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# 7. Niobium 1992

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*CONTENTS*

## *INTRODUCTION*

This review is intended to cover the literature on the coordination chemistry of niobium for the year 1992 through coverage of *Chemical Abstracts* volumes 116 (July-Dec), 117 and 118 (Jan-June). To keep the review within managable length, we have chosen to limit the study, in a similar fashion to the 1991 review, to low nuclearity inorganic coordination systems only; consequently several areas have had to be omitted. Specifically, organic/organometallic systems have only been included where there was good reason on account of the non-carbon based components of the coordination sphere, high-nuclearity cluster chemistry (including polyoxometallates) and solid state and materials science have been excluded unless again there was a strong reason to include them from an inorganic/coordination chemistry viewpoint.

The layout of the review focuses on the different oxidation states of niobium which range from +5 down to −2. However, most compounds of niobium in oxidation states lower than +5 are found to be stabilised by carbon-based organic ligands and as such lie outside the scope of the present review. Consequently 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

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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.

For background material 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 coordination chemistry for 1991 [2].

## *7.1 NIOBIUM(V)*

### *7.1.1 Complexes with group 17 ligands*

Niobium(V) is a hard Lewis acid and consequently forms complexes readily with hard Lewis bases such as halide anions. Many such homoleptic halide complexes have been studied in detail previously, but there is still current interest in these species, in for example electrochemical, spectroscopic, spectrophotometric studies and in synthetic chemistry particularly involving metallo-organic systems. Some of these applications are outlined below.

The crystal structure of $[Et_3NH][Nb(O)F_4.H_2O]$ has been reported. The structure is orthorhombic containing a six-coordinate niobium coordination sphere in the anion with the oxo function and the water ligand occupying mutually *trans* positions [3]. In a similar vein, the monoclinic compounds $Na[NbCl_6]$ and its isomorphous tantalum analogue also contain octahedral coordinated metal centres and are in turn isomorphous to compounds such as $Na[SbCl_6]$, $K_2[PtCl_6]$ [4]. The Kα fluorescence spectra of many transition metal salts, including $[NH_4][NbF_6]$ have been measured with a high resolution two-crystal vacuum spectrophotometer [5].

In the field of metal ion extraction and spectrophotometric determinations [6,7], the alternative and simultaneous spectrophotometric determination of niobium and tantalum was examined by using the colour development between *o*-hydroxyhydroquinonaphthalein and niobium and tantalum in the presence of hexadecyltrimethylammonium chloride in strong acid media [7].

Quasi-fluoride glasses were prepared in the LiF-$Ba[NbOF_5]$ binary and LiF-$AlF_3$-$Ba[NbOF_5]$ ternary systems. The LiF content can reach 67.5%. Various properties of the obtained glasses, including chemical durability, thermal behaviour, density, refractive index, UV-VIS and IR transmission have been determined. The relationships between some physical properties of obtained glasses and their composition were studied. LiF dependence of the stability $(T_c - T_g)/T_g$ for the glasses is discussed according to a random polyhedra packing structural model [8].

The $^{93}Nb$ NMR spectral chemical shifts in the complexes $[NbX_{6-n}Y_n]^-$ (n = 0-6; X,Y = F, Cl, Br) have been calculated by the Hartree-Fock method. The calculated values are in very good agreement to the experimental values. Theoretical analyses reveal that the niobium chemical shifts are dominated by the paramagnetic contributions and are due to the *d-d** transition mechanism, in which the critical factor is a variation in the excitation energy ΔE. Based on an orbital interaction picture, ΔE is found to depend on the overlap interactions between the niobium-4*d* and ligand n*p* orbitals. It is also observed that the niobium chemical shift is related to the electronegativity of the ligand donor atom, the niobium net charge and the *d*-electron population of the central niobium metal [9]. Solid state studies on niobium complexes have also been used to summarise the theory for the second-order quadrupolar effects on the centre band for magic angle spinning-solid state NMR spectra of spin-$^1/_2$ nuclei dipolar coupled to the quadrupolar $^{93}Nb$ nucleus [10].

The stability constants of a number of complexes of lithium, zinc and niobium with the ligand, 6,6,6',6'-tetramethyl-4,4'-spirobishexahydro-2,2'-pyrimidinone (L) have been investigated ($NbCl_5.L.2H_2O.Me_2CO$) [11].

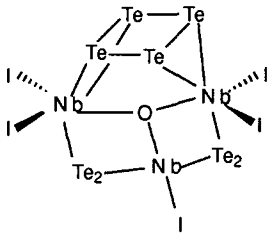
Metallo-organic systems have again been developed from halide containing precursors. For example, $[(\eta^5\text{-}C_5Me_5)NbCl_4]$ has been employed for the synthesis of various reduced species of niobium containing carbonyl and tertiary phosphine ligands [12]. Furthermore, the complex $[Nb(\eta^6\text{-mesitylene})_2]$ (where mesitylene is 1,3,5-trimethylbenzene) has been synthesised by exhaustive reduction of $NbCl_5$ by a reducing mixture of $Al/AlCl_3$ in the presence of mesitylene and dimethoxyethane (dme) or thf [13].

### *7.1.2 Complexes with group 16 ligands*

Within the general area of group 16 donor ligands, (i) oxo, (ii) alkoxo and (iii) sulfur based systems form the bulk of published studies.

In the field of oxo chemistry we have already mentioned above the studies on $[Et_3NH][Nb(O)F_4.H_2O]$ [3] and quasi-fluoride glasses [8].

The high temperature reaction of niobium, $[Nb(O)I_3]$, tellurium and iodine produces $[Te_4Nb_3O(Te_2)_2I_6]I$ which contains a square planar $Te_4$ ring and two $Te_2$ groups coordinated to a trinuclear metal cluster (**1**) [14].

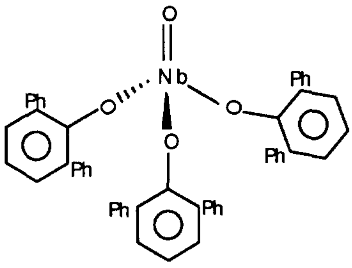


(**1**)

The crystal structure of $[Nb(O)(O\text{-}2,6\text{-}Ph_2C_6H_3)_3]$ (**2**) has been determined by Rothwell and co-workers. The compound is orthorhombic with the expected monomeric, pseudo-tetrahedral geometry and with d(Nb-O) of 1.896Å (average) and d(Nb=O) of 1.685(9)Å [15].

Along similar lines, the synthesis and characterisation *via* spectroscopic and analytical techniques of the four-coordinate compounds $[Nb(O)(O\text{-}2,6\text{-}R_2C_6H_3)_3]$ (R = Me, $^tBu$) have been reported [16]. Presumably, these two species have structures similar to that of (**2**).

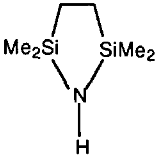
The complex $[Nb(O)(OCH_2CH_2OMe)_3]$ has been prepared by reaction of the respective OEt and $O^iPr$ compounds with $HOCH_2CH_2OMe$ [17].



(2)

A sequence of metathesis reactions has been investigated by Gibson and co-workers. Oxo (M=O), imido (M=NR) and alkylidine (M=CHR) exchange reactions occur readily between the coordinatively unsaturated centres of $[MQ_2X_2]$ (M = Mo, W; Q = O, NR, CHR'; X = $O^tBu$; R = $2,6\text{-}^iPr_2C_6H_3$; R' = $CMe_2Ph$, $^tBu$) and $[M(\eta^5\text{-}C_5R''_5)QX_2]$ (M = Nb, Ta; Q = NR, CHR'; X = Cl, $O^tBu$). A kinetic study of the reaction between $[Mo(O)_2(O^tBu)_2]$ and $[Mo(NR)_2(O^tBu)_2]$ indictaes that the exchange proceeds *via* a four-centre transition state [18].

