PHD

Bis(cyclopentadienyl)titanium(IV) derivatives of carboxylic acids containing additional donor atoms and their use as building blocks for heterobimetallic complexes

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Bis(cyclopentadienyl)titanium(IV) Derivatives of Carboxylic Acids Containing Additional Donor Atoms and Their Use as Building Blocks for Heterobimetallic Complexes.

Submitted by Timothy John Paget
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1996

Timothy John Paget

Summary

The work presented in this thesis has been concerned principally with bis(cyclopentadienyl)titanium(IV) derivatives of carboxylic acids which contain additional donor functions. The compounds have been synthesised *via* a number of preparative routes and their structures investigated to elucidate the nature of the bonding between the bifunctional carboxylate ligand and the titanocene moiety. The carboxylic acids chosen were in the main derivatives of acetic acid or benzoic acid with a Group 15 or 16 heteroatom incorporated into the structure, such as cyanoacetic acid, salicylic acid and thiophenoxyacetic acid.

In addition, these bifunctional carboxylate ligands have been used to link titanium to late transition metals producing heterobimetallic compounds. The crystal structure of one of these complexes containing titanium and palladium, $[Cp_2Ti(O_2CCH_2PPh_2)_2PdCl_2]$, has been determined and displays discrete molecular entities in which the geometry of the titanium atom seems to be unaffected by the presence of the second metal atom.

As starting materials to heterometallic complexes, a range of *P*-coordinated diphenylphosphinoacetic acid-transition metal complexes were prepared. Mass spectrometry evidence suggests that some of these complexes e.g. $[(HO_2CCH_2PPh_2)CuCl]$ and $[(HO_2CCH_2PPh_2)AuCl]$ are expected to have interesting hydrogen-bonded interactions in the solid state. This was confirmed for $[(HO_2CCH_2PPh_2)AuCl]$ and *trans*-$[(HO_2CCH_2PPh_2)_2PdCl_2]$ by X-ray crystallography.

Finally, the X-ray crystal structure of silver(I) cyanoacetate, a compound used as a starting material in the titanocene chemistry, was determined. The interaction between the two silver atoms at the centre of the dimeric arrangement found in the structure was investigated by EHMO calculations the results of which suggest a weak bond.

Acknowledgements

Appropriately, I would like to start my acknowledgements by thanking my supervisor Dr. Dennis Edwards. His encouragement and guidance throughout this period of research is greatly appreciated. I would particularly like to thank him for his assistance in the final stages of this thesis, for proof reading the whole thing at a very busy period - the start of term.

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I have enjoyed my time working in Lab 2.10 and would like to take this opportunity to thank all my colleagues who have provided advice, company, friendship and a good laugh in various measures along the way. In particular, I must thank those members of the lab who were around at the start of my studies and showed me my way around, namely John McGinley, Rob Harker, Paul Deacon, Dave Smith, Chris Rainford, Natalie Devylder and Sean Becket, but also the newer arrivals; Virginie Ogrodnik, Phil Wright, Jo Stanley, Mike Maxwell, and Sonali Bhandari.

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The extended Hückel molecular orbital calculations were performed with the assistance of Dr. Rob Deeth (now of Warwick University) and his research group at the time, namely Paul Sheen, Sarah Langford and Veronica Burton (now Paget!).

This PhD has been such a large part of my life that I feel I have not only to thank people who have helped directly with my work, but also those who have kept me going, and made life fun over the last three years and to this end I thank all my friends, but in particular Simon and Alastair who have always been around for a good chat when ever I've needed one. I would also like to mention my former house mates; Simon, Steve and Gareth from Bloomfield Rise plus Alison, Tony, Robin, Warren and Alan from Southcot Place for their company, and for putting up with me.

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My family deserves a VERY BIG mention, for supporting me in many ways too difficult to describe in words. I'll just say thanks mum, dad, Dave, Gail, Steve, Karen, Ali, Andy, Katey, Rachel, Hannah, Chris, Anna, Sarah and Abigail. I'm also very grateful for the support of my parents-in-law, particularly during the final stages of writing up.

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"Whatever you do, work at it with all your heart,
as though you were working for the Lord."

Colossians 3:23.

Contents

Abbreviations

Cp	cyclopentadienyl, C_5H_5
Cp*	pentamethylcyclopentadienyl, C_5Me_5
Cp'	monosubstituted cyclopentadienyl, RC_5H_4
Me	methyl
Et	ethyl
^{n}Pr	n-propyl
^{i}Pr	iso-propyl
^{t}Bu	tertiary-butyl
Ph	Phenyl
Cy	Cyclohexyl
EHMO	extended Hückel molecular orbital
FAB	fast atom bombardment
IR	infrared
MS	mass spectrometry
NMR	nuclear magnetic resonance
br	broad
d	doublet
m	medium
s	singlet (NMR)
	strong (IR)
sh	shoulder
t	triplet
vs	very strong
vw	very weak
w	weak

Chapter 1.

Introduction.

1.1. Titanocene Compounds

Of the various types of titanium complexes containing direct Ti-C bonds, the most prolific are those involving the anionic η^5-bonded cyclopentadienyl ligand or derivatives thereof.[1] In particular, bis(cyclopentadienyl)titanium compounds, or 'titanocenes', where there are two cyclopentadienyl ligands π-bonded to titanium are well represented in the literature. The main thrust of this research effort over the last thirty years or so has focused principally on the synthesis and characterisation of novel titanocenes and their application as catalysts in industrially important processes, chiefly Ziegler - Natta polymerisation, but also as catalysts and reagents in organic synthesis.

The first bis(cyclopentadienyl)titanium complexes were reported by Wilkinson and co-workers in the mid 1950's.[2] Their work arose from an interest in cyclopentadienyl compounds of transition metals initiated by the isolation of bis(cyclopentadienyl)iron(II) ('ferrocene') in 1948 by Miller, Teboth and Tremaine,[3] and the elucidation of its structure reported in 1952.[4] Since then many titanocene complexes have been reported and have involved titanium in oxidation states of +2, +3 and +4.[1]

The utility of titanocene complexes has been enhanced in some cases by incorporating various substituents on the cyclopentadienyl ring. Changing a proton for a range of groups such as alkyl, aryl, silyl, phosphido, etc. not only induces additional steric constraints, but also has an effect on the electronic properties of the Cp_2Ti moiety.[5] In addition, linking the two cyclopentadienyl rings *via* a carbon chain or heteratom has produced a subgroup of bis(cyclopentadienyl)titanium compounds called *ansa*-titanocenes.[6]

The inclusion of bulky substituents on the cyclopentadienyl rings and/or the rigid framework generated in *ansa*-titanocenes has enabled chemists to tailor the titanium environment in titanocenes to a high degree of precision. The catalysts or reagents developed, many of which are chiral, can function in a highly stereospecific manner. Titanocene compounds have also been synthesised using annulated ring systems such as the indenyl and fluorenyl anions.

1.1.1. Structure and Bonding

The structures of bis(cyclopentadienyl)titanium complexes are dominated by a bent metallocene arrangement. The two cyclopentadienyl rings are inclined so that their planes form an angle γ (Fig. 1) generally between 45°-55° although this angle can be increased to ~65° for certain *ansa*-titanocenes.[6]

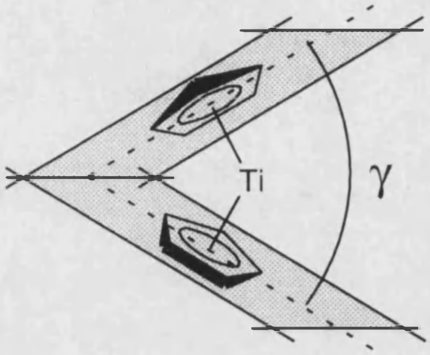


Figure 1. The geometry of the Cp_2Ti fragment.

The non-linear arrangement of the cp rings found in titanocene complexes contrasts with the classic sandwich type structure in ferrocene.[4b] This difference can be rationalised using the 18-electron rule which is considered to be a useful tool in predicting the stability of organometallic transition metal compounds.[7]

In the case of ferrocene, each cyclopentadienyl anion donates 6VE (VE = valence electrons) to the d^6 iron(II) giving a total valence electron count of 18VE. For the titanium(II) analogue, similar electron counting predicts an unstable 14VE species and it is unlikely that the compound exists in the form of simple sandwich-type entities.[8]

By adopting a bent metallocene geometry, the titanium atom can bond to additional electron donating ligands to increase its valence electron count. There are numerous examples of bis(cyclopentadienyl)titanium(II) compounds in which the titanium achieves a stable 18VE configuration by accepting additional neutral ligands.[9]

With Ti(III) and Ti(IV) the metal is more electron deficient and again the Cp_2Ti moiety adopts a bent structure. However in these instances, the titanium is frequently unable to reach a formal 18VE configuration because the steric bulk of the cyclopentadienyl rings usually limits the number of additional ligands to a maximum of two. This is in contrast to the analogous zirconium and hafnium compounds in which the larger metals regularly accept up to three additional ligands. The vast majority of bis(cyclopentadienyl)titanium(IV) compounds have a formal valence electron configuration of 16VE.

Bent metallocene structures have been studied in some detail by molecular orbital theory.[10] These investigations have provided insight into the structure and reactivity of such compounds and have shown that there are three principal frontier orbitals for the Cp_2M fragment. These orbitals lie in a central plane which bisects the Z-M-Z' (Fig. 2, Z and Z' represent the centres of the two cyclopentadienyl rings).

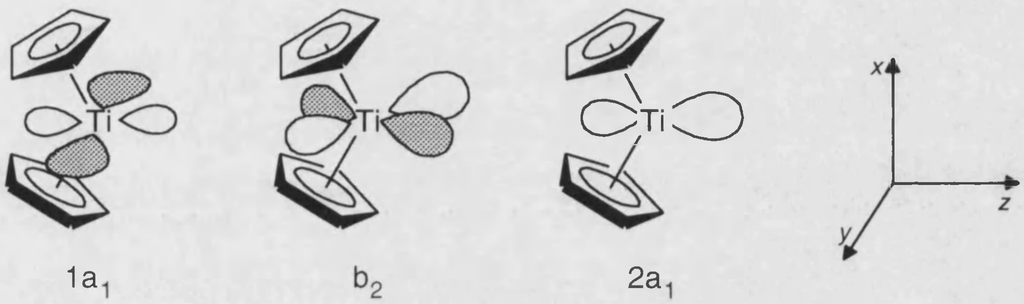
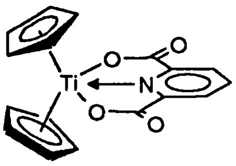


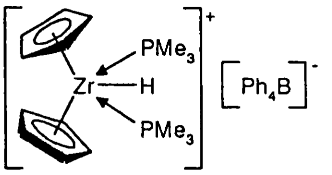
Figure 2. The three frontier orbitals of the Cp_2Ti fragment. The energies of the orbitals increase in the order $1a_1 < b_2 < 2a_1$.

Using the coordinate system shown in Figure 2, the three orbitals $1a_1$, b_2 and $2a_1$ extend largely in the *yz* plane. Calculations by Lauher and Hoffmann show that the b_2 orbital is in the main d_{yz} in character. The $1a_1$ orbital is directed along the *y*-axis and can be described as similar to a 'd_{y^2}' orbital, the principal contributions from the metal orbitals being $d_{x^2-y^2}$ and d_{z^2}. Finally the $2a_1$ orbital also contains contributions principally from the $d_{x^2-y^2}$ and d_{z^2}, but also significant amounts of s and p_z characteristics. Contributions to this latter orbital from the cyclopentadienyl ligands concentrates the orbital away from the metal centre along the *z*-axis.

The utility of this frontier orbital picture of the bent metallocene species is evident when explaining the chemistry of such systems. In the case of group IV and group V metallocenes with d^0 configurations the three frontier orbitals are unoccupied and the metal fragment can accept up to three donor ligands, e.g. $[Cp_2Ti(dipicolinate)]$ **1**,[11] $\{[Cp_2Zr(H)(PMe_3)_2][Ph_4B]\}$ **2**,[12] $[Cp_2Nb(H)_3]$ **3**.[13] However the d^2 complex $[Cp_2Mo(H)_2]$ **4** is able to act as a donor itself by coordinating *via* the occupied $2a_1$ orbital to a $Mo(CO)_5$ moiety.[14]



1



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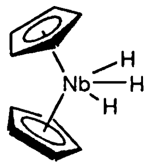

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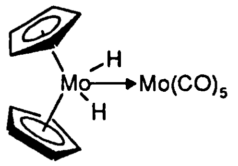


4

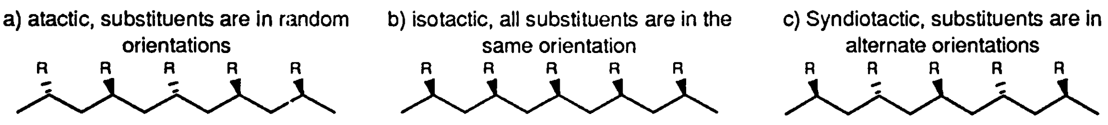
In addition to the *steric* implications to metallocene chemisty, substituents on the cyclopentadienyl ligands also alter the electronic properties of the metal centres. Alkylation of the Cp rings produces an electron donating inductive effect,[5,15] while a stereoelectronic effect is observed in *ansa*-metallocenes.[16] These changes in the electronic character of the metal modify the reactivity of these species and can give rise to catalytic systems with increased activity.

1.1.2. Applications

1.1.2.1. Olefin Polymerisation

As mentioned, a large proportion of investigations carried out on titanocenes have concentrated on applications to Ziegler - Natta olefin polymerisation. The catalytic nature of a mixture of $TiCl_4$ and $AlEt_3$ toward ethene polymerisation was demonstrated by K. Ziegler in the mid 1950's.[17] Subsequent development of this system to include other olefins was achieved by G. Natta.[18] In contrast to the industrial processes at that time, these so called Ziegler - Natta systems yielded high density, highly crystalline polymers at room temperatures and pressures. Polymers with such characteristics have greater strength and enhanced thermal properties.

The beneficial bulk physical properties produced by the above heterogeneous assemblies are due to the ordered nature of the polymer at a molecular level (Fig. 3). This stereoregulation in the polymerisation reaction is induced by the surface restrictions about the active metal centre. The asymmetry of the last inserted unit controls the orientation of the incoming olefin segment (Fig. 4). The polymerisation of propene using modern heterogeneous Ziegler - Natta catalysts yields highly isotactic polypropene.



a) atactic, substituents are in random orientations

b) isotactic, all substituents are in the same orientation

c) Syndiotactic, substituents are in alternate orientations

Figure 3. The tacticity of polymers.

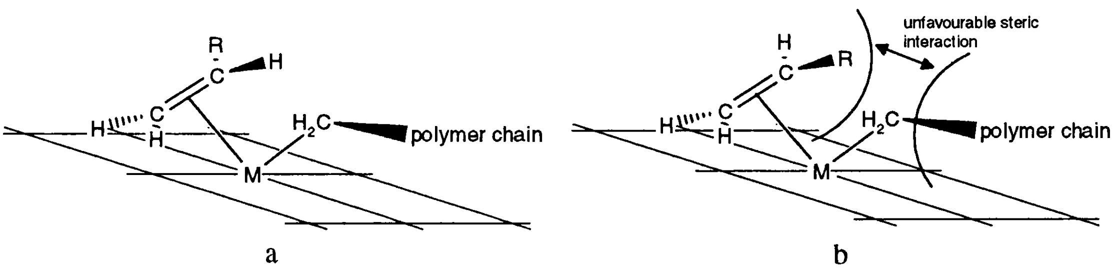
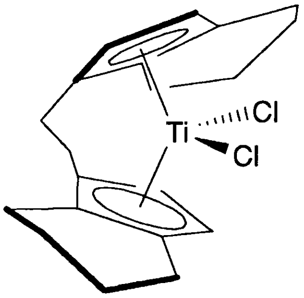


Figure 4. Stereoregulation in heterogeneous Ziegler - Natta catalysts. Proposed transition states showing a) the prefered and b) the disfavoured approach of the incoming monomer. The local surface environment controls the orientation of the growing polymer chain which in turn directs the insertion of the next monomer unit.

Group IV metallocenes also form effective olefin polymerisation catalysts themselves.[19] Early investigations involved the activation of Cp_2TiCl_2 with diethylaluminium chloride (Et_2AlCl) to give a homogeneous catalytic system that produced polyethene under similar conditions to the heterogeneous catalysts.[20] However without the restrictions of a solid support, homogeneous systems involving simple cyclopentadienyl ring derivatives do not induce stereoregulation at normal temperatures and pressures. Control of stereochemistry is observed with simple systems at low temperatures and operates *via* a similar mechanism to that observed in heterogeneous systems.[21]

High temperature stereochemical control can be brought about in homogeneous systems by using large *ansa*-metallocene precursors such as ethylenebis(tetrahydroindenyl)titanium dichloride **5**, in which access to the metal centre is restricted.[22] The stereochemical control factors in these cases are thought to be different to that in the heterogeneous case and involve the chirality of the metallocene complexes.[22]



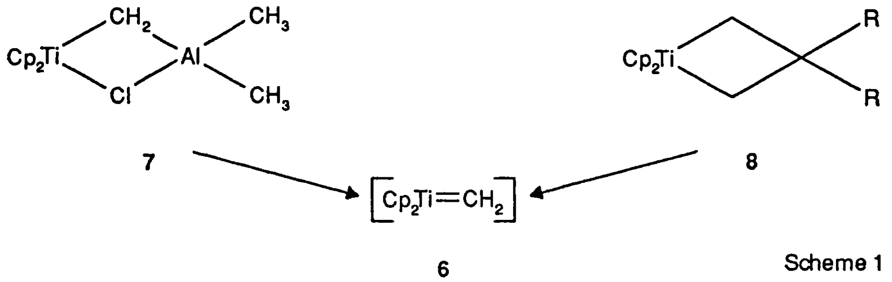
Ethylenebis(tetrahydroindenyl)titanium dichloride **5**

Unfortunately, even with very large, bulky chiral metallocenes, the stereoselectivity of homogeneous Ziegler - Natta catalysts is not as high as that of heterogeneous systems. This is particularly prevalent at temperatures and pressures used commercially. However, the advantage of the single phase procedure is that polymers of very narrow molecular weight distributions are produced. This low polydispersity suggests identical reaction kinetics occur at each of the active centres and, therefore, that polymer growth arises from only one catalytic species.

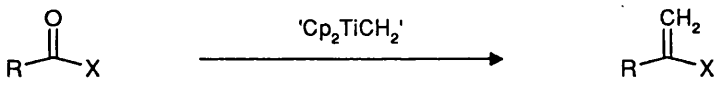
1.1.2.2. Organic Synthesis

The application of titanium compounds in organic synthesis has been investigated extensively and several texts and reviews[23,24] have explored this area. Specifically, bis(cyclopentadienyl)titanium complexes have been utilised in a number of organic transformations either as catalysts or as stoichiometric reagents.

The titanium carbene [Cp_2TiCH_2] **6** generated in situ from Tebbe's complex[25] **7** or from titanacyclobutanes[26] **8** provides a useful alternative to Wittig-type reagents for the conversion of aldehydes and ketones to olefins. In contrast to other methylenation systems, titanium mediated reactions can also be applied to esters and lactones.



Scheme 1

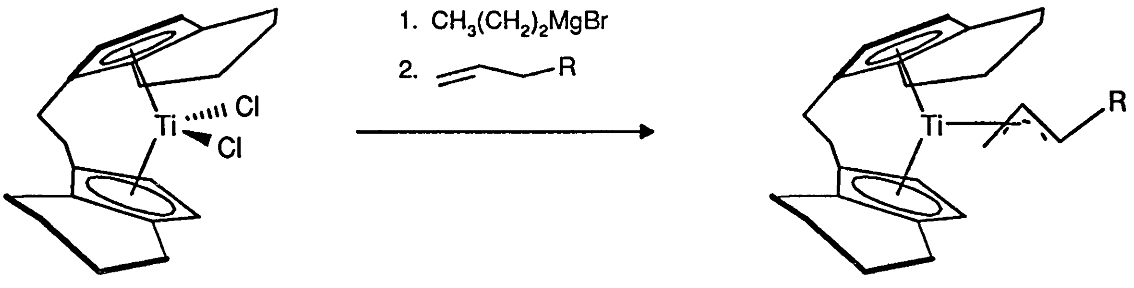


X = H, alkyl, aryl, vinyl, OR

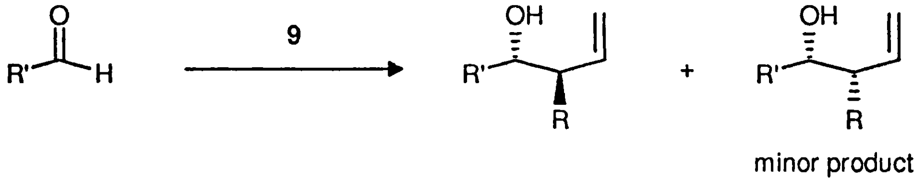
Scheme 2

A later development for this type of transformation is the use of the so-called Petasis reagent, dimethyltitanocene.[27] Reactions with this reagent are thought to proceed *via* the same carbene intermediate and avoid some of the practical difficulties associated with earlier titanocene complexes.

Diastereoselective synthesis of homoallylic alcohols from aldehydes has been achieved using the reduced titanium(III) allyl derivative of ethylenebis(tetrahydroindenyl)titanium dichloride **5**.[28]

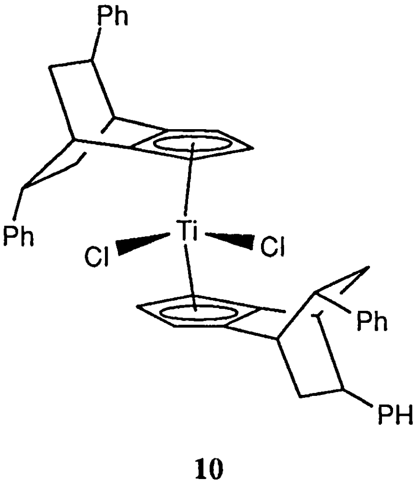


5 **9** Scheme 3



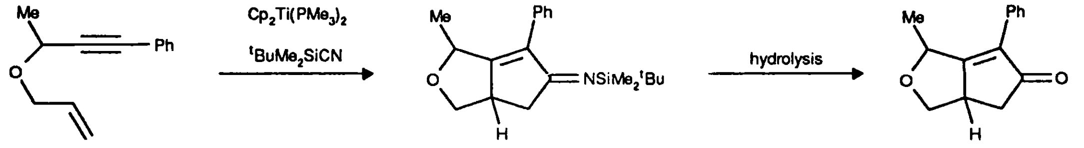
R' = Ph, R = Me; 90%
ratio of diastereoisomers - 40:1 Scheme 4

Hydrogenation catalysts have been produced using titanocene dichlorides as precursors. Conversion of 1-hexene to hexane was effected using substituted titanocenes and NaH as co-catalyst (Scheme 5).[29] Highly enantioselective hydrogenation has been achieved using the sterically hindered, chiral titanocene complex **10**.[30]

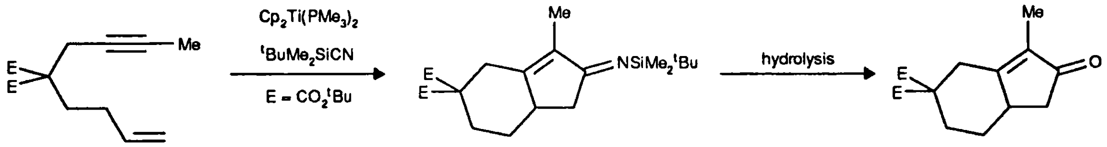


10

The Ti(II) complex [$Cp_2Ti(PMe_3)_2$] in the presence of ^{t}butyldimethylsilylcyanide, is able to catalyse the cyclisation reactions of 1,6- and 1,7-enynes.[31] The bicyclo[n.3.0]alkenones obtained after hydrolysis are useful intermediates in the synthesis of natural products containing cyclopentane groups (Schemes 5 and 6).

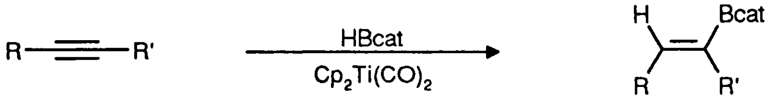


Scheme 5

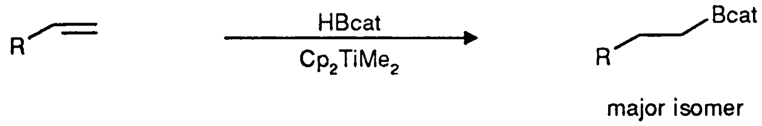


Scheme 6

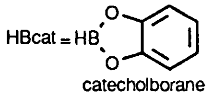
Recently, titanocene dicarbonyl and dimethyltitanocene have been shown to act as efficient, selective catalysts for the hydroboration of alkynes and alkenes, respectively.[32]



Scheme 7



Scheme 8



1.1.2.3. Cancer Therapy

Titanocene dichloride has the potential of being a particularly useful anticancer drug due to its high activity against certain tumour types, and its relatively low toxicity.[33] It is particularly potent against colonic, lung and breast cancers and is currently undergoing clinical trials.

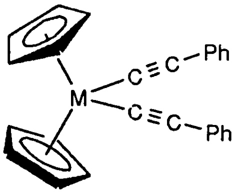
The cytostatic activity of titanocene dichloride was first reported by Köpf and Köpf-Maier in 1979.[34] The discovery was part of an on-going search for new transition metal containing antitumour agents after *cis*-diamminedichloroplatinum(II) (better known as cisplatin in cancer therapy) was found to prevent cell division in certain bacteria cultures.[35] It has since been shown that other bent metallocene compounds have similar but lower activity *in vivo.*

The mode of action of titanocene agents against cell growth is not fully understood. It might be expected that titanocene reagents would behave in a comparable way to cisplatin due to the similarities in their structures and certain aspects of their chemistries.[34] However, although titanocene derivatives are thought to interact with DNA and prevent its replication as occurs with the platinum drug, the actual mechanisms involved are thought to be different.

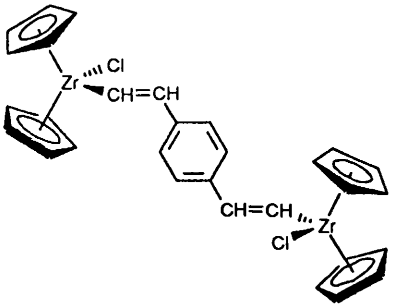
1.1.2.4. Materials Applications

Group IV metallocene complexes have been investigated for their non-linear optical properties, a phenomenon that is used in a range of optical devices.[36] The acetylide complexes **11** (M = Ti, Zr, Hf) and the alkenyl complex **12** display reasonably large coefficients of third order non-linearity. The effect is thought to be due to the conjugated π network which includes the Cp_2M moiety and the delocalised bonds of the carbon systems.[37,38]

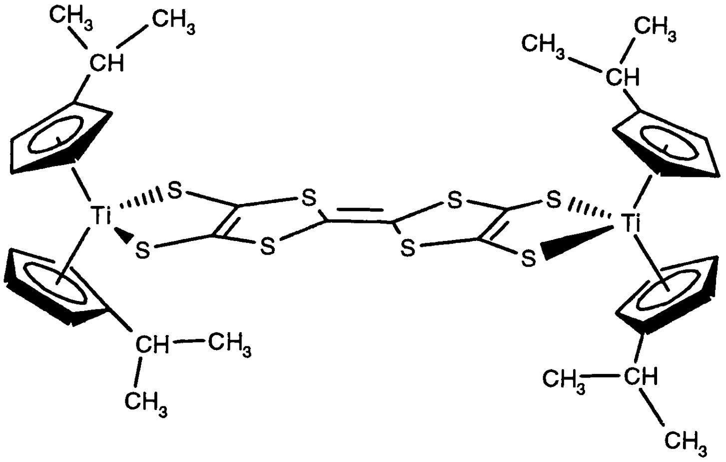
Recently, a building block for new materials with potential superconducting properties or applications as a molecular metal has been synthesised. The complex **13** contains two Cp'_2Ti moieties ($Cp' = RC_5H_4$, where $R = {}^iPr$) linked by a tetrathiafulvalene unit.[39]



11



12



13

1.2.Metal Carboxylates[40,41]

Mankind has made use of metal carboxylates for thousands of years. As early as 1400 BC the lubricating qualities of calcium derivatives of fatty acids were utilised in chariot wheel grease and the first application of lead linoleate was probably in paints for mummification. Alkali metal salts of naturally occuring carboxylic acids have also been used since ancient times in the production of soap. A rapid development of carboxylate chemistry came with the demand for better lubricants and paints during the industrial revolution.

Today, metal carboxylates are an important class of compounds both to research and industry. As end products, they are used in paints, lubricants, soaps, agrochemicals and pharmaceuticals, but are also extensively employed as reagents and catalysts.

For the research chemist, carboxylates display a fascinating variety of structures. There are a huge range of carboxylic acids that can be used to form metal complexes. Some contain simple alkyl or aryl groups, others contain bulkier components such as tertiary butyl and mesityl, while others contain additional donor functions such as amino, hydroxyl, phosphino, pyridyl, and carboxyl to name but a few.

It is therefore possible to alter the properties of a metal complex by varying the carboxylate ligand. Interesting supramolecular structures have been generated and investigated for potential applications in areas such as liquid crystals, non-linear optics, and molecular conductors.[42,43] Smaller molecular units have been studied, among other reasons,for their interesting bonding features and catalytic activity.[44,45]

The proliferation of the carboxyl group in living organisms has also encouraged numerous studies on metal complexes containing carboxylate ligands. Many of these investigations have probed the important roles of metals such as iron, copper and zinc in plants, animals and microorganisms.[46,47] Other researchers have analysed the effect on living tissues of metals not normally found in biological systems. This has led to the development of pharmaceutical drugs containing certain metals such as platinum and gold and the therapeutic use of technetium complexes as imaging agents.[48,49]

1.2.1. Synthesis

Due to their importance many synthetic routes to metal carboxylates have been devised. Some of the more important methods are summarised below, most examples being taken from recent literature.

i) Direct reaction of an electropositive metal with a carboxylic acid

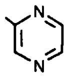
$$M + RCOOH \xrightarrow[M = Na, K, Rb, Cs]{} MO_2CR + \tfrac{1}{2}H_2 \qquad \text{Eq. 1}$$

ii) Neutralisation reactions involving a metal oxide, hydroxide, alkoxide or carbonate and a carboxylic acid, acid anhydride or acid chloride.

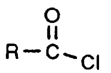
$$NaOH + HO_2CCH_3 \xrightarrow{H_2O} NaO_2CCH_3 + H_2O \qquad \text{Eq. 2}$$

$$MnCO_3 + 2HO_2CR \xrightarrow{H_2O} Mn(O_2CR)_2 + CO_2 + H_2O \qquad \text{Eq. 3}^{50}$$

R =



$$Bi_2O_3 + 3(CF_3CO)_2O \longrightarrow 2Bi(O_2CCF_3)_3 \qquad \text{Eq. 4}^{51}$$



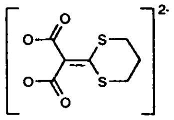
$$L_2PtX_2(OH)_2 \xrightarrow{R-C(=O)-Cl} L_2PtX_2(O_2CR)_2 \qquad \text{Eq. 5}^{52}$$

e.g. $L = NH_3$, $X = Cl$, $R = (CH_2)_{12}CH_3$

iii) Metathesis reactions.

$$BaCl_2 + K_2(DTEYM) \xrightarrow{H_2O} Ba(DTEYM) + 2KCl \qquad \text{Eq. 6}^{53}$$

DTEYM = 1,3-dithiepen-2-ylidenemalonate,



$$PtCl_2(PPh_3)_2 + 2AgO_2CCF_3 \longrightarrow Pt(O_2CCF_3)_2(PPh_3)_2 + 2AgCl \qquad \text{Eq. 7}^{54}$$

iv) Reaction of a metal halide and carboxylic acid.

$$2NbCl_5 + 2HO_2CC_6F_5 \xrightarrow{CHCl_3} [NbCl_4(O_2CC_6F_5)]_2 + 2HCl \qquad \text{Eq. 8}^{55}$$

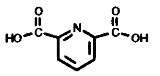
- and in the presence of base.

$$2BrMn(CO)_5 + 2HO_2CC_6H_4SH \xrightarrow[-4CO/-Et_3NHBr]{xs\ Et_3N} [Et_3NH]_2[Mn_2(O_2CC_6H_4S)_2(CO)_6] \qquad \text{Eq.9}^{56}$$

v) Exchange of carboxylate ligand.

$$Pd(O_2CCH_3)_2 + (HO_2C)_2C_5H_3N \longrightarrow Pd[(O_2C)_2C_5H_3N] + 2HO_2CCH_3$$ Eq. 10[43]

$(HO_2C)_2C_5H_3N$ =



vi) Reactions involving the cleavage of metal-hydrogen or metal-carbon σ-bonds.

$$Cp_2ZrH_2 + \text{xs } CF_3COOH \longrightarrow Cp_2Zr(O_2CCF_3)_2 + 2H_2$$ Eq. 11[57]

$$CH_3Cu(PPh_3)_2 + CH_3COOH \longrightarrow (CH_3CO_2)Cu(PPh_3)_2 + CH_4$$ Eq. 12[58]

vii) Oxidation of a metal carbonyl.

$$Mo(CO)_6 + \text{xs } RCOOH \xrightarrow{(RCO)_2O} Mo_2(O_2CR)_4$$ Eq. 13[59]

viii) Insertion of CO_2 into metal-alkyl or -aryl bonds.

$$[HM(CO)_5]^- + CO_2 \xrightarrow[M = Cr, Mo, W]{} [(HCO_2)M(CO)_5]^-$$ Eq. 14[60]

$$[CH_3W(CO)_5]^- + CO_2 \longrightarrow [(CH_3CO_2)W(CO)_5]^-$$ Eq. 15[61]

ix) Reaction of metal thiolates with acid anhydrides.

$$Sn(SR)_4 + 4(R'CO)_2O \longrightarrow Sn(O_2CR')_4 + 4R'COSR$$ Eq. 16[62]

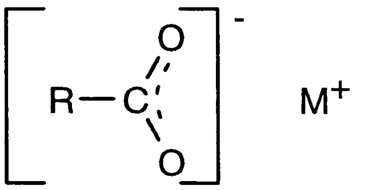
Other methods include the reactions of carboxylic acids with tetrahydroborato complexes[63] and the insertion of carbon monoxide into alkali hydroxides.

1.2.2. Metal-Carboxylate Interactions

1.2.2.1. Crystal Structure Data

A wealth of information on the solid state structures of metal carboxylates exists in the literature. From this data the bonding interactions of the carboxylate function have been classified into four major types; namely: ionic, unidentate, bidentate chelating, and bridging.

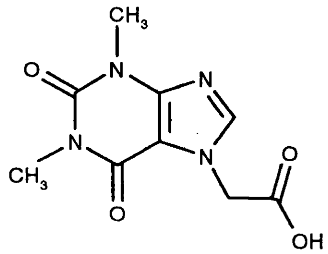
i) ionic



eg. NaO_2CH[64]

This bonding mode is observed with electropositive metals and is typified by the highly symmetrical nature of the carboxyl function. Ideally, equal C-O bond distances are present, and a small difference, $\Delta[\nu_{asym(O-C-O)}-\nu_{sym(O-C-O)}]$ between the symmetric and asymmetric stretches of the O-C-O group is observed in the infrared spectrum.

Uncoordinated carboxylate anions can also be observed with other metals. The nickel(II) complex of theophylline-7-acetate **14**, a ligand used to model the guanosine nucleoside in DNA, contains an octahedral nickel surrounded by six molecules of water. The two carboxylate anions are not bonded to the metal but take part in extensive hydrogen bonding.[65]



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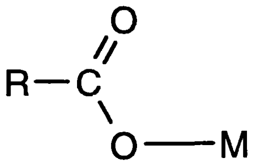
The carboxyl groups in $[Cu(O_2CCH_2CN)_2H(PPh_3)_2]$ are also not directly attached to the metal, but form intermolecular hydrogen bonds with the proton. Uniquely, the cyanoacetate ligands are *N*-bonded to the copper *via* the nitrile functions (see Chapter 2, compound **51**).[66]

As well as being important starting materials in metal carboxylate chemistry, ionic sodium and potassium salts are useful as standards when comparing structural and spectroscopic features.

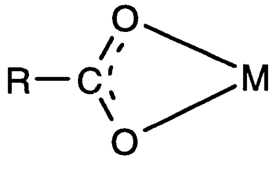
ii) unidentate



This mode is frequently observed with coordinatively saturated metal centres. The unsymmetrical nature of the carboxylate bonding is often displayed by a significant difference in the C-O bond distances and a large value of $\Delta[\nu_{asym(O\text{-}C\text{-}O)}\text{-}\nu_{sym(O\text{-}C\text{-}O)}]$. For example, in the triorganotin(IV) derivative of 2-benzoylbenzoic acid $[(2\text{-}C_6H_5COC_6H_4CO_2)Sn(^nBu)_3]$,[67] the carboxylate ligand is attached to the metal through one oxygen of the carboxyl function [Sn-O, 2.109(7)Å] and by the carbonyl oxygen of the benzoyl group [Sn-O", 2.675(10)Å]. The second carboxyl oxygen is not bonded to tin [Sn-O', 3.077(8)Å] and the asymmetry of the O-C-O moiety is illustrated by the C-O bond distances [C-O, 1.296(13)Å; C-O', 1.229(12)Å] and the difference between the asymmetric and symmetric bands in the IR spectrum {$\nu_{asym(O\text{-}C\text{-}O)}$ = 1662, 1597, 1578cm^{-1}; $\nu_{sym(O\text{-}C\text{-}O)}$ = 1338cm^{-1}; $\Delta[\nu_{asym(O\text{-}C\text{-}O)}\text{-}\nu_{sym(O\text{-}C\text{-}O)}]$ = 324-241cm^{-1}}.

