

4. Titanium 1992

José C. Vites and Mary M. Lynam

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INTRODUCTION

This review surveys the titanium literature for 1992 of interest to coordination chemists. It is based on a literature search of volumes 116, 117 and 118 (1–10) of *Chemical Abstracts*. Its format is in a similar vein to the 1991 review [1]. Additionally, major inorganic chemistry journals from January to December 1992 were searched separately. The assistance of Heidi Mercado of the Eastern Michigan University Library with a computer literature search is gratefully appreciated.

4.1 TITANIUM(IV)

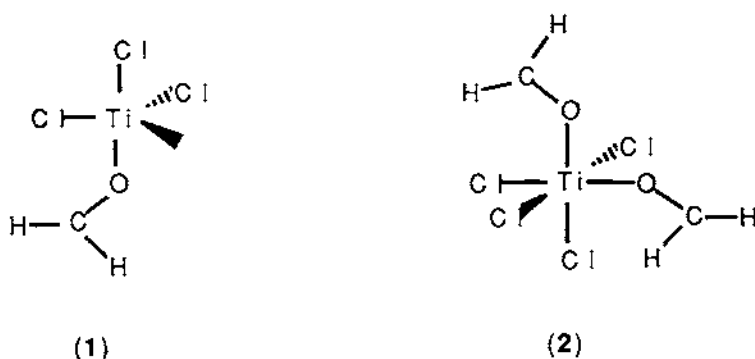
4.1.1 Complexes with halide ligands

Investigation of a class of complex anions $M(OTeF_5)_6^{n-}$, has led to the synthesis of the compound $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$ [2]. The X-ray crystal structure shows the anion to

possess an octahedral TiO_6 core. A salient feature of the structure is the absence of Ag-O bonds; each $[\text{Ag}(\text{CH}_2\text{Cl}_2)_3]^+$ cation is extremely weakly coordinated to the $\text{Ti}(\text{OTeF}_5)_6^{2-}$ anion by two $\text{Ag}\cdots\text{F}$ contacts of 3.029(8) and 3.033(6) Å. This anion has been found to be less coordinating, more stable in the presence of electrophilic cations and much more solubilizing in weakly coordinating solvents than any previously reported anions.

The one-electron oxidation of $(\text{Cp})_2\text{TiCl}_2$ in acetonitrile was studied and the product generated $[(\text{Cp})_2\text{TiCl}(\text{CH}_3\text{CN})]^+$ was characterized by electrochemical, and ^1H NMR and UV-VIS spectroscopic methods [3]. It has been suggested that formation of this cation may be due to abstraction of an electron from a Ti-Cl bond with concomitant release of Cl^- upon coordination by CH_3CN .

Complexes formed between titanium tetrachloride and formaldehyde have been studied by ab initio self consistent molecular orbital methods (SCF-MO) recently [4]. In particular, 1:1 and 2:1 complexes, their different structures and the interconversion between them have been examined. For the 1:1 case, the most stable complex, which has a trigonal bipyramidal structure, was found to have the H_2CO molecule in an axial position (1) whereas in the 2:1 complex, which is octahedral, a *cis* isomer (2) is the most stable one. Furthermore, the formation of an $(\text{H}_2\text{CO}-\text{TiCl}_4)_2$ complex via the dimerization of $\text{H}_2\text{CO}-\text{TiCl}_4$ has also been explored and results indicate that the interaction between formaldehyde and TiCl_4 is stronger than in the monomeric cases. All results are in agreement with what has been observed experimentally.



4.1.2 Complexes with oxygen donor ligands

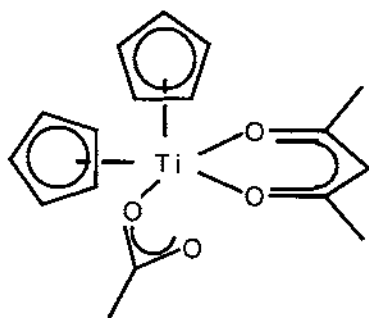
The complexes $[\text{tmtaa}]\text{Ti}=\text{O}$ and $[\text{tmtaa}]\text{Ti}=\text{S}$ have been demonstrated to undergo addition and cycloaddition reactions where $\text{tmtaaH}_2 = 7,16$ -dihydro-6,8,15,17-tetramethyl-dibenzo[*b,i*][1,4,8,11]tetrazacyclotetradecine [5]. These complexes have been characterized by IR and NMR spectroscopies, FAB MS and X-ray crystallography.

The synthesis and characterization of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{W}_5\text{O}_{18}\text{H})]^{3-}$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{W}_5\text{O}_{18}\text{H})]^{2-}$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{W}_5\text{O}_{18}\text{H}_2)]^-$ have been documented [6]. An X-ray diffraction study on the monoprotonated anion shows it to contain hydrogen-bonded dimers of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{W}_5\text{O}_{18}\text{H})]^{2-}$ ions protonated at OTiW doubly-bridging oxygens. Using HCl, the

diprotonated anion $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{W}_5\text{O}_{18}\text{H}_2)]^-$ was obtained; its crystal structure indicates that a pair of *cis*-OTiW oxygens are protonated.

