ELSEVIER

Coordination Chemistry Reviews
164 (1997) 5–25

COORDINATION CHEMISTRY REVIEWS

Titanium 1994

Elke Manek, Dirk Hinz, Gerd Meyer *

Universität zu Köln, Inst. für Anorganische Chemie, Greinstrasse 6, D-50939 Köln, Germany

Contents

1. Introduction

This review aims to highlight advances in titanium coordination chemistry for 1994. It does not cover organometallic complexes. It is based on a literature search of volumes 120 and 121 (numbers 1-26) of *Chemical Abstracts*. For completeness, a separate search in the Science Citation Index of 1994 was carried out. All figures were produced using the program DIAMOND [1].

2. Titanium(IV)

2.1. Complexes with halide ligands

The reaction of $[Ti(Cp)Cl_3]$ with $SbCl_5$ as chloride abstractor provided hexachloroantimonate(V) salts of $[Ti(Cp)Cl_2]^+$, $[Ti(Cp)Cl]^{2+}$ and $[Ti(Cp)]^{3+}$,

---

* Corresponding author.

PII S0010-8545(97)00026-X

respectively [2]. With equimolar amounts, red–brown crystals of $[Ti(Cp)Cl_2(MeCN)_3][SbCl_6]$ and with a 1:2 ratio, light blue crystals of $[Ti(Cp)Cl(MeCN)_4][SbCl_6]_2$ are obtained. Complete removal of the chloride ions from $[Ti(Cp)Cl_3]$ requires a 1:6 excess of $SbCl_5$; purple–blue crystals of $[Ti(Cp)(MeCN)_5][SbCl_6]_3$ may then be isolated. These products were characterized by analytical and spectroscopic (IR, ^{1}H–NMR spectroscopies) methods. Proton NMR spectroscopic studies indicate the presence of intermediate halide-bridged $[Ti(\mu\text{-}Cl)_2Sb]$ species in solution during the sequential halide abstraction. Crystals of $[Ti(Cp)(MeCN)_5][SbCl_6]_3$, obtained as the bis(solvate) from recrystallization in acetonitrile, are characterized by a crystal structure determination. It shows discrete cations and anions and a pseudo-octahedral coordination sphere for Ti^{IV}, built up from five N-bonded acetonitrile ligands and an η^5-bonded cyclopentadienyl anion. The four 'equatorial' nitrogen atoms are coplanar to within 0.01 Å, while the Ti–N bond lengths, in the range 2.089(11)–2.098(10) Å, are shorter than in similar complexes.

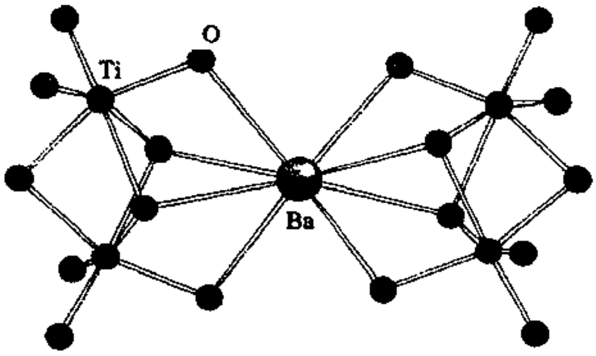
Single crystals of dibromo-bis(cyclopentadienyl)titanium(IV), $Ti(C_5H_5)_2Br_2$, were obtained from an NMR sample dissolved in deuterochloroform. The compound appears to be isostructural with the corresponding chloride [3].

2.2. *Complexes with oxygen donor ligands*

The complex $TiCl_3(OSiPh_3)$ has been prepared from titanium tetrachloride and $HOSiPh_3$. The complex was characterized by IR spectroscopy and by crystal structure determination [4]. There are two crystallographically independent monomers in the unit cell in which the titanium atom is tetrahedrally coordinated by three chlorine atoms and the oxygen atom of the siloxy group. The bond lengths for Ti–O of 1.706(3) Å for the first monomer and 1.714(3) Å for the second one are very short and correspond to single bonds.

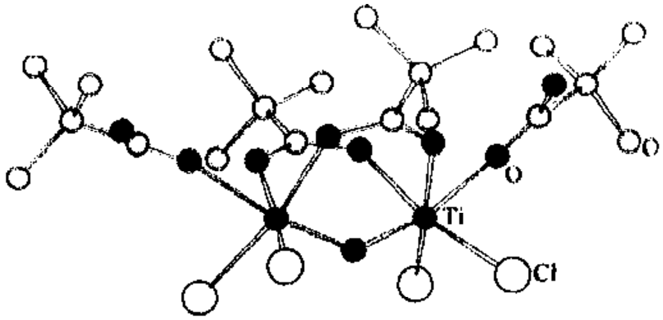
Reaction of Cp_2TiCl_2 with triphenylsilanole in the presence of piperidine gave rise to the compound $Cp_2TiCl(OSiPh_3)$ [5]. It forms orange needles which were characterized by X-ray crystallography and IR spectroscopy. The crystal structure determination shows that the complex forms monomeric molecules in which Ti^{4+} is in a distorted tetrahedral environment. The Ti–O bond length of 1.842 Å is 0.14 Å longer than in $TiCl_3(OSiPh_3)$ while the Si–O bond length of 1.615 Å is 0.075 Å shorter. The π-bonding of the Ti–O bond is therefore enhanced in the latter.

In the system $Ca(OEt)_2$-$Ti(OEt)_4$-L ($L = EtOH$, C_6H_6) only one complex, $[Ca\{Ti_2(OEt)_9\}_2]$, was observed, whereas in the analogous Ba system three complexes, $[Ba\{Ti_2(OEt)_9\}_2]$ (1), $[Ba\{Ti_2(OEt)_{10}\}]\cdot 5EtOH$ and $\{Ba_4\{Ti_2O(OEt)_{14}\}\}\cdot 8EtOH$ were obtained [6]. Single crystal X-ray investigations of $[M\{Ti_2(OEt)_9\}_2]$ ($M = Ca$, Ba), confirmed unambiguously that the central atoms (Ca or Ba) in the molecules are eightfold coordinated (distorted tetragonal antiprism) by two face-sharing bioctahedral $[Ti_2(OEt)_9]$ groups via two μ_3- and two μ-OR groups. The M^{II}-OEt bond lengths are similar to those in the corresponding metal oxides $M^{II}O$ while the Ti–O bond lengths exhibit a clear cut correlation with the bonding mode of the OR groups [Ti-O (terminal) < Ti-(μ-OM) < Ti-μ-OTi < Ti = (μ_3-OTi)]. This provides evidence for the high stability of the [$Ti_2(OEt)_9$] group.



(1)

The new dinuclear complex compound [{$TiCl_2(O_2CBu^t)(Bu^tCO_2H)$}$_2$] (**2**) was synthesized by reaction of $TiCl_4$ with 2,2-dimethylpropanoic acid [7]. The X-ray crystal structure analysis shows that the titanium atoms are bridged by an oxo and two carboxylate groups. The Ti–O distances range from 1.77 Å (Ti-μ-O) and 1.99-2.09 Å (Ti-μ-O (acid anion)) to 2.09–2.14 Å (neutral acid ligand). At 40°C the compound decomposes to the trinuclear species [{$Ti_3Cl_3(O_2CBu^t)_5O_2$], and at higher temperatures (100–120°C) to another dinuclear oxo derivative [{$TiCl(O_2CBu^t)_2$}$_2$O]. Syntheses using *para*-substituted aryl acids generally yield trinuclear complexes [{$Ti_3Cl_3(O_2CC_6H_4X$-*p*)$_5O_2$] (X = Cl or Br) although the *p*-Bu^t acid forms [{$TiCl(O_2CC_6H_4Bu^t$-*p*)$_2$}$_2$O]. The *ortho*- and *meta*-substituted acids yield either [$Ti_3Cl_4(O_2CR)_4O_2$] (R = C_6H_4Cl-*o* or -*m*) or [$Ti_4Cl_5(O_2CR)_7O_2$] (R = C_6H_4Me-*o*) derivatives.

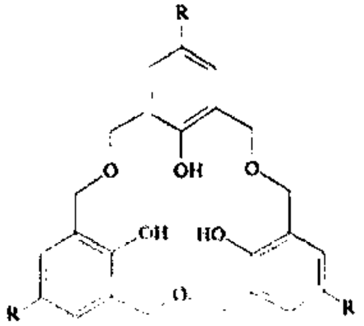


(2)

The peroxo complexes of titanium(IV) [$Ti(O)(O_2)C_6H_4(NH_2)_2(H_2O)$], [$Ti(O)(O_2)L_2$], [$Ti(O_2)L'_2$] and [$Ti(O)(O_2L''')$] (where L = ethylenediamine, 2-aminopyridine; L′ = aminophenoxido, oxoquinolino; L‴ = diethyltriamine; L″ = pyridine, triphenylphosphine oxide) have been synthesized and were characterized by elemental analysis, conductivity measurements and IR spectral studies [8]. The complexes contain monodentate and didentate ligands. They oxidize both PPh_3 and

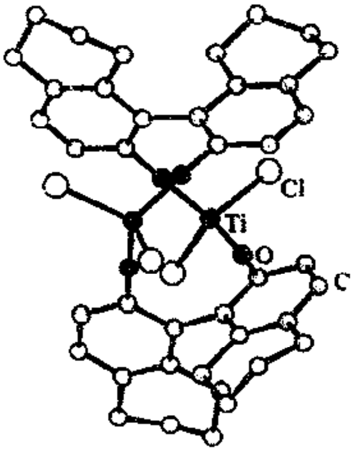
$AsPh_3$. Those with tridentate and tetradentate ligands are more stable and inert towards oxidation. The complexes are consistent with six-coordinate Ti(IV), only one complex, $[Ti(O)(O_2)(en)_2]$, shows a coordination number of seven.