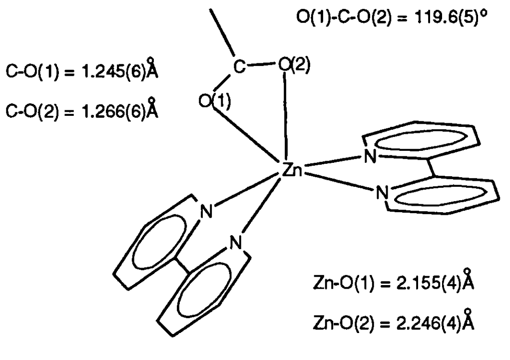
However, there are numerous examples of unidentate coordination where the C-O distances of the carboxy function are very similar, usually due to hydrogen bonding taking place. For example, $[Pd(2,9\text{-dmphen})(CH_3CO_2)_2].0.40CH_2Cl_2.0.30H_2O$ (2,9-dmphen = 2,9-dimethyl-1,10-phenanthroline); C-O = 1.24(1), 1.25(1)Å; C-O' = 1.23(1), 1.23(1)Å,[68] $[Mn(phen)(Me_3NCH_2CO_2)(H_2O)_2]$ (phen = 1,10-phenanthroline); C-O = 1.244(5)Å, C-O' = 1.249(5)Å[69] and $\{Co[O_2CC_6H_3(NO_2)_2\text{-}3,5]_2(H_2O)_4\}.4H_2O$; C-O = 1.253(4), 1.250(4)Å, C-O' = 1.248(4), 1.248(4)Å.[70]

iii) chelating



Chelating coordination can be symmetrical[71,72]or more commonly asymmetrical.[73,45] The symmetrical chelating systems show similarity to ionic and certain bidentate bridging carboxylates in that the two C-O bonds are equivalent. This gives rise to small $\Delta[\nu_{asym(O-C-O)}-\nu_{sym(O-C-O)}]$ stretching frequency differences, which are lower than those of ionic systems. In common with unsymmetrical systems, symmetrical chelates have small O-C-O and O-M-O angles. For example, one of the bimalonate carboxyl functions in $[\{La(H_2O)_2(O_2CCH_2CO_2)(O_2CCH_2CO_2H)\}.H_2O]$ has similar C-O and La-O bond lengths for both oxygen atoms [C-O: 1.253(6), 1.265(6)Å; La-O: 2.613(3), 2.598(3)Å] and an O-C-O angle of 120.8(4)°.[72] The cadmium(II) complex $[\{Cd(H_2O)(O_2CC_5H_4N)(Br)\}_n]$ ($HO_2CC_5H_4N$ = nicotinic acid) exhibits almost identical Cd-O bond lengths for the carboxylate oxygen atoms [2.348(3) and 2.331(3)Å] and a small chelate angle, ∠O-Cd-O = 56.0(1)°.[74] For comparison, sodium formate contains C-O bond lengths of 1.27Å and an O-C-O angle of 124°.

The zinc(II) cations **15** and **16** in $[Zn(bpy)_2(MeCO_2)](ClO_4).H_2O$ (bpy = 2,2'-bipyridine)[75] and $[Zn(phen)_2(MeCO_2)]ClO_4$ (phen = 1,10-phenanthroline)[76] display two types of asymmetrical chelating acetates. In the first complex the asymmetry is observed in the Zn-O and C-O bond distances. With the second example, the C-O bond lengths are identical despite the large difference in the Zn-O distances.



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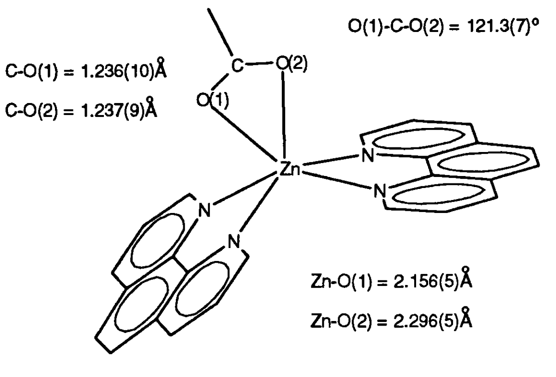

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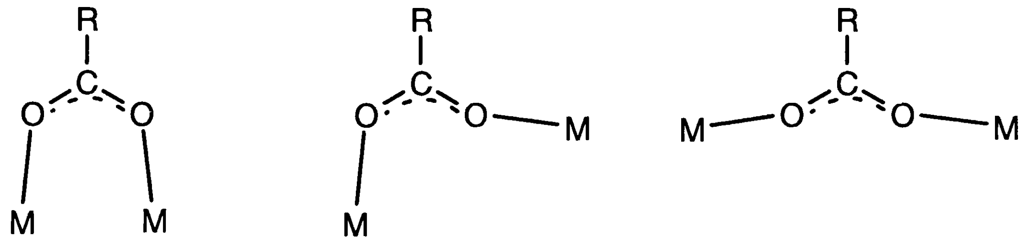
iv) bridging

The bridging mode is the most frequently observed coordination type for metal carboxylates. This class of complexes can be further subdivided depending on how many metal centres are linked together, the occurence or non-occurence of chelation, and how the metal-oxygen bonds are orientated with respect to the carboxyl function.

Figure 5 shows the reported carboxyl bridging types involving two metal centres. The *syn, syn* bidentate bridging mode (Type **I**) is observed in dinuclear transition metal carboxylates which take up the familiar 'paddle wheel' structure (Fig. 6). These compounds have been studied as a result of their interesting metal-metal interactions arising from the close proximity of the metal centres imposed by the bridging carboxylate functions.



μ-*O,O'-syn, syn*
I

μ-*O,O'-syn, anti*
II

μ-*O,O'-anti, anti*
III

μ-η^2,η^1
IV

μ-η^1,η^1-monatomic
V

Figure 5. Bridging modes of the carboxyl function between two metal centres.

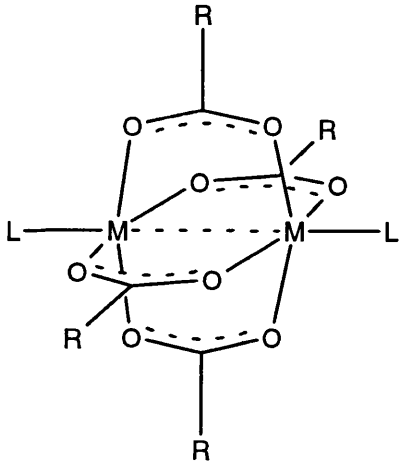


Figure 6. 'Paddle wheel' structure involving *syn, syn* bridging (Type **I**) carboxylates

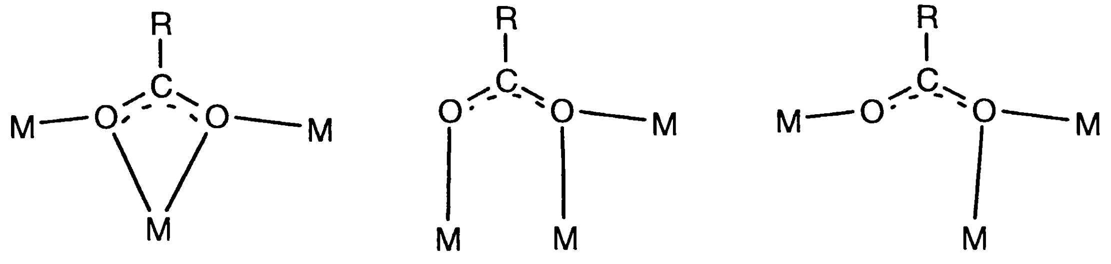
Trinuclear complexes containing *syn, syn* bridging carboxylates are also known, and take the form $[M_3(O)(O_2CR)_6L_3]^{n+}$ where L is some neutral ligand and n = 0 or 1 depending on the oxidation states of the metal centres. The oxygen sits in the centre of an equilateral triangle of the three metal atoms, each pair of which are bridged by two carboxylates. The iron(III) complex, $[Fe_3(O)(O_2CC_6H_5)_6(CH_3OH)_3](NO_3)(CH_3OH)_2$[77] and the iron(II/III) complex $[Fe_3(O)(O_2CCH_3)_6$(3-ethylpyridine)$_3].CH_3CCl_3$[78] are recent examples of this type of structure.

The *syn, anti*' and *anti, anti* bridging modes (Types **II** and **III**) generally lead to chain or layer compounds as in $[Co(H_2O)_2(O_2CCH_2OPh)_2]$[79] in which the *syn, anti* carboxylate groups are observed and in $[\{Cu(O_2CH)_2(H_2O)_2\}.2H_2O]$[80] in which *anti, anti* carboxylate groups are observed. However, discrete molecular entities are present in $[Mn_4(2\text{-}SC_6H_4CO_2)_2(CO)_{16}]$[56] and $[\{Zn_2(4\text{-}HOC_6H_4CO_2)_4L_2\}.2H_2O]$ (L = *N,N*-diethylnicotinamide)[81] despite both compounds displaying carboxylate groups that are *syn, anti* bridging. The *anti, anti* bridging mode is much less well represented in the literature than types **I**, **II**, **IV** or **V**.

Type **IV** bridging which is a combination of chelating and unidentate coordination modes is observed in the polymeric copper(II) and lead(II) complexes $[Cu(dien)(O_2CCH_3)][ClO_4]$ (dien = diethylenetriamine)[82] and [Pb(bzgly-*O*)$_2$(H$_2$O)$_2$].2H$_2$O (bzgly-*O* = *N*-benzoylglycinato-*O*).[83]

The monoatomic bridging mode (Type **V**) is displayed by the mercury(II) and copper(II) complexes $[Hg(O_2CCH_3)_2P(C_6H_{11})_3]_2$[84] and $[Cu_2(O_2CCH_3)_2$(7-amino-4-methyl-5-aza-3-hepten-2-onato)$_2]$.[85]

Figure 7 shows the possible coordination modes for carboxyl functions bridging three metal centres. The most common of these involves the chelating and *anti, anti* bridging type **VI** which occurs in barium cyanoacetate[86] and in the slightly more exotic barium 1,3-dithiepan-2-ylidenemalonate.[53] Type **VII** features in certain 'paddle wheel' structures when the axial ligand L, is a carboxyl function of an adjacent bimetallic unit[87], in related planar Cu(I) and Ag(I) dimeric systems (Fig. 8),[88,89] and in the unusual structure of the silver(I) betaine complex $[\{Ag_4(Me_3NCH_2CO_2)_6\}_n](ClO_4)_{4n}$.[90]



VI VII VIII

Figure 7. Bridging modes of the carboxyl function between three metal centres.

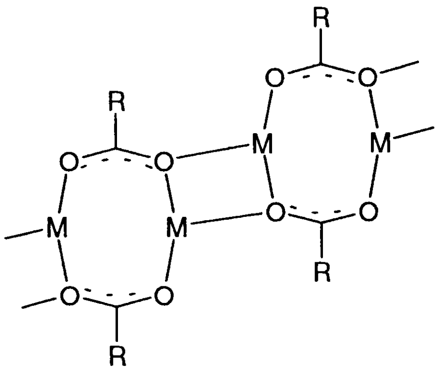


Figure 8. Type **VII** bridging as seen in certain Cu(I) and Ag(I) carboxylates.

The final bridging mode between three metal centres, type **VIII** has recently been reported for the copper(II) complex $[\{Cu_2L(pyca)(H_2O)\}_n][ClO_4]_4.2nH_2O$ (H_2L = *N,N'*-bis(2-aminoethyl)oxamide, Hpyca = pyridine-4-carboxylic acid). The C-O bond distances display the asymmmetry of the O-C-O moiety which is attached to three metal atoms via one short [1.953(4)Å] and two longer Cu-O distances [2.492(5), 2.444(5)Å].[91]

Bridging to four metal atoms (Type **IX**, Fig. 9) occurs in the benzene solvated silver(I) carboxylate, bis[silver(I)trifluoroacetate]benzene.[92]

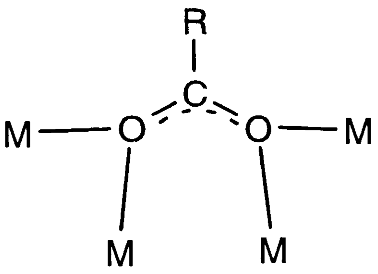


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Figure 9. Carboxylate bridging to four metal centres as observed in the crystal structure of $[(AgO_2CCF_3)_2C_6H_6]$.

1.2.2.2. Infrared Spectroscopy

The bonding modes of the carboxylate function have frequently been predicted, although not always successfully, from the difference in energy between the symmetric and asymmetric stretches of the O-C-O group. The basis of these speculations has been the inequivalence of the two carbon-oxygen bonds in certain coordination modes. For unidentate coordination where the asymmetry of the carboxyl group is large, a shift of the asymmetric stretch to higher frequency compared to the free ion is expected. This gives rise to large values of $\Delta[\nu_{asym(O\text{-}C\text{-}O)}\text{-}\nu_{sym(O\text{-}C\text{-}O)}]$. With more symmetric coordination modes, the difference between the symmetric and asymmetric stretches is expected to be lower than that found in the free ion.

The structures of metal acetates have been reviewed with the specific intent of drawing correlations between the bonding mode of the carboxylate function and the value of $\Delta[\nu_{asym(O\text{-}C\text{-}O)}\text{-}\nu_{sym(O\text{-}C\text{-}O)}]$.[93] This work concluded that (i) large separations $\{\Delta[\nu_{asym(O\text{-}C\text{-}O)}\text{-}\nu_{sym(O\text{-}C\text{-}O)}] > 200cm^{-1}\}$ between the two carboxyl stretching modes are indicative of unidentate coordination, (ii) separations significantly lower than ionic values $\{\Delta[\nu_{asym(O\text{-}C\text{-}O)}\text{-}\nu_{sym(O\text{-}C\text{-}O)}] < 150cm^{-1}\}$ are indicative of bridging or chelating coordination and (iii) very low separations $\{\Delta[\nu_{asym(O\text{-}C\text{-}O)}\text{-}\nu_{sym(O\text{-}C\text{-}O)}] < 105cm^{-1}\}$ point to chelating coordination. These values compare with $\Delta[\nu_{asym(O\text{-}C\text{-}O)}\text{-}\nu_{sym(O\text{-}C\text{-}O)}] = 164cm^{-1}$ for the acetate group in NaO_2CCH_3 taken as the free ion. The analogous values for trifluoroacetate derivatives were also assessed with similar correlations being noted and it was suggested that extension to other carboxylate systems would be valid although less precise.

The above rules can prove useful in proposing the type of carboxyl interaction present in a metal complex when no diffraction data are available. In particular, infrared data are commonly used to differentiate between unidentate and all other coordination modes. The main draw-backs occur in the assignment of the symmetric and asymmetric stretches and with practical difficulties in recording IR spectra. In addition, features such as hydrogen bonding can lead to less asymmetry in unidentate carboxylates with the possibility of significantly lowering the value of $\Delta[\nu_{asym(O\text{-}C\text{-}O)}\text{-}\nu_{sym(O\text{-}C\text{-}O)}]$. In summary, IR data can give an indication of the carboxylate bonding in a complex, but should not form the sole basis of any structural conclusions.

1.3. Bis(cyclopentadienyl)titanium(IV) Carboxylates

The first titanocene carboxylate complexes were reported in a patent in 1961.[94] Since then there have been many reports on the synthesis, reactivity and applications of these compounds.[1, 95] The bulk of this research has concentrated on synthetic methods and structural characterisation but they have also been investigated for applications in cancer therapy, organic synthesis and polymeric materials.

1.3.1. Synthesis

Many synthetic routes that apply to metal carboxylates in general apply to titanocene carboxylates. However, the sensitivity of products towards hydrolysis and their thermal instability must be taken into account.

Bis(cyclopentadienyl)titanium(IV) carboxylates have been prepared principally by metathesis reactions. Frequently the sodium or potassium salt of the appropriate carboxylic acid is treated with a bis(cyclopentadienyl)titanium dihalide in an organic solvent under anhydrous conditions. Refluxing THF was used in the first synthesis of titanocene carboxylates and these conditions have since been used in the preparation of a range of alkyl carboxylates (Equation 17).[94,96]

$$(CH_3C_5H_4)_2TiCl_2 + 2NaO_2CR \xrightarrow{THF/reflux} (CH_3C_5H_4)_2Ti(O_2CR)_2 + 2NaCl \qquad \text{Eq. 17}$$

$R = Me, Et, {}^nPr, Ph, CH_2Cl, CHCl_2.$

Benzene has been commonly used as the solvent for aryl derivatives, the reactions taking place at lower temperatures (Equation 18)[97,98] and the monocarboxylato compound [$Cp_2TiCl(O_2CPh)$] was prepared in refluxing toluene from a 1:1 mixture of sodium benzoate and Cp_2TiCl_2.[99]

$$Cp_2TiCl_2 + 2NaO_2CAr \xrightarrow{C_6H_6/30^\circ C} Cp_2Ti(O_2CAr)_2 + 2NaCl \qquad \text{Eq. 18}$$

The heterobimetallic complexes $Cp_2M[(O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ (M = Ti or Zr) were prepared in dichloromethane at 0°C (Equation 19).[100] Other chlorinated solvents have also been used.[101,102]

$$Cp_2TiCl_2 + 2Na[(O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]$$

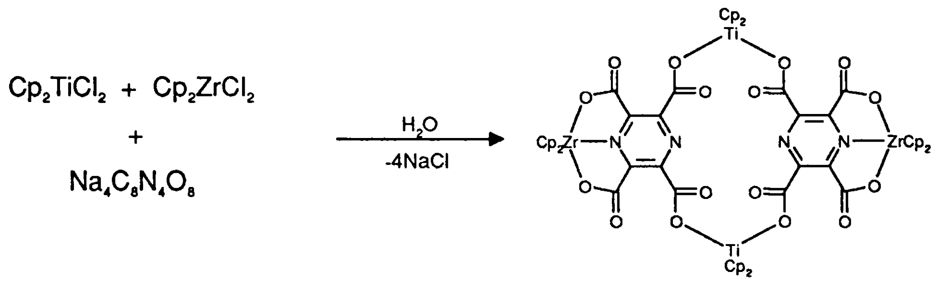
$$\xrightarrow{CH_2Cl_2/0^\circ C} Cp_2Ti[(O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2 \qquad \text{Eq. 19}$$

Metathesis reactions have also been carried out successfully in aqueous media to yield a range of carboxylate compounds (Equation 20),[103,104] including the tetranuclear terephthalate (Equation 21).[105] Although convenient, it has been remarked by Meirim *et al* that aqueous mediated routes are not as widely applicable as anhydrous methods.[106]

$$Cp_2TiCl_2 + 2NaO_2CPh \xrightarrow{H_2O} Cp_2Ti(O_2CPh)_2 + 2NaCl \qquad \text{Eq. 20}$$

$$4Cp_2TiCl_2 + 4Na_2(O_2CC_6H_4CO_2) \xrightarrow{H_2O} [Cp_2Ti(O_2CC_6H_4CO_2)]_4 + 8NaCl \qquad \text{Eq. 21}$$

The binuclear complexes $\{Cp_2Ti[O(CH_2CO_2)_2]\}_2$, $[Cp_2Ti(O_2CCH{=}CHCO_2)]_2$ and $[Cp_2Ti(C_8N_2O_8)TiCp_2]_2$ ($H_4C_8N_2O_8$ = pyrazine tetracarboxylic acid) and the mononuclear penta-coordinate complex $\{Cp_2Ti[O(CH_2CO_2)_2]\}$ were prepared in the two phase system of $H_2O/CHCl_3$ from the sodium carboxylates and Cp_2TiCl_2.[107,108,109] The heterobinuclear complex $[Cp_2Ti(C_8N_2O_8)ZrCp_2]_2$ was prepared in a similar manner from equimolar quantities of Cp_2TiCl_2, Cp_2ZrCl_2 and tetrasodium pyrazine tetracarboxylate (Equation 22) the zirconium atom displaying a higher coordination number than titanium.[108]



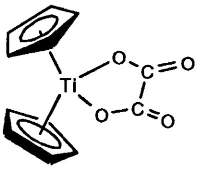
Eq. 22

In addition to alkali metal salts, silver(I) and mercury(I) carboxylates have also been used to prepare the titanocene derivatives.[110,111]

A related method to transmetallations is the reaction of the free acids with metal halides in the presence of a base such as triethylamine (Equation 23).[112,113,114,115,116]

$$Cp_2TiCl_2 + 2HO_2CPh + Et_3N \longrightarrow Cp_2Ti(O_2CPh)_2 + 2Et_3NHCl \qquad \text{Eq. 23}$$

Under aqueous conditions and in two phase systems, Cp_2TiCl_2 reacts with dicarboxylic acids to give the chelating oxalate derivative **17**, the mononuclear bis(hydrogenmaleato) complex **18** and the bridging acetylene dicarboxylates **19** and **20** (Equations 24 and 25)[117,118]



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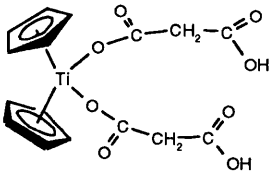

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$[Cp_2Ti(O_2CC{\equiv}CCO_2)]_2$

19

$[Cp_2Ti(O_2CC{\equiv}CCO_2)]_4$

20

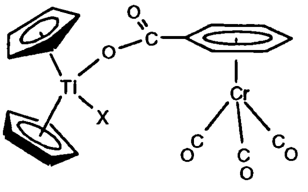
$$Cp_2TiCl_2 + xs\ HO_2CCH_2CO_2H \xrightarrow{H_2O} Cp_2Ti(O_2CCH_2CO_2H)_2 + 2HCl \qquad \text{Eq. 24}$$

$$Cp_2TiCl_2 + xs\ HO_2CC{\equiv}CCO_2H \xrightarrow{H_2O/CH_2Cl_2} [Cp_2Ti(O_2CC{\equiv}CCO_2)]_n + 2HCl \qquad \text{Eq. 25}$$

n = 4 with phase transfer reagent Bu_4NBr and in alternative solvent system H_2O/dioxane
n = 2 without phase transfer reagent

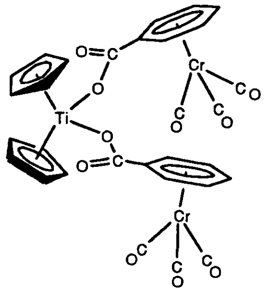
A particularly useful method which has been reported is the reaction of bis(cyclopentadienyl)bis(methyl)titanium(IV) with free carboxylic acids to liberate methane (Equation 26).[119,120] The heterobimetallic complexes **21** and **22** were prepared in this manner. In certain cases this route is more convenient than the methods mentioned above which can sometimes generate insoluble products.[11]

$$Cp_2TiMe_2 + 2HO_2CR \longrightarrow Cp_2Ti(O_2CR)_2 + 2MeH \qquad \text{Eq. 26}$$



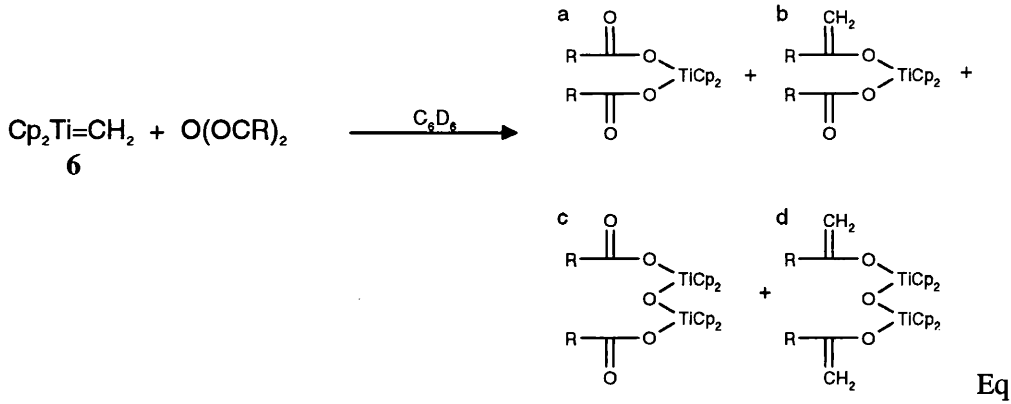
X = Me, Cl, Br

21



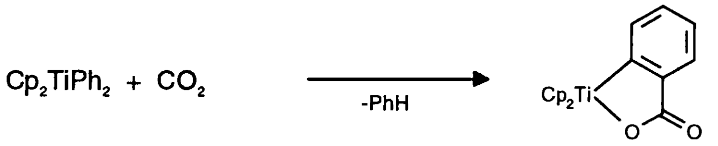
22

A related reaction which has been used to produce bis(cyclopentadienyl)titanium(IV) carboxylates involves the treatment of acid anhydrides with the titanium alkene complex **6** generated from titanacyclobutanes (see earlier). Reaction of acetic, propionic or butyric anhydrides with **6** in C_6D_6 gave a mixture of products as indentified by ^1H NMR (Equation 27)[121]



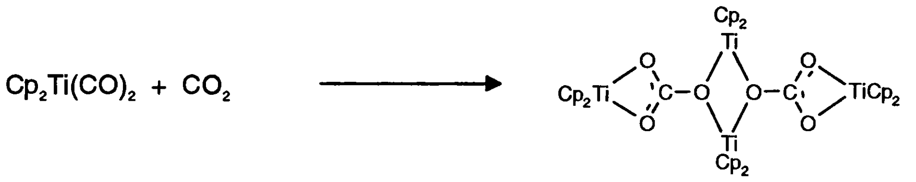
Eq. 27

Insertion of carbon dioxide into the Ti-C σ-bonds of bis(cyclopentadienyl)bis(phenyl)titanium gives the titanacyclic carboxylate **23** (Equation 28).[122] Interestingly, reaction of CO_2 and the titanium(II) compound $Cp_2Ti(CO)_2$ yields the tetranuclear titanium(III) carbonate complex **24** (Equation 29).[123]



23

Eq. 28



24

Eq. 29

Recently, ionic titanocene complexes have been reported consisting of a metal-centred cation with amino acid ligands bound *via* monodentate carboxyl functions and chloride counter ions.[124,125] They have been prepared by the reaction of Cp_2TiCl_2 and the amino acid in methanol (Equation 30). The choice of solvent appears to be important.[126]

$$Cp_2TiCl_2 \; + \; 2aa \xrightarrow{MeOH} [Cp_2Ti(aa)_2]^{2+} [Cl]^-_2 \qquad \text{Eq. 30}$$

aa = glycine, L-alanine, 2-methlyalanine (Ref. 124)
= DL-phenylalanine, DL-4-fluorophenylalanine (Ref. 125)

Other methods include the reaction of organic peroxides with bis(σ-aryl)bis(cyclopentadienyl)-titanium (Equation 31)[127], the oxidation of various bis(cyclopentadienyl)titanium(II) complexes (Equation 32),[128] and the substitution of a thienyl ligand (Equation 33).[129]

$$\mathrm{Cp_2TiPh_2 + (RCO)_2O_2 \longrightarrow Cp_2Ti(O_2CR)_2} \qquad \text{Eq. 31}$$

$$\mathrm{Cp_2Ti(C_2Me_2) + (CF_3CO)_2O \longrightarrow Cp_2Ti(O_2CCF_3)_2 + MeCHCHMe} \qquad \text{Eq. 32}$$

$$\mathrm{Cp_2TiCl(L) + RCO_2H \longrightarrow Cp_2TiCl(O_2CR) + HL} \qquad \text{Eq. 33}$$

L = 2-thienyl, R = CCl_3, CBr_3, C_6F_5, $C_6H_4NO_2$-o

An unusual substitution reaction occurs to yield monocarboxylato titanocenes when certain alkoxides are treated with carboxylic acids (Equation 34).[130]

$$\mathrm{Cp_2Ti(CH_3)OR + HO_2CR' \longrightarrow Cp_2Ti(CH_3)(O_2CR') + HOR} \qquad \text{Eq. 34}$$

R = $CHPh_2$, menthyl, (1S-)bornyl; R' = $CHPh_2$, CH=CHPh, Ph.

The same researchers also reported that reaction of $Cp_2Ti(CH_3)Cl$ with one equivalent of carboxylic acid yields a 1:1 mixture of titanocene dichloride and the bis(carboxylato) titanocene derivative (Equation 35). No mixed ligand products could be detected by NMR.

$$\mathrm{2Cp_2Ti(CH_3)Cl + 2HO_2CR \xrightarrow[R\,=\,CF_3,\ CHPh_2.]{toluene/24hrs} Cp_2TiCl_2 + Cp_2Ti(O_2CR)_2} \qquad \text{Eq. 35}$$

1.3.2. Structures

The carboxylates of bis(cyclopentadienyl)titanium(III) and mono(cyclopentadienyl)titanium(III) or (IV) show a variety of structures with the carboxylates as monodentate, chelating or bidentate bridging ligands and the titanium adopting coordination numbers[†] from 4 up to 7.[131]

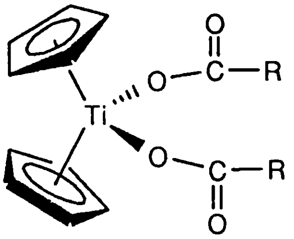
Conversely, bis(cyclopentadienyl)titanium(IV) carboxylates generally contain monodentate carboxyl functions, with distorted pseudo-tetrahedral geometry at the metal, **25**. In particular, of the twenty or more reported crystal structures of bis(cyclopentadienyl)titanium(IV) compounds containing two carboxyl functions bonded to each titanium atom (Table 1), only four show a different metal coordination geometry and all of them contain carboxylates which are exclusively monodentate.

[†] Assuming the cyclopentadienyl rings occupy one coordination site each

Table 1. Structurally characterised bis(carboxylato)bis(cyclopentadienyl)titanium(IV) complexes including compounds containing cyclopentadienyl derivatives.

	coordination number of Ti[a]	reference
$Cp_2Ti(O_2CH)_2$	4	132
$Cp_2Ti(O_2CCF_3)_2$	4	128
$Cp_2Ti(O_2CC_6H_5)_2$	4	102, 104, 112
$Cp'_2Ti(2\text{-}CH_3C_6H_4CO_2)_2$	4	98
$Cp' = CH_3C_5H_4$		
$Cp_2Ti(3\text{-}CH_3OC_6H_4CO_2)_2$	4	137
$Cp_2Ti(4\text{-}NO_2C_6H_4CO_2)_2$	4	133
$[Cp_2Ti\{O_2CC(CH_3)_2NH_3\}_2][Cl]_2$	4	124
$[Cp_2Ti(O_2CR)_2][AsF_6]_2$[b]	4	125
O_2CR = D,L-4-fluorophenylalanine		
$[Cp_2Ti(O_2CC{\equiv}CCO_2)]_2$	4	118
$[Cp_2Ti(O_2CC{\equiv}CCO_2)]_4$.5(solvent)	4	118
solvent = dichloromethane or dioxane		
$[Cp_2Ti(4\text{-}O_2CC_6H_4CO_2)]_4$	4	105
$Cp_2Ti(O_2CCH{=}CHCO_2)]_2$	4	107
$Cp_2Ti(O_2CCO_2)$	4	117
$Cp_2Ti(O_2CCH_2CO_2H)_2$	4	117
$[Cp_2Ti\{3,5\text{-}C_5H_3N(CO_2)_2\}]_2$	4	115
$3,5\text{-}C_5H_3N(CO_2H)_2$ = pyridine-3,5-dicarboxylic acid		
$Cp_2Ti(O_2CCH_2OCH_2CO_2)$	5	109
$[Cp_2Ti(O_2CCH_2OCH_2CO_2)]_2$	4	109
$Cp_2Ti\{2,6\text{-}C_5H_3N(CO_2)_2\}$	5	11
$2,6\text{-}C_5H_3N(CO_2H)_2$ = pyridine-2,6-dicarboxylic acid (dipicolinic acid)		
$[Cp_2Ti(C_8N_2O_8)TiCp_2]_2.2H_2O.2CHCl_3.3CH_3NO_2$	4, 5	108
$C_8N_2O_8H_4$ = pyrazinetetracarboxylic acid		
$Cp_2Ti(C_8N_2O_8H_2).2H_2O,CH_3NO_2$	5	108
$C_8N_2O_8H_4$ = pyrazinetetracarboxylic acid		
$[Cp_2Ti(C_8N_2O_8)ZrCp_2]_2.CH_3NO_2.6CHCl_3$	4	108
$C_8N_2O_8H_4$ = pyrazinetetracarboxylic acid	(Zr-5)	
$CpTi[(O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$	4	100
$Cp'_2Ti(O_2CR)_2$: Cp' = ethylene(tetrahydro-1S-indenyl)[c]	4	116
ethylene(tetrahydro-1R-indenyl)[c]	4	116
HO_2CR = *O*-acetyl-R-mandelic acid		

a - Assuming each cyclopentadienyl moiety occupies one coordination site. b - Preliminary structure only.
c - Both diastereoisomers characterised by independent structure determinations



25

Bis(cyclopentadienyl)bis(trifluoroacetato)titanium(IV) has a solid state molecular structure that is typical for titanocene carboxylates of Ti(IV) (Fig. 10).[128] The titanium atom is surrounded by two cyclopentadienyl ligands [C(10)-C(14), C(20)-C(24)]and two monodentate carboxyl functions of the trifluoroacetates. The distances from the centres of the cyclopentadienyl rings to the titanium atom are 2.06 and 2.05Å, with a angle between these two vectors of 133.3°.

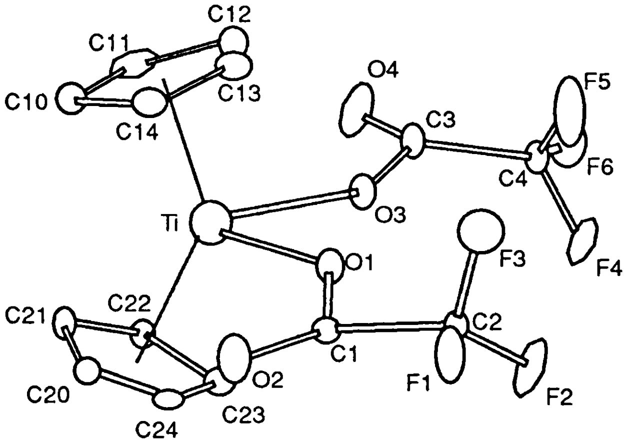


Figure 10. The molecular structure of $Cp_2Ti(O_2CCF_3)_2$.

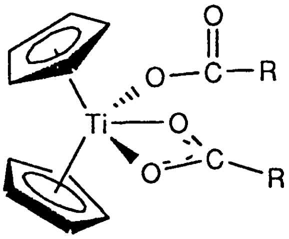
The geometries of the two carboxyl functions are very similar in this particular instance. The Ti-O-C and O-C-O angles are reasonably similar for both ligands [Ti-O-C: 142.8(5), 149.2(6)°; O-C-O: 127.9(5), 126.4(9)°]. An alternative arrangement where the two carboxyl functions are quite different is also frequently observed and there are several reports of complexes displaying both types in different polymorphs (see later).

Another point worth noting is the magnitude of these angles which tend to be fairly large. The Ti-O-C angles in $Cp_2Ti(O_2CR)_2$ compounds range from approximately 130-170° and the averages of the two angles in each complex are around 145-155°. Typical M-O-C values for complexes containing monodentate carboxylates range between 105-135°.

The large O-C-O angles are an indication of the monodentate coordination mode of the trifluoroacetate group. This is also reflected in the C-O bond lengths [C(1)-O(1) = 1.265(8)Å, C(1)-O(2) = 1.217(10)Å; values for the second carboxylate were not reported].

The O-Ti-O angle of 89.7(2)° is slightly lower than those found in other structures which range between 90.5-92.5°.

An alternative structural type **26** has been suggested on the basis of infrared data,[113] but these predictions have not been confirmed crystallographically for compounds containing either one or two carboxylate ligands.



26

From a consideration of the 18 electron rule, one might expect that structures of type **26** would be more stable than type **25**. The formal electron count at titanium in **26** is 18VE as opposed to 16VE in **25**. However, the large Ti-O-C angles and short Ti-O bonds in Ti(IV) titanocene bis(carboxylates) suggest that there is significant double bond character between titanium and oxygen. It can therefore be proposed that the titanium atoms in structures of type **25** achieve an effective 18VE configuration through extra π-donation from oxygen.

Table 2 gives the parameters for the carboxyl-titanium bonding in the monoclinic and orthorhombic modifications of bis(benzoato)bis(cyclopentadienyl)titanium(IV).

