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2. Titanium

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CONTENTS

INTRODUCTION

Interest in the use of titanium for materials science applications as well as for catalysts and supports is evidenced by the body of published papers for 1991. Many of these papers are beyond the scope of this review and will not be dealt with here. This review aims to highlight advances in titanium chemistry of interest to coordination chemists for 1991. It is based on a literature search of volumes 114, 115, and 116 (numbers1-10) of Chemical Abstracts. For completeness, a separate search of major inorganic chemistry journals from January to December 1991 was carried out. I would like to thank Dr. Catherine E. Housecroft for giving me the opportunity to do this review and also Dr. José C. Vites for constructive comments.

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2.1 TITANIUM(IV)

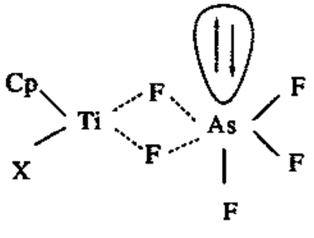
2.1.1 Complexes with halide ligands

The $MeTiCl_3$ complex has been the focus of isotopic NMR [1] and IR [2] spectroscopic studies recently. The relative sign of the $^2J(H\text{-}D)$ coupling constant in $(CH_2D)TiCl_3$ was redetermined and found to be negative. Infrared spectra from $^{12}CH_3TiCl_3$ in the gas and solid phase, $^{12}CD_3TiCl_3$ in the gas phase, and $^{13}CH_3TiCl_3$ and CHD_2TiCl_3 in the gas phase were obtained. The results of both these studies indicate the absence of an agostic interaction and are consistent with the presence of a normal methyl group geometry.

The interaction between Cp_2TiF_2 and Cp_2TiCl_2, and HCl has been studied using the matrix isolation technique in conjunction with IR spectroscopy. One-to-one complexes have been isolated and characterized with spectral data indicating that hydrogen-bonded complexes are formed. The HCl binds to both of the halogens of the dihalide in a bidentate fashion [3].

The structure of trichloro(η^5-methylcyclopentadienyl)titanium(IV) has been determined recently. All five of the ring carbon atoms along with the three chlorine atoms give rise to a piano-stool coordination about the Ti atom. The dihedral angle between the Cp* plane and the Cl_3 plane is 2.7°. The Ti-Cl distances range from 2.2229 (9) Å to 2.228 (1) Å and the Ti-C distances range from 2.301(3) Å to 2.379(3) Å [4].

The complex $[Ti(Cp)_2(S_4N_4)][AsF_6]_2$ has been characterized in SO_2 solutions by ^1H, ^{14}N, and ^{19}F NMR spectroscopy [5]. The AsF_6^- ions were shown by ^{19}F NMR spectroscopy not to be coordinated but to exist in an undistorted octahedral geometry. ^{14}N NMR spectroscopic data indicate that two of the four nitrogen atoms of S_4N_4 are coordinated to the titanocene fragment. Attempts to prepare the Se_4N_4 version of this complex led instead to the formation of $Ti(Cp)_2F_2AsF_3$ (**1**). ^1H, IR and mass spectroscopy are indicative of the structure shown below. $[Ti(Cp)F_3]AsF_3$ (**2**) was also characterized in this study.



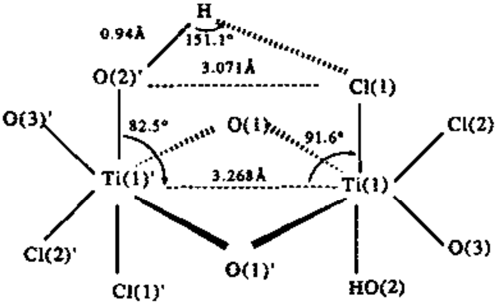
X = Cp (**1**)
X = F (**2**)

$Ph_3TeX.TiX'_4$ (X, X' = Cl, Br, I) have been obtained by the reaction of Ph_3TeX with TiX'_4 [6]. ^1H NMR spectroscopy, conductivity studies and molecular weight determinations are consistent with dissociation in solution to form Ph_3Te^+ and TiX'_4X^- or Ph_3Te^+ and TiX'_4X^{2-} units.

The lack of Te-Ti and Te-X vibrations in the far IR spectra of these compounds reflects the transfer of a halogen atom from Ph_3TeX to TiX'_4 with the resultant formation of halo(mixed) titanate(IV) ions.

2.1.2 Complexes with oxygen donor ligands

Intramolecular O-H····Cl hydrogen bonding, previously unrecognized, has recently been demonstrated in a titanium chloride alkoxide dimer $[TiCl_2(OCH_2CH_2X)_2.HOCH_2CH_2X]_2$ (X = Cl, Br, I) [7]. In the case where X = Cl, (3), addition of titanium tetrachloride to a solution of excess 2-chloroethanol (3-4 equiv) in dichloromethane at –78°C, followed by warming to room temperature and removal of volatile organic materials yielded a white crystalline solid. Crystallization of this solid from dichloromethane/hexane gave $[TiCl_2(OCH_2CH_2Cl)_2.HOCH_2CH_2Cl]_2$ in 74% yield as large, well-formed colourless crystals. Treatment of titanium tetrachloride with 2-bromoethanol, and 2-iodoethanol gave the complexes $[TiCl_2(OCH_2CH_2Br)_2.HOCH_2CH_2Br]_2$ and $[TiCl_2(OCH_2CH_2I)_2.HOCH_2CH_2I]_2$ respectively in 54% and 46% yields as pale yellow crystalline solids. Characterization by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, elemental analysis and a crystal structure determination for (3) indicates that these complexes exist as dimers in the solid state. The dimeric structure appears to be strongly favoured by the presence of O-H·····Cl bonding within the dimer (bond strengths < 5kcal/mol) which was established by structural distortions namely the O(2)'-Ti(1)'-Ti(1) is 82.5° indicating that O(2)' of the coordinated alcohol is bent toward the Cl(1) atom. This was further corroborated by the -OH IR stretching frequencies in nujol and low temperature solution NMR spectroscopic studies in (3).



(3)

The application of an ^{17}O NMR spectroscopic technique to study the structures of Ti(IV) polyoxoalkoxides formed in solution upon hydrolysis of $Ti(OEt)_4$ in 1/3 v/v $CH_3C_6H_5$/EtOH has been described [8]. These species have been selectively enriched at their oxide rather than alkoxide oxygen sites. The solution and X-ray structures of $[Ti_7O_4](OEt)_{20}$, $[Ti_8O_6](OBz)_{20}$ (Bz = $CH_2C_6H_5$) and $[Ti_{10}O_8](OEt)_{24}$ have been discussed.

Synthesis and structural studies of two polymorphs of the condensed species $[Ti_{16}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_8(\mu\text{-}OEt)_{16}(OEt)_{16}]$, a condensation product of $[Ti(OEt)_4]$, have been reported [9]. A monoclinic and tetragonal form have been obtained and comprise different packings of the same $Ti_{16}O_{48}$ cores. A comparison of both structures reflects slight differences in the orientations of the alkoxo groups and in the titanium-oxygen networks. The initial hydrolysis product of titanium tetraethoxide $[Ti_7O_{16}(OEt)_{32}]$ has been prepared by a new route, its structure has been redetermined and all ethyl groups were located.

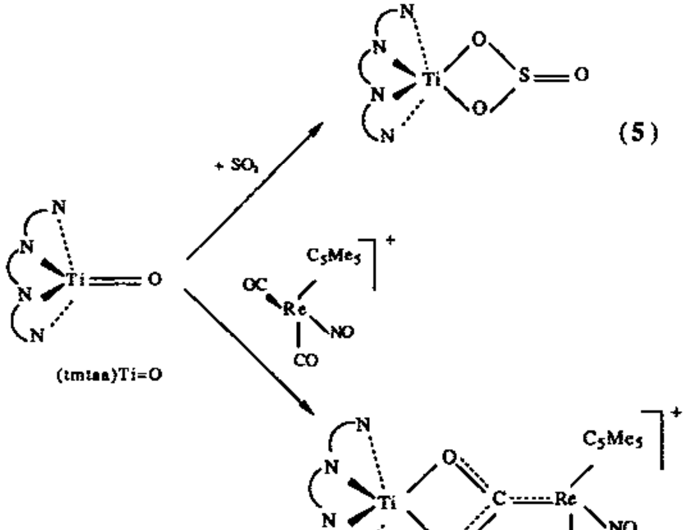
The reaction of barium metal with $Ti(O^iPr)_4$ in isopropyl alcohol gave rise to crystals containing molecules of two different kinds [10]. X-ray crystallography shows a bimetallic oxoalkoxide complex, the structure of which may be represented as $[Ba_4Ti_4O_4(OR)_{16}(ROH)_4][Ba_4Ti_4O_4(OR)_{16}(ROH)_3]$, R = ^{i}Pr. The two crystallographically independant complexes differ mainly in the number of solvating alcohol molecules and both have the same metal-oxygen core: a distorted cube comprised of alternating Ba and O(oxo) atoms at its vertices. Each oxo atom is bonded to one of the titanium atoms which are also linked to the Ba_4O_4 core by bridging alkoxide groups: Ti-OR-Ba. Two different types of Ba, Ti, and oxo-O atoms were distinguished. In the first kind, the coordination polyhedra of titanium is best described as distorted tetrahedral pyramids with oxo atoms comprising the apex and *O*-alkoxide ligands at the base. In the second kind coordination about the Ti atoms may be considered to be trigonal bipyramidal with oxo groups and terminal alkoxide groups in the axial positions. Each Ba atom has a coordination number of 7, the two kinds differing in their disposition of ligands in the coordination sphere. Ti-O(oxo) range from 1.699 (8) to 1.715 (8) Å for the first type and 1.80 (1) to 1.810 (7) Å for the second type. Ti-OR distances are 1.881-1.999 Å. The structure may be regarded as ionic, consisting of four pairs of Ba^{2+} {or $Ba(ROH)^{2+}$} cations and $[TiO(OR)_4]^{2-}$ anions.

