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Coordination chemistry of cyclopentadienyl titanium carboxylates and related complexes

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CONTENTS

ABSTRACT

The coordination chemistry of cyclopentadienyltitanium carboxylate and its related complexes has been reviewed, with an emphasis on developments in the last decade. The syntheses of these coordination compounds can be carried out in different media, *i.e.* organic, aqueous or even two-phase systems. The aqueous-phase synthesis provides a complementary method for some compounds. By using di- and tetracarboxylic acids, the two-phase system has proven to be very effective for the preparation of novel multinuclear cyclic molecules and polymers, depending upon the reaction conditions. Thus, a variety of new complexes have been prepared and characterized. The molecular structures of most cyclopentadienyltitanium carboxylates have revealed a tetracoordinate, pseudo-tetrahedral coordination geometry. Penta-

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and higher coordinate complexes have also been reported recently and their structures determined by X-ray analyses. A commonly used criterion for distinguishing the M–OOCR coordination mode is the frequency difference between the asymmetric and symmetric OCO stretching modes (*i.e.* $\Delta\nu = \nu(\mathrm{OCO})_{as} - \nu(\mathrm{OCO})_{s}$), which is 200 cm^{-1} or more for monodentate bonding and up to 100 cm^{-1} for chelating bonding. The X-ray data are more supportive for determining the Ti–OOCR bonding nature, and these data have confirmed the monodentate nature of the two carboxylate ligands in $Cp_2Ti(OOCR)_2$ and that of the one carboxylate ligand in $Cp_2TiCl(OOCR)$ complexes. Titanocene carboxylates react with various amines to give amides, this is a new method using organometallics for peptide synthesis under severe conditions. The nuclear magnetic resonance data of meta- and para-substituted benzoate titanocenes of the type $Cp_2Ti(OOCC_6H_4X)_2$ have been analysed, showing good to excellent correlations between the chemical shifts and substituent parameters. The results also indicate a long-range interaction between the substituent X and the cyclopentadienyl ring carbon atoms. In the search for new antitumor agents, some titanocene carboxylates have been tested and found to be active against Ehrlich ascites tumor. In comparison with titanocene dihalides, for example, the hydrogenmaleinate complex is fairly soluble in water and the toxicity of titanocene trichloroacetate is particularly low.

1. INTRODUCTION

The study of π-cyclopentadienyltitanium complexes is generally associated with theoretical and synthetic interests. A number of derivatives have been investigated for potential applications as catalysts in organic synthesis, especially in asymmetric synthesis [1–3], antitumor agents [4], and non-linear optical [5] and polymer materials [6]. These applications in turn provide a great stimulus to fundamental research.

Coordinate compounds of cyclopentadienyltitanium carboxylates represent an important class of complexes in organotitanium chemistry. Some titanocene aliphatic and aromatic carboxylates were first reported, together with their catalytical activities towards polymerization, more than 30 years ago [7,8]. Over the last decade, however, this chemistry has received much more attention, mainly because of the emergence of new complexes with novel structures and reactivities, antitumor activities, as well as other potential uses. Hence, it seems to be appropriate and useful to review these developments.

The present survey will concentrate on recent work, with literature coverage until mid-1993. The theme is the syntheses and structures of mononuclear tetra- and higher coordinate compounds and of multiple nuclear complexes. This review will also cover the advances in mass and nuclear magnetic resonance (NMR) spectral studies and in applications to organic syntheses, antitumor agents, as well as polymer materials. Metal carboxylates, such as halotitanium and tantalum carboxylates, cyclopentadienylzirconium carboxylates and some others, are also included because of their relevance to their cyclopentadienyltitanium counterparts.

2. SYNTHESES AND STRUCTURES

2.1. *Synthetic methodology*

Syntheses have been carried out in organic and aqueous media. The most frequently used method of preparation involves the reaction of titanocene dihalide with a metal salt of an appropriate carboxylic acid in tetrahydrofuran (THF) or other organic solvents [9,10], *i.e.*

$$Cp_2TiX_2 + MOOCR \rightarrow Cp_2Ti(OOCR)_2 + 2MX \tag{1}$$

where M = Na, K, Ag, etc. The replacement of two halides requires a ratio of 1:2 of Cp_2TiX_2 to RCOOM or even in excess of two molar equivalents of RCOOM [11–14].

A modified non-aqueous method of preparation is accomplished by the reaction of Cp_2TiCl_2 with a free carboxylic acid in the presence of a base such as Et_3N or $NaNH_2$. This procedure is applicable to different types of complex, such as $Cp_2Ti(OOCR)_2$ [15–17] and $Cp_2TiX(OOCR)$. $Cp_2TiX(OOCR)$ has been prepared in a 1:1:1 ratio, *i.e.*

$$Cp_2TiCl_2 + HOOCR + base \rightarrow Cp_2TiCl(OOCR) + base \cdot HCl \tag{2}$$

The reported examples of such complexes include cyclopentadienyltitanium complexes of ferrocenecarboxylates [18,19], thiophenylcarboxylates [20], pyridinecarboxylates [21] and N-protected amino acids [22]. It is of interest to note the importance of the ratio Cp_2TiCl_2:carboxylic acid:base in reactions of titanocene dichloride with N-protected amino acids. The ratios 1:1:1 and 1:2:1 give exclusively monocarboxylate derivatives $Cp_2TiCl(OOCR)$, whereas the ratio 1:2:2 yields biscarboxylates $Cp_2Ti(OOCR)_2$, which may also be obtained by the treatment of $Cp_2TiCl(OOCR)$ with one equivalent of RCOOH in the presence of triethylamine [22]. The reaction between Cp_2TiCl_2 and PhCOOH in a molar ratio of 1:1 affords $Cp_2TiCl(OOCPh)$. However, when a molar ratio of 1:2 is used in the presence of NaH, to obtain $Cp_2Ti(OOCPh)_2$, displacement occurs to give $CpTiCl(OOCPh)_2$ [23], which is unusual for the reaction between Cp_2TiCl_2 and RCOOM (M = Na, K, Ag) [11–14,24,25].

Some chlorotitanocene carboxylates also have been prepared by two other methods, as shown by [26,27].

$$Cp_2TiCl_2 + (RCOO)_2Hg_2 \rightarrow Cp_2TiCl(OOCR) \tag{3}$$

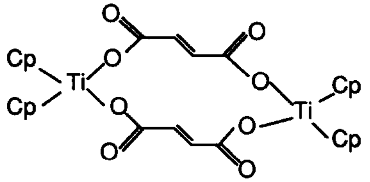
where R = Me, Et, Pr, Ph, and

$$Cp_2TiCl(L) + RCOOH \rightarrow Cp_2TiCl(OOCR) + HL \tag{4}$$

where L = 2-thienyl and R = CCl_3, CBr_3, C_6F_5, $C_6H_4NO_2$-*o*.

A series of carboxylates of the type $(CH_3C_5H_4)_2Ti(OOCR)_2$ is obtained from the sodium salt in water, provided the pH value of the solution is carefully controlled and the aqueous solution of $(CH_3C_5H_4)_2TiCl_2$ is stable up to pH 3 [28]. The reaction of Cp_2TiCl_2 with oxalic acid or maleic acid in boiling water yields the bidentate complex $Cp_2Ti(C_2O_4)$ and the monodentate complex $Cp_2Ti(OOCCH{\dagger}CHCOOH\text{-}cis)_2$ [29] respectively. A separate group has reported on this bidentate complex, though possibly with a different structure and/or composition [30]. Thus, the aqueous phase synthesis provides a complementary method for obtaining some carboxylate compounds [28,31,32]. Doppert and Thewalt obtained the polynuclear complex $[Cp_3Ti_3(OOCH)_3(OH)_3O]OOCH \cdot 2HCOOH$ by the reaction of Cp_2TiCl_2, dissolved in water, with an aqueous solution of NaOH and C_6H_5OH (1:2:1). The precipitate is filtered off and then dissolved in formic acid. The solution is layed with ether. Crystals of the complex grow within a few days [33].

Thewalt and Lunam have also described the two-phase system $H_2O + CHCl_3$ or CH_2Cl_2 and applied it to obtain structurally interesting molecules [34,35]. For example, mixtures of $[Cp_2Ti(OOCCH{=}CHCOO\text{-}trans)]_2$ (**1**) and of the solvate $[(Cp_2Ti(OOCCH{=}CHCOO\text{-}trans)]_2 \cdot 2CHCl_3$ have been prepared by stirring a $CHCl_3$ solution of Cp_2TiCl_2 and an aqueous solution of disodium fumarate in a molar ratio of 1:1. Crystals grow at low temperatures [35]. Similarly, the tetranuclear terephthalate titanium (IV) complex $[Cp_2Ti(OOCC_6H_4COO)]_4$, containing a 36-membered ring, forms as a yellow precipitate upon the treatment of an aqueous solution of Cp_2TiCl_2 with disodium terephthalate (1:1). The preparation of crystals of this complex has also been reported [36]. Other examples include the mononuclear pentadentate complex $Cp_2Ti[O(CH_2CO_2)_2]$, the dinuclear tetra-coordinate complexes $\{Cp_2Ti[O(CH_2CO_2)_2]\}_2 \cdot 2CH_2Cl_2$ [37], $[Cp_2Ti(OOCC{\equiv}CCOO\text{–})]_2$, the tetranuclear complexes $[Cp_2Ti(\mu\text{–}OOCC{\equiv}CCOO)]_4 \cdot 5CH_2Cl_2$ [38], $[Cp_2Ti(C_8N_2O_8)TiCp_2] \cdot 12H_2O$ (pyrazinetetracarboxylate), as well as the heterometallic complex $[Cp_2Ti(C_8N_2O_8)ZrCp_2]_2$ [39].



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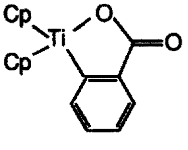
Brintzinger and co-workers found [40] by careful studies on aqueous phase synthesis of salicylate and phthalate titanocene complexes that the exposure time of the product complexes to the aqueous environment is critical. Too short a reaction time leaves large quantities of adducts unreacted or semi-reacted and not easy to separate, whereas prolonged contact with the water medium causes significant decomposition of the complexes, manifested in the loss of the Cp ligand and concomitant formation of additional Ti–O bonds. The aqueous phase synthesis, while exceedingly convenient and certainly useful for some complexes (*vide supra*), has clear limitations and cannot generally replace the clean, albeit cumbersome, anhydrous method of synthesis.

Cyclopentadienyltitanium σ-alkyl and σ-aryl compounds are also useful starting materials. The reaction of CO_2 with Cp_2TiPh_2 gives a five-membered ring carboxylate, *i.e.* $Cp_2Ti(OOCC_6H_4\text{–}o)$ (**2**) [41]. A similar cyclic carboxylate, *i.e.*



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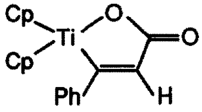

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$Cp_2Ti(OOCCH{=}(Ph)$ (**3**), is obtained by the hydrogenation of Cp_2TiMe_2 under H_2 and with light radiation, followed by treatment with toluene solution of phenylpropiolic acid; however, without H_2, the reaction furnishes $Cp_2Ti(OOCC{\equiv}CPh)_2$ in toluene as an air-stable orange crystalline solid [42].