The synthesis and characterization of group 4 metal-iron complexes bridged by carboxylate substituted cyclopentadienyl groups has been reported [7]. In particular, the complexes $\text{Cp}_2\text{M}[\mu\text{-O}_2\text{CC}_5\text{H}_4\text{Fe}(\text{CO})_2(\text{CH}_2\text{C}_6\text{H}_5)]_2$, $\text{M} = \text{Ti}$ or Zr were prepared and characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy. The crystal structure for the titanium case shows that the two carboxylate groups coordinate to the titanium atom in a monodentate fashion with Ti-O distances of 1.923 and 1.972 Å.

Compounds of the type $[\text{Cp}_2\text{Ti}(\text{RCOCHCOR}')(\text{XCOO})]$ (3), where $\text{R} = \text{R}' = \text{CH}_3$ or $(\text{CH}_3)_3\text{C}$; $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_6\text{H}_5$; $\text{X} = \text{Cl}_2\text{CH}$ or Cl_3C , have been synthesized and characterized by elemental analysis, electrical conductance, magnetic measurements, and IR and NMR spectroscopic studies [8].



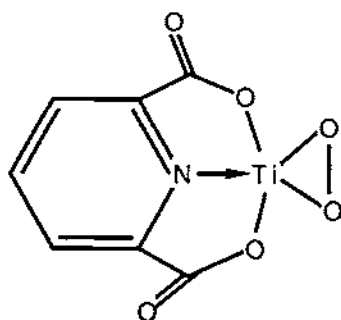
(3)

A study of complex formation in concentrated sulfate solutions using salt additives such as NaF, KF, NH_4F , KCl, RbCl, CaCl_2 and BaCl_2 has been described [9]. Identification of the solid phases showed that $\text{Ti}[\text{O}(\text{OH})_2]$, TiOSO_4 and $\text{TiO}(\text{SO}_4)_2^{2-}$ were among the complexes formed.

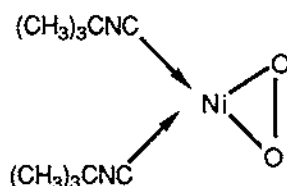
The reaction of titanium tetrachloride with 4-methoxyphenol in a 1:4 molar ratio in benzene gave $\text{Ti}(\text{OC}_4\text{H}_4\text{OMe-4})_4$ which has been characterized using elemental analysis, conductance, molecular weights and NMR spectroscopic studies [10].

The synthesis and crystal structure of cesium-bis(oxalato)oxo-titanate(IV) hydrate $\text{Cs}_4[\text{TiO}(\text{C}_2\text{O}_4)_2]_2 \cdot 3\text{H}_2\text{O}$ have been described [11]. Its structure comprises $(\text{TiO})_4$ rings with Ti in a distorted octahedral environment; Ti-O bonds within the ring system range from 1.796 to 1.829 Å while those to the oxalate are about 2.00 Å. The orientation of the $(\text{TiO})_4$ rings gives rise to holes of up to 6.00 Å in diameter which are occupied by cesium atoms and crystal water.

The bonding between the metal atom and the peroxo fragment in η^2 -peroxotransition metal complexes has been investigated using ab initio calculations [12]. In particular, the electronic structures of peroxotitanium(IV) 2,6-pyridinedicarboxylate (4) and peroxonickel(II) bis(*tert*-butylisocyanate) (5) have been calculated and their bonding compared using orbital population and frontier orbital analyses. The ground state of the titanium complex is 1A_1 while that of the nickel complex is 3B_2 .

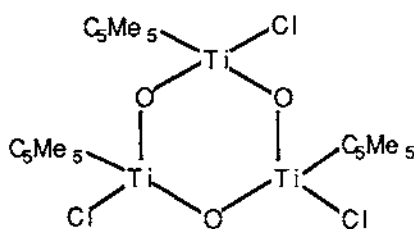


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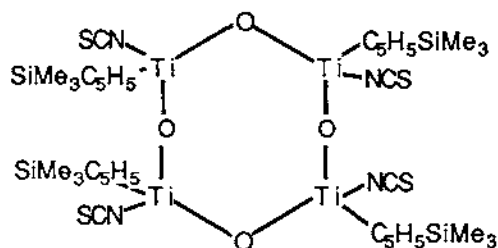


(5)

By hydrolysis of the precursor $[\text{TiLCl}_3]$, the syntheses in high-yield of the monocyclopentadienyloxochloro complexes $[(\text{TiLCl}_2)_2(\mu\text{-O})]$, $[(\text{TiLCl})_4(\mu\text{-O})_4]$, $[(\text{TiL})_4(\mu\text{-O})_6]$ and $[(\text{TiLCl})_3(\mu\text{-O})_3]$ (6), where $\text{L} = \eta^5\text{-C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{Me}$, $\text{C}_5\text{H}_4(\text{SiMe}_3)$ or C_5Me_5 were achieved [13]. Additionally, $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)\}\text{Br}_3]$, $[\text{Ti}_4\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)\}_4\text{Br}_4(\mu\text{-O})_4]$ and $[\text{Ti}_4\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)\}_4(\text{NCS})_4(\mu\text{-O})_4]$ (7) have been prepared. The crystal structures of (6) and (7) where $\text{L} = \eta^5\text{-C}_5\text{Me}_5$ have been obtained. In the former complex, the titanium and oxygen atoms define a six-membered ring having an almost flattened half-boat conformation; the Ti-O bond distances and Ti-O-Ti angles reflect a significant Ti-O double bond character. In the latter species, the titanium and oxygen atoms are arranged giving an eight-membered ring which is roughly planar with coordination about each titanium atom described as trigonal planar. Extended Hückel molecular orbital calculations have been performed on some of these complexes.



