Coordination Chemistry Reviews, 57 (1984) 301—343
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

8. TITANIUM

JOHN R. UFFORD [1] AND NICK SERPONE [1,2]

CONTENTS

INTRODUCTION

The chemistry of titanium continues to be an active area of research. While this review attempts to provide as comprehensive a survey as possible of developments during the 1981 calendar year, the emphasis strictly reflects the interests of the authors.

Unlike the previous review by Fay [3] in this series, which was subdivided in terms of the chemistry of the various oxidation states of titanium, this review presents it in terms of subject matter. The areas which are covered are the preparation and properties of coordination compounds of titanium, photocatalytic reactions involving TiO_2, and the use of titanium compounds as catalysts in polymer and organic syntheses. Solid-state aspects are not treated directly, but are treated in connection with other areas of interest.

Since the review by Fay [3], another review by Pez and Armor [4] has appeared. This latter article deals with the synthesis, structure and properties of formally divalent and trivalent titanium metallocene compounds. The aim of the review was to describe and critically evaluate the confusing data reported for these low-valent titanium and zirconium metallocenes.

The present review article covers the material in the major journals for the 1981 calendar year and the foreign and less well known journals for the period covered by Chemical Abstracts from Volume 93, number 19, to Volume 95,

0010-8545/84/$12.90

number 24; however, articles dated 1980 and abstracted in these volumes [190-260] have not been considered.

8.1 PREPARATION AND CHARACTERISATION OF TITANIUM COMPOUNDS

Reaction of $[(cp)_2TiCl_2]$ with o-$C_6H_4\{CH(SiMe_3)Li(Me_2NCH_2CH_2NMe_2)\}$ in diethyl ether is stereospecific, generating the *meso*-metallacycle $[(cp)_2Ti\{CH(SiMe_3)C_6H_4CH(SiMe_3)$-$o\}]$ in high yield [5]. Cyclic voltammetry in tetrahydrofuran shows a reversible one-electron reduction yielding a relatively persistent titanium(III) anion. Reactions of dicyclopentadienyltitanium(IV) dichloride with dibasic tri(SBN_2) or tetradentate ($S'B'H_2$) Schiff bases have yielded the monomeric (in boiling chloroform) penta- and hexa-coordinated complexes $[(cp)_2TiSB]$ and $[(cp)_2Ti(S'B')]$ [6]. Coordination of azomethine nitrogen and phenolic and alcoholic oxygens to titanium atoms has been substantiated by infrared (IR), nuclear magnetic resonance (NMR), and mass spectral studies.

A series of compounds of the type $[ABTiL]^+X^-$ (where A = cp, B = η^5-MeC_5H_4, L is the conjugate base of acetylacetone, and X is ClO_4^-, BF_4^-, $ZnCl_3(H_2O)^-$, $SnCl_3^-$, $CdCl_3^-$, $FeCl_4^-$, Br^-, or I^-) has been prepared and characterised [7]. The ligand L appears chelated and the titanium atom is essentially tetra-coordinated. The preparation of $[(cp)_2TiCO(PF_3)]$ by the photolysis of $[(cp)_2Ti(CO)_2]$ in hexane in the presence of excess PF_3 is reported to be the first trifluorophosphine derivative of titanium [8]. Properties of the compound are included. The trinuclear complexes $[(cp)TiAl_2Cl_{8-x}Et_x]$ (x = 1-4) have been prepared by the reaction of $[(cp)TiCl_3]$ with two equivalents of ethylaluminium compounds [9]. The composition of ethylated titanium complexes formed in the system $[(cp)TiAl_5Cl_8$-$Et_{3-x}AlCl_x]$ (x = 0, 1, 2) was determined from electron paramagnetic resonance (EPR) spectral data and from the position of d-d absorption bands. In the system $[C_6H_6 \cdot TiAl_2Cl_8$-$Et_{3-x}AlCl_x]$, only $[C_6H_6 \cdot TiAl_2Cl_7Et]$ and $[C_6H_6 \cdot TiAl_2Cl_6Et_2]$ could be detected. In both titanium(III) and titanium(II) series, the stability of the complexes decreases with increasing content of ethyl groups. Properties of the (cp)Ti(III) trinuclear complexes are compared with those of the binuclear complexes $[(cp)_2TiAlCl_{4-x}Et_x]$ (x = 0, 1, 2). Results are also reported for a series of bromo complexes.

When $[(cp)_2TiCl]$ is reacted with lithium alkyls, the product obtained is $[(cp)_2TiR]$ (R = CH_3, C_2H_5, n-C_4H_9, s-C_4H_9, or t-C_4H_9) [10]. Reaction of this product with 2,6-xylyl isocyanide, phenyl isocyanide or carbon dioxide results in the insertion of these ligands into the titanium-alkyl bond with the formation of iminoacyl, amido, and carboxylate derivatives. With ketones, a pinacol-type dimerisation takes place.

Reduction of [(cp)$_2$TiCl$_2$] with LiAlH$_4$ in boiling methylbenzenes or tetralin yields (η^5:η^5-fulvalene)-di-μ-hydrido-bis(η^5-cyclopentadienyl)titanium in yields of >90% [11]. Reduction occurs via the bis(η^5-cyclopentadienyl)titanium(III) chloride dimer which is further transformed into the unstable [(cp)$_2$TiH] species. Thermal decomposition of this occurs with hydrogen evolution and the formation of μ-(η^5:η^5-fulvalene)-μ-hydrido-μ-chloro-bis-(η^5-cyclopentadienyl)titanium. The first fulvalene containing compound observed in the system is formed by hydrido-chloro exchange of this latter compound with [(cp)$_2$TiCl$_2$] and aluminium chlorohydrides.

Dicyclopentadienyl(trimethylsilyl)titanium chloride has been synthesised by the reaction of [(cp)$_2$TiCl$_2$] and tris(trimethylsilyl)aluminium coordinated with diethyl ether, or lithium tetrakis(trimethylsilyl)aluminate [12]. Condensation of sodium atoms at -100 °C in tetrahydrofuran solutions containing [(cp)$_2$TiCl$_2$] and excess trimethylphosphite produces [(cp)$_2$Ti(P(OMe)$_3$)$_2$] [13]. The reaction of chlorodiphenylphosphine with [(cp)(η^7-C$_7$H$_6$Li)Ti] gives [(cp)(η^7-C$_7$H$_6$P(C$_6$H$_5$)$_2$)Ti] in good yields [14]. A new ring compound [{(cp)TiClO}$_3$] is reported to be one of the probable products of [(cp)$_2$TiCl$_2$] in tetrahydrofuran [15]. The tetramer [{(cp)TiClO}$_4$] is known to form in the hydrolysis of [(cp)TiCl$_3$]. The preparation and properties of [(cp)$_2$TiCH$_2$(Me$_3$Si·CCPh)] have been described [16]. The synthesis and structures of [(cp)TiMo$_5$O$_{18}$][MoO$_2$Cl]$^{2-}$ and [(cp)TiMo$_5$O$_{18}$][Mn(CO)$_3$]$^{2-}$ were reported [17]. Preparation of [η^5-C$_5$(CH$_3$)$_5$Ti(CH$_2$=CHCH$_3$)$_3$] and the analogous η^4-butadiene and η^3-methallyl compounds are reported; the compounds appear to be very reactive towards CO and other small molecules [18].

A study of the magnetic exchange interactions of binuclear dicyclopentadienyltitanium(III) complexes propagated by unsaturated and aromatic dicarboxylate dianions has been reported [19]. One curious observation was made. The magnetic susceptibility *versus* temperature data for the supposedly monomeric benzoate complex [(cp)$_2$Ti(O$_2$CPh)] are characteristic of the strongest antiferromagnetic interactions in all of the dicarboxylate-bridged complexes.

[(cp)$_2$Ti-X-Ti(cp)$_2$] (where X is the dianion of thymine, 3,6-dihydroxypyridazine, 2,3-dihydroxyquinoxaline, etc.) was prepared by the oxidative addition of a heterocycle to two mols of [(cp)$_2$Ti(CO)$_2$]. Each bridging species is bis-bidentate and chelates each metal ion in a four-membered ring [20].

The preparation and characterisation of eight binuclear titanium(III) metallocenes [(cp)$_2$Ti]$_2$[O$_2$C(CH$_2$)$_n$CO$_2$] (where n = 0-4, 6, 8, 10) have been reported [21]. The oxalate anion ($n = 0$) bridges in a bis-bidentate fashion and forms five-membered chelate rings with each titanium ion. In other cases, the anion bridges in a bis-bidentate way forming only four-membered chelate rings. An investigation of the propagation of magnetic-exchange interactions by the methylene groups of these aliphatic dicarboxylate anions was included. Six binuclear titanium(III) metallocenes of the type $[(cp)_2Ti]_2B$ (where B is a cycloaliphatic dicarboxylate anion) have been synthesised and characterised [22]. The dianion bridges the two titanium(III) in a bis-bidentate fashion with the formation, also, of four-membered chelate rings. Magnetic-exchange interactions by the methylene groups of the dianions are also reported and discussed.

Metallocene compounds of the form $[(cp)_2TiRR']$ (where R is $CH_2M'Me_3$ [M' = C, Si, Ge, Sn, or $CH(SiMe_3)_2$] and R' is an alkyl group or Cl) have been prepared [23]. The reaction of HCl in diethyl ether with $[(cp)_2Ti(CH_2SnMe_3)Cl]$ gives mainly the products of $CH_2{-}SnMe_3$ scission rather than that due to $Ti{-}CH_2$ scission. The dialkyls containing one or two CH_2SnMe_3 ligands give largely RH and R'H. The relative ability of R as a leaving group decreases in the sequence $CH_2SnMe_3 > CH_2CMe_3 > CH_2SiMe_3 > CH_2GeMe_3 > CH_3$.

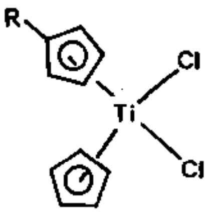
Preparation and characterisation of the compounds $[(cp)_2Ti(CO)_2]$ [24], $[(C_5H_4Me)_4Ti_2S_6]$ [25], phenolic derivatives of $[(\eta^5{-}C_5H_4Me)_2TiCl_2]$ [26], hydroxy-coumarin complexes of $[(cp)_2TiCl_2]$ [27], and $[(cp)_2Ti(CH_3){-}(OC)_3Mo(cp)]$ [28] have been published.

The compound $[(\mu{-}O_2){-}(\mu{-}(\eta^1{:}\eta^5{-}C_5(CH_2)(CH_3)_4)Ti(\eta^5{-}C_5(CH_3)_5)_2]$ has been characterised and is the first to contain a $[\eta^1{:}\eta^5{-}C_5(CH_2)(CH_3)_4]$ ligand. One methyl group of a $C_5(CH_3)_5$ ring attached to one titanium has become a methylene bridge to a second titanium atom [29].

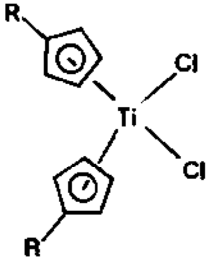
Pentasulphide and pentaselenide complexes of bis(methylcyclopentadienyl)titanium(IV) and (cyclopentadienyl)(methylcyclopentadienyl)titanium(IV) have been reported [30]. The compounds are monomeric, non-electrolytes. A chair configuration was assigned to the TiS_5 and $TiSe_5$ rings in these complexes on the basis of proton NMR spectra.

Tris(*N*,*N*-diisopropyldithiocarbamato) compounds of the type $[(cp)Ti(S_2CN^iPr_2)_3]$ and $[(C_5H_4Me)Ti(S_2CN^iPr_2)_3]$ have been synthesised by the reaction of $[(cp)_2TiCl_2]$ or $[(MeC_5H_4)_2TiCl_2]$ and anhydrous $Na(S_2CN^iPr_2)$ in refluxing dichloromethane or tetrahydrofuran [31]. The compounds are monomeric, non-electrolytes. Infrared data suggest seven-fold coordination; proton NMR spectral data show the compounds to be stereochemically rigid. The suggested structure for these complexes is the rare mono-capped trigonal prism. A crystal structure determination would appear to be in order to verify this suggestion.

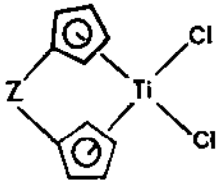
Monosubstituted 1,1'-disubstituted and 1,1'-bridged titanocene dichlorides, $[(RC_5H_4)(C_5H_5)TiCl_2]$ (R = Me, Et, SiM_3; *1-3*), $[(RC_5H_4)_2TiCl_2]$ (R = Me, CMe_3, $SiMe_3$, $SiMe_2Bu$, $GeMe_3$; *4-8*), and $[Z(C_5H_5)_2TiCl_2]$ [Z = $(CH_2)_3$, CH_2, CHMe, SiHMe, $SiEt_2$, $GeMe_2$; *9-15*] can be prepared by metallation of cyclopentadienes RC_5H_5 and $Z(C_5H_5)_2$ with BuLi and according to reactions (*1-5*) with $[(C_5H_5)TiCl_3$ or $TiCl_4]$, respectively [32]. The resulting compounds (*1*) through (*15*), as well as the indenyl and tetrahydroindenyl derivatives,



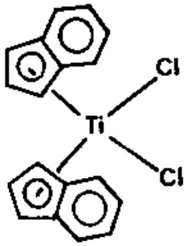
(1-3)



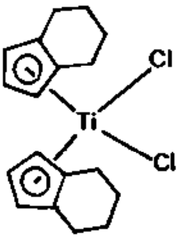
(4-8)



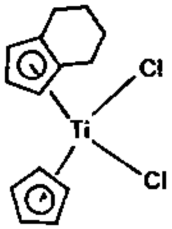
(9-15)



(16)



(17)



(18)

$[(C_9H_7)_2TiCl_2]$, $[(C_9H_{11})_2TiCl_2]$, and $[(C_9H_{11})(C_5H_5)TiCl_2]$ (*16-18*) have also been investigated with respect to their anti-tumour activity against Ehrlich ascites tumour in mice [32].

Exposure of $[(cp)_2TiCl_2]$ in various media to ^{60}Co γ-rays at 77 °K yields the corresponding titanium(III) complex, $[(cp)_2TiCl_2]^-$, characterised by its EPR spectrum [33]. At >77 °K in methanol solutions, this species changes irreversibly into a second titanium(III) complex suggested to be $[(cp)_2TiCl]$. Similar treatment of $[(cp)TiCl_3]$ gives $[(cp)TiCl_3]^-$, the EPR spectrum of which suggests a major contribution from a $d_{x^2-y^2}$ configuration rather than a d_{z^2} configuration as found for the previous complex [33]. Correspondingly, $TiCl_4$ in the pure state at 77 °K forms $TiCl_4^+$ ions, having an EPR spectrum comparable

$$\begin{tikzcd}
2\ \mathrm{RC_5H_5} \arrow[r, "2\ \mathrm{BuLi}"] & 2\ \mathrm{RC_5H_4Li} \arrow[r, "\mathrm{TiCl_4}"] \arrow[d, "2\ \mathrm{(C_5H_5)TiCl_3}"] & \mathrm{(RC_5H_4)_2TiCl_2} \\
& 2\ \mathrm{(RC_5H_4)(C_5H_5)TiCl_2} &
\end{tikzcd} \tag{1}$$

$$2\ \mathrm{SiMe_2Cl(C_5H_5)} \xrightarrow{4\ \mathrm{BuLi}} 2\ \mathrm{SiMe_2Bu(C_5H_5)Li} \xrightarrow{\mathrm{TiCl_4}} \mathrm{(SiMe_2BuC_5H_4)_2TiCl_2} \tag{2}$$

$$\begin{tikzcd}
& & \mathrm{(CH_2)_3(C_5H_4)_2TiCl_2} \\
2\ \mathrm{C_5H_6} \arrow[r, "\substack{1.\ 2\ \mathrm{Na} \\ 2.\ \mathrm{(CH_2)_nBr_2}}", "\substack{3.\ 2\ \mathrm{Na} \\ 4.\ \mathrm{TiCl_4}}"'] & {} \arrow[ur, "n = 3"] \arrow[dr, "n = 2"'] & \\
& & \mathrm{(CH_3CH_2C_5H_4)(C_5H_5)TiCl_2}
\end{tikzcd} \tag{3}$$

$$\mathrm{Z(C_5H_5)_2} \xrightarrow{\mathrm{BuLi}} \mathrm{Z(C_5H_4Li)_2} \xrightarrow{\mathrm{TiCl_4}} \mathrm{Z(C_5H_4)_2TiCl_2} \tag{4}$$

$$\begin{tikzcd}
2\ \mathrm{C_9H_8} \arrow[r, "\mathrm{BuLi}"] & 2\ \mathrm{C_9H_7Li} \arrow[r, "\mathrm{TiCl_4}"] \arrow[d, "\substack{1.\ 2\mathrm{(C_5H_5)TiCl_3} \\ 2.\ 4\mathrm{H_2},\ [\mathrm{Pt}]}"] & \mathrm{(C_9H_7)_2TiCl_2} \arrow[d, "4\mathrm{H_2},\ [\mathrm{Pt}]"] \\
& \mathrm{(C_9H_{11})(C_5H_5)TiCl_2} & \mathrm{(C_9H_{11})_2TiCl_2}
\end{tikzcd} \tag{5}$$

with that of Cl_2^- together with $TiCl_4^-$; the latter ion possesses a distorted structure with the extra electron in a predominantly d_{z^2} orbital [33].

