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Niobium and tantalum 1995

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Contents

Introduction

This review is intended to cover the literature on the co-ordination chemistry of niobium and tantalum through the year 1995 as reflected in the Bath Information and Data Services, Science Citation Index database. Searching was performed using keyword analysis with 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 1994 review, to low nuclearity inorganic co-ordination 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 components of the co-ordination sphere or its unusual nature.

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

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to separate the +5 oxidation state from the others since most co-ordination chemical studies have inevitably dealt with the former state. Within each main section the subsections are organised according to the nature of the co-ordinated 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 reader's attention is directed to a comprehensive review of the co-ordination chemistry of niobium and tantalum covering the years 1985–87 especially for areas of cluster chemistry, solid state and materials related science [1] and to previous annual reports in this journal [2–4].

1. Niobium(V) and tantalum(V)

1.1. Complexes with group 17 donor ligands

The reactions of $[Nb(C_5H_5)Cl_4]$ or $[Nb(CH_3C_5H_4)Cl_4]$ compounds with four equivalents of various pentadienyl anions led initially to $Nb(RC_5H_4)(\eta^5-Pdl)(\eta^3-Pdl)$ complexes, for $Pdl = C_5H_7$ or $2,4\text{-}C_7H_{11}$(C_7H_{11} = dimethylpentadienyl). For the $2,4\text{-}C_7H_{11}$ complexes, subsequent intramolecular coupling between the two Pdl ligands occurs at room temperature, leading to $Nb(RC_5H_4)(\eta^8$-2,4,7,9-tetramethyl-1,3,7,9-decatetraene) complexes [5]. These contain one η^4-*cis*-diene and one η^4-*trans*-diene coordinated to the metal centre. This has been confirmed, using crystallography, for the R = H complex, which crystallises in the orthorhombic space group Pcc2 with $a = 14.061(3)$, $b = 14.273(3)$, $c = 8.045(1)$ Å, and $Z = 4$. For related tantalum reactions, a different course is followed, leading to isolation of $Ta(C_5H_5\eta^3\text{-}Pdl)$ complexes ($Pdl = 2,3\text{-}C_7H_{11}$; $2,4\text{-}C_7H_{11}$; $1,5\text{-}(Me_3Si)_2C_5H_5$), apparently via disproportionation. A structural study on the $2,3\text{-}C_7H_{11}$ complex revealed that its mode of coordination involved localised Ta–C and Ta–olefinic interactions through the 1, 4 and 5 positions of the open dienyl ligand. The compound crystallises in the monoclinic space group $P2_1/c$ with $a = 7.887(2)$, $b = 14.433(3)$, $c = 12.645(3)$ Å, and $\beta = 97.93(2)°$ for $Z = 4$. However, for the 1, $5\text{-}(Me_3Si)_2C_5H_5$ complex, the more usual allylic mode of coordination was observed. This compound crystallises in the monoclinic space group P2(1)/n, with $a = 7.422(1)$, $b = 23.934(5)$, $c = 13.059(2)$ Å, and $\beta = 97.52(1)°$ for $Z = 4$ [5].

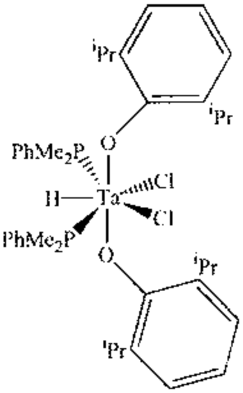
An easy way to produce the scarcely known mononuclear divalent coordination compounds of titanium and niobium by reduction of higher-valent species with potassium graphite, KC_8, in thf or thf-pyridine solutions has been described [6]. Also reported are the preparations and X-ray structural characterisation of several *trans*-dichlorotetrakis(pyridine)metal(II) species, including three crystal forms of *trans*-$NbCl_2(py)_4$. The latter crystallise unsolvated in a tetragonal and a monoclinic form but the third type has thf in the crystals. The propeller-like arrangement of the pyridine planes in the niobium polymorphs is very similar, but differs considerably from that of the titanium analogue in which the pairs of *trans* pyridine molecules are co-planar. For comparison purposes, the structure of *trans*-$MnCl_2(py)_4$ has also been reported. The variation of the M–N bond distances for the high-spin *trans*-$MCl_2(py)_4$ species of the first transition series shows the pattern expected from ligand field considerations with maxima at titanium and manganese and minima at vanadium and nickel [6].

1.2. Complexes with group 16 donor ligands

The reaction of $TiCl_4$ with potassium 2,3,5,6-tetramethylbenzenethiolate (KS-2,3,5,6-Me_4C_6H) in thf gives [Ti(S-2,3,5,6-$Me_4C_6H)_4$] in 50 % yield. This compound possesses a distorted tetrahedral structure with Ti–S bonds of 2.292(6) Å. One of the thiolate groups has a very acute M–S–C angle of 86.5(5)°. The reaction of $TaCl_5$ with excess tetramethylbenzenethiolate (LiS-2,3,5,6-Me_4C_6H) in hexane gives [Ta(S-2,3,5,6-$Me_4C_6H)_5$] which is also a monomeric compound this time with a distorted five-coordinate geometry. The average Ta–S bond distance is 2.37(3) Å and average TaS–C-angle is 116(7)°. Structural comparisons of both the titanium and tantalum compounds with analogous phenolate complexes reveal large values for Δ[(MS)-(MO)]. The extent of the S to M π-bonding in these electron deficient early transition metal thiolates is considerably reduced compared to the O to M π-bonding in phenolate analogues [7].

A series of seven-coordinate, mononuclear tantalum–hydride compounds [$Ta(OC_6H_3Pr^i_2$-2,6$)_2L_2(Cl)_{3-n}(H)_n$](1), n = 1; (**2**), n = 2; (**3**), n = 3; $OC_6H_3Pr^i_2$-2,6 = 2,6-diisopropylphenoxide; L = tertiary phosphines) can be obtained either by hydrogenolysis of the corresponding tantalum alkyl substrate, or by reacting the trichloride [$Ta(OC_6H_3Pr^i_2$-2,6$)_2(Cl)_3$] with one or two equivalents of Bu_3SnH in the presence of a ligand [8]. The hydrogenolysis of [$Ta(OC_6H_3Pr^i_2$-2,6$)_2$($CH_2C_6H_4$-4-Me$)_3$] in the presence of PMe_2Ph or $PMePh_2$ produces [$Ta(OC_6H_3Pr^i_2$-2,6$)_2(H)_3L_2$] (**3a**). L = PMe_2Ph;(**3b**), L = $PMePh_2$), while the compounds [$Ta(OC_6H_3Ph_2$-2,6$)_2(R)_3$] (R = $CH_2C_6H_4$-4-Me, CH_2SiMe_3) produce [$Ta(OC_6H_3Cy_2$-2,6$)_2(H)_3(L)_2$] (**3c**), L = PMe_2Ph; (**3d**), L = $PMePh_2$) with the 2,6-dicyclohexylphenoxide ligand being generated by intramolecular hydrogenation of the ortho phenyl rings in the 2,6-diphenylphenoxide substrate. The hydrogenolysis of the bisalkyl [$Ta(OC_6H_3^iPr_2$-2,6$)_3$($CH_2C_6H_4$-4Me$)_2$] in the presence of PMe_2Ph produces the six-coordinate [$Ta(OC_6H_3^iPr_2$-2,6$)_3(PMe_2Ph)(H)_2$], (**4b**), which will exchange the phosphine ligand to produce a series of substituted derivatives. A related series of six-coordinate dihydride compounds are produced by addition of Bu_3SnH (2 Sn per Ta) to [$Ta(OC_6H_3^tBu_2$-2,6$)_2Cl_3$] in the presence of added L. Single crystal X-ray diffraction analyses of seven-coordinate (1), (**2b**), and (**3c**) (all cases L = PMe_2Ph) show them to adopt pentagonal bipyramidal geometries with *trans* axial aryloxide ligands.

In monohydride (**1**) the unique hydride ligand is *cis* to both phosphine ligands, whilst in dihydride (**2b**) the hydride ligands are mutually *cis* but *trans* to the chloride group within the pentagonal plane. A crystallographic 2-fold axis in trihydride (**3c**) passes through the unique Ta–H bond and bisects the remaining *cis* hydride ligands within the pentagonal plane. The solution ^1H NMR spectra of (**1**), (**2**) and (**3**) are



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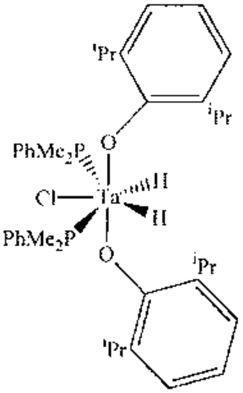
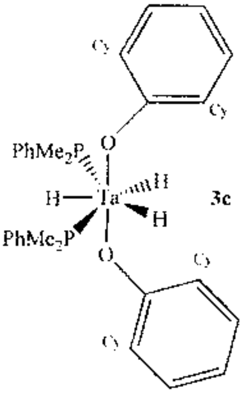
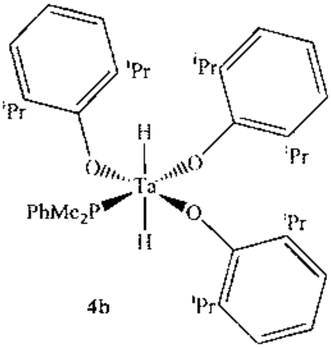


2b



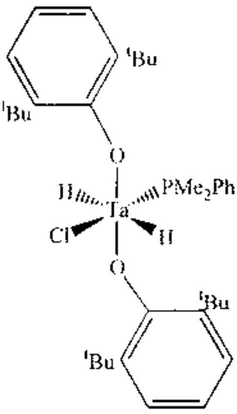
3c

consistent with the solid state structures being maintained in solution. Furthermore, analysis and simulation of the downfield hydride resonances in (**2**) and (**3**) show these seven coordinate molecules to be stereochemically rigid on the NMR spectroscopic time scale. The coupling constants obtained from simulations conclusively rule out the formulation of (**2**) or (**3**) as containing η^2-H_2 ligands. The solid state structures of six-coordinate $[Ta(OC_6H_3^iPr_2\text{-}2,6)_3(PMe_2Ph)(H)_2]$, (**4b**), and $[Ta(OC_6H_3^tBu_2\text{-}2,6)_2(PMePh_2)(Cl)(H)_2]$, (**5c**), show a geometry severely distorted from octahedral. In both compounds the mutually *trans* hydride ligands are bent toward the phosphine ligand with H–Ta–P angles of 66(2)° and 69(1)° for (**4a**) and 56(2)° and 62(2)° for (**5b**). A steric origin to this distortion is ruled out by the structure of (**5b**) in which the hydride ligands are bent toward the bulky phosphine ligand and away from the Ta–Cl bond. Strong support for the distorted structures of (**4**) and (**5**) comes from solution and solid state infrared spectra where two sharp (Ta–H) vibrations are observed. Analysis of the intensity ratio for the symmetric and asymmetric bands yields predicted H–Ta–H angles very close to these observed in the solid state structure [8].