The heterometallic complexes $Cp_2TiX[(OOCC_6H_5)Cr(CO)_3]$ ($X = Cl, Br, CH_3$) have been synthesized by the reaction of $Cp_2TiX(CH_3)$ with $(HOOCC_6H_5)Cr(CO)_3$ (1 : 1). When two molar equivalents of $(HOOCC_6H_5)Cr(CO)_3$ are used, the reaction of $Cp_2M(CH_3)_2$ affords $Cp_2M[(OOCC_6H_5)Cr(CO)_3]_2$ ($M = Ti, Zr$) [43]. Upon heating CO_2 and $Cp_2Ti(CH_3)_2$ together, CO_2 inserts into Ti–CH_3 bond(s) and $Cp_2Ti(OOCCH_3)_2$ is reported to be the product [44].

The reaction of $(RC_5H_4)_2TiCl(CH_3)$ ($R = H, CH_3, CO_2CH_3$) with acetic or chloroacetic acid has been investigated kinetically [45], *i.e.*

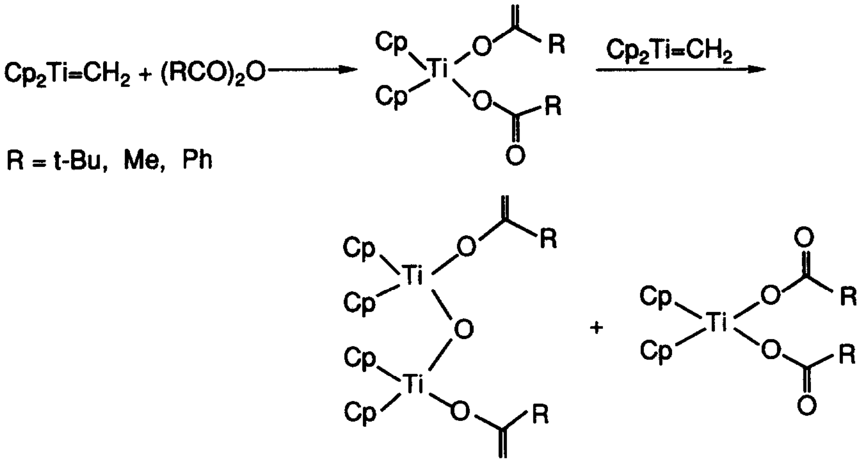
$$(RC_5H_4)_2TiCl(CH_3) + HOOCR' \rightarrow (RC_5H_4)_2TiCl(OOCR') + CH_4 \qquad (5)$$

The rates are determined with pseudo-first-order conditions in acid and are complicated by the second equilibrium

$$2(RC_5H_4)_2TiCl(OOCR') \rightarrow (RC_5H_4)_2TiCl_2 + (RC_5H_4)_2Ti(OOCR')_2 \qquad (6)$$

Schobert and co-workers described some unexpected substitution reactions of alkoxy-, acyloxy- and chlorobis(cyclopentadienyl)methyltitanium(IV) complexes with carboxylic acids [46]. Exclusive substitution of the alkoxy ligand is observed in the reactions of $Cp_2TiOR(CH_3)$ ($R = CHPh_2$, menthyl, (1s)bornyl) with R'COOH ($R' = CHPh_2$, $CH = CHPh$, Ph). The treatment of $Cp_2TiCl(CH_3)$ with one equivalent of R'COOH ($R' = CHPh_2, CF_3$) yields an exact 1 : 1 mixture of titanocene dichloride and the biscarboxylate complexes. No complexes with a mixed-ligand distribution could be detected by NMR and thin layer chromatography (TLC) [46].

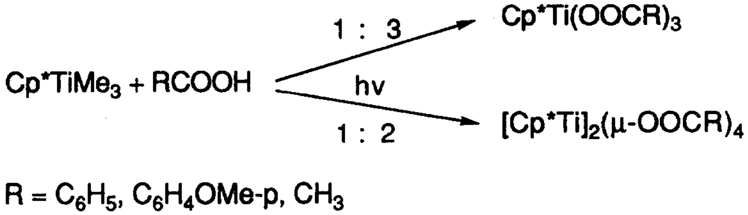
The reactive 16-electron species $Cp_2Ti = CH_2$, generated *in situ* from either its aluminum alkyl adducts or olefin adducts [47], react with acid anhydrides to yield carboxylate complexes, some of which are otherwise difficult to synthesize [48]:



(7)

The acetylene complexes $Cp_2Ti(PMe_3)(CH{\equiv}CH)$ and $Cp_2Ti(PMe_3)(CH_3CH{\equiv}CCH_3)$ react with trifluoroacetic acid to give very unstable alkenyl complexes, *i.e.* $Cp_2Ti(RC{=}CHR)(OOCCF_3)$ (R = H, CH_3). Treatment of these two alkenyl complexes with water and trifluoroacetic acid affords the oxo-bridged dinuclear complex $[Cp_2Ti(OOCCF_3)]_2\mu$-O and the biscarboxylate complex $Cp_2Ti(OOCCF_3)_2$ [49,50]. The $Cp_2Ti(OOCCF_3)_2$ was previously reported by a separate group [51].

The trimethyl complex $Cp^*Ti(CH_3)_3$ is highly reactive towards carboxylic acids and the reaction products are carboxylate compounds [52,53].

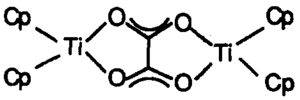


(8)

Two titanocene dipicolinate derivatives have been synthesized by the reaction of $Cp_2Ti(CH_3)_2$ or $(CH_3)_2C_2(C_5H_4)_2Ti(CH_3)_2$ with pyridine-2,6-dicarboxylic acid [54]. Initial attempts to make these complexes failed, because other methods commonly employed for the synthesis of titanocene biscarboxylate complexes, such as the reaction of Cp_2TiCl_2 with free carboxylic acids in the presence of triethylamine, or with two equivalents of sodium carboxylate [10], in the case of dipicolinic acid or its disodium salt, gave mainly products insoluble in $CHCl_3$ or THF.

Low-valent titanium reagents are most widely used in carbonyl coupling reactions of organic and organometallic compounds [3,55–59]. Low-valent organotitanium species frequently used include $[CpTiCl_2]_n$, $[Cp_2TiCl]_2$, $Cp_2Ti(CO)_2$, $Cp_2Ti(PMe_3)_2$ and others generated by the reduction of Cp_2TiCl_2 with a number of reducing agents [3,9,60,61]. The preparative methods for titanium (IV) carboxylate complexes are also applicable to those carboxylate compounds in which titanium has a formal oxidation state below 4 [9,34,59].

Compounds of the type $[\mathrm{CpTi(OOCR)_2}]_2$ have been obtained by the treatment of $[\mathrm{CpTiCl_2}]_n$ with the sodium salt of the appropriate carboxylic acid in THF solution or with the free carboxylic acid in the presence of *n*-butylamine or triethylamine [62].



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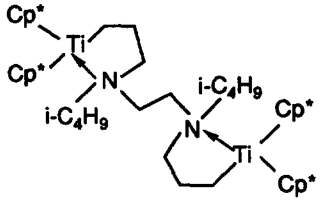
Dititanocene oxalate $(\mathrm{Cp_2Ti})_2(\mathrm{C_2O_4})$ (4) can be prepared by the reaction of oxalic acid with $\mathrm{Cp_2TiH_2BH_2}$ (from $\mathrm{Cp_2TiCl_2}$ and $\mathrm{NaBH_4}$ in THF) in benzene as dark-blue crystals [63]. This compound also has been described as a purple precipitate obtained by the treatment of a deoxygenated water solution of $[\mathrm{Cp_2TiCl}]_2$ with a fourfold molar excess of aqueous solution of $\mathrm{K_2C_2O_4}$. The precipitate may be recrystallized from THF+ether to give a solvate $[\mathrm{Cp_2Ti}]_2\cdot 1/2\mathrm{OEt_2}$. Solvent-free crystals also have been reported [64]. A third preparative method involves the reaction of $\mathrm{Cp_2Ti(CO)_2}$ with a THF solution of oxalic acid (2:1). Dark-blue crystals may be obtained by recrystallization from toluene [65].



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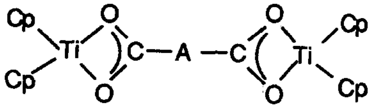
$(\mathrm{Cp^*_2Ti})_2(\mathrm{C_2O_4})$ has been obtained from $[\mathrm{Cp^*_2Ti}](\mathrm{C_{16}H_{34}N_2})$ (5) and $\mathrm{CO_2}$ in benzene [66], as given by

$$2[\mathrm{Cp^*_2Ti^{III}}]_2(\mathrm{C_{16}H_{34}N_2})+6\mathrm{CO_2}\rightarrow 2\mathrm{Cp^*_2Ti^{IV}}(\mathrm{OOCC_{16}H_{34}N_2COO}) + [\mathrm{Cp^*_2Ti^{III}}]_2(\mathrm{C_2O_4}) \qquad (9)$$

Dicarbonyltitanocene $\mathrm{Cp_2Ti(CO)_2}$ has been employed in the preparation of a series of compounds with dicarboxylate bridges other than oxalate the oxalate $\mathrm{Cp_2Ti(OOC\text{-}A\text{-}COO)TiCp_2}$ (6). $\mathrm{Cp_2Ti(CO)_2}$ reacts with the dicarboxylic acid (2:1) in THF to give a green–blue powder, which can become dark-blue crystals upon crystallization from toluene [65,67]. If the carboxylic acid is unsaturated, it is hydrogenated to varying extents, depending on the particular acid. It was confirmed by labelling experiments that the acidic hydroxy groups are the source of the



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hydrogen atoms in the hydrogenation reaction [68]. Also, since the low-valent titanium compounds are less stable, protection conditions are required to avoid oxidation of the products.

The inorganic counterparts of cyclopentadienyltitanium carboxylates have been readily obtained at room temperature by the reaction of $TiCl_4$ with carboxylic acids [69–74]. Heterobimetallic carboxylates $TiMgCl_4(OOCR)_2 \cdot 2EtOAc$ are obtained by the reaction of the complex $TiMgCl_6 \cdot 4EtOAc$ with 2 mol acid RCOOH (R = Ph, PhCH = CH, p-Me_3CPh, Me_2CCH) [75].

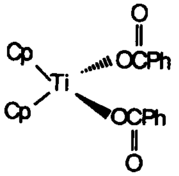
2.2. *Mononuclear tetra-coordinate complexes*

The molecular structures of a vast number of dicyclopentadienyltitanium (IV) compounds studied to date have invariably revealed a tetra-coordinate, pseudo-tetrahedral coordination geometry. The examples of such carboxylate complexes are numerous. The dicyclopentadienyltitanium biscarboxylates of the type $Cp_2Ti(OOCR)_2$ have been studied for decades [9,10], where R is alkyls, halogenated alkyls [76], alkenyls such as CH=CHCOOH [29,77], alkynes, such as C≡CPh [42], a series of unsubstituted and substituted phenyls [11,15,24,25], heterocycles [20–22], as well as organometallic moieties [12,18,19,39]. Substituted cyclopentadienyl and indenyltitanium carboxylates are also known [14,28,30,31].