Oxidation of $[Nb(\eta^5\text{-}C_5Me_5)_2Cl_2]$ with $O_2$ in thf containing traces of $H_2O$ gave $[\{Nb(\eta^5\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)]$ (3) and polymeric $[Nb_2Cl_2O_4(thf)_3]_n$. Compound (3) exists as two isomers distinguished by the relative orientation of $(\eta^5\text{-}C_5Me_5)$ and bridging ligands. Reduction of complex (3) with zinc powder gave $[\{Nb(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)(\mu\text{-}O)\}_3]^+$ (4) which was isolated in combination with the anions $[\{ZnCl_2(\mu\text{-}Cl)\}_2]^{2-}$, $[\{ZnCl\}_4(\mu\text{-}Cl)_6]^{2-}$ and $[\{\{ZnCl\}_6(\mu\text{-}Cl)_8\}^{2-}]_n$. The cluster (4) contained $Nb_3{}^{13+}$, was diamagnetic and had an equilateral triangle of niobium atoms (average Nb-Nb distance 2.876(1)Å) each edge of which is bridged by chlorine and oxygen atoms (average Nb-Cl 2.542(1)Å, average Nb-O 1.937(3)Å) [19]. The geometry and electronic structure of (4) are compared with those of $\{[Re(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)]_3\}^{2+}$ and $\{Nb(\eta^6\text{-}C_6Me_6)(\mu\text{-}Cl)_2]_3\}^{n+}$ (n = 1, 2). Oxidation of the salts of (4) in dichloromethane solution with $O_2$ gave $\{[Nb(\eta^5\text{-}C_5Me_5)Cl]_3(\mu\text{-}Cl)(\mu\text{-}O)_2(\mu_3\text{-}OH)(\eta_3\text{-}O)\}^+$ (5) isolated as the $\{[ZnCl_2(\mu\text{-}Cl)]_2\}^{2-}$ salt. This complex (5) has an isosceles triangle of niobium atoms (Nb-Nb distances of 3.028(2)Å and 3.318(2)Å). The shorter of the two niobium-niobium distances is bridged by chlorine. The $\mu_3$-O atom has much shorter distances to the two niobium atoms forming the long edge (average distance 2.046(8)Å) than to the third niobium (2.228(8)Å). The $\mu_3$-OH ligand has equal distances to all three niobium atoms (2.207(8)Å) [19].



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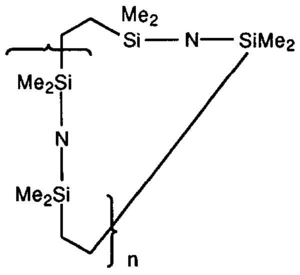


(7)

Complexes of the form [$L_3M{=}O$] (M = Nb, Ta; HL = (**6**)) are accessible by the reaction of [$M(O)Cl_3$] with LiL in 30% and 19% isolated yield respectively. The new silazanes (**7**) (n = 2, 3) are prepared from $Me_2ClSiCH_2CH_2SiClMe_2$ and $NH_3$ [20].

In the area of organometallic chemistry, mixtures of $Et_3Al$ or RMgBr (R = alkyl) reducing agents and 2,6-dimethylphenoxo complexes of tungsten(VI) or niobium(V) have been found to be catalyst precursors for the polymerisations of alk-1-ynes. The number of aryloxo functions on the metal centre controls the activity of the polymerisations of monoalkyl substituted alkynes resulting in the formation of high molecular mass polymers [21].

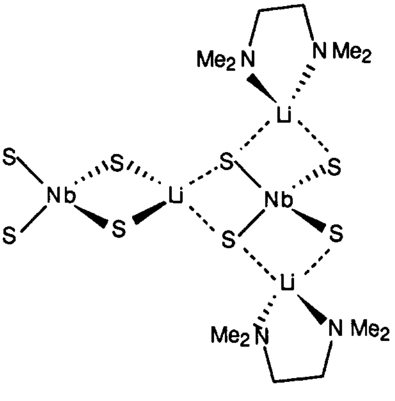
The carbenoid-like complex [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br$] reacts with one equivalent of several ketenes $R^1R^2C{=}C{=}O$ to give the niobium(V) complexes, [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(C,O\text{-}R^1R^2CCO)$] ($R^1 = R^2$ = Ph; $R^1 = R^2$ = Me; $R^1$ = Ph, $R^2$ = Me; $R^1$ = Ph, $R^2$ = Et) with the expected carbon and oxygen bonding mode as found in several early transition metal moieties. The protonation of these moieties with one equivelent of $H^+$ (ethereal solution of $HBF_4$) affords the cationic niobocene [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(R^1R^2HCCO)$]$^+$ ($R^1 = R^2$ = Ph; $R^1 = R^2$ = Me; $R^1$ = Ph, $R^2$ = Me; $R^1$ = Ph, $R^2$ = Et). Both of the above ketene complexes undergo a 2-electron reduction without transformation of the ketene moiety to give the same anionic niobium(III) species [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(C,O\text{-}R^1R^2CCO)$]$^-$ [22].

The tris(4-methylbenzyl) compound [$Nb(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(CH_2C_6H_4Me\text{-}4)_3$] (**8**) acts as a catalyst precursor for the hydrogenation of a variety of aryl phosphine ligands. Triphenylphosphine gave tricyclohexylphosphine and $Ph_2P(CH_2CH_2)_nPPh_2$ gave $Cy_2P(CH_2CH_2)_nPCy_2$ (n = 1,3) [23]. The same compound (**8**) is also a useful catalyst precursor for the hydrogenation of many polynuclear aromatic hydrocarbons [24]. Typical conditions involve heating cyclohexane solutions of (**8**) and the substrate (*ca.* 20 equivalents) to 80°C under an atmosphere of hydrogen (1200 psi) for 24 h. Under these conditions, naphthalene, 1-Me- and 2-Me-naphthalene, anthracene, and acenaphthene produce tetralin, 1,2,3,4-tetrahydro-5-methylnaphthalene, 1,2,3,4-tetrahydro-6-methylnaphthalene 1,2,3,4,5,6,7,8-octahydroanthracene and 1,2,2a,3,4,5-hexahydroacenaphthylene respectively in >95% yields. Phenanthrene is hydrogenated more slowly to afford a mixture of 9,10-dihydrophenanthrene (20%) and 1,2,3,4,5,6,7,8-octahydrophenanthrene (70%) with 10% remaining as unreacted substrate. Since 9,10-dihydrophenanthrene is not converted to the octahydro derivative under the conditions of the reaction the product mixture must be subject to kinetic control [24].

The complex [$Mn\{Nb(O^iPr)_6\}_2$] has been synthesised by the interaction of the appropriate potassium alkoxometallate in the desired molar ratio with $MnCl_2$ in mixed benzene-alcohol solvent. Chloride replacement reactions lead to the formation of [$\{Nb(O^iPr)_6\}Mn\{Al(O^tBu)_4\}$]. These species have been characterised by elemental analyses, infrared and ESR spectroscopies, and magnetic susceptibility measurements [25].

The third main area of group 16 ligand chemistry concerns those ligand systems bound by sulfur. A spectrophotometric method for the determination of sulfur has been developed based on the extraction of a ternary complex with $SCN^-$ and methotrimepyrazin from 1-2 M HCl medium into trichloroethylene [26]. The absorbance of the organic phase was measured at 400 nm and the method applied to the detection of niobium in standard minerals.