(6)



(7)

An *ab initio* study of bonding in rutile-type compounds including TiO_2 , carried out by means of band structure calculations, has been reported [14]. From these calculations, electron densities, densities of states, total energies and structure factors were derived. Using the calculated densities of states, the chemical bonding in these structures was interpreted. Results indicate that an MX_6 cluster model where $\text{M} = \text{Ti}$, Zn , V , Cr or Ru , $\text{X} = \text{O}$ or F , accounts for only part of the bonding mechanism. In the crystalline environment, the anionic ligands reduce their amount of π -bonding in the MX_6 cluster at the expense of increased σ -bonding with all three nearest neighbours in the M_3X units. This reduction leads to an increase in metal-metal bonding across the shared

edges of the MX_6 octahedra. The observed lattice geometry may be viewed as an optimum balance between maximizing stabilization of the MX_6 and M_3X units. Results from these studies have been compared with experimental results and other calculations.

The synthesis of $[TiO(dmso)_5](CF_3SO_3)_2$ and a complete variable-temperature and pressure study of dmso exchange on $[TiO(dmso)_5]^{2+}$ in deuterated nitromethane CD_3NO_2 diluent has been described [15]. The complex displays two distinct dmso-exchange processes namely, a D mechanism has been suggested for the fast exchange of loosely bound axial dmso with the bulk. The second process which is slower takes place via the migration of the axial dmso to the equatorial plane concomitant with the loss of an equatorial dmso molecule in a concerted process which has an expanded transition state.

The reactions of dibasic hydrazones, benzothiazoline and other chelating ligands with $[Cp_2MCl_2]$ $M = Ti$ or Zr have been described [16]. Structures have been proposed for the products based on elemental analyses, molar conductance, molecular weight, IR, UV-VIS and 1H NMR spectroscopy.

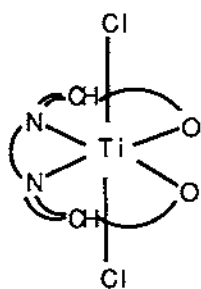
A large intramolecular ferromagnetic interaction has been observed in a $Ti(IV)$ complex composed of two tridentate Schiff base semiquinonato radical ligands [17]. Results from X-ray crystallography, cyclic voltammetry and magnetic susceptibility measurements indicate that this behaviour is due to the topological degeneracy of the magnetic orbitals of the radicals.

The synthesis and characterization of $Ti(IV)$ and $Mo(V)$ complexes with diesters has been described [18]. The crystal structures of $[O-C_6H_4(CO_2CH_2CH_2Ph)Cl_4Ti]$, $[C_2O_4(CH_2CH_2Ph)_2Cl_4Ti]$ have been determined, with titanium being octahedrally coordinated in both structures and surrounded by four chlorine and two oxygen atoms of coordinated *O*-diester molecules in the *cis* position.

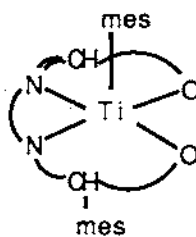
4.1.3 Complexes with oxygen and nitrogen donor ligands

A detailed study on the alkylation reactions of $[Ti(salen)Cl_2]$ (8) where salen is the tetradentate Schiff's-base dianion *N,N'*-ethylenebis(salicylideneimine) has been reported [19]. Complex (9) the first octahedral *trans*-dimethyltitanium(IV) derivative, is the result an aryl migration to the ligand in the reaction of $MgBr(mes)$, ($mes = 2,4,6-Me_3C_6H_2$) with (8) yielding a complex in which one mesityl group is bonded to the metal atom while the second one is attached to the carbon atom of an imino group in the salen ligand. The alkylation reaction is dependant on the solvent used, when alkylation or arylation is carried out in thf with $MgBrR$ ($R = Ph$ or mes) the reductive arylation of (8) occurs with isolation of the corresponding $Ti(III)$ derivatives.

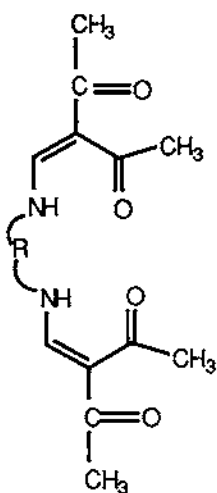
Bis(cyclopentadienyl)titanium and zirconium complexes $[Cp_2M(J-R)]$ where H_2J-R is a Jager type ligand with bridging R groups (10) have been synthesized [20]. The subsequent condensations of the complexes ($R = o$ -phenylene) with *o*-phenylenediamine leading to ring closure and formation of cyclic complexes have also been studied. These complexes were characterized by elemental analysis, electrical conductance, magnetic susceptibility and electronic, IR and 1H NMR spectroscopy.