The individual molecules in the orthorhombic modifications contain one short and one long Ti-O distance. The shorter bond corresponds with the wider Ti-O-C angle and implies a bonding situation as shown in Figure 11a where titanium achieves an effective 18VE configuration through Ti-O single and double bonds.

Table 2. Bond lengths (Å) and bond angles (°) for the carboxyl-titanium moieties in the monoclinic and two orthorhombic modifications of bis(benzoato)bis(cyclopentadienyl)-titanium(IV).

	Ti-O	Ti-O-C	Ti-O'	Ti-O'-C
monoclinic[a]	1.922(7)	148.6(4)	1.930(5)	147.9(7)
orthorhombic[b]	1.894(4)	168.7(3)	1.995(3)	135.2(3)
orthorhombic[c]	1.913(6)	157.0(7)	1.976(5)	135.4(6)

a - Ref. 112, b - Ref. 104, c - Ref. 102.

The monoclinic benzoate and trifluoroacetate derivatives have similar Ti-O distances and Ti-O-C angles for both carboxylate ligands and suggest a bonding situation as shown in Figure 11b. Both carboxylates contribute additional electron density from the titanium bound oxygens *via* π-interactions to give two Ti-O partial double bonds.

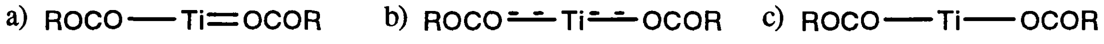
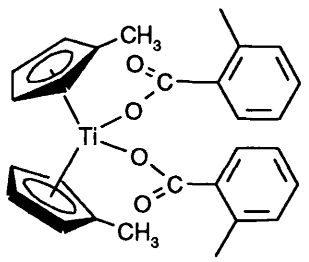


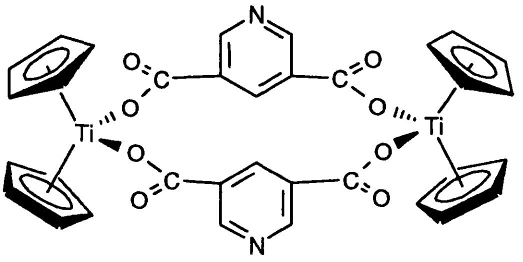
Figure 11. Suggested Ti-O bonding in titanocene bis(carboxylates). a) 18VE configuration attained though double and single Ti-O bonds. b) 18VE configuration attained though two partial Ti-O double bonds. c) 16VE configuration attained.

With sterically restricted systems such as $[(CH_3C_5H_4)_2Ti(O_2CC_6H_4Me\text{-}2)_2]$ **27**[98] and $[Cp_2Ti(\text{pyridine-3,5-dicarboxylate})_2TiCp_2]$ **28**[115] it is possible that a bonding situation similar to that shown in Figure 11c occurs. The titanium atoms in these cases have 16VE configurations.



Ti-O = 1.961(3)Å; Ti-O-C = 137.9(7)°
Ti-O' = 1.979(3)Å; Ti-O'-C = 138.6(4)°

27

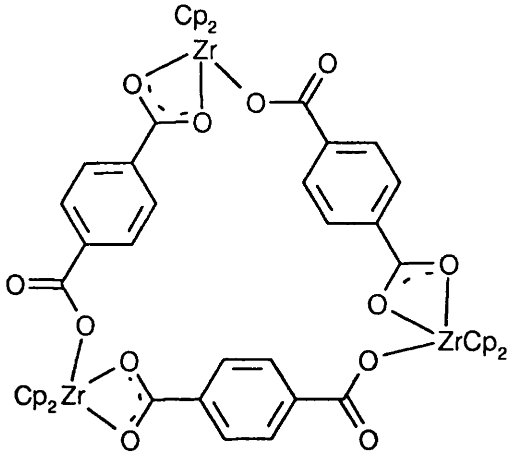


Ti-O = 1.961(3)Å; Ti-O-C = 134.3(2)°
Ti-O' = 1.958(3)Å; Ti-O'-C = 135.7(3)°

28

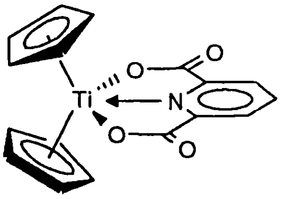
In addition to the above hypotheses, EHMO calculations on the model complex $[Cp_2Ti(O_2CH)_2]$, have shown that there is a destabilizing interaction between the cyclopentadienyl rings and the carboxylato ligands which is significantly greater for structures having a chelating carboxylate.[112]

With the larger zirconium atom in the analogous zirconocene carboxylates, chelation of carboxyl functions is observed. For example, in the dicarboxylato complex $[Cp_2Zr(O_2CC_6H_4CO_2\text{-}4)]_3$, each bridging terephthalato ligand contains one chelating and one unidentate carboxyl function forming a trimeric metallocycle **29**.[134] Similar chelating and unidentate arrangements are seen in the dimeric dimethoxylfuran-2,5-dicarboxylato[135] and the polymeric acetylene dicarboxylato[136] complexes.



29

When a third donor atom is held in close proximity to the titanium atom by a dicarboxylato ligand (eg. 2,6-dipicolinato or oxydiacetato) penta-coordinate geometries can be generated **1**, **30**, **31**.[11,108,109] These 18-electron species show greater stability than the four-coordinate compounds. For example, the 2,6-dipicolinato derivative **1** can be purified by silica-gel column chromatography and reacts slowly (30min. for complete conversion to Cp_2TiCl_2) with gaseous HCl. The reaction of four-coordinate carboxylates with HCl is almost instantaneous.



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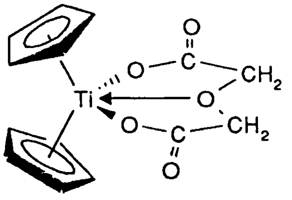

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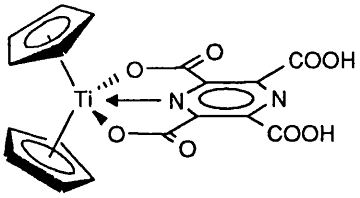


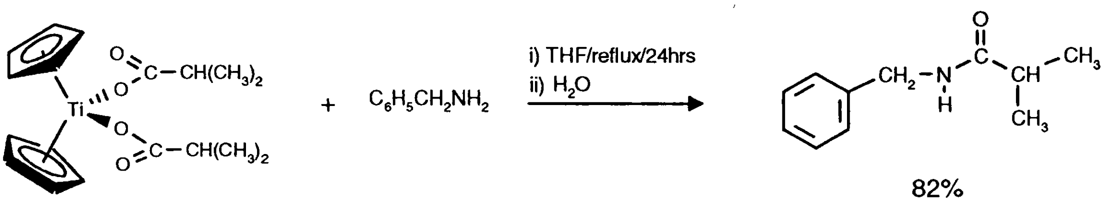
31

1.3.3. Reactivity

Titanocene bis(carboxylate) derivatives are reasonably air stable in the solid state. In solution however, they are sensitive to air and moisture, and readily form oxo bridged species. It is rather surprising that they can be prepared from aqueous media, although this synthetic route is not applicable to all carboxylates, and the contact time of the complex with water must be monitored carefully. They are also generally thermally unstable, decomposing around 100°C.

Reaction of $[Cp_2Ti(O_2CC_6H_5)_2]$ with bromine in tetrachloromethane yields $C_5H_5Br_3$ and $C_5H_5Br_5$ in a stereospecific manner *via* cleavage of the cyclopentadienyl rings.[102] The stereoselectivity of this reaction was explained in terms of the non-equivalence of the two benzoato ligands which results in one side of the Cp_2Ti moiety being less sterically hindered for electrophilic attack. This assumes that the asymmetry between the two carboxyl functions observed in the solid state remains in solution. Other researchers have also suggested that the non-equivalence of the Ti-O bonding is not restricted to the solid state.[137]

The reaction of titanocene carboxylates with amines has been investigated with a view to producing synthetically useful reagents for amide bond formation.[138] The isobutyrate derivative **32** reacted with benzylamine to give *N*-benzylisobutyramide in 82% yield (Scheme 9). The peptide **34** was produced in a similar manner from the amino acidato-titanocene complex **33** and alanine methyl ester hydrochloride in the presence of triethylamine (Scheme 10). Unfortunately the conditions used to induce a reaction are too harsh and too long for practical peptide synthesis.



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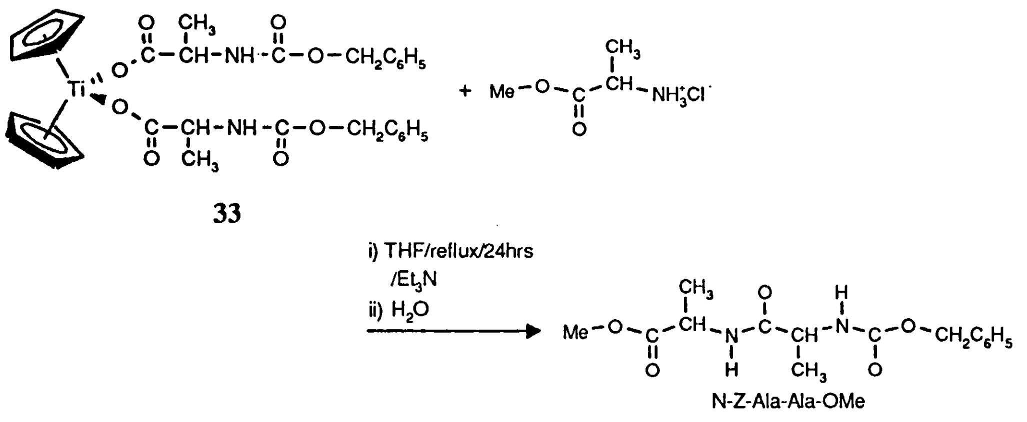
Scheme 9



33

34

45%

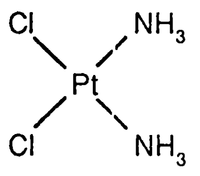
Scheme 10

1.3.4. Applications

1.3.4.1. Antitumour Activity

Although not fully developed as a registered drug, the titanium(IV) compound, titanocene dichloride, is currently undergoing clinical testing (see earlier). In the meantime a number of studies have been carried out on the cytotoxic activity of various other titanocene derivatives. These investigations have shown that modifying the cyclopentadienyl rings causes a loss of activity whereas the nature of the non-cyclopentadienyl ligands is not important for antitumour effects *in vitro*.[139,140] It has also been verified that the chemotherapeutic effects are due to the activity of titanium species and not the cyclopentadienyl ligands.[141]

The therapeutic range and toxic side effects of the well established anticancer agent *cis*-diamminedichloroplatinum(II) 35 have been modified beneficially by replacing the chloride ligands for other anionic ligands. In particular, the carboxylate derivative diammine(cyclobutane-1,1-dicarboxylate)platinum(II) 36 has been developed in a second generation of platinum-based drugs and is used clinically under the name carboplatin.



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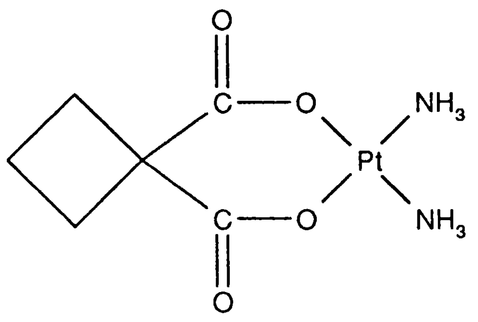


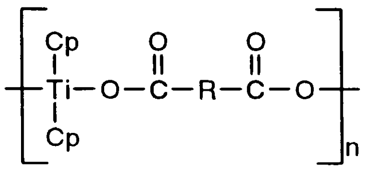
36

In an analogous manner to the platinum reagents, substitution of the chloride ligands in Cp_2TiCl_2 for other halides or pseudohalides such as carboxylate could lead to new drugs with different or enhanced therapeutic ranges and/or lower toxicities. Several groups have investigated titanocene carboxylates for this very reason.[114,125,142]

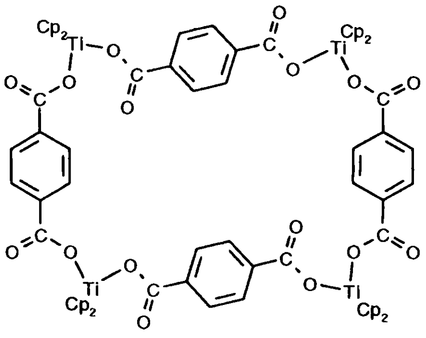
Investigations using experimental tumours on mice has revealed that the trichloroacetate and hydrogen malonate titanocene derivatives have slightly enhanced activities compared to the dichloride. In addition, the trifluoroacetate has low toxicity, and the hydrogen malonate derivative is particularly water soluble. Microbiological studies on the ionic amino acid complex $[Cp_2Ti(O_2CCH(NH_3)CH_2C_6H_4F\text{-}4)_2][Cl]_2$ have shown that the compound produces a similar elongation of bacteria cells to those observed by Rosenberg and coworkers with **35**.[35] Rosenberg's observations eventually lead to the development of cisplatin as a drug.

1.3.4.2. Polymeric Materials

Several research groups have investigated the use of dicarboxylic acids to produce polymeric materials containing organometallic segments **37**. The first reported synthesis by Carraher[143] was later questioned by Döppert[144] due to the lack of analytical data on the compounds produced. In addition, some of the systems investigated by Carraher have since been used to synthesise cyclic oligomers such as the tetrameric terephthalate **38**.[105]

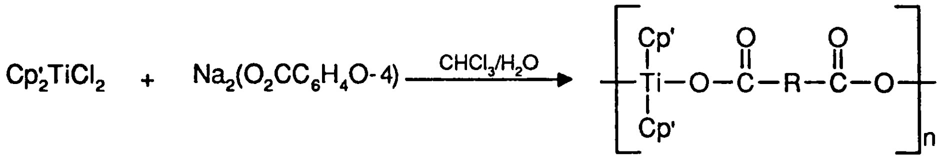


37

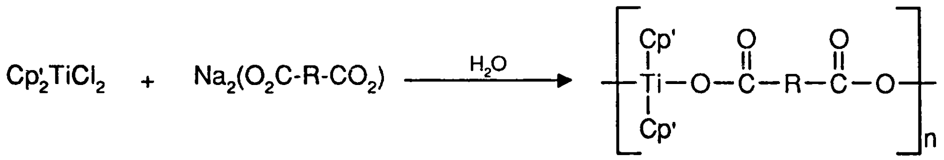


38

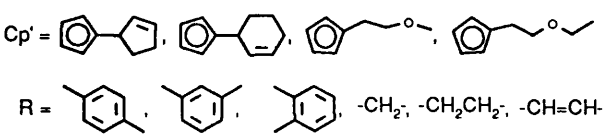
A later study by Shen *et al* produced materials that were slightly soluble in polar organic solvents.[145] Adding substituents to the cyclopentadienyl rings of the titanocene moiety such as cyclopentenyl, cyclohexenyl or alkoxyalkyl residues was reported to yield polymeric materials with 4-hydroxybenzoic acid (Scheme 11) and several dicarboxylic acids (Scheme 12) which were soluble in 2-chloroethane. The number average molecular weights of these materials were estimated to be between 10^4 and 10^5.



Scheme 11

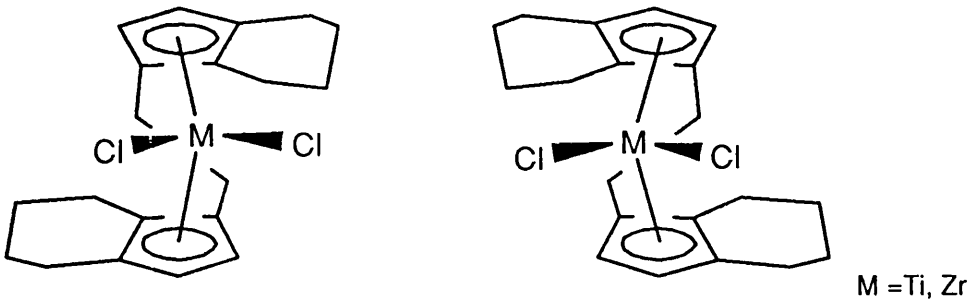


Scheme 12

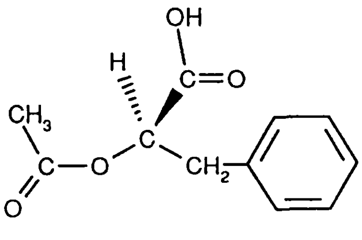


1.3.4.3. Resolution of Chiral Metallocene Catalysts

The separation of racemic mixtures of *ansa*-metallocene dichlorides has been achieved using naturally occuring chiral carboxylic acids. Derivatisation of rac-ethylenebis(tetrahydro-1-indenyl)titanium and zirconium dichlorides **39** with *O*- acetyl-R-mandelic acid **40** yields diastereoisomers which can be differentiated by their solubilities and further more isolated independently by fractional crystallisation.[116]



39



O-acetyl-R-mandelic acid 40

1.4. Heterometallic Compounds

Complexes containing two or more metals of the same type have been known for many years and several reviews have dealt with this subject.[146] Attention towards these compounds arose due to the interesting metal - metal interactions that are often present and the possible applications to materials chemistry and catalysis.[147] In addition, the discovery that binuclear metallic species are the active sites in a number of enzymes and co-enzymes has led to renewed research effort in this field.[148]

A more recent development is the preparation and reactivity of heterometallic complexes, where two or more very different metals are brought together. Much of this work has been devoted to the development of catalysts, or models for catalytic systems,[149,150] although there has also been an interest in modelling biological systems,[151] and even therapeutic applications.[152]

Metal centres have been connected *via* a variety of linkages (Fig. 12). Short metal-metal distances have been achieved using ligands such as carbonyl, amido, phosphido, hydrido, halide, thiolato and selenato as bridging groups (Fig. 12a). Carbon based bridges are also known (Fig. 12b), for example in Tebbe's reagent **7**, and complexes can be found in which the metal nuclei are linked solely through direct metal-metal bonds (Fig. 12c).

Rather longer metal-metal distances have been produced using bifunctional ligands. Often these involve bridging ligands having a delocalised π-system and a donor atom (Fig. 12d), as observed in *P*-coordinated complexes of the commercially available 1,1'-bis(diphenyphosphino)ferrocene.[153] Compounds containing metal-carbon σ-bonded organic groups with addtional donor functions can also form heterometallic species (Fig. 12e).

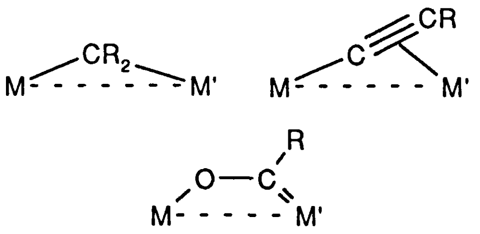
Of relevence to this work are the class of heteronuclear complexes bridged by ligands containing two or more donor atoms which have different affinities for certain metals, usually by containing hard and soft donors (Fig. 12f).

a)

X = CO, NR_2, PR_2, H, Cl, Br, SR, SeR

e.g. $Cp_2Ti(thf)(\mu\text{-}CO)Mo(CO)_2Cp$[154]
$CpTi(\mu\text{-}NMe_2)_3Cr(CO)_3$[155]
$Cp_2Zr(\mu\text{-}PR_2)_2RhH(CO)PPh_3$[156]
$Cp_2Zr(O_2CH)(\mu\text{-}H)(\mu\text{-}N^tBu)IrCp^*$[157]
$[Cp_2Ti(\mu\text{-}Cl)_2]_2Zn$[158]
$[Cp_2Ti(\mu\text{-}SEt)_2CuPPh_3]PF_6$[159]
$[Cp_2Ti(\mu\text{-}SeMe)_2Fe(NO)_2$[160]

b)

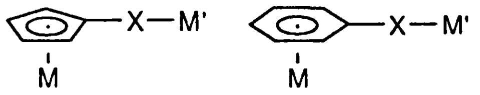


e.g. $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$ 7[25]
$Cp_2Ta(\mu\text{-}CH_2)CoCp$[161]
$(Me_3SiC_5H_4)_2Ti(\mu\text{-}C{\equiv}CSiMe_3)_2Cu(\eta^1\text{-}C_6H_2Me_3\text{-}2,4,6)$[162]
$[(Me_3SiC5H4)_2Ti(\mu\text{-}C{\equiv}CSiMe_3)_2]AgNO_2$[163]
$Cp_2TiCl(\mu\text{-}OCMe)Cr(CO)_5$[164]

c)

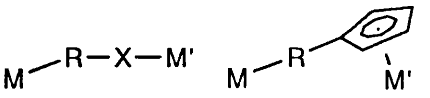
e.g. $[(Me_3SiC_5H_4)_2Nb(AuPPh_3)_2]PF_6$[165]
$[CH_2(CH_2NSiMe_3)_2Zr\{M(CO)_2Cp\}_2]$
(M = Fe, Ru)[166]
$Cp_2Ti[Co(CO)_4]_2$[167]

d)



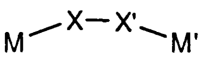
e.g. $[Fe(\mu\text{-}C_5Me_4PPh_2)]AuCl$[168]
$Cp_2Ti[(\mu\text{-}OC_6H_4CH_3)Cr(CO)_3]_2$[169]
$Ti(\mu\text{-}C_5H_4PPh_2)(\mu\text{-}C_7H_6PPh_2)Mo(CO)_3H$[170]

e)



e.g. $[Cp_2Zr(\mu\text{-}CH_2PPh_2)_2Cr(CO)_4]$[171]
$[Cp_2Zr(\mu\text{-}CH_2PPh_2)_2]_2Ni$[172]
$(Me_3SiC_5H_4)_2Ti[(\mu\text{-}C{\equiv}CC{\equiv}CC_5H_4)FeCp]_2$[173]

f)

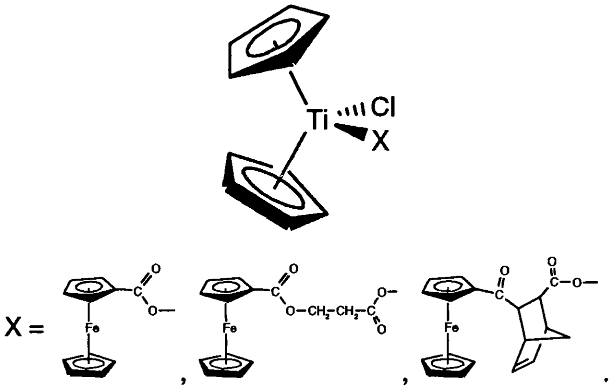


e.g. $Cp^*Zr(\mu\text{-}OCH_2PPh_2)_3Ni(CO)$[174]
$[Cp_2Zr(\mu\text{-}OC_6H_4PPh_2\text{-}2)_2\{Rh(CO)Cl\}]_n$[175]
$Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2PPh_2)_2Ni(CO)_2$[176]

Figure 12. Types of metal-metal interactions in heterobimetallic complexes.

There are very few examples of titanocene complexes containing additional heterometallic species where a carboxylate is the bridging ligand. The first report involved the substituted ferrocene complexes **41**. The monocarboxylato complex $Cp_2Ti(Cl)[(O_2CC_5H_4)FeCp]$ was prepared in 84%

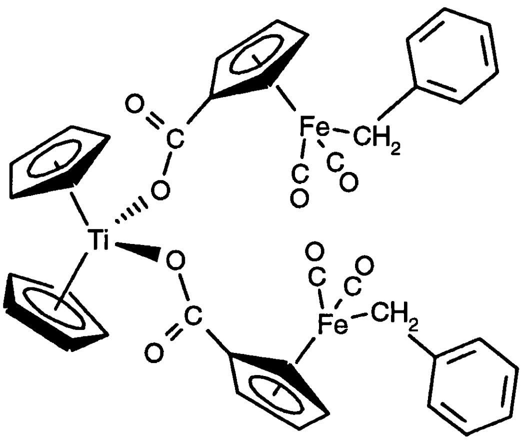
yield from Cp_2TiCl_2 and ferrocene carboxylic acid $[CpFe(C_5H_4CO_2H)]$ in the presence of $NaNH_2$ (Equation 36).[177,178]



41

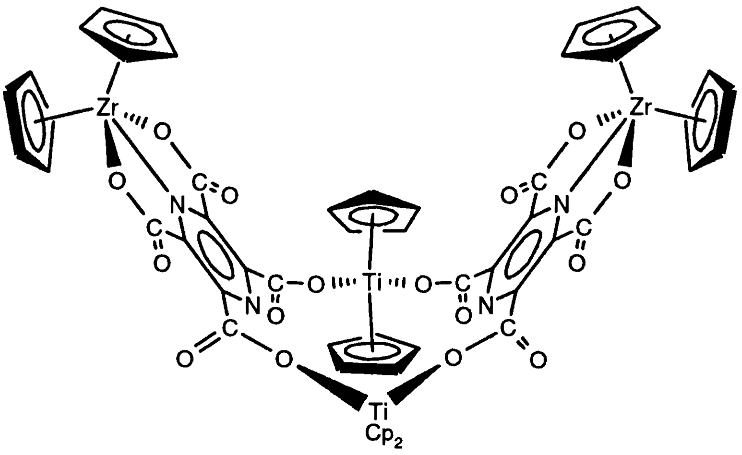
$$Cp_2TiCl_2 + [CpFe(C_5H_4CO_2H)] \xrightarrow[\text{-NaCl/-NH}_3]{\text{benzene/NaNH}_2} Cp_2Ti(Cl)[(O_2CC_5H_4)FeCp] \qquad \text{Eq. 36}$$

A later report by different researchers described the structure of the bis(carboxylato) complex $Cp_2Ti[(O_2CC_5H_4)Fe(CO)_2(CH_2Ph)]_2$ **42**, prepared as described earlier (Equation 19).[100] The titanocene carboxylate geometry does not appear to be particularly perturbed by the presence of the iron. Related chromium-arene complexes have also been prepared (Equation 26, see earlier).[120]



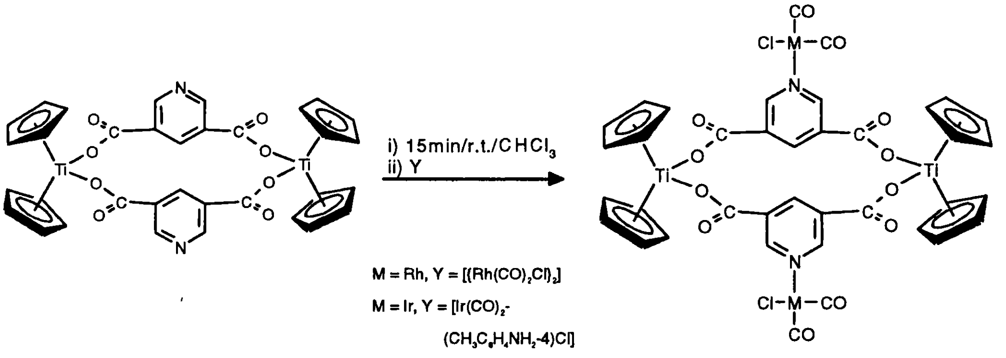
42

The first reported titanocene derivative involving titanium linked to another metal *via* a carboxylate ligand containing an additional donor atom was the Ti/Zr complex of pyrazinetetracarboxylate **43** (Equation 21).[108] The molecular structure contains tetranuclear species with two tianocene and two zirconocene moieties bound by two pyrazinetetracarboxylates acting as (3+1+1)-dentate ligands. The zirconium atoms are coordinated in a tridentate chelating manner similar to that found for 2,6-pyridinedicarboxylate ligands and the pseudo-tetrahedral titanium atoms bridge the two zirconocene species *via* monodentate carboxyl groups.



43

Finally, early-late heterobimetallic complexes have been prepared using the titanocene carboxylate **28** which contains uncoordinated pyridine nitrogen atoms. Reaction of **28** with [{Rh(CO)$_2$Cl}$_2$] or [Ir(CO)$_2$(CH$_3$C$_6$H$_4$NH$_2$-4)Cl] yielded the tetranuclear complexes [Cp$_2$Ti{μ-3,5-C$_5$H$_3$N(CO$_2$)$_2$M(CO)$_2$Cl}$_2$TiCp$_2$] (3,5-C$_5$H$_3$N(CO$_2$)$_2$ = 3,5-pyridinedicarboxylate; M = Rh, Ir) **44** (Equation 37).[115]



Eq. 37

28 **44**

Chapter 2.

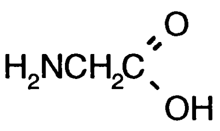
Bis(cyclopentadienyl)titanium(IV) Derivatives of Carboxylic Acids Containing Additional Nitrogen Donors.

2.1. Introduction

Of the types of carboxylic acids containing additional nitrogen donors, amino acids are among the most important. They are the basic building blocks of life, being readily polymerised through amide and other linkages to yield peptides and hence to more complicated structures. The study of amino acid-titanocene derivatives has become of particular importance following the discovery that bis(cyclopentadienyl)titanium dichloride is an effective antitumour agent.[34] Not only is it possible that new, more effective drugs could result but more significantly, investigating amino acid-titanocene interactions should provide insight into the mode of action of titanocene based reagents. To date, very little work has been carried out in this area.

In addition, it might be predicted that titanocene-amino acidate complexes would contain amine functions available for binding to a second metal centre yielding novel heterometallic species.

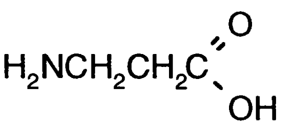
The nitrogen-containing carboxylic acids chosen for this study include three amino acids; glycine **45**, β-alanine **46**, and anthranilic acid **47**. The primary amine and carboxyl functions in these three compounds are separated by different spacers. Glycine, the simplest α-amino acid has a methylene bridge while β-alanine, a β-amino acid has a longer ethylene joining group. As with β-alanine, there is a two carbon link between the functional groups in anthranilic acid although in this case these atoms are part of a six-membered aromatic ring.



$H_2NCH_2C(=O)OH$

glycine

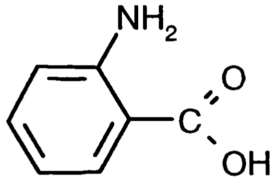
45



$H_2NCH_2CH_2C(=O)OH$

β-alanine

46

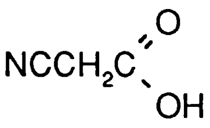


anthranilic acid

(2-aminobenzoic acid)

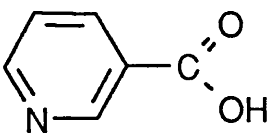
47

Two other related acids were also studied, namely cyanoacetic acid **48** and nicotinic acid **49**. Cyanoacetic acid was chosen as an analogue of simple amino acids such as **45**, and because it possesses a nitrile group which can act as an additional donor function. The nitrile function is often involved in bonding to transition metals, sometimes even without participation of the carboxylate group.[66] Nicotinic acid contains a pyridyl group which could either bond to titanium, or be available for binding a second metal.



cyanoacetic acid

48



nicotinic acid

(pyridine-3-carboxylic acid)

49

2.2. Preparation and characterisation of some bis(cyclopentadienyl)titanium(IV) carboxylates

Microanalysis data for compounds **N1-N5** and selected infra-red data for compounds **N1-N4** are given in Tables 3 and 4 respectively. Table 5 contains the ^1H NMR data for compounds **N1-N5** and ^{13}C NMR chemical shifts are listed for **N1**, **N2** and **N4** in Table 6.

Table 3. Microanalysis data for complexes N1-N5. Calculated values for the quoted formulae are given in parentheses.

		%C	%H	%N
$Cp_2Ti(O_2CCH_2CN)_2$	N1	55.4 (55.5)	4.01 (4.08)	7.98 (8.09)
$Cp_2Zr(O_2CCH_2CN)_2$	N2	48.8 (49.3)	3.56 (3.62)	7.05 (7.19)
$Cp_2Ti(O_2CC_6H_4NH_2)_2$	N3	63.3 (64.0)	4.82 (4.92)	5.98 (6.22)
$Cp_2Ti(O_2CC_5H_4N)_2$	N4	62.9 (62.6)	4.30 (4.30)	6.66 (6.63)
$[Cp_2Ti(O_2CCH_2NH_3)_2]Cl_2$	N5	41.7 (42.1)	5.10 (5.05)	6.75 (7.02)

2.2.1. Bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1

With the intent of using cyanoacetic acid as a model for amino acids, bis(cyanoacetato)-bis(cyclopentadienyl)titanium(IV) **N1** was prepared *via* several methods to test different synthetic schemes. These schemes are outlined in Equations 38 - 41, with yields obtained being given.

Method A.

$$Cp_2TiCl_2 + 2NaO_2CCH_2CN \xrightarrow{THF/reflux} Cp_2Ti(O_2CCH_2CN)_2 + 2NaCl \quad \text{Eq. 38}$$

66%

Method B.

$$Cp_2TiCl_2 + 2NaO_2CCH_2CN \xrightarrow{H_2O} Cp_2Ti(O_2CCH_2CN)_2 + 2NaCl \quad \text{Eq. 39}$$

75%

Method C.

$$Cp_2TiCl_2 + 2AgO_2CCH_2CN \xrightarrow{H_2O} Cp_2Ti(O_2CCH_2CN)_2 + 2AgCl \quad \text{Eq. 40}$$

81%

Method D.

$$Cp_2TiMe_2 + 2HO_2CCH_2CN \xrightarrow{CH_2Cl_2} Cp_2Ti(O_2CCH_2CN)_2 + 2MeH \quad \text{Eq. 41}$$

83%

The above reactions yielded orange powders which could be recrystallised to give blood red cube-like crystals. The microanalyses, IR and ^1H NMR data of these products were in good agreement with one another, and with the predicted results for a compound of the formula $(C_5H_5)_2Ti(O_2CCH_2CN)_2$. Solutions of the products in organic solvents showed signs of decomposition when exposed to the air for extended periods (10-20 hours) however, in the solid state the compounds were stable. A crystal of the material prepared *via* Equation 38 was selected for an X-ray analysis from which the molecular structure shown in Fig. 14 was determined.

The reaction of the silver carboxylate and bis(cyclopentadienyl)titanium dichloride, Method C, was one of the more convenient preparative routes. Silver cyanoacetate was easily synthesised (see Appendix 1 for a description of its structure) and the reaction with the titanocene reagent proceeded cleanly to give **N1** in good yield and high purity. The use of bis(cyclopentadienyl)-bis(methyl)titanium(IV) was not as effective as with other carboxylic acids (described later) despite the high product yield. This was due to the hygroscopic nature of cyanoacetic acid and care was needed to ensure the absence of significant quantities of water in the reaction mixture.

For the aqueous preparation of **N1** the generation of sodium cyanoacetate could be perfomed *in situ* from cyanoacetic acid and sodium hydroxide in equimolar amounts. Method B was therefore the simplest as the reagents were off-the-shelf. The purity and yield of the product was not as high as with Method C, but for producing larger quantities of **N1**, this aqueous route was preferred.

Table 4. IR data for compounds N1-N4.[a]

		ν(C-H)[b]	ν(C=C)[b]	δ(C-H)[b]	ν(O-C-O)		other
					(asym)	(sym)	
		(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})
$Cp_2Ti(O_2CCH_2CN)_2$	N1	3110	1447	1019	1666	1308	2255 [ν(CN)]
		3098		826			
$Cp_2Zr(O_2CCH_2CN)_2$	N2	3117	1456	1019	1663	1309	2265 [ν(CN)]
		3094		826	1553		
$Cp_2Ti(O_2CC_6H_4NH_2)_2$	N3	3112	1458[c]	1019	1578	1331	3441 [ν(NH)asym]
				818	1541		3330 [ν(NH)sym]
$Cp_2Ti(O_2CC_5H_4N)_2$	N4	3106	1423	1028	1634	1350	
		3049		824		1306	

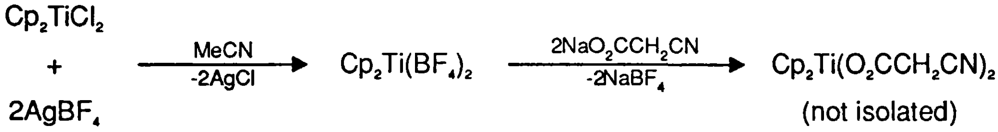
a - Further data including relative peak intensities are given in Chapter 7. b - Characteristic cyclopentadienyl vibrations. c - Coincides with nujol ν=1460cm^{-1}.

The IR spectrum displays characteristic vibration modes of the cyclopentadienyl ligands (ν=3110, 3098, 1447, 1019 and 826cm^{-1}), along with the C-N stretch of the nitrile groups at ν=2255cm^{-1} and the C-O asymmetric and symmetric stretches of the carboxylate groups at ν=1666 and 1308cm^{-1}. Only two signals are observed in the ^1H NMR spectrum of **N1** (δ=6.63 and 3.47ppm) the integrals of which are in the ratio of 10:4, as expected for equivalent cyclopentadienyl and cyanoacetate ligands. The chemical shift of δ=6.63ppm for the cyclopentadienyl protons is typical for this type of compound.