Bonding modes for the carboxylates have been discussed in a number of papers, where two structural features have been proposed. The question concerns whether the carboxylate ligand is monodentate or bidentate to the titanium center.

A commonly used criterion [78,79] for distinguishing the M–OOCR coordination mode is the frequency difference between the asymmetric and symmetric OCO stretching modes ($\Delta\nu = \nu(OCO)_{as} - \nu(OCO)_s$), which is 200 cm^{-1} or more for monodentate bonding and up to 105 cm^{-1} for chelate bonding. For the compounds $(CH_3C_5H_4)_2Ti(OOCR)_2$, the difference $\Delta\nu$ is less than 100 cm^{-1}, so the two carboxylate ligands were described as bidentate [28]. Ever since, this structure assignment has been claimed also for other similar carboxylate complexes [20–22,80,81], but with little confirmatory evidence, especially a lack of X-ray structure analysis data.

New results have confirmed the monodentate nature of the two carboxylate ligands in $Cp_2Ti(OOCR)_2$. The X-ray analyses of $Cp_2Ti(OOCPh)_2$ (7) show that the molecule has a distorted tetrahedral structure in which the titanium atom is attached to two η-C_5H_5 groups and two monodentate benzoate ligands. The two carboxylate



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ligands are different, one of which has a Ti—O—C angle of 147.9(7)° [15], 135.2(3)° [82] or 135.4(6)° [13], and longer Ti—O (1.930(5) Å [15], 1.995(3) Å [82] or 1.976(5) Å [13]) and O—C (1.299(2) Å [15], 1.275(5) Å [82] or 1.267(10) Å [13]) bonds, while the other has a Ti—O—C angle of 148.6(4)° [15], 168.7(3)° [82] or 157.0(7)° [13], with shorter Ti—O (1.922(7) Å [15], 1.894(4) Å [82] or 1.913(6) Å [13]) and O—C (1.204(10) Å [15], 1.208(5) Å [82] or 1.267(10) Å [13]) bonds.

The relatively short Ti—O bond lengths and large Ti—O—C bond angles suggest that $Cp_2Ti(OOCR)_2$ complexes, which are formally 16-electron complexes if only Ti—O σ bonding is considered, achieve an effective 18-electron configuration via Ti—O π bonding. Extended Hückel molecular orbital (EHMO) calculations confirm the existence of a strong π-type interaction, involving the $1a_1$ orbital of the Cp_2Ti^{2+} fragment and in-plane p orbitals of the coordinated benzoate oxygen atoms. EHMO calculations and geometrical considerations indicate that the alternative coordination geometry which has one monodentate and one bidentate carboxylate ligand is precluded by O–C steric interactions [15].

The structural feature of $Cp_2Ti(OOCPh)_2$ has been used to explain its reaction with bromine. The structural consequences of the bonding mode are that the approach to the titanium atom is hindered on the side of the less bent carboxylate (*i.e.* with a large Ti—O—C bond angle). Thus, attack by Br_2 occurs preferentially on one side of the molecule, giving the ring cleaved product of $C_5H_5Br_3$ or $C_5H_5Br_5$ in which bromination indeed occurred stereospecifically [13].

The monodentate nature of the two carboxylate ligands is also confirmed by X-ray analyses of the phenyl-substituted derivatives $Cp_2Ti(OOCC_6H_4OCH_3\text{-}m)_2$ (**8**) [83] (Fig. 1), $(CH_3C_5H_4)_2Ti(OOCC_6H_4CH_{3-o})_2$ [14], as well as other complexes such as $Cp_2Ti(OOCHC{=}CHCOOH\text{-}cis)_2$ and $Cp_2Ti(OOCCF_3)_2$ [29,49].

For more complicated systems, such as $Cp_2Ti[(OOCC_5H_4Fe(CO)_2(CH_2C_6H_5)]_2$ (**9**) [12], $Cp_2TiX[(OOCC_6H_5)Cr(CO)_3]$ (X=Cl, Br, CH_3) and $Cp_2Ti[(OOCC_6H_5)Cr(CO)_3]_2$ [43], the coordination of the carboxylate ligand(s) is not perturbed by the iron and chromium metal, respectively, as it is in monodentate mode. However, for their zirconium counterparts, such as $Cp_2Zr[(OOCC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ and $Cp_2Zr[(OOCC_6H_5)Cr(CO)_3]_2$, the IR spectra indicate one monodentate and one bidentate attachment to the zirconium metal. Furthermore, the NMR data suggest fast interconversion between the two carboxylate groups at room temperature, *i.e.* $Cp_2Zr(OOCR)_2$ (**10**) [12,43] (Scheme 1).

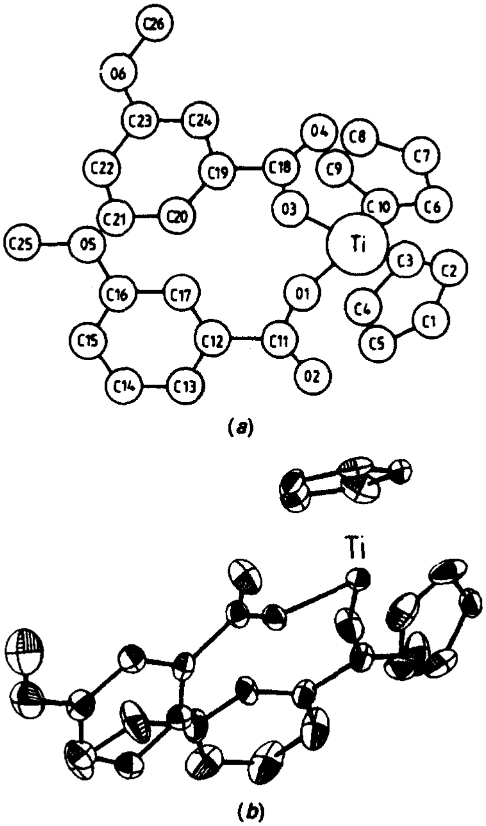
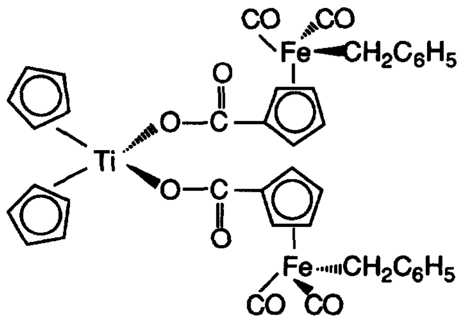


Fig. 1. (a) Structural formula and atomic numbering scheme of $Cp_2Ti(OOCC_6H_4OCH_3-m)_2$ (**8**) and (b) ORTEP view.



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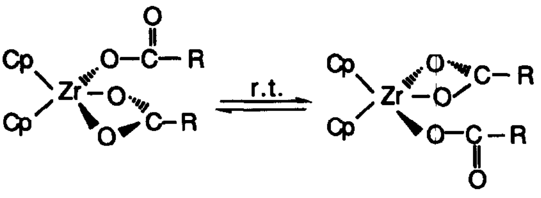

R = $(C_5H_4)Fe(CO)_2(CH_2C_6H_5)$, $(C_6H_5)Cr(CO)_3$

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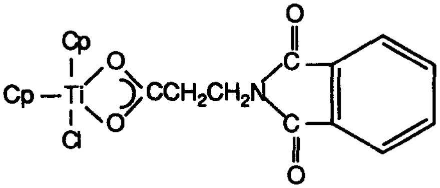
Scheme 1. $Cp_2Zr(OOCR)_2$ (**10**).

It would be interesting to see if the carboxylate acts as a bidentate ligand in the complexes of the type $Cp_2TiX(OOCR)$, where R is ferrocenyl [18,19], thiophene [20] or pyridine [21]. X-ray analyses would be very helpful to confirm the carboxylate ligand bonding mode of the following $Cp_2TiCl(OOCCH_2CH_2NO_2$-$C_2C_6H_4$-*o* (**11**) structure, which was proposed on the basis of IR data [81].



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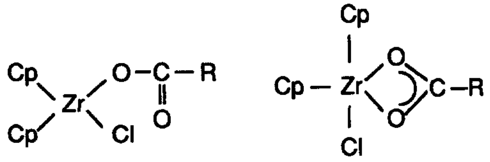
IR spectral data also have been used to discern the carboxylate bonding modes of the chlorozirconocene carboxylates $Cp_2ZrCl(OOCR)$ (R = H, CH_3, $C(CH_3)_3$, Ph), giving monodentate η^1-O (**12a**), and bidentate or chelating η^2-O, O′ (**12b**).

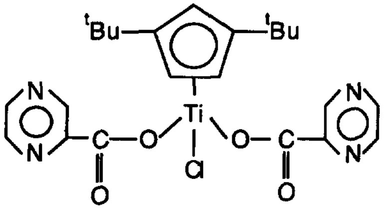


a **b**

12

The formate (R = H) exists as a mixture of monodentate η^1-O (**12a**; $\nu(COO)_{as}$ 1628 cm^{-1}/$\nu(COO)_s$ 1372 cm^{-1}) and bidentate η^2-O, O′ (**12b**; $\nu(COO)_{as}$ 1562 cm^{-1}/$\nu(COO)_s$ 1372 cm^{-1}) structures. The other three chlorozirconocene carboxylates favor the chelating form (**12b**) [84]. This proves that the Zr—OOCR bonding modes are indeed different from the corresponding Ti—OOCR bonding modes. More convincing results are obtained by X-ray analysis.

Since a large $\Delta\nu$ value (335 cm^{-1}) is observed in the pyrazine carboxylate complex of mono(1,3-di-*t*-butyl-cyclopentadienyl)titanium (IV) trichloride which was prepared by stirring overnight a mixture of $(1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)\text{TiCl}_3$ and 2-pyrazine carboxylic acid (molar ratio 1 : 1) in benzene, the monodentate mode of bonding is most likely (**13**) [85]. However, earlier studies showed small $\Delta\nu$ values (less than 100 cm^{-1}) in mono(cyclopentadieny)titanium derivatives with caprylic, lauric, myristic, palmitic, stearic and behenic acids, and the carboxylate ligand was assigned to be bidentate (**14**) [86].



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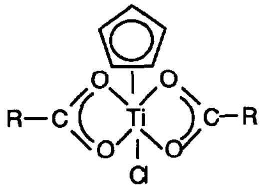

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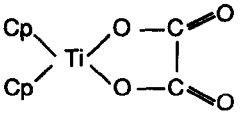
The single-crystal X-ray structures of four mononuclear carboxylate derivatives of titanocene metallacycles have been determined: $\text{Cp}_2\text{Ti}(\text{C}_2\text{O}_4)$ (**15**) [29], $\text{Cp}_2\text{Ti}(\text{OOCC}_6\text{H}_5)$ (**16**) [87] $\text{Cp}_2\text{Ti}(\text{OOCC}_6\text{H}_4\text{-}o)$ (**2**) [41] and $\text{Cp}_2\text{Ti}(\text{OOCCH{=}CC}_6\text{H}_5)$ (**3**) [42].