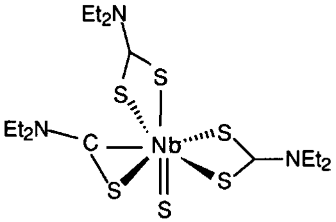
The anion $[NbS_4]^{3-}$, previously known only as an intractable solid prepared at high temperature, was prepared in the system $Nb(OEt)_5/(Me_3Si)_2S/LiOMe$ (1:4:3) in acetonitrile solvent at ambient temperature. The initial product is orthorhombic $Li_3[NbS_4].4\ CH_3CN$. A pure stable product can be obtained by crystallisation of the tetramethylethylenediamine (TMEDA) adduct, $Li_3[NbS_4].2$ TMEDA (**9**) [27].



(**9**)

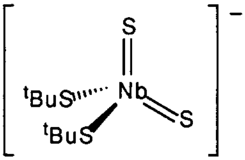
Compound (**9**) contains discrete, essentialy tetrahedral $[NbS_4]^{3-}$ species with imposed $D_{2d}$ symmetry and four S-S edges bridged by $Li^+$ in a distorted tetrahedral coordination. Opposite edges are bridged by $Li^+$ to form a linear chain of $[NbS_4]^{3-}$ units, two other edges are bridged by $Li^+$ coordinated to two molecules of $CH_3CN$ or a single molecule of TMEDA. Differences in colour of the three chromophores in the series of compounds $[MS_4]^{3-}$ (M = V, Nb, Ta) arise from a progressively high-energy shift of the first L-M charge transfer band ($1t_1$-2e) in the series, M = V (501, 561 nm), Nb (340 nm), Ta (300 nm). $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ are the simplest of the few discrete soluble chalcogenoniobates and tantalates that have thus far been prepared. The role of $Li^+$ in stabilising and solubilising the product compounds is considered and unknown tetrathiometallates that might be obtained by the cation stabilising aspect of the methods used here are pointed out [27].

$Nb(S)(\eta^2\text{-}SCNEt_2)(\eta^2\text{-}S_2CNEt_2)_2$ has been prepared from the reaction of $NaS_2CNEt_2$ with $Nb_2Cl_6(THT)_3$ (THT = tetrahydrothiophene) and characterised by spectroscopic methods and *via* a single-crystal X-ray diffraction study. $Nb(S)(\eta^2\text{-}SCNEt_2)(\eta^2\text{-}S_2CNEt_2)_2.{}^1/_4\ C_6H_6$ (**10**) is triclinic. The coordination sphere around the niobium(V) atom consists of a single sulfur atom, two chelating dithiacarbamate (dtc) ligands and one thiocarbamyl ligand bound through both carbon and sulfur. The resulting structure is a seven-coordinate pentagonal bipyramid with the sulfur atom and one of the sulfur atoms of the dtc ligands occupying polar positions. The formation of the sulfur and thiocarbamylligands results from oxidative addition of one of the C-S bonds to the metal centre in the (III) oxidation state with concomitant cleavage of the dimeric structure of the precursor complex. A dimeric compound with bridging tridentate dtc ligands is proposed as a necessary intermediate for the oxidative addition reaction to occur [28].



(10)

The syntheses of $[Ph_4P][Nb(S)_2(SCMe_3)_2]$ **(11)** and $[Et_4N][Nb(S)(SCMe_3)_4]$ **(12)** in the reactions of $NbCl_5$ with $NaSCMe_3$ in acetonitrile solvent are described. The synthesis of **(11)** can also be accomplished by the oxidation of **(12)** with stoichiometric quantities of sulfur. Compound **(11)** and $[Et_4N][Nb(S)(SCMe_3)_4]_{0.9}[Nb(S)_2(SCMe_3)_2]_{0.1}$ **(13)** have been studied by single-crystal X-ray diffraction. The site of the anion in **(13)** is occupied by $[Nb(S)(SCMe_3)_4]^-$ to the extent of 90% and by $[Nb(S)_2(SCMe_3)_2]^-$ to the extent of 10% as verified by $^1H$ NMR spectroscopy. The monoanions in **(11)** and **(13)** show the metals to be in tetrahedral and trigonal bipyramidal coordination environments respectivly. The (Nb=S) bonds in **(11)** and **(13)** are 2.187(3)Å and 2.194(2)Å. The (Nb-S) bonds in **(11)** and the equatorial (Nb-S) bonds in **(13)** of 2.377(4)Å and 2.38(1)Å are significantly shorter than the axial bond in **(13)** at 2.567(2)Å. The latter, in a position *trans* to the (Nb=S) bond is subject to a pronounced *trans* influence. The $^1H$ NMR spectrum of **(11)** in $CD_3CN$ solvent shows a single resonance for the $^tBuS$ ligands at δ 1.38 ppm whereas for **(12)** this same resonance appears at δ 1.58 ppm. Mass spectrometric studies of reaction biproducts suggest that the sulfido ligands in **(11)** and **(12)** form as a result of both heterolytic and homolytic C-S bond cleavage reactions that occur in parallel [29].



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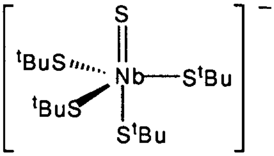


(13)

The reaction of $[Nb(\eta^5\text{-}C_5H_4{}^tBu)_2H_3]$ with sulfur was investigated with regard to the kinetic stabilisation of as yet elusive intermediates during the formation of the polysulfide complex, $[Nb_2(\eta^5\text{-}C_5H_4{}^tBu)_4S_9]$. Therefore, the complexes $[Nb(\eta^5\text{-}C_5H_4{}^tBu)S_3H]$ and $[Ta(\eta^5\text{-}C_5H_4{}^tBu)S_2H]$ were synthesised in a related reaction and structurally investigated [30]. Despite the problematic location of the hydrogen atom during X-ray characterisation, both of these two complexes contain $M(\eta^2\text{-}S_2)$ cores to which either an SH or H group are attatched. Attempts to prepare metallocene sulfides by metathesis reactions of $[Nb(\eta^5\text{-}C_5H_4{}^tBu)_2Cl_2]$ and $Li_2S_5$ gave the polynuclear compounds $[Nb_3(\eta^5\text{-}C_5H_4{}^tBu)_3S_{10}O]$ and $[Nb_4(\eta^5\text{-}C_5H_4{}^tBu)_4S_{13}]$ [30].

### *7.1.3 Complexes with group 15 ligands*

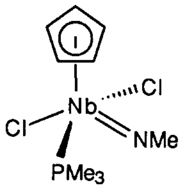
The most predominant systems with ligands bearing donor atoms from group 15 are those with nitrogen-based ligands. Since nitrogen is a harder donor atom than phosphorus or any of the lower congeners, its complexes with the hard acid Nb(V) tend to be energetically more favourable. Within the area of nitrogen-based ligands, the imido (nitrene, =NR) ligand has continued to be amoung the most widely studied. In many cases the imido function is present as a spectator ligand, providing electronic control over the metal oxidation state and steric control over the metal primary coordination sphere. Nevertheless, certain systems have come to light recently which involve the imido group undergoing a transformation. A selection of this year's imido based chemistry is outlined below.

The compound $[Nb(=NMes)_2Cl_2(py)_2]$ (Mes = 2,4,6-$Me_3C_6H_2$) has been prepared from the reaction between $[Nb(NEt_2)_2Cl_3]_2$ with two equivalents of LiNHMes per niobium. The compound $[Nb(NEt_2)_2Cl_3]_2$ also reacts with excess LiNHMes in thf solvent to afford $[Li(thf)_2]_2[Nb(=NMes)_3(NHMes)]$ [31]. The tantalum analogues can be synthesised using an analogous procedure. Subsequent experiments have suggested that the tris(imido) function arises *via* an intermolecular deprotonation of $[Nb(NMes)(NHMes)_2]^-$. The complex $[Li(thf)_2]_2[Nb(=NMes)_3(NHMes)]$ reacts with a single equivalent of $^nBuLi$ to afford the metathesis product complex, $[Li(thf)_2]_2[Nb(=NMes)_3Bu]$ [31].