Investigation of titanium(III) solutions in molten alkali chlorides by Raman spectroscopy has shown that the solvent cations affect the nature of the complex anions formed [34]. A detailed study of the effect of LiCl on the anion $[TiCl_6]^{3-}$, the only species present in a titanium(III) solution in CsCl at 700 °C, is presented. At twenty mol percent LiCl, a new band appears in the $[TiCl_6]^{3-}$ spectrum. This band appears not to be associated with any vibration of $[TiCl_6]^{3-}$ or $[TiCl_4]^-$. It is probably due to $[Ti_2Cl_9]^{3-}$ [34]. The following equilibria were suggested in molten chloride solution.

$$[TiCl_6]^{3-} \rightleftharpoons [TiCl_4]^- + 2\ Cl^- \qquad (6)$$

$$2\ [TiCl_6]^{3-} \rightleftharpoons [Ti_2Cl_9]^{3-} + 3\ Cl^- \qquad (7)$$

Solid $TiCl_3$ can be transported by Al_2Cl_6 via $TiAlCl_6$ in a temperature gradient as shown by mass spectrometric studies [35]. No indication of $TiAl_2Cl_9$ was found as is often assumed in the literature. Transport of $TiCl_2$ with Al_2Cl_6 involves disproportionation. This can be prevented by the addition of titanium, and the compound $Ti_{17}Cl_{16}$ can be prepared. $Ti_{17}Br_{17}$ can also be formed. Thermal decomposition studies of these are reported.

Raman and infrared studies of $[CH_3TiX_3]$ and $[CD_3TiX_3]$ (where X = Cl, Br, or I) have been carried out [36]. Studies at one atmosphere between 4000 and 20 cm^{-1} are reported as well as at a pressure of 4 atmospheres and 350 °K. Raman spectra of the solids at 4.2 °K are included in the data.

A series of complex cyanides $Rb_5Ti(CN)_8$, $Cs_4Ti(CN)_7$, and $K_3Ti(CN)_6$ have been prepared [37]. Reduction of $K_3Ti(CN)_6$ with one equivalent of potassium in liquid ammonia yields $K_2Ti(CN)_4$. The extremely reactive $K_4Ti(CN)_4$ was prepared by potassium reduction of $TiBr_3$ and KCN also in liquid ammonia. $K_5Ti(CN)_8$, $Rb_5Ti(CN)_8$, and $Cs_4Ti(CN)_7$ are believed to have seven-coordinated titanium, while $K_3Ti(CN)_6$ probably contains an octahedral anion.

The formation of complexes between $TiCl_4$ (M) and the lactam 2-methyl-2-azabicyclo-(2,2,2)-octa-3-one (L) of composition M_2L, ML, and ML_2 have been reported [38]. The characterisation of the complexes was concluded from analysis of Raman spectral data and proton and C-13 NMR data. Two forms of the ML_2 complex are reported. Hexacovalent titanium is found in M_2L and ML compounds; in ML_2 titanium is probably five-coordinate. The report proposes structures for the four compounds and characterises the dynamics of the exchange of lactam between the ML_2 complexes and the free lactam.

The reaction of $Ti(OR)_4$ with amidoximes under different conditions results in the formation of crystallisable amidoximates [39]. Rates of reaction and degree of molecular association are influenced by the nature of the alkyl group; a tertiary-butyl group results in a monomer, an ethyl group yields a trimer, while an isopropyl group yields an equilibrium mixture of monomer and dimer.

Preparation of $[TiCl\{N(SiMe_3)_2\}_3]$ by the reaction of $TiCl_4$ with an excess of $Li[N(SiMe_3)_2]$ is reported by other workers [40]. Structural and spectroscopic data are discussed in terms of steric effects and the nature of the metal-ligand bond. There is evidence for fluxional behaviour of the bulky ligands.

Reaction of $TiCl_4$ with $P(NCO)_3$ and $P(CN)_3$ in anhydrous benzene yields $[TiCl_3P(NCO)_2]$ and $[TiCl_3P(CN)_2]$ [41]. IR spectral bands have been assigned on the basis of C_{3v} symmetry. A detailed investigation of the reaction between $TiCl_4$ and 8-quinolinol-N-oxide has also been published [42].

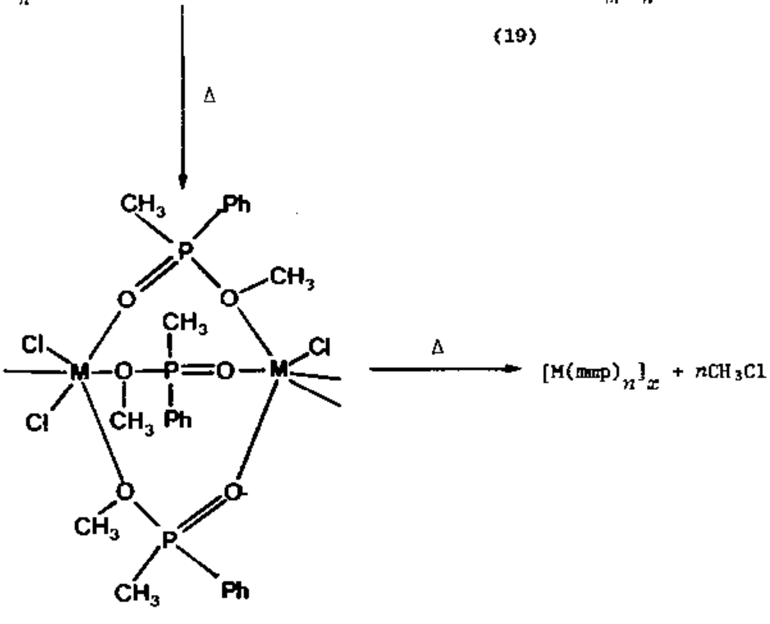
Novel titanium chelates with azo ligands have been synthesised and their dyeing properties investigated [43]. In attempts to prepare such chelates, 2-hydroxy- and 2,2'-dihydroxy-azo compounds were respectively allowed to react with titanium tetraisopropoxide; with the 2-hydroxy-azo ligands, the products were not isolated but with the 2,2'-hydroxy-azo compounds the reaction gives a neutral 1:2 titanium chelate. Among these chelates, water-soluble ones have good affinity for fibres of wool, silk, and nylon but dyeing tests reveal that these chelates possess an inferior fastness to light, potting, and washing than the conventional chromium chelates. The water-insoluble chelates obtained for polystyrene show that these colour the resin black and also show excellent properties on staining power and light fastness in comparison to the Vali Fast Black (a chromium chelate). Reaction of MCl_4 (M = Ti, Sn) with L and Q (L = $Me_2NCH_2NMe_2$, $Me_2NCH_2CH_2NMe_2$, $Et_2NCH_2CH_2NEt_2$; Q = 1,3,5-trimethyl-1,3,5-triazacyclohexane) yields the monomeric $MCl_4 \cdot L$, dimeric $TiCl_4 \cdot Q$, and the polymeric $Q \cdot 3TiCl_4$, characterised by infrared spectroscopic methods [44]. Ionisation constants and heats of complexation have also been determined.

The compound $[Cl_2Ti(O_2PCl_2)_2]$ was reported to be formed when $TiCl_4$ reacts with either $Cl_2PO_2SiMe_3$ or with $P_2O_3Cl_4$ [45]. Vibrational and P-31 NMR spectral data are also reported. Red chelate compounds $[(R_2PS_2)TiCl_2]$ are obtained when $TiCl_4$ is reacted with $R_2P(S)SH$ where R is a methyl or ethyl group [46]; the compounds are very sensitive to hydrolysis. The crystal structure of the ethyl compound shows a twisted TiS_4Cl_2 octahedral chromophore with a *cis* configuration.

Structures involving linear, ligand-bridged polymeric species are reportedly formed when (MeO)Ph(Me)P=O, mpp, is reacted at elevated temperatures with various metal trichlorides, including $TiCl_3$ (reaction 8). The structures were suggested on the basis of IR and magnetic data [47]. The reaction proceeds by the formation of adduct (*19*) followed by the coordination of the oxygen atoms in the MeO group to the metal ion to form the polymer (*20*).

$$MCl_n + m[(MeO)Ph(Me)P{=}O] \longrightarrow M[O{=}P(Me)Ph(OMe)]_m Cl_n \qquad (8)$$

(19)



(20)

Elimination of methyl chloride results in the precipitation of polymer $[M(mpp)_n]_x$ material.

Reaction of AgOCN with bromine in dichloromethane at -70 °C yields a solution of $(OCN)_2$. Addition of an equimolar amount of $TiCl_4$ produces $TiCl_4(NCO)_2$ [48]. Infrared and Raman spectral data indicate the NCO ligand is bonded to the metal through the nitrogen atoms. Using alcohol interchange techniques, metal derivatives of β-methallyl alcohol with the formula $Ti[OCH_2C(CH_3){=}CH_2]_4$ have been prepared [49]. Molecular weight determinations in benzene indicate the compound to be a dimer, characterised by infrared and NMR spectral methods. Complexes of titanium(IV) and 2-methoxyethanol have been reported, and their probable structures discussed [50].

Reaction between $TiCl_4$ and Ph_4AsN_3 in dichloromethane yields orange crystals of $[Ph_4As]_2[TiCl_4(N_3)_2]$ [51]. X-ray crystal structural data indicate the solid to crystallise in the space group C2/c. The $[TiCl_4(N_3)_2]^{2-}$

anion has C_2 symmetry with the two azido groups in *trans* positions. IR data have also been reported and band assignments made. Complexes of the general type $TiCl_4 \cdot B$ have been reported, where B is *N*,*N'*-dimethyloxamide, *N*,*N'*-dimethylmalonamide, *N*,*N'*-dimethyldithiooxamide, and *N*,*N'*-diethyloxamide [52]. Infrared and NMR spectra reveal chelation involves either [O-O] or [S-S] coordination to the metal ion with the S donors more strongly bonded to the metal than the O donors; the compounds are covalent.

Two complexes of composition TiL_2 (where L are the lactams 1-methyl-1-azahepta-2-one and 1-methyl-1-azacyclonona-2-one) have been described [53]. Analysis of proton and ^{13}C NMR spectra in 1,1,2,2-tetrachloroethane-d_2 and $CDCl_3$ solutions at mole ratios L/Ti > 2 indicate TiL_2 to have different geometrical arrangements.

The synthesis of polydyes of titanium using interfacial techniques has been reported [54]. Application of the polydyes that takes advantage of their potential permanent non-leaching nature, in contrast to the monomeric dyes, has been emphasised. The polydyes are fluorescent and can be impregnated into paper, cloth, paint, and doped into plastics; dyes used were Congo Red, Nigrosine, Bromphenol Blue, Bromthymol Blue, Indigo Carmine, and Eriochrome Black T.

Calorimetric and cryoscopic studies of $SnCl_4$ and $TiCl_4$ complexes with dibenzo-24-crown-8 (L) reveal the formation of $L \cdot 2SnCl_4$ and $L \cdot 2TiCl_4$; the heats of formation are, respectively, -203.0 and -228.9 kJ/mol [55]. Complexing of 1,2-diethoxyethane and 1,2-dimethoxybenzene with the Lewis acids $SnCl_4$, $TiCl_4$, $AlBr_3$, and CF_3CO_2H have also been investigated and their dipole moments determined. In addition, in mixed fluoride-nitrate melts of $LiNO_3$-KNO_3-KF, tetrahedral compounds of TiF_4^- and CoF_4^- are formed at 150-250 °C [56]. Electronic spectral studies indicate the crystal field 10Dq is 10,000 cm^{-1} for TiF_4^- under such melt conditions.

$MeSiCl_3$ reacts with TiO_2 in a fluidised bed at a temperature of 600 °C and leads to homolytic cleavage of Si-C and Si-H bonds and formation of polysiloxane-modified TiO_2 [57].

The monomeric tetrathiocyanato-bis(ligand)titanium(IV) species are formed when $TiCl_4$ and $[TiCl_x(NCS)_yL_2]$ are reacted with alkali thiocyanates in tetrahydrofuran or acetonitrile (x = 1,2,3; y = 3,2,1; and L is CH_3CN or C_4H_8O) [58]. Desolvation of $[Ti(NCS)_4(THF)_2]$ leads to polymeric $[Ti(NCS)_4]_x$ materials. The compounds were characterised by analysis, conductivity measurements and IR and electronic spectra.

The diphenoxybis(dithiocarbamato)titanium(IV) complexes, $[(C_6H_5O)_2M(S_2CNR_2]$ and $[(C_6H_5O)_2M(S_2CNRR')_2]$ (where R = Me, Et, ^iPr, and R' = cyclohexyl) have been prepared by the reaction of stoichiometric amounts of diphenoxytitanium(IV) dichloride and sodium salts of dithiocarbamic acid in refluxing THF [59]. Infrared and electronic spectral data show the dithiocarbamate portion behaves as a bidentate ligand. Conductance measurements indicate the compounds are non-electrolytes; magnetic data, NMR and visible spectral data are also reported.

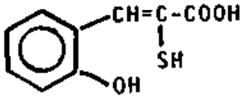
New S-(methyl or benzyl)-β-N-(2-hydroxyphenyl)methylene dithiocarbazate complexes of titanium(IV) have been reported [60]. Data are given for IR, NMR and electronic spectra upon which, along with electrical conductance measurements, probable structures are suggested. The thermograms for the methyl compound are reported.

A new simpler method for preparing tris(dithiolene)titanium compounds has been described, using standard anaerobic techniques and light petroleum as solvent [61]. Solutions of the dithiol and the amine are mixed and stirred at ambient temperature overnight; after filtering under nitrogen, yields of products are in the 90% range. The dark green solid $[Et_3NH]_2[Ti(S_2C_6H_3CH_3)_3]$ and the black compound $[Et_2NH_2]_2[Ti(S_2C_6H_3CH_3)_3]$ are diamagnetic solids, and insoluble in benzene and chloroform. Both yield deep violet solutions in acetone and acetonitrile; both are stable to atmospheric moisture in the solid state, but are sensitive to moisture in solutions.

The systems titanium(IV)-catechol-3,5-disulphuric acid (Tiron) and some aminopolycarboxylic acids were studied in acid solutions [62], and evidence for the existence of chelates with components in the ratio 1:1:1 reported.

Two new compounds have been reported starting with freshly precipitated titanium hydroxide, selenic acid, and hydrogen peroxide under controlled pH conditions [63]. At pH 0.5, a solid of composition $K_2[Ti(O_2)(SeO_4)_2]\cdot 3H_2O$ forms and at pH 1.5 the product has the composition $K_2[TiO(O_2)SeO_4]\cdot 3H_2O$. Both show characteristic peroxo and selenato IR bands. The solid obtained at pH 1.5 shows the presence of $(TiO)^{2+}$ with a band observed at 1040 cm^{-1}. Reaction between $TiCl_4$ and $(SeCN)_2$ in CS_2 produces the compound $TiCl_3(NCSe)$ [64]. Vibrational spectral data indicate the selenocyanate group forms a bridge between metal atoms via nitrogen atoms.

The ligand 3-(2-hydroxyphenyl)-2-mercaptopropenoic acid, H_2R, has been used to extract titanium(IV) and manganese(II) from prepared stock solutions of their chloride and nitrate salts, respectively, in a proper solvent [65]. The



(21; H_2R)

effect of pH, reagent concentration in the organic phase, presence of electrolytes and masking agents, on the equilibrium has also been studied [65]. For titanium(IV), the compound of the extracted metal ion is probably $Ti(OH)_3(HR)$ determined from the method of equilibrium shift. New methods have also been developed for the spectrophotometric determination of titanium in the concentration range 0.05-0.5 g [66]. A mechanism is proposed on the basis of a kinetic study. In 3M HCl, the titanium species is $[Ti(OH)_2]^{2+}$; at pH 2.5, where the reaction with the extracting agent, bromopyrogallol red, has been studied, titanium(IV) exists predominantly as $Ti(OH)_3^+$ formed as per reaction (9) that precedes complexation. The predominating form of

$$[Ti(OH)_2]^{2+} + H_2O \overset{K_{th}}{\rightleftharpoons} Ti(OH)_3^+ + H^+ \tag{9}$$

bromopyrogallol red (H_4DG) at pH 2.5 is H_3DG^-; it undergoes a deprotonation equilibrium (reaction 10) followed by complexation with $Ti(OH)_3^+$ according

$$H_3DG^- \overset{K'}{\rightleftharpoons} HDG^{3-} + 2\ H^+ \tag{10}$$

to reaction (11). The "complex" composition was determined to be 1:1 and 1:2

$$Ti(OH)_3^+ + HDG^{3-} \xrightarrow{k} \text{"complex"} \tag{11}$$

by Job's method [66].

8.2 STRUCTURAL STUDIES

Two new ternary compounds, $BaNd_2Ti_3O_{10}$ (1:1:3) and $BaNd_2Ti_5O_{14}$ (1:1:5), have been identified in the $BaO/Nd_2O_3/TiO_2$ system [67]. The former compound crystallises in the orthorhombic space group Cmcm or Cmc2, while the latter crystallises in the orthorhombic space group Pbam or Pba2. Single crystals of the binary compound $Nd_4Ti_9O_{24}$ are also orthorhombic, space group Fddd [67].