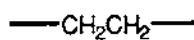
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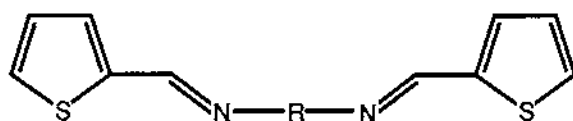
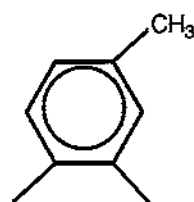
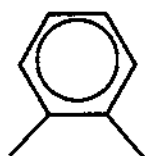
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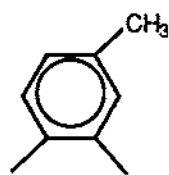
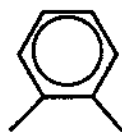
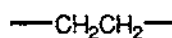
(10)



R =



R =



(11)

4.1.4 Complexes with oxygen and sulfur donor ligands

The synthesis and structural characterization of (cyclopentadienyl)titanium and zirconium derivatives with Schiff bases derived from thiophene-2-aldehyde (11) has been reported [21]. Two types of derivatives ($\text{Cp}_2\text{MCl}_2\text{-L}$) and $[\text{Cp}_2\text{MCl}(\text{L})_2]\text{Cl}_2$ were isolated and characterized by elemental analysis, electric conductance, magnetic moment measurements, IR, ^1H NMR, and ^{13}C NMR spectroscopy.

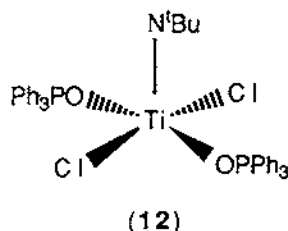
4.1.5 Complexes with sulfur donor ligands

The synthesis and properties of the four-membered titanacycles $\text{Cp}_2\text{TiS}_2\text{Si}(\text{C}_6\text{H}_5)_2$, $\text{Cp}_2\text{TiS}_2\text{Ge}(\text{C}_6\text{H}_5)_2$ and $\text{Cp}_2\text{TiS}_2\text{Sn}(\text{C}_6\text{H}_5)_2$ have been reported [22]. Mass and UV spectroscopy and ^1H NMR spectroscopy were used to characterize these compounds.

4.1.6 Complexes with nitrogen donor ligands

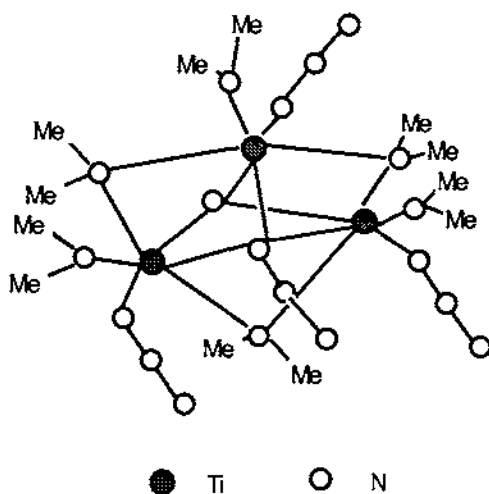
The gas phase thermal average molecular structures of $\text{Ti}(\text{NMe}_2)_4$, $\text{V}(\text{NMe}_2)_4$, and $\text{V}(\text{O}^i\text{Bu})_2$ have been elucidated [23]. Gas phase electron diffraction obtained with nozzle temperatures of 130-156°C indicate S_4 symmetry, and the T-N bond distances are 1.917(2) Å. The N-Ti-N valence angle of 114.2(17)° indicates that the coordination tetrahedron of Ti may be slightly flattened. The shapes of the coordination tetrahedra in these molecules have been discussed in terms of donation of π electrons from N or O into low-lying d orbitals on the metal atom.

Research on the preparation of model complexes involved in chemical vapor deposition (CVD) has resulted in the synthesis and characterization of two titanium nitrogen complexes [24]. Treatment of TiCl_4 with *tert*-butylamine (6-8 equiv) in dichloromethane at -78°C followed by warming to room temperature and workup yielded $[\text{TiCl}_2(\text{NH}^i\text{Bu})_2(\text{NH}_2^i\text{Bu})_2]_n$ as bright orange crystals. Treatment of this complex with triphenylphosphine oxide in dichloromethane at room temperature yielded the complex $[\text{TiCl}_2(\text{N}^i\text{Bu})(\text{OPPh}_3)_2]$ (12) in which the Ti-N bond length is 1.672(7) Å. When the former was volatilized at 500°C a gold film ensued which was identified as titanium nitride while volatilization of the latter produced an amorphous blue-black substance. Mass spectroscopy on the former provided evidence for monomeric and dimeric imido complexes in the CVD process.



The synthesis of molecular precursors to titanium nitride using azide as the nitrogen source has been pursued [25]. A stoichiometric amount of azidotrimethylsilane was reacted with $\text{Ti}(\text{NMe}_2)_4$ in benzene at approximately 5°C yielding a brick red oil which was extracted with

toluene, filtered and recrystallized from hexane yielding air-sensitive red-orange crystals of $[\text{Ti}(\text{NMe}_2)(\text{N}_3)(\mu\text{-NMe}_2)]_3(\mu_3\text{-N}_3)(\mu_3\text{-NH})$ (13). The structure which is the first Ti complex containing a triply bridging azide, comprises a six-membered $(\text{TiNMe}_2)_3$ titanacycle in a pseudo-chair configuration. The six-coordinate titanium atoms are connected through bridging dimethylamide groups which are bent towards a triply bridging azide cap on one face of the cycle. The other face of the ring is capped by a triply bridging imide group. The $\text{Ti-N}_3(\text{cap})$ bond length is $2.30\text{\AA}$ is significantly longer than the terminal $\text{Ti-N}_3(\text{terminal})$ bond lengths of 1.91 and $2.01\text{\AA}$. The mechanism for formation of the imide has not been fully established but is thought to be derived from a capping azide ligand.