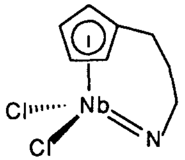
The mixed imido-amido complex $[Nb(=NSiMe_2H)(N(SiHMe_2)_2)_3]$ has been formed *via* the reaction of $LiN(SiHMe_2)_2$ and $NbCl_5$. It was noted that no decomposition *via* β-hydrogen elimination or abstraction was observed for this compound [32].

Gibson and co-workers have reported on a sequence of chiral-at-metal, half-sandwich complexes of niobium of the form $[Nb(\eta^5\text{-}C_5H_5)(=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(PMe_3)L]$ (L = CO, $C_2H_4$, $C_3H_6$, MeCCMe, PhCCPh) starting from the di-chlorinated complex $[Nb(\eta^5\text{-}C_5H_5)(=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2]$ [33]. The structure of the propene complex shows the expected distorted three-legged piano stool geometry. The same group have followed up this line of research with an investigation of half-sandwich methylimido complexes of niobium, $[Nb(\eta^5\text{-}C_5R_5)(=NMe)Cl_2]$ (R = H, Me) prepared by treatment of $[Nb(\eta^5\text{-}C_5R_5)Cl_4]$ with $NMe(SiMe_3)_2$ in $CH_3CN$ solvent. The sterically hindered alkyl and arylimido analogues $[Nb(\eta^5\text{-}C_5H_5)(=NR)Cl_2]$ (R = $^tBu$, -2,6-$^iPr_2C_6H_3$) and $[Nb(\eta^5\text{-}C_5Me_5)(=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2]$ are obtained upon treatment of $[Nb(\eta^5\text{-}C_5R_5)Cl_4]$ with two equivalents of $NHR(SiMe_3)$ in chlorocarbon solvent. Four complexes have been studied by single-crystal X-ray diffraction analyses, which reveals that all the complexes are monomeric with quasi-linear imido ligands [34]. The (M=N) bond distances range from 1.744(3)-1.780(5)Å which are consistent with pseudo triple bonds. The imido complexes react with tertiary phosphine ligands ($PR_3$) to give eighteen-electron adducts of the form $[Nb(\eta^5\text{-}C_5H_5)(=NR)Cl_2(PR_3)]$. The single-crystal X-ray study of the complex with R = Me (**14**), shows the expected distorted four-legged piano stool geometry with the phosphine ligand coordinated *cis* to the imido ligand and to one of the chloro ligands [34]. Alkoxo and aryloxo analogues can be prepared in a similar manner by metathesis reactions with two equivalents of LiOR reagents in $Et_2O$ solvent. Fenske-Hall calculations indicate that there exists a close relationship between the $[Nb(\eta^5\text{-}$

$C_5H_5)(=NR)]$ fragment and the bent-metallocene moiety $[M(\eta^5\text{-}C_5H_5)_2]$ for the group 4 transition elements [34].



**(14)**



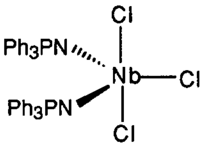
**(15)**

In a similar fashion, the complex **(15)** has been prepared in a one-pot reaction between $NbCl_5$ and $C_5H_4(SiMe_3)(CH_2)_3N(SiMe_3)_2$. A single-crystal X-ray study on the $PMe_3$ adduct has confirmed the novel intramolecular chelating imido ligand [35].

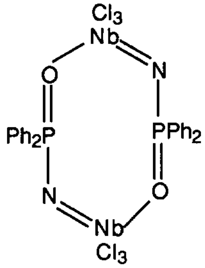
It has been demonstrated recently that the imido ligand may not be quite the spectator ligand that is normally considered to be its only role. Oxo, imido and alkylidine exchange reactions occur readily between the coordinately unsaturated centres of $[MQ_2X_2]$ (M = Mo, W; Q = O, NR, CHR'; X = $O^tBu$; R = $2,6\text{-}^iPr_2C_6H_3$; R' = $CMe_2Ph$, $^tBu$) and $[M(\eta^5\text{-}C_5R''_5)QX_2]$ (M = Nb, Ta; Q = NR, CHR'; X = Cl, $O^tBu$) [18].

Since the imido ligand is so widespread in the coordination chemistry of the earlier transition elements, several results from electronic structure calculations are worthy of note. A wide range of transition metal imido complexes have been examined by *ab initio* molecular orbital (MO) calculations. The agreement between geometries for calculated models and their experimental counterparts ranges from very good to excellent, as found in previous studies of multiply bonded group 4 complexes. Together, these data suggest that the accuracy one has come to expect for the prediction of structural properties for main-group compounds may become a reality for transition metal compounds [36]. The accurate prediction of molecular structure also leads one to infer that the bonding in these complexes is also accurately described. The MC/LMO/CI (multiconfiguration/localised MO/configuration interaction) technique shows that eight resonance structures are most convenient in the description of the metal-imido linkage. Three of these account for approximately two thirds of the total contributions; two resonance structures, both possessing a dative $\sigma$-bond correspond to novel bonding descriptions for transition metal imido complexes. The dative character of the $\sigma$-bond is largely unappreciated. The MC/LMO/CI results also indicate that the metal imido bond is intermediate between a double and a triple bond. Nucleophilic resonance structures decrease as one goes to the right in the transition series while electrophilic ones show the reverse behaviour, in agreement with the observed reactivity [36].

The compound $[NbCl_3(NPPh_3)_2]$ **(16)** was prepared from $NbCl_5$ and $Me_3SiNPPh_3$ in $CH_3CN$ solvent. Colourless, moisture sensitive crystals proved suitable for asingle crystal X-ray structure determination which reveals that the complex is monomeric containing the niobium atom in a distorted trigonal bipyramidal geometry [37]. The nitrogen atoms of the two phosphiniminato ligands are in equatorial positions along with a single chlorine ligand. The (Nb-N) and (P-N) distances are in accordance with single bonds whilst with a mean value of 2.42Å, the (Nb-Cl) distances are remarkably long.



**(16)**



**(17)**

In a similar fashion to **(16)**, the eight-membered ring compound **(17)** has been prepared from the reaction of $NbCl_5$ and $Me_3SiOPPh_2NSiMe_3$. Recrystallisation from $CH_3CN$ affords crystals suitable for X-ray diffraction study which confirms the presence of the novel eight-membered heterocyclic ring system [38].

The compound $[Na(15\text{-crown-}5)][NbF_6(NPPh_3)]$ has been prepared by the reaction of $[NbCl_4(NPPh_3)]_2$ with excess NaF in $CH_3CN$ solvent in the presence of 15-crown-5. Partial hydrolysis of $[Na(15\text{-crown-}5)][NbF_6(NPPh_3)]$ leads to $[Ph_3PNH_2][NbF_5(NPPh_3)]$. Single-crystal X-ray determination of both of these two complexes reveals that they both form ion pairs in which the niobate anions contain almost linear $[MNPPh_3]$ moieties [39].

### *7.1.3 Complexes with other donor ligands*

Amongst ligands with donor atoms from other groups of the periodic table, silicon based ligands have been the subject of increasing attention, especially systems containing transition metal-silicon single and multiple bonds.