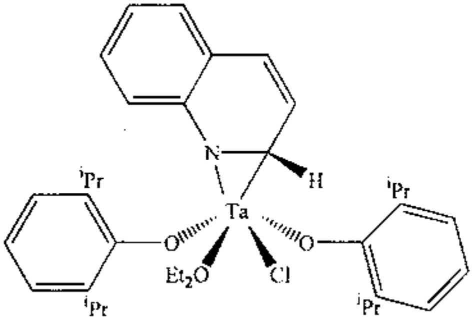
4b

5c



Reaction of $(C_5H_5)_2Ta(=S)H$ with $M'(CO)_5(thf)$ (M' = Cr, Mo, W) gives rise to the formation of adducts in which the $[M'(CO)_5]$ fragments are coordinated to the Ta–S double bond as established by means of ^{1}H NMR spectroscopy and, in the case of M' = W, by single crystal X-ray diffraction [9].

The heterocyclic complexes [η^1-N-QUIN]Ta(OAr)$_3$Cl$_2$ (**6**) and [η^1-N-6MQ] Ta(OAr)$_3$Cl$_2$ (**7**) (where Ar = 2,6-diisopropylphenyl, QUIN = quinoline, and 6MQ = 6-methylquinoline) have been prepared from Ta(OAr)$_3$Cl$_2$(OEt$_2$) and QUIN or 6MQ in pentane. [η1-N-6MQ]Ta(OAr)$_2$Cl$_3$ (**8**) is prepared similarly from Ta(OAr)$_3$Cl$_2$(OEt$_2$) [10]. Upon rapid, two-electron reduction of these complexes, an η^1-N > η^2-(N,C) bonding rearrangement is effected and the thermally sensitive, [$\eta^2-N,C-$QUIN]Ta(OAr)$_3$ (**9**), [$\eta^2-N,C-$6MQ]Ta(OAr)$_3$ (**10**), and [$\eta^2-N,C-$6MQ]Ta(OAr)$_2$Cl(OEt$_2$) (**11**) can be isolated. Alternatively, (**11**) can be prepared in higher yield from ($\eta^6-C_6Me_6$)Ta(OAr)$_2$Cl and 6MQ. The trimethylphosphine adducts [η^2-N,C-QUIN]Ta(OAr)$_3$(PMe$_3$) (**12**) and [$\eta^2-N,C-$6MQ]-Ta(OAr)$_3$(PMe$_3$) (**13**) can be prepared by simple coordination of PMe$_3$ to the base-free compounds. When Ta(OAr)$_2$Cl$_3$(OEt$_2$) is reduced by one electron in the presence of QUIN, 6MQ, or pyridine, the d^1 bis-ligand complexes [η^1-N-QUIN]$_2$Ta$_2$(OAr)$_2$Cl$_2$ (**14**), [η^1-N-6MQ]$_2$Ta$_2$(OAr)$_2$Cl$_2$ (**15**) and [η^1-N-py]$_2$Ta$_2$(OAr)$_2$Cl$_2$ (**16**) can be isolated. Under mild hydrogenation conditions, the only heterocyclic ligands which are hydrogenated are those bound in the η^2-N,C mode to a d^2 metal. Structural studies on [$\eta^2-N,C-$6MQ]Ta(OAr)$_3$(PMe$_3$) (**13**) and [$\eta^2-N,C-$6MQ]Ta(OAr)$_2$Cl(OEt$_2$) (**11**) have been undertaken [10].



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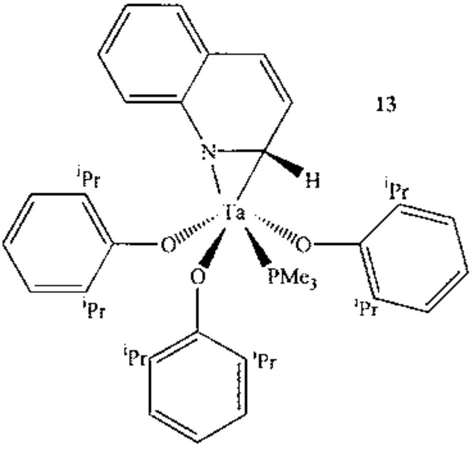

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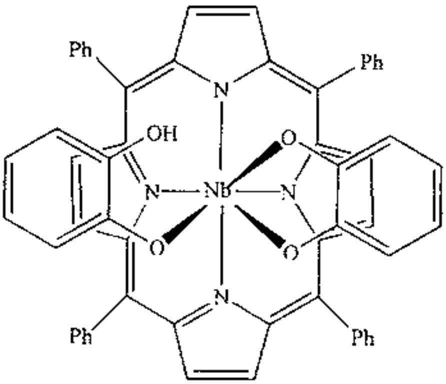
The synthesis and characterisation by powder X-ray diffraction analysis of niobium and tantalum dichalcogenides, MX$_2$(M = Nb, Ta; X = S, Se, Te) as well as of their intercalation products with polyethylenoxide (PEO) have been described. New metallic modifications were obtained for TaS$_2$ and TaSe$_2$. X-Ray diffraction patterns of the PEO intercalated phases indicate structures similar to the pristine dichalcogenides but with interplanar spacings increased in about 10 Å [11].

The syntheses, spectroscopic properties, crystal and molecular structures and bonding of several cyclopentadienyl or pentamethylcyclopentadienyl niobium and tantalum calixarene complexes have been described [12]. Included are the mononuclear complexes [Cp*Ta(calix[4]arene)], [Cp*Ta(*p-tert*-butylcalix[4]arene)], and [CpNb(*p-tert*-butylcalix[4]arene)], in which the electron-deficient metal centres are protected in the *exo*-calix position by sterically bulky ligands. These complexes are well suited to bind small-molecule guests within their macmcyclic pockets, as demonstrated in the solid state and in solution for the complexes [Cp*Ta(*p-tert*-butylcalix[4]arene)]. toluene, [Cp*Ta(OH$_2$)(*p-tert*-butylcalix[4]arene)], and [Cp*Ta(NCCH$_3$)(*p-tert*-butylcalix[4]arene)]. In [Cp*Ta(calix[4]arene)], the calixarene cavity is elliptically shaped as a result of two sets of *trans*-Ta–O–Ph interbond angles, one wide and one narrow, a geometry that nicely accommodates the toluene guest molecule in complexes [Cp*Ta(*p-tert*-butylcalix[4]arene)].toluene. In [Cp*Ta(OH$_2$)(*p-tert*-butylcalix[4]arene)] and [Cp*Ta(NCCH$_3$)(*p-tert*-butylcalix[4]arene)], however the cavity is cylindrical. Insights into these differences and bonding in these compounds are provided by Fenske–Hall molecular orbital calculations on [Cp*Ta(calix[4]arene)], a model of [Cp*Ta(calix[4]arene)] with C_{4v} symmetry, [Cp*Ta(OH$_2$)(calix[4]arene)], and [Cp*Ta(NCCH$_3$) (calix[4]arene)] [12].

The formation of metal alkoxo-niobates has been studied using the physicochenlical analysis method, namely the investigation of solubility isotherms for the $M(OR)_nNb(OR)_5ROH$ systems ($M = Li$, Ba, Sc, La; $R = Et$,^{i}Pr) [13]. The following compounds crystallised: $LiNb(OEt)_6$, $[LiNbO(OEt)_4(EtOH)]_2$, $[BaNbO(OEt)_5(EtOH)]_4$, $BaNb_2(O^iPr)_{12}[(PrOH)]_2$ and $LaNb_2(O^iPr)_{13}$. It has been found that the dimetallic isopropoxide of scandium and molybdenum does not exist in the solid state. The oxo complexes are formed on storage (or more rapidly on refluxing) of solutions of non-ore compounds in alcohols in the presence of dry air and are, in fact, the products of the oxidation of these compounds by oxygen. The structure of $[LiNbO(OEt)_4(EtOH)]_2$ is built of dimeric molecules with the metal-oxygen core analogous to that of $Ti_4(OMe)_{16}$. $[BaNbO(OEt)_5(EtOH)]_4$ is constructed around the $[Ba_4O_4]$ cubane-like unit, whose oxygen vertices are occupied by the oxo atoms of $NbO(OEt)_5$ octahedra. The structures of $BaNb_2(O^iPr)_{12}[(PrOH)]_2$ and $LaNb_2(O^iPr)_{13}$ and the recently studied $Nb(O^iPr)_5$ are based on the common motif featuring the M_2O_2 four-membered cycles in edge sharing octahedra. All the observed [Nb-M-Nb] units are non-linear, the molecule of $LaNb_2(O^iPr)_{13}$ being asymmetric, for the, central $[LaO_6]$ octahedron is sharing simultaneously an edge with one $[NbO_6]$ octahedron and a face with the other. The conditions leading to the formation of oxo groups and the influence of the latter on the complexation process have been discussed. The literature data on the existence of 3d transition metals alkoxo-niobates have not been confirmed. It has been found that interaction of Nb and Co or Ni isopropoxides takes place only due to preliminary micro-hydrolysis or pyrolysis and leads to formation of oxoalkoxo-niobates [13].