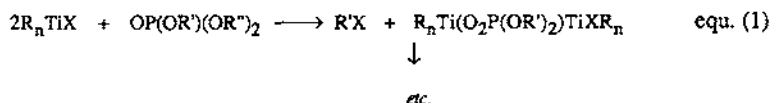
(13)

The synthesis and X-ray structure determination of the compounds $(\text{RC}_5\text{H}_4)\text{TiCl}_2\{\text{NH}(\text{tBu})\}$ ($\text{R} = \text{H}, \text{CH}_3$), both of which contain short Ti-N bonds, have been achieved [26]. The overall geometry of the molecules may be derived from the piano-stool arrangement of $(\text{C}_5\text{H}_5)\text{TiCl}_3$ and $(\text{CH}_3\text{C}_5\text{H}_4)\text{TiCl}_3$ by substitution of a chloro by an amido ligand. An *anti*-conformation with respect to the Ti-N bond for the amido and cyclopentadienyl ligands is adopted. The Ti-N distances are short, $1.879(3)\text{\AA}$ for $\text{R} = \text{H}$ and $1.871(5)\text{\AA}$ for $\text{R} = \text{CH}_3$ and, together with the planar environment about the N atom, are indicative of multiple bonding. A variable-temperature NMR spectroscopic study was conducted to further explore the Ti-N bond. Rotational barriers of approximately 5 kcal mol^{-1} were obtained indicating free rotation about the Ti-N vector.

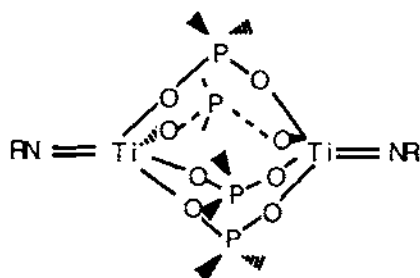
4.1.7 Complexes with phosphorus donor ligands

Exploration of phosphato-titanium chemistry in order to gain a better understanding of KTiPO_4 , a nonlinear optical material, has resulted in the preparation of several new diverse phosphato-titanium coordination compounds [27]. Three families of compounds were prepared by

elimination reactions as shown in equation 1. The stable compounds obtained



possess phosphates bridging two titanium centres, while monomeric nonbridged compounds have been implicated as reaction intermediates. Compound (14) is synthesized from imido-bridged dimeric compounds $[(Me_2N)_2Ti(\mu-NR')]_2$ when the phosphato groups are introduced in the synthesis the bridging imido groups assume terminal positions through a mechanism thought to involve monomeric intermediates. The X-ray crystal structure of $[^tBuN=Ti(O_2P(OSiMe_3)_2)_4Ti=N^tBu]$ reveals a Ti-N separation of 1.667(5) Å.



(14)

4.1.8 Clusters

A facile route to titanium-oxo cluster compounds obtained in high yields by the reaction of carboxylic acids with titanium tetrachloride has been reported [28]. X-ray crystallography on the benzoate derivative $\{Ti_4Cl_6(\mu_2-O_2CPh)_6(\mu_3-O)_2\}$ indicates a Ti_4O_2 core structure previously unknown in which there are two types of titanium environments. Notably, the carboxylate bridges lie principally on one side of the molecule thereby vesting it with hydrophobic character whereas the halogen substituents lie on the other side and remain accessible for further reaction.

In a related paper [29], the reaction of $TiCl_4$ with a series of *para*-substituted benzoic acids $p-XC_6H_4CO_2H$; X = Me, Et, F or I giving rise to the trinuclear oxo clusters of general formula $[Ti_3Cl_3(O_2CR)_5O_2]$ has been described. The reaction conditions are simple, heating $TiCl_4$ (1 mol) with acid (2-2.5 mol) either in refluxing light petroleum (b.p. 100-120°C) or in the absence of solvent at temperatures up to 150°C. After evolution of HCl pale yellow or yellow-orange solids precipitate. For the X = Me case an X-ray crystal structure shows the molecule to consist of a central $Ti_3(\mu-O)(\mu_3-O)$ unit with a unique carboxylate group bridging two titanium atoms and the other four carboxylates forming two sets of bridging groups. All titanium atoms are in a distorted octahedral environment. Work is ongoing to try to identify the subtle effects influencing the type of product formed *i.e.* a tetranuclear cluster when benzoic acid is used versus trinuclear clusters when *para*-substituted benzoic acids are used.

4.2 TITANIUM(III)

4.2.1 Complexes with hydride ligands.

The synthesis and characterization by EPR and IR of a novel μ -indenyl μ -dihydrido mixed-valence Ti(III)/Ti(II) compound has been achieved [30]. The Ti-Ti distance from X-ray crystallography 2.745 Å is the shortest so far observed an indicative of a metal-metal bond in addition to a fairly strong Ti(II) arene bond forcing a shorter metal-metal separation.

4.2.2 Complexes with halide ligands.

The thermal decomposition products of trichlorotitanium complexes TiCl_3L_n , $\text{TiCl}_3\text{L}_2\text{L}$, and TiCl_3LL_2 where L = thf, alcohols, MeCN, py and its derivatives, $n = 3$ or 4, were studied in the 20 - 400°C range and characterized using magnetic susceptibility measurements [31]. The decomposition pathways were found to vary depending on the properties of the ligands present in the parent complex.