The electronic structure of complexes arising from the formation of a double bond between a silylene ligand [SiRR'] and a high valent transition metal fragment have been investigated using *ab initio* wave functions including the effects of electron correlation [40]. Using the analogy of carbon, these complexes may be referred to as Schrock-type silylidenes. A prime motivation for this work is that complexes of this type, unlike their carbon counterparts, have so far eluded successful experimental characterisation. Several conclusions can be reached from the calculations; (i) the inclusion of electron correlation is necessary for an accurate description of the [M=Si] $\pi$-bond while the [M=Si] $\sigma$-bond is adequately described at the Hartree-Fock level, (ii) the GVB overlap (an indicator of kinetic stability) and [M=Si] force constants (an indicator of thermodynamic stability) increase upon replacement of hydrogens with other ligands ($H_nM{=}SiH_2$ to $Cl_nM{=}SiH_2$) and substituents on the silicon atom ($H_nM{=}SiH_2$ to $H_nM{=}SiCl_2$) that are more electron-withdrawing than hydrogen, (iii) the [M=Si] force constants are larger for group 5 rather than group 4 systems in the same period (Nb > Zr and Ta > Hf) and (iv) analysis of the molecular and electronic structural data using the MC/LMO/CI approach leads to the conclusion that stronger [M=Si] double bonds arise when the [M=Si] π-bond is made more back-bonding in character. The results suggest several strategies for synthesising a silylidene which is stable enough to allow for experimental characterisation [40].

Another theoretical study has been made of the stabilities and reactivities of Schrock-type metal-silylene complexes of the forms [$MeH_2Nb{=}SiR_2$] (R = H, OH) as well as the Fischer- type systems [$(CO)_5Cr{=}SiR_2$] and [$(CO)_4Fe{=}SiR_2$] (R = H, OH) [41]. The stability of the [Nb=Si] bond in [$MeH_2Nb{=}SiR_2$] is larger than that of the iron and chromium complexes which have been synthesised recently. This suggests that the Schrock-type silylene can be synthesised as a stable compound. An orbital correlation diagram shows that there is an obvious [M=Si] double bond in [$MeH_2Nb{=}SiR_2$]. Both electrophiles and nucleophiles will attack niobium, although nucleophilic attack at silicon is possible. The first $^0S$ and $^1T$ excited states lie within 1 eV of the ground state and excitations to these levels apparently do not weaken the niobium-silicon bonding [41].

## *7.2 LOWER OXIDATION STATES OF NIOBIUM*

### *7.2.1 Complexes with group 17 ligands*

Most studies of lower oxidation state complexes of niobium containing ligands with group 17 donor atoms have involved their use as synthetic precursors, especially in the field of metallo-organic chemistry.

Pedersen has reported on the reduction of $NbX_5$ (X = Cl, Br) with $Bu_3SnH$ in either thf or dme solvent to afford [$NbX_4(thf)_2$] and [$NbX_3(dme)$] respectively [42].

Green and co-workers have reported on the reaction between [$NbCl_4(thf)_2$] with $LiC_9H_7$ or $NaC_9H_7$ which gives [$Nb(\eta\text{-}C_9H_7)_2Cl_2$] which reacts in turn with $NaBH_4$ to give [$Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)$]. The bridging and terminal $BH_4$ hydrogens exchange on the NMR spectroscopic timescale with ΔG of activation of *ca.* 55 kJ $mol^{-1}$ [43]. [$Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)$] reacts with $PMe_2Ph$ or pyridine *via* $BH_3$ extrusion to afford [$NbH(\eta\text{-}C_9H_7)_2L$] (L = $PMe_2Ph$, pyridine). The pyridine ligand undergoes restricted rotation about the [Nb-N] bond (ΔG of activation of *ca.* 52 kJ $mol^{-1}$). Many other synthetic studies on the complex [$Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)$] are reported [43].

The complex [$Nb(\eta^6$-mesitylene$)_2$] (where mesitylene is 1,3,5-trimethylbenzene) has been synthesised by reduction of $NbCl_5$ by a reducing mixture of $Al/AlCl_3$ in the presence of mesitylene and dimethoxyethane (dme) or thf [13] as mentioned above. [$Nb(\eta^6$-mesitylene$)_2$] is oxidised to [$Nb(\eta^6$-mesitylene$)_2X$] by reaction with 1,1'-dimethyl-4,4'-bipyridinium halides (X = Cl, I). The reaction of both halo compounds with carbon monoxide yielded the niobium(I) derivatives [$Nb(\eta^6$-mesitylene$)_2CO$][$Nb_2(\mu\text{-}X)_3(CO)_8$]. In the case of X = I, infrared studies show the presence of intermediate carbonyl compounds at low temperature, presumably [$Nb(\eta^6$-mesitylene$)_2I(CO)$] and [$Nb(\eta^6$-mesitylene$)_2(CO)$]$^+$. The ionic iodide derivative was shown by single-crystal X-ray diffraction to consist of discrete [$Nb(\eta^6$-mesitylene$)_2(CO)$]$^+$ cations and [$Nb_2(\mu\text{-}X)_3(CO)_8$]$^-$ anions. The two mesitylene groups in the cation are bent and in an eclipsed conformation [13].

Reaction of $LiCH_2PPh_2$ with $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$ gives the paramagnetic complex $[Nb(\eta^5\text{-}C_5H_5)_2(CH_2PPh_2)_2]$ [44]. The complex $[Nb(\eta^5\text{-}C_5H_5)_2(CH_2PPh_2)Cl]$ is observed only as an unstable intermediate. Oxidation of $[Nb(\eta^5\text{-}C_5H_5)_2(CH_2PPh_2)_2]$ by $AgBF_4$ affords $[Nb(\eta^5\text{-}C_5H_5)_2(CH_2PPh_2)_2][BF_4]$ whereas reduction with $Na/C_{10}H_8$ gives $Na[Nb(\eta^5\text{-}C_5H_5)_2(CH_2PPh_2)_2]$. Both are isolable in analytically pure form as stable diamagnetic solids.

Reactions of alkynes RCCR' (R = R' = Me, Et, Ph; R = H, R' = Ph) with the dinuclear halide bridged complexes $Et_4N[Nb_2X_3(CO)_8]$ (X = Br, I) in thf solvent at room temperature gives pale yellow air-sensitive $[NbX(CO)_2(RCCR')_2]_2$ (X = Br, R = R' = Ph; X = I, R = R' = Ph, Et, Me; X = I, R = H, R' = Ph) in moderate yields [45]. The compounds have been characterised by FAB-mass spectrometry, infrared and NMR spectroscopies but spectral data alone have not permitted an unambiguous structural assignment. Treatment of $[NbI(CO)_2(RCCR')_2]_2$ (R = R' = Ph, Et, Me) with $PEt_3$ gave red thf solutions of $[NbI(CO)_2(RCCR')(PEt_3)_2]$. An eighteen-electron configuration in the compounds $[NbX(CO)_2(RCCR')_2]_2$, in the absence of a metal-metal double bond is attained with the alkyne ligands acting as three-electron donors; a postulate that receives some some support from the $^{13}C$ NMR spectral chemical shifts of the alkyne carbon atoms [45].

### *7.2.2 Complexes with group 16 ligands*

Amongst the chalcogens, ligands containing oxygen, sulfur, seleniun and tellurium donor atoms have been studied.

Ether donor ligands have mainly be used as spectator or ancilliary ligands. Thus, the seventeen-electron compounds $[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)]$ undergoes a reversible one-electron oxidation to afford $[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)(thf)][PF_6]$ [46].

The two-electron reduction of $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl_2]$ in the presence of one equivalent of $Ph_2CHCHO$ yields $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(\eta\text{-}C,O\text{-}Ph_2CHCHO)]$ which has been characterised by electron spin resonance (ESR) spectroscopy [47].