The $[(\eta^5\text{-}MeC_5H_4)_2Ti(\mu_2\text{-}MoO_4)]_2$ dimer has been synthesised and its structure determined [11]. It displays limited thermal stability depending on the nature of the solvent. The complex is composed of a cyclic tetranuclear eight-membered centrosymmetric structure in which the four metal atoms are coplanar with 2 oxygen atoms tilted up and 2 oxygen atoms tilted down. Structural parameters for the Mo-O-Ti fragment are indicative of significant Mo-O multiple bond character and a long Ti-O bond.

Using highly sterically hindered cyclopentadienyl ligands hydrolysis of $[(\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]TiCl_3$ with $1/2$ equiv. of water gave the μ-oxo complex $[(\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]_2Ti_2Cl_4(\mu\text{-oxo})$, which upon further reaction with water gave the dinuclear complex $[(\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]_2Ti_2Cl_2(\mu\text{-oxo})_2$ [12]. The crystal structure of the latter reveals a dimer composed of two $(Si_3Cp)TiClO_2$ tetrahedra sharing an O-O edge and having a planar $Ti_2(\mu\text{-}O)_2$ core. The Ti-O distances are 1.814 (1) Å and 1.835 (1) Å and angles of 84.23 (3)° about the titanium atom and 95.78 (3)° about the oxygen atom. The short Ti-Ti distance of 2.707 Å suggests that transannular bonding may be involved. The bulky cyclopentadienyl groups are arranged in a *trans* configuration.

The molecular structure and electrochemical behaviour of the complex $[HNEt_3][Ti(tripace)].1.5MeCN$ (tripace = tricatechol) has been reported [13]. This anion contains a hexacoordinated Ti(IV) atom which is located at the centre of a distorted octahedron defined by six catechol oxygen atoms. The central nitrogen atom in the tripace ligand is in the "in" conformation and is protonated. The electrochemical properties were studied to determine if the tripace ligand is capable of stabilizing highly oxidized transition metals. Results indicate that it is stable towards reduction up to $E_{1/2} = -1.02V$ vs the standard calomel electrode.

The compounds $[M(O_2CNR_2)_4]$ (M = Ti, Zr, or Hf; R = Et or ^{i}Pr) were synthesised by reacting the corresponding metal tetrachloride with CO_2-NHR_2 in toluene [14]. Comparison of IR spectroscopic data for these complexes and an X-ray study on $[Hf(O_2CN^iPr_2)_4]$, strongly suggests that independent of the nature of the metal, all the isopropyl derivatives of this class have the same structure. The X-ray structure shows the central hafnium atom surrounded by eight oxygen atoms of the four *N,N*-diisopropylcarbamato groups in a slightly distorted dodecahedral arrangement. The four carbamato groups chelate the hafnium atom in a symmetrically bidentate fashion. The redox reaction between $[Ti(O_2CNEt_2)_4]$ and $[V(Cp^*)_2]$ gave $[\{Ti(O_2CNEt_2)_3\}_n]$ and $[\{V(Cp^*)(O_2CNEt_2)\}]$.



The remarkable nucleophilicity of the oxo ligand in (tmtaa)Ti=O (tmtaa = dianion 7,16-dihydrido-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine) has been exploited in a variety of addition and cycloaddition reactions with several organic and inorganic substrates [15]. In particular it is sufficiently reactive to attack the carbonyl ligand of $[CpRe(CO)_2(NO)]^+$ inducing cycloaddition to form the bimetallic (4) which possesses a μ_2-η^3-CO_2 ligand. Reaction with SO_2 gave the first reported $\eta^2(O_2)$-sulphito complex of titanium (5).

The synthesis, characterization and crystal structure determination of monomeric and dimeric titanatranes have been achieved [16]. In particular, the crystal structures for Z-$\overline{Ti(OCH_2CH_2)_3N}$, Z = $OSiPh_3$ and O_2CMe show interesting geometries. The former is monomeric presumably due to the nature of the bulky siloxy group, the geometry about Ti is nearly trigonal bipyramidal with Ti being a little above the plane of equatorial oxygen atoms. The linear Si-Ti-O axis contains a transannular Ti-N bond with a length of 2.26 Å. The latter complex is dimeric and is in striking contrast to the former by the fact that each Ti is seven-coordinate. The geometry around each Ti atom may best be described as a distorted trigonal prism of oxygen atoms with the nitrogen atom near a rectangular face. The Ti-Ti distance of 3.290 (2) Å is not indicative of any substantial interaction. ^1H and ^{13}C NMR spectroscopic studies show the siloxy complex is monomeric in solution at room temperature whereas the acetato complex is a dimer which undergoes a fluxional gearing motion at room temperature but becomes monomeric upon warming up. In a subsequent paper [17], the crystal structure of $Me_2N\overline{Ti(OCH_2CH_2)_3N}$ was reported and discussed. This is a dimer where, in contrast to the $OSiPh_3$ and O_2CMe complexes, the N of the Me_2N is *trans* to an oxygen atom rather than a nitrogen atom. This is probably due to the fact that the more electron donating Me_2N group prefers to be *trans* to an alkoxy oxygen rather that to the more electron donating tertiary bridgehead nitrogen. The axial Me_2N is labile to substitution by a variety of OR groups in reactions with the corresponding ROH reagent to give in better than 90 % yield the O^iPr, $OSiPh_3$, O^tBu, OPh, and $OCMe_2Et$ derivatives. RSH compounds also cleanly react with this complex to give in 85% yield in most cases SEt, S^iPr, $SCMe_2Et$, SPh, and S-allyl derivatives.

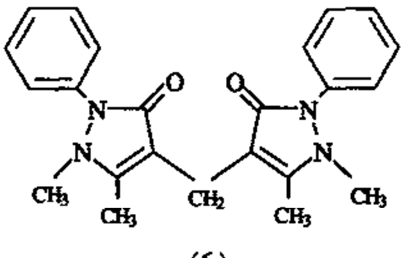
The compound $[Ti(Cp^*)Me_3]$ reacts with 3 equivalents of carboxylic acids HO_2CR R = Me, Ph or *p*-$MeOC_6H_4$ to give tris(carboxylates) $[Ti(Cp^*)(O_2CR)_3]$ [18]. The crystal structure for the R = Ph derivative has been determined and the geometry around the metal atom may be described as a distorted pentagonal bipyramid with the three carboxylate groups binding in a bidentate fashion. The mean Ti-O distance is 2.152 Å.

The preparation, chemistry and crystal structures of some unique chlorotitanium carboxylate compounds $[TiCl_3(O_2CR)]$ which lack Cp ligands was reported [19]. The reaction of $TiCl_4$ with a 1 mol equivalent of a carboxylic acid at temperatures of 50°-100°C yielded the trichloro(carboxylate) compounds $[TiCl_3(O_2CR)]$, R = Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, $CMePh_2$, Me_3C, C_9H_6N, CH=CHPh and CH=CHMe. For R = Me_3C, a crystal structure has been obtained. The compound is trimeric with a triangular arrangement of titanium atoms. Each titanium atom reveals a distorted octahedral coordination due to four chlorine and two oxygen atoms. The carboxylic groups symmetrically bridge two titanium atoms and there is one double and one triply bridging chlorine atom. In particular, one of the Ti-Cl bonds in the triple bridge is very long (2.839 (2) Å) in comparison to the other two bonds (2.565 (2) and 2.577 (2) Å). This is consistent with the break up in solution into dimers, loss of the third titanium unit generates a vacant coordination position which is presumably occupied by weak donation from the solvent. In reactions of $[TiCl_3(O_2CRH)]$ intermediates of composition $[Ti_2Cl_7(O_2CR)(RCO_2)]$ were obtained. For R = *p*-ClC_6H_4, and CH=CHMe crystal structures were obtained. Both display similar structures with a carboxylate anion bridging a bent Ti_2Cl_6 unit, and a neutral acid molecule rather than an acid anion, the orientation of these acid groups is such that there is close contact between the -OH group of the acid and a terminal Cl ligand. The Ti-Cl bonds involved in these contacts are significantly lengthened (2.22, 2.27 Å) compared to the other Ti-Cl terminal bonds.