Reaction of $[(cp)_2Ti(CF_3SO_3)_2]$ with $(Et_3NH)NO_3$ in tetrahydrofuran yields $[(cp)_2Ti(NO_3)_2]$; the crystal structure has been determined [68]. $[(cp)_2Ti(NO_3)]$ and water react in acetone to form the diaquo complex $[(cp)_2Ti(H_2O)_2](NO_3)_2$ which crystallises in the orthorhombic system [69]; hydrolysis in THF yields $[(cp)_2Ti(NO_3)]_2O$ for which the structure reveals that the NO_3 groups act as monodentate ligands [70]. The preparation and the structural parameters for $CsM^{II}Ti^{III}F_6$ {where M^{II} is Mg, Ni, Zn, Co, V, Fe, or Mn, and $CsM^{I}_{0.5}Ti^{III}_{1.5}F_6$ (M^I is K or Rb)} have been reported [71], as well as the crystal structures of Ti_7Cl_{16} and Ti_7Br_{16} [72].

The colourless oxonium compound $[O_2]_2{}^+[Ti_7F_{30}]^{2-}$ has been synthesised by reacting TiO_2 with a mixture of F_2/O_2 at a pressure $P(F_2/O_2)$ of ∿ 300-3500 atm and at a temperature of ∿ 300-400 °C; the compound crystallises in the space group P_3 [73]. The crystal structure reveals that $[O_2]_2[Ti_7F_{30}]$ possesses isolated columns of partially distorted TiF_6 octahedra (the column structure) which are connected only quite loosely by (disordered) $[O_2]^+$ cations; $\nu_{O_2{}^+}$ is at 1857 cm^{-1} and μ_{eff} = 2.35 BM (295 °K) as expected for a "spin-only" case [73]. The structure of the complex $Ti(C_4H_8O)_3Cl_3$, space group $P2_1/c$, was reported [74]; the complex is neutral with octahedrally coordinated titanium(III) and possesses the meridional configuration. The two independent molecules in the asymmetric unit are similarly oriented with exception of the THF ligands which are *trans* to the Cl atoms. The $Ti-O_{thf}$ bond distance for the two THF ligands *trans* to each other is 2.08 Å, whereas the $Ti-O_{thf}$ bond *trans* to the Cl atom is 2.18 Å ascribed to the presence of a *trans* effect. The compound $Ti(THF)_3Cl_3$ thermally decomposes according to reaction (12) where the released THF is the one *trans* to the Cl atom [74].

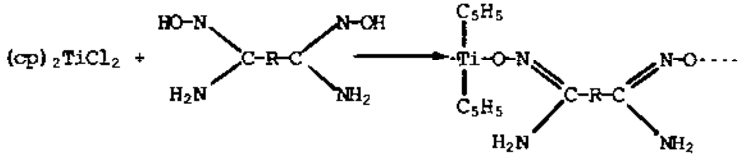
$$Ti(THF)_3Cl_3 \longrightarrow Ti(THF)_2Cl_3 + THF \qquad (12)$$

Raman data on $M^{II}(H_2O)_6SiF_6$ (M = Ni, Fe, Mg, Zn) and $M^{II}(H_2O)_6TiF_6$ (M = Ni, Zn) have been given [75]. Results allowed a positive identification of the symmetric M-O stretching frequency for the first time in these salts; the range for ν_s(M-O) is 374-405 cm^{-1}. Also, the following spectral frequencies are given: ν_{as}(Ti-F) at 450 cm^{-1} for M = Ni; ν_s(Ti-F) at 613 cm^{-1} and 610 cm^{-1} for M = Ni and Zn, respectively; δ(F-Ti-F) occurs at 272 cm^{-1} for M = Ni and at 262, 300 cm^{-1} for M = Zn [75]. Crystal structures of the unsymmetrically bridging imido complex $[(CH_3)_2(t\text{-}BuN)W]_2(\mu\text{-}t\text{-}BuN)_2$ and the symmetrically bridging imido complex $\{[(CH_3)_2N]_2Ti]_2(\mu\text{-}t\text{-}BuN)_2$ have been determined [76], both compounds crystallising in the space group $P2_1/n$ with two molecules in the unit cell. The compound $\{(cp)_2Ti[(\eta\text{-}C_5H_4)(CO)_3Mn]_2\}$ has been prepared according to reaction (13) and its structure determined by X-ray

$$(cp)_2TiCl_2 + Li[Mn(\eta\text{-}C_5H_4)(CO)_3] \xrightarrow[5:1]{THF/Et_2O} (cp)_2Ti[(\eta\text{-}C_5H_4)(CO)_3Mn]_2 \qquad (13)$$

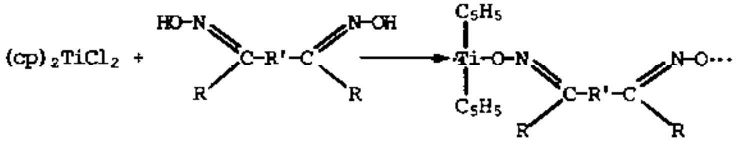
methods [77]. As well, the crystal structure of $[\mu\text{-}(C_2O_4)][(cp)_2Ti]_2\cdot 0.5Et_2O$ has been reported [78].

The synthesis and the structural characterisation of titanium polyoximes derived from $[(cp)_2TiCl_2]$ has been described [79]. Dioximes were selected on the basis of geometrical dissymmetry, potential biological activity, and the potential for extended conjugation through the polyoxime chain. The product yields and chain lengths seem to depend on the electronic character of the oxime, with the product chain length also dependent on polymer solubility. Two polyoxime forms (*22*) and (*23*) can be obtained [79] according to reaction (14) and (15). While the reaction is known to occur almost exclusively only at oxime sites, reaction at amine sites does occur with excess [$(cp)_2TiCl_2$] leading to branched and crosslinked products. In the case of reaction (15), however, branching and crosslinking is precluded.



(14)

(*22*)



(15)

(*23*)

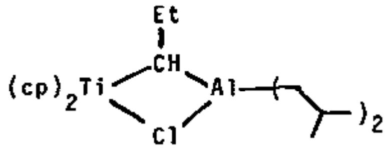
A reaction between diphenyltitanocene and phenyl(pentafluorophenyl)-acetylene in refluxing benzene produces, in 44% yield, 1,1-bis(η^5-cyclopentadienyl)2-phenyl-3-(pentafluorophenyl)benzotitanole [80]. Degradation of the product with $HCl/CHCl_3$ affords titanocene dichloride and Z-1,2-diphenyl-1-(pentafluorophenyl)ethene. Reaction of [$(cp)_2Ti(C_6H_5)_2$] and $C_6H_5C{\equiv}CC_6F_5$ in benzene, under photolysis conditions, results in the exclusive formation of 1,1-bis(η^5-cyclopentadienyl)2,5-diphenyl-3,4-di(pentafluorophenyl)titanole [80]. This latter product was also obtained in 77% yield from a reaction between [$(cp)_2Ti(CO)_2$] and $C_6H_5C{\equiv}CC_6F_5$ in hexane solution. Structural elucidation of these and related metallacycles was accomplished by ^{13}C NMR spectroscopy and from degradation studies [80].

An X-ray analysis of the product of reaction (16) reveals that titanium is tetrahedrally coordinated [81].

$$(cp)_2Ti(ClO_4)_2 + H_2O \xrightarrow{THF} [(cp)_2Ti(H_2O)](ClO_4)_2\cdot 3THF \qquad (16)$$

The methyltriphenylphosphonium hexachlorotitanate(IV) compound, $[MePh_3P][TiCl_6]$, crystallises in the monoclinic space group $P2_1/n$ with $[TiCl_6]^{2-}$ occupying an inversion centre and having a slightly distorted octahedral shape; Ti–Cl distances are 2.33-2.35 Å [82]. A co-precipitation technique was used to prepare the rare earth titanates $Ln_2Ti_2O_7$ (Ln = a rare earth), $Ln_2Ti_2O_5$ and $Ln_2Ti_4O_{11}$ (Ln = La, Nd) from mixtures of titanium salts and rare earth salts in aqueous ammonia solutions at pH 8.5-9.5; the crystal structures of these titanates are also reported [83].

Webster and Wood [84] report that the compound previously thought by R.E. Collin (1969) to be Ti(acac)OCl is really $Sn(acac)Cl_2$ on the basis of X-ray crystallographic and analytical evidence; apparently, the error (1969) resulted from the fact that Sn had been added to the reacting system during the preparation. The synthesis and characterisation of a "long chain" alkylidene-bridged heterobimetallic complex (*24*) has been reported but not isolated; it was identified by spectral measurements [85].



(24)

8.3 PROPERTIES OF Ti COMPOUNDS

The enthalpies of formation of solid $[(cp)_2Ti(O_2CPH)_2]$ and $[(cp)_2Ti(O_2CCF_3)_2]$ are −775.2±8.1 kJ/mol and −2219.0±8.0 kJ/mol, respectively; Ti–O bond energies were estimated to be ∿ 432 kJ for Ti–OOCPh and ∿ 417 kJ for $Ti{-}OOCCF_3$ [86]. Heats of solution of some Lewis acids and bases in acetic anhydride have been determined and the following order of their relative strengths was proposed [87]: $SbCl_5 > SO_3^{2-} > SnCl_4 > TiCl_4 > AsCl_3 \sim$ piperidine > *n*-butylamine > $KOOCCH_3 > NaOOCCH_3$ > α-picoline > quinoline. Heats of neutralisation of these Lewis acids and bases in acetic anhydride suggest that the major enthalpy change in these neutralisation reactions is due to the combination of a proton and the $(CH_3COOCOCH_2)^-$ ion, resulting in the formation of acetic anhydride.

The compound (η-cyclooctatetraene)(η^5-fluorenyl)titanium has been studied by electron paramagnetic resonance in fluid and frozen solutions, and in addition by near-infrared and uv-visible spectroscopy [88].

Spectra and studies on the coordination chemistry of titanium chlorides in some fused salt solvents have been reported [89]. These spectra of titanium(III) and titanium(II) were obtained in $AlCl_3$-KCl melts ($1.00 > X_{AlCl_3} > 0.49$) at temperatures 471-894 °K and in the LiCl-KCl eutectic melt at temperatures 658-1185 °K. Titanium(III) was found to be octahedrally coordinated in pure $AlCl_3$ (liquid and in $AlCl_3$-KCl melts for $X_{AlCl_3} > 0.67$ while octahedral-tetrahedral coordination equilibria seem to be established at lower $AlCl_3$ contents. On the other hand, titanium(II) possesses octahedral coordination at compositions (mole fraction of $AlCl_3$) between 0.51 and 1.00, but a disproportionation equilibrium occurs for $X_{AlCl_3} \cong 0.60$, culminating at $X_{AlCl_3} \cong 0.49$ where titanium(II) is unstable and the spectrum of titanium(III) in an octahedral-tetrahedral coordination equilibrium is observed [89]. In the LiCl-KCl eutectic melt, titanium(III) is also present in an octahedral-tetrahedral coordination equilibrium; however, titanium(II) has octahedral coordination in this melt but a disproportionation equilibrium is established [89]. Electron paramagnetic resonance, Raman, infrared, and visible absorption spectroscopic, as well as magnetic circular dichroism and magnetic susceptibility measurements have been performed on $Cs_3Ti_2Cl_9$ [90]. Infrared and magnetic data proved unambiguously that, for each of the $[TiCl_6]^{3-}$ units, the trigonal field is very large, with ${}^2A_1$ lying about 1500 cm^{-1} (Δ) below ${}^2E$. The lowest lying terms in $[Ti_2Cl_9]^{3-}$ are suggested to be ${}^1A_1$ and ${}^3A_2''$ arising from the exchange interaction between two ${}^2A_1$ states; the energy gap ${}^1A_1' - {}^3A_1''$ is $J = -525$ cm^{-1} [90]. These above values for the trigonal field Δ and J were obtained using a static model, but a discrepancy between the susceptibility data and the model predictions led Briat and co-workers [90] to improve on the theory. They showed that vibronic coupling might be responsible for the observed increase of $|J|$ when temperature is lowered from 298 °K to liquid helium temperature.

Crystals of $LaTiO_3$ and $CeTiO_3$ show metallic resistivity behaviour between 300 and 125 °K ($LaTiO_3$) and at 60 °K for $CeTiO_3$ [91]. Below these temperatures, materials act as semiconductors with activation energies 0.01 eV ($LaTiO_3$) and 0.001 eV ($CeTiO_3$). The susceptibility of $LaTiO_3$ (300-125 °K) is temperature independent, but below this temperature evidence for weak ferromagnetism was found, $\mu_{SAT} = 7 \times 10^{-3}\mu_B$ (4.2 °K). $CeTiO_3$ orders magnetically below 116 °K, but above this temperature, the susceptibility data can be fitted to a Curie-Weiss plus a TIP term yielding $C_m = 0.55$, $\theta_C = 5$, and $X_{TIP} = 850 \times 10^{-6} cm^3/mol$ [91].

Reduction of $Ti(O^iPr)_4$ by $LiAlH_4$ at room temperature gives the mixed valence complex $[Ti_4(O^iPr)_{12}O]$ shown by electron paramagnetic resonance spectroscopy to contain titanium(III) and titanium(IV); the solid exhibits singlet-triplet states arising from interactions between two titanium(III) atoms [92]. The results of a study of the redox reaction between $[Ru(en)_3]^{3+}$

and titanium(III) has provided detailed information on the outer-sphere mechanistic path; the acid dependence of the rate indicates $Ti(OH)^{2+}$ is the reductant species rather than Ti^{3+} [93].

The significance of the absence of chelation in the functioning of salicylate ion as a bridging ligand for electron transfer between ruthenium(III) and titanium(III) has been assessed [94]. It had been suggested previously by Martin and Gould (1976) that chelation of titanium(III) to the bridging ligand occurs prior to electron transfer in reactions between titanium(III) and several salicylato-Co(III) complexes. Recent data by Bose and Earley [94] demonstrate that a different mechanism operates in the reduction of the corresponding (salicylato)pentaammineruthenium(III) complex. The results were interpreted in terms of the mechanism described by reactions (16-19); the first-order rate constant for outer-sphere ruthenium(III)-

$$A_5MSalH^{2+} + Ti^{3+} \xrightleftharpoons[k_{-1}]{k_1} A_5MSalHTi^{5+} \qquad (16)$$

$$A_5MSalHTi^{5+} \xrightleftharpoons[k_{-2}]{k_2} \underset{\text{"ring closure"}}{A_5MSalHTi^{4+} + H^+} \qquad (17)$$

$$A_5MSalHTi^{5+} \xrightarrow{k_3} \text{products} \qquad (18)$$

$$A_5MSalHTi^{4+} \xrightarrow{k_4} \text{products} \qquad (19)$$

titanium(III) electron transfer is $\sim 60\ s^{-1}$ [94]. Bromopentaamminecobalt(III) reacts with $Ti(OH)^{2+}$ ($k_2 = 0.18\ M^{-1}s^{-1}$) while the fluoro analogue reacts with Ti^{3+} with $k_2 = 1 \times 10^{-3} M^{-1}s^{-1}$ [95]. For reactions of $Co(en)_2(H_2O)OH^{2+}$ ions with Ti^{3+}, $k = 50\ M^{-1}s^{-1}$ (*trans*) and $20\ M^{-1}s^{-1}$ (*cis*); for the same oxidants, rate constants for the reaction with $Ti(OH)^{2+}$ are $3 \times 10^3\ M^{-1}s^{-1}$ (*cis*) and $4 \times 10^3\ M^{-1}s^{-1}$ (*trans*). Reactions with rate constants close to $10^3\ M^{-1}s^{-1}$ were interpreted as substitution-limited inner-sphere processes [95]. The Br^- ion is a poor bridging ligand for Co(III)-Ti(III) electron transfer, while OH^- and particularly F^- are efficient bridging ligands; cross bridge interactions are most important for reactions of titanium(III) than for reactions of Co(III) [95].

Absorption and reflectance spectra of *cis*-dihalobis(2,4-pentanedionato)-titanium(IV) complexes and other group IV metals have been measured under water- and alcohol-free conditions [96]. The majority of absorption spectral bands in the uv-visible region arise from π-π^* transitions of the acetylacetonate ligands which are subject to the effect of different degrees of metal-ligand π-electron bonding. Significant π bonding, as is the case for titanium compounds, leads to electron delocalisation over the complex molecule and increases the splitting of the various π-π^* band components [96]. Ligand-to-metal-charge-transfer transitions are likely only for the iodo complexes: however, π-bonded acetylacetonate intermixes ligand-to-metal charge-transfer states into π-π^* excited states, that is particularly effective in titanium(IV) complexes. Halogen ligands are capable of perturbing this mechanism effectively when π-electron delocalisation is large [96].

The complexes Ti(acac)$_2$XY (X = Cl or Br; Y = O^{i}C$_3$H$_7$ or 2,6-(^{i}C$_3$H$_7$)$_2$C$_6$H$_3$O; acac = anion of 2,4-pentanedione) have been characterised by NMR spectroscopy; the diastereotopic probe was placed on the monodentate Y ligand to follow the course of configurational rearrangements in these and analogous complexes [97]. Where Y is isopropoxide, the isopropyl methyl NMR signal remains a sharp doublet down to -63 °C; diastereotopic splitting is observed when Y is 2,6-(^{i}C$_3$H$_7$)$_2$C$_6$H$_3$O. On the basis of earlier work, it appears that rearrangements probably occur via twist processes [97]. The complexes Ti(tibm)$_2$Cl$_2$, Sn(tibm)$_2$Cl$_2$, and Ti(thd)$_2$Cl$_2$ have also been characterised by NMR techniques in dichloromethane and 1,1,2,2-tetrachloroethane solutions; the tibm ligand (anion of 1,1,1-trifluoro-5-methyl-2,4-pentanedione) contains a diastereotopic probe [98]. These complexes, which contain unsymmetrical AB bidentate ligands, adopt the three *cis*-X$_2$ diastereomeric configurations. Terminal group exchange in the bidentate ligands occurs in parallel with inversion of the molecular configuration; these changes are described by an averaging set A_6''' which was shown earlier to scramble the terminal groups and the -CH= protons of the diketonate ligand amongst all possible non-equivalent sites of the *cis*-X$_2$ diastereomers, and in addition leads to Λ-Δ interconversion. Here also the rearrangements occur via twist processes [98].