The $^{13}C\{^1H\}$ NMR spectrum of **N1** displays four signals. A very intense peak at δ=119.4ppm is assigned to the cyclopentadienyl carbons, which is similar to other bis(cyclopentadienyl)-titanium(IV) carboxylates. The chemical shifts of a medium intensity signal at δ=26.9ppm and a weak signal at δ=167.2ppm correspond well with the values of the methylene and carboxylato carbons in cyanoacetic acid (δ=24.1, 166.7ppm; 270MHz, D_2O). The remaining signal at δ=115.2ppm of weak intensity can be assigned to the nitrile carbon.

A fifth attempted route to prepare **N1** was *via* the reaction of bis(cyclopentadienyl)-bis(tetrafluoroborato)titanium with sodium cyanoacetate (Equation 42).

Method E.



$$\begin{matrix} Cp_2TiCl_2 \\ + \\ 2AgBF_4 \end{matrix} \xrightarrow[-2AgCl]{MeCN} Cp_2Ti(BF_4)_2 \xrightarrow[-2NaBF_4]{2NaO_2CCH_2CN} \underset{\text{(not isolated)}}{Cp_2Ti(O_2CCH_2CN)_2} \quad \text{Eq. 42}$$

Evidence for the formation of compound **N1** *via* Method E is supported by the solution ^1H NMR spectrum only, which contains two peaks at δ=3.49 and 6.64ppm with integrals in the ratio of 10:4. A number of other signals were also observed. This route was not pursued as it was less convenient to follow than Methods A-D and because it did not result in an easily isolable pure product.

Table 5. ^1H NMR data for compounds N1-N5.

		Chemical Shift, δ (ppm)		
		CH_2	C_5H_5	other
$Cp_2Ti(O_2CCH_2CN)_2$	N1	3.47	6.63	
$Cp_2Zr(O_2CCH_2CN)_2$	N2	3.43	6.36	
$Cp_2Ti(O_2CC_6H_4NH_2)_2$	N3		6.59	6.02 (NH_2), 6.62, 7.24, 7.85 (*phenyl*)
$Cp_2Ti(O_2CC_5H_4N)_2$	N4		6.66	7.42, 8.28, 8.76, 9.21 (*pyridyl*)
$[Cp_2Ti(O_2CCH_2NH_3)_2]Cl_2$	N5	3.65	6.57	

Solvent $CDCl_3$, except N5 (D_2O). Further data including peak integrals and multiplicities are given in Chapter 7.

2.2.2. Bis(cyanoacetato)bis(cyclopentadienyl)zirconium(IV) N2

For comparative purposes the zirconium analogue of **N1**, bis(cyanoacetato)bis(cyclopentadienyl)zirconium **N2** was prepared. Reaction of bis(cyclopentadienyl)zirconium dichloride and silver cyanoacetate gave a high yield of a white, air sensitive material (Equation 43).

$$Cp_2ZrCl_2 + 2AgO_2CCH_2CN \xrightarrow{CHCl_3} Cp_2Zr(O_2CCH_2CN)_2 + 2AgCl \qquad \text{Eq. 43}$$

N2, 74%

Recrystallisation of the product from dichloromethane or acetonitrile gave large diamond or square plate-like crystals respectively but unfortunately neither batch were suitable for single crystal X-ray analysis due to crystal twinning.

The ^1H NMR, $^{13}C\{^1H\}$ NMR and IR spectra of the two metallocene cyanoacetate analogues **N1** and **N2** are very similar. The ^1H NMR of **N2** shows two singlets with integrals in the ratio of 4:10 and the $^{13}C\{^1H\}$ data contain the expected four peaks. In the IR spectrum bands due to the nitrile, carboxylate and cyclopentadienyl groups can all be clearly seen.

Table 6. $^{13}C\{^1H\}$ NMR data for compounds **N1**, **N2** and **N4**.

		Chemical Shift, δ (ppm)				
		-CO$_2$-	*C$_5$H$_5$*	*-CH$_2$-*	*-CN*	*pyridyl*
$Cp_2Ti(O_2CCH_2CN)_2$	**N1**	167.2	119.4	26.9	115.2	
$Cp_2Zr(O_2CCH_2CN)_2$	**N2**	170.5	115.0	26.5	113.8	
$Cp_2Ti(O_2CC_5H_4N)_2$	**N4**	170.1	118.8			123.2, 129.2, 137.2, 151.0, 152.0

Solvent $CDCl_3$. All signals were observed to be singlets.

2.2.3. Bis(anthranilato)bis(cyclopentadienyl)titanium(IV) N3

The reaction of bis(cyclopentadienyl)titanium dichloride and excess sodium anthranilate in toluene (Equation 44), gives an orange solid which is sparingly soluble in mildly polar solvents.

$$Cp_2TiCl_2 + 2NaO_2CC_6H_4NH_2 \xrightarrow{toluene/40^{\circ}C} Cp_2Ti(O_2CC_6H_4NH_2)_2 + 2NaCl \qquad \text{Eq. 44}$$

N3

The microanalysis of this product gives rough agreement with the values expected for bis(cyclopentadienyl)bis(anthranilato)titanium **N3**, although the nitrogen content is a little low.

The ^{1}H NMR spectrum also supports the formation of the bis(anthranilato) derivative giving a strong singlet at δ=6.59ppm due to the cyclopentadienyl protons, followed by three multiplets at δ=6.66, 7.24 and 7.85ppm arising from the anthranilato aromatic protons. A broad signal at δ=6.02ppm can be assigned to the amine hydrogens. Peak integrals could not be employed very accurately in the interpretation of the ^{1}H NMR data due to the lack of resolution between signals in the region δ=6.5 to 6.8ppm.

An earlier study of this compound by Wang *et al.* reported the chemical shift of the cyclopentadienyl protons as δ=6.55ppm, along with multiplets due to the anthranilate aromatic protons between δ=6.58 and 7.87ppm.[103] A broad peak at δ=5.73ppm was assigned to the protons of the amine function. The chemical shifts given in Table 5 correspond closely with these previously published values.

In the IR spectrum of **N3**, the vibrations characteristic of cyclopentadienyl ligands are weak. In contrast the symmetric and asymmetric stretches of the amine and carboxylate groups are very strong.

The aqueous phase synthesis of **N3** from bis(cyclopentadienyl)titanium dichloride and sodium anthranilate gives similar results to the anhydrous method.

2.2.4. Bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4

Bis(cyclopentadienyl)bis(nicotinato)titanium(IV) **N4** has been previously reported by Dixit *et al.* and was prepared by the reaction of bis(cyclopentadienyl)titanium dichloride, nicotinic acid and triethylamine (1:2:2 molar ratio respectively) in tetrahydrofuran.[113a] The synthesis of **N4** has been repeated *via* a related route to complement the limited data published in the initial paper and with an intent to investigate the donor ability of the pyridyl groups with respect to further metal centres.

Complex **N4** was recovered in high purity from the reaction of bis(cyclopentadienyl)titanium dichloride and sodium nicotinate (Equation 45), by layering the reaction mixture with hexanes and cooling. The bright orange-red cube-like crystals produced were suitable for a single crystal X-ray diffraction study from which the molecular structure shown in Figure. 15 was determined. The reaction was performed only once and therefore the non-optimised conditions resulted in a low yield of the desired product. However the compound was fully characterised by elemental analysis, ^{1}H NMR, ^{13}C NMR and IR spectroscopy and mass spectrometry.

$Cp_2TiCl_2 + 2NaO_2CC_5H_4N \xrightarrow{THF/reflux} Cp_2Ti(O_2CC_5H_4N)_2 + 2NaCl$ Eq. 45

15%

The microanalysis of **N4** is in excellent agreement with the calculated values for a compound of the formula $(C_5H_5)_2Ti(O_2CC_5H_4N)_2$. The IR spectrum displays the characteristic bands for cyclopentadienyl groups and strong bands for the stretching modes of the carboxyl functions. The ^1H NMR data indicate five resonances all above 6ppm with integrals in the ratio of 10:2:2:2:2 which is consistent with two equivalent nicotinate ligands. The pyridyl protons clearly exhibit coupling between one another although the coupling constants could not be resolved accurately. The expected seven resonances are observed in the $^{13}C\{^1H\}$ NMR spectrum.

The values for the asymmetric carboxyl stretch and the cyclopentadienyl proton chemical shift of 1634cm^{-1} and 6.66ppm respectively compare favourably with those reported in the previous study (1640cm^{-1} and 6.6ppm).[113a]

2.2.5. Studies involving glycine and β-alanine

Attempts to prepare non-ionic bis(cyclopentadienyl)titanium(IV) complexes containing glycinate or β-alaninate ligands have proved unsuccessful. Conditions employed for the synthesis of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) **N1** do not result in a reaction, the starting materials being identified as the major components of the final reaction mixtures.

Treating bis(cyclopentadienyl)titanium dichloride with sodium or silver glycinate in more polar solvents such as acetonitrile does give rise to a reaction, but the products of these procedures have not been elucidated due to the complexity of the spectroscopic data. Likewise, attempted syntheses in either tetrahydrofuran or acetonitrile using the tetrafluoroborate derivative of bis(cyclopentadienyl)titanium(IV) yield equally confusing analytical data. The ^1H NMR spectra suggest a number of cyclopentadienyl proton environments are present.

Analogous reactions with β-alanine in polar solvents, and *via* bis(cyclopentadienyl)-bis(tetrafluoroborato)titanium(IV) produced similar results.

One complicating factor in these experiments could be amide bond formation by condensation of amino acid units. Bis(cyclopentadienyl)titanium(IV) carboxylates have been shown to act as acylating agents for amines and O-protected amino acids.[138]

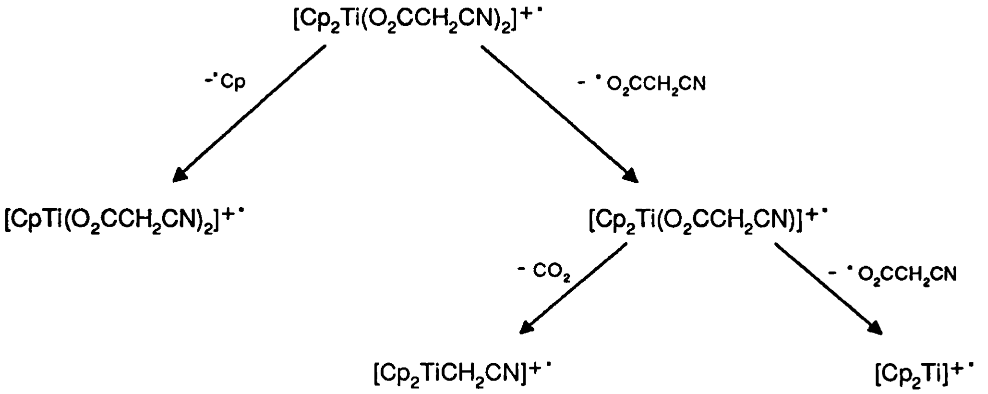
The ionic complex, bis(cyclopentadienyl)bis(glycine)titanium dichloride **N5** was prepared to confirm recent work by Klapötke and co-workers which was published while this research was in progress. **N5** was synthesised by the method described in ref. 124 and characterised by microanalysis and ^{1}H NMR spectroscopic data which are in good agreement with the proposed structure. The chemical shifts of the methylene and cyclopentadienyl protons (δ=3.65, 6.57ppm) are close to the reported[124] values of δ=3.68ppm and 6.57ppm.

2.3. Mass spectra

The FAB mass spectra for the complexes **N1** and **N4** show quite different fragmentation patterns. The detected fragments and their relative intensities for the cyanoacetate derivative (see Table 7) are similar to those found by Dang *et al.*[97] for a range of bis(substituted benzoato) complexes of bis(cyclopentadienyl)titanium(IV). The postulated principal fragmentation pathways are shown in Scheme 13.

Table 7. Selected MS FAB data for **N1** and **N4**. Relative intensities are given in parentheses.

		m/z (intensity as % of base peak)
$Cp_2Ti(O_2CCH_2CN)_2$	**N1**	FAB+: 344 (33), 281 (9), 262 (100), 218 (70), 178 (45).
		FAB- : 346 (25), 84 (100).
$Cp_2Ti(O_2CC_5H_4N)_2$	**N4**	FAB+: 423 (1), 344 (50), 300 (100).
		FAB- : 510 (46), 466 (64), 422 (26), 303 (30), 275 (100).



Scheme 13

Bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4 fragments quite differently. Although the molecular ion and some of its fragment ions can be observed, a large number of negatively charged ions can be assigned to species arising from ion association. The principal fragments observed are listed in Table 7 and their proposed structures are illustrated in Figure 13.

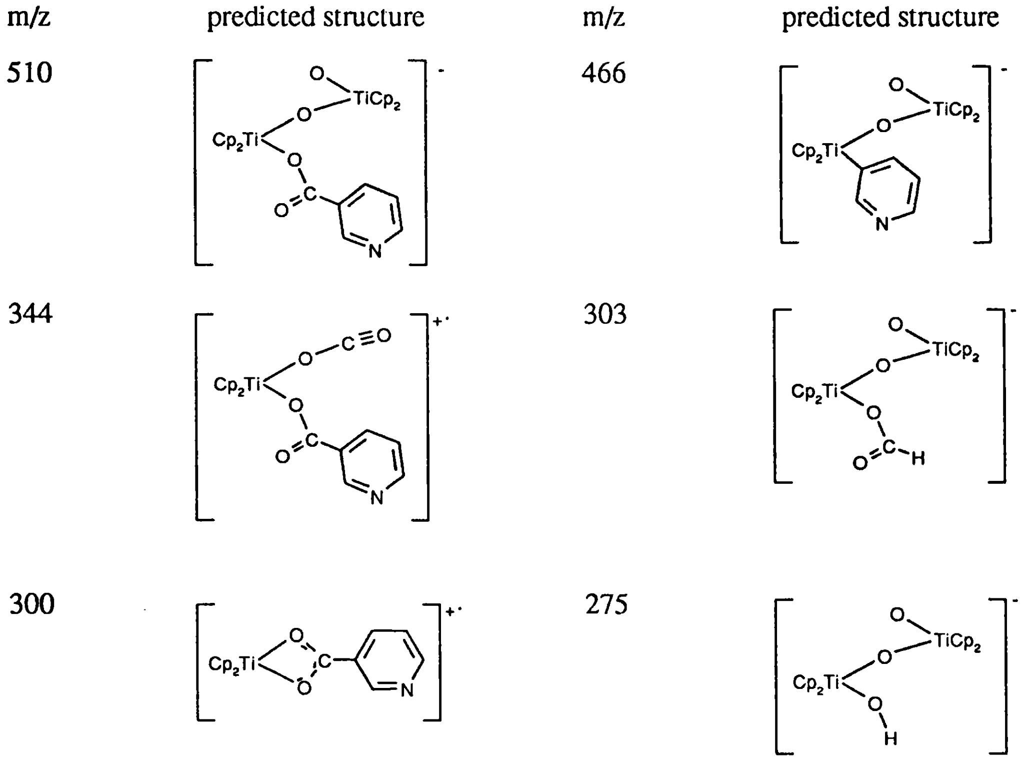


Figure 13. Proposed structures of ions in the FAB mass spectrum of **N4**.

2.4. Structural studies.

2.4.1. Predictions from IR Spectroscopy

As stated in the introduction, IR data can be used to give an indication of the bonding mode of carboxylates. However, these speculations must be treated with caution due to problems associated with the interpretation of IR spectra. Errors can arise from the incorrect assignment of symmetric and asymmetric carboxylate stretching bands, exchange of anion between the complex and the alkali halide support, and in the case of spectra recorded using potassium bromide discs as the support, pressure induced changes can effect the values of $\nu(O\text{-}C\text{-}O)_{asym}$ and $\nu(O\text{-}C\text{-}O)_{sym}$.[93]

Table 4 gives the most probable assignments for the symmetric and asymmetric stretches of the carboxyl functions in complexes **N1**-**N4**. Assignment of the peaks was complicated by the number of bands in the frequency range ν=1300-1670cm^{-1}. Nonetheless, with these considerations in mind, it can be said that the IR data for complexes **N1**, **N3** and **N4** suggest unidentate coordination of the carboxylate ligand.

In contrast, the appearance of two asymmetric stretching frequencies in the spectrum of **N2** suggest there may be two different carboxylate environments in the solid state. The band at 1663cm^{-1} is shifted to a higher frequency relative to the asymmetric carboxyl stretch observed in sodium cyanoacetate[179] (ν=1596cm^{-1}) and the band at 1553cm^{-1} is shifted to a lower frequency. A similar pattern has been observed in the zirconocene terephthalate **29**, described earlier where two asymmetric and two symmetric stretching frequencies are assigned to bands at 1650, 1525, 1420, and 1290cm^{-1}. It is probable that the zirconocene cyanoacetate **N2** adopts a similar structure to the terephthalate **29** with regard to the environment around zirconium, i.e. the cyanoacetate ligands coordinate to zirconium *via* their carboxyl functions one being monodentate and the other bidentate chelating. As stated earlier, this could not be definitely confirmed by X-ray crystallography since all crystals examined were twinned.

The nitrile functions in both **N1** and **N2** are predicted to be uncoordinated to a metal centre as indicated by the ν(CN) values of 2255 and 2265cm^{-1} which are close to that found in the sodium salt (ν=2254cm^{-1}).

2.4.2. X-ray crystallography

For both **N1** and **N4** these structural predictions are confirmed by X-ray crystallographic data. The molecular structures of these two compounds are shown in Figures 14 and 15 and selected bond lengths and angles are listed in Tables 8 and 10.

The geometry of the ligands around the central titanium atoms in complexes **N1** and **N4** are similar to those found in previous structural reports of bis(cyclopentadienyl)titanium(IV) carboxylates. If the cyclopentadienyl groups are considered to occupy one coordination site each, then the titanium atom in both structures can be described as adopting a distorted tetrahedral arrangement with a formal electronic configuration of 16 valence electrons. The carboxylates are attached to the metal in a monodentate fashion and none of the nitrogen containing functional groups in either molecule bond to the metal.

TABLE 8. Selected bond lengths (Å) and bond angles (°) for bis(cyanoacetato)-bis(cyclopentadienyl)titanium **N1**.

Ti(1)-O(1)	1.963(4)	Ti(1)-O(3)	1.966(4)
Z(1)-Ti(1)	2.053	Z(2)-Ti(1)	2.061
C(11)-O(1)	1.282(4)	C(14)-O(3)	1.284(4)
C(11)-O(2)	1.202(4)	C(14)-O(4)	1.195(4)
C(13)-N(1)	1.137(5)	C(16)-N(2)	1.140(5)
O(3)-Ti(1)-O(1)	89.3(2)	Z(1)-Ti(1)-Z(2)	131.5
C(11)-O(1)-Ti(1)	143.5(2)	C(14)-O(3)-Ti(1)	147.4(2)
O(1)-C(11)-O(2)	126.4(4)	O(3)-C(14)-O(4)	126.6(4)
C(12)-C(13)-N(1)	178.4(4)	C(15)-C(16)-N(2)	179.7(2)

Z(1) and Z(2) refer to the centres of the cyclopentadienyl rings, C(1)-C(5) and C(6)-C(10) respectively.

2.4.2.1. Bis(cyanoacetato)bis(cyclopentadienyl)titanium N1

The solid state structure of the cyanoacetate derivative shows a large degree of similarity to that of bis(cyclopentadienyl)bis(trifluoroacetato)titanium(IV).[128] A comparison of various solid state parameters is given in Table 9.

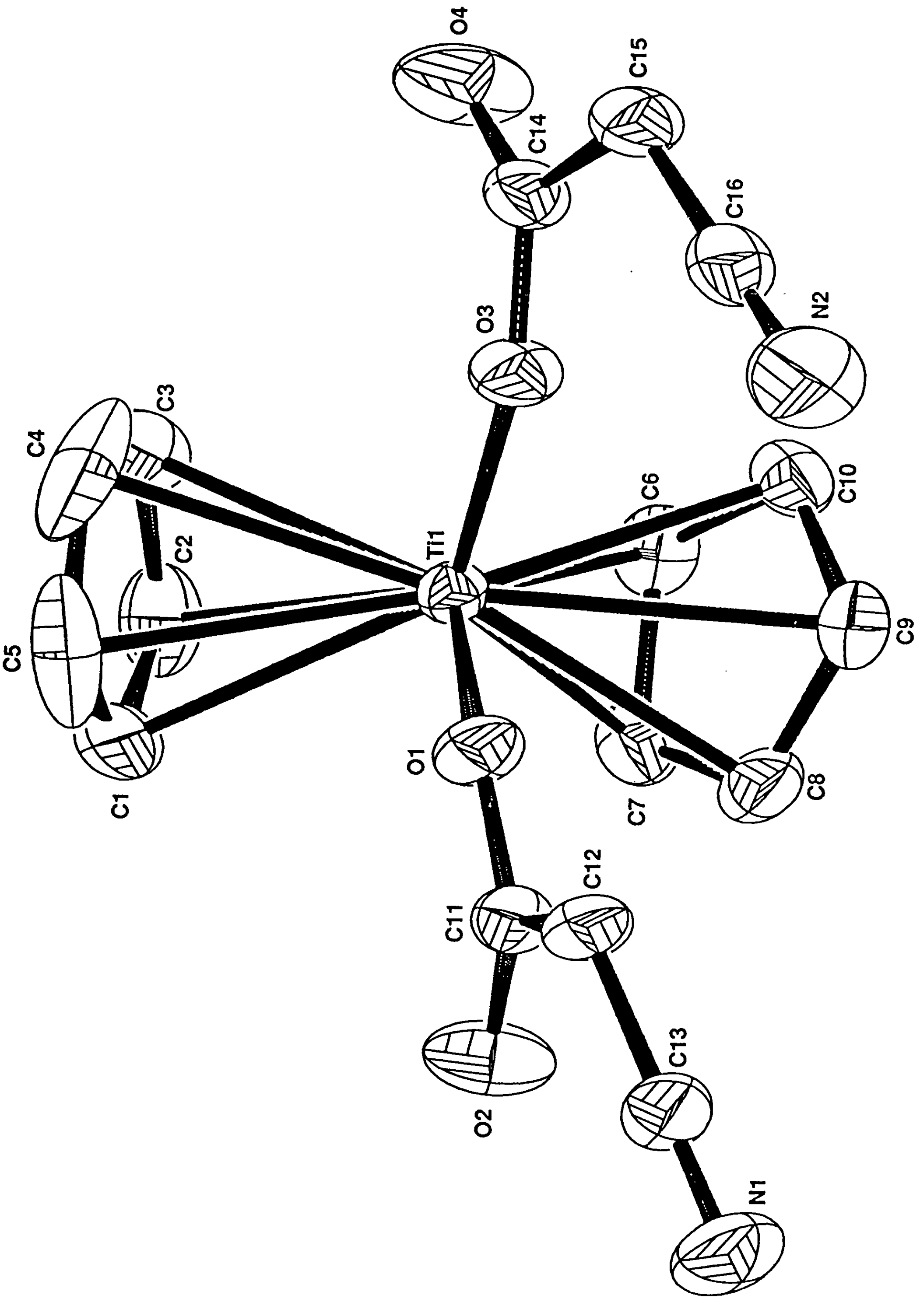


Figure 14. The molecular structure of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1.

Table 9. Comparison of selected solid state molecular parameters of the cyanoacetate and trifluoroacetate derivatives of bis(cyclopentadienyl)titanium(IV).

	bond length (Å)		bond angle (°)			
	Ti-O	Ti-Z	O-Ti-O	Z-Ti-Z	Ti-O-C	O-C-O'
$Cp_2Ti(O_2CCH_2CN)_2$	1.963(4)	2.053	89.3(2)	131.5	143.5(2)	126.4(4)
	1.966(4)	2.061			147.4(2)	126.6(4)
$Cp_2Ti(O_2CCF_3)_2$	1.970(6)	2.05	89.7(2)	133.3	142.8(5)	127.9(7)
	1.979(5)	2.06			149.2(6)	126.4(9)

Z refers to the centroids of the Cp rings, O' refers to the oxygen atoms which are not bonded to titanium

The monodentate coordination of the cyanoacetate ligands is clearly displayed by the large difference in C-O bond distances of the carboxyl functions [Ti-O bond: C(11)-O(1)=1.282Å, C(14)-O(3)=1.284(4)Å; no Ti-O bond: C(11)-O(2)=1.202(4)Å, C(14)-O(4)=1.195(4)Å]. Large differences in C-O bond lengths are observed in the cyanoacetate derivative of zinc(II) hydrotris(3-phenylpyrazoyl)borate where monodentate coordination of the carboxylate is also present [C-O=1.280(5), 1.208(5)Å].[180] The copper(I) and tungsten(0) complexes $(Cy_3P)_2Cu(O_2CCH_2CN)$ (Cy = cyclohexyl) and $[Et_4N][W(CO)_5O_2CCH_2CN]$ are further examples of cyanoacetates where the carboxyl group binds to the metal in a monodentate manner. However, in these instances the difference in C-O bond lengths is not as marked.[180, 181]

In the iron species $[Fe_3O(O_2CCH_2CN)_6(H_2O)_3]$,[182] the C-O distances are approximately equal at 1.25Å, as expected for the bidentate bridging coordination mode of the carboxylates.

The average C-N bond distance of 1.139Å is comparable to the bond lengths found in cadmium(II) cyanoacetate where there are two types of ligand.[183] One is joined to three cadmium atoms *via* an *O,O':O*-bridging bidentate carboxyl function. The nitrile group is not bound to cadmium and has a C-N bond length of 1.132(10)Å. The second type is also joined to three cadmium centres however in this case *via* an *O,O'*- bridging bidentate carboxyl function and the nitrile group which has a C-N bond length of 1.139(9)Å.

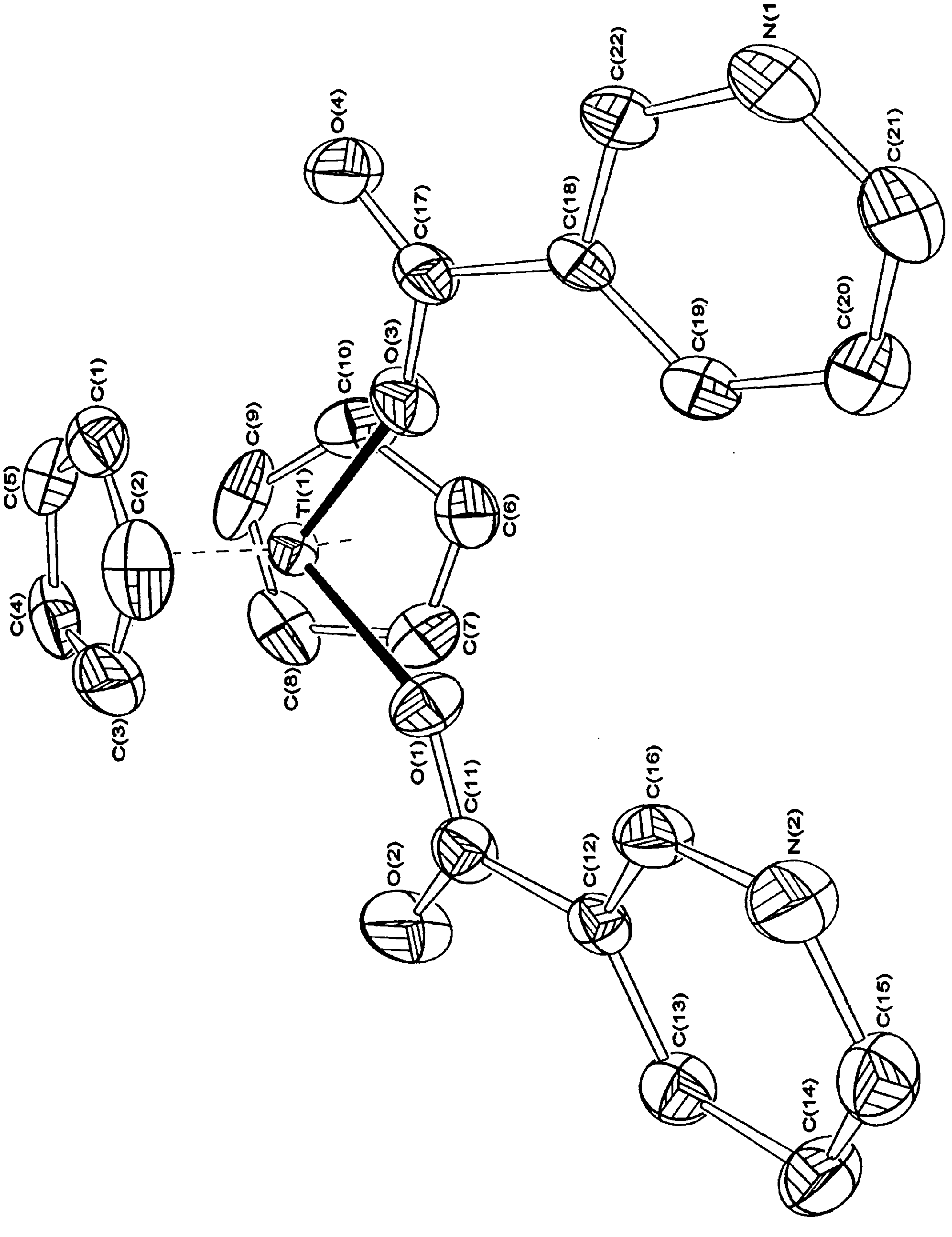


Figure 15. The molecular structure of bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4.

TABLE 10. Selected bond lengths (Å) and bond angles (°) for bis(cyclopentadienyl)-bis(nicotinato)titanium N4.

Ti(1)-O(1)	1.951(2)	Ti(1)-O(3)	1.922(3)
Z(1)-Ti(1)	2.054	Z(2)-Ti(1)	2.055
C(11)-O(1)	1.296(4)	C(14)-O(3)	1.279(3)
C(11)-O(2)	1.207(4)	C(14)-O(4)	1.201(4)
O(3)-Ti(1)-O(1)	90.71(10)	Z(1)-Ti(1)-Z(2)	133.3
C(11)-O(1)-Ti(1)	144.3(2)	C(14)-O(3)-Ti(1)	156.6(2)
O(1)-C(11)-O(2)	124.5(3)	O(3)-C(14)-O(4)	124.5(3)

Z(1) and Z(2) refer to the centres of the cyclopentadienyl rings, C(1)-C(5) and C(6)-C(10) respectively.

2.4.2.2. Bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4

The bond lengths and bond angles around the titanium atom in N4 are all within the ranges of analogous values for previously reported bis(cyclopentadienyl)titanium(IV) carboxylate structures. The distances between the centroids of the cyclopentadienyl rings and titanium (2.054, 2.055Å) and the angle between these two vectors (133.3°) are identical to those found in the trifluoroacetate structure (Table 9).

The parameters associated with the TiO_2 moiety [Ti-O: 1.922(3), 1.951(2)Å; O-Ti-O: 90.71(10)°] are however more comparable with those carboxylate structures where the carboxyl function is a substituent on a six-membered aromatic ring [eg. monoclinic $Cp_2Ti(O_2CC_6H_5)_2$; Ti-O: 1.922(7), 1.930(5)Å; O-Ti-O: 91.4(3)°].[112] The shorter Ti-O distance is accompanied by the widening of the Ti-O-C angle to 156.6(2)° which can be interpreted as the oxygen tending towards sp hybridisation and partial Ti-O double bond formation. The corresponding angle for the other carboxylate group (144.3°) is also quite wide.

The monodentate coordination of the nicotinate groups to titanium results in the differences in the C-O bond distances of the carboxyl function [$\Delta\{(C\text{-}O)-(C\text{-}O')\}=0.078, 0.089$Å]. The O-C-O' angles are also consistent with this mode of carboxylate bonding. This appears to be the only reported example of the nicotinate anion adopting solely monodentate coordination through its carboxyl function that has been confirmed crystallographically.

Monodentate nicotinate ligands are observed in the crystal structures of *trans*-$[M(nic)_2(H_2O)_4]$ (M = Cr, Zn; Hnic = nicotinic acid)[184] but bonding is through nitrogen. Monodentate coordination of the carboxyl function occurs in the structure of $[(PPh_3)_2Cu(nic)]$ and

$\{NH_4[Ag(nic)_2].H_2O\}_n$ however in these compounds, the ligand bridges to a second metal centre *via* the pyridyl nitrogen.[185, 186] Carboxyl bidentate bridging and bidentate chelating coordination modes are common in nicotinate complexes of the lanthanides[187] and is also displayed in the structure of silver(I) nicotinate where a third metal atom is coordinated *via* the pyridyl group.[185]

The nicotinate anion acts as a tridentate ligand in several other complexes. Tridentate bridging and chelating of the carboxyl function occurs in the calcium complex $[Ca(nic)_2(H_2O)_2].3H_2O$[188] and is also observed in a third of the nicotinate ligands in a praseodymium complex discussed in Reference 186c. The cadmium complex $[Cd(nic)_2(H_2O)]$ contains nicotinate groups bonded to two cadmium atoms through a bidentate chelating carboxyl function and the pyridyl nitrogen.[189]

The nicotinic acid ligands in *trans*-$[Cr(nicH)_2(NH_3)_4](ClO_4)_3.2H_2O$ are monodentate, coordinated through the carboxyl group, the pyridyl nitrogens being protonated.

The two pyridyl rings in N4 have very similar bond angles and bond lengths. The average C-C bond length in both groups is 1.375Å, the distribution of these lengths being limited to a very small range [C(12)-C(16): 1.365(4)-1.380(4)Å; C(18)-C(22): 1.370(5)-1.383(4)Å]. The C-N-C angles [116.4(3), 116.2(3)] are slightly more acute than the corresponding parameters in the crystal structures of the free acid [∠C-N-C = 117.7°],[190] the hydrated calcium complex [∠C-N-C = 117.3(2)°] or the uncoordinated ligand observed in $\{[Mg(H_2O)_6](nic)_2(H_2O)_4\}$ [∠C-N-C = 117.7(7)°].[179] This is probably a result of the nitrogen atoms of N4 not being involved in any strong bonding interactions such as hydrogen bonding which occurs in the above three examples.

2.5. Heterobimetallic compounds

Only two of the titanocene carboxylate complexes containing additional nitrogen donors were investigated for their ability to bind to a further transition metal species. Many of the products from these reactions were insoluble powders which were difficult to purify and it was necessary to start with reagents that were of high quality. The microanalysis and ^1H NMR of bis(anthranilato)bis(cyclopentadienyl)titanium(IV) N3 suggested a small proportion of some impurity and attempts to eliminate this were unsuccessful, therefore subsequent reactions of this compound were not studied.

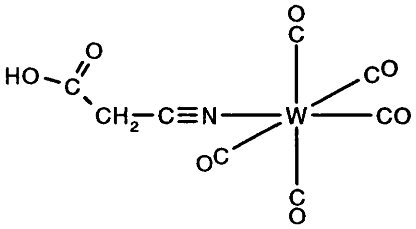
The glycine complex prepared **N5**, was not suitable for coordination studies because the nitrogens in this compound are not available to metallic species, being already protonated in the zwitterionic form.

As suggested by their solid state structures, **N1** and **N4** contain nitrogen donor functions which are available for binding to other metal centres. Therefore, these were the complexes chosen for an investigation of the possible synthesis of heterometallic compounds.

2.5.1. Bimetallic compounds involving bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1

Despite efforts with various different metals it was not possible to coordinate an additional metal species *via* the nitrile functions of **N1** using the methods described here. Attempts to prepare bimetallic compounds by treating **N1** with $AgBF_4$, $Mo(CO)_6$, $[Cu(MeCN)_4][ClO_4]$ or $PdCl_2$ resulted in either the starting materials being recovered or a decomposition reaction.

These results are rather surprising when one considers the range of coordination compounds known to involve nitrile ligands. Indeed, cyanoacetic acid acts solely as a nitrogen donor in several well characterised complexes. The neutral tungsten complex $[W(CO)_5(NCCH_2CO_2H)]$ **50** is one example,[191] and in the copper(I) complex $[(PPh_3)_2Cu(O_2CCH_2CN)_2H]$ **51** both carboxylate and carboxylic acid ligands are coordinated to the metal *via* the nitrile function, while the carboxyl groups are merely involved in intermolecular hydrogen bonding.[66]



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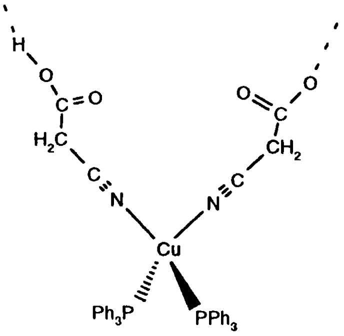


51

Treating **N1** with molybdenum hexacarbonyl in toluene at ambient temperature was not sufficient to displace any of the carbonyl ligands with nitrile functions. Heating the reaction to

65°C probably only resulted in a slight amount of decomposition of the cyanoacetate complex, the main species in the reaction mixture being **N1** as indicated by ^1H NMR spectroscopy.

2.5.2. Bimetallic compounds involving bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4

The reaction of **N4** with palladium(II) or platinum(II) chloride species yielded orange insoluble compounds. Due to their insolubility neither product was characterised satisfactorily. The analytical data give a rough agreement with the calculated values for the predicted 1:1 compounds (Table 11). The palladium containing complex **N6** was further characterised by IR spectroscopy, selected data of which is given in Table 12 along with the data for **N4** and palladium(II) chloride for comparison.