The crystal structure of the monoclinic form of bis(cyclopentadienyl)bis(m-methoxybenzoato)titanium(IV) was investigated. Of interest is the presence of asymmetric Ti-O bonds in the title compound where Ti-O1 = 1.895 Å and Ti-O3 = 1.962 Å indicative of double and single bond character respectively with oxygen contributing 3 electrons in the former and 1 electron in the latter. ^{13}C NMR and mass spectroscopy indicate that this situation is favoured by an effect known as localized polarization. This effect may be brought about in titanocene benzoates by the presence of substituents with inductively electron-withdrawing properties. It is believed that mesomeric donating properties may be tolerated provided the substituent is suitably positioned [20].

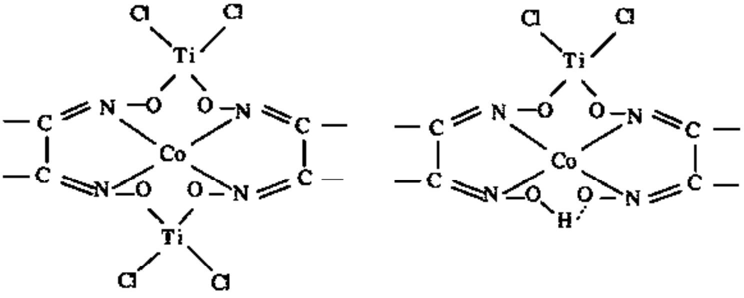
The structure of $[Ti(\mu\text{-}O)(OC_6H_3\text{-}2,6^iPr_2)_2(NC_5H_4\text{-}4NC_4H_8)]_2$, a simple oxygen bridged Ti(IV) dimer, has been determined [21]. Each Ti atom posseses pseudo trigonal bipyramidal geometry with two aryl oxide O atoms and one bridging O atom forming the trigonal plane. Pertinent bond lengths include Ti-O (bridge) = 1.847 Å (av.); Ti-O(aryl oxide) = 1.825 Å (av.); and Ti-Ti (non-bonding interaction) = 2.796 (1) Å. Its structure has been compared with that of $[Ti(\mu\text{-}O)(acac)_2]_2$.

The formation of eight-membered chelate rings and aromatic ring stacking has recently been demonstrated in Ti(IV)-4,4'-methylenebis(antipyrine) complexes [22]. $TiCl_4$ was reacted with 4,4'-methylenebis(antipyrine), also called diantipyrylmethane, (dam), (6), in perchloric acid solution to give orange crystals and a yellow powder of composition $[Ti(dam)_3](ClO_4)_4$. X-ray crystallographic studies show that in both complexes Ti(IV) is hexacoordinated by oxygen atoms with Ti-O average distances of 1.93 Å in the former and 1.94 Å in the latter and are shorter when compared with other complexes. The average bite angles 91° and 93° respectively, are larger in comparison to cathecholate or acetylacetonate complexes. A striking feature of these complexes is the aromatic ring stacking between a pyrazolone moiety of one ligand and a phenyl ring of another thereby imparting extra stability to them. Both complexes exhibit a CT band at 385 nm due to transfer of electron density from the phenyl group to the pyrazolone ring.

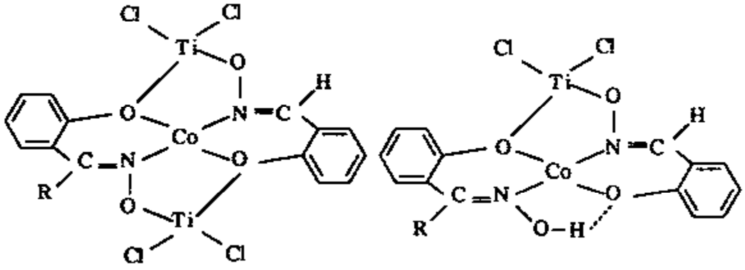


(6)

Some 1:2 and 1:1 addition compounds have been prepared by reaction of $TiCl_4$ with Co(II) bischelates of dimethylglyoximate (dmgoxH), salicylaldoximate (saloxH), and *o*-hydroxy-acetophenoximate (haaoxH) [23]. On the basis of elemental analysis, magnetic susceptibility measurements, infrared and electronic spectra tentative structures have been assigned and are shown below (7). The square planar complexes are coloured, paramagnetic amorphous powders which may possess antitumour activity of related Co(II) bis(chelates).



dmgoxH 2:1 dmgoxH 1:1



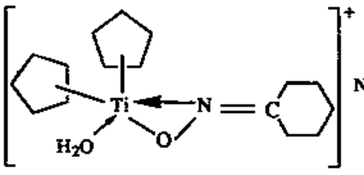
R = H - saloxH

R = CH_3- haaoxH

(7)

Reaction of Cp_2TiCl_2 with oximes in the two phase system ($CHCl_3$, Cp_2TiCl_2)/(H_2O, NaOH, oxime) led to ionic complexes of the type $[Cp_2Ti(H_2O)(\text{oximato})]^+X^-$ [24]. The complexes $[Cp_2Ti(H_2O)(ONC_6H_{10})]NO_3$ (**8**), $[Cp_2Ti(H_2O)(ONC_6H_8NOH)]Cl.H_2O$ (**9**), and the dinuclear complex $[Cp_2Ti(H_2O)(ONC_6H_8NO)(H_2O)TiCp_2](NO_3)_2.4H_2O$ (**10**), were characterized by X-ray structure determinations. The ON-fragment of the oximato ligand displays side-on bonding donating three electrons such that the Ti atom has an 18-electron configuration.

The synthesis, characterization, electrochemical and structural studies of two complexes of the form $Ti(OAr')_4$ where Ar' = C_6H_4(2-tBu) and C_6H(2,3,5,6,-Me$)_4$ have been documented [25]. Both complexes are monomeric and this may be attributed to the steric bulk of the ligands. The Ti atom is in a pseudo-tetrahedral environment with O-Ti-O angles ranging from 108.6 (1) to 111.3 (2)° in the former and 107.1 (8) to 111.8 (7)° in the latter. The Ti-O distance is 1.779(3) Å in the former while it ranges between 1.76(2) and 1.79(2) Å in the latter and are indicative of Ti-O dπ-pπ bonding. Chemical reduction with sodium amalgam affords the anionic Ti(III) species $[Ti(OC_6H(2,3,5,6,\text{-}Me)_4)_4]^-$. Attempts to couple and complex this anion with $[(cod)Rh(\mu\text{-}Cl)]_2$ in order to generate $(C_6H(2,3,5,6,\text{-}Me)_4O)_2Ti(\mu\text{-}OC_6H(2,3,5,6,\text{-}Me)_4)_2Rh(COD)$ failed, with oxidation of titanium(III) to titanium(IV) and reduction of rhodium(I) to rhodium(0).



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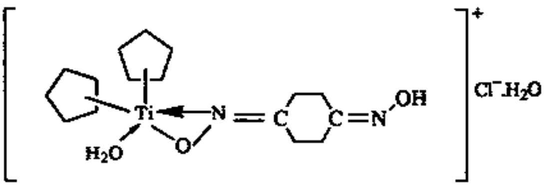

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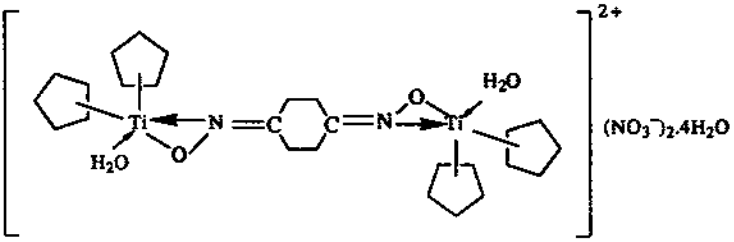
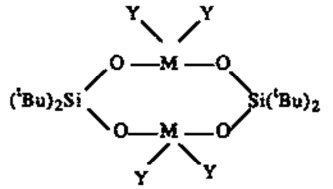


(10)

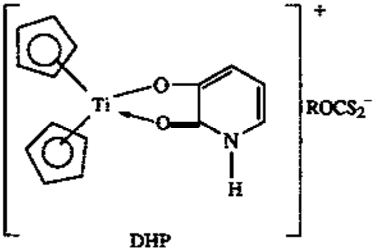
The synthesis and structures of eight-membered titanium containing siloxane rings has been achieved [26]. X-ray structural analysis on (11) and (12) shows the titanium atom to be in a tetrahedral environment with short Ti-O bonds indicating multiple bonding.