The electron spin resonance spectra of a series of compounds of formula $[\text{Ti}(\text{C}_5\text{H}_5-n\text{Me}_n)\text{X}]$ ($n = 0, 1, 3, 4$ or 5; X = Cl, Br or I) in toluene and 2-methyltetrahydrofuran (mthf) solvents at 77 and 298K have been recorded [32]. These spectra reveal that compounds with $n = 3-5$ are monomeric in toluene whereas those with $n = 0$ or 1 are dimers. The dimers dissociate in mthf, this being concomitant with solvent coordination.

An ab initio configuration interaction study of the metal-metal coupling in some titanium and zirconium dimers was undertaken recently [33]. The metal-metal distance in $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2]$ and $[\text{Cp}_2\text{Zr}(\mu\text{-Ph}_2)]_2$ was optimized and the computed equilibrium distances were found to be Ti-Ti 3.965 Å and Zr-Zr 3.77 Å. Singlet-triplet splitting was also computed being 10,065 cm^{-1} for the titanium dimer and 14,000 cm^{-1} for the zirconium dimer.

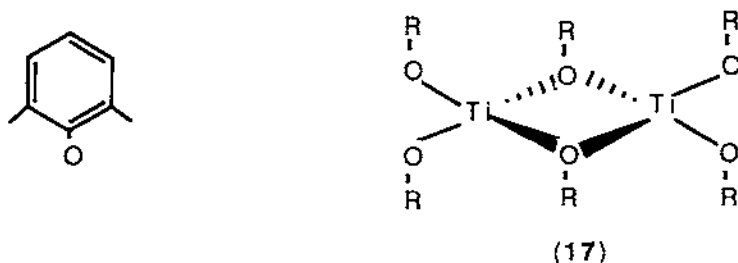
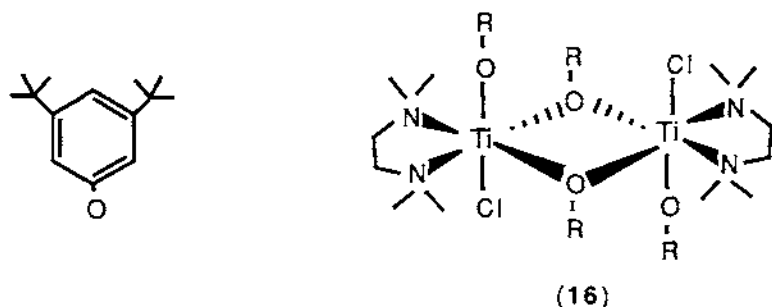
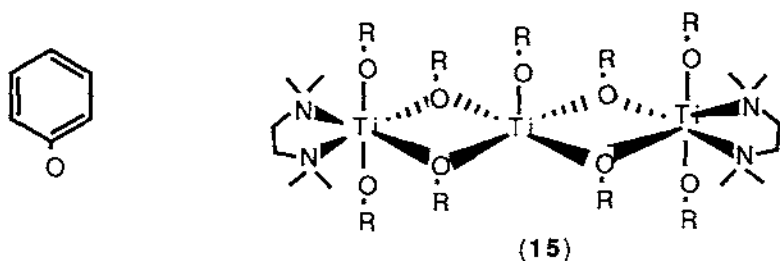
4.2.3 Complexes with oxygen donor ligands.

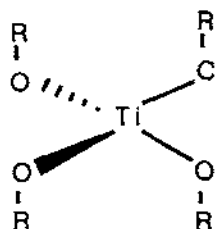
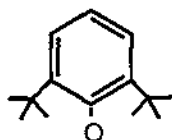
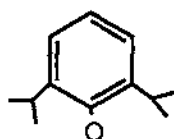
Treatment of $\text{TiCl}_3(\text{thf})_2$ with 3.0 equiv of $\text{Na}(\text{silox})$, $\text{silox} = ^t\text{Bu}_2\text{SiO}^-$, in thf gave $(\text{silox})_3\text{TiCl}$ which when reacted with L generated various thermally unstable adducts $(\text{silox})_3\text{TiL}$ (L = dme, CNMe, CN^tBu , NC^tBu , PMe_3 and NH_3) whereas when reacted with ketones and aldehydes gave ketyls or compounds indicative of ketyl reactivity [34]. The reaction of $(\text{silox})_3\text{TiCl}$ with acetone gave $(\text{silox})_3\text{Ti}(\text{OCMe}_2\text{H})$ and $(\text{silox})_3\text{Ti}(\text{OMeC}=\text{CH}_2)$ while acetaldehyde gave $(\text{silox})_3\text{TiOEt}$ and $(\text{silox})_3\text{TiOCH}=\text{CH}_2$. These complexes were characterized using UV-VIS and EPR spectroscopy.

The synthesis, crystal structure and EPR spectra of $[\text{Cp}_2\text{Ti}(\mu\text{-OCH}_3)]_2$ and $[\text{Cp}_2\text{Ti}(\mu\text{-OC}_2\text{H}_5)]_2$ have been described [35]. The Ti-Ti distances 3.35 Å in both compounds are noticeably short. Both are paramagnetic dimers exhibiting antiferromagnetic behaviour with $J = -268 \pm 4 \text{ cm}^{-1}$ for the methoxy dimer.