The IR spectrum of **N6** (Table 12) displays the characteristic bands due to cyclopentadienyl and carboxyl functions and the frequencies of the vibrations are similar to those of the parent compound **N4**. **N6** also shows a signal due to the Pd-Cl stretch around 360cm^{-1}.

Table 11. Microanalysis data for complexes **N6** and **N7**. Calculated values for the quoted formulae are given in parentheses.

		%C	%H	%N
$Cp_2Ti(O_2CC_5H_4N)_2PdCl_2$	**N6**	44.0 (44.1)	3.41 (3.03)	4.57 (4.67)
$Cp_2Ti(O_2CC_5H_4N)_2PtCl_2$	**N7**	37.0 (38.4)	2.79 (2.64)	4.40 (4.07)

Table 12. Selected IR data for **N6**.[a]

		v(C-H)[b]	v(C=C)[b]	δ(C-H)[b]	v(O-C-O)		other
					(asym)	(sym)	
		(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})
$Cp_2Ti(O_2CC_5H_4N)_2PdCl_2$	**N6**	3108	1462	1019 828	1642	1319	358 [v(PdCl)]
$Cp_2Ti(O_2CC_5H_4N)_2$	**N4**	3106 3049	1423	1028 824	1634	1350 1306	
$PdCl_2$							340cm^{-1} [v(PdCl)]

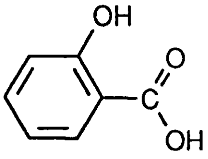
a - Further data are given in Chapter 7. b - Characteristic cyclopentadienyl vibrations.

Chapter 3.

Bis(cyclopentadienyl)titanium(IV) Derivatives of Carboxylic Acids Containing Additional Oxygen Donors.

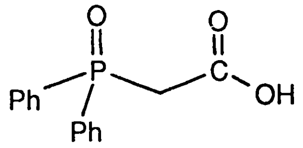
3.1. Introduction

Two carboxylic acids with additional oxygen donor functions were studied. The first, salicylic acid (2-hydroxybenzoic acid) **52** contains an extra phenolic oxygen, while the second, diphenylphosphinylacetic acid **53** has a phosphine oxide group.



salicylic acid

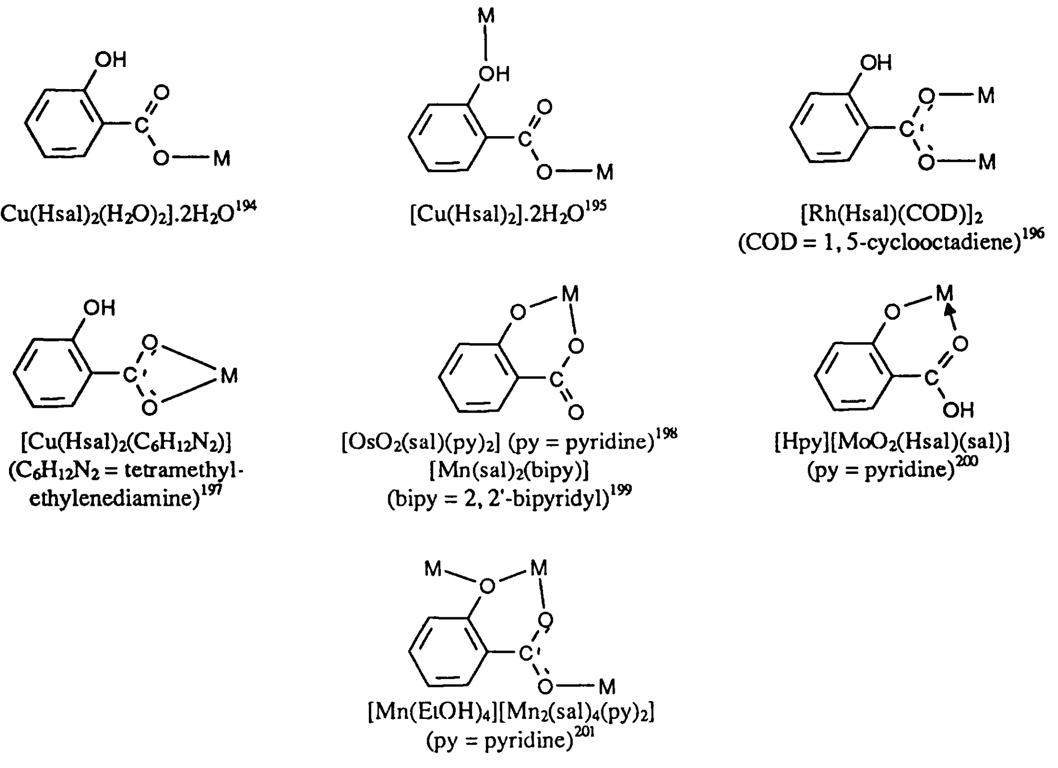
52



diphenylphosphinylacetic acid

53

Salicylic acid (H_2sal) is a well known and important compound. It's metal complexes have been studied quite recently with a view to understanding the mechanism of certain biological processes involving metal centres, and to producing useful catalytic species.[192,193] The coordination chemistry of the salicylate anions, both the singly ($Hsal^-$) and doubly (sal^{2-}) deprotonated forms, show a variety of structural motifs (Fig.16).



$[Cu(Hsal)_2(H_2O)_2].2H_2O$[194]

$[Cu(Hsal)_2].2H_2O$[195]

$[Rh(Hsal)(COD)]_2$
(COD = 1,5-cyclooctadiene)[196]

$[Cu(Hsal)_2(C_6H_{12}N_2)]$
($C_6H_{12}N_2$ = tetramethylethylenediamine)[197]

$[OsO_2(sal)(py)_2]$ (py = pyridine)[198]
$[Mn(sal)_2(bipy)]$
(bipy = 2,2'-bipyridyl)[199]

$[Hpy][MoO_2(Hsal)(sal)]$
(py = pyridine)[200]

$[Mn(EtOH)_4][Mn_2(sal)_4(py)_2]$
(py = pyridine)[201]

Figure 16. Coordination modes of the salicylate mono- and di- anions.

Two bis(cyclopentadienyl)titanium(IV) salicylate compounds have been previously reported. One involves the doubly deprotonated dianion and it is suggested that the salicylate chelates to titanium *via* one carboxylate oxygen and the phenolate oxygen.[106] The second is said to involve monodentate coordination solely through the carboxylate functions of two monodeprotonated salicylates.[103] Neither of these predictions have been confirmed by crystallographic data.

The synthesis of both of the above compounds was attempted to a) establish the structures of the reported compounds and b) to investigate the ability of either of these compounds, particularly the bis(salicylato) complex, to coordinate to additional transition metal species.

Diphenylphosphinylacetic acid is less well known than salicylic acid and few reports of it's metal complexes have appeared in the literature to date. Grim and Satek published a synthesis of the acid in 1977 and included in this publication are descriptions of the Ni(II), Cu(II), Hg(II), Pb(II) and uranyl derivatives.[202] Ng and Zuckerman studied the organotin compounds, $[Ph_2P(O)CH_2CO_2SnR_3]$ (R=Me, Et, ^nPr, ^nBu, Cy and Ph) and $[\{Ph_2P(O)CH_2CO_2\}_2SnR_2]$ (R=Me and Ph)[203] and recently, Cross *et al.* have investigated the coordination chemistry of the related anion 2-(diphenylphosphinyl)propanoate to a range of metal centres.[204]

This latter study suggests that in many cases the 2-(diphenylphosphinyl)propanoate anion acts as a bidentate chelating ligand, coordinating to the metal centre *via* one of the carboxylate oxygens and the phosphine oxide group. This prediction is verified in the case of the V(III) derivative $[V\{O_2CCH_2P(O)Ph_2\}_3]$, by an X-ray single crystal structure analysis. Analogous behaviour would be expected for the diphenylphosphinylacetate anion.

The titanocene complex was prepared to investigate the possibility of linking titanium to a second metallic species *via* the diphenylphosphinylacetate moiety.

3.2. Preparation of the bis(cyclopentadienyl)titanium(IV) derivatives **O1-O3**

The microanalyses and ^1H NMR data for compounds **O1-O3** are given in Tables 13 and 15 respectively. Selected IR and $^{13}C\{^1H\}$ NMR data for the doubly deprotonated salicylate and diphenylphosphinylacetate derivatives are contained in Table 14 and 16.

Table 13. Microanalysis data for complexes **O1-O3**. Calculated values for the predicted structures on the left are given in parentheses

		%C	%H
$Cp_2Ti(O_2CC_6H_4O)$	**O1**	64.6 (65.0)	4.42 (4.49)
$Cp_2Ti(O_2CC_6H_4OH)_2$	**O2**	63.6 (63.7)	4.44 (4.46)
$Cp_2Ti(O_2CCH_2P(O)Ph_2)_2$	**O3**	63.4 (65.5)	4.90 (4.92)

3.2.1.Bis(cyclopentadienyl)(salicylato)titanium(IV) O1

Bis(cyclopentadienyl)(salicylato)titanium **O1** was prepared in aqueous media by the equimolar reaction of bis(cyclopentadienyl)titanium dichloride with salicylic acid in the presence of 1 equivalent of sodium hydroxide and 1 equivalent of triethylamine (Equation 46).

$$\begin{matrix} Cp_2TiCl_2 + HO_2CC_6H_4OH \\ + NaOH + Et_3N \end{matrix} \xrightarrow{H_2O/\text{room temp.}} \begin{matrix} Cp_2Ti(O_2CC_6H_4O) + NaCl + H_2O \\ + Et_3NHCl \end{matrix} \qquad \text{Eq. 46}$$

The product of this reaction is an air stable dark maroon powder which can be recrystallised from a dichloromethane solution layered with hexanes. The dark purple diamond shaped crystals produced were suitable for single crystal X-ray analysis. The molecular structure determined from this crystallographic study is shown in Figure 17.

The microanalysis is in good agreement with the predicted values for **O1**. The IR spectrum of **O1** displays cyclopentadienyl ring vibrations similar to those observed with compounds **N1-N4** along with strong bands at v=1622 and 1327cm^{-1} due to the asymmetric and symmetric stretches of the carboxylate group. This compares with v=1616 and 1320cm^{-1} for the previously reported preparation of this compound.[106]

The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra contain the correct number of signals expected for **O1**, assuming the cyclopentadienyl ligands are equivalent. The chemical shifts are typical for compounds of this type and the value for the cyclopentadienyl protons (δ = 6.40ppm) compares favourably with that of the earlier report (δ = 6.39ppm).[106]

Table 14. IR data for compounds **O1** and **O3**.

		ν(C-H)* (cm^{-1})	ν(C=C)* (cm^{-1})	δ(C-H)* (cm^{-1})	ν(O-C-O) (asym) (cm^{-1})	(sym) (cm^{-1})	other (cm^{-1})
$Cp_2Ti(O_2CC_6H_4O)$	**O1**	3073	1450	1013	1622	1337	
				820			
$Cp_2Ti(O_2CCH_2P(O)Ph_2)_2$	**O3**	3054	1437	1019	1636	1294	1190
				826			[ν(P=O)]

*Charcateristic cyclopentadienyl vibrations.

Table 15. ^1H and $^{31}P\{^1H\}$ NMR data for compound **O1-O3**.

		Chemical Shift, δ (ppm)				
		CH_2	C_5H_5	*phenyl*	other	$^{31}P\{^1H\}$
$Cp_2Ti(O_2CC_6H_4O)$	**O1**		6.40	6.63, 6.88, 7.38, 8.16		
$Cp_2Ti(O_2CC_6H_4OH)_2$	**O2**		6.67	6.89, 7.01, 7.44, 7.83	11.93 (O*H*)	
$Cp_2Ti(O_2CCH_2P(O)Ph_2)_2$	**O3**	3.35	6.34	7.53, 7.89		28.7^a

solvent $CDCl_3$. a- $^2J(^{31}P-^1H)$=13.7Hz.

Table 16. $^{13}C\{^1H\}$ NMR data for compounds **O1** and **O3**.

		C_5H_5 δ(ppm)	-CO_2- δ(ppm)	other δ(ppm)
$Cp_2Ti(O_2CC_6H_4O)$	O1	118.6	170.3	118.5, 119.3, 120.5, 132.3, 133.3, 167.3 (*phenyl*)
$Cp_2Ti(O_2CCH_2P(O)Ph_2)_2$	O3	118.6	170.0	40.3 (-CH_2-), 128.3, 130.6, 131.6, 132.8 (*phenyl*)

solvent $CDCl_3$

The most abundant peak in both the positive and negative FAB mass spectra of **O1** is due to the molecular ion. This unusual behaviour for bis(cyclopentadienyl)titanium(IV) carboxylates demostrates the greater stability of this compound due to the chelated ligand. Enhanced stability has also been reported for the thiosalicylate (2-thiobenozate) analogue of **O1**, which was purified by column chromatography.[99] Most titanocene carboxylates are unstable on chromatography columns.

Further less intense peaks are observed for fragment ions involving loss of the cyclopentadienyl rings, reactions within the salicylate ligand including loss of carbon dioxide and loss of the salicylate ligand altogether (Table 17).

Table 17. FAB MS data for **O1**. Relative intensities are given in parentheses.

	m/z (intensity as % of base peak)	
FAB+	315 (100)	$[HCp_2Ti(O_2CC_6H_4O)]^+$
	250 (7)	$[HCpTi(O_2CC_6H_4O)]^+$
	205 (21)	$[CpTi(C_6H_4O)]^+$
	178 (10)	$[Cp_2Ti]^+$
FAB-	314 (100)	$[Cp_2Ti(O_2CC_6H_4O)]^{-}$
	265 (51)	
	137 (50)	$[O_2CC_6H_4OH]^-$

The structure of **O1** was investigated by a single crystal X-ray study to determine the precise nature of the salicylate-titanium coordination. A perspective view of the molecule is shown in Figure 17 along with the atomic labelling scheme adopted. Selected bond lengths and bond angles are given in Table 18.

As shown by the molecular structure in Figure 17, the salicylate dianion adopts a chelating coordination mode where both the carboxyl and phenoxy functions are involved in bonding to titanium.

The coordination sphere about the titanium atom formed by O(1), O(2) and the centroids of the two cyclopentadienyl rings gives rise to the typical Cp_2TiL_2 distorted tetrahedral geometry. Any additional distortion caused by titanium being part of a six-membered metallocycle seems to be slight as only a small contraction in the O-Ti-O angle is evident [$\angle$O(1)-Ti-O(2)=88.5(3)° compared to 89.7(2)° for $Cp_2Ti(O_2CCF_3)_2$[128]]. In contrast, a five-membered metallocycle such as that found in $Cp_2Ti(C_2O_4)$ has a much more dramatic effect, yielding an O-Ti-O angle of 79.4°.[117] It appears that the O-Ti-O angle has no influence over the angle between the centroids of the Cp rings and titanium [**O1**, $\angle$Z(1)-Ti-Z(2)=132.9°, $Cp_2Ti(O_2CCF_3)_2$, $\angle$Z(1)-Ti-Z(2)=133.3°, $Cp_2Ti(C_2O_4)$, $\angle$Z(1)-Ti-Z(2)=133.3°].

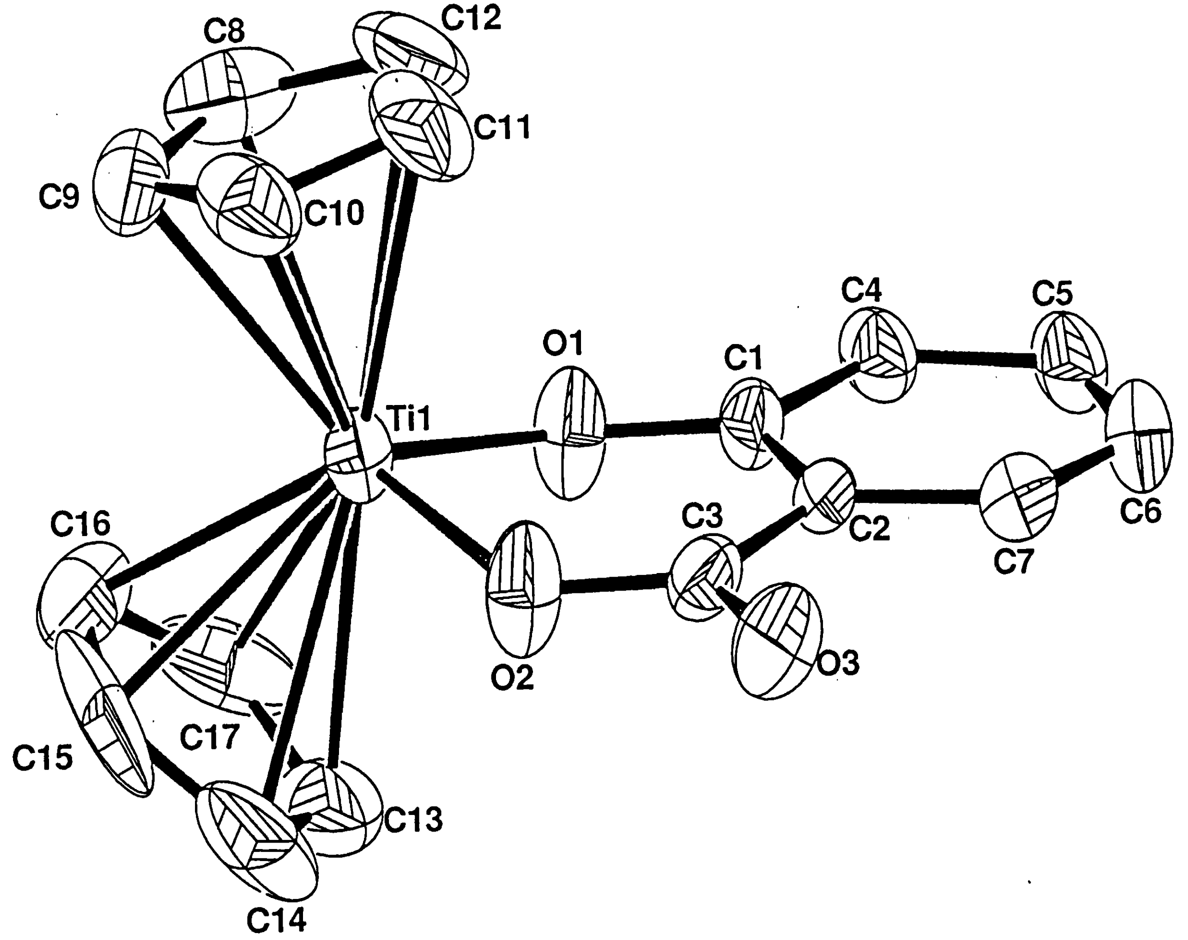


Figure 17. The molecular structure of bis(cyclopentadienyl)(salicylato)titanium(IV) O1.

TABLE 18. Selected bond lengths (Å) and bond angles (°) for bis(cyclopentadienyl)-salicylatotitanium **O1**.

Ti(1)-O(1)	1.909(6)	Ti(1)-O(2)	1.940(7)
C(1)-O(1)	1.321(8)	O(2)-C(3)	1.297(8)
C(3)-C(2)	1.488(9)	C(3)-O(3)	1.221(8)
C(1)-C(2)	1.405(9)	C(2)-C(7)	1.385(9)
C(7)-C(6)	1.359(9)	C(6)-C(5)	1.385(10)
C(5)-C(4)	1.373(9)	C(4)-C(1)	1.403(9)
Z(1)-Ti(1)	2.060	Z(2)-Ti(1)	2.071
O(2)-Ti(1)-O(1)	88.5(3)	Z(1)-Ti(1)-Z(2)	132.9
O(2)-C(3)-O(3)	120.5(8)	O(1)-C(1)-C(2)	123.5(8)
O(2)-C(3)-C(2)	118.6(7)	C(1)-C(2)-C(3)	123.7(7)
C(1)-C(2)-C(7)	119.0(8)	C(2)-C(7)-C(6)	121.5(8)
C(7)-C(6)-C(5)	120.3(8)	C(6)-C(5)-C(4)	119.7(8)
C(5)-C(4)-C(1)	120.8(8)	C(4)-C(1)-C(2)	118.7(8)

Z(1) and Z(2) refer to the centres of the cyclopentadienyl rings, C(8)-C(12) and C(13)-C(17) respectively.

The Ti-O distances for the phenolate [Ti-O(1), 1.909(6)Å] and carboxylate [Ti-O(2), 1.940(7)Å] functions are of the same order as the corresponding values in $Cp_2Ti(OPh)_2$ [Ti-O, 1.907(3)Å][99] and in the monoclinic form of $Cp_2Ti(O_2CPh)_2$ [Ti-O, 1.922(7), 1.930(3)Å]. The difference between the M-O(phenolate) and M-O(carboxylate) bond lengths compares with those found in $[Mn(sal)(bpy)(H_2O)_2].ClO_4.H_2O$ [bpy=bipyridyl, Mn-O(phenolate), 1.830(2)Å, Mn-O(carboxylate), 1.871(4)Å],[192a] where the salicylate dianion adopts the same bidentate coordination as in the present study.

The distances to the centres of the cyclopentadienyl rings from the metal atom (2.060, and 2.071Å) are similar to the observed lengths in $Cp_2Ti(O_2CPh)_2$ [monoclinic, 2.057(7) and 2.065(17)Å][112] but are slightly longer than those in $Cp_2Ti(O_2CPh)_2$ [orthorhombic, 2.045(7) and 2.048(6)Å][102] and $Cp_2Ti(m\text{-}O_2CC_6H_4OMe)_2$ [2.045(8) and 2.057(9)Å].[137] The rings are contracted in comparison to all three of the above compounds [**O1**, C(8)-C(12), $C\text{-}C_{av}$=1.355Å, C(13)-C(17), $C\text{-}C_{av}$=1.322Å, $Cp_2Ti(O_2CPh)_2$ (monoclinic), $C\text{-}C_{av}$=1.385, 1.379Å, $Cp_2Ti(O_2CPh)_2$ (orthorhombic), $C\text{-}C_{av}$=1.378, 1.370Å, $Cp_2Ti(m\text{-}O_2CC_6H_4OMe)_2$ $C\text{-}C_{av}$=1.35, 1.37Å].

Comparison of the carboxylate C-O bond lengths clearly demonstrates the unidentate coordination of this group to titanium [C(3)-O(2), 1.297(8)Å, C(3)-O(3), 1.221(8)Å]. A similar difference is seen in the structure of $Cp_2Ti(C_2O_4)$ [C-O, 1.294(6), 1.295(6)Å, C-O', 1.205(6), 1.213(6)Å] in which coordination of the carboxylate moieties is also monodentate.

The magnitude of the doubly deprotonated salicylate bite angle at titanium in **O1** [88.5(3)°] lies between the corresponding values found in the molybdenum(VI) complexes; $[pyH][MoO_2(Hsal)(sal)]$ (py=pyridine) and $[NMe_4][MoO_2(sal)_2].2H_2O$ of around 81°[200,205] and the manganese(III) and copper(II) complexes; $[Mn(sal)(bpy)(H_2O)_2].ClO_4.H_2O$ (bpy=bipyridyl)[192a] and $[Cu_2(amp)_2(sal)_2].4(CH_3)_2CHOH$ (amp=2-amino-2-methyl-1-propanol)[206] where ∠O-Mn-O=94.1(1)° and ∠O-Cu-O=93.8(1)°.

The salicylate atoms C(1)-C(7) and O(1)-O(3) form a planar system with a maximum deviation from the least squares plane of 0.044Å at C(1). The titanium atom is raised above this plane by 0.322Å. The phenyl ring [C(1), C(2) and C(4)-C(7)] exhibits minor deviations from regularity, with C-C bond lengths in the range 1.359(9)Å to 1.405(9)Å ($C\text{-}C_{av}$=1.385Å) and bond angles 118.7(8)° to 121.5(8)°.

3.2.2. Bis(cyclopentadienyl)bis(salicylato)titanium(IV) O2

On the basis of ^1H NMR data the reaction of bis(cyclopentadienyl)titanium dichloride with 4 equivalents of sodium salicylate in toluene at 35°C gave two cyclopentadienyl containing products in the approximate ratio of 2.5:1 (Scheme 14). The major product was assigned as bis(cyclopentadienyl) bis(salicylato)titanium **O2** where the salicylate is the monoanion and is deprotonated only at the carboxylate function. The minor product was assigned as bis(cyclopentadienyl)(salicylato)titanium **O1** where the salicylate is the dianion with deprotonation at both the carboxylate and phenolate functions.

$$Cp_2TiCl_2 + xsNaO_2CC_6H_4OH \longrightarrow \underset{\text{major product}}{Cp_2Ti(O_2CC_6H_4OH)_2} + Cp_2Ti(O_2CC_6H_4O)$$

Scheme 14

The ^1H NMR spectrum of the mixed products is shown in Figure 18. The singlet at δ=6.42 and the doublet of doublets at δ=8.20ppm integrate to give an approximate ratio of 10:1 and are in similar positions to those found in **O1**. Evidence that the major isomer is the bis(salicylato) derivative comes from the resonance of the phenolic proton at δ=11.94ppm. The integrals of this signal and the four major multiplets in the aromatic region are of a similar magnitude and can be assigned to the salicylate ligands of **O2**. The cyclopentadienyl protons of **O2** appear as

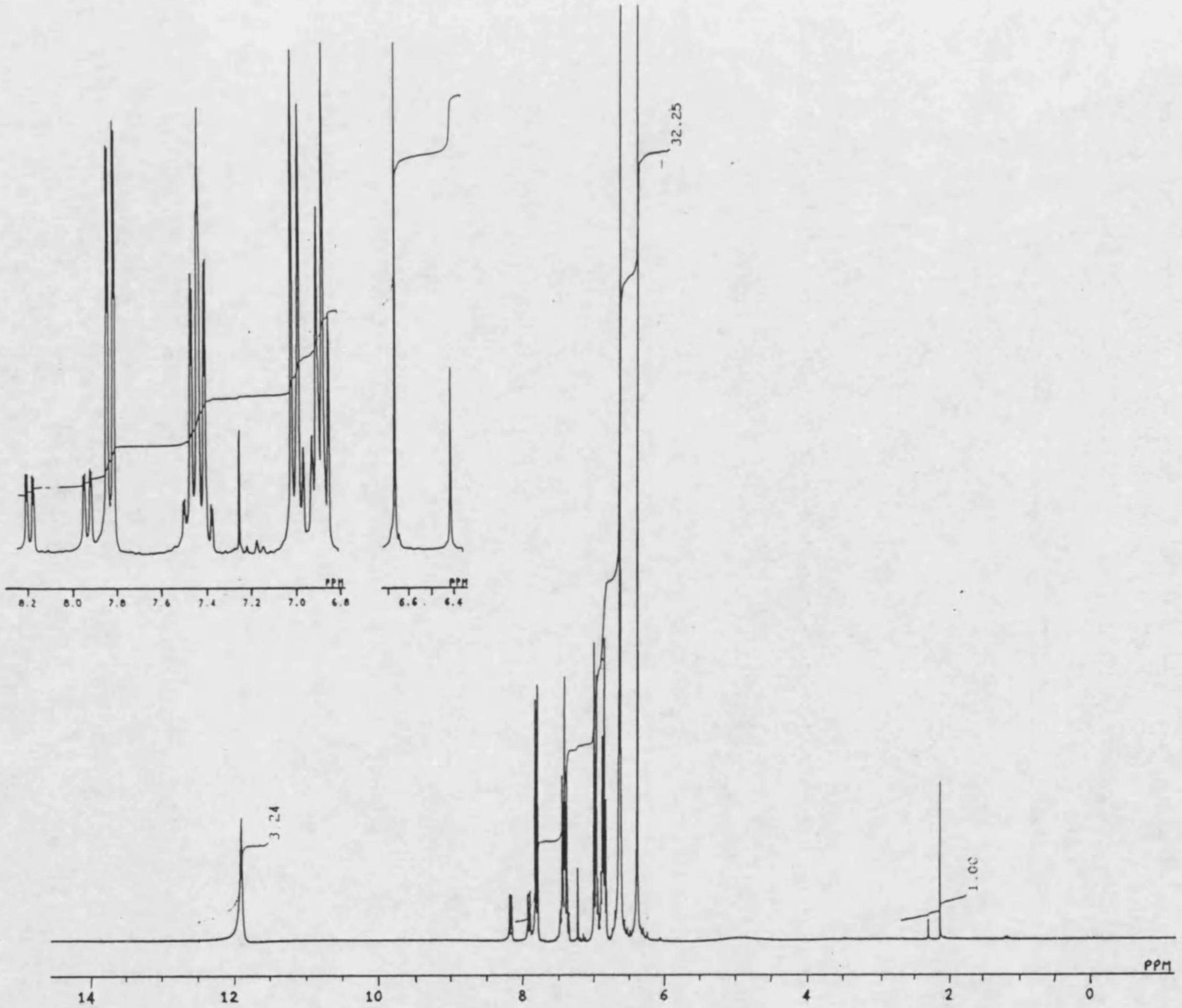


Figure 18. ^{1}H NMR spectrum of the titanium containing products of the reaction of bis(cyclopentadienyl)titanium dichloride with excess sodium salicylate.

an intense singlet at δ=6.67ppm. The reported aqueous phase synthesis of this product gives the chemical shift of the cyclopentadienyl protons as δ=6.66ppm ($CDCl_3$).[103]

Further evidence for the formation of the two salicylato derivatives is given by the observation of a doublet of doublets at δ=7.94ppm, and the rather broader, weak signals at δ=6.97 and 6.93ppm. These peaks suggest the presence of free salicylic acid, which is a necessary by-product if the monosalicylate derivative **O1** is to be formed under the reaction conditions applied (Equations 47-49).

$$Cp_2TiCl_2 + 2NaO_2CC_6H_4OH \xrightarrow{\text{toluene/35°C}} Cp_2Ti(O_2CC_6H_4OH)_2 + 2NaCl \qquad \text{Eq. 47}$$

$$Cp_2Ti(O_2CC_6H_4OH)_2 \xrightarrow{\qquad} Cp_2Ti(O_2CC_6H_4O) + HO_2CC_6H_4OH \qquad \text{Eq. 48}$$

or alternatively

$$\begin{tikzcd}
Cp_2TiCl_2 + NaO_2CC_6H_4OH \arrow[r, "\text{toluene/35°C}"] & Cp_2Ti(O_2CC_6H_4OH)Cl + NaCl \arrow[d, "NaO_2CC_6H_4OH"] & \\
& Cp_2Ti(O_2CC_6H_4O) + HO_2CC_6H_4OH + NaCl & \text{Eq. 49}
\end{tikzcd}$$

The above reaction carried out in aqueous media, and the reaction of bis(cyclopentadienyl)-bis(methyl)titanium with salicylic acid in toluene, produces a similar mixture of products.

Attempts to prepare pure bis(cyclopentadienyl)bis(salicylato)titanium(IV) **O2** *via* the procedure used by Wang *et al.*[103] were unsuccessful. Contrary to the observations published, precipitation of the desired product did not occur when an aqueous solution of bis(cyclopentadienyl)titanium dichloride pretreated with acetyl acetone was reacted with an aqueous solution of sodium salicylate. Further analysis of the reaction mixture did not support the exclusive fomation of **O2**.

3.2.3. Bis(cyclopentadienyl)bis(diphenylphosphinylacetato)titanium(IV) **O3**

Bis(cyclopentadienyl)bis(diphenylphosphinylacetato)titanium(IV) **O3** was prepared by the reaction of the free carboxylic acid and bis(cyclopentadienyl)bis(methyl)titanium(IV) in dichloromethane (Equation 50).

$$Cp_2TiMe_2 + 2HO_2CCH_2P(O)Ph_2 \xrightarrow{CH_2Cl_2\,/\text{-}2MeH} Cp_2Ti(O_2CCH_2P(O)Ph_2)_2 \qquad \text{Eq. 50}$$

The bright orange product is reasonably air stable in the solid state, but deuterochloroform solutions prepared for NMR analysis showed significant amounts of decomposition products after a day, even when sealed under nitrogen.

The analysis data for **O3** are in approximate agreement with a complex of formula $Cp_2Ti(O_2CCH_2P(O)Ph_2)_2$. Due to the instabilty of the compound in solution, **O3** was not purified by recrystallisation and this may account for the discrepancy in the carbon content. The complex was however satisfactorily characterised by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy and mass spectrometry. Selected FAB mass spectrometry data are given in Table 19.

In addition to showing vibrations due to the cyclopentadienyl and carboxyl functions, the IR spectrum (Table 14) also displays a strong band at $1190cm^{-1}$ which can be assigned to the P=O moiety. The ^1H and $^{13}C\{^1H\}$ NMR spectra (Tables 15 and 16) contain the correct number of signals for the predicted structure and this is also confirmed by the ratio of the proton integrals.

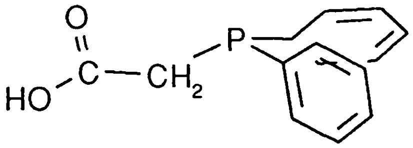
The proton decoupled ^{31}P NMR spectrum shows just one phosphorus resonance at δ=28.7ppm which compares with δ=26.3ppm for the free acid[202] and δ=26.0-28.9ppm for a range of organotin derivatives.[203] The methylene protons couple to the ^{31}P nucleus to give a coupling constant of 13.7Hz which is comparable to the values reported for the Hg(II), Pb(II) and uranyl complexes [$^2J(^{31}P\text{-}^1H)$=11-14Hz].[202] The free acid gives a coupling constant also within this range of $^2J(^{31}P\text{-}^1H)$=13.9Hz.

The FAB mass spectrum for **O3** contains a large number of peaks that are difficult to assign, particularly from ions carrying a negative charge. However, there is an intense signal due to the fragment ion of the carboxylate ligand and a weak signal (10% of the base peak due to the carboxylate ligand) which corresponds with the loss of a carboxylate ligand from the parent ion (Table 19).

Table 19. Selected MS FAB data for O3. Relative intensities are given in parentheses.

		m/z (intensity as % of base peak)
$Cp_2Ti(O_2CCH_2P(O)Ph_2)_2$	O3	FAB+: 437 (10), 261 (100), 201 (32).
		FAB- : 259 (100), 215 (60).

Diphenylphosphinylacetic acid, **53** acid used in the preparation of the above compound was initially obtained as a by product from the synthesis of a related compound diphenylphosphinoacetic acid **54**.



54

During the synthesis of the phosphine derivative **54**,[207] colourless crystals were isolated from an aqueous phase. The identity of this material as diphenylphosphinylacetic acid was established by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy, microanalysis and FAB mass spectrometry and further confirmed by a single crystal X-ray structure determination. Direct preparation of **53** *via* the reaction of diphenylphosphine oxide and chloroacetic acid in the presence of sodium ethanoate[202] yields a material that is spectroscopically identical to the above.

The structure of **53** was determined to establish the nature of the hydrogen bonding within the extended structure. Several possibilities exist; intermolecular hydrogen bonding between adjacent carboxyl functions, as commonly seen in many carboxylic acids, could occur resulting in dimerisation. The formation of six-membered rings could arise from intramolecular bonding between the carboxyl and phosphine oxide functions. Finally, intermolecular interactions between the carboxyl and phosphine oxide functions could give rise to an oligomeric or polymeric supramolecular structure.

A perspective view of the molecule is shown in Figure 19 along with the atomic labelling scheme. In the phenyl ring containing carbons C(7)-C(12), atoms C(8)-C(12) were observed to be disordered with positions C(8A)-C(12A) in the ratio of 1:1. Figure 20 is a projection of the unit cell down the b axis and displays the formation of 1-dimensional linear polymers in the

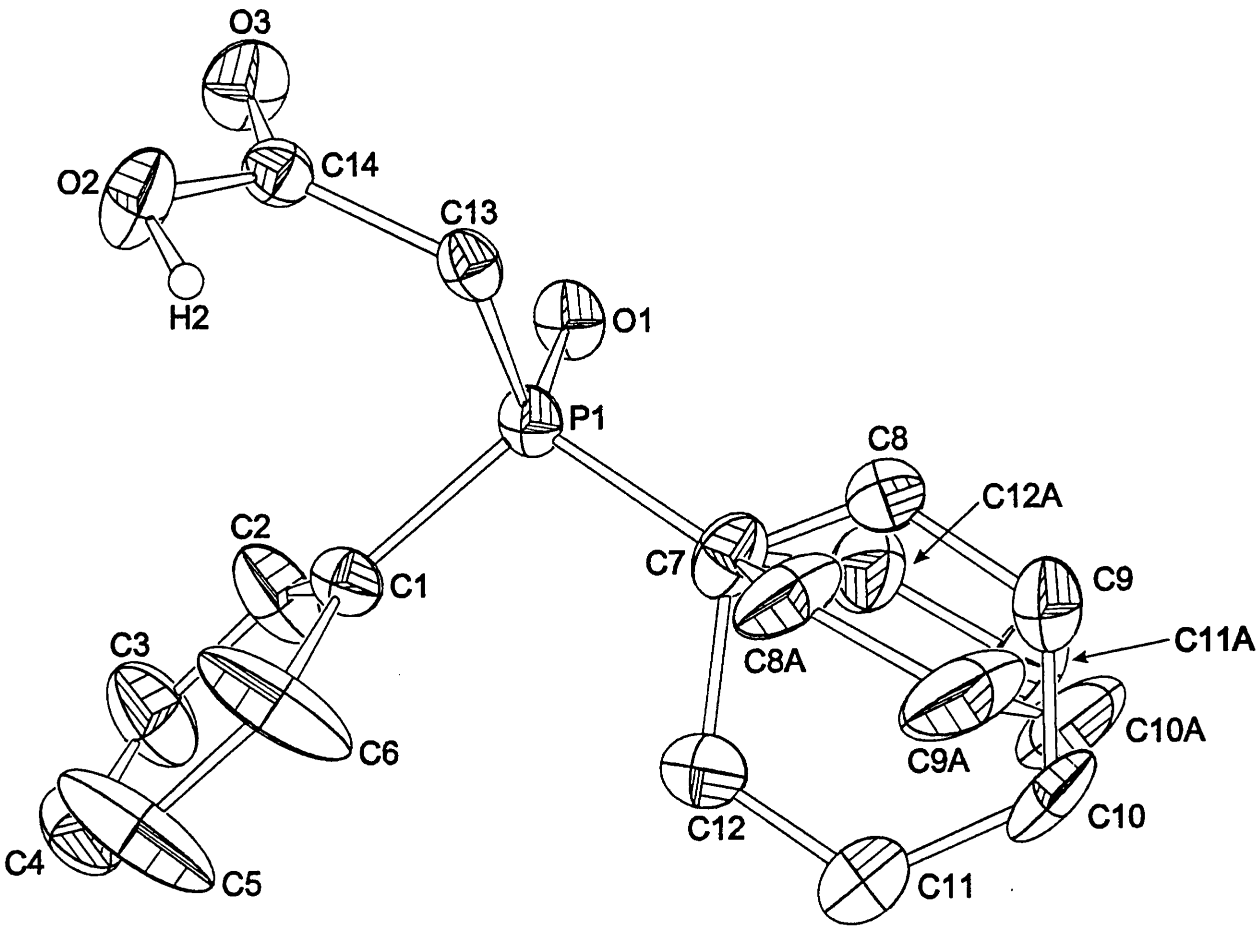


Figure 19. The molecular structure of diphenylphosphinylacetic acid, $HO_2CCH_2P(O)Ph_2$.