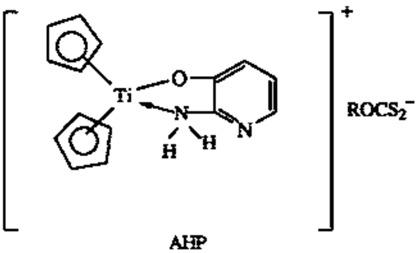
	X	Y	M
(11)	H	Cl	Ti
(12)	H	Br	Ti

Bis(cyclopentadienyl)titanium dichloride was treated with 2,3 dihydroxypyridine (DHP), (13) and 2-amino-3-hydroxypyridine (AHP), (14) in aqueous medium, forming soluble ionic derivatives of the type $[(Cp)_2TiL]^+Cl^-$. Further reaction of these complexes with xanthate anions in aqueous solution gave rise to ionic complexes of the type $[(Cp)_2TiL]^+ROCS_2^-$ *where* R = Me, Et,

^{i}Pr. Based on elemental analysis, conductance measurements, electronic, IR and ^{1}H NMR spectroscopic studies the structures (**13**) and (**14**) were assigned [27].

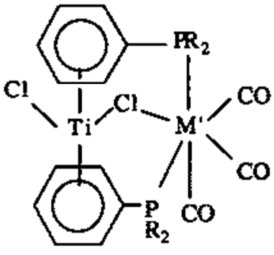


(**13**)

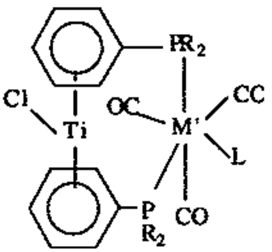


(**14**)

The dinuclear complex (**15**) was synthesised from mononuclear precursors $TiCl_2(C_5H_4PR_2)_2$, R = C_6H_5, 4-$C_6H_4CH_3$ and $M'(CO)_3L_3$, M' = Cr, Mo, W. For the case where L = CO or $P(OMe)_3$ irreversible cleavage of the chloro bridge occurs with the formation of adducts [$MM'Cl_2(\mu$-$C_5H_4PR_2)_2(CO)_3L$] (**16**). ^{t}BuO$^-$ may replace a terminal Cl$^-$ ligand at titanium whereas MeS$^-$ substitutes both terminal and bridging Cl$^-$. The latter complexes are inert towards CO or $P(OMe)_3$ substitution [28].

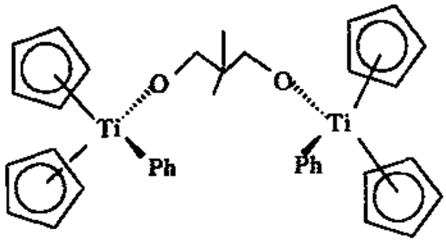


(**15**)



(**16**)

The reaction of Cp_2TiPh_2 with 2,2-dimethylpropanediol proceeds smoothly at 65°C over 18 hours. ^{1}H NMR spectroscopic results and combustion analysis suggested the formulation $Cp_2Ti(Ph)(\mu$-$OCH_2C(CH_3)_2CH_2O)(Ph)TiCp_2$ (**17**) which was confirmed by X-ray crystallography. The coordination spheres of the titanium atoms are pseudo tetrahedral with Ti-O distances of 1.80 (1) and 1.82 (1) Å, and Ti-O-C angles of 146.4 (9)° and 148.0 (9)°. The Ti···Ti separation is 6.725 Å. The driving force responsible for its formation rather than a chelated mononuclear species is not understood, but may arise as a result of Ti-O multiple bond character. The phenyl rings are oriented towards each other in an "inside" conformation thereby avoiding steric interactions of the Cp rings with substituents of the bridging alkoxide moiety [29].



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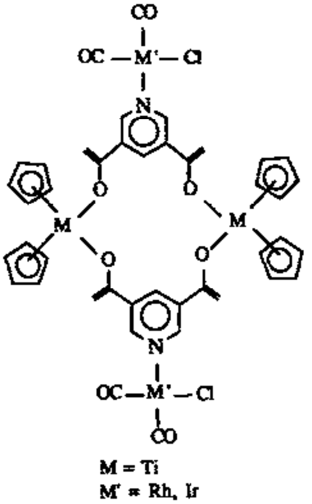


(18)

The results of attempts to couple Ti(IV) and Rh(I) and Ir(I) complexes by means of pyridine-3,5-dicarboxylato ligands have been reported [30]. The complex $[Cp_2Ti\{\mu\text{-}3,5\text{-}C_5H_3N(CO)_2\}_2TiCp_2]$ was synthesised by reaction of $TiCp_2Cl_2$ with pyridine-3,5-dicarboxylic acid in the presence of NEt_3 in THF at room temperature yielding a yellow air-stable crystalline solid. X-ray crystallography established its dimeric nature in which two Cp_2Ti units are linked by two pyridine-3,5-dicarboxylato ligands. Only one oxygen atom of each carboxylato ligand is bonded to each Ti atom giving a 16-membered ring; Ti-O distances of 1.961(3) and 1.958(3) Å have been found. The pyridine rings are almost coplanar with the nitrogen atoms lying to the exterior of the ring. The Ti atoms are in a distorted tetrahedral environment. To explore the reactivity of the uncoordinated pyridine nitrogen atoms, this dimeric complex was reacted with $[\{Rh(CO)_2Cl\}_2$ and $[Ir(CO)_2(p\text{-}MeC_6H_4NH_2)Cl]$ to give tetranuclear complexes as yellow air-stable solids. FAB mass spectra did not give satisfactory information on the nature of these complexes but IR and ^1H NMR spectroscopic data are in accord with the proposed structures (**18**).

The complex $[Ti(tartrate)(OR)_2]_2$, an active catalyst for asymmetric epoxidation of allylic alcohols by tertiary alkyl hydroperoxides, has been shown to be the dominant species in equimolar mixtures of titanium tetraalkoxides and dialkyl tartrate esters. It has been characterized by IR, ^1H, ^{13}C and ^{17}O NMR spectroscopy. Based on spectroscopic results and an X-ray crystal structure of a previously reported titanium tartramide complex, a dimeric structure was proposed. Each Ti atom is six coordinate with bridging tartrate ligands and terminal alkoxide ligands [31].

Dichlorobis(methylsalicylato)titanium(IV) reacts with potassium or amine salts of dialkyl or diaryl dithiocarbamates in 1:1 and 1:2 molar ratios in anhydrous benzene at room temperature or in boiling CH_2Cl_2 to yield mixed ligand complexes: $(AcOC_6H_4O)_2Ti(S_2CNR_2)Cl$ and $(AcOC_6H_4O)_2Ti(S_2CNR_2)_2$, Ac = CH_3CO, R = Et, ^nPr, ^nBu, *cyclo*-C_4H_8 and *cyclo*-C_5H_{10}. These compounds were found to be moisture sensitive and highly soluble in polar solvents. IR, ^1H, and ^{13}C NMR spectroscopic data are suggestive of coordination number 7 and 8 respectively, around titanium [32].

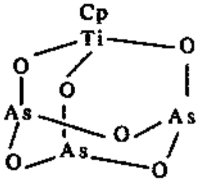
Interest in the use of complexes formed from titanium alkoxides and $MgCl_2$, for use as potential catalysts, has led to the synthesis and X-ray crystal structure of $[Ti_2(OEt)_8]_2Mg_2(\mu\text{-}Cl)_2$ [33]. The reaction of $Ti(OEt)_4$ and $MgCl_2$ in the 2:1 stoichiometric ratio yielded, after recrystallization from n-heptane single crystals of the title compound. The molecule is centrosymmetric and lies on a crystallographic center of symmetry. The asymmetric unit consists of three face-shared pseudotetrahedra centered on two Ti and Mg atoms which are surrounded by eight ethyl groups. A double chlorine bridge between the two Mg atoms serves to bond the two asymmetric units together.

Coordination compounds of Ti(IV) in carbonate solutions have been studied [34]. For $[Ti^{4+}] > 10^{-3}$mol/L dinuclear ions $Ti_2O(CO_3)_5(OH)_3^{5-}$ were produced with a formation reaction equilibrium constant of $(4.02 + 2.44) \times 10^{-2}$. When $[Ti^{4+}] < 10^{-3}$mol/L both mononuclear $TiO(CO_3)_3^{4-}$ and dinuclear ions are produced. The formation reaction equilibrium constant for the mononuclear ions was $(2.21+0.28) \times 10^{-11}$.

The synthesis and crystal structure of $[TiCl_4(EtCO_2Et)]_2$ has been reported [35]. It is a dimer with two Cl bridges between the Ti atoms which are coordinated by five Cl atoms and the carbonyl oxygen of the ester in an almost perfect octahedral environment.

Recently, $[(C_5HMe_4)TiBr(\mu\text{-}O)]_4$ and $[(C_5Me_5)TiBr(\mu\text{-}O)]_3$ were accidently obtained in pure form as byproducts in the preparation of titanocene dibromides resulting from the use of substoichiometric amounts of cyclopentadienyllithium compounds with respect to $TiBr_3$ [36]. The former tetranuclear compound contains a planar 8-membered $(\text{-}Ti\text{-}O\text{-})_4$ cycle with the C_5HMe_4 and Br lying alternately above and below the cycle plane. In the latter, the $(\text{-}Ti\text{-}O\text{-})_3$ cycle is not planar.with one of the oxygen atoms lying 0.4Å from the plane containing all the Ti and oxygen atoms.