Some Ti(IV) coordination compounds of the general formula Ti(L)X, where L represents the trianion of the oxacalix[3]arene (**3**) macrocycle and X is an isopropoxide or acetylacetonate ligand, have been prepared and were characterized [9]. The Ti(L)(acac) complex exhibits a dynamic interconversion on the ^{1}H-NMR time scale. At room temperature, the macrocyclic ligand in the complex has C_{3v} symmetry and the acac methyl groups are equivalent. In contrast, at low temperatures, the macrocycle possesses C_s symmetry and the acac methyls are inequivalent. Computer simulations of variable-temperature NMR spectroscopic experiments have provided rate constants and activation parameters for the interconversion process. Rapid isomerization of trigonal bipyramidal isomers via turnstile or Berry pseudorotation processes is proposed to explain the dynamic behaviour of this complex.

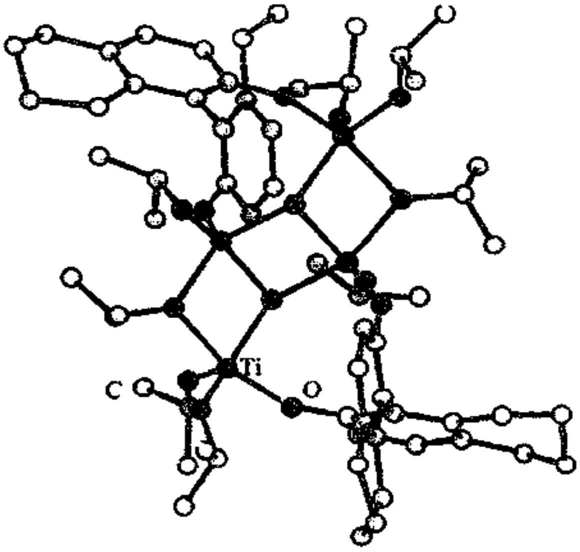


(**3**)

The reaction between the bis(trimethylsilyl)ether of 5,5′,6,6′,7,7′,8,8′-octahydrobinaphthol, **HYDBINO(TMS)$_2$**, and $TiCl_4$ generates a new unusual complex: a 14-membered dititanium-macrocycle with the empirical formula **Ti(HYDBINO)Cl$_2$** (**4**). The ^{1}H and ^{13}C-NMR spectra of this complex reveal only one set of tetrahydronaphtholate resonances over the temperature range of −60° to +30°C. A solution molecular weight study revealed that the complex exists as a dimer in solution. The X-ray structure determination confirmed this observation for the solid state. The four-coordinate titanium complex shows extremely short Ti–O bond lengths at an average of 1.742 Å, and the Ti–O–C angle is nearly linear with 168°, indicating an unusually large degree of π-bonding character. The reaction of partially hydrated **HYDBINOH$_2$** with $Ti(O\text{-}i\text{-}Pr)_4$ generated the first member of a new class of titanium oxo-alkoxide complexes: a tetratitanium-di-μ_3-oxo cluster, **Ti$_4$(HYDBINO)$_2$(O-i-Pr)$_8$O$_2$** (**5**) [10]. A crystal structure determination shows, that the complex consists of a $Ti_4(\mu_3\text{-}O)_2$ core with virtually C_2 symmetry, in which both oxo ligands adopt a μ_3 environment. The complex contains a relatively planar Ti_4O_2 core, with a Ti1-Ti2-Ti3-Ti4 dihedral angle of 178°. The Ti-μ_3-O-Ti angles average to 102°, approximating a zigzag arrangement. Each titanium centre adopts a distorted square pyramidal geometry with Ti–O bond distances increasing in the order terminal alkoxide < phenoxide < oxo < bridging isopropoxide.



(4)



(5)

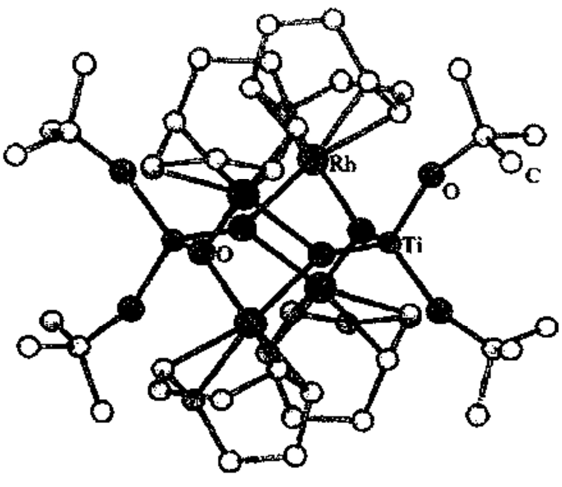
Reaction of $Ti(OR)_4$ (R = i-Pr and Et) with fluoroalcohols, HOR^f ($R^f = CH(CF_3)_2$, C_6F_5, $2,6\text{-}F_2C_6H_3$, $2,4\text{-}F_2C_6H_3$, $4\text{-}FC_6H_4$, C_6H_5), results in the formation of a series of $Ti(OR^f)_x(OR)_{4-x}(HOR)_n$ compounds with x = 2-4 and n = 0 or 1. Only in the cases of $R^f = CH(CF_3)_2$ (x = 2) and $2,6\text{-}F_2C_6H_3$ (x = 2 and 3) is n = 0 [11]. The degree of substitution can be correlated to the electron withdrawing ability of the R^f group, with highly electron withdrawing groups disfavouring complete substitution. These compounds have been characterized by combustion elemental analysis, IR, ^1H- and ^{19}F-NMR spectroscopy. Single-crystal X-ray diffraction studies of $Ti(OR^f)_x(OR)_{4-x}(HOR)$ ($R^f = CH(CF_3)_2$, R = Et, and x = 2; $R^f = C_6F_5$, R = i-Pr, and x = 3) revealed centrosymmetric dinuclear structures, held together by bridging oxygen atoms. The coordination geometries approximate edge-sharing bioctahedra with the coordinated alcohol molecules hydrogen-bonded across the dinuclear unit to an oxygen atom of an alkoxide. The coordination geometry defined by the oxygen atoms of the alkoxide ligands approximates a square-based pyramid, with an isopropoxide in the apical site [Ti(1)-O(4) = 1.718(6) Å and Ti(1)-O(4)-C(4) = 159.6(6)°]. One of the terminal phenoxides has a nearly linear angle (169.3(6)°), while the other one has a relatively acute angle (123.3(4)°). The phenyl group of the latter is oriented such that a fluorine atom fills the site trans to the isopropoxide. Ti(1)-F(1) = 2.704(5) Å is nearly identical to the sum of the van der Waals radii of fluorine and Ti(IV). The two compounds that do not coordinate alcohol (R = i-Pr; $R^f = 2,6\text{-}F_2C_6H_3$, x = 3, and $R^f = CH(CF_3)_2$, x = 2), also do not form stable complexes with Lewis bases such as acetonitrile or thf. This contrasts with $Ti[OCH(CF_3)_2]_4$ which forms volatile $Ti[OCH(CF_3)_2]_4L_2$ (L = MeCN and thf) compounds. The structure of $Ti[OCH(CF_3)_2]_4(NCMe)_2$ has been determined using X-ray crystallography. The nitrile ligands occupy *cis* positions in the distorted octahedral coordination geometry.

A dimetallic lead titanium alkoxide-acetate complex was isolated from a solution of $Pb(OAc)_2$ and $Ti(OEt)_4$. It was characterized by single-crystal X-ray diffraction, in addition to spectroscopic methods and chemical analysis. The structure determination of crystalline $[PbTi_2(\mu_4\text{-}O)(OOCCH_3)(OCH_2CH_3)_7]_2$ revealed a dimeric structure [12]. Half of the molecule consists of a basic triangular $PbTi_2(\mu_3\text{-}O)$ unit with proper ligand attachments, and two units are linked at the Pb and μ_3-O ions through formation of a $Pb_2(\mu_4\text{-}O)_2$ parallelogram as well as by μ_2-OEt ligands. Within each monomeric unit, the Ti1–Ti2 base of the triangle is spanned by a μ_2-OEt and a μ_2-OAc group and three other OEt^- ligands at each Ti cation. Both Ti cations have a sixfold coordination with a distorted octahedral geometry. The average Ti–O distance is 1.975 Å. The coordination number of Pb is five, with a pseudo-square-pyramidal configuration, attributed to interactions of the bonding electron pairs with stereochemically active lone pair of electrons at the Pb(II) center. $[PbTi_2(\mu_4\text{-}O)(OOCCH_3)(OCH_2CH_3)_7]_2$ was also characterized in solution by ^{1}H- and ^{13}C-NMR spectroscopy in benzene-d_6 at ambient temperature. The thermal decomposition of $[PbTi_2(\mu_4\text{-}O)(OOCCH_3)(OCH_2CH_3)_7]_2$ was examined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transformed infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDXA), as is relevant to the understanding of the evolution of structure in the formation of ceramic dielectrics.