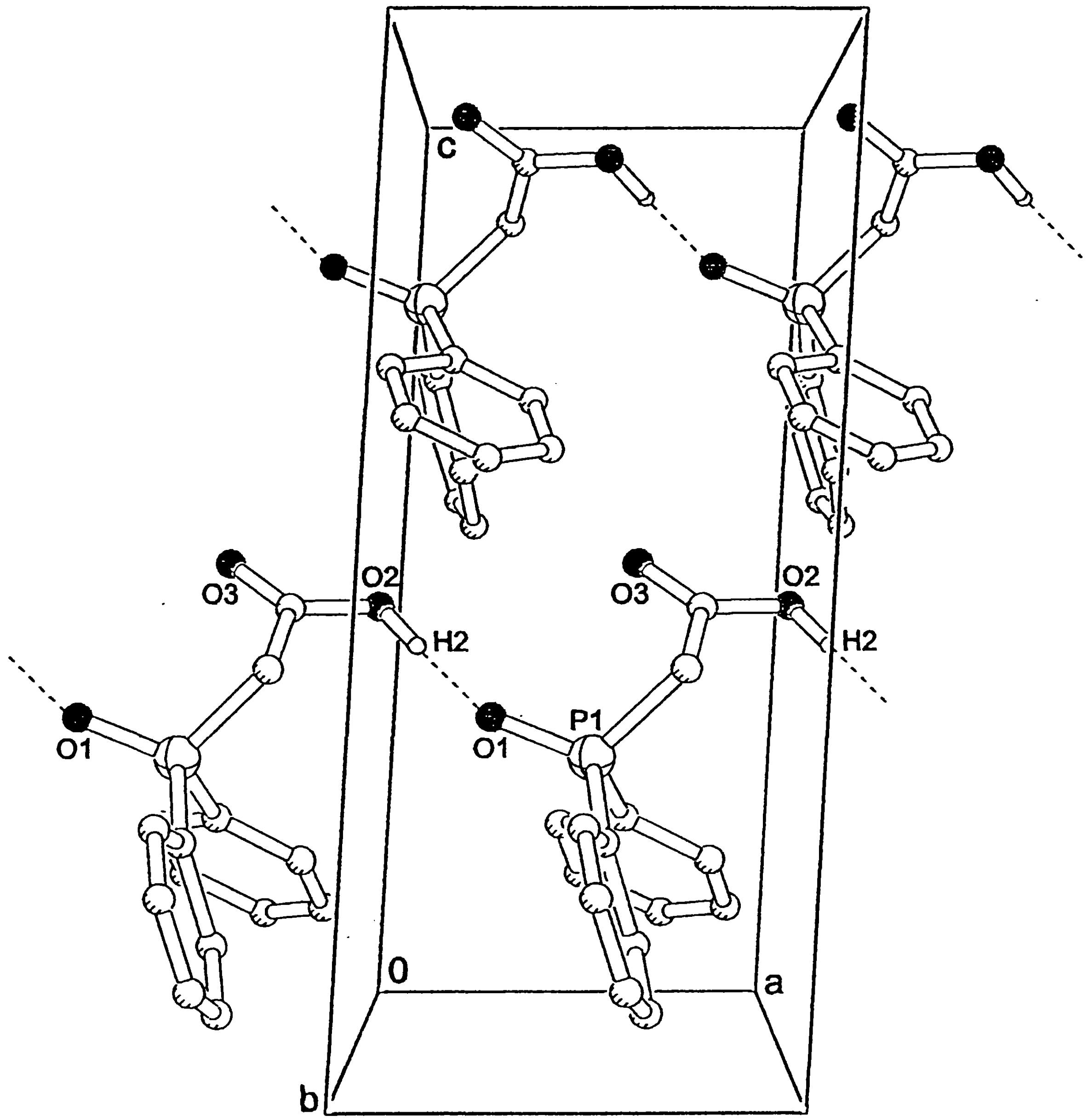


Figure 20. Projection of the unit cell down the b axis of diphenylphosphinylacetic acid.

supramolecular structure. Selected bond lengths and angles are given in Table 20 and hydrogen bond parameters in Table 21.

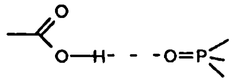
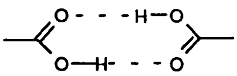
Table 20. Selected bond lengths (Å) and angles (°) for **53**.

P(1)-O(1)	1.490(3)	H(2)-O(1)#1	1.653(7)
P(1)-C(1)	1.790(4)	O(2)-C(14)	1.316(5)
P(1)-C(7)	1.793(5)	O(3)-C(14)	1.202(5)
P(1)-C(13)	1.804(4)		
O(1)-P(1)-C(1)	111.6(2)	C(1)-P(1)-C(7)	107.9(2)
O(1)-P(1)-C(7)	111.1(2)	C(1)-P(1)-C(13)	107.3(2)
O(1)-P(1)-C(13)	113.4(2)	C(7)-P(1)-C(13)	105.2(2)
O(3)-C(14)-O(2)	120.3(4)	O(2)-H(2)-O(1)#1	176(6)

Symmetry transformations used to generate equivalent atoms: #1 *-1+x, y, z*

The polymeric intermolecular association in **53** contrasts the dimeric arrangement of **54**[208] and many other carboxylic acids. Intermolecular hydrogen bonding occurs between the carboxylic proton H(2), in the molecule as presented, and the oxygen atom O(1), of the phosphine oxide moiety in the lattice neighbour generated *via* the symmetry operator -1+x, y, z. As a consequence the hydrogen bond is shorter and the variation in the carboxylic C-O bond lengths is greater than in **54** (Table 21).

Table 21. Hydrogen bond parameters of diphenylphosphinylacetic acid **53** and comparison with those of diphenylphosphinoacetic acid **54**.

System		Bond Length (Å)				Bond Angle (°)
		C=O	C-O	O-H	H- - -O	O-H- - -O
	**53**	1.202(5)	1.316(5)	0.93(7)	1.653(7)	176(6)
	**54**	1.208(5)	1.283(6)	1.03(6)	2.36(7)	178(8)

The phosphorus atom has a distorted tetrahedral geometry with the P-C linkages folded away from the P=O bond giving C-P-C angles less than 109.5°. The average C-P-C angle (106.8°) is similar to that found in triphenylphosphine oxide (average C-P-C angle, 107.1°,[209] 106.5°,[210] 106.6°[211]) and the variation in the C-P-C angles is of the order of that found in one of these determinations.[210] This represents a relative widening of the cone formed by phosphorus and its three nearest carbon atoms when compared to the structure of **54** (average C-P-C angle 100.9°) where oxygen has been replaced by a more sterically demanding lone pair. A similar effect is observed when comparing the structures of triphenylphosphine oxide and triphenylphosphine (average C-P-C angle 102.8°).[212]

As a result of the larger C-P-C angles in **53**, the P-C bond lengths (average P-C length 1.796Å) are contracted compared to those in **54** (average P-C length 1.836Å), although as with **54**, the $P\text{-}C_{phenyl}$ distances (1.790, 1.793Å) are shorter than the $P\text{-}C_{methylene}$ distance (1.804Å). The P=O bond length of 1.490(3)Å is longer than that found in any of the triphenylphospine oxide polymorphs (P=O: 1.46,[209] 1.483,[210] 1.484Å[211]) and comparable to P=O distances found in bis(triphenylphosphine oxide)dimethylmalonic acid (P=O; 1.492, 1.493Å)[213] where similar hydrogen bonding occurs.

The phenyl groups [C(1)-C(6), ring 1, and C(7)-C(12), ring 2] show large distortions from the regular benzene structure, more so than in either **54** or triphenylphosphine oxide, with C-C bond lengths and internal angles over the ranges 1.300(8)-1.389(9)Å, 115.3(5)-122.8(5) ° (ring 1) and 1.187(12)-1.526(13)Å, 115.6(9)-126(3) ° (ring 2). The average C-C bond length of ring 1 (1.346Å) is also shorter than the comparable values in **54** (1.370, 1.378Å), triphenylphosphine oxide (1.40, 1.40, 1.41,[209] 1.380, 1.370, 1.377,[210] 1.376, 1.378. 1.363Å[211]) or in ring 2 (1.37Å). This is possibly a result of the disorder described above.

3.3. Heterometallic complexes

No investigations were undertaken to establish the ability of complexes **O1**-**O3** to form heterobimetallic compounds with additional transition metal species. The nature of the salicylate ligand in the chelate complex **O1** does not suggest that any of the oxygen atoms would be good donor atoms. The difficulty in preparing a pure sample of the bis(salicylato) complex **O2** and the instability of **O3** in solution precluded either of these compounds from further studies.

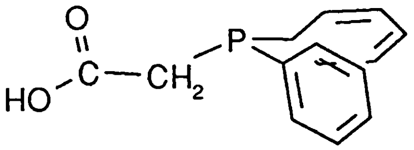
Chapter 4.

Bis(cyclopentadienyl)titanium(IV) Derivatives of Carboxylic Acids Containing Additional Phosphorus Donors.

4.1. Introduction

The previous two chapters have dealt with titanocene derivatives of carboxylic acids which contain additional hard donor atoms. In this chapter, we descend the periodic table from nitrogen to consider the softer donor atom properties of phosphorus.

The carboxylic acid chosen for these studies was diphenylphosphinoacetic acid 54. This acid contains a diphenylphosphino moiety separated from the carboxyl function by a methylene bridge which provides a certain degree of flexibility without introducing a large separation between the two functional groups.



54

The synthesis of diphenylphosphinoacetic acid was first reported by Issleib and Thomas in 1960.[214] Over the last thirty years, the coordination chemistry of the free acid, the anion and some ester derivatives have been studied by a number of researchers. A selection of transition metal complexes of the free acid and certain derivatives have been investigated for their potential use in organic synthesis[215] and as polymerisation catalysts.[216] Other workers have used the acid to incorporate the diphenylphosphino moiety into biologically important molecules and polymeric materials *via* reaction at the carboxyl function.[217,218]

In general, compounds containing phosphorus and oxygen donor functions are of interest for their capacity to form hydrophilic or even water soluble metal-phosphine complexes,[219] their use as bridging groups in heterometallic materials[175] and as chelating ligands.[220] In the latter, the ability of the phosphine moiety to stabilise transition metal species in low oxidation states is coupled with the enhanced binding properties of an O, P-bidentate ligand.

Both diphenylphosphinoacetic acid 54 and it's anion have been shown to behave as *O*- or *P*-donor ligands or as *O,P*-chelates. In the mercury(II) and palladium(II) complexes $[Hg_2(Ph_2PCH_2CO_2H)_2(Br)_2(\mu\text{-}Br)_2]$[221] and *trans*-$[(Ph_2PCH_2CO_2H)_2PdBr_2]$,[222] the free acid acts as a phosphine ligand, the carboxy group participating only in intermolecular hydrogen bonding. Calcium diphenylphosphinoacetate contains the anion bound *via* the carboxyl function in a tridentate bridging and chelating coordination mode,[223] and in the rhodium(I) and platinum(II) complexes [$Rh(CO)(Ph_2PCH_2CO_2)(Ph_2PCH_2CO_2H)$][224] and [$Pt(Br)(Ph_2PCH_2CO_2)(Ph_2PCH_2CO_2H)_2$].$H_2O$,[225] the anion is *O,P*-chelating while the acid is bonded *via* the phosphorus atom.

Bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1** has been prepared and investigated for its' ability to further coordinate to other transition metal species. In addition, a range of *P*-coordinated diphenylphosphinoacetic acid-transition metal complexes **P2**-**P8** were synthesised and their suitability assessed as starting materials for the production of heterobimetallic compounds containing the titanocene moiety.

4.2. Bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) P1

4.2.1. Preparation and characterisation

Bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1** was prepared in good yield from the reaction of bis(cyclopentadienyl)bis(methyl)titanium(IV) and diphenylphosphinoacetic acid in dichloromethane (Equation 51). The microanalysis, NMR and IR data for the product of this reaction are given in Table 22.

$$Cp_2TiMe_2 + 2HO_2CCH_2PPh_2 \xrightarrow{CH_2Cl_2/-2MeH} \underset{\textbf{P1}, 95\%}{Cp_2Ti(O_2CCH_2PPh_2)_2} \qquad \text{Eq. 51}$$

Table 22. Microanalysis, NMR and IR data for **P1**.

analysis[a]		%C: 67.6 (67.7); %H: 5.13 (5.17)
NMR δ(ppm)[b,c]	^1H	2.96(-C*H*$_2$-), 6.01(C$_5$*H*$_5$), 7.10(*phenyl*), 7.29(*phenyl*)
	$^{13}C\{^1H\}$	37.6(-*C*H$_2$-), 118.2(*C*$_5$H$_5$), 128.3(*phenyl*), 128.6(*phenyl*), 132.6(*phenyl*), 138.4(*phenyl*), 175.4(-*C*O$_2$-)
	$^{31}P\{^1H\}$	-17.6
IR (cm^{-1})[c]		$\nu(C\text{-}H)_{Cp}$: 3100, 3056; $\nu(C{=}C)_{Cp}$: 1464; $\delta(C\text{-}H)_{Cp}$: 1019, 824 $\nu(O\text{-}C\text{-}O)$: 1618, 1325

a - Calculated values for $(C_5H_5)_2Ti(O_2CCH_2PPh_2)_2$ are given in parentheses. b - Solvent: $CDCl_3$. c - Further data contained in Chapter 7.

The analytical data for **P1** are in good agreement with the predicted formula of this compound. The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra display the correct number and position of signals expected and the peak integrals of the protons are in the approximate ratio of 4:10:22; CH_2:C_5H_5:*phenyl* (theoretical; 4:10:20). The ^{1}H, ^{13}C and ^{31}P chemical shift values are altered very little in comparison to the free acid (see Table 22).

The symmetric and asymmetric stretches of the carboxylate functions (1325, 1618cm^{-1}) compare with those of 1379cm^{-1} and 1593cm^{-1} for the sodium salt and suggest monodentate coordination. Characteristic bands due to the cyclopentadienyl rings can be observed, however some of these may be confused with vibrational modes of the phenyl groups of similar frequency.

The FAB mass spectrum of **P1** (Table 23) shows similar fragmentation patterns to those described for **N1** (Scheme 13) and the earlier study on bis(substituted benzoato) titanocene derivatives.[97] Weak or zero intensities for parent ions are common in these spectra, the more abundant peaks arising from loss of carboxylate and cyclopentadienyl ligands. In addition to the above, further fragment ions generated by disintegration of the diphenyphosphinoacetate ligands are observed.

Table 23. FAB MS data for **P1**. Relative intensities are given in parentheses.

	m/z (intensity as % of base peak)	
FAB+	665 (1)	$[HCp_2Ti(O_2CCH_2PPh_2)_2]^+$
	599 (4)	$[CpTi(O_2CCH_2PPh_2)_2]^+$
	522 (7)	$[CpTi(O_2CCH_2PPh_2)(O_2CCH_2PPh)]^{+\cdot}$
	437 (36)	$[Cp_2Ti(O)(O_2CCH_2PPh_2)]^+$
	421 (82)	$[Cp_2Ti(O_2CCH_2PPh_2)]^+$
	344 (24)	$[Cp_2Ti(O_2CCH_2PPh)]^{+\cdot}$
	261 (26)	$[H(HO_2CCH_2P(O)Ph_2)]^+$
	245 (100)	$[H(HO_2CCH_2PPh_2)]^+$
FAB-	664 (7)	$[Cp_2Ti(O_2CCH_2PPh_2)_2]^-$
	587 (15)	$[Cp_2Ti(O_2CCH_2PPh_2)(O_2CCH_2PPh)]^-$
	259 (40)	$[O_2CCH_2P(O)Ph_2]^-$
	243 (100)	$[O_2CCH_2PPh_2]^-$

4.2.2. X-ray crystal structure determination

Bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1** was further characterised by an X-ray single crystal structure determination from which the molecular structure shown in Figure 21 was calculated. Selected bond lengths and bond angles for **P1** are given in Table 24.

The molecular structure of bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1** shows a titanium environment that is typical for bis(cyclopentadienyl)titanium(IV) carboxylates. A pseudo-tetrahedral titanium atom is bonded to two η^5-cyclopentadienyl rings and two monodentate carboxylates, the bond angles and bond lengths all being within the range of those found in similar structures [Ti-O: 1.925(5), 1.972(4)Å; Ti-Z: 2.061, 2.059Å; O-Ti-O: 91.5(2)°; Z-Ti-Z: 132.4°. Z represents the centre of the cyclopentadienyl rings].

Table 24. Selected bond lengths (Å) and angles (°) for **P1**.

Ti(1)-O(1)	1.972(4)	Ti(1)-O(3)	1.925(5)
Ti(1)-Z(1)	2.061	Ti(1)-Z(2)	2.059
O(1)-C(11)	1.282(8)	O(3)-C(25)	1.300(7)
O(2)-C(11)	1.216(8)	O(4)-C(25)	1.189(8)
P(1)-C(12)	1.856(6)	P(2)-C(26)	1.830(7)
P(1)-C(13)	1.830(7)	P(2)-C(27)	1.845(7)
P(1)-C(19)	1.842(7)	P(2)-C(33)	1.837(8)
O(3)-Ti(1)-O(1)	91.5(2)	Z(1)-Ti(1)-Z(2)	132.4
C(11)-O(1)-Ti(1)	136.1(5)	C(25)-O(3)-Ti(1)	143.4(4)
O(2)-C(11)-O(1)	125.0(7)	O(4)-C(25)-O(3)	123.3(7)
C(12)-P(1)-C(13)	101.8(3)	C(26)-P(2)-C(27)	100.2(3)
C(13)-P(1)-C(19)	99.8(3)	C(27)-P(2)-C(33)	101.9(3)
C(19)-P(1)-C(12)	98.8(3)	C(33)-P(2)-C(26)	101.4(4)

Z(1) and Z(2) refer to the centres of the cyclopentadienyl rings, C(1)-C(5) and C(6)-C(10) respectively.

The two carboxylate ligands are quite different in their attachment to titanium, the shorter Ti-O distance to O(3) [1.925(5)Å] corresponding with the wider Ti-O-C angle (143.4°). As mentioned earlier, the wide Ti-O-C angles observed in the molecular structures of bis(cyclopentadienyl)titanium(IV) carboxylates has been explained by partial double bond formation between titanium and oxygen. In this case, the variation in bond angles and bond lengths between the two carboxylate ligands could be due to differing degrees to which

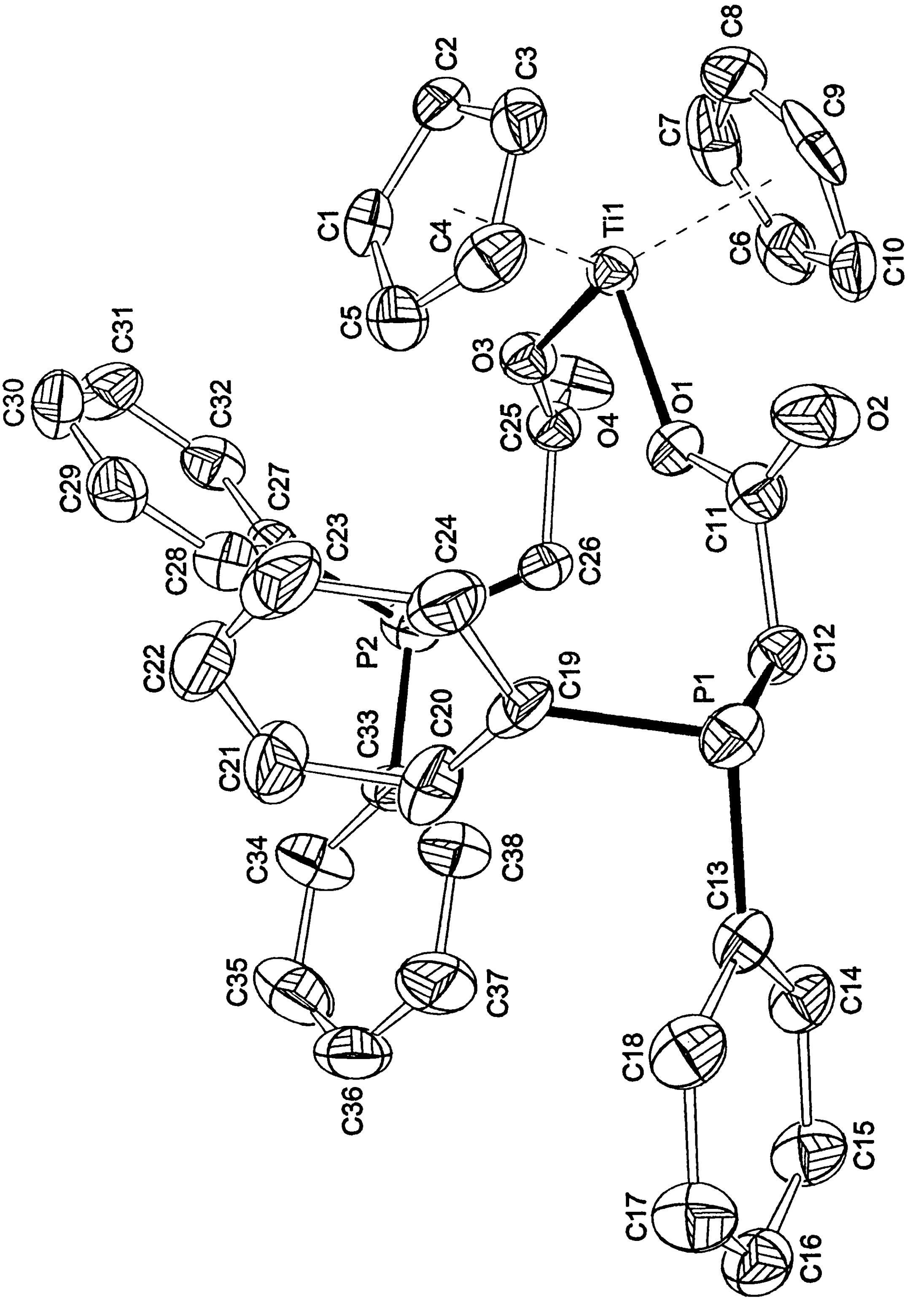


Figure 21. The molecular structure of bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) P1.

additional electron density is exchanged between the oxygen and titanium atoms. Alternatively, the discrepancy could result from crystal packing effects.

The dissimilarity in the titanium-carboxyl bonding between the two carboxylates is also reflected in the C-O distances. For the shorter Ti-O bond, a difference of 0.111Å is observed in the carboxyl C-O bond lengths [C(25)-O(3)=1.300(7)Å, C(25)-O(4)=1.189(8)Å] compared to that of 0.066Å for the other carboxylate [C(11)-O(1)=1.282(8)Å, C(11)-O(2)=1.216(8)Å]. In either case the difference is quite large and confirms the expected unidentate nature of the carboxylate ligands.

As with the nicotinate, the bis(cyclopentadienyl)titanium(IV) derivative of diphenylphosphinoacetate appears to be the first example of this ligand coordinating in a solely monodentate fashion *via* the carboxyl function to be confirmed crystallographically. This fact further emphasises the tendency of the bis(cyclopentadienyl)titanium(IV) moiety to favour the monodentate form of carboxylate bonding.

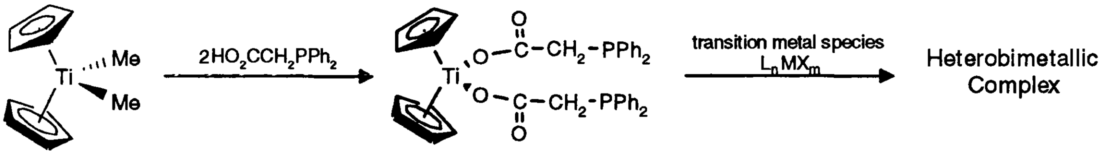
The O-C-O angles [$\angle$O(1)-C(11)-O(2)=125.0(7)°, $\angle$O(3)-C(25)-O(4)=123.3(7)°] compare with those of 124.7(6)° and 124.4(6)° for the palladium(II) complex [$Pd(O_2CCH_2PPh_2)_2$] where the diphenylphosphinoacetate ligand is bidentate chelating through phosphine and monodentate carboxyl functions.[226]

The phosphine moieties are arranged so that the lone pairs of the phosphorus atoms are directed away from each other. The bond angles and bond lengths around phosphorus are very similar to those found in the free acid[208] [**P1**: $\angle$(C-P-C)$_{av.}$=100.7°, P-C$_{av.}$=1.840Å; $HO_2CCH_2PPh_2$: $\angle$(C-P-C)$_{av.}$=100.9°, P-C$_{av.}$=1.836Å], as are the dimensions of the phenyl rings. The C-P-C angles around the phosphorus atoms in both **P1** and the free acid, deviate significantly from the ideal tetrahedral angle due to the sterically demanding lone pairs.

4.3. Heterometallic compounds

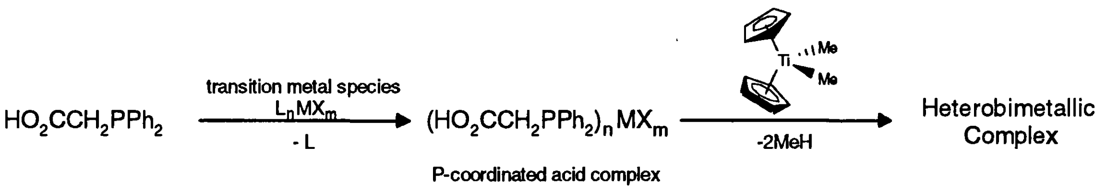
4.3.1. Synthetic strategy

Two alternative routes were proposed for the preparation of heterobimetallic complexes involving the bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) moiety. The first involves initially isolating the bis(cyclopentadienyl)titanium(IV) carboxylate followed by treatment of this complex with a transition metal species (Scheme 15). The second involves the treatment of a transition metal species with diphenylphosphinoacetic acid to give the *P*-coordinated acid complexes, and the subsequent reaction of these complexes with bis(cyclopentadienyl)bis(methyl)titanium(IV) (Scheme 16).



P1

Scheme 15



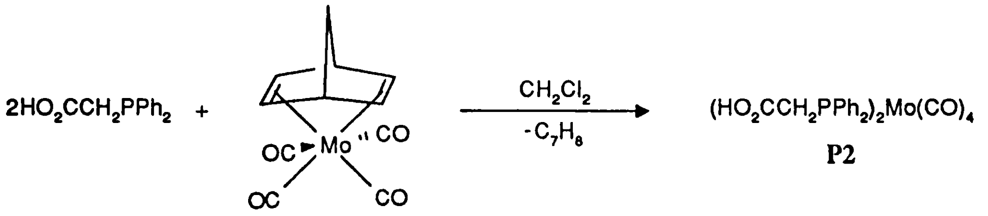
Scheme 16

In several cases, transition metal precursors that had neutral labile ligands were chosen to achieve coordination of the phosphine functions of **P1** or the free acid. As a result of this, preparation of the heterometallic materials *via* the sequence of reactions proposed in Scheme 16 yielded better results. Once the *P*-coordinated acid complexes had been purified and isolated the final step, involving treatment with bis(cyclopentadienyl)bis(methyl)titanium(IV) generates methane as the only by-product, provided the reaction proceeds cleanly. On the other hand, the final step of Scheme 15 entails the substitution of a labile ligand L which remains in the reaction mixture. This ligand has the potential of complicating the isolation of the heterometallic compound or even worse, reacting further with species in solution.

4.3.2. *P*-Coordinated diphenylphosphinoacetic acid transition metal complexes

4.3.2.1. Preparation

The synthesis of heterometallic complexes *via* the route proposed in Scheme 16 initially required the preparation of diphenylphosphinoacetic acid-transition metal complexes. This was achieved either by direct reaction of the free acid with a metal halide or by displacement of a suitable labile ligand from a transition metal species (Equations 52-58).



P2 Eq. 52

$$4\mathrm{HO_2CCH_2PPh_2} + \mathrm{[(MeCN)_6Ni][BF_4]_2} \xrightarrow[-6\mathrm{MeCN}]{\mathrm{CH_2Cl_2}} \mathrm{[(HO_2CCH_2PPh_2)_4Ni][BF_4]_2}$$

P3 Eq. 53

$$2\mathrm{HO_2CCH_2PPh_2} + \mathrm{(C_6H_5CN)_2PdCl_2} \xrightarrow[-2\mathrm{C_6H_5CN}]{\mathrm{CH_2Cl_2}} \mathrm{(HO_2CCH_2PPh_2)_2PdCl_2}$$

P4 Eq. 54

$$2\mathrm{HO_2CCH_2PPh_2} + \mathrm{(C_6H_5CN)_2PtCl_2} \xrightarrow[-2\mathrm{C_6H_5CN}]{\mathrm{CH_2Cl_2}} \mathrm{(HO_2CCH_2PPh_2)_2PtCl_2}$$

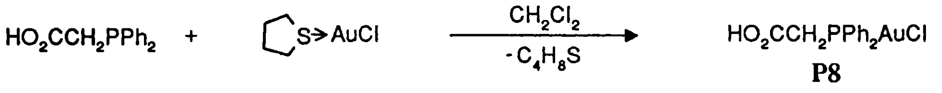
P5 Eq. 55

$$\mathrm{HO_2CCH_2PPh_2} + \mathrm{CuCl} \xrightarrow{\mathrm{CH_2Cl_2}} \mathrm{HO_2CCH_2PPh_2CuCl}$$

P6 Eq. 56

$$3\mathrm{HO_2CCH_2PPh_2} + \mathrm{CuCl} \xrightarrow{\mathrm{CH_2Cl_2}} \mathrm{(HO_2CCH_2PPh_2)_3CuCl}$$

P7 Eq. 57



P8 Eq. 58

The complexes **P2-P8** were characterised by microanalysis, IR and NMR spectroscopy and FAB mass spectrometry. The analyses and ^{1}H and ^{31}P{^{1}H} NMR data for compounds **P2-P8** are given in Tables 25 and 26. ^{13}C{^{1}H} NMR data for compounds **P2** and **P6-P8** are listed in Table 27.

The analytical data for all the compounds P2-P8 are in good agreement with the predicted formulae. The palladium and platinum compounds **P4** and **P5**, contain very low percentages of nitrogen suggesting the presence of a small quantity of impurities where benzonitrile remains coordinated to the metal centres.

Table 25. Microanalysis data for complexes P2-P8. Calculated values for the quoted formulae are given in parentheses.

		%C	%H
$(HO_2CCH_2PPh_2)_2Mo(CO)_4$	**P2**	55.1 (55.2)	3.72 (3.76)
$[(HO_2CCH_2PPh_2)_4Ni][BF_4]_2$	**P3**	54.5 (55.6)	4.37 (4.33)
$(HO_2CCH_2PPh_2)_2PdCl_2{}^a$	**P4**	50.1 (50.5)	3.88 (3.94)
$(HO_2CCH_2PPh_2)_2PtCl_2{}^b$	**P5**	45.2 (44.6)	3.49 (3.47)
$(HO_2CCH_2PPh_2)CuCl$	**P6**	49.1 (49.0)	3.80 (3.82)
$(HO_2CCH_2PPh_2)_3CuCl$	**P7**	59.9 (60.7)	4.75 (4.73)
$(HO_2CCH_2PPh_2)AuCl$	**P8**	35.2 (35.3)	2.70 (2.75)

a - 0.54% N. b - 0.26% N.

4.3.2.2. NMR Spectroscopy

The ^1H NMR spectra of the seven compounds **P2-P8** are all very similar to that of the free acid (Table 24). The variation in chemical shift of the methylene resonance is probably an effect of the solvent used and seems to be insensitive to the bonding taking place between phosphorus and the transition metal centres. The shape of the methylene peak however, is slightly more informative with a departure from the simple singlet seen in the spectrum of the free acid occuring in the spectra of complexes **P2**, **P4**, **P5** and **P8**.

The tetrahedral nature of the phosphorus atom in compounds **P4**, **P5** and **P8** is displayed by the splitting of the methylene signal into a doublet with coupling constants $^2J(^{31}P-^1H) \approx 12Hz$. These values compare with that of 13.92Hz for the phosphine oxide derivative.

Complex **P2** contains a more complicated signal due to an effect known as "virtual coupling".[227] This phenomenon arises when two equivalent phosphorus atoms around a transition metal centre are strongly coupled to one another. Under the correct conditions, certain protons on the phosphine ligands can couple equally to both phosphorus nuclei producing a sharp 1:2:1 triplet instead of the expected doublet. In the case of **P2**, the coupling between the two phosphorus atoms in a *cis* arrangement is not large enough to produce a triplet with the ideal 1:2:1 ratio of peak integrals, rather a sharp doublet is observed with a broad peak in the middle (Fig. 22).

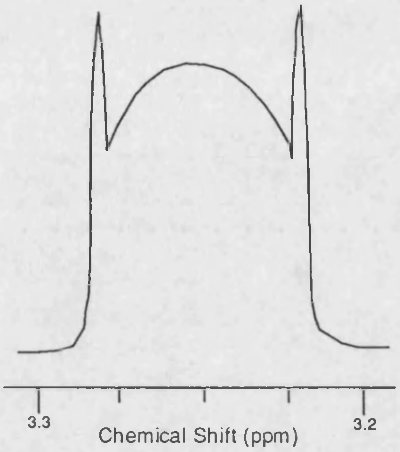


Figure 22. A redrawing of the methylene peak from the ^{1}H NMR spectrum of **P2**.

The ^{1}H NMR spectra of **P3**, **P6** and **P7** are broad and therefore it is not possible draw information from splitting patterns.

Table 26. ^{1}H and $^{31}P\{^1H\}$ NMR chemical shifts for complexes **P2**-**P8**. For comparison, the free acid and its' phosphine oxide derivative are included.^{a}

		^{1}H δ(ppm)			^{31}P
		-C*H*$_2$-	*phenyl*	-O*H*	δ(ppm)
$HO_2CCH_2PPh_2$^{b}		3.11	7.33-7.48	11.5	-15.1
$(HO_2CCH_2PPh_2)_2Mo(CO)_4$^{c}	**P2**	3.25	7.39, 7.51		25.0
$[(HO_2CCH_2PPh_2)_4Ni][BF_4]_2$^{b}	**P3**	3.16	7.29		-13.0
$(HO_2CCH_2PPh_2)_2PdCl_2$^{d}	**P4**	3.71	7.31, 7.54, 7.83		12.4
$(HO_2CCH_2PPh_2)_2PtCl_2$^{d}	**P5**	3.63	7.28-7.67		3.0^f
$(HO_2CCH_2PPh_2)CuCl$^{d}	**P6**	3.42	7.48, 7.68, 7.78-7.83	6.87	-13.3
$(HO_2CCH_2PPh_2)_3CuCl$^{b}	**P7**	3.16	7.13, 7.32	10.07	-9.5
$(HO_2CCH_2PPh_2)AuCl$^{b}	**P8**	3.83	7.56, 7.82		25.0
$HO_2CCH_2P(O)Ph_2$^{e}		3.68	7.47-7.60, 7.82	12.54	26.3

a - Further data (eg. multiplicity, proton integrals, etc.) are given in Chapter 7. Solvent: b - $CDCl_3$, c - d_6-acetone, d - CD_3CN, e - d_6-DMSO. f - $^2J(^{195}Pt-^{31}P)$=3790Hz.