Peroxo complexes of niobium have been synthesised and characterised [14]. Although the complexes fail to oxidise alcohols and olefins stoichiometrically, they act as active catalysts in presence of *tert*-butyl hydroperoxide (TBHP), resulting in the formation of oxidation products. Competitive epoxidation of cycloolefins does not suggest coordination of olefins to metal ions [14].

A novel catecholato complex. Nb^V(tpp)(cat)(Hcat) (**17**), where cat and Hcat are two distinct catechol ligands (a didentate catecholate dianion and a monodentate catecholate monoanion, respectively) and tpp is 5,10,15,20-tetraphenylporphyrin dianion, has been isolated in the reaction of Nb^V(tpp)(O)(AcO) with catechol, where AcO is an acetato ligand [15]. Its molecular structure has been determined by X-ray crystallography which confirmed that no oxo ligand was present and in this respect it is unique among the niobium(V) porphyrins.



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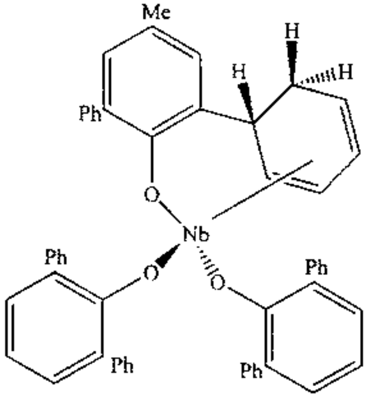
The didentate and monodentate ligands are located on the same side of the porphyrin ring. The hepta-coordinate niobium atom is bonded to the four pyrrole nitrogen atoms and to three oxygen atoms in the catechols. The niobium atom is displaced by 1.02 Å from the mean plane of the four nitrogen atoms [15]. The structure of the complex in solution and the mechanism of the Nb=O cleavage have been investigated by means of ^{1}H NMR spectroscopy. The bidentate catechol is oriented in C_s symmetry with respect to the porphyrin plane, and the monodentate catechol is located perpendicular to both the didentate catechol and the poiphyrin plane. A unique route to Nb=O cleavage is proposed that involves an intramolecular electron transfer from the catechol ligand coordinated at the first stage through a ligand exchange with AcO. Both protonation and electron transfer to the Nb=O moiety play important roles in the cleavage process. The sodium amalgam reduction (2Na per Nb) of hydrocarbon solutions of the niobium compounds [Nb(OC$_6$H$_3$Ph$_2$-2.6)$_3$Cl$_2$], (OC$_6$H$_3$Ph$_2$-2,6=2,6-diphenylphenoxide) and [Nb(OC$_6$H$_2$Ph$_3$-2,4.6)$_3$Cl$_2$], (OC$_6$H$_3$Ph$_3$-2,4.6=2,4,6-triphenylphenoxide) under 1 atmosphere of H$_2$ leads to the deep-red. η^4-cyclohexadiene complexes [Nb(OC$_6$H$_3$Ph-η^4-C$_6$H$_7$)(OC$_6$H$_3$Ph$_2$-2,6)] and [Nb(Nb(OC$_6$H$_3$Ph-η^4-C$_6$H$_7$)(OC$_6$H$_2$Ph$_3$-2.4,6)], respectively [16]. The spectroscopic properties of [Nb(OC$_6$H$_3$Ph-η^4-C$_6$H$_7$)(OC$_6$H$_3$Ph$_2$-2,6)] and [Nb(Nb(OC$_6$H$_3$Ph-$\eta 4$-C$_6$H$_7$)

$(OC_6H_2Ph_3\text{-}2,4,6)]$ are consistent with one of the aryloxide ligands having undergone 1,2-hydrogenation of a phenyl substituent, leading to a cyclohexadiene group which is strongly coordinated to the metal centre. This is confirmed by a single crystal X-ray diffraction analysis of $[Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OC_6H_3Ph_2\text{-}2,6)]$ (**18**), showing the coordination sphere about niobium to consist of two, normal 2,6-diphenylphenoxide ligands and one chelating, partially hydrogenated aryloxide group. The η^4-bonding of the chelated cyclohexadiene group is slightly distorted with Nb–C distances of 2.27(1), 2.27(2), 2.37(1) and 2.40(1) Å [16]. Hydrocarbon solutions of $[Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OC_6H_3Ph_2\text{-}2,6)]$ and $[Nb(Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OC_6H_2Ph_3\text{-}2,4,6)]$ will react further with hydrogen (200–1200 psi) to produce upon hydrolysis 2-cyclohexyl-4-phenylphenol and 2,6-dicyclohexylphenol and 2-cyclohexyl-4,6-diphenylphenol and 2,6-dicyclohexyl-4-phenylphenol respectively. The intramolecular hydrogenation of aryl-phenoxide groups has also been achieved by treating mixtures of the chloride compounds $[Nb(OC_6H_3Ph_2\text{-}2,6)_nCl_{5-n}]$ or $[Nb(OC_6HPh_4\text{-}2,3,5,6)_nCl_{5-n}]$ $(n=2,3)$ with $(5-n)$ equivalents of BuLi under hydrogen. Spectroscopic (^1H, ^{13}C NNM) analysis of the phenols obtained in all cases indicated that exclusive-hydrogenation of *ortho*-phenyl groups occurs with no evidence of attack on either the *meta*-or *para* phenyl substituents or upon the central phenoxy ring [16]. The use of D_2 as reagent gas leads to dicyclohexylphenols containing up to 11 deuterium atoms per cyclohexyl ring due to the presence of H/D exchange processes. Analysis of the stereochemical positions of the remaining protons in the cyclohexyl rings indicates that the hydrogenation of the phenyl rings occurs via two regiochemically distinct reaction pathways.



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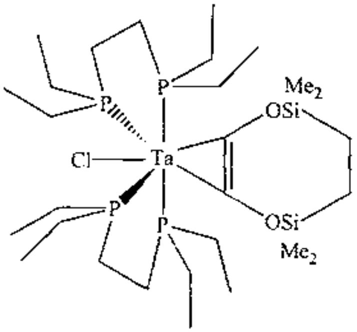
Eight new complexes $\alpha_2\text{-}M_{7-m}H_m[P_2W_{17}NbO_{62}]\cdot H_2O$ and $\alpha\text{-}1,2,3\text{-}M_{8-m}H_m[P_2W_{15}Nb_3O_{62}]\cdot XH_2O$ (M = K,TMA,TEA,TBA) were synthesised and characterised by IR and UV spectroscopies, polarography, XPS and XRD methods [17]. ^{31}P and ^{183}W NMR spectroscopic studies show that the niobium atoms in the anions are on the polar sites. The crystal of $\alpha_2\text{-}M_{7-m}H_m[P_2W_{17}NbO_{62}]\cdot 30H_2O$ is hexagonal with cell parameters $a = 19.836(4)$, $b = 19.836(9)$, $c = 15.498(6)$ Å, ($\alpha = \beta = 90$, $\gamma = 120°$) [17].

The synthesis and structural characterisation of three new elementary chalcogenometallates is reported. The $[(O)Nb(S_2)_2(SH)]^{2-}$ and corresponding tetranegative anions have been obtained in the reactions of the $[Nb(S)_3(S^tBu)]_{2-}$ anion with elemental sulfur and Et_3N, respectively, in the presence of water. The $[(O)Nb(S_2)_2(SH)]^{2-}$ anion reacts with Et_3P to give the $[Nb(S)_3(SH)]^{2-}$ anion [18].

1.3. Complexes with group 15 donor ligands

The heterodimetallic complex $[Cp_2Ta(CO)(\mu\text{-}PMe_2)Cr(CO)_5]$ was prepared by reaction of $[Cp_2Ta(CO)(PMe_2)]$ with $[Cr(CO)_5thf]$ [19]. Irradiation of $[Cp_2Ta(CO)(\mu\text{-}PMe_2)Cr(CO)_5]$ afforded the dibridged compound $[Cp_2Ta(CO)(\mu\text{-}PMe_2)_2Cr(CO)_4]$. Addition reactions between the latter and Lewis bases L (L = phosphines, or isonitriles) produced adducts with L regiospecifically coordinating to chromium. Depending on L, the reaction may be stereospecific, since coordination of L may lead to *cis* or *trans* arrangements on the chromium site [19].

Convenient syntheses of dicarbonyl complexes of the type $[M(CO)_2(depe)_2Cl]$ (depe = 1,2-bis(diethylphosphino)ethane, M = Ta, Nb) and $[M(CO)_2(dbpe)_2Cl]$ (dbpe = 1,2-bis(dibutylphosphino)ethane, M = Ta, Nb) having increased steric demands at the high coordinate metal centres are described [20]. Reductive coupling of the CO ligands occurs to provide products of the type $[M(R_3'SiOC{=}COSiR_3')(R_2PCH_2CH_2PR_2)_2]_x$. Single crystal X-ray structural studies were carried out for two reductively coupled products prepared with 1,2-bis(chlorodimethylsilyl)ethane as the electrophile, $[V(Me_2SiOC{=}COSiMe_2)(dmpe)_2Cl]$ (**19**) and $[Ta(Me_2SiOC{=}COSiMe_2)(depe)_2Cl]$ (**20**).



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In these complexes, the acetylene is contained within a newly formed eight-membered ring, and the ligands are arranged in a pentagonal bipyramid geometry comprising two axial phosphorus atoms and five equatorial ligands, the coupled carbons, a *trans* chloride and the remaining two phosphorus atoms [20].