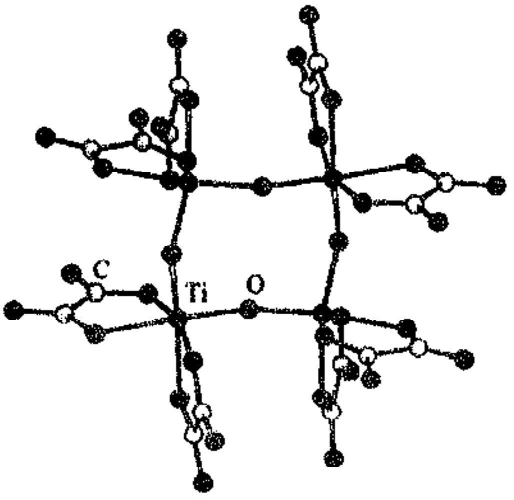
The reaction of $[(\mu\text{-}OH)Rh(cod)]_2$ with $CH_3Ti(O^tC_4H_9)_3$ gives alkylation of the Rh^I complex at lower temperatures whereas at room temperature a new oxo-bridged complex $[(\mu_3\text{-}O)_4\{Rh(cod)\}_4\{Ti(^tC_4H_9O)_2\}_2]$ (**6**) is formed in the course of a protolysis reaction. An X-ray structure determination shows that the complex has a dimeric structure [13]. The average Ti–O distance is 1.80 Å and the O–Ti–O angles differ between 108.8 and 111.8 . The coordination of Ti^{IV} is therefore nearly ideally tetrahedral. The coordination sphere of Rh^I is square-planar with an average Rh–O distance of 2.08 Å an Rh–O–Rh angle of 84.0°. The Rh-Rh distance is with 2.79 Å one of the shortest distances that was ever found for dimeric anion bridged Rh^I complexes.

The synthesis and crystal structure of dipotassium bis(oxalato)oxotitanate(IV) dihydrate, $K_2[TiO(C_2O_4)_2]\cdot 2H_2O$ is described [14]. The anions, (**7**), of the compound form eight-membered rings of four Ti and four O atoms. Each Ti atom is in a distorted octahedral environment. Distances between Ti and O in the non-planar ring system, possessing an inversion centre, range from 1.789(3) to 2.138(3) Å. The K^+ ions exhibit eight- or tenfold coordination with typical distances between 2.649(17) and 3.158(5) Å. Some of the K^+ ions and the water molecules are disordered.

The complex $[TiCl_4(TPPO)_2]$ (TPPO = tripiperidinophosphine oxide) was obtained by reaction of $[TiCl_4(NH_3)_2]$ with two equivalents of TPPO [15]. A slow reaction ensued and resulted in the complex. The crystal structure was determined. It exhibits an ideally octahedral geometry around the titanium atom and reveals



(6)



(7)

trans TPPO ligands. The Ti–Cl bond lengths are 2.341(1) and 2.343(1) Å. The Ti–O bond length is with 1.923(3) Å shorter than a Ti–O single bond and clearly contains a significant π-bonding component.

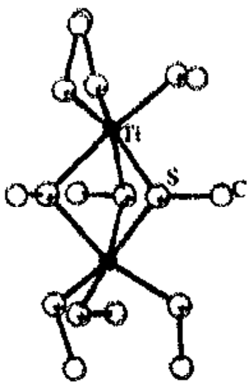
Reaction of triphenylarsine oxide with $TiCl_4$ leads to crystals of tetrachlorobis(triphenylarsineoxide)-titanium(IV), $((C_6H_5)_3AsO)_2TiCl_4 \cdot 2CH_2Cl_2$ [16]. The Ti(IV) atom is sixfold coordinated. The geometry can be described as an octahedron.

After the successful synthesis, the crystal structure of a monomeric titanocene-α-amino-acid complex could be solved for the first time [17]. Reaction from $[Cp_2TiCl_2]$ with the amino acids (glycine, L-alanine, 2-methylalanine) yielded orange-red complexes which are stable at room temperature and insensitive to air and moisture. ^1H-NMR and IR spectroscopic studies were carried out. A structure determination of the complex containing 2-methylalanine shows that the coordination sphere of the titanium atom is a distorted tetrahedron and has approximately

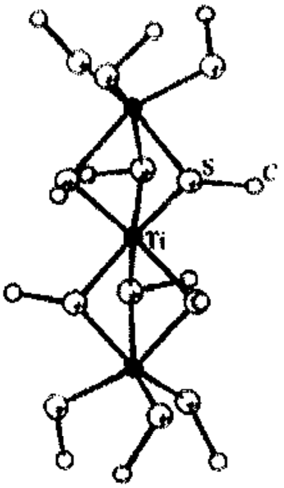
C_2 symmetry. The Cp rings are in an ecliptic conformation. The Ti–O bond length, 1.961 Å, is consistent with a single bond. The complex is one of the few examples in which the amino acid is bound exclusively to the metal centre via the oxygen atom.

2.3. *Complexes with sulfur donor ligands*

The reaction of [Ti(NMe$_2$)$_4$] with seven equivalents of MeSH yields [NMe$_2$H$_2$][Ti$_2$(SMe)$_9$]. A crystal structure determination shows that the two titanium atoms are coordinated by three terminal and three bridging MeS-ligands. The [Ti$_2$(SMe)$_9$]$^-$ (**8**) unit is described as a flat, face sharing double octahedron which is new for *S*-donor ligands. Both TiS$_6$ units in [Ti$_2$(SMe)$_9$]$^-$ are trigonally distorted to D_{3h} symmetry. The reaction of four equivalents of MeSH with [Ti(NMe$_2$)$_4$] yielded single crystals of [Ti$_3$(SMe)$_{12}$] (**9**) [18]. The three titanium atoms are linearly arranged. The two outer titanium atoms are sixfold coordinated by three terminal and three bridging MeS ligands while the central titanium atom is coordinated by six bridging MeS ligands. The geometry of the Ti$_3$S$_{12}$ unit may be described as a trigonal-prismatic central unit with two face-sharing octahedra. The two outer TiS$_6$ units are trigonally distorted octahedra while the inner TiS$_6$ unit is unusually close to D_{3h} symmetry. The trigonal distortion of the TiS$_6$ unit in both complexes is not expected. A symmetry reduction may be induced by a secondary Jahn–Teller effect which should be stabilized by a trigonally distorted O_h symmetry of the coordination polyhedron. First ^{1}H-NMR spectroscopic studies in solution indicate that by dissolving [NMe$_2$H$_2$][Ti$_2$(SMe)$_9$], the complex [Ti$_3$(SMe)$_{12}$] and at least one further compound is formed.



(**8**)



(**9**)

2.4. *Complexes with selenium or tellurium donor ligands*

The reaction of Cp$_2$Ti(EAr)$_2$ with M(dppe)(ClO$_4$)$_2$ and M(PhCN)$_2$Cl$_2$, respectively, yields heterodimetallic complexes of the type

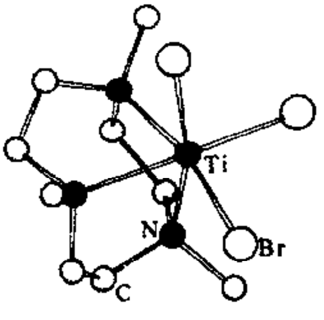
$[Cp_2Ti(\mu\text{-}EAr)_2M(dppe)](ClO_4)_2$, (M = Ni, Pt; E = Se, Te), (Ar = Ph, C_6H_4-4-Me, C_6H_4-4-OMe, C_6H_4-4-OEt) and $[Cp_2Ti(\mu\text{-}TeAr)_2MCl_2]$ (M = Pd, Pt). The reaction of $Cp_2Ti(SeAr)_2$ with $M(PhCN)_2Cl_2$, however, leads to the formation of Cp_2TiCl_2 and a polymeric material $[(M/SeAr)_2]_n$ [19].