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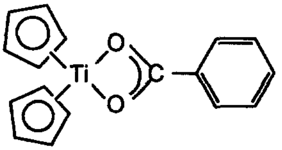

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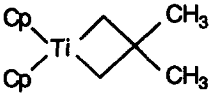
There are two independent $\text{Cp}_2\text{Ti}(\text{OOCC}_6\text{H}_5)$ molecules in the unit cell; both have similar bond distances and angles. The angles and distances within the titanium coordination sphere are those expected for pseudo-tetrahedral coordination [87]. The benzoate group acts as a bidentate chelating ligand. The compound was prepared either via the reaction of $[Cp_2TiCl]_2$ and $KOOCC_6H_5$ in H_2O or via the reaction of $Cp_2Ti(CO)_2$ and $HOOCC_6H_5$ in THF.

The X-ray structure analysis of the dark-red compound $[Cp_2Ti(OOCCH{=}CC_6H_5)\cdot C_6H_5C{\equiv}CCOOH]$ showed the unit cell to be composed of a titanocene metallacycle in which titanium is η^5 bonded to two cyclopentadienyl rings and to one oxygen atom in a five-membered metallacycle. It has a larger Cnt(1)–Ti–Cnt(2) angle of 134.9° compared with that of 133.3° in $Cp_2Ti(C_2O_4)$ (**4**) [29] and that of 134° in $Cp_2Ti(OOCC_6H_4\text{-}o)$ (**2**) [41].

NMR experiments suggested the formation of seven- and eight-membered titanocene metallacycle carboxylates. Upon reaction with $Cp_2Ti(C_5H_{10})$ (**17**), phthalic anhydride yielded ^1H NMR data consistent with the formation of the proposed enolate $Cp_2Ti(O_3C_3H_2C_6H_4\text{-}o)$ (**18**), while a similar treatment of glutaric anhydride indicated the formation of the proposed enolate $Cp_2Ti(C_6H_8O_3)$ (**19**). However, they were not isolated [48].



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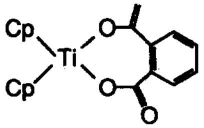

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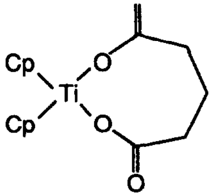

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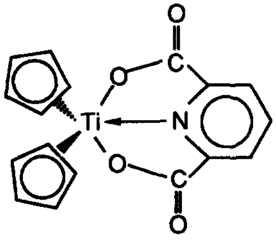
2.3. Mononuclear penta- and higher coordinate complexes

Titanocene dipicolinate $Cp_2Ti(C_7H_3NO_4)$ is the first reported penta-coordinate carboxylate complex of titanocene determined by X-ray diffraction. The compound is prepared by stirring a mixture of a toluene solution of dimethyltitanocene $Cp_2Ti(CH_3)_2$ and a suspension of dipicolinic acid in THF at room temperature. Upon evaporation of the solvents and subsequent recrystallization from toluene + hexane, the complex is obtained as a yellow solid which is readily soluble in methylene dichloride, diethyl ether or toluene. Slow evaporation from a chloroform solution gives crystals suitable for X-ray crystal structure determination [54]. Its aqueous phase preparation also has been reported [40].

The molecular structure shows that the dipicolinate ligand is bound to the titanium center by its pyridine nitrogen atom and two of the carboxylate oxygen atoms, which occupy the central and the two lateral coordination sites of the titanocene fragment ($Cp_2Ti(C_7H_3NO_4)$) (**20**). The Ti–N and Ti–O distances of 2.16 Å and 2.11 Å are significantly longer than the Ti–N= bonds (1.96–2.02 Å) [88–90] and Ti–O bonds (1.86–1.90 Å) [91–93] in comparable tetra-coordinate titanocene complexes. The O–Ti–N angle of 71.1° is within the range 65–73° found for other penta-coordinate, non-hydridic metallocene derivatives [94,95]. Two identical chelate bite angles of only 71° make the dipicolinate ligand particularly suited to forming a remarkably stable titanocene derivative with penta-coordinate geometry [54]. This has been further confirmed by the crystal structure of another nitrogen-chelating titanocene carboxylate $Cp_2Ti(C_8H_2N_2O_8)$ (**21**) [39].



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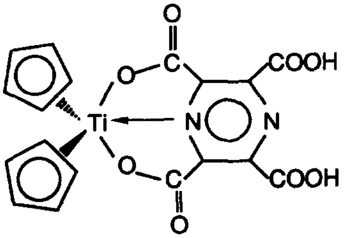

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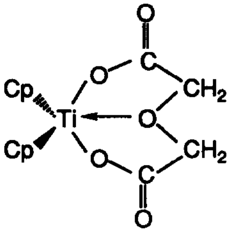
Unlike titanocene biscarboxylate derivatives, titanocene dipicolinate is quite inert to ligand exchange reactions. The hydrolysis of $Cp_2Ti(C_7H_3NO_4)$ in mixed aqueous solvents, such as H_2O + THF or H_2O-saturated chloroform, proceeds at a remarkably slow rate. Even conversion into Cp_2TiCl_2 by treatment with gaseous HCl in chloroform requires about 30 min for completion [54].

The reaction of Cp_2TiCl_2 with dipicolinic acid in the presence of triethylamine gives $Cp_2TiCl(C_7H_4NO_4)$ (1:1:1) and $Cp_2Ti(C_7H_4NO_4)_2$ (1:2:2) respectively. A penta-coordinate geometry is proposed for the chlorotitanocene dipicolinate and a hexa-coordinate geometry for the bisdipicolinate derivative. In both cases, the dipicolinate group is a bidentate ligand and the nitrogen atom is not bound to the titanium atom. The assignments are based on the small $\Delta\nu$ values (70–120 cm^{-1}) and lack support from crystal structure determinations [21].

The disodium salt of oxydiacetic acid $NaOOCCH_2OCH_2COONa$, which has a potential chelating oxygen atom, reacts with Cp_2TiCl_2 in the two-phase system of $H_2O + CHCl_3$ to give $Cp_2Ti[O(CH_2COO)_2]$. Its crystal structure determined by X-ray diffraction shows a mononuclear penta-coordinate geometry, *i.e.*



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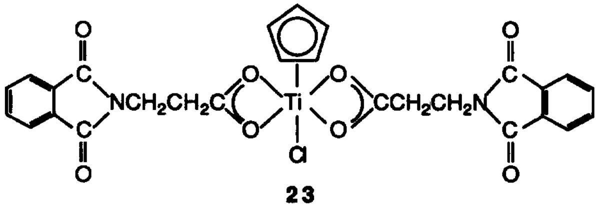
$Cp_2Ti[O(CH_2COO)_2]$ (**22**). The analogous reaction with Cp_2ZrCl_2 affords $Cp_2Zr[O(CH_2COO)_2]$, which is isostructural with the titanocene derivative (**22**) [37].

In comparison with titanocene dipicolinate, titanocene oxydiacetate has an expectedly longer Ti<O bond (2.21 Å) and an even shorter Ti–O bond (2.10 Å). The O–Ti<O angle is 69.7° [37].

Many other titanocene carboxylates are proposed without X-ray data to be penta- or hexa-coordinate species such as thiophenecarboxylates [20], pyridinecarboxylates [21], N-protected amino acid derivatives [22,81]



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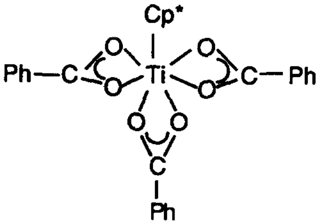
$(CpTiCl(OOCCH_2CH_2NC_2O_2C_6H_4\text{-}\phi)_2$ (**23**)), and carboxylates with bidentate and tridentate atom(s) [32,86].

A hepta-coordinate geometry has been assigned to the trisbenzoate compound



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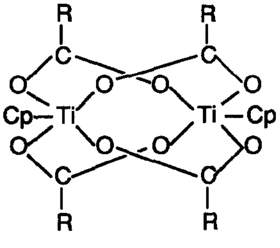
$Cp^*Ti(OOCPh)_3$ (**24**) which is readily obtained by the reaction of $Cp^*Ti(CH_3)_3$ with PhCOOH. The molecular structure shows one benzoate group nearly perpendicular to the other two, suggesting a distorted pentagonal bipyramidal coordination (**24**) [52,53]. The bidentate nature of the three benzoate ligands is further confirmed by the facts that the three O–Ti–O angles of 59.06°, 61.4° and 60.0° are close to those of 60.9° and 60.5° found in $Cp_2Ti(OOCPh)$, in which the Ti–O bond distances of 2.13 and 2.15 Å are also within the range 2.10–2.21 Å in $Cp^*Ti(OOCPh)_3$ [53].

More recently, some zirconocene dipicolinate and related biscarboxylate complexes have been obtained, and their coordination geometries and reactivities investigated [96].

2.4. Binuclear complexes

In the 1970s, studies confirmed the binuclear nature of a series of cyclopentadienyltitanium (III) biscarboxylates. $CpTiCl(OOCR)_2$ (**25**) shows the general structure, where $R = CF_3$, Me, Et, Pr, Ph [60,62,63,94,95].



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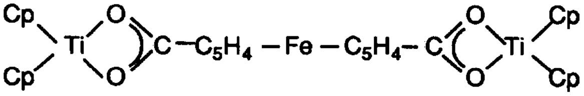
An X-ray structure determination of cyclopentadienyltitanium (III) bisbenzoate has been described, showing the formation of four carboxylate bridges. The intramolecular Ti–Ti distances are 3.63 and 3.74 Å, indicating that there is no Ti–Ti bonding [97] (**25**, R = Ph).

In the 1980s, a number of dititanocene carboxylates were synthesized, in which the two titanocene fragments were bridged by a dicarboxylate dianion group (**6**). In **6**, A represents a hydrocarbon, such as a saturated [–$(CH_2)_n$–], an unsaturated

(–CH=CH– or –C≡C–), a cyclic, an aromatic ($–C_6H_4–$), or an organometallic [$(C_5H_4)_2Fe$] species [65,67,68,87,98].

The compounds are paramagnetic. The electron paramagnetic resonance (EPR) spectra of over 20 binuclear titanocene carboxylates of the type shown in **6** have been recorded and the question of whether or not a saturated bridge could propagate a magnetic exchange interaction between two distant Cp_2Ti^{III} moieties investigated.