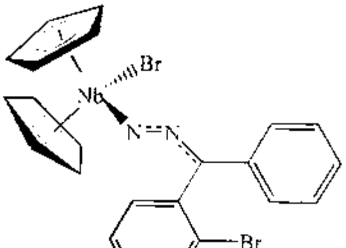
The compound $[TaCp^*Cl_4](Cp^* = \eta^5\text{-}C_5Me_5)$ reacts with isocyanides and amines to give the pseudo-octahedral adducts $[TaCp^*Cl_4L]$ ($L = 2,6\text{-}Me_2C_6H_3NC$; $2,4,6\text{-}Me_3C_6H_2NC$; ${}^tBuNC$; or $C_6H_5NH_2$,). Reduction of $[TaCp^*Cl_4]$ in the presence of stoichiometric amounts of isocyanide, with two equivalents of Na/Hg gives the diamagnetic pseudo-octahedral tantalum(III) complex, $[TaCp^*Cl_2(CN\text{-}2,6\text{-}Me_2C_6H_3)_3]$. All the complexes have been characterised by standard IR and NMR spectroscopic methods and the molecular structure of $[TaCp^*Cl_4L]$ ($L = 2,6\text{-}Me_2C_6H_3NC$) was confirmed by X-ray diffraction methods [21]. In a similar fashion, $[NbCp^*Cl_4]$ reacts with one molar equivalent of isocyanides and phosphines to give pseudo-octahedral adducts $[NbCp^*Cl_4 \cdot L]$, ($L = 2,4,6\text{-}Me_3C_6H_2NC$; PMe_3; PMe_2Ph; $PMePh_2$,) and the dinuclear complex $[(NbCp^*Cl_4)_2(\mu\text{-dmpe})]$ [22]. Reactions of $[NbCp^*Cl_4]$ with appropriate amounts of MeMgCl yield the corresponding dimethyl $[NbCp^*Cl_2Me_2]$, and tetramethyl $[NbCp^*Me_4]$ derivatives. Again, all new complexes have been characterised by IR and NMR spectroscopies, and most of them were examined also by mass spectrometry [22].

The reaction between $[NbCpCl_4]$ and the phosphine ligands PMe_xPh_{3-x}($x = 0, 1, 2, 3$) has been investigated [23]. While no reaction occurs with PPh_3, stable adducts are formed with all the other ligands in the above series. These have been isolated and characterised by elemental analysis, ${}^1H$ and ${}^{31}P$-NMR spectroscopy, and an X-ray structural determination of the $PMePh_2$ adduct. The three phosphines PMe_3, PMe_2Ph and $PMePh_2$, however, also engage in a subsequent reduction process with formation of chlorine radicals and Nb(IV) complexes. $[NbCpCl_3(PMe_3)_2]$ has been independently synthesised from $[NbCpCl_4]$, sodium and PMe_3 in a 1:1:2 ratio and have been fully characterised. The relative rate of reduction depends on the nature of the phosphine, increasing in the order $PMePh_2 < PMe_2Ph < PMe_3$.

OsO_2R_2($R = CH_2^tBu, CH_2CMe_2Ph$) or $OsO_2(CH_2SiMe_3)_2]_n$ reacts with one or two equivalents of $Ta(NAr)(O^tBu)_3$($NAr = N\text{-}2,6^iPr_2C_6H_3$) to form complexes of the type $OsO(NAr)R_2$ or $Os(NAr)_2R_2$. $OsO(NAr)(CH_2^tBu)_2$ reacts with two equivalents of HCl or Me_3SiI in CH_2Cl_2 or dme to form $Os(NAr)(CH_2^tBu)_2Cl_2$ or $Os(NAr)(CH_2^tBu)_2I_2$, respectively, or with $SiMe_3X$ in CH_2Cl_2 to form green, crystalline, $Os(NAr)(CH_2^tBu)_2(OSiMe_3)X$ ($X = Cl, OTf$) [24].

Reaction of $[TaCp^*Cl_2Me_2]$ with two equivalents of isocyanide or addition of one equivalent of isocyanides to azatantalacyclopropane complexes $[TaCp^*Cl_2(\eta^2\text{-}NRCMe_2]$ ($R = 2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$) at room temperature afforded new imido derivatives $[TaCp^*Cl_2(NR)]$ ($R = 2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$) in almost quantitative yields, with simultaneous elimination of the imino ketene, $RN{=}C{=}CMe_2$ [25]. When the same reactions were carried out in the presence of traces of water, small amounts of cyclic η^2-amido-carbene species $[TaCp^*Cl_3(\eta^2\text{-}NRCMe_2\text{-}CNHR')]$ ($R = R' = 2,6\text{-}Me_2C_6H_3$, $R = 2,6\text{-}Me_2C_6H_3$, $R' = 2,4,6\text{-}Me_3C_6H_2$) were simultaneously obtained. These latter complexes can also be prepared by heating the corresponding trichloroisopropylamido complexes $[TaCp^*Cl_3(NR^iPr)]$, at 90° in the presence of isocyanide and decompose by further heating at 120° to give the imido compounds $[TaCp^*Cl_2(NR)]$. A similar reaction of $[TaCp^*Cl_nMe_{4-n}](n=0,1)$ with one equivalent of $CN(2,6\text{-}Me_2C_6H_3)$ afforded mono- and dimethylated azatantalacyclopropane derivatives $[TaCp^*Cl_nMe_{2-n}[\eta^2\text{-}N(2,6\text{-}Me_2C_6H_3)CMe_2]$ ($n=1$; $n=0$), which react with one additional equivalent of isocyanide to give imido alkenylamido species $[TaCp^*X[N(2,6\text{-}Me_2C_6H_3)](NR'CMe=CMe_2)](X=Cl, R'=2,6\text{-}Me_2C_6H_3,$ and $2,4,6\text{-}Me_3C_6H_2$; $X=Me$, $R'=2,6\text{-}Me_2C_6H_3$, and $2,4,6\text{-}Me_3C_6H_2$.). All compounds have been characterised by IR and ^1H and ^{13}C NMR measurements, and the activation barrier to rotation around the [C=C] double bond of the alkenyl group of $[TaCp^*X[N(2,6\text{-}Me_2C_6H_3)](NR'CMe=CMe_2)]$ was determined in solution [25].

The complexes $[Cp_2Nb(H)(\eta^1-NNCPhAr)](Ar=Ph$ or $o\text{-}C_6H_4Br)$ were found to undergo easy substitution of a hydride ligand for a halogen atom by the reaction of $[Cp_2Nb(H)(\eta^1\text{-}NNCPhPh)]$ with various alkylhalides with high yields of $[Cp_2Nb(X)(\eta^1\text{-}NNCPh_2)]$ (X=Cl, Br or I). $[Cp_2Nb(Br)(\eta^1\text{-}NNC(Ph)\text{-}o\text{-}C_6H_4Br)$ and $[Cp_2Nb(Br)(\eta^1\text{-}NNCPh_2)]$ were found to be formed in a halogen exchange reaction, and also by the thermolysis of $[Cp_2Nb(H)(\eta^1\text{-}NNCPh(o\text{-}C_6H_4Br))]$ [26]. Halide diazoalkane niobocene complexes clearly exhibit marked polarity of the metal centre. Nucleophilic substitution of bromine in $[Cp_2Nb(Br)(\eta^1\text{-}NNCPh_2)]$ yielded $[Cp_2Nb(Me)(\eta^1\text{-}NNCPh_2)]$. The results of X-ray analysis of $[Cp_2Nb(Br)(\eta^1\text{-}NNC(Ph)\text{-}o\text{-}C_6H_4Br)$ (**21**) are also provided.



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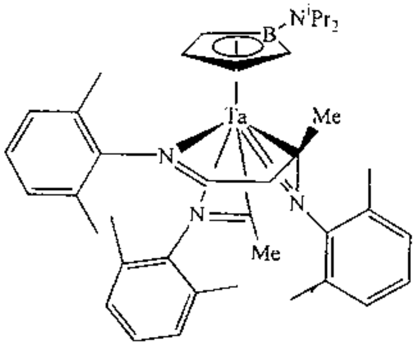

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The hydrido complexes $[NbCp_2H(L)]$ [L=CO or $P(OMe)_3$] reacted with MeI to afford the iodo derivatives $[NbCp_2IL]$ [27]. The reaction of $[NbCp_2IL]$ with NaSEt leads to the terminal thiolato complexes $[NbCp_2L(SEt)]$. These compounds were used to bind the metal carbonyl fragments $[Fe(CO)_4]$ and $[M(CO)_5]$ from $[Fe_2(CO)_9]$ and $[M(CO)_5(thf)]$ (thf=tetrahydrofuran), respectively. The corresponding monothiolato-bridged complexes $[NbCp_2L(\mu\text{-}SEt)]_3$ (M=Fe, n=4: M=Mo or W, n=5) were obtained only in the case of L=CO and no dibridged μ-SEt, μ-CO complex was formed. The new complexes have been characterised by IR, ^1H and ^{31}P NMR spectroscopies. The X-ray analysis of $[NbCp_2(CO)(\mu\text{-}SEt)]$ showed an *endo* position of the ethyl group with respect to the CO ligand bound to the niobium. The results of extended-Hückel molecular orbital (EHMO) conformational calculations carried out on the model complexes $[NbCp_2(CO)(PMe_2)]$ and $[NbCp_2(CO)(SMe)]$ are compared, and the importance of electronic and steric effects deduced. An explanation for the non-formation of dibridged μ-SEt, μ-CO complexes is attempted on the basis of EHMO and X-ray results [27].

1.4. Other donor sets

Reaction of Me_3TaCl_2 with $Li_2[C_4H_4BN(CHMe_2)_2]$ (thf) produces $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]Me_2Ta[\mu\text{-}\eta^5\text{-}C_4H_4BN(CHMe_2)_2]TaMe_4$ which is a formally electron deficient (24 electron) triple decker complex [28]. Similarly, mononuclear produces $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]TaMe_3PMe_3$ is obtained when $Me_3TaCl_2PMe_3$ is used as the metal source. Compound $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]TaMe_3PMe_3$ undergoes clean migratory insertion chemistry with 2,6-dimethylisocyanide to afford the metallabicyclic complex $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]Ta[\eta^2\text{-}MeCN(2,6\text{-}Me_2C_6H_3)][\eta^3\text{-}2,6\text{-}Me_2C_6H_3)NCHCH_2C(Me)N(2,6\text{-}Me_2C_6H_3)]$ (**22**) which has been structurally characterised.