A ^{13}C and ^{19}F NMR study of difluorobis(1,1,1-trifluoro-4-(2'-thienyl)-butane-2,4-dionato)titanium(IV) has been carried out in CDCl$_3$ and CD$_3$CN [99]. A value of μ of 8.36 D indicates a *cis* structure. In CD$_3$CN, the carbonyl carbon at 182.5 ppm showed splitting indicating a non-rigid *cis* structure in solution; at room temperature the process appears to involve R group exchange.

Proton and fluorine NMR spectra of methoxypentafluorophenyltitanocene complexes indicate a possible coupling between the methyl protons of the methoxy group and the two *ortho* fluorine atoms of the pentafluorophenyl ligand [100]. Also, anisochrony of the two *ortho* and the two *meta* fluorine atoms has been detected in some cases [100].

The character of experimental absorption spectral bands and several calculated parameters have been compared for complexes of titanium(IV) with the phenolic ligands, chromotropic acid, α-naphthol, β-naphthol, 1-hydroxy-2-naphthoic acid, 2-hydroxy-3-naphthoic acid, 2-hydroxy-1-naphthoic aldehyde, pyrocatechol, and salicylic acid [101]. Complexes of titanium(III) with several hydroxy and polymeric acids have been studied by EPR techniques; formation of polynuclear complexes with various multiplet states has been proposed to account for the unusual spectra when the acid is mandelic acid [102]. EPR methods have also been employed to study the oxidation reaction of the Ti(III)-EDTA system with hypochlorous acid in the presence of maleic acid [103]. Formation of OH radicals was noted in the single electron oxidation reaction of this system.

Infrared spectra of the products obtained from the interaction of $TiCl_4$ with acetone, methyl ethyl ketone, acetophenone, benzophenone, diethyl ether, and tetrahydrofuran have been obtained and assignment of absorption bands in the spectral regions 475-450, 411-402, and 390-385 cm^{-1} to Ti-Cl stretching modes carried out [104]. The first two bands belong to the adduct $TiCl_4 \cdot D$ and the third band to $TiCl_4 \cdot 2D$. An increase in the donor content displaces the equilibrium towards formation of the $TiCl_4 \cdot 2D$ adduct.

Oxidising properties of $[TiCl_3 \cdot 3L]^+$ show a linear dependence on the sum of Taft constants of functional groups of L; L is pentyl chloroacetate, butyl formate, isopropyl formate, ethyl acetate, butyl acetate, isopentyl acetate, isopropyl acetate, ethyl isovalerate, pentyl propionate, and ethyl capronate [105]. Acid dissociation constants of HSO_4^- at 25 °C have been determined as a function of ionic strength to calculate the compositions and stability constants of titanium(IV) complexes [106]. For example, values of β_1 for $Ti(OH)(SO_4)^+$ decrease from 19.0±1.0 at an ionic strength of 0.6 to 3.4±0.2 at an ionic strength of 3.30. The mechanism and the thermodynamic factors influencing the reactions of coordinated peroxide complex $Ti^{IV}(O_2^-)$ with the reducing agent titanium(III) and with OH radicals have been analysed theoretically, based on new and published kinetic data [107].

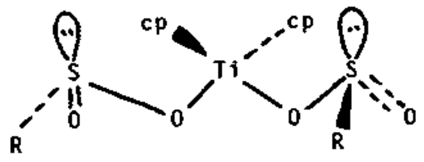
Adsorption of Rh^{3+}-chloride complexes on hydrated TiO_2 and ZrO_2 from dilute solutions reveals that the kinetics and the equilibrium of sorption depend on the concentration of Rh^{3+} in the solutions, on ageing of solutions, and on the nature and concentration of the supporting electrolyte [108]. Aquation of Rh^{3+} complexes retards adsorption; chloride complexes are believed to be sorbed by an ion-exchange mechanism. The adsorbed Rh^{3+} complexes undergo aquation in the sorbent phase.

The X-ray emission of the $K_{\beta 2.5}$- and L_α-bands of titanium have been studied in the nitrides $TiN_{0.8}$, $TiN_{0.9}$, and $TiN_{1.0}$ along with the $K_{\beta 2.5}$- and

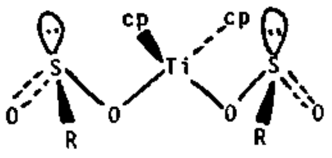
Lα-bands of titanium and Kα-bands of carbon in the carbides $TiC_{0.6}$, $TiC_{0.8}$, and $TiC_{0.95}$ as well as the X-ray photoelectron spectra of base levels of carbides and nitrides and the photoelectron spectrum of the $TiC_{0.6}$ valence zone [109]. The energy bond of the Ti $2p_{3/2}$-level in carbides is greater than in pure titanium, and the energy of the s-level bond of C in carbides is lower than in graphite. This indicates an increase in electron delocalisation in the C atom and a decrease in the Ti atom sphere in carbides in comparison to the charges in the initial titanium and graphite. A similar situation is observed for $TiN_{0.9}$. The carbides and nitrides of titanium possess an ionic component of the bond, but its value would presumably not be great owing to the low value of transferred charge. The specific surface of titanium nitride, prepared by evaporating Ti particles in a high temperature plasma, can be altered by varying the conditions of quenching of the reaction products [110]. With an increase in the specific surface of titanium nitride, the temperature for the start of oxidation is reduced and the amount of adsorbed oxygen is increased with contact with air.

8.4 CHEMICAL REACTIONS OF Ti COMPOUNDS

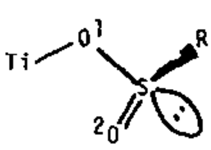
Reaction of $[(cp)_2TiCl_2]$ with 1 or 2 molar equivalent of $LiN(SiMe_3)_2$ yields $[(cp)_2Ti(CH_2SiMe_2NSiMe_3)]$ [111]. Both $[(cp)TiCl_3]$ and $[(cp)TiClO]_4$ react with dilute HNO_3 to give $[(cp)Ti(NO_3)_3]$ via the monocyclopentadienyltitanium(IV) aqua complexes [112]. Tetrabenzyltitanium and its dicyclohexylamine adduct react with CO to form acylbenzyltitanium compounds; infrared spectra reveal $[(PhCH_2)_4Ti(CO)_2]$ and $[(PhCH_2)_4Ti(CO)(amine)]$ as potential intermediates [113]. Interestingly, CO inserts exclusively into the $Ti-CH_3$ bond of $[(cp)_2Ti(C_6F_5)CH_3]$ while cyclohexylcyanide inserts only into the $Ti-C_6F_5$ bond to give $[(cp)_2Ti\{CN(C_6H_{11})C_6F_5\}CH_3]$ [114]. This represents the first example of an insertion reaction into a transition meta-perfluorocarbon ligand bond. However, starting with the non-fluorinated compound $[(cp)_2Ti(C_6H_5)CH_3]$ one obtains only $[(cp)_2Ti\{CN(C_6H_{11})C_6H_5\}CH_3]$ [114]. Insertion of SO_2 into two Ti-C bonds of $[(cp)_2TiR_2]$ complexes gives a mixture of the two diastereomeric forms of the disulphinates $[(cp)_2Ti(SO_2R)_2]$ [115]. In the case of the *meso* form, inversion of one chiral S transforms this *meso* form to racemise, and *vice-versa*. The cyclopentadienyl groups are diastereotopic and the R groups are enantiotopic in the *meso* disulphinate compounds, whereas for the enantiomers of the racemic mixture (E + E') both cp and R groups are equivalent [115]. The E *meso* isomerisation results from rocking of SO_2R groups on the Ti atom. This can occur in two ways as indicated in reactions (20) and (21).



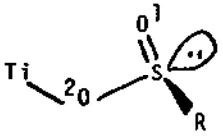
(25; E or E')



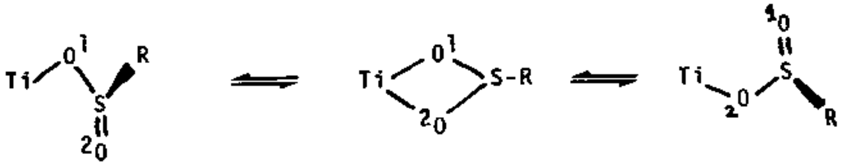
(26; *meso*)



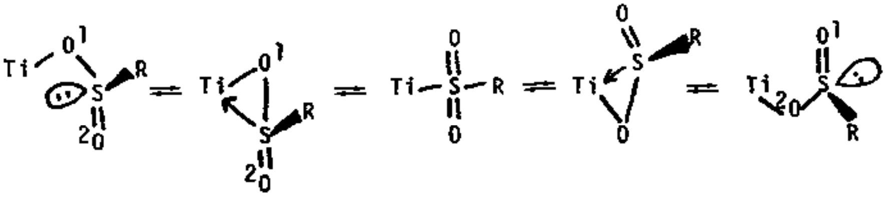
(27)



(28)

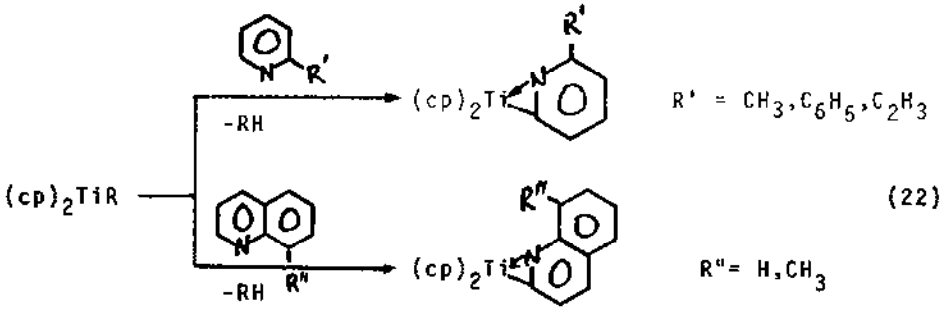


(20)

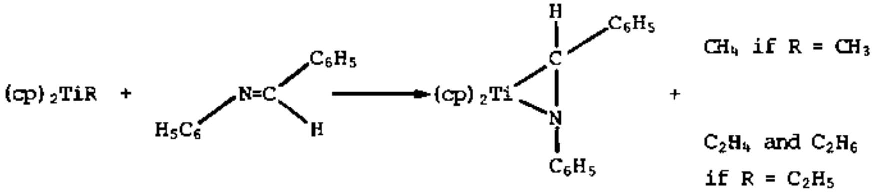


(21)

Reaction of [(cp)$_2$TiR] (R = alkyl) with 2-substituted-pyridines and with quinolines leads to α-metallation of these ligands with formation of triangular titanocycles containing titanium(III) (reaction 22) [116]. Evidence of the metallation at the α-position is afforded by reactions of the titanocycles with iodine and D_2O/DCl which yield the corresponding iodo- and deutero-pyridine and -quinoline derivatives. Reaction of [(cp)$_2$TiR] with the structually related ligand benzalaniline leads to a side-on coordinated benzalaniline complex of titanocene (reaction 23) [116]. Reactions of the



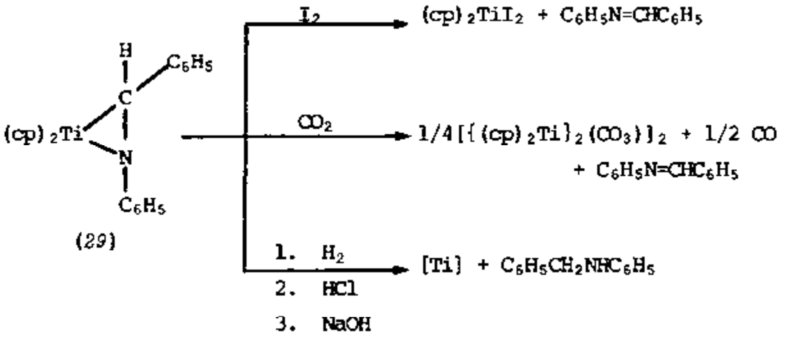
(22)



(29)

(23)

diamagnetic complex (*29*) formed from reaction (23) with iodine, CO_2 and H_2 are described in reactions (24), (25), and (26), respectively.



(24)

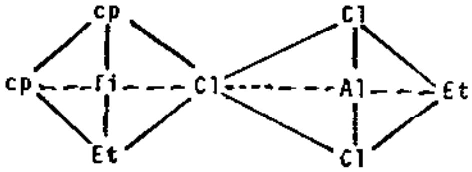
(25)

(26)

The dititanium compound $[(C_8H_8TiCl\cdot THF)_2]$ reacts with acetylenes RC CR', where R = R' = Ph, R = R' = p-tolyl, R = Ph and R' = Me, ^{i}PrMgCl, to give the binuclear complexes $[C_8H_8TiRC{\equiv}CR']_2$ [117]. Infrared, NMR, and mass spectral data are reported. Thermal heating of these acetylenic binuclear compounds produces $[C_8H_8TiC_4{-}R_2R'_2]$. $[(cp)_2M(SH)_2]$ (M = Ti or Zr) react to form $[(cp)_2MS]$ when treated with mono- and di-sulphur transfer agents; treatment of $[(cp)_2TiCl_2]$ with Li_2S_2 gave $[(cp)_2TiS_5]$ in better yields [118]. The interaction of t-butylisocyanide with $[(cp)_2TiMe_2]$ leads to insertion products in which methyl groups are transferred to the isocyanide ligand [119].

Heterometallic coordination polymers containing alternating Ni and Ti metal ions have been synthesised by the reaction of titanium(IV) isopropoxide with Ni(II) bis-chelates of some *ortho*-hydroxyoximes [120]. Dinitrogen compounds of poly {1-[4-(chlorodicyclopentadienyltitanio)phenyl]ethylene-co-1-(4-bromophenyl)ethylene-co-1-phenylethylene} have been synthesised [121]. An equilibrium exists between the mononuclear and binuclear species. Yields of NH_3, formed after hydrolysis of the reaction mixtures resulting from the above poly compounds and lithium naphthalide in a nitrogen atmosphere, increase dramatically with decreasing content of titanocene in the polymer [121].

The most rapid reaction in the soluble Ziegler catalyst system $(cp)_2TiEtCl/AlEtCl_2$ is the formation of the primary complex equilibrium [122]. Kinetic data and thermodynamic data for this equilibrium were obtained via ^{13}C NMR and quantitative lineshape analyses. Formation of the primary complex is a diffusion-controlled process 10^{10}-10^{11} $M^{-1}s^{-1}$ at 240 °K, the equilibrium constant is $5 \times 10^3\ M^{-1} < K < 5 \times 10^4\ M^{-1}$. The aluminium isotherm proved to be Al/Ti = 1:1 [122]. Elementary processes of the soluble Ziegler catalysts of the type $(cp)_2TiRCl/AlEt_nCl_m$ have also been investigated by ^{13}C NMR spectrsocopy [123]. Using ^{13}C enriched CH_2CH_2 in the NMR experiment it was possible (for the first time) to directly follow the reacting and polymerising system. There appears to be no pre-coordination of the monomer on the primary complexes and insertion occurs unambiguously in the Ti-C bond [123]. The following systems were studied in toluene-d_8 solutions:
$(cp)_2TiEtCl/AlEtCl_2/^{13}C_2H_4$, $(cp)_2TiCl/AlEt_3/^{13}C_2H_4$, and
$(cp)_2TiMeCl/AlEtCl_2/^{13}C_2H_4$ [123].



(30)

Nitric oxide rapidly oxidises dicyclopentadienyltitanium(III) complexes according to reactions (27-29) [124]. Reaction (29) is complicated by formation of small amounts of the NCO complex; for example, $[(cp)_2Ti(CO)_2]$ and NO react in toluene to give $[(cp)_2TiNCO]$ and $[(cp)_2TiO]_n$ with traces of $(cp)_2Ti(III)$ products. EPR, infrared, and product analysis suggest that

$$[(cp)_2TiCl]_2 + 2\ NO \longrightarrow [(cp)_2TiCl]_2O + N_2O \qquad (27)$$

$$2\ (cp)_2TiNCO + 2\ NO \longrightarrow [(cp)_2TiNCO]_2O + N_2O \qquad (28)$$

$$[\{(cp)_2Ti\}_4(CO_3)_2] + 4\ NO \longrightarrow 4\ [(cp)_2TiO]_n + 2N_2O + 2CO_2 \qquad (29)$$

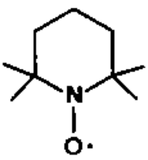
$[(cp)_2Ti(CO)_2]$ and NO initially give an equilibrium between $[(cp)_2Ti(CO)NO]$ and $[(cp)_2TiNO]$; a subsequent oxygen abstraction from $[(cp)_2TiNO]$ gives $[(cp)_2TiNCO]$ [124]. The moiety $(cp)_2Ti$ reacts with excess NO to yield $[(cp)_2TiNO]$ which appears to contain titanium(IV) and bridging N_2O_2, and bridging and non-bridging cp ligands.