$^{13}C\{^1H\}$ NMR data were collected for complexes **P2** and **P4**-**P8**. Due to the low solubility of **P4** and **P5** however, only partial information was obtained which is given in Chapter 7, but not discussed here. The remaining compounds (**P2**, **P6**-**P8**) gave six ^{13}C resonances at approximately the same chemical shifts as the free acid (Table 27).

In addition, the spectrum of **P2** shows two further signals due to the carbonyl ligands (δ=210.2, 216.1ppm) which confirms the *cis* arrangement expected from displacement of the norbornadiene moiety. The symmetry of the molybdenum coordination sphere is further established by the observation of four bands in the carbonyl region of the IR spectrum (Table28).

Table 27. $^{13}C\{^{1}H\}$ chemical shifts for complexes **P2**, **P6-P8**. For comparison, the free acid and its' phosphine oxide derivative are included.

		^{13}C δ(ppm)		
		-CH_2-	-CO_2H	*phenyl*
$HO_2CCH_2PPh_2{}^{a}$		35.1	177.2	128.4, 129.0, 132.4, 136.7
$(HO_2CCH_2PPh_2)_2Mo(CO)_4{}^{b,e}$	P2	37.8	169.4	129.0, 130.4, 133.1, 137.3
$(HO_2CCH_2PPh_2)CuCl^{c}$	P6	34.7	170.1	129.6, 131.6, 133.2, 133.5
$(HO_2CCH_2PPh_2)_3CuCl^{a}$	P7	33.5	171.9	128.3, 129.8, 131.5, 132.4
$(HO_2CCH_2PPh_2)AuCl^{a}$	P8	35.0	168.7	129.9, 130.3, 133.3, 134.2
$HO_2CCH_2P(O)Ph_2{}^{d}$		37.8	167.4	128.6, 130.6, 131.7, 134.2

Solvent: a - $CDCl_3$, b - d_6-acetone, c - CD_3CN, d - d_6-DMSO. e - Carbonyl resonances: δ = 210.2, 216.1ppm. Additional information regarding multiplicities and coupling constants is given in Chapter 7.

As expected, the $^{31}P\{^{1}H\}$ chemical shifts for compounds **P2-P8** are more informative of phosphorus coordination. All values are shifted downfield relative to the free acid (Table 26) and represent a general deshielding of the phosphorus nuclei. This can be explained as a result of the phosphorus lone pair being involved in bonding or as a consequence of the phosphorus atom becoming tetrahedral. A similar downfield shift is observed when the phosphorus is bonded to oxygen in the phosphine oxide derivative of the free acid.

The extent to which deshielding occurs does vary. For the molybdenum and gold complexes the change in chemical shift is relatively large (40ppm). For the first row transition metal complexes **P3**, **P6** and **P7** however, the effect is small, which could possibly reflect weaker interactions of the phosphine ligand with nickel and copper.

The large ^{195}Pt-^{31}P coupling constant [$^{1}J(^{195}Pt$-$^{31}P)$=3790Hz] observed for **P5** suggests the expected *cis* arrangement of the ligands. This follows from a study by Grim *et al.* who investigated the ^{31}P NMR spectra of a range of phosphine complexes of platinum(II) chloride.[228] Comparison of the $^{1}J(^{195}Pt$-$^{31}P)$ values revealed that the *cis* isomers have significantly larger coupling constants than the *trans* isomers [$^1J(^{195}Pt-^{31}P)$; *cis*: 3500-3650Hz, *trans*: 2400-2500Hz]. The corresponding value for **P5** compares with that of 3616Hz for one of these complexes, *cis*-[$(CH_3PPh_2)_2PtCl_2$].

4.3.2.3. IR Spectroscopy

The asymmetric and symmetric stretches observed in the IR spectra of complexes **P2**-**P8** are very similar to those displayed by the uncoordinated diphenylphosphinoacetic acid (Table 28). The palladium complex **P4** shows a slight departure from this pattern and is possibly due to a weak interaction between one of the carboxyl oxygens and the metal as detected in the *trans* dibromo complex *trans*-[$(HO_2CCH_2PPh_2)_2PdBr_2$].[222]

Table 28. Selected IR data for complexes **P2**-**P8** and uncoordinated diphenylphosphinoacetic acid.

		ν(O-C-O) cm^{-1}		low frequency[a] cm^{-1}		other cm^{-1}
		asym	sym	ν(M-X)		
$HO_2CCH_2PPh_2$		1700[b]	1301, 1291		310vw, 247w	
$(HO_2CCH_2PPh_2)_2Mo(CO)_4$	**P2**	1701	1296			2027, 1921,[c] 1897 [CO vibrations]
$[(HO_2CCH_2PPh_2)_4Ni][BF_4]_2$	**P3**	1700	1287			1069, 745 [BF_4^- vibrations]
$(HO_2CCH_2PPh_2)_2PdCl_2$	**P4**	1732, 1707	1350	318m	297m, 262s, 238w	
$(HO_2CCH_2PPh_2)_2PtCl_2$	**P5**	1696[d]	1300	332m, 303m	270sh, 260s	
$(HO_2CCH_2PPh_2)CuCl$	**P6**	1705	1294		340sh, 330s, 300sh, 240w	
$(HO_2CCH_2PPh_2)_3CuCl$	**P7**	1700[e]	1290	247w	340m	
$(HO_2CCH_2PPh_2)AuCl$	**P8**	1700	1300	335vs	346w, 240w	

All spectra recorded as nujol mulls on CsI discs. a - Intensities are relative to peaks in the region 200-400cm^{-1} only, and are annotated as: vw - very weak, w- weak, m - medium, s - strong, vs - very strong, sh - shoulder. Relative intensities of other peaks are given in Chapter 7. b - Shoulder at 1718cm^{-1}. c - Shoulder at 1910cm^{-1}. d - Shoulder at 1734cm^{-1}. e - Shoulder at 1725cm^{-1}.

Recrystallisation of **P4** from ethanol produced yellow crystals, the microanalysis and IR spectrum of which were significantly different to the data relating to the non-purified product (Table 32). This crystalline material **P4'** was subsequently identified *via* a single crystal X-ray structure determination and found to contain *trans*-bis(diphenylphosphinoacetic acid)-

palladium(II) chloride and solvent molecules of water and ethanol. A description of the structure is presented later in this chapter.

The nickel(II) complex **P3** contains broad bands above 3200cm^{-1} (3216, 3463 and 3528cm^{-1}) which are probably due to water. This water was not detected in the ^{1}H NMR spectrum of the initially prepared brown complex. On standing in air for several days however, the colour of the complex changed from brown to green and the uptake of atmospheric moisture is the most likely cause of this. The presence of water could also explain the slight discrepancies in the analysis which yields lower carbon and higher hydrogen contents than the proposed structure.

Also observed in the IR spectrum of **P3** are vibrational modes due to the BF_4^- anion at 1069 and 745cm^{-1}.

The low frequency region (200-400cm^{-1}) of the spectra for complexes **P4, P5, P7** and **P8** contains the metal-chloride bond stretching modes. Unfortunately, it also contains ligand vibrations at 310 and 247cm^{-1} which makes designation of the bands particularly difficult when the resolution of the spectra is low as in the case of the copper(I) complex **P7**. The assignment of the low frequency vibrations are given in Table 28 although some of these assignments are only tentative.

4.3.2.4. Magnetic moment of P3

The magnetic moment of the green nickel(II) complex **P3** was determined *via* the Evans' NMR method. The value of 2.04B.M. obtained is lower than that predicted by the spin-only formula of 2.83B.M. and suggests that either the compound was not pure or that large errors were incurred during measurement. However, a reading of 2.04B.M. does suggest that the material is paramagnetic and therefore that the geometry of the nickel atom is either octahedral or tetrahedral and not square planar.

4.3.2.5. Mass spectrometry

The FAB mass spectrometry data for complexes **P2-P4** and **P6-P8** are given in Table 29. Nearly all the complexes show signals above the calculated weight from the empirical formulae indicating the high degree of molecular association in the solid state. This is to be expected considering the potential for hydrogen bonding by the carboxylic acid functions. Most fragmentations occur at the metal generating ions containing a metal centre and different proportions of ligands. The loss of CO_2 is also a common feature with all of the complexes.

Table 29. Selected FAB MS data for complexes **P2-P4** and **P6-P8**. Peak intensities are given in parentheses and are expressed as a % of the base peak.

$(HO_2CCH_2PPh_2)_2Mo(CO)_4$, **P2**				$[(HO_2CCH_2PPh_2)_2Ni][BF_4]_2$, **P3**			
m/z	FAB+	m/z	FAB-	m/z	FAB+	m/z	FAB-
698 (5)	$[(HA)_2Mo(CO)_4]^+$	697 (11)	$[(HA)(A)Mo(CO)_4]^-$	545 (35)	$[(HA)(A)Ni]^+$	87 (100)	BF_4^-
670 (2)	$[(HA)_2Mo(CO)_3]^+$	669 (9)	$[(HA)(A)Mo(CO)_3]^-$	302 (20)	$[(HA)(A)Ni]^+$		
642 (13)	$[(HA)_2Mo(CO)_2]^+$	453 (97)	$[(A)Mo(CO)_4]^-$	261 (70)	$[H(HO_2CCH_2P(O)Ph_2)]^+$		
614 (1)	$[(HA)_2Mo(CO)]^+$	425 (100)	$[(A)Mo(CO)_3]^-$	245 (62)	$[H(HA)]^+$		
586 (7)	$[(HA)_2Mo]^+$			201 (100)	$[H(H_3CPPh_2)]^+$		
454 (33)	$[(HA)Mo(CO)_4]^+$						
426 (17)	$[(HA)Mo(CO)_3]^+$						
342 (17)	$[(HA)Mo]^+$						
297 (10)	$[(CH_2PPh_2)Mo]^+$						
245 (100)	$[H(HA)]^+$						

$(HO_2CCH_2PPh_2)_2PdCl_2$, **P4**				$(HO_2CCH_2PPh_2)CuCl$, **P6**			
	FAB+	m/z	FAB-	m/z	FAB+	m/z	FAB-
1186 (10)	$[(HA)(A)_3Pd_2]^+$	1257 (5)	$[(HA)_3(A)Pd_2Cl_2]^-$	1336 (1)	$[(HA)_4Cu_4Cl_3]^+$	1372 (2)	$[(HA)_4Cu_4Cl_4]^{-\cdot}$
942 (3)	$[(A)_3Pd_2]^+$	665 (8)	$[(HA)(A)PdCl_2]^-$	895 (2)	$[(HA)_3Cu_2Cl]^+$	1128 (6)	$[(HA)_3Cu_4Cl_4]^{-\cdot}$
631 (46)	$[(HA)_2PdCl]^+$	628 (54)	$[(HA)(A)PdCl]^-$	857 (3)	$[(HA)_2(A)Cu_2]^+$	882 (24)	$[(A)_2Cu_4Cl_4]^-$
593 (100)	$[(HA)(A)Pd]^+$	585 (48)	$[(HA)(H_3CPPh_2)PdCl]^-$	651 (60)	$[(HA)_2Cu_2Cl]^+$	638 (40)	$[(A)Cu_4Cl_4]^-$
549 (65)	$[H(A)(CH_2PPh_2)Pd]^+$	541 (24)	$[(H_3CPPh_2)_2PdCl]^-$	551 (100)	$[(HA)_2CuI]^+$	539 (86)	$[(A)Cu_3Cl_3]^-$
350 (20)	$[(HA)Pd]^+$	384 (46)	$[(A)PdCl]^-$	407 (34)	$[(HA)Cu_2Cl]^+$	341 (80)	$[(A)CuCl]^-$
		341 (65)	$[(H_3CPPh_2)PdCl]^-$	342 (10)	$[(HA)CuCl]^{+\cdot}$		
		188 (100)	$[HO_2CP(Cl)Ph]^{-\cdot}$	263 (68)	$[(H_3CPPh_2)Cu]^+$		
				245 (68)	$[H(HA)]^+$		

$(HO_2CCH_2PPh_2)_3CuCl$, **P7**				$(HO_2CCH_2PPh_2)AuCl$, **P8**			
m/z	FAB+	m/z	FAB-	m/z	FAB+	m/z	FAB-
859 (7)	$[(HA)_2(A)Cu_2]^+$	893 (3)	$[(HA)(A)_2Cu_2Cl]^-$	917 (22)	$[(HA)_2Au_2Cl]^+$	951 (25)	$[(HA)(A)Au_2Cl_2]^-$
795 (2)	$[(HA)_3Cu]^+$	793 (4)	$[(HA)(A)_2Cu]^-$	685 (3)	$[(HA)_2Au]^+$	475 (45)	$[(A)_2AuCl]^-$
651 (3)	$[(HA)_2Cu_2Cl]^+$	585 (12)	$[(HA)(A)CuCl]^-$	476 (7)	$[(HA)AuCl]^{+\cdot}$	431 (100)	$[(CH_2PPh_2)AuCl]^-$
551 (100)	$[(HA)_2Cu]^+$	549 (18)	$[(A)_2Cu]^-$	441 (100)	$[(HA)Au]^+$		
263 (50)	$[(H_3CPPh_2)Cu]^+$	341 (75)	$[(A)CuCl]^-$				
245 (25)	$[H(HA)]^+$	188 (100)	$[HO_2CP(Cl)Ph]^{-\cdot}$				

HA = $HO_2CCH_2PPh_2$.

Several compounds display fragmentations specific to their structure. The molybdenum complex **P2** contains a parent ion at m/z=698 and four subsequent fragments at 28 mass unit intervals due to the sequential loss of the CO ligands. The tetrafluoroborate anion is clearly present in the spectrum of the nickel(II) complex **P3** at m/z=87.

A number of ions in the mass spectrum of the copper(I) complex **P6** involve a Cu_4Cl_4 moiety which might suggest this compound contains the CuCl cubane structure found in $[(PPh_3)CuCl]_4$.[229] The tetranuclear CuCl cubes could be linked together *via* hydrogen bonding through the free carboxylic acid groups (Fig. 23).

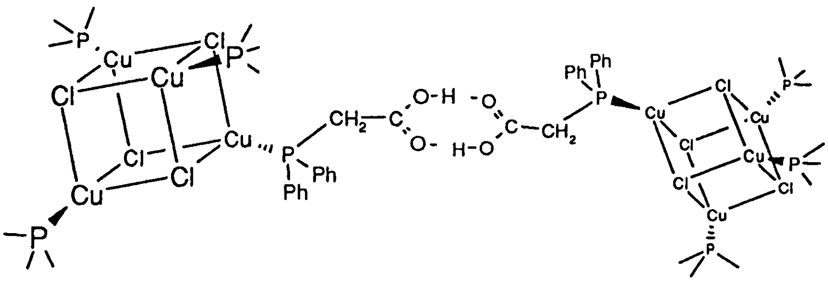


Figure 23. Suggested structure of $HO_2CCH_2PPh_2CuCl$ **P6**

A hydrogen bonded dimeric arrangement similar to that found in the crystal structure of the free acid[208] is predicted for the gold(I) complex **P8**. The mass spectrum contained very few peaks in comparison to those of the other complexes **P2-P4**, **P6** and **P7** but gave strong signals (>20% of base peak) at m/z=951 and 917 due to the dimeric parent ion and the parent ion after loss of one chloride ligand.

This prediction is also in agreement with the IR data which have carboxylate stretching frequencies identical to the free acid. In addition, a strong metal-halide stretch at $335cm^{-1}$ suggests a linear arrangement at gold and terminal chloride ligands. The Au-Cl stretching frequency observed in the IR spectrum of chloro(triphenylphosphine)gold(I) is close to the above value at $325cm^{-1}$.[230]

4.3.2.6. Crystal structure of (diphenylphosphinoacetic acid)gold(I) chloride P8

Confirmation of the dimeric arrangement of (diphenylphosphinoacetic acid)gold(I) chloride was achieved *via* single crystal X-ray diffraction. The structure of the dimer is shown in Figure 24. Selected bond lengths and angles are given in Table 30.

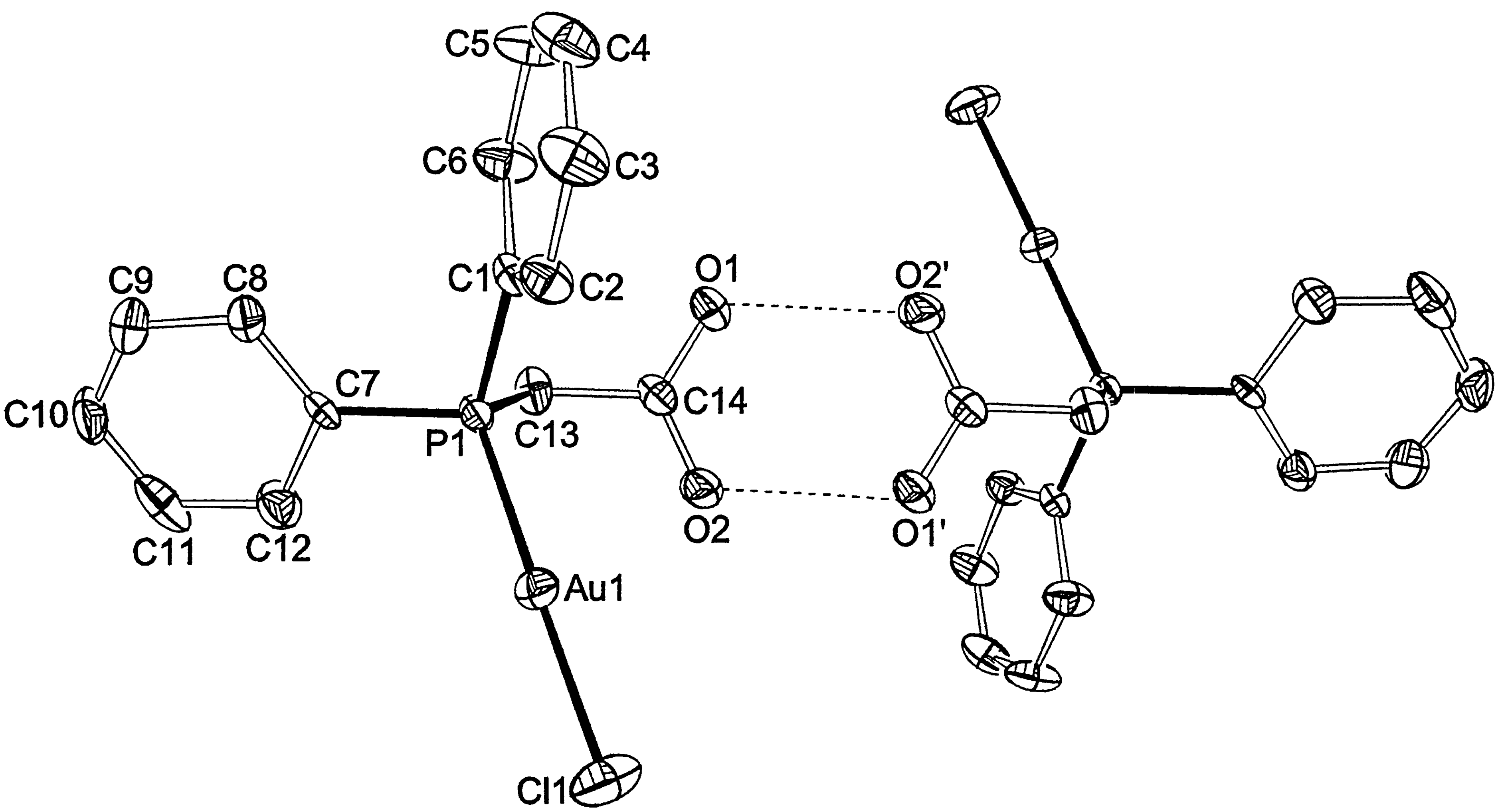


Figure 24. ORTEX plot of the hydrogen bonded dimer contained in the crystal structure of (diphenylphosphinoacetic acid)gold(I) chloride P8.

Figure 24 shows two adjacent hydrogen bonded molecules which are related by an inversion centre. Unfortunately the carboxyl protons were not located but the short O(1)···O(2)' distance [2.618(9)Å] is comparable to the analogous parameter in more common carboxylic acids such as benzoic acid [O···O': 2.64Å][231] and terephthalic acid [O···O': 2.62Å][232] and to that found in the uncoordinated free diphenylphosphinoacetic acid [O···O': 2.660(7)Å].[208] The mercury(II) and palladium(II) complexes, dibromo(diphenylphosphinoacetic acid)mercury(II)[221] and dibromobis(diphenylphosphinoacetic acid)palladium(II)[222] also contain intermolecular hydrogen bonding, but the O···O' contacts are longer in these cases [Hg(II), 2.858(9)Å; Pd(II), 2.710(7)Å].

Table 30. Selected bond lengths (Å) and angles (°) for **P8**.

Au(1)-P(1)	2.220(2)	Au(1)-Cl(1)	2.270(3)
P(1)-C(1)	1.808(8)	C(14)-O(1)	1.237(10)
P(1)-C(7)	1.803(8)	C(14)-O(2)	1.265(11)
P(1)-C(13)	1.824(9)	C(13)-C(14)	1.514(12)
O(1)-O(2)#1	2.618(9)		
P(1)-Au(1)-Cl(1)	179.0(1)	C(1)-P(1)-C(7)	106.6(4)
C(1)-P(1)-Au(1)	114.4(3)	C(7)-P(1)-C(13)	101.5(4)
C(7)-P(1)-Au(1)	113.4(3)	C(13)-P(1)-C(1)	106.4(4)
C(13)-P(1)-Au(1)	113.5(3)	O(1)-C(14)-O(2)	122.5(8)

Symmetry transformations used to generate equivalent atoms: #1 *1-x,1-y,2-z*

The carbonyl group does not show a large difference between the two C-O bond distances [C(14)-O(1)=1.237(10)Å, C(14)-O(2)=1.265(11)Å, Δ=0.028Å]. This is not the case for the free acid or for the mercury(II) or palladium(II) complexes mentioned above where the difference between the two bond lengths ranges from 0.075Å for the free acid to 0.095Å for the Pd(II) complex. The O-C-O angle for **P8** of 122.5(8)° compares to that of 122.2(4)° for the free acid and 123.3(9)° for the Hg(II) complex.

A comparison of important bond lengths and angles between chloro(triphenylphosphine)gold(I)[233] and **P8** is given in Table 31. Substituting one phenyl ring for a CH_2CO_2H moiety appears to have very little effect on the geometries of the gold and phosphorus atoms. The Au-Cl distances [2.270(3)Å vs 2.279(3)Å] are identical to within

Table 31. Comparison of certain structural parameters of (diphenylphosphinoacetic acid)gold chloride and chloro(triphenylphosphine)gold(I).

	bond lengths (Å)			bond angles (°)		
	Au-Cl	Au-P	P-C	P-Au-Cl	C-P-Au	C-P-C
$(HO_2CCH_2PPh_2)AuCl$	2.270(3)	2.220(2)	1.808(8)	179.0(1)	114.4(3)	106.6(4)
P8			1.803(8)		113.4(3)	106.4(4)
			1.824(9)		113.5(3)	101.5(4)
			av: 1.812		av: 113.8	av: 104.8
$(PPh_3)AuCl$[a]	2.279(3)	2.235(3)	1.803(13)	179.63(8)	114.8(5)	103.3(4)
			1.866(12)		113.3(5)	105.8(4)
			1.792(13)		112.5(5)	106.2(5)
			av: 1.820		av: 113.5	av: 105.1

a - Ref. 233.

The cone formed by phosphorus and its three nearest carbon atoms of the gold complex is opened wider in **P8** than in the free acid [**P8**: $\angle$(C-P-C)$_{av}$=104.8°; diphenylphosphinoacetic acid: $\angle$(C-P-C)$_{av}$=100.9°]. As a result, the P-C bond lengths of **P8** are shorter [**P8**: P-C$_{av}$=1.812Å; diphenylphosphinoacetic acid: P-C$_{av}$=1.836Å]. In the case of **P8** the lone pair of electrons are less sterically demanding because they are involved in charge donation to the metal atom. This effect was also noted earlier in the structure of the phosphine oxide derivative, diphenylphosphinylacetic acid.

As with both diphenylphosphinoacetic acid and its phosphine oxide derivative, the P-C bond lengths in **P8** involving the sp^2 hybridised carbon atoms in the phenyl rings are slightly shorter than the P-C distance involving the sp^3 hybridised carbon [sp^2, P-C$_{av}$=1.806Å; sp^3, P-C=1.824(9)Å]. In comparison to the uncoordinated acid, the methylene carbon C(13) is involved in a slightly shorter bond to phosphorus [1.824(9)Å vs 1.855(5)Å] and a slightly longer bond to the carboxyl carbon C(14) [1.510Å vs 1.489(6)Å]. The angle P(1)-C(13)-C(14) of 112.6(6)° is marginally less acute than that of 110.2(4)° for the free acid.

The remaining bond lengths and angles of the two phenyl rings C(1)-C(6) [C-C$_{av}$=1.37Å]and C(7)-C(12) [C-C$_{av}$=1.38Å] are very similar to those found in diphenylphosphinoacetic acid.

4.3.2.7. Crystal structure of *trans*-bis(diphenylphosphinoacetic acid)palladium(II) chloride.1/3EtOH.1/3H_2O, **P4'**.1/3EtOH.1/3H_2O

As mentioned earlier, recrystallisation of the yellow-green powder **P4** isolated from the reaction of two equivalents of diphenylphosphinoacetic acid with one equivalent of bis(benzonitrile)palladium(II) chloride produced yellow crystals **P4'** which gave a significantly different microanalysis and IR spectrum to the non-purified product. These results are presented in Table 32

Table 32. Comparison of the microanalysis and IR data of **P4** and **P4'**.

		microanalysis[a]		IR (cm^{-1})[c]			
		%C	%H	ν(O-C-O)		low frequency	
				asym	sym	ν(M-Cl)	
$(HO_2CCH_2PPh_2)_2PdCl_2$	**P4**	50.1 (50.5)	3.88 (3.92)	1732, 1707	1350	318	297, 262
$C_{86}H_{86}Cl_6O_{14}P_6Pd_3$[b]	**P4'**	50.1 (50.6)	4.57 (4.20)	1705, 1694	1302	370	

a - Calculated values for the quoted formulae are given in parentheses. b - Empirical formula based on one molecule of water and one molecule of ethanol per three molecules of the palladium complex as determined crystallographically. c - Further data given in Chapter 7.

From the IR data presented in Table 32 it can be seen that on recrystallisation of **P4** from ethanol, the vibrations associated with the carboxylic acid group are altered. In the purified complex **P4'**, the asymmetric and symmetric stretching frequencies of the carboxyl functions are much closer to those of the free acid and the other *P*-coordinated diphenylphosphinoacetic acid-metal complexes reported in Table 28.

The frequency of the ν(Pd-Cl) vibration also changes significantly. For **P4'**, the Pd-Cl stretch at 370cm^{-1} is close to that of *trans*-$[(PPh_3)_2PdCl_2]$[234] where ν(Pd-Cl)=360cm^{-1} and contrasts with ν(Pd-Cl)=318cm^{-1} for **P4**. The spectrum of **P4** displays two further bands in the low frequency region at 297 and 262cm^{-1}, possibly due to Pd-Cl bending modes. An increase in the number of M-Cl vibrational modes for a *cis* arrangement of the ligands compared to a *trans* arrangement has previously been observed in several bis(phosphine)platinum(II) chloride complexes [*cis*- and *trans*-$(R_3P)_2PtCl_2$: R=Me and Et;[235] R=Ph[236]] which might suggest that the diphenylphosphinoacetic acid ligands are *cis* in the initial complex **P4**.

The *trans* arrangement of the phosphorus ligands in **P4'** has been confirmed crystallographically. The asymmetric unit was found to contain three half molecules of the palladium species along with one molecule of water and one molecule of ethanol both at 50% site-occupancy giving on average one water and one ethanol molecule for every three palladium atoms. All three palladium atoms are located at inversion centres intrinsic in the space group symmetry, yielding planar geometry about the metal atoms. Figure 25 shows a portion of the structure of **P4'**.1/3EtOH.1/3H_2O with the asymmetric unit emphasised using labelled atoms which are not primed.

Three independent [$(HO_2CCH_2PPh_2)_2PdCl_2$] moieties are present in the structure. Two of these are similar to each other and involve molecules containing Pd(1) and Pd(2) which form 1-dimensional polymers along the a axis *via* twofold hydrogen bonding through the carboxylic acid groups to lattice neighbours (Fig. 26). These polymers are stacked in the b direction and alternate between Pd(1) and Pd(2) containing molecules at half unit cell intervals.

The complex containing Pd(3) is somewhat different and is not involved in hydrogen bonded polymeric arrays. Rather, discrete hydrogen bonded entities are generated by the interaction of the carboxyl oxygen O(5) with O(8) of the solvent water molecule and subsequent interaction of this oxygen atom with O(7) of the solvent ethanol molecule (Fig. 27). These interactions are complicated by the half occupancy of the solvent molecules.

Unfortunately, protons associated with the carboxylic acid groups, the hydroxy group of the ethanol molecule and the lattice water could not be located. The presence of hydrogen bonding was therefore indicated by short O···O distances.

Selected bond angles and bond lengths for **P4'**.1/3EtOH.1/3H_2O are given in Table 33. Relevant intermolecular distances are given in Table 34

The square planar palladium atoms Pd(1)-Pd(3) all have slightly different coordination environments. The Pd-P and Pd-Cl bond lengths for Pd(1) and Pd(3) are very similar with the Pd-P distances [Pd(1)-P(1): 2.326(1)Å; Pd(3)-P(3): 2.337(2)Å] which compare with those found for *trans*-[$(HO_2CCH_2PPh_2)_2PdBr_2$] [Pd-P: 2.322(2)Å],[222] and are longer than the Pd-Cl

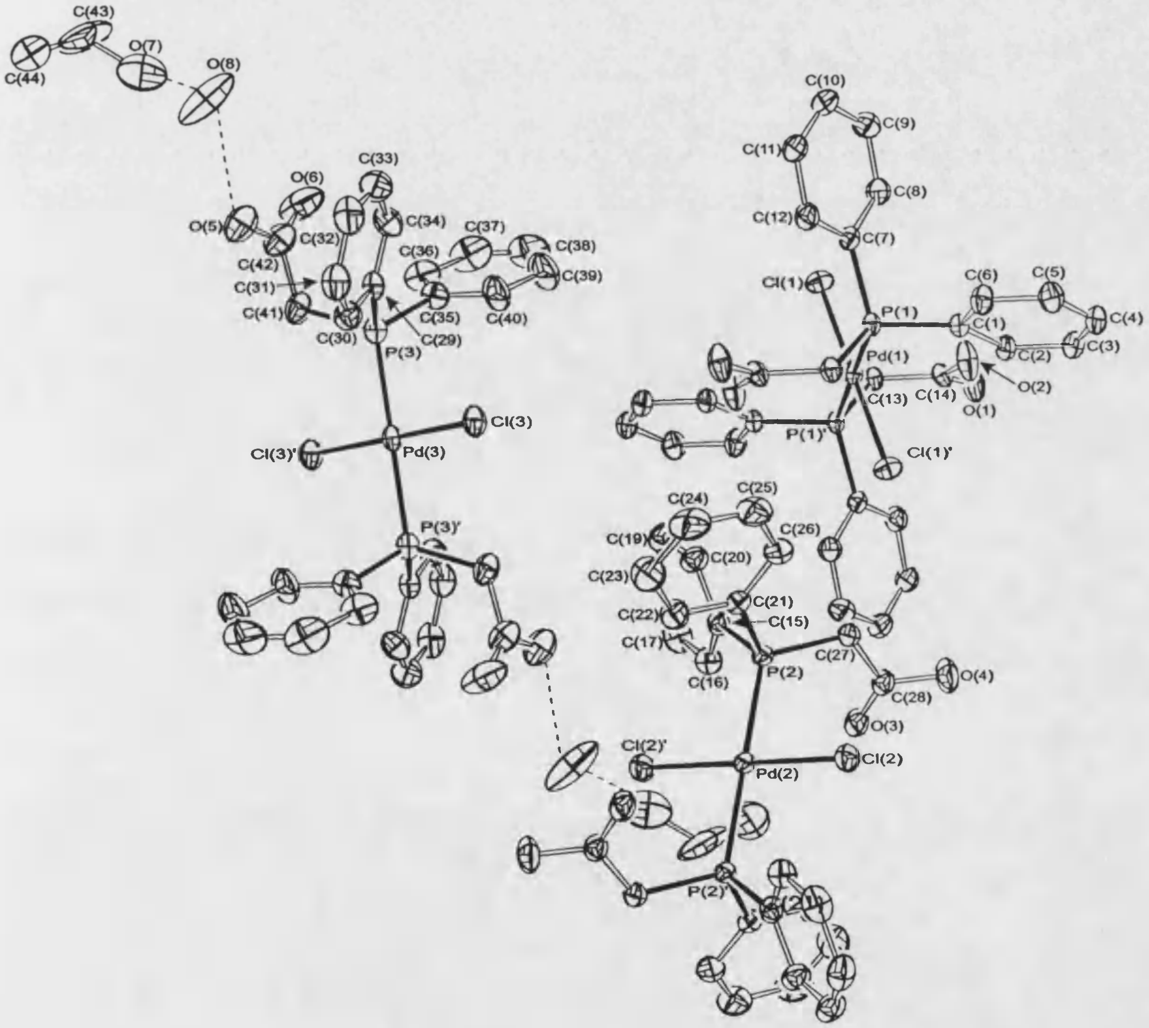


Figure 25. ORTEX plot of a section of the crystal structure of bis(diphenylphosphinoacetic acid)palladium(II) chloride.1/3EtOH.1/3H_2O, **P4'**.1/3EtOH.1/3H_2O. The asymmetric unit is highlighted by labelled atoms which are not primed.