2.5. Complexes with nitrogen donor ligands

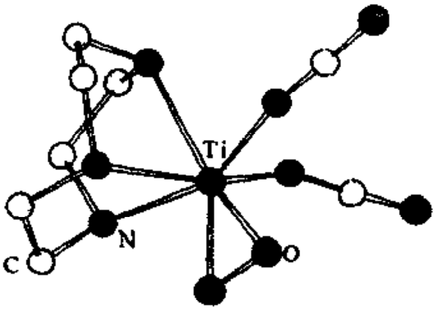
The compound $TiCl_3(NPPh_3)$ has been prepared from titanium tetrachloride and $Me_3SiNPPh_3$ [4]. The complex was characterized by IR spectroscopy and by crystal structure determination. The complex forms monomeric molecules in which the titanium atom is tetrahedrally coordinated by three chlorine atoms and the nitrogen atom of the phosphorone-iminato ligand. For the first time, an extended Ti–N–P axis is observed due to the threefold symmetry. The bond lengths Ti–N of 1.719(4) and P–N of 1.614(4) Å correspond to double bonds.

The oxidation of $[(Me_3tacn)Ti^{III}Br_3]$ (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) in water with $Na_2[S_2O_8]$ leads upon addition of $NaClO_4$ to $[(Me_3tacn)Ti^{IV}Br_3]ClO_4$. The series $[(Me_3tacn)Ti^{IV}Br_x(OCH_3)_{(3-x)}]^+$ (x = 0–2) has been synthesized by oxidation reactions of $[(Me_3tacn)TiBr_3]$ with air [20]. The compounds $[(Me_3tacn)TiBr_3]ClO_4$, $[(Me_3tacn)TiBr(OCH_3)_2]ClO_4$, and $[(Me_3tacn)Ti(OCH_3)_3]BPh_4$ have been structurally characterized by X-ray crystallography. $[(Me_3tacn)TiBr_3]ClO_4$ consists of separated monocations $[(Me_3tacn)TiBr_3]^+$ (**10**) and perchlorate anions. The titanium(IV)ions are in a pseudo-octahedral ligand environment composed of one facially coordinated triamine and three bromide ions. Two peroxotitanium(IV) complexes $[(Me_3tacn)Ti(O_2)(NCO)_2]$ (**11**) and $[(Me_3tacn)Ti(O_2)Cl_2]$ have been isolated from solutions of $[(Me_3tacn)_2Ti_2^{III}(NCO)_4(\mu-O)]$ and $[(Me_3tacn)TiCl_3]$ which had been exposed to air and H_2O_2, respectively. Both complexes contain the $\eta^2-O_2^{2-}$ ligand. Three octahedral titanyl complexes, $[(Me_3tacn)Ti(O)Cl_2]$, $[(tiptacn)Ti(O)(NCS)_2]$, and $[(tiptacn)Ti(O)(NCO)_2]$, were obtained from solutions of $[(Me_3tacn)TiCl_3]$, $[(tiptacn)Ti(NCS)_2]$, and $[(Me_3tacn)Ti(NCO)_2(OCH_3)]$ by interaction with oxygen, where tiptacn represents 1,4,7-isopropyl-1,4,7-triazacyclononane [20]. The complex consists of neutral molecules of $[(Me_3tacn)Ti(O)Cl_2]$. It is the second structurally characterized octahedral titanyl complex. The Ti=O distance was found to be 1.637(3) Å. All new compounds have been studied by IR and Raman spectroscopy in solution and in the solid state. Cyclic voltammograms (CV) of complexes dissolved in acetonitrile containing a 0.10 M $[TBA]PF_6$ supporting electrolyte were recorded at a Pt-button working electrode in the potential range of −2.0 to +2.0 V vs. Ag/AgCl.

The isolation and structural characterization of a mixed amido aryloxide compound of titanium(IV), $[Ti(OC_6H_3{}^tBu_2\text{-}2,6)_2(NMe_2)_2]$ (**12**), containing the sterically demanding 2,6-di-*tert*-butylphenoxide ligand is reported [21]. The compound was obtained by reaction of $[Ti(NMe_2)_4]$ with 2,6-di-*tert*-butylphenol. The crystal structure determination shows that a distorted tetrahedral geometry is adopted around the Ti metal centre with two aryloxide O atoms and two N atoms of the dialkylamido groups. The Ti–O(aryloxide) distances of 1.808(2) and 1.828(2) Å are well within

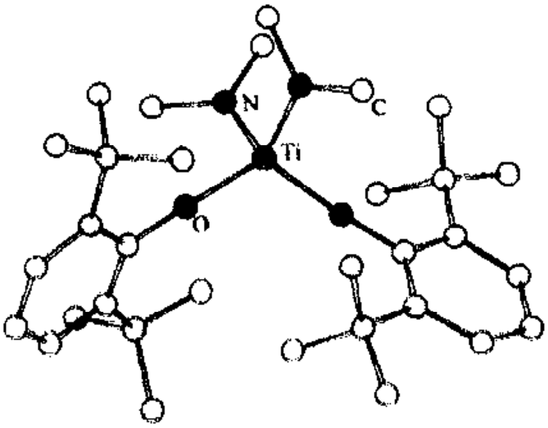


(10)



(11)

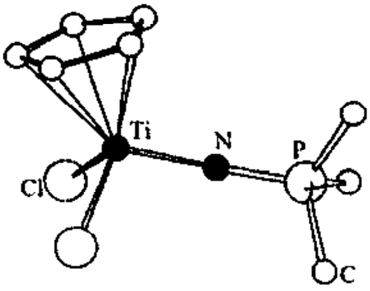
the range of observed values while the Ti–N(amido) distances of 1.892(3) and 1.885(3) Å are shorter than a single bond length of 1.96 Å as estimated from the sum of covalent radii.



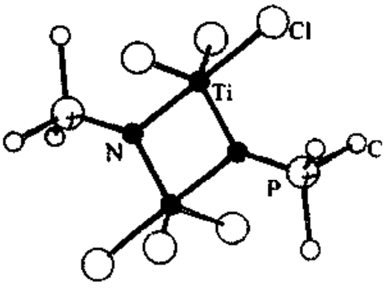
(12)

The reaction of titanium tetrachloride with two equivalents of *N,N',N''*-trimethylethylene-diamine yields a monomeric titanium tetrachloride adduct, $[TiCl_4(Me_2NCH_2CH_2NMeH)]$. The complex $[TiCl_2(Me_2NCH_2CH_2NMeH)_2]$ is prepared by the reaction of titanium tetrachloride with four equivalents of *N,N',N''*-trimethylethylenediamine [22]. The X-ray crystal structure of $[TiCl_4(Me_2NCH_2CH_2NMeH)]$ reveals that it has a distorted octahedral structure with the chelating amine ligand in a delta-*gauche* conformation.

The compounds $CpTiCl_2(NMe)_3$, $[TiCl_3(NPMe_3)]_2$, $[Ti_2Cl_5(NPMe_2Ph)_3]\cdot CH_2Cl_2$ and $[Ti_3Cl_6(NPMe_3)_5][BPh_4]$ are formed from Cp_2TiCl_2 and titanium tetrachloride, and the corresponding phosphane imino compounds $Me_3SiNPMe_3$ and $Me_3SiNPMe_2Ph$, respectively [23]. The tetraphenylborate salt crystallized from the reaction of $[Ti_3Cl_6(NPMe_3)_5]Cl$ with $NaBPh_4$. All compounds were characterized by IR spectroscopy and crystal structure analyses. The structure determination of $CpTiCl_2(NPMe)_3$ (**13**) revealed that the molecules are monomeric with the $(NPMe_3)^-$ ligand in an almost linear arrangement, with an Ti–N–P angle of 170.7°. In $[TiCl_3(NPMe_3)]_2$ (**14**) the titanium atoms, which occur in trigonal bipyramidal coordination, are linked by the N atoms of the $(NPMe_3)^-$ groups to form a centrosymmetric dimer with Ti–N bond lengths of 1.843 and 2.082 Å. The structure determination of $[Ti_2Cl_5(NPMe_2Ph)_3]\cdot CH_2Cl_2$ shows that the compound may be understood as a reaction product of $TiCl_2(NPMe_2Ph)_2$ and $TiCl_3(NPMe_2Ph)$. In the resulting heavily distorted Ti_2N_2 four-membered ring, the Ti–N bond lengths are 1.804, 1.944, 1.992 and 2.346 Å. The largest Ti–N bond is in *trans*-position to the N atom of the terminal $(NPMe_2Ph)^-$ ligand with a Ti–N distance of 1.756 Å.