Ph_2PCl easily inserts into the Ta–H bond of $[Cp_2TaH_3]$ affording an ionic complex $[Cp_2TaH_2(HPPh_2)]Cl$. This species was then found to undergo ready deprotonation to give the first phosphido-substituted tantalocene complex $[Cp_2TaH_2PPh_2]$, which was characterised by NMR spectroscopy and X-ray crystallography. Thermal decomposition of $[Cp_2TaH_2PPh_2]$ as well as its reaction with $HPPh_2$ has also been investigated [29].

2. Lower oxidation states of niobium and tantalum

2.1. Complexes with group 17 donor ligands

The synthesis of a dimeric tantalum complex with two non-symmetric alkylidyne bridging ligands, both of which coordinate with [C=Ta] double bonds to the same tantalum atom (and with C–Ta single bonds to the other tantalum atom), has been reported. The two bridging alkylidyne ligands are involved in an unusual axial-equatorial ligand exchange [30].

The electrochemistry and electronic absorption spectroscopy of the anionic chloride complexes derived from the metal–metal bonded, di-cationic ($z = 2$–5) clusters have been examined in $CH_3CN/[^nBu_4N]PF_6$ at 23 °C and in the room temperature chloroaluminate molten salt, aluminium(III) chloride-1-methyl-3-ethylimidazolium chloride ($AlCl_3$–[MeEtim]Cl) at 40 °C. The following electrochemical reactions were identified in the former solvent (potentials versus Ag/0.10 M Ag^+): $[(Ta_6Cl_{12})Cl_6]_2$ (red-orange) $+ e = [(Ta_6Cl_{12})Cl_6]^-$, $E(1/2) = 1.19$ V; $[(Ta_6Cl_{12})Cl_6]^{2-}$ $+ e = [(Ta_6Cl_{12})Cl_6]^{3-}$ (yellow), $E(1/2) = -0.28$ V; $[(Ta_6Cl_{12})Cl_6]^{3-}$ (yellow) $+ e(-) = [(Ta_6Cl_{12})Cl_6]^{4-}$ (green), $E(1/2) = -0.84$ V; $[(Ta_6Cl_{12})Cl_6]^{4-}$ $+ CH_3CN' = [(Ta_6Cl_{12})Cl_5(CH_3CN)]^{3-}$ (green) $+ Cl^-$. The replacement of chloride ion by CH_3CN in the $[(Ta_6Cl_{12})Cl_6]^{4-}$ complex in the last step shown above takes place in a slow homogeneous reaction that is coupled to the $[(Ta_6Cl_{12})Cl_6]^{3-/4-}$ electrode reaction. This homogeneous reaction is observed on the timescale of bulk controlled-potential electrolysis in $CH_3CN/[^nBu_4N]PF_6$ without added chloride ion, but not during voltammetric experiments. The addition of a large excess of chloride ion to a solution containing $[(Ta_6Cl_{12})Cl_5(CH_3CN)]^{3-}$ converts this complex back to $[(Ta_6Cl_{12})Cl_6]^{4-}$. In the acidic $AlCl_3$–[MeEtim]Cl melt, two reversible redox reactions, analogous to the (4+/3+) and (3+/2+) reactions seen in CH_3CN, were found at E(1/2) = 1.16 and 0.79V (versus Al/Al(III) in the 66.7–33.3 mol% melt), respectively. However, inter-solvent comparisons of the E(1/2) of these reactions referenced to the $FeCp_2(0/+)$ couple indicated that; both are shifted positively by more than 1 V in the molten salt relative to $CH_3CN/[^nBu_4N]PF_6$, suggesting replacement of labile chloride ions on the $[(Ta_6Cl_{12})Cl_6]^{(6-z)-}$ ($z = 2$–4) clusters with $[AlCl_4]^-$ during dissolution in acidic melt to produce species with the general formula. $(Ta_6Cl_{12})Cl_y(AlCl_4)_{6-y}]^{(6-z)-}$ ($y \leq 6$). The Stokes-Einstein products of the $[(Ta_6Cl_{12})Cl_6]^{(6-z)}$ ($z = 3$ and 4) clusters in $CH_3CN/[^nBu_4N]PF_6$ were nearly the same with an average value of ca. 10×10^{-11} g cm s^{-2} K^{-1}. This value is very close to that found for the corresponding anionic niobium clusters in a previous investigation conducted in basic $AlCl_3$-[MeEtim]Cl [31].

The reaction of $[Nb(\eta^5\text{-}C_5H_4R)_2X_2]$ [R = $SiMe_3$, X = Cl; R = $SiMe_3$, X = Br; R = H, X = Cl; R = ^{t}Bu, X = Cl] with nitroso derivatives ArNO[Ar = Ph; $o\text{-}CH_3C_6H_4$; $p\text{-}(CH_3)_2NC_6H_4$] yields paramagnetic complexes formulated as $[Nb(\eta^5\text{-}C_5H_4)R)(\eta^3\text{-}C_5H_4R)X_2(ArNO\text{-}N,O)$, which have been characterised by ESR and IR spectroscopy [32].

Reaction of $[Tp^*NbCl_2(PhC{=}CR)]$ (R = CH_3,Ph) with one equivalent of allyl Grignard gives moderate yields of the five-membered niobacycles $[Tp^*ClNbC(Ph)C(R)CHCH(CH_3)]$ resulting from an allyl-alkyne coupling reaction accompanied by a 1,3-hydrogen shift in the allyl moiety [33]. Both the spectroscopic and X-ray crystal data (**23**) indicate an η^4-butadienyl formulation is appropriate for the new ligand.

Reaction of $NbCl_4(thf)_2$ with three equivalents of Cy_2NLi in toluene afforded

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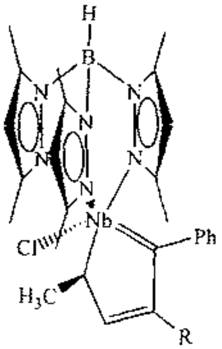


the complex $[(Cy_2N)_2Nb(CyNC_6H_{10})Cl]$ where one cyclohexyl ring has been metallated to form a niobaaziridine ring [34]. Further reaction of $[(Cy_2N)_2Nb(CyNC_6H_{10})Cl]$ with $NaHBEt_3$ in toluene led to the formation of the end-on dinitrogen complex $[(Cy_2N)_3Nb]_2(N_2)$, which was isolated as pale yellow crystals in good yield [34].

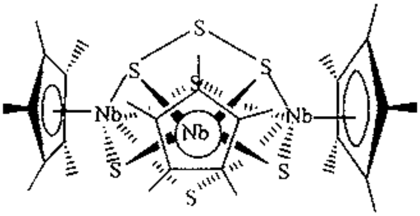
Conditions have been established for the preparation of three different hydrated chloroniobium cluster hydroxide compounds from alkaline solutions: triclinic $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot 4H_2O$ and two cubic compounds whose structures are uncertain with regard to the co-ordination of OH^- ions, $[Nb_6Cl_{12}(OH)_2(H_2O)_{14}]$ and $[Nb_6Cl_{12}(H_2O)_{14}(OMe)_2]$ [35]. Based upon structural data $[Nb_6Cl_{12}(OH)_2(H_2O)_{14}]$ and $[Nb_6Cl_{12}(H_2O)_{14}(OMe)_2]$ may contain either the cation $[Nb_6Cl_{12}(H_2O)_6]^{2+}$ or the neutral cluster $[Nb_6Cl_{12}(OH)_2(H_2O)_4]$ containing hydroxo ligands. In $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot 4H_2O$ distinct distances of 2.147(5) for NB-OH, and 2.250(5) and 2.289(5) Å for $Nb\text{-}OH_2$ were found. In $[Nb_6Cl_{12}(OH)_2(H_2O)_{14}]$ and $[Nb_6Cl_{12}(H_2O)_{14}(OMe)_2]$, only distances of 2.19(1) and 2.193(7) Å, respectively, were found for the [Nb–O] bonds of co-ordinated water (or hydroxide–water averaged). IR spectra of $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot 4H_2O$ show strong [O—H] and [Nb—O] stretching bands that reflect the presence of co-ordinated OH-groups. In $[Nb_6Cl_{12}(OH)_2(H_2O)_{14}]$ and $[Nb_6Cl_{12}(H_2O)_{14}(OMe)_2]$, the IR spectra are less definitive about possible coordination modes of hydroxide [35].

The new compounds $A_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$ (A = Rb, Cs) were synthesised from $In_4[Nb_6Cl_{12}Cl_6]$ by substituting six terminal Cl ligands and the In^+ ions in methanolic solution [36]. An X-ray structure refinement was performed on single-crystal data of $Rb_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$; $a = 9.125(1)$, $b = 9.372(1)$, $c = 10.620(1)$ Å, $\alpha = 96.88(2)$, $\beta = 101.89(1)$, $\gamma = 101.44(2)^\circ$ and $Cs_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$(2) $a = 9.209(5)$, $b = 9.479(7)$, $c = 10.918(7)$ Å, $\alpha = 96.89(6)$, $\beta = 103.35(5)$, $\gamma = 101.60(5)^\circ$. Each of the centro-symmetric $[Nb_6Cl_{12}(N_3)_6]^{4-}$ ions of the isotypic compounds contains six terminal azide groups at the corners of the octahedral niobium cluster. The $[Nb_6Cl_{12}(N_3)_6]^{4-}$ ions are linked via Rb–N and Rb–Cl interactions of the Rb^+ ions to form a three-dimensional structure. Crystals of the compounds react explosively on heating or mechanical pressure [36].

2.2. *Complexes with group 16 donor ligands*

Tantalum alkyne complexes prepared from internal acetylenes and low-valent tantalum ($TaCl_5$ and Zn) in dme and benzene have been shown to react with terminal diynes in the presence of thf and pyridine to give tetra-substituted benzene derivatives in good to excellent yields [37].