Bis(η^4-1,4-cyclopentadiene)nickel(0), $Ni(COD)_2$, reacts with $[(cp)Fe(CO)_2Cl]$, $[(\eta^3\text{-}C_5H_5)Fe(CO)_3Cl]$, $[Mn(CO)_5Cl]$, and $[MnP(OMe)_3(CO)_4]_2$ to give metal-metal bonded coupling products [125]. Partial reduction with $Ni(COD)_2$ was observed with $Ti(acac)_2Cl_2$ (acac = anion of 2,4-pentanedione) and $[(cp)_2TiCl_2]$ which gave $[Ti(acac)_2Cl]_2$ and $[(cp)Ti(py)Cl]$, respectively, in pyridine [125]. Phosphine oxides, with at least one aryl-phosphorus bond, are reduced to the corresponding phosphines by stoichiometric amounts of $Mg/(cp)_2TiCl_2$ in boiling THF [126]. Titanocene dichloride is reduced by Mn powder in some 1,2-dialkoxyethanes at room temperature; the reduction times are much shorter under N_2 than under argon [127]. The effect arises because nitrogen stabilises the reduced species $[(cp)_2TiCl]$ by occupying the fourth coordination site; reduction under an atmosphere of CO was also reported [127]. The reduction of EDTA-Co(III) by titanium(III) species indicates that reduction proceeds via an outer-sphere mechanism [128]. The possibility of the thiocyanate ion as a bridging ligand in the reduction of ruthenium(III) by titanium(III) and by [N-(hydroxyethyl)ethylenediaminetriacetato]titanium(III), Ti(HEDTA), has been reported by Lee and Earley [129]. Titanium(III) reduces $Ru(NH_3)_5NCS^{2+}$ with a second order rate constant of 840 $M^{-1}s^{-1}$ in 2M LiCl; the activation parameters are $\Delta H^{\neq}$ = 35 kJ/mol and $\Delta S^{\neq}$ = 70 J.mol. The Ti(HEDTA) complex reduces the same oxidant, $Ru(NH_3)_5NCS^{2+}$, with $k = 2.8 \times 10^4\ M^{-1}s^{-1}$ (25 °C and 2M LiCl) [129]. Comparison of the results with previously available data led Lee and Earley to conclude that both reactions involve an inner-sphere electron transfer process, that NCS^- is more efficient as a bridging ligand in these redox processes than in Co(III)-Cr(II) systems, and that titanium(III) is less sensitive to labilisation by amino acid ligands than are Ru(III) and Cr(III). The oxalate ion is an efficient bridging ligand for electron transfer between transition metal ions; however, the detailed mechanism of the electron transfer step seems to depend on which metal ions are involved. The results of a recent study of the influence of oxalate ion as a non-bridging ligand on the rate of Co(III)-Ti(III) electron transfer reactions, which also involve oxalate as a bridging ligand, have been reported [130].

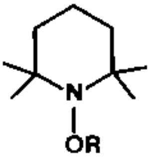
Formation of V(III)-Ti(IV) and Ti(III)-Ti(IV) binuclear complexes in the cross-reaction of Ti(HEDTA) and $VO(HEDTA)^-$ has been noted by Kristine and Shepherd [131]. It appears that a twist mechanism or a dissociative process involving rupture of a carboxylatotitanium(III) bond in $Ti(HEDTA)(H_2O)$ limits the rate of oxidation of this complex by $VO(HEDTA)^-$. Electron transfer occurs via outer sphere, and subsequent to electron transfer a substitution reaction occurs giving a binuclear species containing Ti(IV) and V(III) [131]. The limiting redox process was found to be first order in $[Ti(HEDTA)(H_2O)$ alone with $k_{obs} = 73.6 \pm 5.0\ s^{-1}$ at an ionic strength of 0.50 M (NaCl), pH = 5.0, acetate buffer, and a temperature of 25.2 °C. Relaxation studies indicate [131] a ring opening of a glycinato fragment of the $HEDTA^{3-}$ ligand for $Ti(HEDTA)(H_2O)(OH)^-$ which proceeds by an inverse H^+ pathway ($k_1 = 1.92 \times 10^{-4}\ M^{-1}s^{-1}$) and by reverse ring closure ($k_0 = 6.2\ s^{-1}$). The magnitude of the kinetic parameters support a proton-scavenging pathway involving a monohydroxy-bridged, strained intermediate with a rate-limiting bond-breaking process of $0.33\ s^{-1}$. Formation of the new Ti(III)Ti(IV) binuclear complex occurs with a $k = 3.12 \pm 0.42 \times 10^2\ M^{-1}s^{-1}$ and competes with the dominant outer-sphere cross reaction involving $Ti(HEDTA)(H_2O)$ and $VO(HEDTA)^-$. This new species has a spectral band at ∿ 800 nm ($\varepsilon = 47\ M^{-1}cm^{-1}$); the identical $Ti(III)Ti(IV)(HEDTA)_2$ complex can be prepared by autooxidation of $Ti(HEDTA)(H_2O)$. The redox-active isomer of $Ti(HEDTA)(H_2O)$ can be produced through a first order process ($k \sim 0.14\ s^{-1}$) above pH 4.0 (at pH 4.0, the Ti(III)Ti(IV) ion is thermodynamically unstable) by dissociation of Ti(III)Ti(IV). The initial products of the $Ti(HEDTA)(H_2O)/VO(HEDTA)^-$ cross reaction are $TiO(HEDTA)^-$ and $V(HEDTA)(H_2O)$, which subsequently can combine ($k \sim 23\ M^{-1}s^{-1}$) to yield a third binuclear species $Ti(IV)V(III)(HEDTA)_2$ having a charge-transfer spectral band at 453 nm ($\varepsilon \sim 380\ M^{-1}cm^{-1}$). A binuclear complex containing the reverse oxidation states Ti(III)-V(IV) has been detected competitively early in the cross reaction ($k \sim 1.23 \times 10^4\ M^{-1}s^{-1}$); however, this species is not the precursor complex to the $Ti(IV)V(III)(HEDTA)_2$ complex [131]. In fact, the Ti(III)-V(IV) is non-productive for inner-sphere electron transfer.

In a subsequent paper, Shepherd and co-workers [132] report on the structural nature of $TiO(EDTA)^{2-}$ in solution and on the reaction of $TiO(EDTA)^{2-}$ with H_2O_2 in the pH range 2.0-5.2 that gives $Ti(O_2)(EDTA)^{2-}$. The former oxo complex exists as an equilibrium mixture of at least six isomeric and protolytic forms which vary in whether a water molecule is bonded or whether the EDTA ligand occupies five coordination positions at titanium(IV). Two distinctly different primary coordination spheres in terms of spectral properties and reactivities toward H_2O_2 were observed for $TiO(EDTA)^{2-}$ solution in the above pH range [132]. These are the aquated forms (A), $TiO(EDTAH_n)(H_2O)^{n-2}$, having two carboxylates and two ethylenediamine nitrogen atoms of the EDTA ligand and one coordinated water molecule, and the fully chelated (B) forms, $TiO(EDTAH_n)^{n-2}$, with three carboxylates and two ethylenediamine nitrogens of EDTA attached to titanium(IV). The displacement of the oxo ligand by peroxo is first order in $[H_2O_2]$ and $[TiO(EDTA)^{2-}]$; $k_A = 5.25 \pm 0.25 \times 10^6\ M^{-1}s^{-1}$ for the A forms which have a $[H_3O^+]^{1.0}$ dependence, but the B forms have only an acid-independent path, $k_B = 49 \pm 5\ M^{-1}s^{-1}$ at 25 °C. The mechanism has been interpreted [132] to be the associative displacement of oxo by peroxo in which the available pendant functional groups assist the reorganisation of the titanium(IV) coordination sphere. The formation of $Ti(O_2)(EDTA)^{2-}$ by the reaction of O_2 with $Ti(EDTA)(H_2O)^-$ has been examined; substitution and intramolecular electron transfer occur by an H^+-independent path [132]. In addition, the superoxo transient $Ti(O_2)(EDTA)^-$ is rapidly scavenged by $Ti(EDTA)(H_2O)^-$ ($k \sim 10^6\ M^{-1}s^{-1}$), via presumably an outer-sphere process. A comparison has also been made for the reduction of O_2^- and O_2^{2-} coordinated to Co(III) and Ti(IV) by one-electron reductants and the affinities of the O_2^{3-} or O_2H^{2-} radical toward these centres [132].

$MeTiCl_3$ reacts with the compounds (*31*) and (*32*) (where R is $TiCl_3$ and Me) to give a 1:2 $MeTiCl_3$-(*31*) complex which initially forms and decomposes in the rate-determining step to yield Me radicals; these in turn react with the complex and with the reactants and solvent [133]. The mechanism of complex formation of titanium with disulphophenylfluorene (A) and N-cetypyridinium chloride (B) giving the complex TiA_2B_4 has been elucidated [134].



(31)



(32)

8.5 ELECTROCHEMICAL STUDIES

A few electrochemical studies of titanium compounds have been reported. These include a one-electron study of $[(cp)_2TiCl_2]$ in various solvents by polarography and voltammetry [135], as well as the electrochemical oxidation of [(cp)$_2$TiClL] (L = tetrahydrofuran, dimethylphenylphosphine) by voltammetry and controlled potential electrolysis [136]. A one-electron reduction of [(cp)$_2$TiCl$_2$] in tetrahydrofuran has been examined in detail and found to be reversible; this contradicts an earlier report [137]. A study of [(cp)$_2$TiCl$_2$] in 0.8:1 molar ratio of AlCl$_3$-butylpyridinium chloride melt reveals a reversible one-electron reduction of the cation in a process dependent upon chloride concentration [138]. Half-wave potentials as well as the equilibrium constant for reaction (30) have been determined [139]. A

$$[TiCl_6]^{3-} + AlOCl_2^- \rightleftharpoons AlCl_4^- + [TiOCl_4]^{2-} \qquad (30)$$

potentiometric and spectroscopic study of the reaction between fluorescein isothiocyanate with an amine, chemically bound to a titanium electrode, has been reported [140].

$TiCl_4$ gives four polarographic reduction waves with equal height in dimethylsulphoxide solutions containing Et_4ClO_4 [141]. The limiting current of each wave is diffusion-controlled and proportional to the concentration of $TiCl_4$; controlled potential coulometry at a potential on the plateau of the fourth wave shows an uptake of four electrons per molecule. These four reduction waves were attributed to reduction of Ti(IV) to Ti(III), Ti(II), Ti(I), and Ti(0) [141].

8.6 PHOTO-ELECTROLYSIS

Titania, anatase, or simply, TiO_2 powder as well as other titanium oxide species have been used extensively in photocatalytic systems. Mercury lamp irradiation of TiO_2 powders mixed with RuO_2 leads to the continuous production of H_2 and O_2 from gaseous H_2O at room temperature; the rate of evolution of H_2 per 100 mg TiO_2/RuO_2 and 20 hours is 11 μmols at a steady state [142]. A mechanism of water decomposition on TiO_2 was proposed from the dependence of the reactivity on the surface treatments. The photochemical decomposition of hydrocarbons in oxygen-containing solutions at platinised-TiO_2 yields predominantly CO_2 as the reaction product along with the intermediate production of hydroxylated compounds [143]. A mechanism has also been proposed for the reaction based on the photo-regeneration of OH radicals at the TiO_2 surface [143].

Irradiation of aqueous-ethanolic solutions of titanium(IV) with light of $\lambda < 310$ nm yields Ti(III) and hydrogen [144]. The initial rate of formation of Ti(III) during the first 3 hours of photolysis is 2.5×10^{-5} mol/hour and is 100 times greater than the rate of hydrogen formation. Use of C_2D_5OH indicates that the composition of the hydrogen produced is ∿ 50% H_2 and ∿ 50% HD.

Experiments by Sato and White [145] demonstrate that the decomposition of water is catalytic at 23 °C when a platinised powdered TiO_2 catalyst, illuminated with band-gap radiation, is used. The reaction of gas-phase H_2O with active C over illuminated platinised TiO_2 has also been studied at room temperature and 60 °C [146]. The products are H_2, CO_2, and a small amount of O_2. As the reaction proceeds, the rate of product formation decreases because of an accumulation of H_2 and the loss of good contact between the catalyst and carbon; the reaction is zero-order in P(water) and the activation energy is ∿ 5 kcal/mol [146]. The qualitative wavelength dependence of the reaction rate shows an onset a little shorter than observed in the water-gas shift reaction and the H_2O decomposition reaction over the same catalyst. At room temperature, the quantum efficiency is ∿ 2% at the beginning of reaction; when the reaction is carried out in liquid water, the oxidation of C is inhibited and O_2 and H_2 are evolved [146]. Photocatalytic decomposition of water vapour over platinised TiO_2 also takes place when the catalyst is coated with NaOH (∿ 7 wt %) [147]. The quantum efficiency reaches ∿ 7% (20 μmol H_2/hour) at the beginning of the reaction but decreases with accumulation of products owing to thermal back reaction over Pt. This effect of back reaction can be reduced by increasing NaOH loading. Photocatalytic activity of platinised TiO_2 for the water-gas shift reaction increases with increasing NaOH coating and rates of such catalysed reaction are independent of temperature in the range 18-50 °C, but are pH-dependent [147]. Reaction kinetics for the catalysed interaction of gas-phase water with carbon monoxide over platinised TiO_2 under ultraviolet irradiation have been examined from 0 to 60 °C [148]. At 25 °C, the reaction is zero-order in [CO] and $[H_2O]$ when $P(CO) > 0.3$ torr and $P(H_2O) > 5$ torr; activation energy is > 7.5 kcal/mol and the quantum efficiency is ∿ 0.5%. When TiO_2 and H_2, or CO, is placed in an ambient of gas-phase water and illuminated with band-gap radiation, H_2 is evolved [149]. Addition of small amounts of O_2 retards completely this reaction. At temperatures > 200 °C, a dark reaction between reduced TiO_2 and H_2O to produce H_2 also occurs. These results indicate that H_2 evolution is not the result of catalytic H_2O photolysis, but a photo-assisted reaction of H_2O with O_2 vacancies produced by the reduction [149].

A transparent TiO_2 colloidal solution (particle radius ∿ 200 A) can be produced by hydrolysis of titanium tetraisopropoxide in acidic aqueous solutions [150]. When simultaneously loaded with ultrafine Pt and RuO_2 deposits, these particles display an extremely high activity as H_2O

decomposition catalysts. Band-gap excitation of the TiO_2 generates H_2 with a quantum yield ∿ 30±10% with O_2 produced in stoichiometric amounts [150]. If either $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) or rhodamine B are used as sensitisers, H_2O is decomposed by visible light. Addition of methyl viologen (MV^{2+}) increases H_2 yields significantly. Laser photolysis experiments were performed with the $[Ru(bpy)_3]^{2+}/MV^{2+}$ system and reveal the high rate and specificity of the catalytic reactions leading to H_2 and O_2 production from H_2O [150]. Sustained cleavage of water by four quanta of visible light has been achieved in aqueous solutions by Graetzel and co-workers [151,152] using a bifunctional redox catalyst composed of Pt and RuO_2 co-supported on colloidal TiO_2 particles. A photochemical model system containing $[Ru(bpy)_3]^{2+}$ as a sensitiser and MV^{2+} as an electron relay species has been used to test the effect of catalyst composition, sensitiser, concentration, pH and temperature on the efficiency of light-induced H_2O decomposition [151]. An electron relay-free system also exhibits high photoactivity [152], and direct band-gap irradiation by ultraviolet light leads to efficient H_2O cleavage in the absence of sensitiser and relay [151]. Amphiphilic surfactant derivatives of $[Ru(bpy)_3]^{2+}$ also exhibit an extremely high activity in promoting the water cleavage process [152]. Adsorption of the sensitiser on TiO_2 particles - water interface, and electron ejection into the TiO_2 conduction band (cb) were evoked (see reactions 31-33) to explain the observations [152].

$$(TiO_2/RuO_2) \xrightarrow{h\nu} {}^*(TiO_2/RuO_2) \longrightarrow (TiO_2/RuO_2)^+ + e^-_{cb} \qquad (31)$$

$$(TiO_2/RuO_2)^+ + H_2O \longrightarrow 2H^+ + 1/2\ O_2 \qquad (32)$$

$$e^-_{cb} \xrightarrow[\text{surface}]{\text{Pt}} (Pt;e^-)_{surface} \xrightarrow{H_2O} 1/2\ H_2 + OH^- \qquad (33)$$

Irradiation of a TiO_2 suspension (grain size < 0.06 mm, 3-15 mg/ml) in acidic solutions containing 10^{-3} M Ce^{4+} leads to enhanced evolution of oxygen [153], with the yield of O_2 dependent on the amount of TiO_2 in the suspension and on temperature. A suspension of TiO_2 (band gap ∿ 3.1 eV, λ < 400 nm) in dilute H_2SO_4 leads to H_2 and O_2 evolution in the ratio 2:1. In both systems, TiO_2 apparently acts as an efficient electron donor [153]. Reaction mechanisms (34 to 42) for the two systems have been proposed by Vonach and Getoff [153]. Reaction (36) can occur according to reactions (36 a-d) where H_2O^+ transients are presumably formed on the particle surface where $OH^\cdot$ radicals are also oxidised. An increase in temperature yields more oxygen in this above system. It was also found that at the higher temperature

$$TiO_2 \xrightarrow[\lambda > 360\ nm]{h\nu} TiO_2^* \longrightarrow (TiO_2^+, e^-)_{surface} \quad (34)$$

$$(TiO_2^+, e^-)_{surface} + Ce^{4+} \longrightarrow TiO_2^+ + Ce^{3+} \quad (35)$$

$$4\ TiO_2^+ + 2\ H_2O \longrightarrow 4\ TiO_2 + 4\ H^+ + 2\ O_2 \quad (36)$$

$$H_2O + TiO_2^+ \longrightarrow TiO_2 + H_2O^+ \quad (36a)$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\cdot \quad (36b)$$

$$OH^\cdot + TiO_2^+ \longrightarrow TiO_2 + H^+ + O \quad (36c)$$

$$2\ O \longrightarrow O_2\ \text{(very fast)} \quad (36d)$$

(60 °C) the oxygen evolution process is photocatalytic and thermochemical, but at the lower temperatures (10 °C) the photocatalytic process is predominant [153]. For the H_2SO_4/H_2O aqueous system, the H_2 and O_2 yields increase with increase in H_2SO_4 concentration, and the mechanism was described [153] as beginning with reaction (34) above, followed by reactions (37–39) with oxygen evolution as shown in reaction (36). Without TiO_2 in this second system,

$$(TiO_2^+, e^-) + H^+_{aq} \longrightarrow H + TiO_2^+ \quad (37)$$

$$H + H \longrightarrow H_2;\quad k = 1.15 \times 10^{10}\ M^{-1}s^{-1} \quad (38)$$

$$H + H_2O \longrightarrow H_2 + OH^\cdot;\quad k = 10\ M^{-1}s^{-1} \quad (39)$$

very little H_2 and O_2 is produced because of direct photolysis of H_2SO_4 through reactions (40–42) which can be suppressed using light of $\lambda > 350$ nm.

$$SO_4^{2-} \xrightarrow{h\nu} {}^*SO_4^{2-} \longrightarrow SO_4^{-\cdot} + e^-_{aq} \quad (40)$$

$$e^-_{aq} + H^+_{aq} \longrightarrow H;\quad k = 2.3 \times 10^{10}\ M^{-1}s^{-1} \quad (41)$$

$$2\ SO_4^{-\cdot} \longrightarrow S_2O_8^{2-} \quad (42)$$

TiO_2-supported noble metal catalysts such as Pt-, Pd-, and Rh-TiO_2 are much more active for the NO-CO reaction in the presence or absence of H_2O, H_2, and O_2 than the corresponding Al_2O_3 or other supported catalysts [154]. They are effective even in an oxidative gas composition range for the NO-CO-(H_2O)-H_2-O_2 reaction producing no ammonia. Comparison of the catalytic activity and properties of Pt-TiO_2 with those of other supported catalyst suggests that the higher activity of the TiO_2-supported catalysts could be attributed to their ability to activate NO molecules by dissociative adsorption at lower temperatures [154].