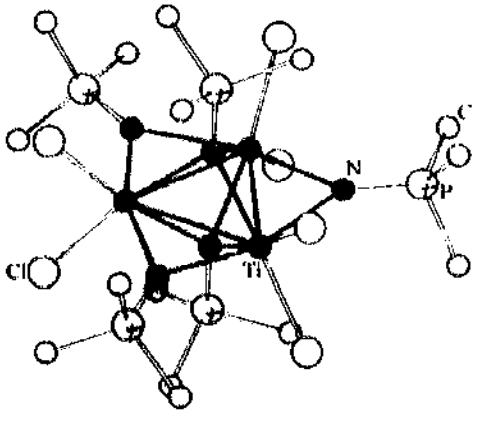


(13)



(14)

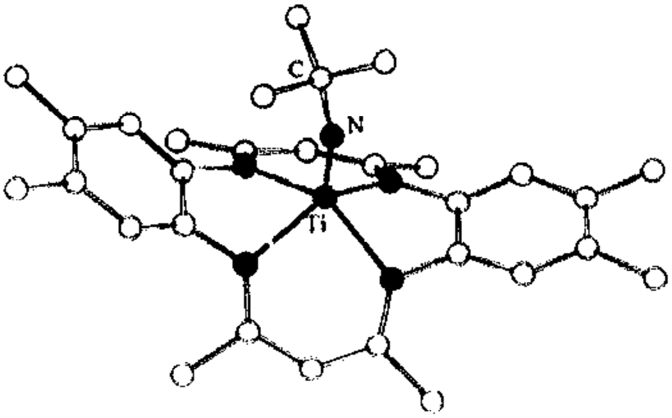
The structural data for $[Ti_3Cl_6(NPMe_3)_5][BPh_4]$ (**15**) show that the three titanium atoms along with three $(NPMe_3)$ groups with μ_2-N functions and two $(NPMe_3)$ groups with μ_3-N functions form a trigonal bipyramid. Each titanium atom accomplishes a coordination number of six with two terminal chlorine atoms.



(15)

The complex $[Ti(NBu^t)Cl_2(Bu^tpy)_2)]$ (Bu^tpy = 4-*tert*-butylpyridine) is a useful precursor for monomeric titanium imido complexes. It is rapidly prepared from $TiCl_4$, Bu^tNH_2 and Bu^tpy. Reaction of $[Ti(NBu^t)Cl_2(Bu^tpy)_2)]$ with one equivalent of $Na[C_5H_5]$ or $Li[C_5H_5]$ gave the monomeric half-sandwich cyclopentadienyl complexes $[Ti(\eta\text{-}C_5R_5)(NBu^t)Cl(Bu^tpy)]$ (R = H or Me). Treatment of the complex with two equivalents of $Na[C_5H_5]$ in thf followed by recrystallization afforded the bis(η-cyclopentadienyl) derivative $[Ti(\eta\text{-}C_5H_5)_2(NBu^t)(Bu^tpy)]$. The reaction of $[Ti(NBu^t)Cl_2(Bu^tpy)_2)]$ with one equivalent of $Li[C_9H_4Me_3]$ ($C_9H_4Me_3$ = trimethylindenyl) yielded the first 4-indenyl-imido derivative

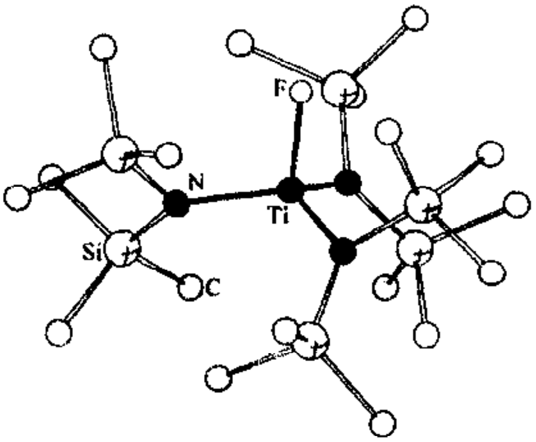
[Ti(η-C$_9$H$_4$Me$_3$)(NBu^t)Cl(Bu^{t}py)] [24]. The preparation of *N*-donor half-sandwich derivatives of the {Ti(NBu^t)} unit was also carried out. [Ti(NBu^t)Cl$_2$(Bu^{t}py)$_2$)] reacted smoothly at room temperature with K(dmbpz) in thf to give [Ti(dmbpz)(NBu^t)Cl(Bu^{t}py)]. The tris(3-isopropylpyrazolyl)borate and the tris(3-isopropyl-4-bromopyrazolyl)borate analogues may be prepared similarly. [Ti(dmbpz)(NBu^t)Cl(Bu^{t}py)] is the first example of a titanium pyrazolylborato–imido derivative. Reaction of [Ti(NBu^t)Cl$_2$(Bu^{t}py)$_2$] with one equivalent of the dilithium salts Li$_2$[Me$_4$taa] or Li$_2$[Me$_8$taa] (Me$_4$-/Me$_8$taa = tetra- and octamethyldibenzotetraaza[14]annulene) in thf afforded the macrocyclic imido derivatives [Ti(Me$_4$taa)(NBu^t)] and [Ti(Me$_8$taa)(NBu^t)], respectively. The crystal structure of [Ti(Me$_8$taa)(NBu^t)] (**16**) was determined. The Ti atom lies 0.76 Å out of the macrocycle's N$_4$ plane, and the Me$_8$taa ligand is saddle-shaped as expected. The Ti–N–Bu^t angle of 164.3(3)° is sufficiently close to linearity so that it may be inferred that the Bu^{t}N ligand is acting as a four-electron donor. The Ti≡NBu^t bond length [Ti–N(5) = 1.724(4) Å] is quite long compared to titanium-imido linkages in general [ranging from 1.672(7) to 1.723(4) Å, seven examples]. The largest one is found for a Ti–NBu^t linkage. The complex is formally a fourteen-valence-electron species.



(**16**)

Complexes with the formulae TiClL^1 have been synthesized by reacting titanium tetrachloride with the Schiff bases derived from salicylaldehyde and substituted 2-aminopyridines (C$_5$H$_4$NR; R = H, 3-CH$_3$, 4-CH$_3$, 5-CH$_3$, 6-CH$_3$; L^1 ligands) or from *N*-methylpyrrole-2-carboxaldehyde and various amines (H$_2$NR; R = C$_6$H$_5$, 2-CH$_3$C$_6$H$_4$, 4-CH$_3$C$_6$H$_4$, CH$_2$C$_6$H$_5$, (CH$_2$)$_2$CH$_3$, CH(CH$_3$)$_2$, (CH$_2$)$_5$CH$_3$, (CH$_2$)$_7$CH$_3$; L^2 ligands) [25]. They have been characterized by elemental analysis along with ^{1}H-NMR and IR spectroscopy. The L^1 ligands appear to coordinate via their pyridine nitrogen and phenolic oxygen atoms. Ti(IV) has the coordination number six in these complexes. The L^2 ligands are monodentate coordinating via the imine nitrogen atoms. When the complexes are monomers, the coordination number of the metal atom is five, but if they are dimers or polymers formed by halogen bridges, the coordination number of the titanium atom is six.

The complex FTi[N(SiMe$_3$)$_2$]$_3$ (**17**) was obtained from the reaction of TiF$_4$ with three equivalents of LiN(SiMe$_3$)$_2$. An X-ray crystal structure determination shows that the molecule consists of a neutral monomeric $FTi[N(SiMe_3)_2]_3$ molecule [26]. The titanium atom is tetrahedrally coordinated by the fluorine atom and the three nitrogen atoms of the $N(SiMe_3)_2$ groups. Only small differences are observed for the Ti–N distances (average: 1.913 Å). The presence of three bulky $N(SiMe_3)_2$ ligands around the titanium atom shields the fluorine atom and reduces the reactivity of the Ti–F bond (1.792(4) Å). A ^{1}H-NMR spectroscopic study shows the equivalence of the three $N(SiMe_3)_2$ ligands, one singlet at $\delta = 0.31$ ppm. Mass spectrometric (MS) analysis, thermoanalytical studies (TGA/DTA/MS) and CVD experiments are also discussed.

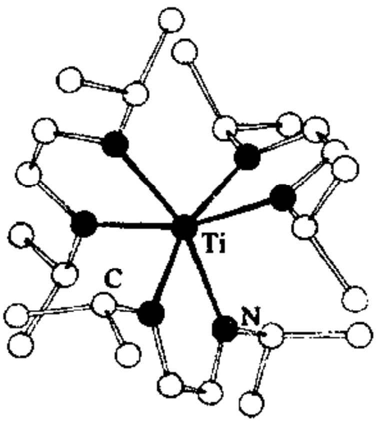


(17)

Reactions of $[(\eta^5\text{-}C_5H_5)TiCl_3]$ with dialkyl and diarylamido-lithium complexes in 1:1, 1:2 or 1:3 molar ratios afford the mono(pentamethylcyclopentadienyl)titanium(IV) dialkylamido-complexes $[(\eta^5\text{-}C_5H_5)TiCl_{3-n}(NR_2)_n]$ (n = 1; R = Me or Si Me$_3$) (n = 2, R = Me or Ph; n = 3, R = Me or Et). Similar reactions of $[\{\eta^5\text{-}C_5Me_5)TiCl_2\}_2(\mu\text{-}O)]$ and $[\{\eta^5\text{-}C_5Me_5)TiCl\}_3(\mu\text{-}O)_3]$ gave the corresponding complexes $[\{\eta^5\text{-}C_5Me_5)TiCl_{2-n}(NR_2)_n\}_2(\mu\text{-}O)]$ (n = 1; R = Me or Ph) (n = 2; R = Me) and $[\{\eta^5\text{-}C_5Me_5)Ti_3Cl_{3-n}(NMe_2)_n(\mu\text{-}O)_3]$ (n = 1 or 3) [27]. The crystal structure of $[\{\eta^5\text{-}C_5Me_5)Ti(NMe_2\}_3]$ has been determined by X-ray crystallography and it shows that it has a piano-stool structure with a symmetry plane defined by Ti(1)–N(2)–Cp*(centroid). The N(1)–, N(2)–, N(1A) plane is essentially parallel to the Cp* plane. All compounds were characterized by IR, ^{1}H- and ^{13}C-NMR spectroscopy.