Reactions of $[Cp'Ta_2(S_2)H]$ ($Cp' = {}^tBuC_5H_4$) and $[Cp(x)_2Nb(S_2)H]$ ($Cp(x) = C_5Me_4Et$) with S_8, I_2, and CH_3I are investigated. Sulfur insertion into the M H bond of $[Cp'Ta_2(S_2)H]$ results in the formation of $[Cp'_3Ta_3S_{12}]$ and $[Cp'_4Ta_4S_{13}]$, where structures are known by analogy, and $[Cp'_6Ta_8S_{17}]$, which has been characterised spectroscopically. $[Cp(x)_2Nb(S_2)H]$ gives in the analogous reaction $[Cp(x)_3Nb_3S_{12}]$ as the only product. This compound desulfurises in boiling decane to give $[Cp(x)_3Nb_3S_7]$ [38]. An X-ray diffraction analysis of $[Cp(x)_3Nb_3S_7]$ (**24**) revealed an unusual M_3S_7 core containing four monosulfide and one trisulfide ligand. The polysulfide ligand is arranged in such a way that its inner sulfur atom is at the top of the molecule in a noncoordinating fashion. Whereas reaction of $[Cp'Ta_2(S_2)H]$ or $[Cp(x)_2Nb(S_2)H]$ with I_2 gives spectroscopically characterised $[Cp'Ta_2(S_2)I]$ and $[Cp(x)_2Nb(S_2)I]$ by an H/I exchange, only the reaction of $[Cp'Ta_2(S_2)H]$ with CH_3I leads to well defined products. At 0 °C, $[Cp'Ta_2(S_2CH_3)H]I$ is formed as an intermediate product which converts into $[Cp'Ta_2(=S)I]$ at higher temperatures. The attack of CH_3I at the disulfide ligand gives rise to the formation of a chiral sulfur site as inferred from ^1H NMR spectroscopic data [38].



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2.3. Complexes with group 15 donor ligands

A series of dinuclear diamagnetic niobium(IV) complexes of the types $Nb_2Cl_8[Ph_2P(CH_2)_nPPh_2]_2$ (where $n=1$–6), $Nb_2Cl_8[Ph_2PCH=CHPPh_2]_2$ and $Nb_2Cl_8[(p\text{-}FC_6H_4)_2P(CH_2)_2Ph_2]_2$ have been synthesised by the reaction of niobium(IV) chloride tetrahydrofuran adduct in thf with symmetrical and unsymmetrical ditertiary phosphines, viz. 1,2-bis(diphenylphosphino)methane (dppm); 1,2-bis(diphenylphosphino)ethane (dppe); 1,3-bis(diphenylphosphino)propane (dppp); 1,4-bis(diphenylphosphino)butane (dppb);1,5-bis(diphenylphosphino) pentane (dppent); 1,6-bis(diphenylphosphino)hexane (dpph); cis-1,2-bis(diphenylphosphino)ethene (dppen) and 1-diphenylphosphino-2-[bis (*p*-fluoro)]phosphinoethane (dp(pf)pe). All these complexes have been characterised by elemental analyses. IR and ^1H, ^{13}C, ^{31}P-NMR spectroscopies and magnetic susceptibility measurements [39].

The trihydrides $[Cp_2MH_3]$ (M = Nb or Ta) react with diphosphines $R_2P(CH_2)_nPR_2$ (R = Me or Ph, $n=1$ or 2) affording the monohydrides $[Cp_2M(H)]$. The dimetallic dihydride $[Cp_2M(H)(\mu\text{-dppp})]$ (dppp = $Ph_2P(CH_2)_3PPh_2$) is obtained by reaction of dppp with $[Cp_2NbH_3]$. The complexes $[Cp_2M(H)(\text{diphosphine})]$ (M = Nb or Ta) are able to bind $[M'(CO)_4]$ fragments (M′ = Cr,Mo or W) and lead to the dibridged complexes $[Cp_2M(\mu\text{-}H)(\mu\text{-diphosphine})M'(CO)_4]$ [40].

The reaction of $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran) with bis(tertiaryphosphinoethyl)amides $Li[N(CH_2CH_2PR_2)_2]$ (R = Me or Pr) results in the formation of new niobium dialkylamides [41]. The specific complexes generated depend on the stoichiometry of the reaction and the bulk of the tertiary phosphine substituents. Thus, with the bulky diisopropylphosphino function, monomeric paramagnetic mono- and bis-ligand complexes are obtained, $[NbCl_3L_2]$ and $[NbCl_2L_2]_2$. However with the less sterically encumbered dimethylphosphino function only the diamagnetic dinuclear complex, $[NbCl_2L_2]_2$, can be isolated; its crystal structure shows equivalent bridging terdentate amide ligands with two bridging chlorides for each dimeric unit resulting in eight-co-ordinate niobium atoms. In contrast, the bis(2-diethylaminoethyl)amide $Li[N(CH_2CH_2NEt_2)_2]$, analogue of the smaller phosphine, only gave rise to paramagnetic monomeric derivatives [41].

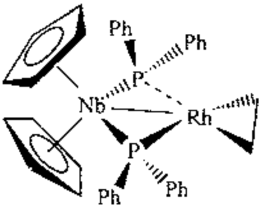
Niobium and tantalum metallophosphines give rise to phosphonate complexes of the type $[Cp_2M(PR_2Me)(POR'R'')]$ by intramolecular Arbuzov rearrangement probably involving nucleophilic attack by phosphorus as shown by ^1H and ^{31}P NMR spectroscopies. The reaction rate depends both on the phosphido group and the metal atom. The Lewis basicity of the phosphoryl group in $[Cp_2M(PR_2Me)(POR'R'')]$ is used in reactions with $Cr(CO)_6$ to synthesise a dimetallic complex as shown by its ^1H and ^{31}P NMR and IR spectroscopies [42].

Convenient syntheses of dicarbonyl complexes of the type $[M(CO)_2(depe)_2Cl]$ (depe = 1,2-bis(diethylphosphino)ethane, M = Ta, Nb) and $[M(CO)_2(dbpe)_2Cl]$ (dbpe = 1,2bis(dibutylphosphino)ethane, M = Ta, Nb) having increased steric demands at the high coordinate metal centres have been described [43]. Reductive coupling of the CO ligands of 1–4 occurs to provide products of the type $[M(R'_3SiOC{=}COSiR'_3)(R_2PCH_2CH_2PR_2)_2]X$. A single crystal X-ray structural study has been carried out for the reductively coupled product prepared with 1,2-bis(chlorodimethylsilyl) ethane as the electrophile $[Ta(Me_2SiOC{=}COSiMe_2)(depe)_2Cl]$ (monoclinic, space group Cc, $a = 11.512(1)$, $b = 18.311(3)$, $c = 18.493(3)$ Å, $\beta = 97.322(7)^\circ$). In this complex, the acetylene is contained within a newly formed eightmembered ring, and the ligands are arranged in a pentagonal bipyramid geometry comprising two axial phosphorus atoms and five equatorial ligands, the coupled carbons, a *trans* chloride, and the remaining two phosphorus atoms [43]. The formation of species derived by O-acylation of the CO ligands in the $[Ta(CO)_2(dmpe)_2]^-$ and $[Ta(CO)_2(depe)_2]^-$ anions was indirectly established by isolation and characterisation of products in which two CO ligands had coupled to form acetylene complexes. Addition of two equivalents of acetyl chloride to $Na[Ta(CO)_2(dmpe)_2]$ or $Na[Ta(CO)_2(depe)_2]$ yielded the acetylene complexes $[Ta(AcOC{=}COAc)(dmpe\ or\ depe)_2Cl]$. The structure of the dmpe derivative was confirmed in a single-crystal X-ray determination. Additional proof of direct alkylation at the terminal CO ligands was provided by isolation of mixed siloxy/alkoxyacetylene coupled products $[M(R_3SiOC{=}COR)(dmpe)_2X]$ ($R = Et, Ac, CO_2Me$; $R'Si_3 = {}^tBuPh_2Si, Pr_3Si$) and $[M(R'_3SiOC{=}COR)(depe)_2X]$ ($R = Et, Ae$; $R'Si_3 = {}^tBuPh2Si, Pr_3Si, Me_3Si$) from reactions of the siloxycarbyne precursors $[M(COSiR'_3)(CO)(dmpe)_2]$ and $[M(COSiR'_3)(CO)(depe)_2]$ ($M = Nb, Ta$) with carbon-based electrophiles. The proper choice of carbon-based electrophile and reaction conditions is crucial in order to avoid oxidation of these low-valent metal complexes to $[M(CO)_2(dmpe)_2X]$, which can occur competitively or exclusively [43].

The chelating diamide complexes *mer*-$TaCl_3(BDPP)$, *mer*-$TaCl_3(BDPP)$, and (BDPP)Ta(η^2-RC=CR)Cl (R=Pr; R=Et; R=Ph). (BDPP=2,6-(ArNCH$_2$)$_2$NC$_5$H$_3$; Ar=2,6−Pr$^i_2$C$_6$H$_3$), have been prepared [44]. Proton and carbon NMR spectroscopic data suggest that the alkynes in these complexes rotate rapidly on the NMR time scale. An X-ray study of (BDPP)Ta(η^2-PrC=CPr)Cl revealed a distorted-square-pyramidal geometry with the chloride occupying the apical position.

The compound [NbCl$_4$(thf)$_2$] and four equivalents of LiNPh$_2$ react to give the homoleptic NB(IV) compound [Nb(NPh$_2$)$_4$] [45]. The reactions of [NbX$_4$(thf)$_2$] (X=Cl,Br) with two equivalents of lithium bis(trimethylsilyl)amide lead to the NB(IV) amido halide complexes [Nb(N(SiMe$_3$)$_2$)$_2$X$_2$] but the reaction of [NbCl$_4$(PMe$_3$)$_2$] with two equivalents of LiNH(2,6-C$_6$H$^i_3$Pr$_2$) gives the Nb(V) bis(imido) complex [Nb(N-2,6C$_6$H$^i_3$Pr$_2$)$_2$Cl(PMe$_3$)$_2$]. A better preparation of the bis(imide) involves reacting [Nb(NEt$_2$)$_2$Cl$_3$]$_2$ sequentially with two equivalents of LiNH(2,6−C$_6$H$^i_3$Pr$_2$) and PMe$_3$ [45].