Thermolysis of $As_{2(4)}O_{3(6)}$ with $[(\eta^5\text{-}C_5Me_4R)_2Ti(CO)_2]$ R = Me, Et gave $[(\eta^5\text{-}C_5Me_4R)TiAs_3O_6$ with a $TiAs_3O_6$ skeleton whose structure has been elucidated by X-ray analysis (**19**) [37], with Ti-O(1) =1.831 (1), Ti-O(2) = 1.826 (1), Ti-O(3) = 1.838 (1) Å.



Cp = η^5-C_5Me_4Et

(19)

2.1.3 *Complexes with sulphur donor ligands*

Oxidative addition of RSSX to $Cp_2Ti(CO)_2$ to yield complexes of the type $Cp_2Ti(X)(SSR)$, where X = SR and R = $CHMe_2$, CMe_3, CH_3Ph, and 4-C_6H_4Me; X = phthalimido and R= $CHMe_2$, CMe_3, CH_3Ph, and 4-C_6H_4Me; and X= Cl and R = CPh_3 has been reported [38]. The complexes were characterized using NMR spectroscopy. The presence of the disulfanido ligand RSS^- in the $Cp_2Ti(SR)(SSR)$ complexes was confirmed by reaction of these complexes with $PhCH_2Br$ to give CpTiBr, $PhCH_2SR$ and $PhCH_2SSR$. The complexes were characterized using NMR spectroscopy.

An interesting reaction of $TiCl_4$ with *O,O*-dialkyl and *O,O*-alkylene dithiophosphoric acids has been reported [39]. For the case of the *O,O*-dialkyl acids the reaction proceeds with ready elimination of HCl to yield substituted derivatives $Cl_2Ti[S_2P(OR)_2]_2$. In contrast, cyclic *O,O*-alkylene dithiophosphoric acids form stable 2:1 adducts which are insoluble in common organic solvents but sparingly soluble in CH_2Cl_2, DMSO and DMF. IR, ^1H and ^{31}P NMR spectroscopic methods have been used to characterize these complexes and indicate octahedral geometries for the 2:1 adducts in which the acids are behaving as monodentate ligands. The ligands are arranged in a *cis* fashion with the phosphorothionyl sulphur atom as the donor centre.

Treatment of $Cp^*{}_2TiCl_2$ with Li_2S_5 in THF followed by recrystallization from CH_2Cl_2/pentane yielded large red-black crystals of $[(Cp^*)_2TiS_3]$. The $S_3{}^{2-}$ ligand is chelating with Ti-S bond distances of 2.409 (2) Å and 2.417 (3) Å and is the only characterization of a chelating $S_3{}^{2-}$ ligand thus far [40].

Isomeric titanocene complexes with novel S-O chelating ligands have been synthesised [41]. $Cp'_4Ti_2S_4$ (Cp' = η^5-$CH_3C_5H_4$) reacted spontaneously with thionyl chloride in 1:1 ratio at 0°C in CS_2 to give titanocene dichloride and a pentasulfide complex which is sparingly soluble in CS_2 and precipitates in the form of red crystals. IR and ^1H NMR spectral data indicate that it is present as $Cp'_2Ti(\mu\text{-}S_2)_2S{=}O$, it is readily soluble in $CHCl_3$, CH_2Cl_2 and THF but solutions decompose within 45 minutes at 20°C whereby it is readily converted via ring expansion to an isomeric complex. The latter complex has been characterized by X-ray crystallography and shows a novel OS_5 ligand which is bound to the metal atom via an oxygen and one sulphur atom giving rise to a seven-membered ring. The Ti-S bond is 2.467 Å and the Ti-O bond is 1.946 Å. The oxophilicity of titanium is thought to be the driving force for the isomerization.

2.1.4 Complexes with selenium donor ligands

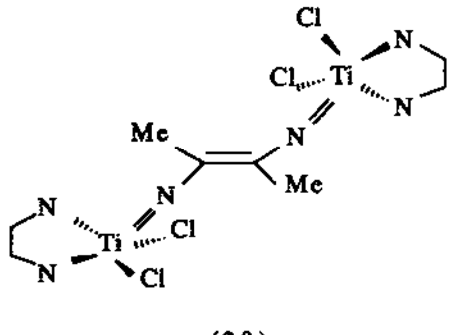
The synthesis of $(CH_3C_5H_4)_2Ti(\mu_2\text{-}Se_2)_2AsCH_3$ has been synthesised and characterized by ^1H NMR, mass and IR spectroscopy [42]. The ^1H NMR spectrum is consistent with a rigid six-membered $TiSe_4As$ metallacycle with As in an axial position.

The techniques of ^{77}Se NMR spectroscopy and X-ray crystallography have been used to characterize $[Ti(Cp)_2Se_xS_{5-x}]$, (x = 0 - 5) mixtures obtained by the reaction of $TiCp_2Cl_2$ with a series of lithium polyselenide and polysulfide mixtures at different molar ratios [43]. A detailed study for the Se:S 3:2 preparation has been carried out. Its structure comprises two cyclopentadienyl rings and a chain of five chalcogen atoms the latter forming a bidentate chelate ring with titanium.

2.1.5 Complexes with nitrogen donor ligands

The compound $(tmed)TiCl_2$ undergoes a reductive coupling reaction with CH_3CN and Ph_2N_2 to give [*trans*-NC(Me)=(Me)CN][$(tmed)TiCl_2$]$_2$ **(20)** and $(tmed)Cl_2Ti{=}NPh$ **(21)** respectively [44]. The geometry around Ti in **(20)** is a slightly distorted square pyramid with a very short Ti-N (eneimidato) distance 1.699 (4) Å, C-N = 1.384 (5) Å and C-C = 1.377(10) Å indicative of considerable electronic delocalization over the organic moiety. In **(21)**, Ti is square pyramidal with a Ti-N distance of 1.702 (6)Å. It has been suggested that the unusual pyramidal geometry may be controlled by electronic factors.

The synthesis of a terminal aryl-imido titanium complex has been reported [45]. It is unknown whether the aryl-imido ligand in (23) is due to the direct fragmentation of the metallacycle in (22) or whether the reaction proceeds through one or more intermediates. The Ti-N(imido) distance is 1.708 (5) Å, while the N-N of the diazo unit is 1.284 (6) Å. The Ti-N(diazo) distances are 2.175 (5) Å and 2.125 (5) Å indicating that the diazo ligand is σ-bound to Ti with no evidence for M-L π-back-bonding.



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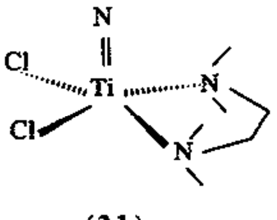

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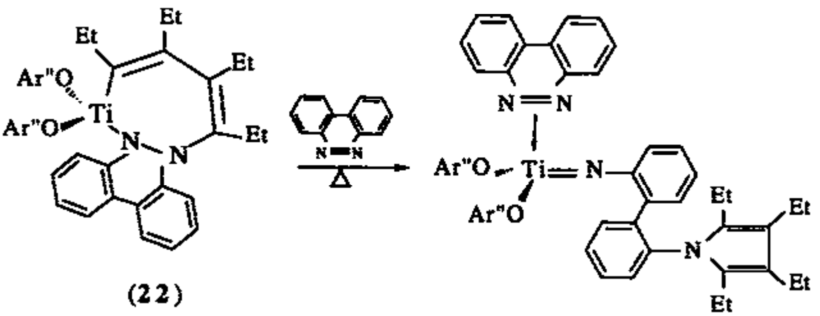


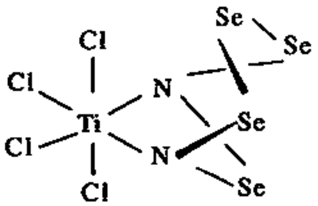
(22)

(23)

The reaction of $TiCl_4$ with $Me_3SiOPPh_2NSiMe_3$ proceeded unexpectedly with elimination of all Me_3Si groups to yield an eight-membered heterocycle $[\{TiCl_2(OPPh_2N)\}_2].4MeCN$ [46]. Its crystal structure was determined and reveals the presence of an almost planar eight-membered heterocycle with very short Ti-N bonds1.741(2) Å, and P-N-Ti angles of 175.9 (1)° A strong *trans* effect is displayed by the coordinated MeCN ligands, the Ti-N bond *trans* to the ring nitrogen is longer by 0.125 (3) Å compared to the one in the *cis* position.

The coordination chemistry of acrylonitrile, $CH_2=CHCN$, methacrylonitrile $CH_2=CMeCN$, and *cis/trans* crotononitrile $MeCH=CHCN$ with $TiCl_4$ has been explored [47]. Some 1:1 and 2:1 addition complexes were prepared and coordination was found to be via donation of the lone pair of the nitrogen to the metal centre. IR and NMR spectroscopy have been used to characterize these complexes. Electrical conductivity experiments indicate that these adducts are non-electrolytes and therefore non-ionic. They are volatile at room temperature with the 2:1 acrylonitrile and methacrylonitrile complexes tending to dissociate in the vapour phase to the 1:1 complex and free ligand.