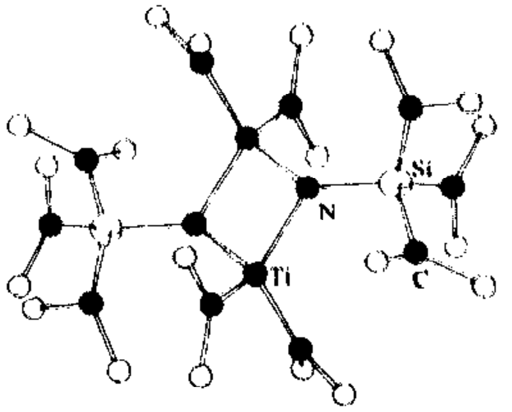
The compound $Ti(NR{=}CH{-}CH{=}NR)_3$ ($R = i\text{-}C_3H_7$) (**18**) was obtained by reaction of $TiCl_4 \cdot thf$ with $Li_2(NR{-}CH{=}CH{-}NR)$ in the presence of the ligand molecules. The compound was characterized by ^{1}H- and ^{13}C-NMR spectroscopies, and mass spectrometry [28]. The structure was determined by X-ray diffraction. The titanium atom is very shielded and this may be the reason for the low reactivity of the compound. The complex may be interpreted as a titanium(IV) compound in which the negative charge is equally delocalized over the three DAD ligands.

Synthesis and spectroscopic data of $[NB(NMe_2)_2Si(NMe_2)_3Ti(NMe_2)_3]$, $[NSi(NMe_2)_3Ti(NMe_2)_2]_2$ and $[N(SiMe_3)Si(NMe_2)_3Ti(NMe_2)_3]$ are reported [29].



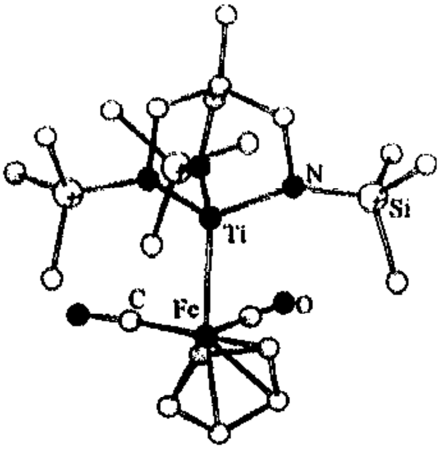
(18)

The complex [NSi(NMe$_2$)$_3$Ti(NMe$_2$)$_2$]$_2$ (**19**) consists of dimers and the molecules have approximately C_{2h} symmetry. The compound is characterized by a planar four-membered Ti$_2$N$_2$ ring with exocyclic tri(dimethylamino)silyl substituents attached to the nitrogen atoms of the ring. The C_2 axis lies in between the two titanium atoms of the Ti$_2$N$_2$ ring and the two symmetry planes go through both of the nitrogen atoms as well as the silicium atoms of the silyl group. The titanium atoms have a tetrahedrally distorted surrounding and the Ti–Ti bond length is 2.807 Å.



(19)

The chemical reactivity at an early transition metal centre upon a single site while effectively shielding the remaining coordination sphere is of interest in the development of polydentate amido ligands. Two types of new tripodal amides are reported: [H$_3$CC(CH$_2$NSiMe$_3$)$_3$TiBr] **A** and [HC(SiMe$_2$NC$_6$H$_4$CH$_3$)$_3$TiBr] **B**. Reaction of the amides **A** and **B** with carbonyl metallate derivatives leads to the coupled, heterodimetallic, dinuclear complexes [H$_3$CC(CH$_2$NSiMe$_3$)$_3$TiBr] [M(CO)$_2$(C$_5$H$_4$)] (M = Fe (**a**) (**20**), Ru (**b**)), [H$_3$CC(CH$_2$NSiMe$_3$)$_3$TiBr][Co(CO)$_3$(PPh$_3$)] (**c**) and [HC(SiMe$_2$NC$_6$H$_4$CH$_3$)$_3$TiBr] [M(CO)$_2$(C$_5$H$_4$)] (M = Fe (**d**), Ru (**e**)), [HC(SiMe$_2$-NC$_6$H$_4$CH$_3$)$_3$TiBr] [Co(CO)$_3$(PPh$_3$)] (**f**), respectively [30]. The Ti–Fe complexes (**a**) and (**d**) are the first compounds with an unsupported Ti–Fe bond that are stable in solution at ambient temperatures and chemically fairly robust towards attack by weak nucleophiles unless activated thermally or photochemically. The existence of Ti–M bonds in the complexes (**a–f**) was initially established by IR spectroscopy. Free rotation about the Ti–M bonds is inferred from the effective threefold symmetry of the titanium-amide moiety observed in the NMR spectra. Cooling solutions of (**a**), (**b**), (**d**), and (**e**) in [D_8]toluene 190 K leads to a broadening of the resonance assigned to the amido ligand. Single crystal X-ray structural analyses of (**a**) and (**b**) have established that, while the compounds differ significantly with regard to their packing in the crystal and thus space group symmetry, their molecular structures are very similar. The central structural unit is the Ti–M bond (M = Fe, Ru). The average Ti–Fe distance of 2.433 Å in (**a**) and the Ti–Ru distance of 2.527(1) Å in (**b**) are significantly shorter than in other compounds. In fact, the Ti–Fe bond length in (**a**) is the shortest observed so far for an unsupported transition metal–metal single bond in a molecule. In order to establish the basic structural arrangement in the dimetallic complex derived from **B**, an X-ray structure analysis of (**e**) was carried out. A striking feature is the lampshade arrangement of the tripodal amide in which the tolyl groups are oriented almost orthogonally to the radial planes spanned by the Ti, N, and Si atoms. That this orientation of the amido tolyl groups is retained in solution may be inferred from the shift of the signals of the Cp protons in the ^{1}H-NMR spectrum of (**e**) to higher field ($\delta = 4.07$ in comparison with 4.99 in (**b**)). The Ti–Ru bond therefore appears less shielded than in (**b**), and it may be due to this situation that the metal–metal bond [d(Ti–Ru) = 2.503(4) Å] is even shorter than that observed in (**b**).

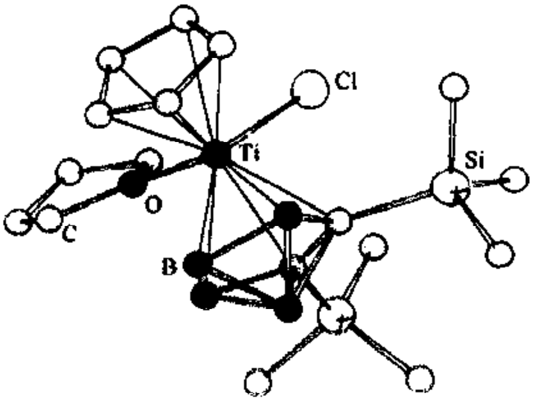


(**20**)

2.6. Complexes with boron donor ligands

The reaction of *closo-exo*-Li-1-Li-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ and anhydrous Cp_2TiCl_2 produced [*commo*-1-Cp-1-Ti-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2$, the first example of a paramagnetic Ti(III) d^1-d^1 dimer not having distinct bridging ligands [31].

Chemical oxidation of the complex gave the previously unknown diamagnetic (d^0) Ti(IV) complex, *commo*-1-Cp-1-Cl-1-thf-1-Ti-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (**21**). For [*commo*-1-Cp-1-Ti-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$$]_2$ the EPR spectrum in frozen toluene at 105 K was recorded. The dimer shows an interesting magnetic behaviour in that it exhibits a broad susceptibility maximum at 60 K with a sudden decrease below and Curie-Weiss behaviour above this temperature. Despite of the paramagnetism useful NMR spectroscopic data were obtained. These and the IR and mass spectra as well are consistent with the molecular structure. The X-ray crystal structure reveals that there are two crystallographically independent half-dimers in the unit cell and a centre of symmetry exists within each dimer. The complex *commo*-1-Cp-1-Cl-1-thf-1-Ti-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ examined by ^1H-, ^{11}B- and ^{13}C-NMR spectroscopies, IR and mass spectrometry. A crystal structure determination shows a distorted tetrahedral coordination for the titanium atoms with Ti-C_2B_3 and Ti-Cp centroid distances very similar to those found for [*commo*-1-Cp-1-Ti-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$$]_2$.