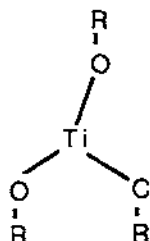
The synthesis and characterization of some trivalent titanium aryloxides obtained from ligand replacement reactions of Ti(II) and Ti(III) halides have been described [36]. Results show

that the steric hindrance of the aryloxy ligand in addition to its fundamental role in determining the geometry and nuclearity of the derivatives also possesses the ability to stabilize the trivalent oxidation states. The crystal structures of (15), (16), (17), (18) and (19) have been obtained. In (15) the Ti-O bridging distances are 2.089(7) vs 1.902(8) Å for the terminal distances on the two terminal titanium atoms with octahedral environments. Notably, the central titanium atom with square pyramidal coordination for which the Ti-O bridging distances are 2.067(7) and 2.030(7) Å whereas the Ti-O apical distance is 1.802(11) Å suggestive of Ti-O multiple bonding. The unusual trigonal planar geometry for (19) reveals that an increase in steric hindrance introduced by two ortho *tert*-butyl groups prevents the aryloxy oxygen atoms from bridging thereby hampering dimerization. Conversely, a slight diminishing of steric hindrance as in the case of 2,6-(*i*Pr)₂C₆H₃O leads to homoleptic and monomeric species, either neutral and diamagnetic (18) or anionic and paramagnetic species (19) depending on the synthetic pathway employed.





(18)



(19)

4.2.4 Complexes with sulfur donor ligands.

A systematic study of the electronic structure of cyclopentadienyl clusters including $[(\eta\text{-C}_5\text{H}_4\text{Me})\text{TiS}]_4$ using PES, UV-VIS spectroscopy, cyclic voltammetry and extended Huckel molecular orbital calculations was carried out [37].

4.2.5 Complexes with nitrogen donor ligands.

The coordination chemistry of titanium(III) and titanium(IV) with the macrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane (L) has been described [38]. The reaction of TiCl_3 with L in CH_3CN at 20°C gave blue $[\text{LTiCl}_3]$ whereas green crystals were obtained using elevated temperatures. The green crystals has been shown to consist of compositionally disordered crystals containing $[\text{LTi}^{\text{III}}\text{Cl}_3]$ and $[\text{LTi}^{\text{IV}}(\text{O})\text{Cl}_2]$ as a probable impurity. The complexes $[\text{LTiBr}_3]$, $[\text{LTiCl}_3]\text{Cl}$ and $[\text{LTi}^{\text{IV}}(\text{O})(\text{NCS})_2]$ were also synthesized. The latter is the first structurally characterized octahedral complex Ti(IV) complex containing a terminal oxo ligand with $\text{Ti}=\text{O}$ bond of 1.638 Å.

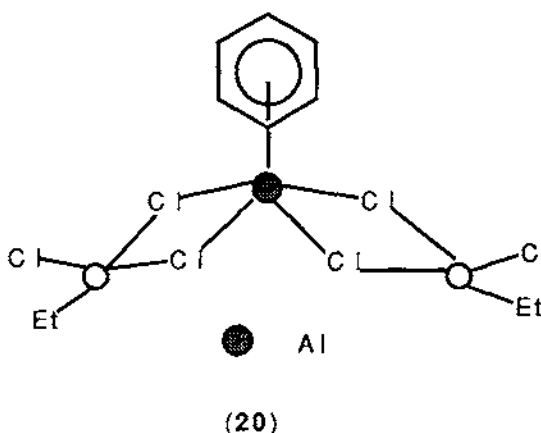
The synthesis of a series of unusual monopyramidal complexes $[\text{M}(\text{N}_3\text{N})]$, $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}$ and Fe ; $\text{N}_3\text{N} = [(\text{tBuMe}_2\text{Si})\text{NCH}_2\text{CH}_2]_3\text{N}$ where a trigonal-monopyramidal (TMP) coordination geometry is enforced by the triamido ligand has been described [39]. These complexes were characterized by magnetic measurements, NMR and IR spectroscopy. They have potential for unusual substrate binding as seen from the reversible binding of CO to $[\text{Ti}(\text{N}_3\text{N})]$ a reaction that is accompanied by a color change from blue to green and a shifting and broadening of the ^1H NMR of the triamido ligand.

A study of dmf exchange on $\text{Ti}(\text{dmf})_6^{3+}$ in neat dmf using ^1H and ^{17}O NMR spectroscopy as a function of temperature and pressure and using two magnetic fields 4.7 and 9.4T has been conducted [40]. The activation volume for dmf exchange was found to be $-5.7 \text{ cm}^3 \text{ mol}^{-1}$ and, together with a very negative entropy of activation ($-73.6 \pm 1.1 \text{ J K}^{-1} \text{ mol}^{-1}$), is consistent with an associative interchange I_a mechanism activation mode.

4.3 TITANIUM(II)

4.3.1 Complexes with halide ligands.

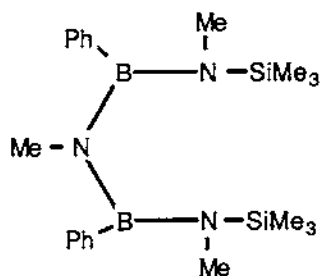
The crystal structure of $(\eta^6\text{-C}_6\text{Me}_6)\text{Ti}[(\mu\text{-Cl})_2(\text{AlClEt})_2]_2$ (20) has been determined [41]. The ethyl groups are in outer positions of the aluminate ligands farthest away from the C_6Me_6 ligands.