An antiferromagnetic exchange interaction has been observed in the solid state of the complexes. The interaction is intramolecular in origin. For example, in the series of complexes bridged by $–OOC(CH_2)_nCOO–$ ($n=0–4$, 6, 8, 10) dianions, it decreases monotonically as the value of n is increased [65] and, in the phthalate-bridged complexes, it decreases as the bridge is changed from the phthalate dianion ($J=-2.8\ \mathrm{cm^{-1}}$) to the isophthalate dianion ($J=-1.4\ \mathrm{cm^{-1}}$) and finally to the terephthalate dianion ($J=-0.7\ \mathrm{cm^{-1}}$). The magnitudes of the exchange parameters for these three phthalate-bridged complexes are intermediate between those of the corresponding cyclic and aliphatic complexes. The antiferromagnetic exchange interactions are propagated by σ orbital overlaps. This is further substantiated by the fact that the exchange interaction seen for the fumarate-bridged complex is the same as that seen for the succinate-bridged complex. The ferrocene-1,1′-dicarboxylate-bridged complex $Cp_2Ti(OOCC_5H_4FeC_5H_4COO)TiCp_2$ (**26**) also exhibits an antiferromagnetic exchange interaction with $J=-0.78\ \mathrm{cm^{-1}}$ and $g=2.03$. The C–Fe–C fragment provides the interconnecting electron density between the two Cp_2TiOOC moieties [67].



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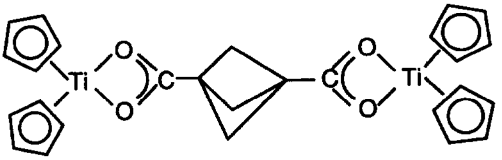
The X-ray structure of binuclear titanocene carboxylate bridged by the bicyclo[1,1,1]pentane-1,3-dicarboxylate dianion, *i.e.* $Cp_2Ti(OOCC_5H_6COO)TiCp_2$ (**27**) shows normal pseudo-tetrahedral distances and angles for each of the titanium (III) ions. The complex is centrosymmetric with the bicyclo[1,1,1]pentane moiety disordered equally in two positions, and with an intramolecular Ti–Ti distance of 9.8509(6) Å, which is found to be 7.8326(11) Å in the binuclear complex $Cp_2Ti(OOCC_4H_6COO)TiCp_2$ (**28**). The complex $Cp_2Ti(OOCC_4H_6COO)TiCp_2$ is



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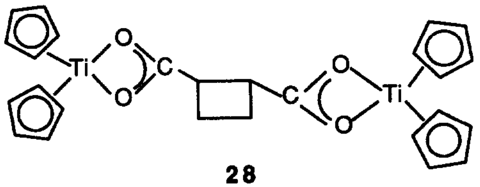

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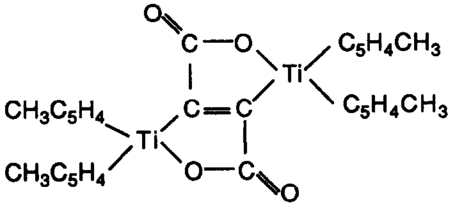
bridged by the *trans*-cyclobutane-1,2-dicarboxylate anion and the cyclobutane ring is non-planar with a dihedral angle of 153° [87].

(μ-Acetylenedicarboxylato)bis[bis(η^5-methylcyclopentadienyl)titanium],



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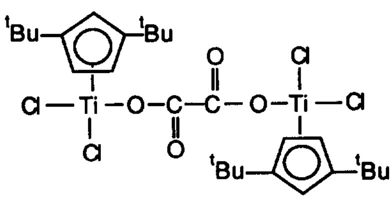
[(CH$_3$C$_5$H$_4$)$_2$Ti(CCOO)]$_2$ (**29**) has been synthesized from the dipotassium salt of acetylenedicarboxylic acid and [(CH$_3$C$_5$H$_4$)$_2$TiCl]$_2$. The molecular structure shows that two titanium atoms coordinate to the two- and three-carbon, respectively, and to a carboxylate oxygen atom to form five-membered chelate rings [68].

The oxalate-bridged binuclear complexes (Cp$_2$Ti)$_2$(C$_2$O$_4$) (**4**) [63–65] and (Cp$^*_2$Ti)$_2$(C$_2$O$_4$) [66] also have five-membered metallacycles. The oxalate group acts as a planar tetradentate bridging ligand, with the titanium atoms displaced in a *cis* fashion out of the C$_2$O$_4^{2-}$ plane [64]. Structural comparison has been made between (Cp$_2$Ti)$_2$(C$_2$O$_4$) (**4**) and Cp$_2$Ti(C$_2$O$_4$) (**15**) [29], showing that the binuclear complex has a longer Ti–O distance (2.16 Å) and a smaller O–Ti–O angle (75.8°), compared with 2.00 Å and 79.4 Å found in the corresponding mononuclear complex.

The treatment of (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$TiCl$_2$ with sodium oxalate (2:1) in THF gives



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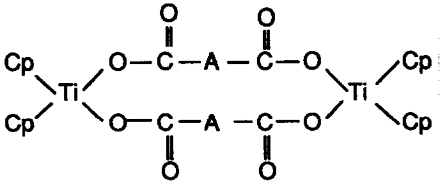
rise to the crystalline compound [(1,3-^{t}Bu$_2$C$_5$H$_3$)TiCl$_2$]$_2$-μ-(C$_2$O$_4$) (**30**), and monodentate bonding has been proposed [85].

There are several binuclear complexes in which two Cp$_2$Ti^{IV} are bridged by



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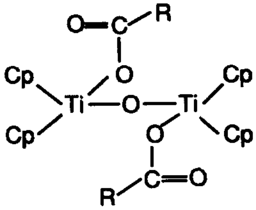
two dicarboxylate dianions, *i.e.* $Cp_2Ti(OOC{-}A{-}COO)_2TiCp_2$ (**31**), where A is $-(CF_2)_n-$ [76], –CH=CH–*trans* [35], –C≡C– [39] and $-CH_2OCH_2-$ [38]. Crystal data for $[Cp_2Ti(OOCCH{=}CHCOO$–*trans*$)]_2$ and the solvate $[Cp_2Ti(OOCCH{=}CHCOO$–*trans*$)]_2 \cdot 2CHCl_3$ are available. X-ray analysis of the solvent-free compound shows that the titanium atoms and the atoms of the dicarboxylate bridges are not coplanar. The molecule lies on a crystallographic center of symmetry. It is different from the solvate complex in the puckering of their central 14-membered rings and in the geometry of the TiOC fragments [35]. In addition, some dicarboxylates, such as 3,4-dimethoxyfuran-2,5-dicarboxylate or isophthalate, form binuclear zirconocene complexes with one bidentate and one monodentate carboxylate ligand [96].

The oxo-bridged binuclear complexes have been known for titanocene carboxylates, *i.e.* $[Cp_2Ti(OOCCH_3)]_2\mu$-O (**32**), and chlorotitanium (IV) carboxylate derivatives. $[Cp_2Ti(OOCCH_3)]_2\mu$-O (**32**, $R=CH_3$) was isolated as an impure product in a yield of 11% from $Cp_2Ti(C_5H_{10})$ (**17**) and acetic acid in ether. The IR band appeared at 730 cm^{-1} (O–Ti–O). Another oxo-bridged complex $[Cp_2Ti(OOCPh)]_2\mu$-O (**32**, R = Ph) was formed together with other products, in the reaction of $Cp_2Ti(C_5H_{10})$ with benzoic anhydride, but it was not isolated from the reaction mixture [48].



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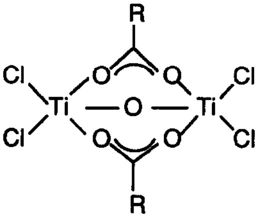
The η^1-alkenyl complexes $Cp_2Ti(CR{=}CHR)(OOCCF_3)$ ($R=H$, CH_3) react with water and trifluoroacetic acid to give the complex $[Cp_2Ti(OOCCF_3)]_2$-μ-O (**32**, $R=CF_3$). The crystal and molecular structures of the oxo-bridged complex have been determined by X-ray diffraction, showing the two Ti–O (bridged) distances to be 1.836 Å and the Ti–O–Ti angle 173.3° [50].

The yellow crystalline binuclear complexes $Ti_2Cl_4(\mu\text{-}O)(\mu\text{-}OOCR)_2 \cdot 2L$ (**33**, L =



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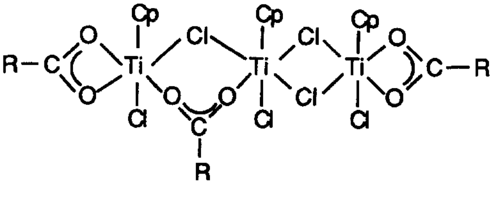
EtOAC, THF) are obtained in a high yield (about 80%) by the reaction of one molar equivalent of water with $TiCl_3(OOCR)$ ($R = CH_3$, Ph) or $TiCl_2(OOCCH_3)_2$ in a solution of the appropriate ligand. The compounds (**33**, $R = CH_3$, Ph) are stable under dry nitrogen, but are slowly hydrolyzed in air. It is noteworthy that the two μ-oxo complexes are formed by hydrolysis of either a Ti–Cl bond in $TiCl_3(OOCCR)$ or a Ti–carboxylate bond in $TiCl_2(OOCCH_3)_2$, indicating the stability of the μ-oxocarboxylate unit formed in the hydrolysis of compounds shown in **33**.

The X-ray structure of the adducts (**33**, R = Ph) shows near-octahedral coordination around the two metal atoms, with the ligand (EtOAC or THF) being *trans* to the bridging oxygen. The acetate derivative (**33**, $R = CH_3$) is isomorphous and virtually isostructural [69,71].

The presence of both bridging oxygen and carboxylate groups is confirmed with a Ti–O–Ti angle of 137.4°, which is much smaller than that of 173.3° found in the oxo-bridged titanocene trifluoroacetate (**32**, $R = CF_3$) [50]. The deviation of this angle from the ideal 180° clearly results from the presence of the two carboxylate bridges. It has been determined that the oxygen atom of the μ-oxo bridge arises from the water added [69].

2.5. *Multinuclear complexes*

$[CpTi(OOCR)Cl_2]_3$ compounds (with the proposed formula shown in **34**) can be prepared by allowing the appropriate carboxylic acid to react with $CpTiCl_3$ in the presence of *n*-butylamine (1:1:1) in THF at room temperature. The product



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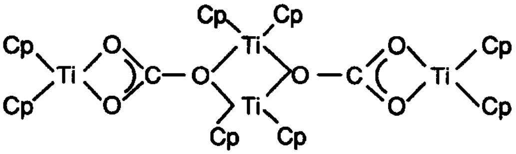
may be recrystallized from benzene to give yields of 75%–80%. The complexes are susceptible to hydrolysis. The trinuclear nature follows from ebullioscopic molecular weight determination in benzene [86].