(**21**)

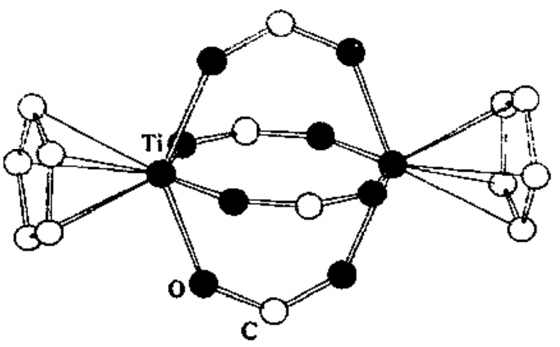
3. Titanium(III)

3.1. *Complexes with oxygen donor ligands*

Dinuclear 'titanocene' $[CpTi]_2(C_{10}H_8,H,H)$ reacts with carboxylic acids resulting in the replacement of its three bridges by four carboxylato bridges. The structure of the resulting formato complex $[CpTi(OCOH)_2]_2$ (**22**) has been determined by X-ray crystallography [32]. The Ti^{III} centres are bridged by symmetric formato groups. The Ti–Ti distance of 3.775(1) Å is too long for a direct Ti–Ti interaction.

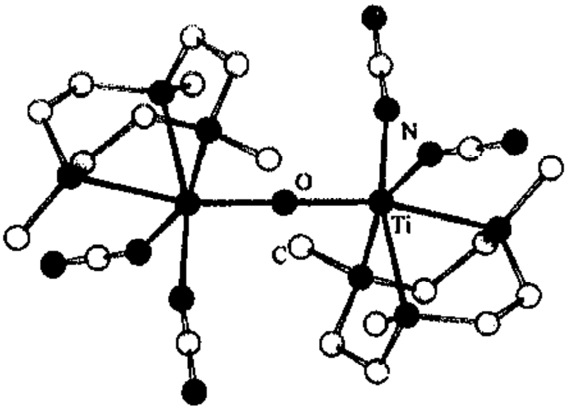
3.2. *Complexes with nitrogen donor ligands*

The compound $Ti^{III}(CH_3CN)_3Cl_3$ reacts with the cyclic triamine 1,4,7-triisopropy-1,4,7-triazacyclononane (tiptacn) with formation of $[(tiptacn)Ti^{III}Cl_3]$. The



(22)

chloro ligands of the complex are readily substituted by thiocyanato groups generating [(tiptacn)Ti^{III}(NCS)$_3$]. From a mixture of thf, NaOCN, water, methanol and [(tiptacn)Ti^{III}Cl$_3$], the complex [(tiptacn)Ti^{III}(NCO)$_3$(OCH$_3$)] was obtained. In the absence of methanol and by using 1,4,7-trimethyl-1,4,7-triazacyclononane (Me$_3$tacn) as the macrocyclic triamine, the neutral (μ-oxo)dititanium(III) complex [(Me$_3$tacn)$_2$Ti$_2$(NCO)$_4$(μ-O)] is formed. The thiocyanato analogue [(Me$_3$tacn)$_2$Ti$_2$(NCS)$_4$(μ-O)] was obtained from an acetonitrile/water mixture with [(Me$_3$tacn)Ti(NCS)$_3$]. The crystal structure of [(Me$_3$tacn)$_2$Ti$_2$(NCO)$_4$(μ-O)] has been determined by X-ray crystallography [33]. The neutral molecules in the complex of [(Me$_3$tacn)$_2$Ti$_2$(NCO)$_4$(μ-O)] (23) contain the linear Ti^{III}–O–Ti^{III} moiety with a Ti–O bond distance of 1.838(1) Å. From temperature dependent magnetic susceptibility measurements (2.0-296 K) it is concluded that the two unpaired electrons in the complexes [(Me$_3$tacn)$_2$Ti$_2$(NCO)$_4$(μ-O)] and [(Me$_3$tacn)$_2$Ti$_2$(NCS)$_4$(μ-O)] exhibit a weak intramolecular antiferromagnetic coupling. Electronic and X-band EPR spectra, electrochemistry and the magnetic properties of all complexes have been investigated in detail.



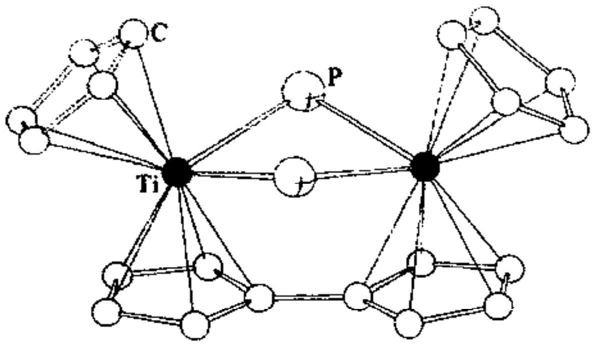
(23)

The reduction of TiCl$_4$ with sodium amalgam and addition of [PhNC(H)NPh]Li affords the titanium(III) compound Ti(DPhF)$_3$. The crystal structure determination shows that, because of the small bite of the ligand, the N–Ti–N* angles within the chelate rings are only 63.3(2)° and the TiN_6 core deviates markedly from being trigonal antiprismatic. Reduction of $TiCl_4$ with $HSn(n\text{-}Bu)_3$ and addition of [PhNC(H)NPh]Li does not produce a Ti^{II} product but rather an imido bridged compound, $Ti_2(\mu\text{-DPhF})_2(DPhF)_2(\mu\text{-NPh})_2$ [34]. The titanium atoms are in a distorted octahedral environment. The main deviation is in the small N–Ti–N* angle in the chelating ring, 61.43(7)°. The bridging Ti–N–Ti units are unsymmetrical, with the Ti–N bond lengths of 1.789(2) and 2.068(2) Å, indicative of alternative single and double bond character.

Reaction of $[(Cy_2N)_2Ti(\mu\text{-Cl})_2Li(TMEDA)]$ (TMEDA = *N,N,N′,N′*-tetramethylethylene-diamine) with MeLi formed different complexes depending on the stoichiometric ratios of the reactants used [35]. The novel Ti(III) complex $[(Cy_2N)_2Ti(\mu\text{-Me})_2Li(TMEDA)]$ formed when two equivalents of the organolithium reagent was used. A crystal structure determination revealed that the coordination geometry around the titanium atom is a distorted tetrahedron with the coordination polyhedron bound to two nitrogen atoms of the two amides and the carbon atoms of the two methyl groups. The trigonal planar geometry of the nitrogen donor atoms together with the rather short Ti–N distances (Ti1–N1 = 1.964(4) Å, Ti1–N2 = 1.941(4) Å) indicate an sp^2 hybridization of the nitrogen atoms, and possibly to some extent Ti–N π-bonding. A tetravalent complex, $[(Cy_2N)_2TiMe_2]$, was obtained when a molar ratio of 1:1 was used. The complex is monomeric and a titanium atom is placed in the centre of a distorted tetrahedron defined by two nitrogen atoms of the two amido ligands and the two terminal methyl groups. $[(Cy_2N)_2TiMe_2]$ rapidly decomposed in toluene at 60°C to form the bridging methylene complex $[(Cy_2N)_2Ti(\mu\text{-CH}_2)_2\text{-Ti}(NCy_2)_2]$. The molecule is dimeric and consists of two identical $(R_2N)_2Ti$ fragments connected by two bridging methylene groups. The coordination polyhedron around each titanium atom is that of a distorted tetrahedron. The $Ti_2(CH_2)_2$ core is planar, forming rather short Ti–Ti contacts (Ti–Ti = 2.934(2) Å).

3.3. *Complexes with phosphorus donor ligands*

The reduction of Cp_2TiCl_2 with primary phosphides K[PHR] (R = t-Bu, $SiPh_3$, $C_6H_2\text{-}2,4,6\text{-}(t\text{-}Bu_3)$) in the presence of the corresponding primary phosphine, PH_2R, is reported. In the first two cases, the products obtained are typical Ti(III) dimers of the form $[Cp_2Ti(\mu\text{-PHR})]_2$ (R = t-Bu, $SiPh_3$). However, in the cases of the reaction of super-mesitylphosphine phosphine, the product obtained is $[CpTi(\mu\text{-PH}_2)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (**24**) [36]. These reactions have been monitored spectroscopically by ^1H- and ^{31}P-NMR and X-band EPR spectroscopies. An X-ray crystal structure determination shows that the two Ti atoms are coordinated to π-bound cyclopentadienyl rings as well as half of the fulvalenide moiety which bridges the two metal centres. The two phosphide (PH_2) moieties also bridge the two metal atoms, thus completing the pseudotetrahedral coordination spheres of the titanium atoms. The Ti_2P_2 unit is not planar. The dihedral angle between the TiP_2 planes is 26.6(2)°.