Along similar lines, the eighteen-electron ketene complexes $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}C,O\text{-}OCCRR')]$ (R = Et, R' = Ph; R = R' = Me, Ph) undergo facile one-electron reduction to the paramagnetic metalloenolate complexes, $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}C,O\text{-}OCCRR')]^-$ [48]. This process has been studied by cyclic voltammetry, electrolysis and infrared spectroelectrochemistry which indicate that the ketene complexes structurally isosmerise during reduction. The metalloenolates have anomolously low $^{93}Nb$ hyperfine splittings (ESR) which is attributed to the delocalisation of unpaired electron density onto the enolate ligand suggesting that the structural reorganisation involves rotation of the enolate to facilitate resonance delocalisation. Results of infrared spectroelectrochemistry indicate that the anions undergo a slow, reversible chloride ligand loss with subsequent ketene fragmentation; the product thus formed is a carbonyl-alkylidine species. Upon re-oxidisation some of the starting niobium ketene complex is regenerated and the overall process is a redox-induced ketene cleavage-formation sequence. In the presence of added acid (either Lewis or Brønsted) the electrochemistry goes *via* a two-electron sequence to give either niobocene alkyl-carbonyl or ketene-hydride complexes [48]. Further studies on this system by the same group [49] have revealed that $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}C,O\text{-}OCCR(CH_2R'))]$ undergo facile reaction with $[Ph_3C][BF_4]$ to give the cationic α,β-unsaturated metal acyls $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}C,O\text{-}OCCR(CHR'))][BF_4]$. Reaction is stereospecific for *E*-alkenes but these undergo slow isomerisation to a mixture of *E*/*Z* isomers. If both ketene substituents contain accessible allylic hydrogens, the reaction shows little regioselectivity. Preliminary mechanistic studies are consistent with a direct hydride extraction rather than an electron transfer/hydrogen-atom transfer sequence [49].

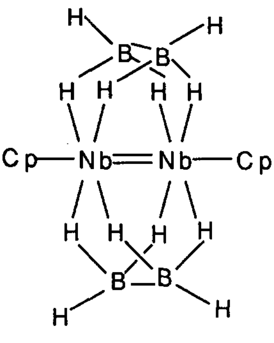
The carbonyl complexes $[Nb(\eta\text{-}C_5H_4Me)_2(CO)R]$ (R = $CH_2Ph$, $CH_2SiMe_3$, $CH_2CMe_3$, Me) react cleanly and quantitatively with di-oxygen ($O_2$) under ambient conditions to produce the corresponding carbon dioxide complexes $[Nb(\eta\text{-}C_5H_4Me)_2(\eta^2\text{-}CO_2)R]$ (R = $CH_2Ph$, $CH_2SiMe_3$, $CH_2CMe_3$, Me). The latter have been characterised spectroscopically and in the case of $[Nb(\eta\text{-}C_5H_4Me)_2(\eta^2\text{-}CO_2)CH_2Ph]$ by single-crystal X-ray diffraction [50]. The stoichiometry of the reaction of $[Nb(\eta\text{-}C_5H_4Me)_2(CO)CH_2Ph]$ with $O_2$ is 2 : 1. Isotopic labelling experiments indicate that the added oxygen atom is derived from $O_2$ and is equally districuted in the two sites of the ($\eta^2$-$CO_2$) ligand.

The interaction of $[Nb(\eta\text{-}C_5H_4Me)_2(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ with several Lewis acids has been found to result in facile decarbonylation. The niobium containing products depend markedly on the nature of the Lewis acid partner. Reaction of $[Nb(\eta\text{-}C_5H_4Me)_2(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ with $LiPF_6$ or $BF_3.Et_2O$ causes both decarbonylation and deoxygenation producing $[Nb(\eta\text{-}C_5H_4Me)_2(F)(CH_2SiMe_3)][Z]$ ([Z] = $PF_6$ or $BF_4$) which have been characterisaed spectroscopically and *via* X-ray diffraction in the case of the $[PF_6]^-$ salt. This complex is also produced in the reaction of the oxo derivative $[Nb(\eta\text{-}C_5H_4Me)_2(O)(CH_2SiMe_3)]$ with $LiPF_6$ or $BF_3.Et_2O$ [51]. $[Nb(\eta\text{-}C_5H_4Me)_2(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ reacts with $ZnCl_2$ first to form an adduct which, based on infrared and NMR spectroscopic data appear to possess a novel μ-$CO_2$ unit bridging both niobium and zinc centres. This adduct is unstable, decomposing with loss of carbon monoxide to form $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)OZnCl_2]_2$ which is, in effect, an adduct of $ZnCl_2$ with the oxo species $[Nb(\eta\text{-}C_5H_4Me)_2(O)(CH_2SiMe_3)]$. Reaction of $[Nb(\eta\text{-}C_5H_4Me)_2(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ with $HgCl_2$ rapidly produces an incompletely characterised product which has been both decarbonylated and dealkylated. Although $CdCl_2$ does not react with $[Nb(\eta\text{-}C_5H_4Me)_2(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ under comparable conditions, $Me_3SiCl$ reacts rapidly to afford $[Nb(\eta\text{-}C_5H_4Me)_2(O)Cl]$ resulting from decarbonylation and dealkylation [51].

Moving onto lower congenors, addition of $LiSCHMe_2$ to $[Nb(\eta\text{-}C_5H_5)Cl_2(PhCCPh)]$ forms $[Nb(\eta\text{-}C_5H_5)(SCHMe_2)_2(PhCCPh)]$ [52]. Complex reactivity ensues upon subsequent addition of $HgCl_2$ or $Co_2(CO)_8$ to $[Nb(\eta\text{-}C_5H_5)(SCHMe_2)_2(PhCCPh)]$. Molecular orbital analysis of the bonding in the complex $[Nb(\eta\text{-}C_5H_5)(Cl)_2(\mu\text{-}SEt)_2Ni(\eta\text{-}C_5H_5)]$ reveals the odd electron to be localised on niobium but a substantial [Nb-Ni] bond still exists. The effects of the bridging ligands on the metal-metal overlap populations are described.

The bonding of $[S_2Fe_2(CO)_6]$ with several electron-deficient fragments including $[Nb(\eta\text{-}C_5H_5)(CO)_2]$, formed photochemically, have been investigated [53]. The product $[Nb(\eta\text{-}C_5H_5)(CO)_2(\mu^3\text{-}S_2)Fe_2(CO)_6]$ has been shown to possess an [Fe-Fe] bond.

An intriguing transformation has been reported upon the reaction of $S_8$ with $[Nb_2(\eta^5C_5Me_4Et)_2(B_2H_6)_2]$ (**18**) which affords the novel complex (**19**) in low (26%) yield [54].



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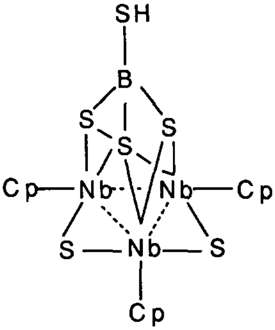

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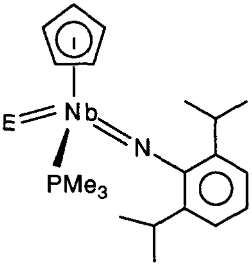


(20)

Treatment of [Nb($\eta^5$-$C_5Me_5$)(=N-2,6-${}^iPr_2C_6H_3$)($PMe_3$)$_2$] with elemental sulfur, selenium or tellurium affords the corresponding terminal chalcogenido complexes [Nb($\eta^5$-$C_5Me_5$)(=N-2,6-${}^iPr_2C_6H_3$)($PMe_3$)(E)] **(20)** (E = S, Se, Te) in 58, 60 and 41% isolated yields respectively. The products are isostructural, monomeric complexes containing terminal chalcogenido units as concluded from infrared, NMR spectroscopic and cryoscopic investigations [55].