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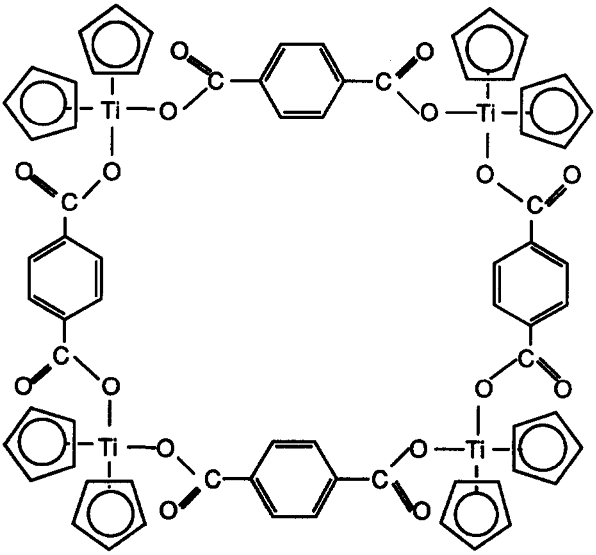
The tetranuclear complex $[(Cp_2Ti)_2CO_3]_2$ (**35**) can be obtained by the reaction of $[Cp_2Ti]_2$ or $[Cp_2Ti]_2O$ with CO_2 in toluene. It is precipitated from the solution by adding hexane. It can be recrystallized from toluene [99,100]. This compound is paramagnetic, with $\mu_{eff} = 1.70\mu_B$ per titanium atom at 293 K [99]. The EPR spectrum of a THF solution at 20°C shows a single line with $g = 1.980$. The solid compound shows no half-field line at -196°C [100].

The solid compound is green. A freshly prepared toluene or THF solution is also green but becomes blue over time — the THF solution sooner than the toluene solution. Evaporation of the solutions provides the solid green starting compound. The color change is probably caused by a tetranuclear (green)↔dinuclear (blue) equilibrium [100]. X-ray structure analysis shows the molecule with crystallographic C_{2h} symmetry [99].

Thewalt *et al.* determined the structures of several tetranuclear titanocene carboxylates by X-ray crystallography. Terephthalate titanocene, $[Cp_2Ti(OOCC_6H_4COO)]_4$ which contains a 36-membered ring (**36**), is shown to be folded in such a way that the two phenyl rings are packed parallel to each other with an interring distance of about 3.7 Å. The average Ti—O distance is 1.94 Å and the average O—Ti—O angle is 90.5°. This complex is unstable in air and is solvated [36].

The acetylenedicarboxylate-bridged compound $[Cp_2Ti(OOCC{\equiv}CCOO)]_4 \cdot 5CH_2Cl_2$, containing a 28-membered ring (**37**),has a crystallographic symmetry of four with a saddle-like conformation. The regions in the crystal structure occupied by the CH_2Cl_2 may be occupied by dioxane, to give $[Cp_2Ti(OOCC{\equiv}CCOO)]_4 \cdot 5C_4H_8O_2$ [38].

Titanocene dichloride reacts with tetrasodium pyrazinetetracarboxylate in the water + $CHCl_3$ system to give the tetranuclear complex $[Cp_2Ti(C_8N_2O_8)TiCp_2]_2$ (**38**, M = Ti), which has been isolated as the hydrate $[Cp_2Ti(C_8N_2O_8)TiCp_2]_2 \cdot 12H_2O$ or the crystalline solvate $[Cp_2Ti(C_8N_2O_8)TiCp_2]_2 \cdot 2H_2O \cdot 2CHCl_3 \cdot 3CH_3NO_2$ from an appropriate mixture of solvents. As shown in **38**, two of the titanium atoms are penta-coordinate (Cp_2TiO_2N arrangement) and the other two are tetra-coordinate (Cp_2TiO_2 arrangement). The pyrazinetetracarboxylate (4-) anions act as (3 + 1 + 1) dentate ligands. The Ti—N and Ti—O distances of 2.20 Å



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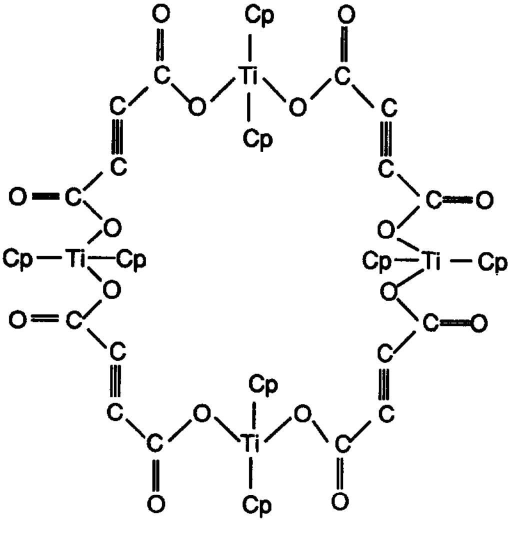

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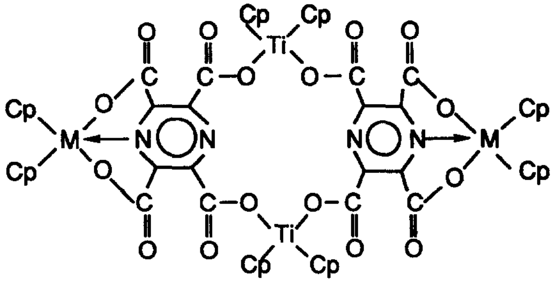
and 2.16 Å are close to those of 2.16 Å and 2.11 Å found in the mononuclear dipicolinate titanocene complex [54]. The O–Ti–N angle of 68.9° is slightly smaller than the other of 70.4° within the Cp_2TiO_2N arrangement in the tetranuclear complex [39].

Several tri- and tetranuclear chlorotitanium carboxylates, such as $Ti_3Cl_3(\mu$-



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$O_2CC_6H_4X$-$p)_5(\mu_2$-$O)(\mu_3$-$O)$ (X = Me, Et, F, I) [73] and $Ti_4Cl_6(\mu$-$OOCPh)(\mu$-$O)_2$ [72], have been obtained and structurally studied.

The heterometallic complex $[Cp_2Ti(C_8N_2O_8)ZrCp_2]_2$ (**38**, M = Zr) can be prepared by the reaction of equimolar amounts of Cp_2TiCl_2 and Cp_2ZrCl_2 with tetrasodium pyrazinetetracarboxylate. The complex which crystallizes as the solvate $[Cp_2Ti(C_8N_2O_8)ZrCp_2]_2 \cdot CH_3NO_2 \cdot 6CHCl_3$ is isostructural with $[Cp_2Ti(C_8N_2O_8)TiCp_2]_2$ [39].

2.6. *Carboxylic acids and/or substituted cyclopentadienyl systems*

A variety of carboxylic acids or their metal salts have been employed and tested for the synthesis of cyclopentadienyltitanium carboxylates. These ligands themselves have unique structures and/or biological activities. For example, terephthalic acid is a versatile ligand which reacts with $Cp_2Ti(CO)_2$ to give the binuclear paramagnetic complex **6** (A = C_6H_4) [66]. Tetranuclear terephthalato titanocene has been obtained by the treatment of an aqueous solution of Cp_2TiCl_2 with disodium terethphalate (**36**) [36]. Terethphalatic acid also has been condensed with substituted dicyclopentadienyltitanium dichlorides, to produce polyesters [101].

Dipicolinic acid is a useful material not only for the preparation of some titanocene dipicolinate complexes [21,54] — one of which is the first pentadentate titanocene [54] — but also for biological interest [102,103]. Also, some amino acids react with titanocene dichloride to give amino acid derivatives of titanocene which are synthetically and biologically useful materials [16,17].

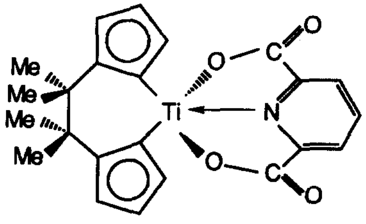
The two organometallic complexes $(HOOCC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ and $(HOOCC_6H_5)Cr(CO)_3$, which contain carboxylic acid groups, have been utilized in the preparation of several early (Ti,Zr)-late (Fe,Cr) bimetallic complexes bridged by carboxylate [12,43].

A series of substituted benzoate derivatives of titanocene have provided a good model for the investigation of substituent effects in the organometallic system [104]. Substituted cyclopentadienyltitanium complexes have received much attention recently. In general, the replacement of one or more hydrogen atoms from the Cp ring(s) by alkyl, aryl or other substituents alters both the steric and electronic effect of the Cp ring(s), resulting in differing reactivities, stabilities, solubilities and spectral properties of the substituted cyclopentadienyltitanium complexes, such as $Cp_2^*TiCl_2$, relative to their well-known (η^5-cyclopentadienyl)titanium counterparts [105]. For example, the reaction between $(C_5HPh_4)_2TiCl_2$ and $AgNO_3$ in THF + H_2O solution results in slow precipitation (days) of AgCl, in contrast to the rapid reaction between Cp_2TiCl_2 and $AgNO_3$ in a THF + H_2O solution [106]. Bulky cyclopentadienylmetal derivatives have been reviewed, indicating that the kinetic stabilization imparted is probably the most important factor for using bulky ligands [107].

Another very active research area has been chiral cyclopentadienyltitanium complexes and their applications in synthetic and catalytic reactions [108,109]. Two reviews appeared in 1992 [1,2]. Chiral cyclopentadienyltitanium complexes can be obtained in two general ways: metallization of chiral or prochiral cyclopentadienyl ligands, or by converting achiral cyclopentadienyltitanium complexes by appropriate functionalization into chiral derivatives [1].

The preparation of C_2-symmetrical bis(cyclopentadienyl)titanium dichlorides containing two equivalents of a chiral, enantiometrically pure monosubstituted cyclopentadiene has been successfully accomplished by the addition of the cyclopentadienyl anion (generally prepared by deprotonation of the chiral cyclopentadiene with *n*-butyllithium) in an ethereal solvent to $TiCl_4$. The addition of the chiral cyclopentadienyl anion to achiral cyclopentadienyltitanium trichloride enables access to titanocences containing one chiral cyclopentadienyl ligand [110]. Metallization of two cyclopentadienyl ligands covalently linked by a one-, two- or three-atom chain produces ansa-titanocenes. Introducing additional substitution on these bridged cyclopentadienyl rings can produce chiral complexes [111,112].

With a number of bulky and/or chiral titanocene dichlorides available, it would be quite possible to explore the corresponding carboxylate complexes and their potential applications. So far, only three highly substituted cyclopentadienyltitanium carboxylate compounds have been reported, *i.e.* $(CH_3)_4C_2(C_5H_4)_2Ti(C_7H_3NO_4)$



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(**39**) [54], $[1,3\text{-}^tBu_2\text{-}C_5H_3TiCl_2]_2\text{-}\mu\text{-}(C_2O_4)$ (**30**), $(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl(OOCC_4H_3N_2)_2$ (**13**) [85].

3. MASS AND NMR SPECTRAL STUDIES

3.1. Electron impact mass spectrometry behavior

Electron impact (EI) mass spectrometry (MS) is a useful tool for the structural characterization of cyclopentadienyltitanium complexes; in particular, carboxylate derivatives [11,23,76,77].