Titanium(IV) complexes with furfuraldazine, 2-thiophenaldazine and 2-pyridinaldazine have been synthesised and characterized by UV and IR spectroscopy, molar conductance and elemental analysis [48]. IR spectra suggest that the azine ligands are tridentate. Molar conductance suggests that the complexes are 1:4 electrolytes at 10^{-3}M concenterations in DMF solutions. The formula $[ML_2]X_4$ where L = azine ligand and X = NO_3^- or Cl^- has been proposed for these complexes.



(24)

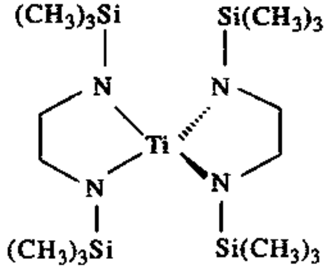
The donor-acceptor complex [$TiCl_4(Se_4N_2)$] has been prepared by reaction of Se_4N_2 with $TiCl_4$ in CH_2Cl_2 suspensions giving red-brown moisture sensitive crystal powders [49]. Based on results from IR spectroscopy it is assumed that both nitrogen atoms bond in a chelating fashion at the titanium atom as shown in (**24**).

Investigation of Lewis acidic titanium species for incorporation into early/late heterobimetallic (ELHB) complexes has led to the synthesis and structural characterization of complexes of the form $Ti(NR_2)_3Cl$ where R = Me and Et [50]. This is the first report to describe the isolation of the R = Et derivative as a crystalline solid. The complexes may be prepared in two ways; by reaction of three equivalents of an amide or by reaction of $Ti(NR_2)_4$ with $TiCl_4$. The geometry about the titanium atom in both complexes may best be described as pseudo-tetrahedral with structural data consistent with Ti-N multiple bonding. Rotation about Ti-N bonds has been investigated, ^1H NMR spectroscopic studies have shown that this barrier is small and extended Hückel and molecular mechanics calculations suggest that steric effects dominate the rotational barriers. Attempts to effect substitution reactions in which phosphido groups replace chloride resulted in redox chemistry giving titanium(III) species.

A new method for the preparation of monoalkylamides of composition $Cp'TiCl_2NHR$ has been reported [51]. The reactants and products are shown in the table below. Compounds (**25-34**) are stable and eliminate HCl only in the presence of a strong base to give $(CpTiClNtBu)_2$ or $(Me_3SiC_5H_4TiClN^tBu)_2$ from a and b respectively. The reactions of (**26**) and (**29**) with $LiN(SiMe_3)_2.Et_2O$ in the presence of pyridine gave $Cp^*TiClNtBu.py$ and $Me_3SiC_5H_4TiClN^tBu.py$ respectively. X-ray crystal structural analysis has been performed on $Cp^*TiCl_2NH^tBu$ and $Cp^*TiClNtBu.py$.

Cp'	R	Compound
C_5H_5	^tBu	(**25**)
$Me_3SiC_5H_4$	^tBu	(**26**)
$(Me_3Si)_2C_5H_3$	^tBu	(**27**)
Me_4C_5H	^tBu	(**28**)
Me_5C_5	^tBu	(**29**)
C_5H_5	CH^iPr_2	(**30**)
$Me_3SiC_5H_4$	CH^iPr_2	(**31**)
$(Me_3Si)_2C_5H_3$	CH^iPr_2	(**32**)
Me_4C_5H	CH^iPr_2	(**33**)
Me_5C_5	CH^iPr_2	(**34**)

A cyclic amide of the form TiL_2 was formed by reaction of $TiCl_3(THF)_3$ with LiL_2, L = [$(CH_3)_3SiNCH_2CH_2NSi(CH_3)_3$] with concomitant disproportionation (**35**). X-ray crystallography shows Ti to be in a strongly distorted tetrahedral environment with approximate D_{2d} symmetry [52]. The complex is monomeric, thermally stable and sublimes readily. It is very sensitive to water and is soluble in all common solvents.



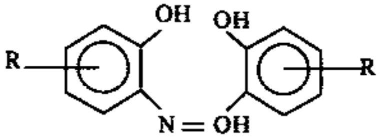
(35)

The reaction of $Me_2NC(S)SN(SiMe_3)_2$ with $TiCl_4$ and $TiBr_4$ yielded $Me_2N\text{-}\overline{CSNTi(Cl_2)S}$ and $Me_2N\text{-}\overline{CSNTi(Br_2)S}$. Reaction of these complexes with pyridine led to the solvates $Me_2N\text{-}\overline{CSNTi(X_2)S}$. 3py with $X^- = Cl^-$, Br^-. These adducts were characterized by X-ray crystallography and display short Ti-N bonds, 1.762 (2) Å for the Cl^- and 1.758 (4) Å for the Br^- complex [53].

The reaction of $TiCl_4$ with $(^iPr)_2P(S)N(SiMe_3)_2$ yields products which are dependent on the basicity of the solvent used to crystallize them. When MeCN was used a dimer $[(^iPr)_2P(S)NTiCl_2.MeCN]_2$ with a planar Ti_2N_2 ring was obtained with asymmetric Ti-N imido bonds 1.863 (2) and 2.060 (2) Å. When pyridine was used the monomer $(^iPr)_2P(S)N{=}TiCl_2.3py$ was obtained with a Ti-N(imido) bond of 1.723 (2) Å [54].

Imido derivatives, $Ti(OCHMe_2)_{4-n}(NHOCR)_n$ (n=1-4; R = Me, Ph, 3-pyridyl) have been prepared [55]. They are stable at ≥ 300°C and were characterized by elemental analysis and IR spectroscopy.

The reactions of acetronitrile with $TiCl_4$ in the presence of $EtCHMeNH_2$, Et_2NH and Et_3N were studied [56]. For all cases insertion into the Ti-Cl bond was observed. The sec-butylamine complex inserts 2 molecules of MeCN giving $TiCl_2(N{:}CMeCl)_2.NH_2CHMeEt.MeCN$. Deprotonation of MeCN was observed with Et_2NH.



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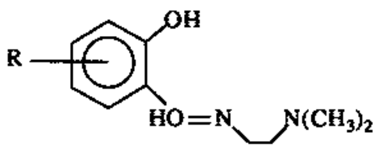
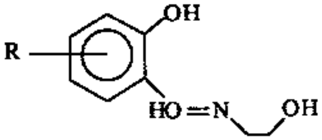


(37)

The synthesis of Ti(IV) complexes with silylated schiff base derivatives *N*-(2-hydroxyphenyl)salycilideneimine - (H_2L^1), (36), *N*-(2-dimethylaminoethyl)salycilideneimine (HL^2)

(**37**) and *N*-(2-hydroxylethyl)salycilideneimine (H_2L^3) (**38**) has been achieved [57]. The complexes have $TiCl_2L^1$, TiL^1_2, $TiCl_3L^2$, and $TiCl_2(HL^3)_2$ stoichiometries. Characterization by ^1H NMR, and IR spectroscopy indicates that coordination is through the imine nitrogen and the phenolic oxygens. In L^2 the tertiary amine group is also coordinated to the metal. In HL^3 the oxygen of the alcohol group is not coordinated.



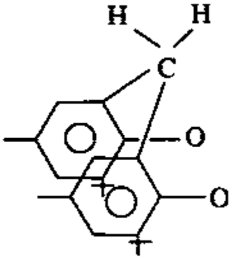
(**38**)

2.1.6 *Complexes with phosphorus donor ligands*

The complex $[(\eta^5\text{-}C_5Me_4PPh_2]_2TiCl_2]$ was found to react with $Mo(CO)_4COD$, $Mo(CO)_5THF$, and $Mo(CO)_6$ giving in each case $[(\eta^5\text{-}C_5Me_4PPh_2]_2TiCl_2]Mo(CO)_4$ as the sole product. whose structure has been elucidated by X-ray crystallography [58]. The molybdenum-titanium distance of 5.194 (1) Å rules out any metal-metal interaction.

2.1.7 *Complexes with boron ligands*

The bisphenoxo dianion ligand (**39**) permitted the isolation of a unique tetrahydroborate titanium(IV) derivative [59]. Using the ^1H NMR spectroscopic signals arising from the diastereotopic hydrogens of the bridging methylene the hapticity of the BH_4^- was studied. An X-ray structure has been reported and shows the titanium atom to be in a tetrahedral environment surrounded by oxygen and boron atoms. The BH_4^- ligands are tridentate based on Ti-H distances and the linearity of the Ti-B-H_t skeleton 171 and 177°. The dioxametallacycle is puckered by 1.038 (4) Å with a boat conformation.



(**39**)

2.2 *TITANIUM(III)*

2.2.1 *Complexes with halide ligands*

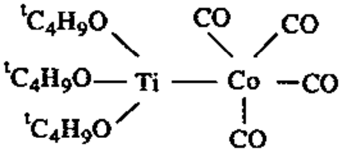
The structure and magnetochemical characterization of fourteen titanium(III) chloro complexes $TiCl_3L_n$ ($n = 3, 4$; L = THF, aliphatic, alcohols, nitriles, py and its derivatives) has been achieved [60]. The magnetic properties and stereochemical arrangement of the complex components have been discussed.