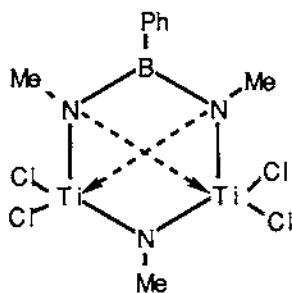
4.3.2 Complexes with nitrogen donor ligands.

The first transition metal containing derivative of borazine (22) has been synthesized recently [42]. The reaction of (21) with TiCl_4 in a 1:1 molar ratio in CHCl_3 gave (22) and the substituted compound BPh_3NMe_3 in 49% yield each. There was no increase in the yield of the reaction when a 1:2 ratio was used, switching the solvent to hexane gave rise to the unstable intermediate (23). The crystal structures of (22) and (23) were obtained, the former is best described as a tetrahedron with two nitrogen and two titanium atoms at its apices. The nitrogen-nitrogen edge is bridged by a boron atom while the titanium-titanium edge is bridged by a nitrogen atom. Two sets of Ti-N bond distances are found, 1.889(3) and 1.863(3) Å to the threefold coordinated nitrogen atoms while those for the fourfold coordinated nitrogen atoms are 2.128(3) and 2.141(3) Å while the Ti-Ti distance is 2.736(1) Å. The latter may be described as a bicyclo[3.1.1]hepane derivative with one Ti in a distorted tetragonal pyramidal environment while the other is in a distorted octahedral environment, the Ti-Ti distance is 3.264(2) Å. There is one long Ti-N bond distance of 2.444 Å while the other Ti-N bond distances average 2.102 Å. Based on the

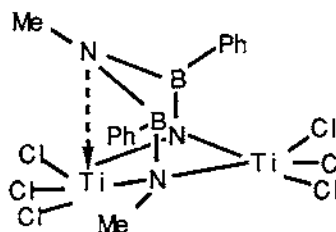
crystal structures a plausible reaction sequence is as follows; (21) reacts with two equivalents of titanium tetrachloride to give (23) which decomposes very rapidly via an S_N1 reaction to give (22) and one equivalent of PhBCl_2 . The latter then reacts with a further equivalent of (23) giving BPh_3NMe_3 and liberating two equivalents of TiCl_4 which then react with (21).



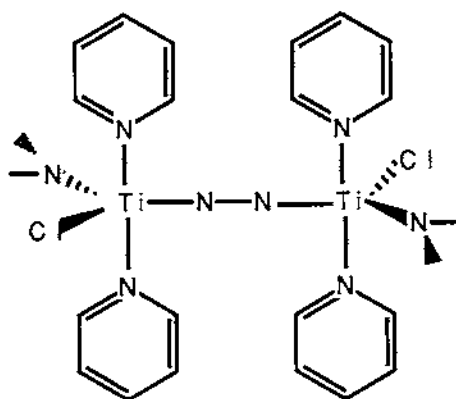
(21)



(22)



(23)



(24)

The first example of the occurrence of dinitrogen activation in a non-organometallic Ti(II) system has been demonstrated recently [43]. The reaction of *trans*-[TiCl₂(tmeda)₂] with one equivalent of LiN(Me₃Si)₂ followed by treatment with pyridine gave rise to a novel titanium dinuclear dinitrogen complex [(TiCl[N(SiMe₃)₂](pyridine)₂]₂(μ-η: η'-N₂) (24). Its crystal structure has been reported and shows both titanium atoms to be in a distorted trigonal bipyramidal environment. The Ti-N(amido) 2.020(4) Å, Ti-N(pyridine) 2.268(4) and 2.251(4) Å and Ti-N(dinitrogen) 1.759(3) Å the latter suggesting some reduction of the dinitrogen moiety.

4.3.3 Complexes with nitrogen and phosphorus donor ligands.

A more convenient one-pot syntheses of half-sandwich η-cycloheptatriene and -enyl derivatives of titanium and zirconium have been described [44]. In a typical experiment MCl₄ (M = Ti or Zr) in toluene was pretreated at -78°C with one equivalent of L₂ [e.g. M = Ti, L₂ = (PMe₃)₂; M = Zr, L₂ = Me₂NCH₂CH₂NMe₂] and the mixture was stirred with 2 equivalents of sodium amalgam in the presence of an excess of cycloheptatriene. Filtration followed by further extraction with more toluene gave crystals at -78°C. These derivatives were characterized by elemental analysis, and ¹H, ¹³C and ³¹P NMR spectroscopy.

4.4 TITANIUM(0)

The syntheses of zerovalent amine carbonyls of titanium, zirconium and hafnium by using labile phosphine carbonyls as precursors have been reported [45]. In particular, acyclic amines did not appear to form isolable carbonyl complexes under various conditions whereas the macrocyclic amines 1,4,7-triazacyclononane, tacn, and 1,4,7-trimethyl-1,4,7-triazacyclononane, Me₃tacn, formed complexes. The phosphine carbonyl was reacted with the cyclic amine in 1,2-dimethoxyethane and stirred under CO(1 atm) for 12 hours at -25°C. A red precipitate formed, was collected and recrystallized from cold CH₃CN/Et₂O giving 70-80% yields in the case of titanium. The molecular structure of the Me₃tacn derivative was determined by X-ray crystallography and is an unexceptional 4:3 piano stool with average Ti-N distances of 2.375(4) Å which are longer than corresponding distances reported for Ti(III, IV) complexes containing Me₃tacn.

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