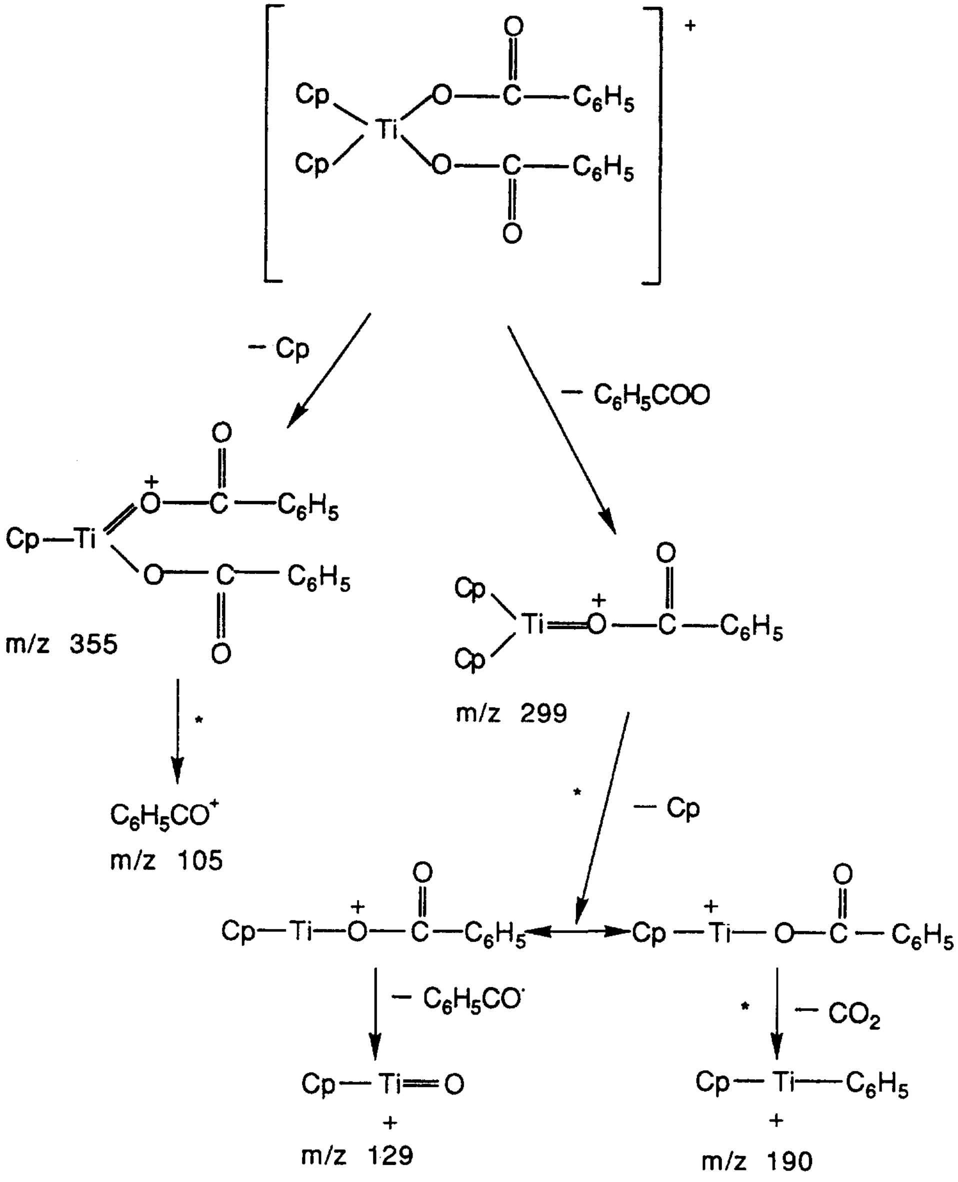
MS data have been reported for the carboxylate derivatives of the type $Cp_2Ti(OOCAr)_2$, where $Ar = C_6H_5$, or a substituted phenyl ring. Although the spectra do not show the parent ions, they do give peaks corresponding to structurally informative ions, such as $(Cp_2TiOOCAr)^+$, $(CpTiOOCAr)^{+\cdot}$, $[CpTi(OOCAr)_2–CO_2]^+$ and $(Cp_2Ti)^+$. Furthermore, numerous ions characteristic of the ligands OOCAr are present, including the molecular ion of the free-substituted benzoic acid HOOCAr [11,13].

The El MS behavior of these complexes has been further studied with the aid of metastable ion analysis, deuterium labelling and determination of the monoisotopic ion masses. Particular attention has been directed to possible hydrogen transfer reactions giving rise to the $(HOOCAr)^{+\cdot}$ ions, halide migration reactions, gas phase ion–molecule and ion–radical reactions, and ortho effects [113].

The El-induced fragmentation is partially rationalized in Scheme 2. The pathways indicated with an asterisk were all supported by establishing parent–daughter relationships, determined by recording either daughter ion spectra or parent ion spectra. The fragment ions $(CpTiOOCC_6H_5)^{+\cdot}$ and $(CpTiC_6H_5)^{+\cdot}$ contain Ti^{III} instead of Ti^{IV}. It is also noteworthy that a loss of $Cp^\cdot$ upon fragmentation of $(Cp_2TiOOCC_6H_5)^+$ ions violates the even-electron rule. This fragmentation behavior may be rationalized by the unusual stability of the delocalized cyclopentadienyl radical and the apparently facile reduction of Ti^{IV} to Ti^{III}.

The ion at $m/z = 178$ corresponds to the $(Cp_2Ti)^+$ ion and was shown to be a daughter ion of the $(Cp_2TiOOCC_6H_5)^+$ ion at $m/z = 299$. The ion at $m/z = 122$, corresponding to benzoic acid ion, has shifted to $m/z = 127$ in the spectrum of $Cp_2Ti(OOCC_6D_5)_2$. All the other peaks in the EI spectrum of $Cp_2Ti(OOCC_6D_5)_2$ showed the expected mass increments, which are consistent with the assignments for the unlabelled product (Scheme 2).

The spectra of all three fluorobenzoate derivatives $Cp_2Ti(OOCC_6H_4F)_2$ show $[CpTi(OOCC_6H_4F)]^{+\cdot}$ at $m/z = 252$, and an ion at $m/z = 271$ containing a second fluorine atom. Parent ion scanning indicated that the $[CpTi(OOCC_6H_4F)_2]^+$ and $[Cp_2Ti(OOCC_6H_4F)]^+$ ions are both precursor ions for the $[CpTi(OOCC_6H_4F) + F]^+$ ion. The formation of the $[CpTi(OOCC_6H_4F) + F]^+$ ion from the $[CpTi(OOCC_6H_4F)_2]^+$ ion can be explained by an intramolecular fluorine migration, whereas the formation of the $[CpTi(OOCC_6H_4F) + F]^+$ ion from the $[Cp_2Ti(OOCC_6H_4F)]^+$ ion may be rationalized by an exchange reaction in which a Cp radical is substituted by a fluorine radical, generated during the primary



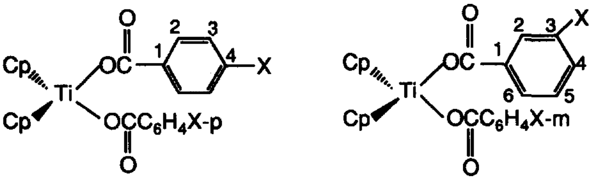
Scheme 2.

decompositions. The intramolecular fluorine migration also may account for the formation of $(CpTiF)^{+\cdot}$ and $(Cp_2TiF)^+$, which were supported by recording parent as well as daughter ion spectra [113]. Such migrations were reported also in other organotitanium compounds bearing perfluorocarbon ligands. The presence of an atom and/or group such as –O–, –S– or –OCO– between the titanium and the perfluoro ligand does not prevent the migrations [76,77,114].

It has been noted that the ortho isomers of the halogen-substituted complexes $Cp_2Ti(OOCC_6H_4X)_2$ (X = F, Cl) show the highest ratio of $[CpTi(C_6H_4X)]^{+\cdot}/[CpTi(OOCC_6H_4X)]^{+\cdot}$, *i.e.* increased loss of CO_2 from the $[CpTi(OOCC_6H_4X)]^{+\cdot}$ ion in the ortho isomers compared with the meta and para isomers. This phenomenon is probably the consequence of the steric effects [113].

3.2. Substituent effects on proton and C-13 NMR chemical shifts

Information about the electronic properties of compounds and mutual interactions of substituents may be obtained by analysing the correlation between NMR chemical shifts and substituent parameters. Over the years, different procedures have been attempted [115–118]; the most effective is the dual substituent parameter (DSP) approach, employing Taft's parameters σ_F and σ_{R_o} [118,119] in conjunction with Reynolds' non-electronic, short-range factors [120]. The DSP procedure has been successfully employed in the analysis of substituent effects on the proton and C-13 chemical shifts for a series of bis(4-substituted benzoato)titanocene derivatives (para series) and for a series of the 3-substituted analogues (meta series), *i.e.* $Cp_2Ti(OOCC_6H_4X)_2$ (**40**).



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The object is to apply the Taft–Reynolds procedure as a tool in the study of the electronic properties and mutual interactions of the substituents in these complexes. The complexes are well suited for this type of research for two reasons. First, the phenyl rings may serve as probes to check the accuracy of the data, as well as the internal consistency of cyclopentadienyl rings to allow the study of propagation, transmission and mutual interaction of electronic substituent effects.

3.2.1. Correlations for phenyl ring carbons and protons

Using the equation [120]

$$\delta = \delta_0 + \rho_F \sigma_F + \rho_R \sigma_R \qquad (10)$$

correlations have been obtained for all the atoms (carbons and protons) of the phenyl ring. Indicators for the goodness of fit show that the correlations are good for the para-atoms. Thus, high values for the correlation coefficient *r* and the *F*-test of the variance are obtained, well above the critical values ($r \geqslant 0.93$ and $F \geqslant 20$) for two and six degrees of freedom at 5% significance. The correlations, however, are rather poor for the non-para-atoms, which is not unexpected. Factor analysis [120,121] and other statistical investigations [122,123] have shown that at least three factors (triple substituent parameter (TSP) approach) are required to correlate the shifts of non-para-carbon atoms in a phenyl ring [120], *i.e.*

$$\delta = \delta_0 + \rho_F\sigma_F + \rho_R\sigma_{R^\circ} + \rho_x\sigma_x \qquad (11)$$

where σ_x represents the appropriate short-range factor and ρ_x is the weighting coefficient. The results indicate a remarkable improvement for some carbons, but only slight or no improvement for others.

3.2.2. *Correlations for side-chain carbons and protons: the carboxylate carbons and the cyclopentadienyl carbons and protons*

The correlations using the DSP approach are good-to-excellent for carboxylate carbons and the Cp carbon shifts, as judged by the goodness-of-fit parameters *r*, *F* ratio and RSD.

For the carboxylate groups, negative values have been observed for ρ_F and ρ_R, indicative of the reverse substituent chemical shifts (SCS) effect, *i.e.* electron-withdrawing substituents cause an upfield shift instead of the usual downfield shift. It is of great interest to note that the ρ_R value, which describes the field-inductive contribution, is equal for the para and meta series, while the ρ_R value, which describes the mesomeric contribution, is twice as large in the para series as that in the meta-series.

For the Cp carbon shifts, much smaller ρ_F and ρ_R values are observed compared with the carboxylate shifts. This is obviously because of the much greater distance between the substituents and the Cp carbons.