The heterogeneous photocatalytic decomposition of benzoic acid and adipic acid on platinised TiO_2 powder has been investigated by Bard and co-workers [155]; the photo-Kolbe decarboxylative route to the breakdown of the benzene ring and to the production of butane were followed.

Measurement of photocurrent *versus* TiO_2 electrode potentials at different electrolyte pH shows that the quantum efficiency for H_2O photo-oxidation is pH-dependent [156]. The results were interpreted in terms of surface OH^- groups and physisorbed OH^- ions acting as intermediates in a double mechanism of hole trapping and charge transfer at the semiconductor/electrolyte interface. The experimental data were analysed according to Wilson's model for electrochemical behaviour of semiconducting photoexcited electrodes that introduce as new parameters, surface electron transfer and surface recombination rates. Mechanisms of charge transfer were described to explain generation of photocurrents on absorption of uv light by TiO_2, with the preferred mechanism being one in which surface OH^- groups and Ti^{3+} ions act as hole traps and donor centres, respectively [156].

The solid state photogalvanic cells involving photochemically deposited metals as active materials have been reported [157]. As these cells possess many excellent features as compared with the usual photogalvanic cells in which both cathodic and anodic materials are dissolved in solutions, they provide a novel storage system for the conversion of solar energy to electrical energy. A typical two compartment cell [TiO_2, aqueous $Ce(SO_4)_2$-$Ce_2(SO_4)_3$//aqueous $AgNO_3$,Pt] could be charged by irradiation of 300-400 nm light on TiO_2 [157].

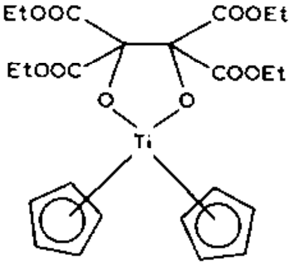
The photosensitisation of $SrTiO_3$ and $BaTiO_3$ anodes under DC conditions affords little improvement in the photo-electrolysis of water [158].

The electronic structure and catalytic activity of cobalt-tetraphenylporphyrin supported on TiO_2 have been studied; this system shows a remarkable activity for H_2-reduction of NO to N_2O at 50 °C [159]. Titanium(II) porphyrin intermediates and dioxygen are generated by photolysis of peroxotitanium(IV)-tetraphenylporphyrin; the observed photo-oxidative behaviour suggests the oxygen to have singlet character [160]. Spectral sensitisation by magnesium tetraphenylporphine (MgTPP) films on $SrTiO_3$ electrodes using hydroquinone as a reductant has been reported [161]. The action spectra reflect the absorption spectra of MgTPP films which show both anodic and cathodic photocurrents depending on the applied potential. An influence of the structure of the MgTPP films on the photocurrents has also been observed [161].

A successful and reproducible manufacturing method for TiO_2 film for photoelectrochemical cell anodes has been described, and the properties and spectral response of the cell along with hydrogen evolution have been studied [162].

8.7 Ti COMPOUNDS IN ORGANIC REACTIONS

Oxidative addition reaction of $[(cp)_2Ti(CO)_2]$ with two equivalents of $OC(CO_2Et)_2$ leads to loss of the two CO groups and formation of the symmetrical metallacycle (*33*) the nature of which was ascertained by NMR and confirmed by an X-ray structural analysis [163]. The chelate ring has a *gauche* conformation, the C atoms being displaced by 0.18 A on opposite sides from the Ti-O-O' plane. $(p\text{-}Me\text{-}C_6H_4N)_2C$, (TCD), couples reductively by $[(cp)_2Ti(CO)_2]$ to give tetra-p-tolyloxalylamidine which acts as a bidentate ligand bonding two $(cp)_2Ti$ units to give $[(cp)_2Ti(TCD)]_2$ containing Ti(III) [163]. The C-N distances in the TCD metallacyclic ring are identical indicating a significant double bond character. Iodine converts this metallacycle to the corresponding diamagnetic Ti(IV) compound, $[(cp)_2Ti(TCD)]_2(I_3)_2$ [163]. Oxidation of $[(cp)_2Ti(TCD)]_2$ with tetracyanoethylene (TCNE) affords a probable charge transfer complex, $[(cp)_2Ti(TCD)]_2(TCNE)_2$, containing the $TCNE^{-\cdot}$ radical anion; the presence of this anion was deduced from the infrared spectrum and magnetic moment (two unpaired electrons per unit). μ-oxobis(dicyclopentadienyl)-



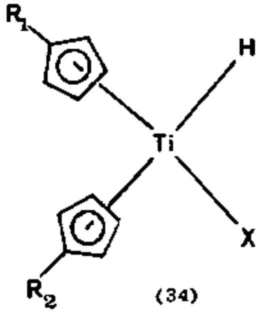
(33)

(alkenyl)titanium(IV) complexes have been prepared from $[(cp)_2Ti(CO)_2]$ and an alkyne in the presence of H_2O, and gave the corresponding *cis*-olefins [164].

The cations $TiCl_4^+$ and $TiCl_3^+$ are the principal ions produced by electron-impact ionisation of $TiCl_4$ [165]. Both cations react with $TiCl_4$ to give $Ti_2Cl_7^+$. Reactions of this and other species of the form $TiCl_3(ligand)^+$ have afforded the determination of an order of relative ligand binding to $TiCl_3^+$:MeF < $TiCl_4$ < MeCl < EtCl < benzene [165]. MeI, propylene, and butenes are also stronger ligands for $TiCl_3^+$ than for $TiCl_4$. Furthermore, a study of halide transfer and proton transfer has led to the determination of some thermochemical dissociation energies: $D(TiCl_3{-}Cl) = 217 \pm 11$ kcal/mol, $D(TiCl_3{-}F) = 254 \pm 4$ kcal/mol, and $D(TiCl_4{-}H^+) = 175 \pm 11$ kcal/mol. Chloride transfer from $MeTiCl_3$ to $TiCl_3^+$ gives $MeTiCl_2^+$ as the major ion at intermediate times in the ion chemistry of $MeTiCl_3$ [165]. This major ion reacts with C_2H_4 to yield $C_3H_5TiCl_2^+$ and hydrogen; $C_3H_5TiCl_2^+$ reacts no further with C_2H_4. With C_2D_4, HD elimination predominates (> 85%) [165].

Ethylene polymerisation catalysed by $[(cp)_2TiEtCl]$ or $[(cp)_2TiMeCl]$ and co-catalysed by oxyaluminium compounds formed by hydrolysis of $AlEtCl_2$, $AlEt_2Cl$, $AlEt_3$, $AlMe_2Cl$, $AlMe_3$, and AlEt(OBu)Cl in benzene solutions has been studied [166]. Co-catalytic activity of oxyaluminium compounds decreases with increase in the number of alkyl substituents in the corresponding alanes, $AlR_xCl_y(OBu)_{3-x-y}$; the oxyaluminium compound formed from AlEt(OBu)Cl is inactive. The oxy compounds of methylalanes are much less active than those from ethylalanes, and if the same aloxane co-catalyst is used, the catalytic activity of $[(cp)_2TiEtCl]$ and $[(cp)_2TiMeCl]$ is about the same [166]. The importance of the chemistry of organo-titanium compounds (following the discovery of Ziegler-Natta catalysts) due to their reference to homogeneous catalysis and chemical fixation of N_2 has led Sharma et al., [167] to prepare several $(cp)_2Ti$-containing compounds with such Schiff bases as N-alkylsalicylaldimine, where alkyl is methyl, ethyl, propyl, isopropyl and n-butyl.

The stereodifferentiating activity of Ziegler-Natta type Ti(IV) catalysts carrying the chiral ligand menthyl and neo-menthyl cyclopentadienyl (Mcp and NMcp) has been investigated in the asymmetric catalytic reduction of a prochiral olefin; 2-phenyl-1-butene is hydrogenated with acceptable optical yields to (R)-(-) or (S)-(+)-2-phenyl-1-butane, respectively [168]. The effect on optical yields of reaction temperature, of the nature of the chiral co-catalyst or of achiral co-catalysts of different bulk has also been studied [168]. The co-catalysts appear to play a negligible role in the asymmetric reduction. The higher optical yields are obtained by compounds carrying the (R)-(-)-menthyl-cyclopentadienyl ligand (Mcp), especially when two such ligands are bound to titanium; with (S)-(+)-NMcp ligand, the optical yields are lower. However, when one or two units of ligand are bound to Ti, the optical yields are about the same for the (S)-(+)-neomenthylcyclopentadienyl ligand. This fact, together with the observation that the absolute configuration of hydrogenated hydrocarbons is dictated by the absolute configuration of the C atom directly attacking the chiral substituent to the cp ring, would indicate that asymmetric induction is principally related to the crowding around the metal atom [168]. The major catalytic species is probably a Ti(IV) complex. The aluminium co-catalyst is probably not directly bound to the titanium catalytic system formed *in situ* by hydride or chloride bridges or other different kinds of bonds, owing to the lack of any influence on the optical yields (but not on the rate of hydrogenation) by the OR substituents bound to the Al atoms [168]. The chiral environment of the titanium atom in a possible Ti(IV) monohydride catalytic intermediate is illustrated by (*34*). The absence of large optical yields with compounds (*37*), (*38*) and (*39*) suggests that chiral groups on the cp ring cannot induce a chiral coordination around titanium as would be possible for a monohydride of the type such as (*34*) above [168].



(34)

X = Cl or $ClAlH(OR)_2$, etc. ...

R_1 = H, CH_3

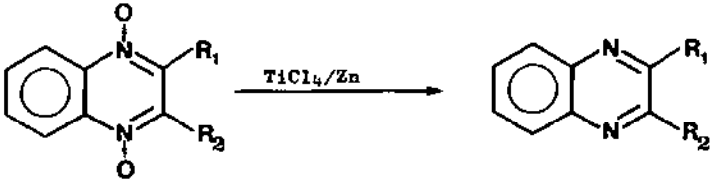
R_2 = (S)-(+)-neomenthyl or (R)-(-)-menthyl

Ti(IV) catalysts used [168]	Co-catalysts used [168]
(*35*) $(\eta^5\text{-Mcp})_2TiCl_2$	$LiAlH_2(OCH_2CH_2OCH_3)_2$
(*36*) $(\eta^5\text{-NMcp})_2TiCl_2$	$LiAlH_2(O\text{-}^tBu)_2$
(*37*) $(\eta^5\text{-Mcp})(\eta^5\text{-cp})TiCl_2$	$LiAlH_2[(-)OMenthyl]_2$
(*38*) $(\eta^5\text{-NMcp})(\eta^5\text{-cp})TiCl_2$	
(*39*) $(\eta^5\text{-Mcp})(\eta^5\text{-cpCH}_3)TiCl_2$	

The systems $(cp)_2TiX/AlH_{3-n}X_n/Et_2O(NEt_3)$ (where X = Cl or Br and n = 0 or 1) have been studied by dielectrometric and colorimetric titration and also by EPR techniques [169]. Bimetallic 1:1 compounds containing hydrogen bridges $Ti{<}\genfrac{}{}{0pt}{}{H}{H}{>}Al$ are formed in all systems. All reaction products, except $(cp)_2TiH_2AlHCl\cdot Et_2O$, formed at 20-25 °C, are monomeric in solution. The monochloro derivative is a dimer containing both ordinary and double hydrogen bridges.

Synthetic methods are given for placing a vinyl group onto 2,2'-bipyridine and 1,10-phenanthroline; the groups have been employed to attach $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ to Pt electrodes by (1) hydrosilylation followed by polycondensation with the electrode, or by (2) cycling the electrode to negative potentials to induce anionic polymerisation at the electrode surface [170]. When electropolymerised at a TiO_2 electrode, the $[Ru(phen)_3]^{2+}$ film, in contact with an aqueous solution containing hydroquinone as a mediator, supports a steady photocurrent stable for > 15 hrs.

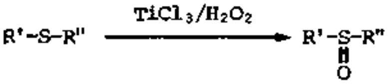
Deoxygenation of 2,3-disubstituted quinoxaline-1,4-dioxides can be carried out under mild conditions with $TiCl_4$/Zn dust to give products in reasonably good yield (range 47-67%) according to reaction (43) [171]. But in practice, $TiCl_4$/Zn dust is the least convenient and sometimes leads to intractable mixtures; the silanes Si_2Cl_6 and Me_3SiI are more convenient. A facile route has been reported for the preparation of tetraphenylfuran in 80% yield from benzoyl chloride and low-valent Ti species, the latter prepared by action of $LiAlH_4$ on $TiCl_3$ [172]. Sulphides can be converted to sulphoxides using $TiCl_3/H_2O_2$ (reaction 44), in alcohols, water, or acetonitrile [173]. Reaction of π-allyldicyclopentadienyltitanium(III) complexes pre-formed or formed *in situ* with aldehydes or ketones proceeds with regiospecificity, high stereoselectivity, and chemospecificity affording, under mild conditions, the corresponding homoallyl alcohols after hydrolysis, and in excellent yields [174].



(43)

R_1 = CH_2Ph, COPh, $COCH_3$, CO_2Et, Ph, CH_3

R_2 = Ph, Ph, CH_3, CH_3, CH_3, CH_3



$$R'\text{-}S\text{-}R'' \xrightarrow{TiCl_3/H_2O_2} R'\text{-}\overset{}{\underset{\underset{\displaystyle O}{\|}}{S}}\text{-}R'' \qquad (44)$$

Synthesis of β-lactams by reaction of ketenesilylacetate with Schiff bases is promoted by $TiCl_4$ [175]. 1-trimethylsilyl-2-butyne reacts with carbonyl compounds in the presence of $TiCl_4$ or tetra-n-butylammonium fluoride to produce mainly α-allenic alcohols [176]. With $TiCl_4$, it is also possible to obtain chloroprenic derivatives only. Propargylmethylsilane reacts also with carbonyl compounds to produce chloroprenic derivatives in the presence of titanium(IV) chloride [177]. A π-allyltitanium complex with a chiral cyclopentadienyl ligand reacts with CO_2 under mild conditions to form a C–C bond providing the first demonstration of asymmetric CO_2 fixation [178]. Use of $(cp)_2Ti$ as a source of $(cp)_2TiCH_2$ for reaction with unsaturated organic and organometallic substrates affords a promising pathway to other metallacyclic and bimetallic methylene bridged systems [179]. Use of $TiCl_4$ [180], $TiCl_3$ [181], alkyltitanium(IV) compounds [182], and $Ti(OR)_4$ [183] in organic syntheses has been reported. The possibility of developing novel syntheses for tri- and tetra-substituted olefins [184], as well as reports on the catalysis of hydrogenation of linear and cyclic olefins with alkyltitanocene compounds [185] have appeared. Tetraneopentyltitanium has been used as a polymerisation catalyst [186].

Disubstituted acetylenes react with isobutyl magnesium halide in the presence of catalytic amounts of $[(cp)_2TiCl_2]$ in ether to afford E-alkenyl Grignard reagents selectively in almost quantitative yields [187]. The regiochemistry of this hydromagnesation reaction is high for alkylarylacetylenes and silylacetylenes giving E-ArC(MgBr)=CHR from alkylarylacetylenes, E-ArC(MgBr)=CH($SiMe_3$) from arylsilylacetylenes, and E-CHR=C(MgBr)$SiMe_3$ from alkylsilylacetylenes, respectively [187]. The reaction offers a novel, selective, operationally simple route for the preparation of tri-substituted olefins.