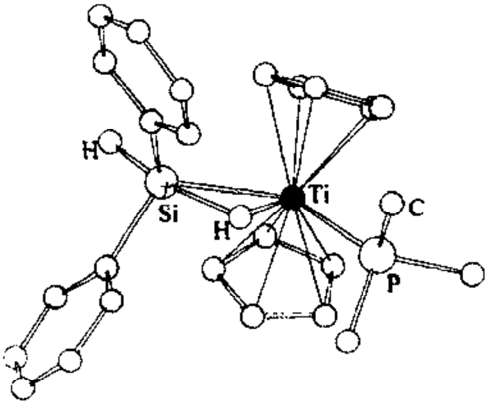


(24)

4. Titanium(II)

Treatment of $(CpTiCl_2)_x$ with n-butyllithium and 1,2-bis(dimethylphosphino)ethene (dmpe) gives a dark-brown solution from which black crystals of $CpTiCl(dmpe)_2$ could be obtained after crystallization from pentane or diethyl ether. Treatment of this compound with methyllithium affords the titanium(II)alkyl $CpTiMe(dmpe)_2$ as black crystals. A similar reaction of $CpTiCl(dmpe)_2$ with n-butyllithium yields the titanium(II)hydride $CpTiH(dmpe)_2$ [37]. All three compounds are diamagnetic. They show sharp ^1H- and ^{13}C-NMR spectroscopic signals for the Cp ring. For each complex there are two PMe_2 resonances for the dmpe ligand. The crystal structures of all three compounds have been determined. All three complexes are best described as pseudo-octahedra with the two dmpe ligands occupying the equatorial positions. The four phosphorus atoms are bent away from the η^5-Cp groups. All compounds are crowded molecules with unusually long metal-ligand bonds. Other titanium(II) pentamethylcyclopentadienyl complexes have also been prepared: treatment of Cp^*TiCl_3 with excess $LiBH_4$ and crystallization from toluene affords the green titanium(III) complex $[Cp^*TiCl(BH_4)]_2$. Treatment of this complex with n-butyllithium in the presence of dmpe or *tert*-butyltris[(dimethylphosphino)methyl]silane (trimpsi) yields dark brown crystals of the titanium(II) complexes $Cp^*Ti(BH_4)$dmpe and $Cp^*Ti(BH_4)$(trimpsi), respectively, after recrystallization from pentane. The compounds $Cp^*Ti(BH_4)$dmpe and $Cp^*Ti(BH_4)$(trimpsi) are paramagnetic. The X-ray crystal structure of the trimpsi complex $Cp^*Ti(BH_4)$(trimpsi) confirms the presence of didentate BH_4^- ligands. Somewhat surprisingly, the potentially tridentate trimpsi ligand is bound to the metal centre in a didentate fashion.

The preparation and characterization of the novel titanocene complex $Cp_2Ti(Ph_2SiH_2)(PMe_3)$ (**25**) is reported [38]. The complex is unstable in solution and decomposes to the dinuclear species $\{(\mu(\eta^1{:}\eta^5\text{-}C_4H_4))(Cp)Ti(PMe_3)\}_2$ and Ph_2SiH_2. The ^1H- and ^{29}Si-NMR and IR spectra were recorded. A single crystal X-ray structure determination was also carried out. The most interesting feature of the structure is the geometry around the silicon atom. This geometry is best described as a distorted trigonal bipyramid with the two hydrogen atoms occupying the apical positions and Ti with two C atoms defining the equatorial plane. Both the spectroscopic and structural data suggest that there is a three-center interaction between silicon, titanium and the hydride ligand.



(25)

References

[1] G. Bergerhoff, DIAMOND: Informationssystem für Kristallstrukturen, Bonn, 1995.
[2] G.R. Willey, M.L. Butcher, M. McPartlin, I.J. Scowen, J. Chem. Soc., Dalton Trans., (1994) 305.
[3] P.G. Jones, C. Kienitz, C. Thöne, Z. Kristallogr. 209 (1994) 85.
[4] T. Rübenstahl, D. Wolff von Gudenberg, F. Weller, K. Dehnicke, H. Goesmann, Z. Naturforsch. 49b (1994) 15.
[5] D. Wolff von Gudenberg, H.C. Kang, W. Massa, K. Dehnicke, C. Maichle-Mössmer, J. Strähle, Z. Anorg. Allg. Chem. 620 (1994) 1719.
[6] E.P. Turevskaya, V.G. Kessler, N.Y. Turova, A.P. Pisarevsky, A.I. Yanovsky, Y.T. Struchkov, J. Chem. Soc., Chem. Commun., (1994) 2303.
[7] H. Barrow, D.A. Brown, N.W. Alcock, H.J. Clase, M.G.H. Wallbridge, J. Chem. Soc., Dalton Trans., (1994) 195.
[8] M.T.H. Tarafder, M. Shamsul Islam, P. Bhattacharjee, S.B. Quaraishi, Indian J. Chem. 33A (1994) 676.
[9] P.D. Hamptom, C.E. Daitch, T.M. Alam, Z. Bencze, M. Rosay, Inorg. Chem. 33 (1994) 4750.
[10] N.W. Eilerts, J.A. Heppert, M.L. Kennedy, F. Takusagawa, Inorg. Chem. 33 (1994) 4813.
[11] C. Campbell, S.G. Bott, R. Larsen, W.G. Van Der Sluys, Inorg. Chem. 33 (1994) 4950.
[12] H.K. Chae, D.A. Payne, Z. Xu, L. Ma, Chem. Mater. 6 (1994) 1592.
[13] D. Selent, J. Pickhardt, P. Claus, J. Organomet. Chem. 468 (1994) 131.
[14] A. Fester, W. Bensch, M. Trömel, Acta Crystallogr., Sect. C 50 (1994) 850.
[15] C.H. Winter, T.S. Lewkebandara, J.W. Proscia, A.L. Rheingold, Inorg. Chem. 33 (1994) 1227.
[16] F. Weller, S. Wocadlo, H.-J. Mai, K. Dehnicke, Z. Kristallogr. 209 (1994) 634.
[17] T.M. Klapötke, H. Köpf, I.C. Tornieporth-Oetting, P.S. White, Angew. Chem. Int. Ed. Engl. 33 (1994) 1518.
[18] W. Stüer, K. Kirschbaum, D.M. Giolando, Angew. Chem. Int. Ed. Engl. 33 (1994) 1981.
[19] A. Khanna, B.L. Khandelwal, Trans. Metal Chem. 19 (1994) 442.
[20] P. Jeske, G. Haselhorst, T. Weyhermüller, K. Wieghardt, B. Nuber, Inorg. Chem. 33 (1994) 2462.
[21] V.M. Visciglio, P.E. Fanwick, I.P. Rothwell, Acta Crystallogr., Sect. C 50 (1994) 896.
[22] S.R. Drake, K.D. Sanderson, M.B. Hursthouse, K.M.A. Malik, Polyhedron 13 (1994) 181.
[23] T. Rübenstahl, F. Weller, K. Harms, K. Dehnicke, Z. Anorg. Allg. Chem. 620 (1994) 1741.
[24] S.C. Dunn, A.S. Batsanov, P. Mountford, J. Chem. Soc., Chem. Commun., (1994) 2007.

[25] C. Parrado, R. Bastida, A. Macias, A. Rodriguez, A. Sousa, Syth. React. Inorg. Met.-Org. Chem. 24 (1994) 1613.
[26] F. Laurent, O. Cyr-Athis, J.P. Legros, R. Choukroun, L. Valade, New J. Chem. 18 (1994) 575.
[27] A. Martin, M. Mena, C. Yélamos, R. Serrano, P.R. Raithby, J. Organomet. Chem. 467 (1994) 79.
[28] K.H. Thiele, B. Richter, B. Neumüller, Z. Anorg. Allg. Chem. 620 (1994) 1627.
[29] O. Wagner, M. Jansen, H.-P. Baldus, Z. Anorg. Allg. Chem. 620 (1994) 366.
[30] S. Friedrich, H. Memmler, L.H. Gade, W.-S. Li, M. McPartlin, Angew. Chem. Int. Ed. Engl. 33 (1994) 676.
[31] N.S. Hosmane, Y. Wang, H. Zhang, J.A. Maguire, E. Waldhör, W. Kaim, H. Binder, R.K. Kremer, Organometallics 13 (1994) 4156.
[32] T. Wöhrle, U. Thewalt, J. Organomet. Chem. 468 (1994) C1.
[33] P. Jeske, K. Wieghardt, B. Nuber, Inorg. Chem. 33 (1994) 47.
[34] A.F. Cotton, W.A. Wojtczak, Polyhedron 13 (1994) 1337.
[35] L. Scoles, R. Minhas, R. Duchateau, J. Jubb, S. Gambarotta, Organometallics 13 (1994) 4978.
[36] J. Ho, D.W. Stephan, Inorg. Chem. 33 (1994) 4595.
[37] Y. You, S.R. Wilson, G.S. Girolami, Organometallics 13 (1994) 4655.
[38] E. Spaltenstein, P. Palma, K.A. Kreutzer, C.A. Willoughby, W.M. Davis, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 10308.