### *7.2.3 Complexes with group 15 ligands*

Since lowering the oxidation state of the niobium centre results in the metal becoming a softer acid centre, it may be expected that ligand systems that do not feature strongly in the chemistry of niobium in its group oxidation state may be more abundant in the lower states. Indeed, this does appear to be the case where group 15 donor ligands are concerned since phosphorus based systems are now more inevidence than they were for niobium(V).

[Nb($\eta^5$-$C_5Me_5$)$Cl_2$($PMe_3$)$_2$] has been prepared by the magnesium reduction of [Nb($\eta^5$-$C_5Me_5$)$Cl_4$] in the presence of $PMe_3$. The product reacts subsequently with carbon monoxide to afford the purple complex [Nb($\eta^5$-$C_5Me_5$)$Cl_2$(CO)$_2$($PMe_3$)] [12].

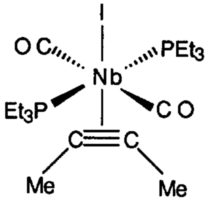
Along similar lines, the novel $d^2$-imido complex [Nb($\eta^5$-$C_5Me_5$)(=N-2,6-${}^iPr_2C_6H_3$)($PMe_3$)$_2$] mentioned in the last section has proved to be a very versatile synthetic precursor to niobium cimplexes in different oxidation states and is accessible *via* magnesium reduction of [Nb($\eta^5$-$C_5Me_5$)(=N-2,6-$^iPr_2C_6H_3$)$Cl_2$] in the presence of $PMe_3$ [56]. [Nb($\eta^5$-$C_5Me_5$)(=N-2,6-$^iPr_2C_6H_3$)$(PMe_3)_2$] reacts with soft bases such as CO, $C_3H_6$, $C_2H_4$, MeCCMe and PhCCPh to afford adducts of the form [Nb($\eta^5$-$C_5Me_5$)(=N-2,6-$^iPr_2C_6H_3$)L($PMe_3$)] (L = CO, $C_2H_4$ and PhCCPh) [33, 56]. [Nb($\eta^5$-$C_5Me_5$)(=N-2,6-$^iPr_2C_6H_3$)$(PMe_3)_2$] can in turn be oxidised by dihydrogen to [Nb($\eta^5$-$C_5Me_5$)(=N-2,6-$^iPr_2C_6H_3$)$H_2$($PMe_3$)]. Novel $\eta^2$-benzyne and benzylidine complexes of niobium can be stablised using the above molecular framework of $PMe_3$, imido and pentamethylcyclopentadienyl ligands [57]. The products have similar structures to the chalcogenido complexes (**20**).

The co-thermolysis of [Nb($\eta^5$-1,3-$^tBuC_5H_3$)$(CO)_4$] with $P_4$ affords the 26-valence electron triple-decker sandwich complex $[Nb(\eta^5\text{-}1,3\text{-}^tBuC_5H_3)]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}P_6)$. The results of single-crystal X-ray diffraction studies show that the middle $P_6$ deck is severly bis-allylically distorted [58]. Extended Hückel molecular orbital calculations were performed to explain this disorder, which is traced to the presence of two electrons in the nearly degenerate $2e'_2$ antibonding orbitals. In 24-valence electron systems, the strong interaction between the metal-metal bonding orbital $a_2''$ and the top most $\pi^*$-orbital of the puckered $P_6$-ring is responsible for the puckering of the $P_6$ ring. Additionally, this type of distortion is favoured by a decrease of energy of the $1e_2''$ orbitals and the larger HOMO-LUMO gap. In comparison to $P_6$ and $As_6$, the $C_6H_6$ ligand is far less susceptible to such an out-of-plane distortion because the high lying $b_{2g}$ orbital provides such a small interaction with the metal-metal bonding orbital. The 24-valence electron triple decker complexes may gain extra stability by three-dimensional delocalisation depending on the middle ring present in the complex [58].

The new compounds [Nb($\eta^6$-$C_7H_8$)$(PMe_3)_2Cl_2$] and [Nb($\eta$-$C_7H_7$)($\eta^4$-$C_7H_8$)($PMe_3$)] have been prepared and the former characterised by single crystal X-ray diffraction which reveals it to possess mutually trans $PMe_3$ ligands [59]. [Nb($\eta$-$C_7H_7$)($\eta^4$-$C_7H_8$)($PMe_3$)] is the first example of an $\eta^4$-$C_7H_8$ ligand whose structure has been examined by a combination of $^{13}C$ NMR spectroscopy and inverse-mode ($^1H$-observed) $^{13}C$-$^1H$ shift correlation NMR spectroscopy. Treatment of [Nb($\eta^6$-$C_7H_8$)$(PMe_3)_2Cl_2$] with magnesium-butadiene reagent gives [Nb($\eta$-$C_7H_7$)($\eta^4$-$C_4H_6$)($PMe_3$)] whilst protonation of [Nb($\eta$-$C_7H_7$)($\eta^4$-$C_7H_8$)($PMe_3$)] occurs readily to afford [Nb($\eta$-$C_7H_7$)($\eta^4$-$C_7H_9$)($PMe_3$)][$PF_6$] and reaction with MeI affords the paramagnetic complex [Nb($\eta$-$C_7H_7$) I$(PMe_3)_2$] which is isomorphous with the analogous sixteen-electron compound [Zr($\eta$-$C_7H_7$)I$(PMe_3)_2$] but has an unusually long [Nb-I] bond. [Nb($\eta$-$C_7H_7$)$(CO)_3$] reacts with DMPE (bis-1,2-dimethylphosphinoethane) to give the monomeric complex, [Nb($\eta$-$C_7H_7$)(DMPE)(CO)]. The analogous $PMe_3$ complex [Nb($\eta$-$C_7H_7$)$(PMe_3)_2$(CO)] is formed by similar reaction involving $PMe_3$ in place of dmpe [59].

The reaction between the seven-coordinate niobium(I) complexes [NbX$(CO)_4$(dppe)] (X = Br, I) or [NbX$(CO)_3(PEt_3)_3$] (X = Cl, Br, I) and alkynes leads to the $d^4$-niobium-alkyne complexes [NbX$(CO)_2$(dppe)($\eta^2$-RCCR)] (R = Ph) and [NbX$(CO)_2(PEt_3)_2$($\eta^2$-RCCR)] (R = H, Me, Et, Ph) [60]. These complexes have been characterised by $^1H$, $^{13}C$, $^{31}P$ and $^{93}Nb$ NMR and infrared spectroscopies. Low field acetylinic hydrogen and carbon resonances confirm the description of the alkyne as a four-electron donor. The $^{93}Nb$ NMR spectral resonances exhibit the expected shielding dependence of halide as Cl < Br < I. A single-crystal X-ray diffraction study of

$[NbI(CO)_2(PEt_3)_2(\eta^2\text{-}MeCCMe)]$ **(21)** reveals a slightly distorted octahedral molecule with carbonyl and phosphine ligands in *trans*-positions.