The bulky group $(Cp_2)(XC_6H_4COO)TiOOC-$ was found to be a very weak inductive acceptor ($\sigma_F = 0.035$) and a moderate resonance acceptor ($\sigma_{R^\circ} = 0.142$).

4. APPLICATIONS

4.1. *Organic syntheses and/or reactions*

Upon boiling the cyclic titanocene carboxylate (**2**) with a 12% solution of BF_3 in methanol, methyl benzoate was detected by gas–liquid chromatography (GLC); however, with CH_3I in benzene, methyl benzoate and methyl *ortho*-toluate were formed. The reaction conditions were severe and the products not isolated [41].

The reactions of $Cp_2Ti(OOCPh)_2$ with a few reagents have been investigated. The treatment of the titanocene bis-benzoate with benzoyl chloride indicated the formation of benzoic anhydride. No reaction was observed with benzyl chloride. The reaction of benzoyl chloride with reduced titanium species generated *in situ* by the reduction of $Cp_2Ti(OOCPh)_2$ with zinc or magnesium showed a complex mixture on gas chromatography and MS analysis. $Cp_2Ti(OOCPh)_2$ was readily reduced to benzyl alcohol with $LiAlH_4$ [124].

As shown by

$$Cp_2ZrCl(OOCR) + [Cp_2Zr(H)Cl]_x \rightarrow [Cp_2Zr(Cl)]_2O + RCHO \qquad (12)$$

three chlorozirconocene carboxylates react with the oligomeric hydride complex $[Cp_2Zr(H)Cl]_x$ in THF to produce the μ-oxo compound plus the requisite aldehyde. These reactions are complete after the reaction mixtures are stirred for a few minutes at room temperature. The μ-oxo complexes were isolated in yields of over 90%, and acetaldehyde and benzaldehyde were quantified (92%–93%) by both IR spectral and GLC procedures [84]. (From a synthetic point of view, it is also useful to examine the reactivity of $[Cp_2Zr(H)Cl]_x$ toward the chlorotitanocene carboxylates $Cp_2TiCl(OOCR)$.)

The observation that metal carboxylates are formally analogous to organic

metal carboxylate organic ester

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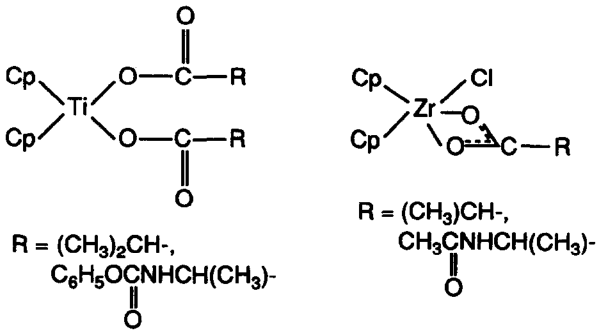
esters, *i.e.* $ML_4(OOCR)$ or RCOOR (**41**) [125], led researchers to consider whether or not transition metal carboxylates could possibly be used as acylating agents. High oxidation state complexes were selected as model compounds, since it was expected that the high positive charge on the metal would increase the reactivity of the carboxylate ligand towards nucleophiles [17].

The ability of titanocene and zirconocene isobutyrates, such as $Cp_2Ti(OOCR)_2$ or $Cp_2ZrCl(OOR)$ (**42**), to act as acylating agents for amide bond formation has



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been demonstrated by their reaction with various amines. Typically, a THF solution of the metallocene isobutyrate and the amine is allowed to reflux under an argon atmosphere. Water is then added to the reaction mixture to precipitate an insoluble metal product. After purification (extraction with acid and base), the yield of analytically pure amides ranges from 42% to 85%. Among a variety of common solvents, THF was found to afford the best yields [17].

Since an important application of amide bond formation is found in peptide synthesis (see, for example, ref 126), the applicability of metallocene carboxylates has been examined as reagents for peptide synthesis. An alanine dipeptide has been successfully synthesized in a yield of 45%, by refluxing titanocene dicarboxylate complex of *N*-benzyloxycarbonyl-L-alanine (Z-ala) in a THF solution of alanine methylester hydrochloride and triethylamine. However, the reaction times and conditions required are far more severe than those required by current methods of amide formation. In contrast, the reaction of $TaCl_4[OOCCH(CH_3)_2]$ with benzylamine occurred readily at room temperature [17]. Furthermore, cyclopentadienyltantalum (IV) amino acid carboxylates have been prepared and reacted with free amino acid esters to give dipeptides in good yields and with high stereochemical purity [127].

The readily prepared species $Cp_2Ti(O_3SCF_3)_2$ and $Cp_2Zr(O_3SCF_3)_2 \cdot THF$ are effective catalysts for the Diels–Alder reaction at very low catalyst loading, giving acceleration by a factor of 10^3–10^5 or more over the corresponding thermal reactions [128].

4.2. Antitumor agents

Studies into the dependence of the antitumor activity of titanocene derivatives upon structural modifications within Cp_2TiX_2 molecules have demonstrated that pronounced antitumor activity against Ehrlich ascites tumor occurs when two non-modified Cp rings are present [23,129,130]. However, the replacement of one or two chlorides by other halide or pseudo-halide ligands does not cause a loss of antitumor activity. Thus, the preferable site for molecular modification is obviously the acido ligands X in Cp_2TiX_2 [4]. Titanocene perfluorocarboxylate complexes are the first reported examples of titanocene carboxylates as antitumor agents [76].

In a search for new antitumor titanocene derivatives, titanocene hydrogen maleinate $Cp_2Ti(OOCCH{=}CHCOOH\text{-}cis)_2$, trichloroacetate $Cp_2Ti(OOCCCl_3)_2$ and other complexes have been tested for antiproliferative activity against Ehrlich ascites tumor in mice. The results show that the introduction of ligands bearing hydrophilic groups, such as carboxylic functions or protonated amino substituents, results in (1) a diminution of the toxic properties, (2) a widening of the therapeutic range and (3) an increase in the water solubility in comparison with that of titanocene dihalides. For example, the therapeutic index (T.I.) values amount to 3.7–3.8 for $Cp_2Ti(OOCCH{=}CHCOOH\text{-}cis)_2$ and 5.5 for $Cp_2Ti(OOCCl_3)_2$, compared with 3.3 for titanocene dichloride. The hydrogenmaleinate complex is quite soluble in water, and is equally active in a DMSO+saline (1:9 by volume) mixture, in pure saline and in buffered solutions. In the case of titanocene bis-trichloroacetate, the toxicity is particularly low (LD_{50}, 100 mg kg^{-1}; LD_{100}, 140 mg kg^{-1}) [77].

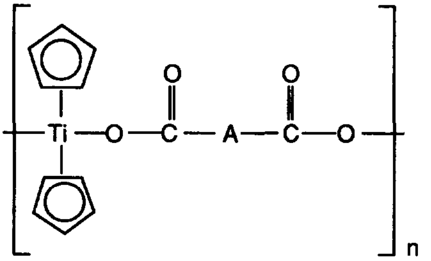
In a series of antitumor platinum compounds, the introduction of carboxylates, such as oxalate, malonate and substituted malonate ligands, also has improved the biological properties, especially the therapeutic effectivity [131–133].

The titanocene complexes $Cp_2Ti(OOCCH{=}CHCOOH\text{-}cis)_2$ and $[Cp_2Ti(bipy)_2^{2+}][O_3SCF_3^{-}]_2$ were evaluated for their *in vitro* antiviral properties and cytotoxicities. The titanocenium salt was found to be active towards the DNA viruses at a concentration 10 times lower than the cytotoxicity threshold [134]. Some other titanocene carboxylates also were reported to show antitumor activities [135,136].

It should be mentioned that the titanocene complexes are unstable under physiological conditions and that cyclopentadiene freed during the decomposition might be the active species [137,138].

4.3. Polymer materials

Titanocene polymers with biscarboxylate bridges were extensively studied in the early 1970s. These compounds, with the proposed structure shown for $-[-Cp_2Ti(OOCACOO)-]_n-$ (**43**),



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can be prepared by three methods [34]:

method A — aqueous synthesis, consisting of the combination of Cp_2TiCl_2 with the disodium salt of the dicarboxylic acid;

method B — interfacial polymerization, where Cp_2TiCl_2 in $CHCl_3$ is rapidly stirred and mixed with an aqueous salt solution of the appropriate dicarboxylic acid;

method C — preparation may be carried out by the reaction of Cp_2TiCl_2 with the organic acid or its salt.

However, it is questionable [139] that polymeric products of the type $[Cp_2Ti(OOCACOO)]_n$ were formed under the reaction conditions reported [140], because it has been shown that large parts of the fumarate and of the terephthalato-bridged products are not polymeric, but have cyclic dinuclear and tetranuclear structures respectively [35,36].

The products are thermally quite stable and insoluble in the common organic solvents. To improve the solubilities, alkyl or alkenyl substituents are introduced into the Cp ring, though with little success as yet. The products which contain groups such as cyclopentenyl, cyclohexenyl or alkoxyalkyl on the Cp ring are soluble in glacial acid and nitromethane [101]. However, trimers and tetramers are quite soluble in the common organic solvents [141].

Titanocene dichloride can be condensed with amino acids. The products are high polymers for all but monopeptides [142]. Parameters in the polymerization with glycyl-glycine, glycine, glycyl-glycyl-L-leucine, glycyl-D-phenylalanine, L-alanyl-glycyl-glycine, and L-isoleucyl-L-alanine have been evaluated [143].

Titanocene dichloride also has been condensed with indole-3-butyric acid and indole-3-propionic acid. The structures of these polymers were determined by MS. The indole-3-butyric acid polymer has a positive effect on rooting of *Hibiscus rosa-sinensis* [144].

5. CONCLUDING REMARKS

This review has outlined the syntheses, structures, reactions, spectra and applications of cyclopentadienyltitanium carboxylates and related coordination compounds. The syntheses can be carried out in organic, aqueous and/or two-phase media. A variety of carboxylic acids or their metal salts have been employed for the syntheses. A carboxylate group may coordinate to the titanium center in a monodentate or bidentate mode, depending on the specific complex, as determined by X-ray analyses. Although a great number of molecules have a mononuclear tetra-coordinate geometry, examples of penta- and higher coordinate, and bi- and multinuclear complexes are also known. Under severe conditions, titanocene dicarboxylates react with reagents such as iodomethane, benzoyl chloride and various amines. The isolated or detected products are synthetically useful. Mass spectra and substituent effects on NMR chemical shifts are discussed in a series of substituted dibenzoate derivatives of titanocene. Antitumor studies show that some titanocene carboxylate complexes, such as titanocene hydrogenmaleinate and the trichloroacetate derivative, are active against Ehrlich ascites tumor. Di- and tetracarboxylic acids are found to be particularly useful for polymers and novel multinuclear cyclic molecules.

As research interest in bulky and/or chiral titanocene dichlorides and in their new applications is increasing rapidly, it is surely anticipated that significant developments in the corresponding titanocene dicarboxylates as reagents or catalysts in organic synthesis, polymerization, and other possible uses will be made in the future.

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