The reaction between [Cp$'_2$Nb(PPh$_2$)$_2$Li] and [ClRh(COD)]$_2$ (COD=cyclooctadiene) in tetrahydrofuran followed by the treatment of the reaction product with Et$_2$O leads to the unprecedented formation of coordinated ethylene to give the new heterodimetallic complexes [Cp$_2$'Nb(PPh$_2$)$_2$RhC$_2$H$_4$] (Cp=C$_5$H$_5$; Cp'=C$_5$H$_4$CH$_3$) and LiCl. The structure of [Cp$'_2$Nb(PPh$_2$)$_2$RhC$_2$H$_4$] (Cp=C$_5$H$_5$) was established spectroscopically and [Cp$'_2$Nb(PPh$_2$)$_2$RhC$_2$H$_4$] (**25**) Cp'=C$_5$H$_4$CH$_3$) by X-ray diffraction. The geometry at rhodium is pseudo-triangular, the [Nb(μ-P$_2$)RhC$_2$] fragment being almost planar; the [Nb–Rh] bond distance is 2.869(2) Å [46].



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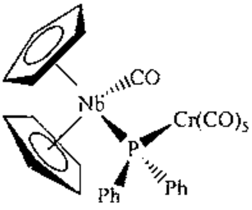
Completely reduced [Cp*$_2$NbCl$_2$] (Cp*=η^5−C$_5$Me$_5$) solutions (two equivalents of Na-Hg) which were previously supposed to contain two isomers A and B of decarnethylniobocene react with sulfur to give products (**26**)–(**29**). ^{1}H and ^{13}C NMR spectroscopic investigations allow for the first time a clear assignment of the structures of A and B. As (**26**) and (**27**) are identical with the previously reported [Cp*$_2$Nb(η-S$_2$)L] derivatives (L=H(26), SH(27)) a bent niobocene structure follows for isomer A. Products (**28**) and (**29**) are in agreement with structures involving an η^1:η^5-tetramethylfulvene ligand which in the case of (**29**) is slightly modified by sulfur insertion into the CH$_2$Nb bond. Thus the structure of isomer B may be derived from bent niobocene by a hydride migration from one CH$_3$ group to niobium [47].

Solutions containing, or made from, the [MCl$_4$] (M=V, Nb, Ta) compounds and alkyl phosphines have been studied [48]. It has been concluded that no [VCl$_4$(PR$_3$)$_2$] species survive, the main reactions being to give various V-III species, such as [VCl$_4$(PR$_3$)$_2$]$^-$ accompanied by varying amounts of [VOCl$_2$(PR$_3$)$_2$] species which are responsible for the observed EPR spectra. When the [*trans*-$MCl_4(PEt_3)_2$] molecules are introduced and the solutions are scrupulously protected from laboratory air, little or no EPR intensity can be recorded.

New terminal monophosphido complexes derived from bent niobocene $Cp(2)Nb(L)PPh_2$ ($L=P(OMe)_3PMe_2H$) have been prepared by a procedure described earlier for [$Cp_2Nb(CO)PPh_2$] [49]. These metallophosphines have been used to bind the [$M(CO)_5$] (M = Cr, Mo, W) fragments. The expected dimetallic monobridged complexes of the type [$Cp_2Nb(L)(\mu\text{-}PPh_2)M(CO)_5$]($L=CO$, $P(OMe)_3$, PMe_2H; M = Cr, Mo, W) are formed. When L = CO the dibridged compounds [$Cp_2Nb(\mu\text{-}PPh_2)(\mu\text{-}CO)M(CO)_4$] (M = Cr, W) are also obtained. All new mono- and dimetallic complexes have been characterised by ^1H and ^{31}P NMR and IR spectroscopies. X-ray diffraction studies of solvated [$Cp_2Nb(CO)(\mu\text{-}PPh_2)M(CO)_5$] (**30**) and [$Cp_2Nb(P(OMe)_3)(\mu\text{-}PPh_2)Cr(CO)_5$] (**31**), indicate that the metallic centres in both complexes are tethered by a single bridge. The large Nb-P-Cr angles (125.94(8) and 129.11(5)°, respectively) and the long Nb-Cr distances (4.653(1) and 4.7575(9) Å, respectively) clearly show the absence of metal-metal interaction [49]



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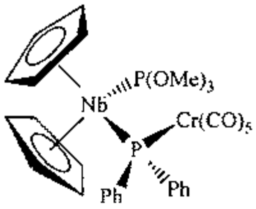

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The electrochemistry and spectroelectrochemistry of the substituted group V carbonyl complexes [$XTa(CO)_4(dppe)$] (X = I, Br) and [$XM(CO)_2(dppe)_2$] (X = I, Br, Cl, H; dppe = 1,2-bis(diphenylphosphino)ethane; M = Nb, Ta) have been investigated [50]. The [$XTa(CO)_4(dppe)$] tetracarbonyl species exhibit irreversible oxidations at $E(a) = +868$ mV ($X^- = Br^-$) and $E(a) = +1276$ ($X^- = I^-$) mV. Spectroelectrochemical oxidation of these complexes at $E(app) = +1000$ mV indicates that CO is evolved with decomposition to non-carbonyl containing products. The reduction chemistry of [$ITa(CO)_4(dppe)$] showed an irreversible cathodic process at $E(c) = -1541$ mV in $TBA+PF_6$-/thf with two coupled oxidation processes [at $E(a) = -530$ mV and $E(a) = +100$ mV]. Spectroelectrochemical reduction of [$ITa(CO)_4(dppe)$] generates [$Ta(CO)_4(dppe)$]$^-$; oxidation of the anion produces [$ITa(CO)_4(dppe)$] at the first coupled process and [$HTa(CO)_4(dppe)$] at the second, respectively. The more highly substituted [$XM(CO)_2(dppe)_2$] compounds exhibit one-electron reversible oxidative processes in $CH_2Cl_2/TBA+PF_6^-$ [E(o) ca. -270 to $+110$ mV] that generate stable (electrochemical time scale) 17-electron species, [$XM(CO)_2(dppe)_2$]$^+$ that were also characterised by IR spectroelectrochemical techniques. EPR spectra observed for these radical cations exhibit ten line signals at $g = 2.04$ ($X^- = Cl^-$) and $g = 2.05$ ($X^- = H^-$) with characteristic coupling to ^{93}Nb ($I = 9/2$) ($A = 115$ G for $X^- = Cl^-$; $A = 113$ G for $X^- = H^-$). Attempts to isolate salts of the $[XM(CO)_2(dppe)_2]^+$ species were unsuccessful [50].

Half–sandwich imido tantalacyclopentane complexes have been prepared via alkene coupling reactions and aspects of their novel insertion chemistry with CO and MeCN reported [51].

Treatment of $[CpCp'Ta(CO)(PPh_3)]Cl$ ($Cp' = \eta^5$-C_5H_5, η^5-C_5Me_5, or η^5-C_5Me_4Et, respectively, Cp, Cp*) with sodium methoxide results in the formation of metallophosphinite complexes $[CpCp'Ta(CO)]$. These compounds exhibit basic properties and Lewis acid fragments [H^+ or $Cr(CO)_5(thf)$] readily undergo coordination at the phosphorus atom: formation of only one stereoisomer is observed [52].

2.4. Other donor sets

Catalyst systems of $[MX_2(\eta^5\text{-}C_5R_5)(\eta^4\text{-diene})]$ (M = Nb and Ta; R = H and CH_3; X = Cl and CH_3) in a combination of methylaluminoxane (MAO) are the precursors of the living polymerisation of ethylene [53]. Mono-diene complexes $[MCl_2(\eta^5\text{-}C_5R_5)(\eta^4\text{-diene})]$ [M = Nb, R = CH_3 (**32**); M = Ta, R = CHS (**33**); M = Ta, R = H (**34**); M = Nb, R = H (**35**); diene = buta-1,3-diene (a), isoprene (b), 2,3-dimethylbuta-1,3-diene (c)] were prepared by the reaction of $[MCl_4(\eta^5\text{-}C_5R_5)]$ with two equivalents of the methylated allyl Grignard reagents in thf. Reaction of (**33**) and (**34**) with MeMgI afforded dimethyl complexes, $Ta(\eta^5\text{-}C_5R_5)(\eta^4\text{-diene})Me_2$[R = CH_3 (**36**); R = H (**37**)], respectively. The polymerisation of ethylene catalysed by 1/MAO, 2/MAO, and 5/MAO at low temperature (−20 °C) gave polyethylene with very narrow polydispersities (M_w/M_n) as low as 1.05). The niobium complexes are superior to the tantalum complexes in terms of the catalyst activity and the polydispersity. When the ligand was Cp instead of Cp*, the catalyst activity of (**34**) for the polymerisation of ethylene at −20 °C increased but the polydispersity of the obtained polyethylene broadened ($M_w/M_n = 1.40$). Protolytic reaction of (**36a**) with one equivalent of triflic acid TfOH produces $[TaCp^*(\eta^4\text{-isoprene})(CH_3)(OSO_2CF_3)]$ (**38**), whose structure has been determined by single-crystal X-ray diffractometry. The molecular structure shows that (**38**) is not a cationic complex and that the tantalum atom is effectively a stereogenic centre surrounded by four different ligands: η^1-triflate, η^5-Cp*, η^4-isoprene, and methyl. A cationic species derived from (**36b**) and $B(C_6F_5)_3$ was detected by ^{1}H NMR spectroscopy and found to be active in ethylene polymerisation. A system of one of the bis-diene complexes of the type $M(\eta^5\text{-}C_5R_5)(\eta^4\text{-2,3-dimethyl-1,3-butadiene})_2$ [M = Nb, R = H; M = Nb, R = CH_3; M = Ta, R = CH_3] in the presence of a large excess of MAO was also found to be an active catalyst for the polymerisation of ethylene [53].