2.2.2 *Complexes with oxygen donor ligands*

The crystal structure of the $[\{Ti(Cp^*)(O_2CPh)_2\}_2]$ has been reported [18]. The molecule consists of two TiCp* fragments bonded through four acetato groups which are situated in two mutually perpendicular planes. The Ti-Ti distance is 3.660 (7)Å indicating the absence of a metal-metal interaction. The geometry about each Ti atom is of the four-legged piano-stool type. The mean Ti-O distance is 2.04 Å and the plane defined by the four oxygen atoms bonded to the metal is almost parallel to the Cp* best plane. The O-C-O angles with mean values of 126° are indicative of bridging rather that chelating acetato groups.

A theoretical analysis using the parameter-free Fenske-Hall model has been carried out on $[(Cp_2Ti)_2(\mu\text{-}C_2S_4)]$ and $[(Cp_2Ti)_2(\mu\text{-}C_2O_4)]$ [61]. Although $(\mu\text{-}C_2S_4)$ and $(\mu\text{-}C_2O_4)$ are electronically equivalent, the tetrathiolate complex is diamagnetic and displays two quasi-reversible one-electron oxidations whereas the oxalate is paramagnetic and undegoes a single two electron oxidation. Molecular orbital calculations have shown that strong bonding interactions between the tetrathiolate π-acceptor orbital and the two Ti atoms gives rise to a nondegenerate HOMO which accounts for spin pairing of the unpaired electron from each Ti atom. For the oxalate case however, the $C_2O_4^{2-}$ π-acceptor orbital is at a higher energy and inaccessible to combine with the titanium orbitals. The HOMO consists of symmetrical and antisymmetrical combinations of titanium atomic orbitals give rise to a degenerate set of half occupied HOMOs each with one unpaired electron. Redox properties were discussed from considerations of HOMO/LUMO compositions.

An unusually stable $[(^tBuO)_3Ti\text{-}Co(CO)_4]$ heterobimetallic has been prepared (40) [62]. IR and mass spectroscopy indicate the absence of bridging carbonyl and alkoxide ligands and C_{3v} symmetry about the Co atom.



(40)

The crystal structure and properties of $[Ti_2(\mu\text{-}Cl)_2Cl_4\{o\text{-}C_6H_4(CO_2Et)_2\}_2].4CH_2Cl_2$ have been described [63]. This compound is novel in Ti(III) chemistry since it lacks cyclopentadienyl ligands which are a common feature in Ti dimers. It is formed by the addition of metallic aluminium turnings to a mixture $TiCl_4$ and diethyl *o*-phthalate in CH_2Cl_2 yielding a brown air-sensitive crystalline compound. The compound has a dimeric structure, each Ti atom is surrounded by two terminal and two bridging chlorine atoms and carbonyl oxygen atoms of the *o*-phthalate molecules forming a slightly distorted edge-sharing di-octahedron. The Ti····Ti distance is 3.629(4) Å. Magnetic susceptibilities were determined between 4.2 K and 293 K and the temperature dependence was found to be typical for an antiferromagnetic d^1-d^1coupling with μ_{eff} per Ti atom 0.43 and 1.43μ_b at 4.2 K and 293 K respectively.

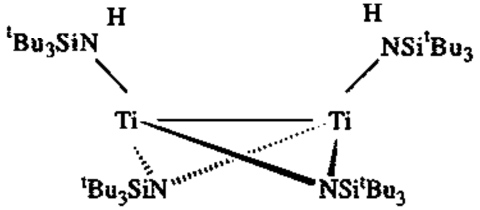
Titanium(III) complexes, $Ti[Cr(NCS)_6].4L$, (L = DMSO, DMF) have been prepared by the reaction of $TiCl_3$ with $K_3[Cr(NCS)_6]$ in solution in the presence of L [64]. They were characterized by IR spectroscopy, X-ray diffraction and thermal decomposition studies. The L ligands are *O*-bonded to the Ti atom and the SCN groups are monodentate, nonbridging and *N*-bonded to the Ti atom.

2.2.3 *Complexes with nitrogen donor ligands*

Recently $[Ti(Cp^*)_2(NMePh)]$ and $[Ti(Cp^*)_2(NMePh)(CNBu^n)$, the first ever titanocene amide Ti(III) complexes to have been characterized by X-ray crystallography have been reported [65]. Although both complexes contain planar amide ligands there is no evidence for Ti-N π-bonding thereby refuting the maxim that the presence of trigonal planar amide ligands can be used as supporting evidence for the existence of nitrogen to metal π-donation. The Ti-N bond distance of 2.054 (2) Å in the former is long, and within experimental error is equal to the sum of single bond radii for titanium and nitrogen. The crowded coordination sphere as evidenced by the small (Cp*)-Ti-(Cp*) angle of 140.5° is likely to contribute to the long Ti-N distance. The geometry around nitrogen is trigonal planar which has been attributed to steric interactions with the Cp* ligands and perhaps conjugation of the nitrogen lone pair with the phenyl ring. In the latter complex the Ti-N bond distance is 2.157 (5) Å which is in the range often observed for N-Ti dative bonding. For both complexes the orientaton of the amide with respect to the $Ti(Cp^*)_2$ unit is such that donation of the lone pair to Ti acceptor orbitals is unlikely.

The various electronic factors responsible for η^1-pyridine-*N* *vs.* η^2-pyridine-*NC* ligation for a series of transition metals have been explored by preparing adducts of the type $(silox)_3ML$ (M = Sc, Ti, V, Ta) [66]. Treatment of $(silox)_3Ti$ (silox = $^tBu_3SiO^-$) with 1 equivalent or an excess of pyridine gave in 67% yield monomeric, ink-blue $(silox)_3Ti(py)$. EPR spectroscopic data are consistent with a localized electron on the titanium atom while the ^1H NMR spectrum is in accord with η^1-*N*-donor binding to a d^1 center. Other pyridine ligands surveyed by η^1-ligation included 4-picoline ($2\text{-}4\text{-}NC_5H_4Me$), 3,5-lutidine ($3,5\text{-}NC_5H_3Me_2$) and $4\text{-}NC_5H_4{}^tBu$. Extended Hückel molecular orbital calculations were carried out to assess the factors responsible for variation in pyridine ligation in this series of adducts.

The X-ray crystal structure of $[(^tBu_3SiNH)Ti]_2(\mu\text{-}NSi^tBu_3).C_6H_6(17C_6H_6)$ (**41**) has been determined and has an unusual C_2 structure with a very short Ti-Ti bond 2.442 (1) Å [67]. Each titanium atom is at the apex of a trigonal pyramid whose basal plane is composed of nitrogens from an amide and two $\mu\text{-}NSi^tBu_3$ bridges. The titanium atoms are 0.58 and 0.60 Å *exo* to the basal planes and are apparently oriented toward empty space. Extended Hückel molecular orbital calculations were carried out to elucidate the electronic factors responsible for the short Ti-Ti bond and the unusual *exo* disposition of the Ti atoms.

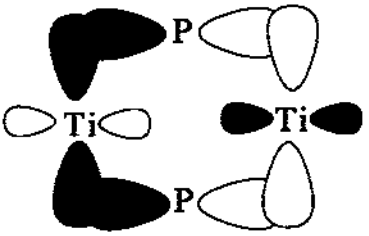


(41)

2.2.4 Complexes with phosphorus donor ligands

The reaction of $[Cp_2TiCl]_2$ with $LiP(SiMe_3)_2$ gave rise to the mononuclear complex $[Cp_2TiP(SiMe_3)_2]$ which is the first example of a complex containing a Ti-P double bond. This complex is paramagnetic and its X-ray structure indicates that Ti is coordinated by two Cp ligands and a $TiP(SiMe_3)_2$ with the geometry around phosphorus being nearly planar and a Ti-P bond length of 2.467 Å indicative of π-interactions. In contrast reaction of $[Cp_2TiCl]_2$ with $LiAs(SiMe_3)_2$ yields the dinuclear $[(Cp_2Ti)_2ClAs(SiMe_3)_2]$ which is also paramagnetic. Reaction of $TiCl_4$ with $P(SiMe_3)_3$ gives rise to the complex $[TiCl_3\{P(SiMe_3)_3\}_2]$ which is also paramagnetic with a trigonal planar Ti atom [68]. In a related paper [69], a theoretical investigation on $[Cp_2TiP(SiMe_3)_2]$ has been reported. HF/SCF calculations on geometry and electronic structure of the model compound $[Cp_2TiP(SiH_3)_2]$, in various low lying electronic states are in close agreement with those from X-ray diffraction and indicate that the Ti-P bond involves π-interactions.