Insertion of diphenylketene into a Ti–O bond of alkyltitanates, $Ti(OR)_4$ ($R = C_2H_5$, ${}^{i}C_3H_7$, C_6H_5, ...) results in the unexpected generation of a Ti–C bond; a series of complexes, $[(RO)_{4-n}Ti(CPh_2C(O)OR)_n]$ (n = 1, 2), was obtained and characterised by spectroscopic data and by hydrolysis products [188]. Action of molecular oxygen changes Ti–C into Ti–O–C (auto-oxidation) and after hydrolysis, α-hydroxyesters (benzilates) are obtained [188].

Hydrogenation of 1-hexene and cyclohexene with $LiAlH_4(cp)_2TiX$ (X = Cl or Br) catalysts is fastest at Al/Ti ratio of 1:2; EPR data suggest the active species is $[(cp)_2Ti]_2AlH_4X$ [189]. No such catalytically active species are formed with $LiBH_4$.

ACKNOWLEDGEMENTS

Our work is supported by the National Sciences and Engineering Research Council of Canada, the Formation de Chercheurs et d'Action Concertée of Québec, and by the North Atlantic Treaty Organisation (No. 046.81). We thank these agencies for their generous support. We also thank Ms. Mary A. Jamieson for assistance.

REFERENCES

1 Department of Chemistry, Concordia University, Montreal, Quebec, Canada, H3G 1M8.
2 To whom correspondence should be addressed.
3 R.C. Fay, *Coord. Chem. Revs.*, 37 (1981) 9.
4 G.P. Pez and J.W. Armor, *Adv. Organomet. Chem.*, 19 (1981) 1.
5 M.F. Lappert and C. Raston, *J. Chem. Soc. Chem. Commun.*, (1980) 1284.
6 R.K. Sharma, R.V. Singh and J.P. Tandow, *Synth. React. Inorg. Met.-Org. Chem.*, 10 (1980) 221.
7 K. Chandra, N.K. Bhatra and B.S. Garg, *J. Ind. Chem. Soc.*, 58 (1981) 122.
8 D.J. Sikora, M.O. Rausch, R.D. Rogers and J.L. Atwood, *J. Am. Chem. Soc.*, 103 (1981) 982.
9 K. Mach, H. Antiopinsova and J. Polacek, *J. Organomet. Chem.*, 194 (1980) 285.
10 E. Klei, J.H. Telgen and J.H. Teuben, *J. Organomet. Chem.*, 209 (1981) 297.
11 H. Antiopinsova, A. Desedlova, V. Hanus and K. Mach, *Transition Met. Chem.*, 6 (1981) 90.
12 L. Roesch, G. Altnau, W. Erb, J. Pickardt and N. Bruncks, *J. Organomet. Chem.*, 197 (1980) 51.
13 M. Chang, P.L. Timms and R.B. King, *J. Organomet. Chem.*, 199 (1980) C3.
14 B. Demerseman and P.H. Dixneuf, *J. Organomet. Chem.*, 210 (1981) C20.
15 H. Koepf, S. Grabowski and R. Vorgtlaender, *J. Organomet. Chem.*, 216 (1981) 185.
16 R.J. McKinney, T.H. Tulip, D.L. Thorn, T.S. Coolbaugh and F.N. Tebbe, *J. Am. Chem. Soc.*, 103 (1981) 5584.
17 V.W. Day, M.F. Fredrick, M.R. Thompson, W.G. Klemperer and R.S. Liu, *J. Am. Chem. Soc.*, 103 (1981) 3597.
18 J. Blenkers, H. deLiefde, H.S. Meijer and J.H. Teuben, *Rec. Trav. Chim. Pays Bas*, 99 (1980) 216.
19 L.C. Francesconi, D.R. Corbin, A.W. Clauss, D.N. Hendrickson and G.D. Stucky, *Inorg. Chem.*, 20 (1981) 2078.
20 D.R. Corbin, L.C. Francesconi, D.N. Hendrickson and G.D. Stucky, *Inorg. Chem.*, 20 (1981) 2084.
21 L.C. Francesconi, D.R. Corbin, A.W. Claus, D.N. Hendrickson and G.D. Stucky, *Inorg. Chem.*, 20 (1981) 2059.
22 L.S. Kramer, A.W. Claus, L.C. Francesconi, D.R. Corbin, D.N. Hendrickson and G.D. Stucky, *Inorg. Chem.*, 20 (1981) 2070.
23 J. Jeffrey, M.F. Lappert, N.T. Luong-Thi, M. Webb, J.L. Atwood and W.E. Hunter, *J. Chem. Soc. Dalton Trans.*, (1981) 1593.
24 D.J. Sikora, M.D. Rausch, R.D. Rogers and J.L. Atwood, *J. Am. Chem. Soc.*, 103 (1981) 1265.
25 C.M. Bolinger, T.B. Rauchfoss and S.R. Wilson, *J. Am. Chem. Soc.*, 103 (1981) 5620.
26 R.S. Arora and R.K. Multani, *Curr. Sci.*, 50 (1981) 716.
27 R. Sharan, G. Gupta and R.N. Kapoor, *Indian J. Chem. Sect. A*, 20A (1981) 94.
28 D.M. Hamilton Jr., W.S. Willis and G.D. Stucky, *J. Am. Chem. Soc.*, 103 (1981) 4255.
29 F. Bottomley, I.J.B. Liu and P.S. White, *J. Am. Chem. Soc.*, 103 (1981) 703.
30 K. Chandra, P. Soni, B.S. Barg and R.P. Singh, *J. Ind. Chem. Soc.*, 58 (1981) 10.

31 K. Chandra, R.K. Sharma, B.S. Barg and R.P. Singh, *J. Inorg. Nucl. Chem.*, 43 (1981) 663.

32 P. Knopf-Maier, W. Kahl, N. Klouras, G. Hermann and H. Koepf, *Eur. J. Med. Chem. Chem. Ther.*, 16 (1981) 275.

33 M.C.R. Symons and S.P. Mishra, *J. Chem. Soc. Dalton Trans.*, (1981) 2258.

34 E. Chassaing, F. Basile and G. Lothioir, *J. Appl. Electrochem.*, 11 (1981) 193.

35 H. Schaefer and R. Laumanns, *Z. Anorg. Allgem. Chem.*, 474 (1981) 135.

36 L. Bencivenni, A. Farina and S. Cesaro, *J. Mol. Struct.*, 66 (1980) 111.

37 D. Nicholls and T.A. Ryan, *Inorg. Chim. Acta*, 41 (1980) 233.

38 J. Lovy, J. Stokr, D. Doskicilova and R. Puffr, *J. Mol. Struct.*, 68 (1980) 119.

39 L. Nigam, V.D. Gupta and R.C. Mehrotra, *Indian J. Chem. Sect. A*, 20A (1981) 61.

40 C. Airoldi, D.C. Bradley, H. Chudzynska, M.B. Hursthouse, K.M.A. Malik and P.R. Raithby, *J. Chem. Soc. Dalton Trans.*, (1980) 2010.

41 M.S. Delgado and V. Fernandez, *Z. Anorg. Allgem. Chem.*, 467 (1980) 225.

42 K.C. Goyal and B.D. Khosla, *J.Ind. Chem. Soc.*, 58 (1981) 617.

43 T. Misono, Y. Abe, Y. Nagao and T. Kajima, *Shikizsi Kyokaishi*, 54 (1981) 15.

44 G.S. Goldin, M.G. Gruntfest and A.I. Luov, *Koord. Khim.*, 7 (1981) 82.

45 A.F. Shihada and Z.S. Salih, *Z. Anorg. Allgem. Chem.*, 469 (1980) 159.

46 W. Kuchen, A. Mamsch, D. Mootz and M. Steffen, *Z. Anorg. Allgem. Chem.*, 472 (1981) 133.

47 C.M. Mikulski, J. Unruh and R. Rabin, *Transition Met. Chem.*, *(Weinheim, Ger.)*, 6 (1981) 79.

48 M.S. Delgrado and V. Fernandez, *Z. Anorg. Allgem. Chem.*, 476 (1981) 149.

49 S.C. Goel and R.C. Mehrotra, *Indian J. Chem. Sect. A*, 20A (1981) 440.

50 R.K. Kanjolia and V.D. Gupta, *J. Ind. Chem. Soc.*, 58 (1981) 340.

51 W.M. Dyck, K. Dehnicke, F. Weller and U. Mueller, *Z. Anorg. Allgem. Chem.*, 470 (1980) 89.

52 S.R. Wade and G.R. Willey, *Inorg. Chim. Acta*, 43 (1980) 73.

53 J. Loevy, R. Puffr and D. Doskocilova, *J. Mol. Struct.*, 73 (1981) 187.

54 C.E. Carraher, R.A. Schwartz, J.A. Schroeder and M. Schwartz, *J. Macromol. Sc. Chem.*, A15 (1981) 773.

55 E.N. Guryanova, L.A. Ganyushin and I.P. Romm, *Zh. Obshch. Khim.*, 51 (1981) 437.

56 S.V. Volkov, V.I. Shapoval, N.I. Buryak and V.G. Lutsenko, *Zh. Neorg. Khim.*, 26 (1981) 528.

57 N.P. Kharitonov, V.I. Spiridonov and V.V. Ostrovskii, *Zh. Prikl. Khim. (Leningrad)*, 54 (1981) 1759.

58 H. Boehland and H. Steinecke, *Z. Anorg. Allgem. Chem.*, 476 (1981) 136.

59 H.S. Sangari, G.S. Sodhi and N.K. Kaushik, *Synth. React. Inorg. Met.-Org. Chem.*, 11 (1981) 373.

60 R.V. Singh, R.K. Sharma and J.P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.*, 11 (1981) 139.

61 J. Jones and J. Douek, *J. Inorg. Nucl. Chem.*, 43 (1981) 406.

62 S. Koch and G. Ackermann, *Z. Anorg. Allgem. Chem.*, 473 (1981) 231.

63 M.K. Gupta and G.V. Jere, *Synth. React. Inorg. Met.-Org. Chem.*, 11 (1981) 455.

64 M.S. Delgrado and V. Fernandez, *Z. Anorg. Allgem. Chem.*, 474 (1981) 226.

65 A. Izquierdo, M. Gine and R. Campano, *J. Inorg. Nucl. Chem.*, 43 (1981) 617.

66 Z. Hausenblasova, I. Nemkova and V. Suk, *Microchem. J.*, 26 (1981) 262.

67 D. Kolar, S. Gabescek, B. Volavsek and H.S. Parker, *J. Solid State Chem.*, 38 (1981) 158.

68 H.P. Klein and U. Thewalt, *J. Organomet. Chem.*, 206 (1981) 69.

69 H.P. Klein and U. Thewalt, *Z. Anorg. Allgem. Chem.*, 476 (1981) 62.

70 U. Thewalt and H.P. Klein, *Z. Anorg. Allgem. Chem.*, 479 (1981) 113.

71 W.D. Griebler and D. Babel, *Z. Anorg. Allgem. Chem.*, 467 (1980) 187.

72 B. Krebs and G. Henkel, *Z. Anorg. Allgem. Chem.*, 474 (1981) 149.

73 G.B. Mueller, *J. Fluorine Chem.*, 17 (1981) 489.

74 M. Handlovic, D. Miklor and M. Zikmund, *Acta Crystallog. Sect. B*, B37 (1981) 811.

75 T.E. Jenkins and J. Lewis, *Spectrochim. Acta, Part A*, 37A (1981) 47.

76 D.L. Thorn, W.A. Nugent and R.L. Harlow, *J. Am. Chem. Soc.*, 103 (1981) 357.

77 R.J. Daroda, G. Wilkinson, M.B. Hursthouse, K.M.A. Malik and M. Thornton-Pett, *J. Chem. Soc. Dalton Trans.*, (1980) 2315.

78 F. Bottomley, I.J.B. Liu and P.S. White, *J. Organomet. Chem.*, 212 (1981) 341.

79 C.E. Carraher, L.P. Torre and H.M. Molloy, *J. Macromol. Sci. Chem.*, A15 (1981) 757.

80 J. Mattra, D.J. Sikora, D.W. Macomber, M.D. Rausch, J.P. Hickey, G.D. Friesen and L.J. Todd, *J. Organomet. Chem.*, 213 (1981) 441.

81 U. Thewalt and H.P. Klein, *J. Organomet. Chem.*, 194 (1980) 297.

82 E. Heyand and U. Mueller, *Z. Naturforsch. B. Anorg. Chem.*, 36B (1981) 135.

83 N.M. Sidorova, K.Y. Merezhinskii and V.B. Glushkova, *Izv. Akad. Nauk. SSR Neog. Mater.*, 17 (1981) 79.

84 M. Webster and J.S. Wood, *J. Chem. Res. Synop.*, 2 (1981) 40.

85 F.W. Hartner Jr. and J. Schwartz, *J. Am. Chem. Soc.*, 103 (1981) 4979.

86 J.C.G. Calado, A.R. Dias, M.S. Salema and J.A.M. Simoes, *J. Chem. Soc. Dalton Trans.*, (1981) 1174.

87 R. Parkash, S.C. Ahlurwalia and S.C. Sud, *Monatsch. Chem.*, 112 (1981) 707.

88 M.K. Cooper, P.A. Duckworth, K. Henrick and M. Paetlin, *J. Chem. Soc. Dalton Trans.*, (1981) 2353.

89 M. Sørlie and H. Øye, *Inorg. Chem.*, 20 (1981) 1384.

90 B. Briat, O. Kahn, I. Morgenstern-Badarau and J.C. Rivoal, *Inorg. Chem.*, 20 (1981) 4193.

91 D.A. MacLean and J.E. Greedan, *Inorg. Chem.*, 20 (1981) 1025.

92 S. Sabo, R. Choukroun and D. Gervais, *J. Chem. Soc. Dalton Trans.*, (1981) 2328.

93 R. Iadevia and J.E. Earley, *Inorg. Chim. Acta*, 53 (1981) L143.

94 R.N. Bose and J.E. Earley, *Inorg. Chem.*, 20 (1981) 2739.

95 S. Ali, C.Z. Chalilpoyil and J.E. Earley, *Inorg. Chim. Acta*, 48 (1981) 57.

96 H.H. Schmidtke and U. Voets, *Inorg. Chem.*, 20 (1981) 2766.

97 D.G. Bickley and N. Serpone, *Inorg. Chim. Acta*, 40 (1980) 213.

98 D.G. Bickley and N. Serpone, *Inorg. Chim. Acta*, 43 (1980) 185.

99 D.T. Haworth, D.L. Grossman and M. Das, *J. Inorg. Nucl. Chem.*, 43 (1981) 1389.

100 J.M. Leblanc and C. Moise, *Org. Magn. Res.*, 14 (1980) 157.

101 A.T. Pilipenko, L.I. Savranskii and N.A. D'Yachenko, *Izv. Vyssh. Uchebn. Zaved Khim. Khim. Teknol.*, 24 (1981) 647.

102 A.N. Glebov, P.A. Vasilev and Y.I. Salnikov, *Zh. Neorg. Khim.*, 26 (1981) 260.

103 Y.N. Kozlov, A.P. Moravskii, A.P. Purmal and V.F. Shuvalov, *Zh. Fiz. Khim.*, 55 (1981) 764.

104 I.V. Ikonitskii, N.A. Buzina, L.K. Kurnosova and E.N. Kropacheva, *Zh. Prikl. Spektrosk.*, 34 (1981) 673.

105 Y.A. Lysenko and E.A. Troshina, *Izv. Vyssk. Uchebn. Zaved Khim. Khim. Teknol.*, 24 (1981) 399.

106 Y.I. Turyan and L.M. Maluka, *Zh. Obshch. Khim.*, 51 (1981) 662.

107 V.M. Berdnikov, L.S. Ryvkina and G.A. Bogdanchikov, *Koord. Khim.*, 7 (1981) 877.

108 L.I. Evdokimova, E.S. Boichinova, S.A. Simanova, V.N. Pak and E.D. Brynzova, *Zh. Prikl. Khim. (Leningrad)*, 54 (1981) 1292.

109 V.V. Nemoshkalenko, M.M. Kindrat, V.P. Krivitskii, B.P. Mamko, V.M. Prokopenko and A.I. Kharlamov, *Metallofizika (Akad. Nauk. Ukr. SSR Otd. Fiz.)*, 3 (1981) 37.

110 I. Grabis, J. Vaivadr, A. Bernaus and T. Millers, *Latv. P.S.R. Akad. Vestus Khim. Ser.*, 4 (1981) 395.

111 S.J. Simpson and R.A. Andersen, *Inorg. Chem.*, 20 (1981) 3627.

112 K. Doeppert and R.D. Sanchez, *J. Organomet. Chem.*, 210 (1981) C9.

113 A. Roeder, K.H. Thiele, G. Palyi and L. Marko, *J. Organomet. Chem.*, 199 (1980) C31.

114 A. Dormond and A. Dahchour, *J. Organomet. Chem.*, 193 (1980) 321.

115 A. Dormond, A. Dahchour and J. Tirouflet, *J. Organomet. Chem.*, 216 (1981) 49.

116 E. Klei and J.H. Teuben, *J. Organomet. Chem.*, 214 (1981) 53.

117 H.R. van der Wal, S.J. Veenstra and H.J. deLiefde, *J. Organomet. Chem.*, 197 (1980) 59.

118 J.M. McCall and A. Shaver, *J. Organomet. Chem.*, 193 (1980) C37.

119 K.W. Chiu, R.A. Jones, G. Wilkinson, A.M.R. Galas and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, (1981) 2088.