The reaction between $[INb(CO)_3(PR_3)_3]$ and diynes yielded the complexes all-*trans*$[INb(CO)_2(PR_3)_2diyne]$ ($PR_3 = PEt_3$; diyne = 2,4-hexadiyne, 1,5-hexadiyne; $PR_3 = PMe_2Ph$, diyne = 2,6-octadiyne). Only one of the acetylenic bonds coordinates.

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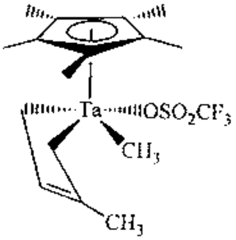
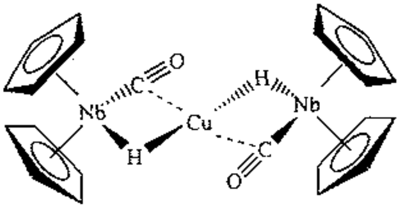


Reaction of $[INb(CO)_3(PMe_2Ph)_3]$ with $Ph_2PC=CPPh_2$ generated $[INb(CO)_2(PMe_2Ph)_2(Ph_2PC=CPPh_2)_2]$, again with the ligands mutually *trans* [54].

Injected ion drift tube techniques, including ion mobility measurements and annealing and fragmentation studies, have been used to examine the isomers present for NbC_n^+ ($n=15$–50) clusters [55]. Isomers attributed to niobium-containing monocyclic and bicyclic rings, graphitic sheets, and metallofullerenes have been identified. Monocyclic rings, where the niobium atom appears to be either inserted into or bound to the outside of the ring, dominate for NbC_n^+ with $n<22$. Isomers assigned to bicyclic rings are first observed and become dominant around NbC_{22}^+. Unlike the bicyclic rings for C_n^+ and LaC_n^+, the NbC_n^+ bicyclic rings do not anneal into monocyclic rings. They probably consist of two rings joined together by a niobium atom. An isomer attributed to NbC_n^+ graphitic sheets is present for $n>22$ and becomes important for clusters with around 30 carbon atoms. Metallofullerenes are first observed for NbC_{28}^+ and become a major isomer for clusters with $n>31$. Both endohedral metallofullerenes and networked metallofullerenes (where the metal atom is part of the cage) have been identified. For clusters with more than around 30 carbon atoms the NbC_n^+ bicyclic rings can be annealed into metallofullerenes and, for the smaller ones, metal-containing graphitic sheets. The isomers observed are similar to those found for pure C_n^+ and LaC_n^+, but the niobium atom has a substantial effect on the properties and the abundances of the different isomers [55].

The reactions of $[Nb(C_5H_4SiMe_3)_2H(CO)]$ with $[Cu(MeCN)_4]BF_4$, $CuPPh_3Cl/TlPF_6$, $AgBF_4$, $AgPPh_3Cl/TlPF_6$, and $Au(tht)Cl/TlPF_6$ lead to the new adducts $[Nb(C_5H_4SiMe_3)_2H(CO)(\mu\text{-}H)_2M]^+$ (M = Cu,Ag,Au), in which the coinage metal cation is only linked to the hydride of each niobium centre, whereas the reaction with $[Au(PPh_3)]^+$ leads to $[Nb(C_5H_4SiMe_3)_2H(CO)(\mu\text{-}H)Au(PPh_3)]PF_6$. The crystal structure of $[\{Nb(C_5H_4SiMe_3)_2(CO)\}_2(\mu\text{-}H)_2Cu]^+$ (**39**) has been determined by X-ray diffraction methods [56]. The crystals are monoclinic, space group $P2_1/c$, with $Z=4$ in a unit cell of dimensions $a=13.048(5)$, $b=12.490(4)$, $c=30.131(9)$ Å, $\beta=94.52(2)°$.

The ethylene complex $[TaCp(\eta^4\text{-butadiene})(\eta^2\text{-}C_2H_4)(PMe_3)]$ was prepared in 77% yield by the reaction of $[TaCpCl_2(\eta^4\text{-butadiene})(\eta^2\text{-}C_2H_4)]$ with two equivalents of EtMgI in the presence of one equivalent of PMe_3. In the absence of PMe_3, $[TaCp(\eta^4\text{-butadiene})(\eta^2\text{-}C_2H_4)(PMe_3)]$ was initially formed but this gradually decomposed to give the known metallacyclic compound $[Ta(CH_2CH_2CH_2CH_2)Cp(\eta^4\text{-butadiene})]$ [57]. Carbonylation of $[TaCp(\eta^4\text{-butadiene})(\eta^2\text{-}C_2H_4)(PMe_3)]$ afforded a monocarbonyl complex [TaCp



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(butadiene)(CO)(PMe_3)] and a dicarbonyl complex [TaCp(butadiene)$(CO)_2$], while reaction with diphenylacetylene under UV irradiation gave a reversible addition product [TaCp(η^4-butadiene)(η^2-PhC=CPh)(PMe_3)] [57].

The preparation and crystal structure of the tantalum-benzyne complex [TaCp*(η^4-buta-1,3-diene)(η^2-C_6H_4)] (**40**) together with its reactions have been studied [58]. The benzyne complex (**40**) was prepared by thermolysis (70 °C, 21 h) of the methyl phenyl complex [Ta(CH_3)(C_6H_5)Cp*(η^4-buta-1,3-diene)] (**41**), which was synthesised by successive treatment of [TaCl_2Cp*(η^4-buta-1,3-diene)] (**42**) with one equivalent of PhMgI and with one equivalent of MeMgI in thf. The rate of thermolysis of (**41**) in C_6D_6 measured at the temperature range between 50 and 75 °C gave the thermodynamic data AG‡(55 °C)=27.2$\pm$0.5 kcal mol^{-1}. In the ^{13}C NMR spectrum of (**40**), a signal due to the *ipso* carbon atoms of benzyne was observed at δ_C 203.0. The monomeric structures of (**41**) and (**40**) were confirmed by single-crystal X-ray analysis. Complex (**40**) is the first example of the parent benzyne complex bearing a metallocene-like [MCp(diene)] fragment and thus expected to react with a wide range of organic substrates. Ethylene and 2-butyne inserted into the tantalum benzyne bond of (**40**) to form the metallacycles [TaCp*($C_6H_4CH_2CH_2$)(η^4-C_4H_6)] (**43**) and [TaCp*(C_6H_4CHMeCHMe)(η^4-C_4H_6] (**44**), respectively. Acetonitrile and carbon dioxide insert also to give [TaCp*(C_6H_4C(Me)=N)(η^4-C_4H_6)] (**45**) and [TaCp*(C_6H_4C(=O)O)(η^4-C_4H_6)] (**46**), respectively. Complex (**40**) was protonated by methanol and 3,3-dimethyl-1-butyne to form phenyl complexes [Ta(OMe)(Ph)Cp*(η^4-C_4H_6) (**47**) and Ta(C=CCMe_3)(Ph)Cp*(η^4-C_4H_6) (**48**,) respectively. The structures of (**44**), (**45**), (**47**) and (**48**) have been elucidated by single-crystal X-ray analysis [58].

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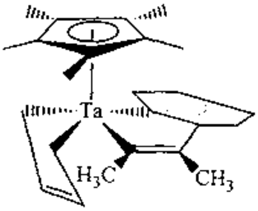

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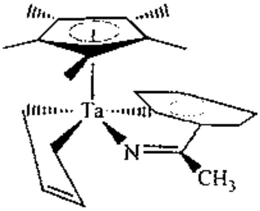

Bulky siloxide and alkoxide ligands, notably silox ^{t}Bu$_3$SiO, and tritox ^{t}Bu$_3$CO, have been employed as ancillary ligands in the chemistry of low-coordinate early transition metal complexes [59]. Related sterically hindered difunctional ligands (e.g. alkoxyalkylphosphines) are utilised to link disparate early and late transition metal

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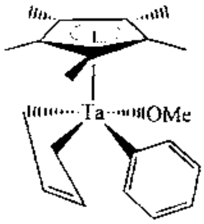

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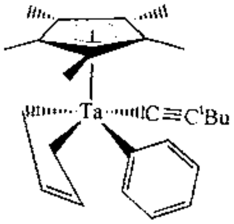

centres together in a quest for cooperative reactivity. This review article focuses on published developments in this area over the past 14 years with emphasis being placed on the rationale for using bulky, hard, anionic donor ligands and the synthesis and reactivity studies of this class of compounds.

The mechanisms of reactions that deoxygenate carbon monoxide (CO) and convert it into longer-chain hydrocarbons are not well understood. A reaction is reported between an early metal methylidene complex and a late transition metal carbonyl species that results in CO deoxygenation along with coupling of the CO carbon to methylidene groups and other CO carbons. The Schrock tantalum-methylene complex $[(\eta^5\text{-}C_5H_5)Ta(=CH_2)CH_3]$ reacts with the trinuclear metal carbonyl species $Ru_3(CO)_{12}$ to yield the cluster complex $[Cp_2(CH_3)Ta(\mu\text{-}O)Ru_3(C_4H_4)(CO)_9]$. This material contains a 4-cumulene ligand that bridges the three late-metal centres. Also formed in this reaction is the unstable free tantalum oxo species, $[(\eta^5\text{-}C_5H_5)Ta(=O)CH_3]$. A crystal structure of the $TaRu_3$ cluster is reported along with a proposed mechanism for this unusual carbon–carbon bond-forming reaction [60].

Treatment of tantalum alkyne complexes with lithium salts of allylic alcohols in dmebenzene-thf (1:1:1) at 25 °C for several hours gives 1,4-dienes stereoselectively in good to excellent yields [61].

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