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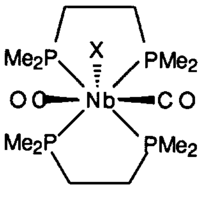


**(22)**

The complexes $[M(CO)_2(dmpe)_2Cl]$ (M = Nb, Ta) are important precursors in the chemistry leading to the reductive coupling of carbon monoxide (CO) ligands to form bis(trialkylsiloxy)acetylenes [61]. Convenient high yield syntheses of $[M(CO)_2(dmpe)_2Cl]$ have been devised by utilising catalytic MgQ (Q = anthracene). When MgQ.3thf is used in the absence of CO, the products obtained are $[Ta(\eta^4\text{-}Q)(dmpe)_2Cl$ and $[Ta(dmpe)_2Cl_2]$. The crystal structure of $[Nb(CO)_2(dmpe)_2X]$ **(22)** (X = Cl, I) are also reported to have a capped trigonal prismatic structure with acute OC-M-CO angles, low ν(CO) stretching frequencies and close, non-bonded carbon-carbon contacts features which indicate their propensity to undergo reductive coupling reactions [61]. Photolysis of $[M(CO)_2(dmpe)_2Cl]$ in the presence of isocyanides RNC affords products of ligand displacement $[M(CNR)(CO)(dmpe)_2Cl]$ (M = Nb, R = Me, $C_6H_{11}$, $^tBu$; M = Ta, R = Me, Et, $^tBu$) [62]. These extremely electron-rich compounds are fluxional in solution displaying low temperature NMR spectra consistent with a capped trigonal prismatic structure similar to **(22)** above. X-ray diffraction analyses on several of the derivatives reveals bent (C-N-C) isocyanide linkages suggesting that the ligands are bound to the metal as heteroallenes. subsequently, reduction of $[M(CNR)(CO)(dmpe)_2Cl]$ (M = Nb, Ta) with 40% Na/Hg followed by addition of $Me_3SiCl$ resulted in reductive coupling of the CO and RNC functions to afford $\{M[(Me_3Si)(Me)NCCOSiMe_3)](dmpe)_2Cl\}$ [63]. An X-ray crystal structure determination on the niobium derivative confimed the presence of the unusual RR'NCCOR acetylene ligand. The reductive coupling proceeds as for coupling of two CO two RNC functions. The first step is formation of an aminocarbyne, a $Ph_3Si$ derivative of which has been characterised. Addition of $Me_3SiCl$ to $\{Nb[CN(Me)(Si^tBuMe_2)](dmpe)_2(CO)\}$ generated the asymmetrically coupled product $\{Nb[(^tBuMe_2Si)(Me)NCCOSiMe_3)](dmpe)_2Cl\}$ demonstrating that aminocarbynes are on the mechanistic pathway to reductive coupling[63].

In thf solvent with 0.2 M $NaBPh_4$ as supporting electrolyte, the one-electron oxidation, at –0.4 V (relative to an aqueous saturated calomel electrode) of the electrogenerated species $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2ClP(OMe)_3]$ yields the cationic niobium(IV) complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2ClP(OMe)_3][BPh_4]$ which has been characterised by ESR spectroscopy [64]. The same result can also be acheived by chemical oxidation.

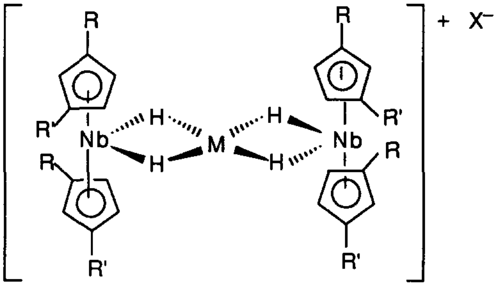
Some studies with nitrogen based ligands coordinated to lower oxidation state niobium systems have been reported. Thus, the electrochemical behavior of the new niobium(IV) derivatives

$[Nb(\eta^5-C_5H_5)_2(L-L)][PF_6]_2$ (L-L = 2,2'-bipyridyl and o-phenanthroline) has been investigated and reduction of the coordinated ligand was observed along with redox processes associated with the metal [65]. An X-ray crystal structure on the bipyridyl complex shows the expected bent metallocene structure with (Nb-N) of 2.226(6) and 2.218(6)Å and an (N-Nb-N) angle of 72.6(3)°. Extended Huckel moleclar orbital calculations showed the absence of back-donation to the low energy acceptor orbitals of the nitrogen ligand.

### *7.2.4 Complexes with other donor ligands*

Most of the ligand types that have not been included in this review may best be described as belonging to the organometallic family and consist predominantly of carbon donors. However, there have been reports of unusual systems comprising novel hydrido and borate type ligands that are worthy of mention in this context.

The reaction of $[Nb(\eta^5-C_5H_4R)_2H_3]$ (R = H, $SiMe_3$) with $[Cu(CH_3CN)_4][PF_6]$ or $AgBF_4$ leads to trinuclear adducts of the form shown below (23) (M = Cu, Ag; X = $PF_6$, $BF_4$; R = R' = H, R = H, R' = $SiMe_3$; R = R' = $SiMe_3$) [66]. In these adducts the Lewis acid is linked to two hydrides of each niobium-trihydride unit as deduced from observation of ABC patterns in the $^1H$ NMR spectra at low temperature and from [H-Ag] coupling constants. The exchange couplingd present in $[Nb(\eta^5-C_5H_5)_2H_3]$ are suppressed. In (23) (M = Cu; X = $PF_6$; R = H, $SiMe_3$; R = H, R' = $SiMe_3$), the absence of apparent couplings could result from superposition of magnetic and exchange couplings opposite in sign. Finally, (23) (M = Ag; X = $BF_4$; R = R' = $SiMe_3$) displays quantum mechanical exchange couplings between the hydrides with the same order of magnitude as in $[Nb(\eta^5-C_5H_4SiMe_3)_2H_3]$. Structural implications of their occurrence, related to the presence of a thermally accessible dihydrogen state, are discussed [66].



(23)

Niobium pentachloride reacts with $NaBH_4$ and $LiC_5Me_4Et$ to afford, depending upon the stoichiometry and temperature, $[Nb(\eta^5-C_5H_5)_2Cl_2]$, $[Nb_2(\eta^5-C_5H_5)_2Cl_2(B_2H_6)]$, $[Nb(\eta^5-C_5H_5)_2BH_4]$ and $[Nb_2(\eta^5-C_5H_5)_2(B_2H_6)_2]$. With a large excess of $NaBH_4$, $[Nb(\eta^5-C_5H_5)_2Cl_2]$ gives $[Nb_2(\eta^5-C_5H_5)_2Cl_2(B_2H_6)]$ at 25°C which reacts further with $NaBH_4$ to give $[Nb_2(\eta^5-C_5H_5)_2(B_2H_6)_2]$ [67]. The synthesis of this latter very stable, deep violet complex can be generalised by using $LiC_5Me_5$, $LiC_5H_4{}^tBu$. All the above compounds have been characterised by infrared, $^{1}H$ and heteroatom NMR spectroscopies. $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$ and $[Nb(\eta^5\text{-}C_5H_5)_2BH_4]$ are analogous to known complexes. In $[Nb_2(\eta^5\text{-}C_5H_5)_2Cl_2(B_2H_6)]$ and $[Nb_2(\eta^5\text{-}C_5H_5)_2(B_2H_6)_2]$ the $B_2H_6$ dianion (which is not stable in the free state) is present as a bridging ligand, orientated perpendicular to the axis defined by the metal-metal vector. So far, the highest $^{93}Nb$ NMR shielding has been observed for $[Nb_2(\eta^5\text{-}C_5H_5)_2(B_2H_6)_2]$, extending the range of known $^{93}Nb$ chemical shifts by 2500 ppm. The temperature dependence of the linewidths of both the $^{11}B$ and the $^{93}Nb$ signals in $[Nb_2(\eta^5\text{-}C_5H_5)_2(B_2H_6)_2]$ allows evaluation of the magnitude of $J_{Nb-B}$ of 50 + 10 Hz [67].

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