120 I. Rani, K.B. Pandeya and R.P. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, 11 (1981) 221.

121 M. Korde, E. Tsuchida and Y. Kurimura, *Makromol. Chem.*, 182 (1981) 749.

122 G. Fink, R. Rottler and C.G. Kreites, *Angew. Makromol. Chem.*, 96 (1981) 1.

123 G. Fink and R. Rottler, *Angew. Makromol. Chem.*, 94 (1981) 25.

124 F. Bottomley and I.J.B. Liu, *J. Chem. Soc. Dalton Trans.*, (1981) 271.

125 M.C. Vanderveer and J.M. Burlitch, *J. Organomet. Chem.*, 197 (1980) 357.

126 F. Mathey and R. Maillet, *Tetrahedron Lett.*, 21 (1980) 2525.

127 L.P. Battaglia, M. Nardelli, C. Pelizzi, G. Prediere and G.P. Chiusoli, *J. Organomet. Chem.*, 209 (1981) C7.

128 H. Ogino, E. Kikkawa, M. Shimura and N. Tanaka, *J. Chem. Soc. Dalton Trans.*, (1981) 894.

129 R.A. Lee and J.E. Earley, *Inorg. Chem.*, 20 (1981) 1739.

130 O. Olubuyide and J.E. Earley, *Inorg. Chem.*, 20 (1981) 3569.

131 F.J. Kristine and R.E. Shepherd, *Inorg. Chem.*, 20 (1981) 215.

132 F.J. Kristine, R.E. Shepherd and S. Siddiqui, *Inorg. Chem.*, 20 (1981) 2571.

133 N.E. Krushch, O.M. Chukanova, F.G. D'Yachkovskii and V.A. Goluber, *Izv. Akad. Nauk. SSR Ser. Khim.*, 6 (1981) 1239.

134 S.B. Sarvin, R.K. Chernova and I.V. Lobacheva, *Zh. Anal. Khim.*, 36 (1981) 9.

135 Y. Muguier, C. Moise and E. Laviron, *J. Organomet. Chem.*, 204 (1981) 61.

136 C. Moise and E. Laviron, *J. Organomet. Chem.*, 210 (1981) 69.

137 N. El Murr and A. Chaloyard, *J. Organomet. Chem.*, 212 (1981) C39.

138 R.J. Gale and R. Job, *Inorg. Chem.*, 20 (1981) 42.

139 H. Linga, Z. Stojek and R.A. Osteryoung, *J. Am. Chem. Soc.*, 103 (1981) 3754.

140 N. Yamamoto, Y. Nagasawa and S. Shuto, *Bull. Chem. Soc. Japan*, 81 (1981) 323.

141 N. Kaneko, H. Nezu and K, Ooka, *Denki, Kagaku Oyobi Kogyo Butsuri Kagaku*, 49 (1981) 302.

142 T. Kawai and T. Sakata, *Chem. Phys. Lett.*, 72 (1980) 87.

143 I. Izum, W.W. Dunn and K.O. Wilburn, *J. Phys. Chem.*, 84 (1980) 3207.

144 I.A. Potapov, M.B. Rozenkevich and Y.A. Sakharovskii, *Koord. Khim.*, 7 (1981) 229.

145 S. Sato and J.M. White, *Chem. Phys. Lett.*, 72 (1980) 83.

146 S. Sato and J.M. White, *J. Phys. Chem.*, 85 (1981) 336.

147 S. Sato and J.M. White, *J. Catal.*, 69 (1981) 128.

148 S. Sato and J.M. White, *Gov. Rep. Announce., Index (US)*, 80 (1980) 4929.

149 S. Sato and J.M. White, *J. Phys. Chem.*, 85 (1981) 592.

150 D. Duonghong, E. Borgarello and M. Graetzel, *J. Am. Chem. Soc.*, 103 (1981) 4685.
151 E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca and M. Graetzel, *J. Am. Chem. Soc.*, 103 (1981) 6324.
152 E. Borgarello, J. Kiwi and E. Pelizzetti, *Nature (London)*, 289 (1981) 158.
153 W. Vonach and N. Getoff, *Z. Naturforsch. A*, 36A (1981) 876.
154 R. Nakamura, S. Nakai, K. Sugiyama and E. Echigoya, *Bull. Chem. Soc. Japan*, 54 (1981) 1950.
155 I. Izumi, F.F. Fan and A.J. Bard, *J. Phys. Chem.*, 85 (1981) 218.
156 P. Salvador, *J. Electrochem. Soc.*, 128 (1981) 1895.
157 H. Hada, K. Takaoka and M. Saikawa, *Bull. Chem. Soc. Japan*, 54 (1981) 1640.
158 G. Campet, M.P. Dare-Edwards and A. Hammett, *Nouv. J. Chim.*, 4 (1980) 501.
159 I. Mochida, K. Tsuji and K. Suetsugu, *J. Phys. Chem.*, 84 (1980) 3159.
160 C.J. Boreham and J.M. Latour, *Inorg. Chim. Acta*, 45 (1980) L69.
161 P.A. Breddels and G. Blasse, *Chem. Phys. Lett.*, 79 (1981) 209.
162 Y.N. Zu and X.R. Ziao, *Tai Yang Neug Hsueh Pao*, 2 (1981) 7.
163 M. Pasquale, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 20 (1981) 349.
164 B. Demerseman and P.H. Dixneuf, *J. Chem. Soc. Chem. Comm.*, (1981) 665.
165 J.S. Uppal, D.E. Johnson and R.H. Staley, *J. Am. Chem. Soc.*, 103 (1981) 508.
166 J. Cihlar, O. Hamuk, P. Hudek and J. Mayer, *Makromol. Chem.*, 182 (1981) 1127.
167 R.K. Sharma, R.V. Singh and S.P. Tandon, *J. Inorg. Nucl. Chem.*, 43 (1981) 410.
168 E. Cesarotti, R. Ugo and R.V. Vitiello, *J. Molec. Cat.*, 12 (1981) 63.
169 B.M. Bulychev, A.L. Kostenko, N.A. Yakovleva and G.L. Soloveichik, *Transition Met. Chem.*, 6 (1981) 32.
170 P.K. Ghosh and T.G. Spiro, *J. Electrochem. Soc.*, 128 (1981) 1281.
171 F.R. Homaidan and C.H. Issodorides, *Heterocycles*, 16 (1981) 411.
172 R. Dams, M. Malinkowski and I. Westdorp, *J. Org. Chem.*, 46 (1981) 2407.
173 Y. Watanabe, T. Numata and S. Oae, *Synthesis*, 3 (1981) 204.
174 S. Sato, S. Iijima and M. Sato, *Tetrahedron Lett.*, 22 (1981) 243.
175 I. Ojima, S. Inaba and M. Nagai, *Synthesis*, 22 (1981) 545.
176 B. Randrianoelina, *Tetrahedron Lett.*, 22 (1981) 1327.
177 J. Pornet, *Tetrahedron Lett.*, 22 (1981) 453.
178 F. Sato, S. Iijima and M. Sato, *J. Chem. Soc. Chem. Comm.*, (1981) 180.
179 K.C. Ott and R.H. Grubbs, *J. Am. Chem. Soc.*, 103 (1981) 5922.
180 A. Itok, T. Saito, K. Oshima and H. Nozaki, *Bull. Chem. Soc. Japan*, 54 (1981) 1456.
181 A. Clerici and O. Porta, *Tetrahedron Lett.*, 21 (1980) 1675.
182 M.T. Reetz, R. Steinbach and B. Wenderoth, *Synth. Commun.*, 11 (1981) 261.
183 D.J. Morgans Jr., K.B. Sharpless and S.G. Traynor, *J. Am. Chem. Soc.*, 103 (1981) 462.
184 T. Yoshida and E. Negishi, *J. Am. Chem. Soc.*, 103 (1981) 1276.
185 S. Samuel, *J. Organomet. Chem.*, 198 (1980) C65.
186 J.C.W. Chieu, J. Wu and M.D. Rausch, *J. Am. Chem. Soc.*, 103 (1981) 1180.
187 F. Sato, H. Ishikawa and M. Sato, *Tetrahedron Lett.*, 22 (1981) 85.
188 C. Blandy and D. Gervais, *Inorg. Chim. Acta*, 47 (1981) 197.
189 E.V. Evdokimova, B.M. Bulychev and G.L. Soloveichik, *Kinet. Katal.*, 22 (1981) 170.
190 V.A. Sharov, N.V. Povarova and E.I. Krylov, *Zh. Neorg. Khim.*, 25 (1980) 2153.
191 Y.A. Turyan and L.M. Maluka, *Zh. Obshch. Khim.*, 50 (1980) 1917.
192 A.G. Sarkisyan, V.M. Arutunyan, V.M. Arakelyan and G. Erevan, *Izv. Akad. Nauk. SSR Fiz.*, 15 (1980) 221.
193 S. Ahn, E.V. Park and B.B. Park, *Taehan Huahakhoe Chi.*, 24 (1980) 91.

194 Y.N. Kafarov, T.D. Alizade and G.A. Gamidzade, *Zh. Neorg. Khim.*, 25 (1980) 2421.

195 F.M. Tulyupa, L. Gerabyutina and L. Karyaka, *Zh. Neorg. Khim.*, 25 (1980) 2677.

196 B.M. Bulychev, V.B. Polyakova and G.L. Soloveichik, *Zh. Neorg. Khim.*, 25 (1980) 2134.

197 M. Zikmund and S. Raprova, *Chem. Zvesti*, 34 (1980) 618.

198 A.G. Sarkisyan, V.M. Arutyunyan and V.M. Arakelyan, *Geliotekhnika*, 6 (1980) 11.

199 M.A. Azizov and K.M. Kantsepolskaya, *Vopr. Formakol. Farmatsii. Tashkent*, (1989) 96.

200 D. Cheng, Y. Li and Z. Lui, *Tai Yang Neug Hseuh Pao*, 1 (1980) 37.

201 S.V. Volkov, V.I. Shapoval and N.I. Buryak, *Zh. Neorg. Khim.*, 25 (1980) 2993.

202 L.M. Dyagileva, O.S. Morozov and N.N. Vyshinskii, *Zh. Obshch. Khim.*, 50 (1980) 1859.

203 L.A. Granyushin, I.P. Romm and E.N. Guryanova, *Zh. Obshch. Khim.*, 50 (1980) 2159.

204 A.I. Kuzmin and G.N. Zviadadze, *Koord. Khim.*, 6 (1980) 1677.

205 M. Zikmund, E. Horvathova and G. Plesch, *Chem. Zvesti*, 34 (1980) 626.

206 A.Y. Nazarenko and I.V. Pyatnitskii, *Org. Reagentry Anal. Khim.*, 3 (1980) 88.

207 R. Gafarova and K.R. Rakhimov, *S.B. Nauch. Tr. Tashkent*, 595 (1979) 62.

208 J.C.J. Bart, I.W. Bassi, G.F. Cerruti and M. Calcaterra, *Gazz. Chim. Ital.*, 110 (1980) 423.

209 N.I. Vorobev, D.I. Medvedev and N.V. Galitskii, *Ukr. Khim. Zh. (Russ. Ed.)*, 46 (1980) 1282.

210 N.V. Povarova, V.A. Sharov and E.I. Krylov, *Zh. Neorg. Khim.*, 25 (1980) 3389.

211 M. Kohutova, J. Dobrovodsky and M. Zikmund, *Chem. Zvesti*, 34 (1980) 740.

212 Z. Krysicki and T. Lubanska, *Pokroky Praskove Metal.*, (1980) 6.

213 J. Lovy, R. Puffr, D. Doskocilova and J. Stokr, *Makrotest.*, (1980) 15.

214 E.A. Iodko, N.A. Noskov and T.V. Noskova, *Dvizhenie Provodyashch. Sred. V. Soln. Magnut. Polyabh.*, (1980) 69.

215 B.L. Wilson and S. Melakasa, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 9.

216 M. Aly and M. Hassan, *Ann. Chim. (Rome)*, 70 (1980) 463.

217 S. Chandra, R.K. Pandey and R.C. Agrawal, *J. Phys.*, 13 (1980) 1757.

218 B. Aurian-Balenji, M. Halmann and J. Manassen, *Sol. Energy*, 25 (1980) 165.

219 Y.L. Kogan and A.M. Vakulenko, *Sol. Energy Mater.*, 3 (1980) 357.

220 K. Dehnicke and R. Loessberg, *Z. Naturforsch. B. Anorg. Chem. Org. Chem.*, 35B (1980) 1587.

221 E. Malyszko and Z. Galur, *Pol. J. Chem.*, 54 (1980) 1385.

222 S. Sato and D. Gervais, *C.R. Séances Adad. Sc. Ser. C*, 291 (1980) 207.

223 Y. Saikali and P. Versaud, *C.R. Séances Adad. Sc. Ser. C*, 291 (1980) 57.

224 H. Lehmkuhl and S. Fustero, *Liebigs. Ann. Chem.*, 9 (1980) 1361.

225 H. Lehmkuhl and S. Fustero, *Liebigs. Ann. Chem.*, 9 (1980) 1353.

226 H. Lehmkuhl and S. Fustero, *Liebigs. Ann. Chem.*, 9 (1980) 1371.

227 J. Armand, P. Chekir and J. Pinson, *J. Heterocycl. Chem.*, 17 (1980) 1237.

228 F. Said and D. Tuck, *Can. J. Chem.*, 58 (1980) 1673.

229 M.T. Reetz and J. Westerman, *Angew. Chem.*, 92 (1980) 933.

230 M. Pal and R.N. Kapoor, *Indian J. Chem. Sect. A*, 19A (1980) 1024.

231 I.N. Unny, S. Gopinathan and C. Gopinathan, *Indian J. Chem. Sect. A*, 19A (1980) 598.

232 V. Baliah and P.V. Stayanaryana, *Indian J. Chem. Sect. B*, 19B (1980) 619.

233 M. Pal and R.N. Kapoor, *Indian J. Chem. Sect. A*, 19A (1980) 912.

234 P.A. Awasarkar, S. Gopinathan and G.C. Sarada, *Indian J. Chem. Sect. A*, 19A (1980) 596.

235 R.S. Arora, S.C. Hau and M.S. Bhalla, *J. Chin. Chem. Soc. (Taipei)*, 27 (1980) 65.

236 K. Chandra and R. Sharma, *Transition Met. Chem.*, 5 (1980) 209.
237 V.E. Lvovsk, E.A. Fushman and F.S. Dyachkovsky, *J. Mol. Catal.*, 10 (1980) 43.
238 J.C. Marchon and J.M. Latour, *J. Mol. Catal.*, 7 (1980) 227.
239 W. Tse, *Diss. Absts. Int. B*, 41 (1980) 1007.
240 R.K. Sharma, R.V. Singh and J.P. Tandon, *J. Inorg. Nucl. Chem.*, 42 (1980) 1382.
241 J.R.R. Mishrake, *J. Ind. Chem. Soc.*, 57 (1980) 769.
242 J.F. Kennedy and B. Kalogerakis, *Biochimie*, 62 (1980) 549.
243 K.S. Siddiqui, N.S. Neelam and T.A. Khan, *Bull. Soc. Chim. Fr.*, (1980) Pt. 1, 360.
244 R. Verhe, N. DeKimpe, L. deBuyck and R. Thierie, *Bull. Soc. Chim. Belg.*, 89 (1980) 563.
245 H. Boehland and H. Steinecke, *Z. Chem.*, 20 (1980) 350.
246 W. Seidel and E. Reisenberg, *Z. Chem.*, 20 (1980) 450.
247 P.B. Chakravarti and H.N. Sharma, *Vijnana Parishad Anusandhan Patrika*, 23 (1980) 309.
248 S. Sato and J.M. White, *Ind. Eng. Chem. Prod. Res. Dev.*, 19 (1980) 542.
249 J.E. Earley, B. Berne, P. Barine and R.N. Bose, *Coord. Chem., 20th Int. Conf.*, (1980) 65.
250 E. Fanti and C.M. Marschoff, *J. Less Common Met.*, 78 (1981) 35.
251 C.C. Valenzuela and J.M. Salas Peregrini, *An. Quim. Ser. B*, 76 (1980) 251
252 M. Kohutova and M. Zikmund, *Proc. 8th Conf. Coord. Chem.*, (1980) 193.
253 G. Plesch, S. Rapiova and H. Zikmund, *Proc. 8th Conf. Coord. Chem.*, (1980) 343.
254 O. Mcic and M.T. Nenadovic, *Energy Storage Trans. Int. Assem. 1st*, (1980) 445.
255 A. Dormond and T. Kolavudh, *Rev. Chim. Miner.*, 17 (1980) 131.
256 I. Rabinovitch, M.S. Sheiman and G.V. Burchalova, *Termodinam. Organ. Soedin. Gorki*, 8 (1989) 22.
257 S. Kano, *Ventron Alembic*, 19 (1980) 1.
258 A. Laurie, W. Shroyer and C. Loberau, *J. Org. Chem.*, 45 (1980) 4296.
259 J.A. Marsella, K.G. Moloy and K.G. Caulton, *J. Organomet. Chem.*, 201 (1980) 389.
260 T.R. Howard, J.B. Lee and R.H. Grubbs, *J. Am. Chem. Soc.*, 102 (1980) 6876.