The complex $[Cp_2Ti(\mu\text{-}PEt_2)]_2$ was synthesised by reaction of Cp_2TiCl_2 with $LiPEt_2$ in 62% yield and its crystal structure determined [70]. It exists as a dimer with a planar Ti_2P_2 core in which the Ti atoms are in a pseudotetrahedral environment. The Ti-P distances range from 2.606 (3) to 2.631 (3) Å and the P-Ti-P angles were found to be 89.1 (1) to 89.9 (1)°. The complex was EPR silent at 298 K and bulk magnetic susceptibility studies indicate that it is diamagnetic implying strong antiferromagnetic coupling between the unpaired electrons on each Ti atom. In THF solution, variable temperature ^1H, and $^{31}P\{^1H\}$ NMR and EPR spectra are consistent with the presence of a paramagnetic, monomeric species Cp_2TiPEt_2. Extended Hückel molecular orbital calculations were carried out to shed some light on the mechanism of antiferromagnetic coupling between the Ti centers. Mixing of the metal $1a_1$ orbitals with the p_z orbitals in the bridging phosphorus atom provides a route for through-ligand coupling of the unpaired electrons on the Ti centres (**42**).



(42)

2.2.5 *Complexes with boron ligands*

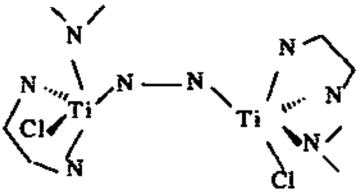
The molecular structure of gaseous $Ti(BH_4)_3$ has been determined from electron diffraction and IR and UV photoelectron spectroscopy on $Ti(BH_4)_3$ and $Ti(BD_4)_3$ [71] The molecule has three tridentate BH_4^- groups giving the molecule overall C_{3h} symmetry and exhibits a planar TiB_3 skeleton. Pertinent structural parameters include r(Ti···B) = 2.175 (4) Å, r(Ti-D_b) = 1.984 (5) Å, r(B-D_b) = 1.276 (5) Å, r(B-D_t) = 1.166 (13) Å. Infrared spectra on gaseous or matrix isolated $Ti(BH_4)_3$ and $Ti(BD_4)_3$ are consistent with the vibrational properties of a molecule possessing C_{3h} symmetry. The UV photoelectron spectrum of $Ti(BH_4)_3$ has an intensity pattern that is characteristic of molecules with tridentate BH_4^- groups. Extended Hückel molecular orbital calculations were carried out on several possible conformers with C_{3h} one lying at an overall minimum on the potential energy surface. The factors responsible for the structure of $Ti(BH_4)_3$ and those of other related tetrahydroborate derivatives are discussed in the light of the results obtained from molecular orbital calculations.

2.3 *TITANIUM(II)*

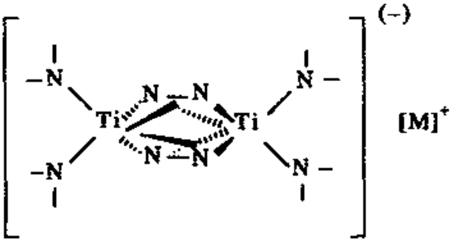
2.3.1 *Complexes with nitrogen donor ligands*

The synthesis and characterization of a novel class of *trans*-Cl_2TiL_4 [L = ½ tmed, *N,N,N'*-trimethylethylenediamine, py, ½ bipy] has been reported [72]. X-ray analysis of the tmed adduct reveals a molecule possessing a *trans* halide octahedral geometry with Ti-Cl = 2.477 (2) Å, Ti-N1 = 2.381 (7) Å, and Ti-N2 = 2.377 Å. A salient feature of its solution chemistry is the remarkable lability of the coordinated tmed ligands thereby facillitating ligand replacement reactions with several amines to form the corresponding derivatives. In a related paper the isolation and characterization of two novel dinitrogen Ti(II) and a mixed valence Ti(II)/Ti(I) amido complex was reported [73]. They were obtained by chlorine replacement from *trans*-$(tmed)_2TiCl_2$. The structures of

$\{[(Me_3Si)_2N]TiCl(tmed)]\}_2(\mu\text{-}N_2)$ (43) and $[\{[(Me_3Si)_2N]_2Ti\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)][(tmed)_2Li]$ (44) were determined by X-ray analysis and are representative of end-on and side-on bonding modes for nitrogen respectively. In (43) coordination about Ti is square pyramidal with Ti-N(N_2) = 1.762 (5) Å and N-N = 1.289 (9) Å suggesting considerable delocalization over the $Ti_2(\mu\text{-}N_2)$ moiety. In (44) Ti is octahedral with Ti-N3 = 2.236 (19) Å and Ti-N4 = 2.290 (13) Å and N3-N4 = 1.379 (21) Å. It is difficult to assess the extent of dinitrogen reduction based on N-N distances owing to the completely different bonding modes exhibited by these two complexes.



(43)



M = [Li(tmed)$_2$]

(44)

The electronic structure of several transition metal amide ions including $TiNH_2^+$ has been studied and compared with available experimental data [74]. Generalized Valence Bond calculations have been performed and indicate that NH_2^- forms a double bond to the metal in an interaction that is primarily electrostatic. The Ti-N distance was found to be 1.92Å. For all states calculated the metal loses electrons to NH_2^-. The charge on Ti in the ground state was found to be +1.34.

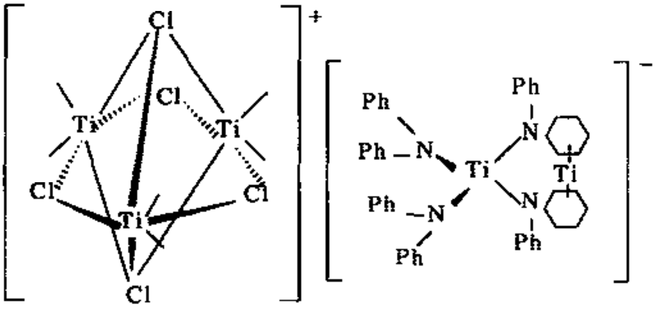
2.3.2 Complexes with phosphorus donor ligands

The ground states of $Ti(CH_3)_2(dmpe)_2$ and $Ti(Cl)_2(dmpe)_2$ have been studied using approximate molecular orbital calculations and ab initio calculations [75]. Experimentally, the dichloro complex was found to have a paramagnetic ground triplet state while the dimethyl was found to have a diamagnetic singlet state. Since Cl^- is a stronger donor it would be expected to cause a larger splitting of the t_{2g} orbitals causing it to be diamagnetic in the ground state. Results from approximate molecular orbital calculations were in agreement with this reasoning and contradictory to experiment. Results from *ab initio* calculations were in qualitative agreement with experimental results provided reasonable basis sets were used. In order to obtain quantitative agreement with experiment significant correlation must be invoked. The differences between the ground states in these complexes is thought to be due to electronegativity differences between Cl^- and CH_3. Since Cl^- is more electronegative, it forms more polar Ti-Cl bonds, thereby causing the Ti atom to have a larger effective nuclear charge which causes the *d* orbitals to contract thereby increasing *d-d* repulsions. These repulsions far outweigh t_{2g} orbital splitting as determinants of ground states of these complexes.

The synthesis and thermal evolution of $Cp_2Ti(CO_2)(PMe_3)$ have been revisited [76]. FT-IR spectroscopic studies in the solid state and in solution (in CH_2Cl_2 and $CHCl_3$) of the complex and its isotopic labelled derivatives ($^{13}CO_2$, $C^{18}O_2$) has been conducted. A normal coordinate analysis with different structural hypotheses was performed assigning a *C*-coordinated CO_2 to Ti.

2.3.3 Clusters

The reaction of *trans*-$(tmed)_2TiCl_2$ with $NaNPh_2$ proceeds instantaneously at room temperature with abstraction of one chlorine atom to give $[(tmed)_3M_3Cl_5]^+[N,N'\text{-}\{Ti[(\text{-}C_6H_5)PhN]_2]^-$ (45) [77] . This reaction is thought to proceed via a complicated disproportionation reaction mechanism involving the formation of zerovalent species. X-ray analysis of the cation shows it to consist of three Ti atoms and three coplanar bridging chlorine atoms. The μ^3-chlorine atoms are symmetrically placed above and below the molecular plane. The M-Cl distances range from 2.456 (5) Å to 2.503 (5) Å with axial and equatorial distances being comparable. The anion consists of a tetracoordinated titanium at the center of a slightly distorted tetrahedron defined by the four nitrogen atoms of the amido groups. In addition two phenyl rings from two different amido groups are parallel and are attached to one Ti atom which is formally zerovalent giving a (η^6-arene)$_2$Ti sandwich. The average Ti-Ti distance is 2.764 Å, which is short and is suggestive of a single bond. The magnetic moment $\mu_{eff} = 1.81\mu_B$ is consistent with the presence of one unpaired electron per molecule, and is likely due to the d^1Ti(III) of the anion; thus the trimetallic cation can reasonably be expected to be diamagnetic. Cleavage of the trimetallic frame was easily achieved via simple treatment with pyridine at room temperature giving rise to monomeric deep blue crystalline $(pyridine)_4TiCl_2$.



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