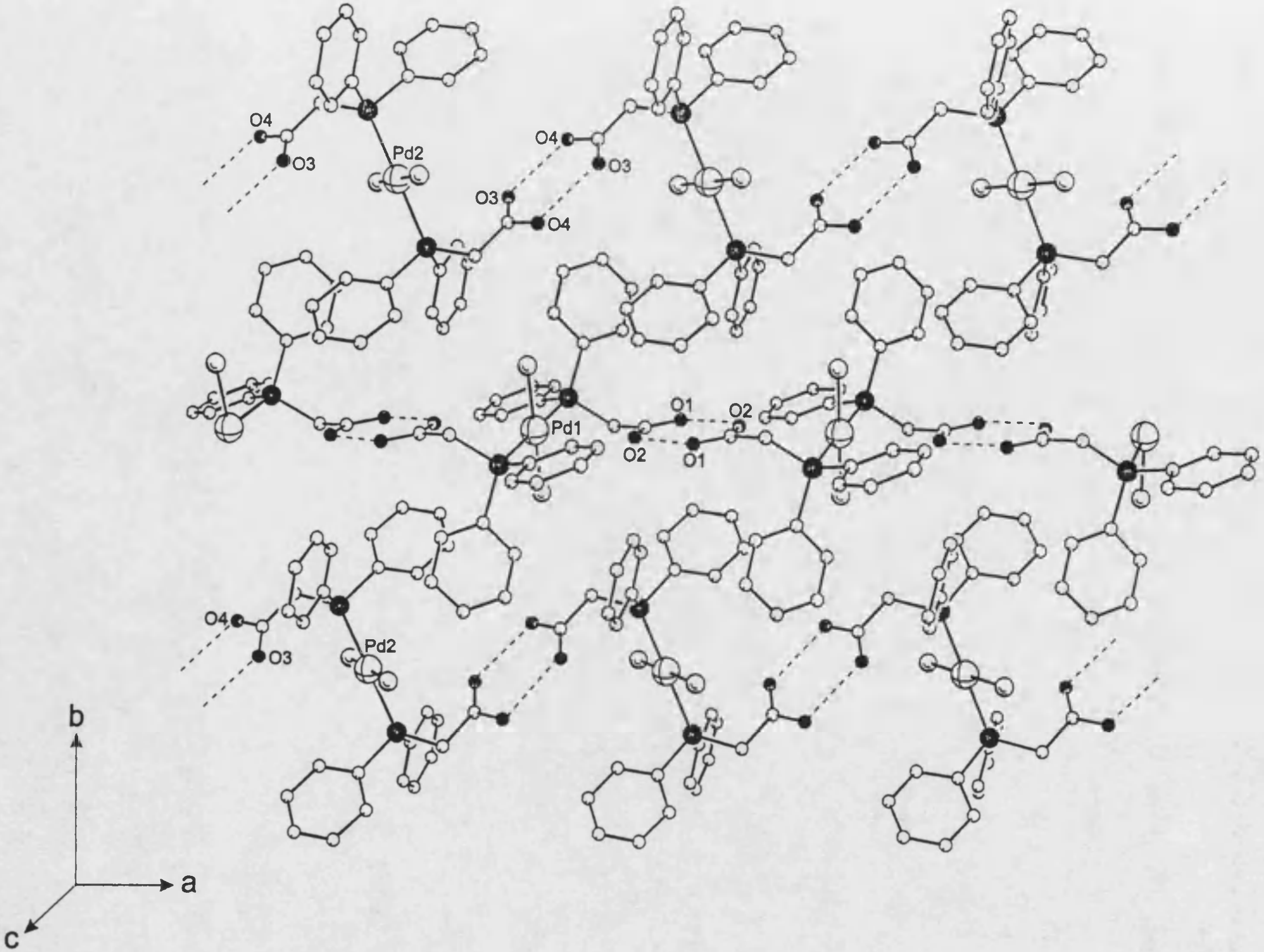


Figure 26. View down the c axis of the crystal structure of **P4'**.1/3EtOH.1/3H_2O displaying the 1-dimensional polymeric chains involving molecules containing palladium atoms Pd(1) and Pd(2)

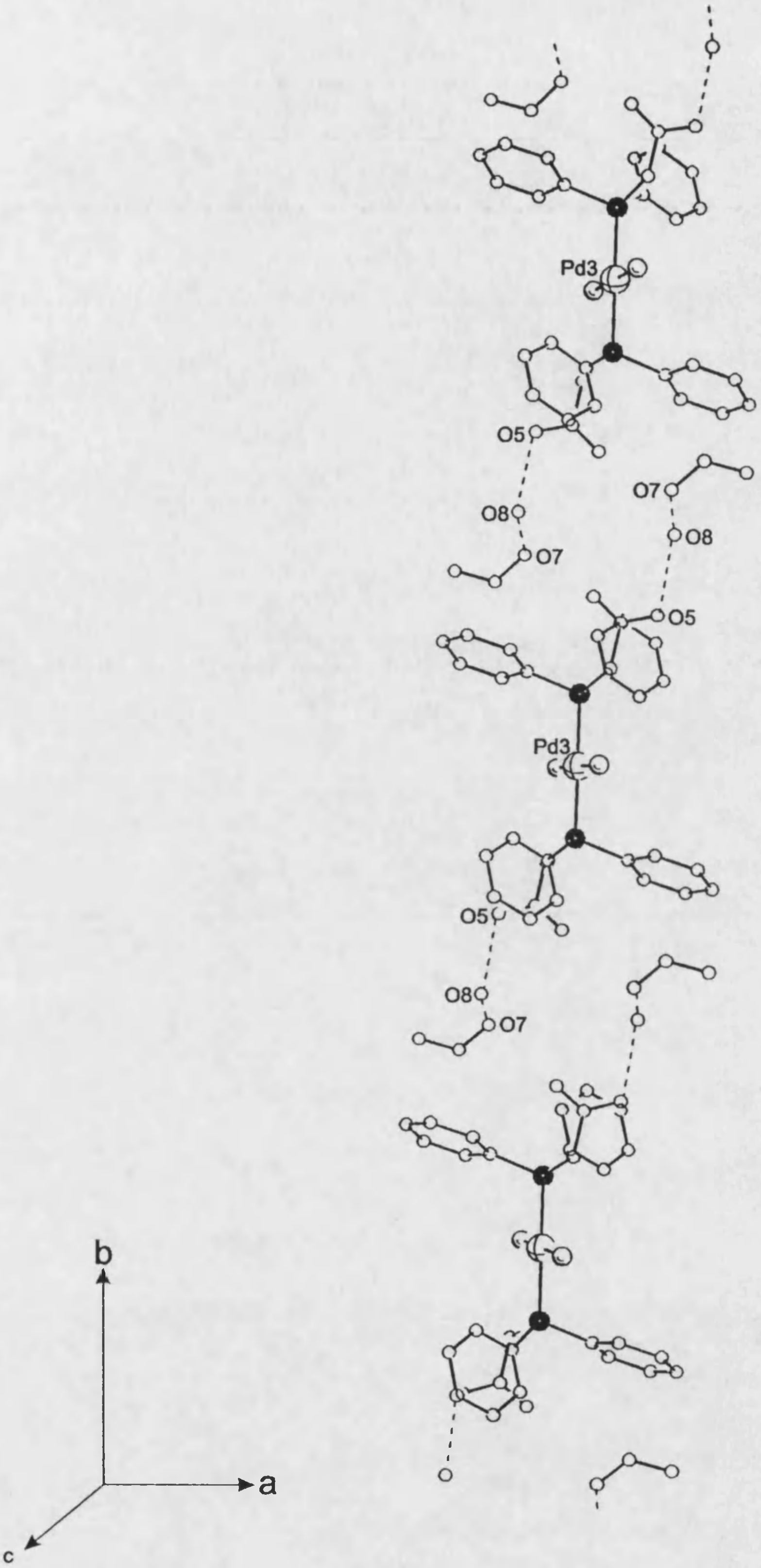


Figure 27. View down the c axis of **P4'**.1/3EtOH.1/3H_2O displaying the discrete intermolecular hydrogen bonded entities involving P(3)-containing species and solvent molecules. Due to disorder, only 50% occupancy of the positions of the solvent molecules is observed.

distances. In contrast, shorter Pd-P bond lengths are observed for the complex **P10**, the palladium(II) chloride derivative of bis(cyclopentadienyl)bis(diphenylphosphinoacetato)-titanium(IV) where the phosphorus atoms are in *cis* positions around the metal.

For Pd(2), the Pd-P and Pd-Cl bond lengths are similar [Pd(2)-P(2): 2.309(1)Å; Pd(2)-Cl(2): 2.303(1)Å].

Table 33. Selected bond lengths (Å) and angles (°) for **P4'**.1/3EtOH.1/3H$_2$O.

Pd(1)-Cl(1)	2.305(1)	Cl(1)-Pd(1)-P(1)	93.24(4)
Pd(1)-P(1)	2.326(1)	Cl(1)-Pd(1)-P(1)#1	86.76(4)
P(1)-C(7)	1.816(5)	C(7)-P(1)-C(1)	101.8(2)
P(1)-C(1)	1.821(4)	C(7)-P(1)-C(13)	104.5(2)
P(1)-C(13)	1.839(5)	C(1)-P(1)-C(13)	103.8(2)
O(1)-C(14)	1.255(6)	O(1)-C(14)-O(2)	122.4(4)
O(2)-C(14)	1.262(6)		
Pd(2)-Cl(2)	2.303(1)	Cl(2)-Pd(2)-P(2)	86.45(5)
Pd(2)-P(2)	2.309(1)	Cl(2)-Pd(2)-P(2)#2	93.55(5)
P(2)-C(15)	1.807(5)	C(15)-P(2)-C(21)	104.6(2)
P(2)-C(21)	1.814(5)	C(15)-P(2)-C(27)	103.8(2)
P(2)-C(27)	1.830(5)	C(21)-P(2)-C(27)	105.3(2)
O(3)-C(28)	1.215(6)	O(3)-C(28)-O(4)	122.4(5)
O(4)-C(28)	1.314(6)		
Pd(3)-Cl(3)	2.295(1)	Cl(3)-Pd(3)-P(3)#3	90.90(5)
Pd(3)-P(3)	2.337(2)	Cl(3)-Pd(3)-P(3)	89.10(5)
P(3)-C(35)	1.808(6)	C(35)-P(3)-C(29)	106.9(3)
P(3)-C(29)	1.807(5)	C(35)-P(3)-C(41)	107.0(3)
P(3)-C(41)	1.847(6)	C(29)-P(3)-C(41)	101.8(3)
O(5)-C(42)	1.264(9)	O(6)-C(42)-O(5)	124.4(7)
O(6)-C(42)	1.212(9)		

All P-Pd-P and Cl-Pd-Cl angles are exactly 180.0° as dictated by symmetry.

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z
#2 -x+1,-y,-z
#3 -x+1,-y+1,-z+1

The species containing Pd(3) has P-Pd-Cl angles close to ideal square planar value of 90° [P(3)-Pd(3)-Cl(3): 89.10(5)°]. The corresponding angles associated with Pd(1) and Pd(2) deviate slightly from the ideal geometry [P(1)-Pd(1)-Cl(1): 86.76(4); P(2)-Pd(2)-Cl(2):

86.45(5)°]. As stated above, all three palladium atoms are situated at inversion centres therefore, all P-Pd-P and Cl-Pd-Cl angles are exactly 180°, and each metal centre is co-planar with the two phosphorus and two chlorine atoms surrounding it.

None of the oxygen atoms O(1)-O(8) coordinate to the metal centres Pd(1)-Pd(3), the shortest Pd···O contact being 3.26Å between Pd(1) and O(2). A shorter Pd···O separation of 3.171(6)Å was quoted as evidence of a weak interaction in the structure of *trans*-$[(HO_2CCH_2PPh_2)_2PdBr_2]$.[222]

Table 34. Distances (Å) pertaining to intermolecular hydrogen bonds for **P4'**.1/3EtOH.1/3H_2O.

O(5) - O(8)	2.673 (16)	O(1) - O(2)#4	2.461 (6)
O(7) - O(8)	2.914 (22)	O(3) - O(4)#5	2.686 (5)
O(6) - O(8)	3.389 (15)		

Symmetry transformations used to generate equivalent atoms: #4 1-x,1-y,z #5 -x,-y,-z

Comparison of the bond lengths of the COOH:::HOOC moieties indicates that the intermolecular hydrogen bonding occurring between units containing Pd(2) is very similar to that found in the dibromo complex[222] where a supramolecular structure involving parallel chains is also observed. There is a large difference between the two C-O distances of the carboxyl functions in both structures, [**P4'**.1/3EtOH.1/3H_2O; C(28)-O(3):1.215(6)Å, C(28)-O(4): 1.314(6)Å; *trans*-$(HO_2CCH_2PPh_2)_2PdBr_2$; C-O: 1.216(9)Å, C-O': 1.311(9)Å] and the O···O contacts between Pd(2) containing molecules [O(3)···O(4): 2.686(5)Å] and in the dibromo compound [O···O: 2.710(7)Å] are slightly longer than that found in the free acid [O···O': 2.660(7)Å].[208]

The second 1-dimensional polymeric arrangement observed in the structure involves molecules containing Pd(1) and exhibits a closer O···O' interaction of 2.461(6)Å. The bond lengths of the carboxyl functions taking part in this shorter interaction do not differ as widely as those described above [C(14)-O(1): 1.255(6), C(14)-O(2): 1.262(6)Å].

The alternative hydrogen bonding arrangement in the structure involves molecules containing Pd(3) and is not polymeric. The two separate O···O' contacts between the O(5) of the Pd complex and O(8) of the solvated water and between O(8) and the oxygen atom of the ethanol molecule O(7) are 2.673(16)Å and 2.914(22)Å respectively. The carboxyl oxygen atom O(6) does not take part in these intermolecular associations as displayed by the large O···O' separation of 3.389(15)Å between O(6) and O(8). This is reflected in the C-O bond distances of the carbonyl function with C(42)-O(5) being slightly longer than C(42)-O(6) [C(42)-O(5): 1.254(9)Å, C(42)-O(6): 1.212(9)Å].

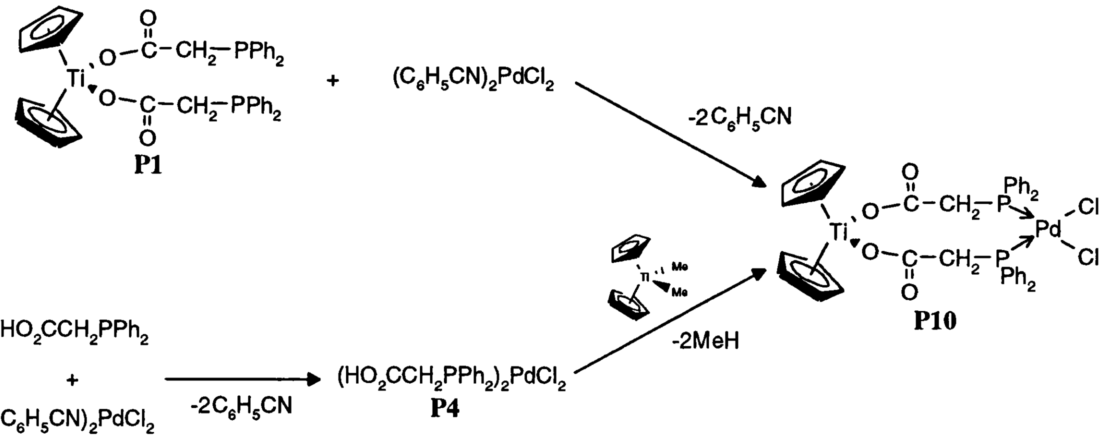
The O-C-O angles in the two units containing Pd(1) and Pd(2) involved in polymeric intermolecular association are identical [O(1)-C(14)-O(2): 122.4(4)°, O(3)-C(28)-O(4): 122.4(5)°] and compare with a slightly wider angle found in the species containing Pd(3) [O(5)-C(42)-O(6): 124.4(7)°] reflecting the difference in the two types of hydrogen bonding present.

The remaining bond lengths and bond angles of the diphenylphosphinoacetic acid moieties are similar to those found in the gold(I) complex **P8**.

4.3.3. Preparation and characterisation of heterometallic complexes

The Ti-Pd heterobimetallic complex **P10** was prepared *via* both of the synthetic strategies outlined in Schemes 15 and 16. Displacement of benzonitrile by the titanium containing phosphine ligand **P1** or treatment of the *P*-coordinated diphenylphosphinoacetic acid-palladium complex **P4** with bis(cyclopentadienyl)bis(methyl)titanium(IV) both yielded the heterobimetallic complex (Scheme 17).

The products were isolated in both instances as red crystalline materials, the analyses of which suggested the presence of solvent molecules within the crystal lattice (Table 35). This was confirmed for the first synthetic route by a single crystal X-ray structure analysis.



Scheme 17

Crystals of **P10**, despite being solvated, were not very soluble in common organic solvents which hindered the characterisation of the compound by NMR techniques. Accordingly, the ^1H and $^{31}P\{^1H\}$ NMR data reported in Chapter 7 do not show the correct number of peaks predicted for the structure **P10** shown in Scheme 17. However, the spectrum recorded in deuterochloroform indicates one main species in solution, the resonances and peak integrals of which are consistent with two equivalent cyclopentadienyl rings and two equivalent diphenylphosphinoacetate ligands as expected for **P10**. These chemical shift values are reported in Table 36.

The remaining resonances in the chloroform spectrum are probably due to impurities which are present in very small quantities in the solid state, but have greater solubility than **P10** and therefore appear more significant in the solution NMR. An alternative possibility is the decomposition of **P10** due to moisture in the NMR solvent. This latter process is probably responsible for the splitting of the cyclopentadienyl signal in the spectrum of **P10** carried out in deuterated acetonitrile.

For the preparation of further heterometallic compounds, reactions of the titanocene carboxylate **P1** with transition metal species did not proceed as cleanly as the alternative route involving the *P*-coordinated diphenylphosphinoacetic acid-metal complexes. In particular, the gold(I) complex **P14** could not be prepared *via* the reaction of **P1** with chloro(tetrahydrothiophene)gold(I). In contrast, **P14** was easily isolated by treating (diphenylphosphinoacetic acid)gold(I) chloride with bis(cyclopentadienyl)bis(methyl)-titanium(IV). The stable golden-coloured product was recovered in 81% yield, and could be recrystallised from chlorinated solvents to give large rectangular solvated crystals. Unfortunately, these crystals rapidly lose their solvent of crystallisation and have so far not been successfully mounted on a diffractometer for a structure determination.

The IR spectrum for **P14** (Table38) shows a ν(Au-Cl) vibration a 335cm^{-1} which is exactly the same as that for the diphenylphosphinoacetic acid complex **P8** suggesting a similar linear arrangement of the gold atom.

The copper(I) analogue of **P14** could be prepared either *via* the reaction of **P1** with copper(I) chloride or by treating (diphenylphosphinoacetic acid)copper(I) chloride **P6** with bis(cyclopentadienyl)bis(methyl)titanium(IV). The products of both reactions were spectroscopically very similar however, the analysis and the intergrals of signals in the proton NMR spectrum suggest the latter method proceeded more cleanly.

Table 35. Microanalysis data for complexes **P9-P14**. Calculated values for the quoted formulae are given in parentheses.

		%C	%H
$[Cp_2Ti(O_2CCH_2PPh_2)_2\}_2Ni][BF_4]_2$	**P9**	57.0 (58.5)	4.59 (4.39)
$Cp_2Ti(O_2CCH_2PPh_2)_2PdCl_2$	**P10**	50.7 (54.2)	3.93 (4.07)
$Cp_2Ti(O_2CCH_2PPh_2)_2PtCl_2$	**P11**	48.0 (49.1)	3.60 (3.68)
$Cp_2Ti(O_2CCH_2PPh_2)_2.2CuCl$	**P12**	52.4 (52.9)	4.11 (3.97)
$Cp_2Ti(O_2CCH_2PPh_2)_2.AgCl$	**P13**	55.3 (56.5)	4.49 (4.24)
$Cp_2Ti(O_2CCH_2PPh_2)_2.2AuCl$	**P14**	40.1 (40.4)	2.92 (3.03)

Preparations *via* the two Schemes 15 and 16 involving nickel(II) species resulted in products which gave identical ^1H and $^{31}P\{^1H\}$ NMR spectra. The signals in the proton spectrum were significantly broadened which made the peak integrals difficult to calculate although they do give an approximate agreement with the predicted structure.

The product of the reaction of the free acid-nickel complex **P3** with bis(cyclopentadienyl)-bis(methyl)titanium(IV) gave an analysis which was slightly low in carbon content and slightly high in hydrogen content for a compound of formula $[\{(C_5H_5)_2Ti(O_2CCH_2PPh_2)_2\}_2Ni][BF_4]_2$ [found (calc.); C: 57.0 (58.5), H: 4.59 (4.39)%]. However, the observance of a broad signal in the ^1H NMR at δ=6.26ppm could indicate the presence of water in which case, with two moles of water per mole of **P9** the theoretical carbon and hydrogen contents can be recalculated at C: 57.1% and H: 4.54%.

The magnetic moment of this hydrated complex **P9**.$2H_2O$ was determined using the Gouy method and found to be 2.35B.M.. This value is below 2.83B.M. predicted by the spin-only formula for two unpaired electrons and suggests the complex is contaminated with some diamagnetic species. No detailed structural predictions can be made from the magnetic properties of **P9** however, the complex is paramagnetic and hence does not contain square planar nickel(II).

The metal is likely to be tetrahedral with four phosphorus atoms in the immediate coordination sphere and water molecules not bound to the metal, but involved in hydrogen bonding to the carboxyl functions. Alternatively, an octahedral environment could be proposed with four phosphorus atoms from the diphenylphosphino moieties and two oxygen atoms from water molecules attached to the metal with the waters in either a *cis* or *trans* arrangement.

The tetrafluoroborate anions are probably not bonded to the metal centre. The IR spectrum displays bands at 1071 and 745cm^{-1} which are tentatively assigned to these groups and are similar those allocated to the uncoordinated species by Nakamoto.[237] In cases where the tetrafluoroborate moiety coordinates to metal centres *via* a weak M-F-BF_3 interaction, splitting of the band at around 1070cm^{-1} has been observed.[238] However, any conclusions derived from the assignment of peaks must be treated with caution due to the large number of bands in this region of the IR spectrum of **P9**.

The $^{31}P\{^1H\}$ NMR chemical shifts for complexes **P9**, **P10** and **P12-P14** show a similar trend to the diphenylphosphinoacetic acid complexes **P2-P8**. Coordination of the phosphorus atom to a metal species produces a downfield shift which varies in magnitude depending on the metal.

Table 36. Selected ^1H and $^{31}P\{^1H\}$ NMR data for complexes **P9**, **P10** and **P12-P14**. Data for complexes **P1** and **O3** are given for comparison.[a]

		^1H δ(ppm)			^{31}P δ(ppm)
		-CH_2-	C_5H_5	*phenyl*	
$Cp_2Ti(O_2CCH_2PPh_2)_2$	**P1**	2.96	6.01	7.10, 7.29	-17.6
$[Cp_2Ti(O_2CCH_2PPh_2)_2\}_2Ni][BF_4]_2$[b]	**P9**	3.08	6.37	7.27	-15.1
$Cp_2Ti(O_2CCH_2PPh_2)_2PdCl_2$[c]	**P10**	3.53	6.30	7.22, 7.59	13.8
$Cp_2Ti(O_2CCH_2PPh_2)_2.2CuCl$	**P12**	3.48	6.23	7.40, 7.68	-12.4
$Cp_2Ti(O_2CCH_2PPh_2)_2.AgCl$	**P13**	3.51	6.10	7.37, 7.66	-1.8[d]
$Cp_2Ti(O_2CCH_2PPh_2)_2.2AuCl$	**P14**	4.11	6.24	7.49, 7.84	24.9
$Cp_2Ti(O_2CCH_2P(O)Ph_2)_2$	**O3**	3.35	6.34	7.53, 7.89	28.7

a - Multiplicites, coupling constants and proton integrals are given in Chapter 7. b - Additional broad peak at δ=6. 26ppm. c - ^1H and $^{31}P\{^1H\}$ spectra contain a number of additional signals. d - $^1J(^{107}Ag-^{31}P)=439.3Hz$, $^1J(^{109}Ag-^{31}P)=506.4Hz$.

Table 37. $^{13}C\{^1H\}$ Chemical shifts for complexes **P12-P14**. Complex **P1** is included for comparison.

		^{13}C δ(ppm)			
		-CH_2-	*C_5H_5*	*-CO_2-*	*phenyl*
$Cp_2Ti(O_2CCH_2PPh_2)_2$	**P1**	37.6	118.2	175.4	128.3, 128.6, 132.6, 138.4
$Cp_2Ti[(O_2CCH_2PPh_2)CuCl]_2$	**P12**	37.3	118.9	172.5	128.9, 130.3, 132.3, 132.7
$Cp_2Ti(O_2CCH_2PPh_2)_2.AgCl$	**P13**	37.9	118.9	171.7	129.0, 130.5, 131.9, 132.8
$Cp_2Ti[(O_2CCH_2PPh_2)AuCl]_2$	**P14**	37.8	119.0	170.6	129.1, 129.9, 131.9, 133.3

Additional information regarding multiplicities and coupling constants is given in Chapter 7.

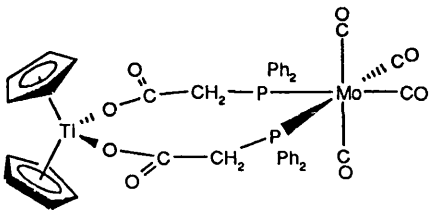
Due to the small quantity produced and its' insolubility, the platinum(II) complex **P11** was not characterised satisfactorily. The IR spectrum shows characteristic bands due to the cyclopentadienyl and carboxylate ligands although the carboxylate stretches are split into several signals which could suggest that the material analysed is not homogeneous (Table 38). The low frequency region of the vibrational spectrum contains very weak bands possibly due to Pt-Cl stretches (v= 375, 322, 310cm^{-1}). Soluble products from reactions *via* either of the two Schemes 15 and 16 gave ^1H and ^{31}P NMR data that indicated a large number of species in solution.

Table 38. Selected IR data for complexes **P9-P14**. Data for complex **P1** are included for comparison.

		cyclopentadienyl ring (cm^{-1})	v(O-C-O) (cm^{-1})	other (cm^{-1})
$Cp_2Ti(O_2CCH_2PPh_2)_2$	P1	3100, 3056, 1464, 1019, 824	1618, 1325	
$[Cp_2Ti(O_2CCH_2PPh_2)_2\}_2Ni][BF_4]_2$	P9	3117, 3056, 1437, 1026, 828	1553, 1396	1071, 745 v(BF_4^-)
$Cp_2Ti(O_2CCH_2PPh_2)_2PdCl_2$	P10	3087, 1435, 1019, 818	1651, 1312, 1275	339, 307 v(Pd-Cl)
$Cp_2Ti(O_2CCH_2PPh_2)_2PtCl_2$	P11	3088, 3052, 1439, 1028, 822	1696, 1647, 1593, 1312	375, 322, 310 v(Pt-Cl)
$Cp_2Ti(O_2CCH_2PPh_2)_2.2CuCl$	P12	3050, 1435, 1017, 828	1634, 1310, 1283	
$Cp_2Ti(O_2CCH_2PPh_2)_2.AgCl$	P13	3050, 1435, 1017, 828	1642, 1273	
$Cp_2Ti(O_2CCH_2PPh_2)_2.2AuCl$	P14	3058, 1439, 1017, 824	1634, 1325, 1292	335 v(Au-Cl)

Additional signals and relative peak intensities are given in Chapter 7.

Attempts to isolate a Ti-Mo heterobimetallic complex of a structure similar to **55** were not successful *via* either of the two routes shown in Schemes 15 and 16. The NMR data for the products from either route indicate a large number of species in solution. The IR data suggest that in both cases the cis-Mo(CO)$_4$ arrangement remains intact.



55

In a similar manner to the reaction involving the molybdenum complex **P2**, treating the copper(I) complex **P7** with bis(cyclopentadienyl)bis(methyl)titanium(IV) resulted in NMR data which were confusing to interpret due to the number of signals.

As an alternative to the synthetic routes proposed in Schemes 15 and 16, the silver(I) complex **P13** was prepared directly from the reaction of silver(I) diphenylphosphinoacetate with bis(cyclopentadienyl)titanium dichloride (Equation 59). The product of the reaction is predicted to be a 1:1 coordination complex of silver(I) chloride and bis(cyclopentadienyl)bis-(diphenylphosphinoacetato)titanium(IV) **P1**. The analytical data is in approximate agreement with this hypothesis.

$$Cp_2TiCl_2 + 2AgO_2CCH_2PPh_2 \xrightarrow{CH_2Cl_2} Cp_2Ti(O_2CCH_2PPh_2)_2.AgCl + AgCl \quad \text{Eq. 59}$$

P13, 77%

The ^1H NMR of the filtered reaction mixture is similar to that of **P1**. However the $^{31}P\{^1H\}$ spectrum displays splitting of the ^{31}P signal due to ^{31}P-^{107}Ag and ^{31}P-^{109}Ag coupling (Fig. 28) [$^1J(^{107}Ag$-$^{31}P)$=439.3Hz, $^1J(^{109}Ag$-$^{31}P)$=506.4Hz]. These coupling constants are consistent with other bis(phosphine) silver(I) complexes. Muetterties *et al.* studied a range of tri-p-tolylphosphine silver(I) complexes and found that the $^1J(^{107}Ag$-$^{31}P)$ coupling constants for a range of compounds [{(p-$CH_3C_6H_4)_3P\}_2AgX$] varies between 278Hz for X=CN and 503Hz for X=ClO$_4$ [X=Cl, $^1J(^{107}Ag$-$^{31}P)$=378Hz].[239] They also discovered that the value of $^1J(^{107}Ag$-$^{31}P)$ decreases with the number of phosphines around silver and is also affected by the substituents on the phosphorus. For example, the tris(phosphine) complex [{(p-$CH_3C_6H_4)_3P\}_3AgCl$] has a

^{31}P-^{107}Ag coupling constant of 280Hz, while the bis(triethyl phosphite) derivative of silver(I) chloride [$\{(C_2H_5O)_3P\}_2AgCl$] has an analogous coupling constant of 550Hz.

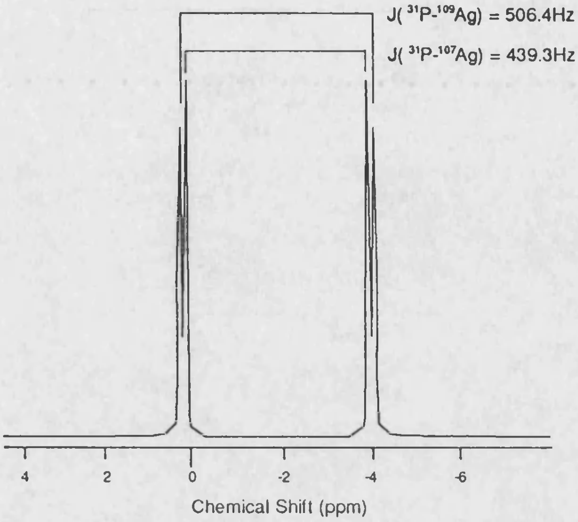


Figure 28. Redrawing of the $^{31}P\{^1H\}$ NMR spectrum of **P13**.

Complexes **P12-P14** were further characterised by FAB mass spectrometry, the spectra of which are summarised in Table 39. An analysis of the Ti-Pd complex **P10** was also undertaken, but the results proved to be very difficult to interpret, with a large number of signals generated.

The complexes studied by mass spectrometry show similar fragmentation pathways to other bis(cyclopentadienyl)titanium(IV) carboxylates, with the addition of further fragments from the second transition metal moiety. The copper and silver complexes **P12** and **P13** display similar behaviour with break up of the complex occurring in the titanocene carboxylate segment through loss of cyclopentadienyl and carboxylate ligands and at the transition metal halide through loss of chloride and metal chloride species.

The gold complex **P14** readily loses the Cp_2Ti fragment to give *P*-coordinated acid species indicating the stability of this combination. The spectrum is very similar to that of **P8**.

Table 39. Selected FAB mass spectrometry data for complexes **P12-P14**.

	$Cp_2Ti(O_2CCH_2PPh_2)_2Cu_2Cl_2$, **P12**		
m/z	FAB+	m/z	FAB-
827 (15)	$[Cp_2Ti(O_2CCH_2PPh_2)_2Cu_2Cl]^+$	864 (4)	$[Cp_2Ti(O_2CCH_2PPh_2)_2Cu_2Cl_2]^{-\cdot}$
762 (20)	$[Cp_2Ti(O_2CCH_2PPh_2)_2CuCl]^{+\cdot}$	762 (25)	$[Cp_2Ti(O_2CCH_2PPh_2)_2CuCl]^{-\cdot}$
727 (95)	$[Cp_2Ti(O_2CCH_2PPh_2)_2Cu]^+$		
697 (15)	$[CpTi(O_2CCH_2PPh_2)_2CuCl]^{+\cdot}$		
662 (70)	$[CpTi(O_2CCH_2PPh_2)_2Cu]^+$		
519 (40)	$[Cp_2Ti(O_2CCH_2PPh_2)CuCl]^{+\cdot}$		
484 (5)	$[Cp_2Ti(O_2CCH_2PPh_2)Cu]^+$		
454 (20)	$[CpTi(O_2CCH_2PPh_2)CuCl]^{+\cdot}$		
	$Cp_2Ti(O_2CCH_2PPh_2)_2AgCl$, **P13**		
m/z	FAB+	m/z	FAB-
915 (2)	$[Cp_2Ti(O_2CCH_2PPh_2)_2Ag_2Cl]^+$		
884 (<1)	$[CpTi(O_2CCH_2PPh_2)_2Ag_2Cl_2]^{+\cdot}$		
850 (1)	$[CpTi(O_2CCH_2PPh_2)_2Ag_2Cl]^+$		
808 (2)	$[Cp_2Ti(O_2CCH_2PPh_2)_2AgCl]^{+\cdot}$		
773 (52)	$[Cp_2Ti(O_2CCH_2PPh_2)_2Ag]^+$		
709 (40)	$[CpTi(O_2CCH_2PPh_2)_2Ag]^+$		
	$Cp_2Ti(O_2CCH_2PPh_2)_2Au_2Cl_2$, **P14**		
m/z	FAB+	m/z	FAB-
1129 (3)	$[H\{Cp_2Ti(O_2CCH_2PPh_2)_2Au_2Cl_2\}]^+$	1128 (3)	$[Cp_2Ti(O_2CCH_2PPh_2)_2Au_2Cl_2]^{-\cdot}$
1093 (13)	$[Cp_2Ti(O_2CCH_2PPh_2)_2Au_2Cl]^+$	951 (15)	$[H(O_2CCH_2PPh_2)_2Au_2Cl_2\}]^-$
1063 (3)	$[H\{CpTi(O_2CCH_2PPh_2)_2Au_2Cl\}]^+$	475 (46)	$[(O_2CCH_2PPh_2)AuCl\}]^-$
1028 (13)	$[CpTi(O_2CCH_2PPh_2)_2Au_2Cl]^+$	431 (100)	$[(CH_2PPh_2)AuCl\}]^-$
917 (14)	$[(HO_2CCH_2PPh_2)_2Au_2Cl]^+$		
441 (100)	$[(HO_2CCH_2PPh_2)Au]^+$		

4.3.4. Molecular structure of the 1:1 coordination complex of palladium(II) chloride and bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) P10

Crystals of the Ti-Pd heterobimetallic complex **P10** formed on allowing dichloromethane solutions to stand. An X-ray structure determination undertaken at -103°C revealed an asymmetric unit containing one Ti-Pd species shown in Figure 29 and three molecules of dichloromethane. Selected bond lengths of the bimetallic compound are given in Table 40.

The crystal structure of **P10**.$3CH_2Cl_2$ shows discrete molecular entities with Ti in a typical pseudo-tetrahedral bent metallocene environment. The bond lengths and angles around titanium are very similar to those of the cyanoacetate described earlier.

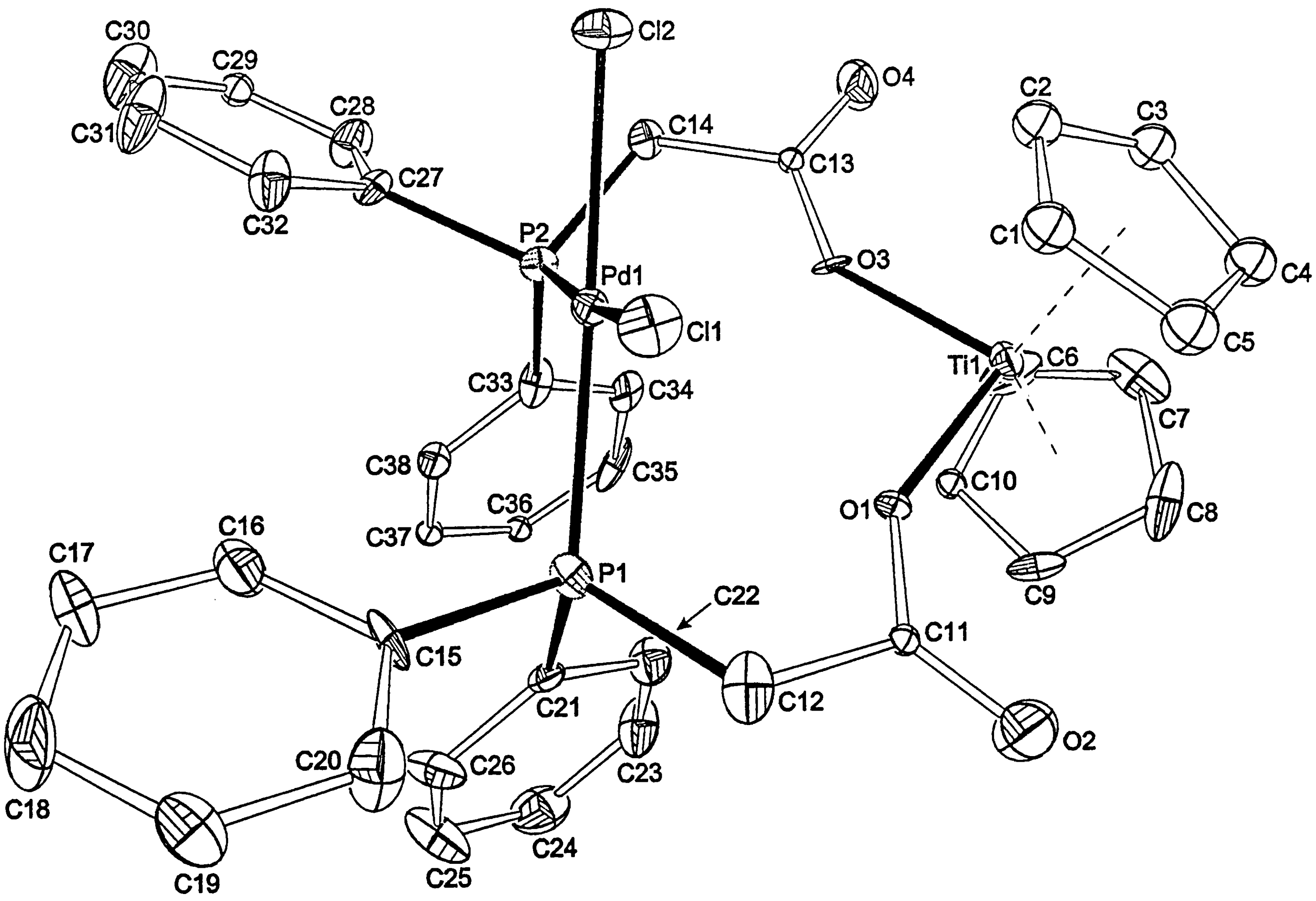


Figure 29. Molecular structure of the 1:1 coordination complex of palladium(II) chloride and bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) solvated with three moles of dichloromethane, P10.3CH_2Cl_2. Solvated molecules are omitted for clarity.

The monodentate carboxyl functions of the diphenylphosphinoacetate ligands differ from those in the structure of bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1**. In contrast to the earlier structure, there is very little difference between the two carboxylate ligands in the bond lengths and angles of the Ti-O_2C- moieties. This could possibly be due to the restrictions imposed by the 10-membered heterobimetallocycle.

Table 40. Selected bond lengths (Å) and angles (°) for **P10**.$3CH_2Cl_2$.

Ti(1)-O(3)	1.961(9)	Ti(1)-O(1)	1.969(8)
Ti(1)-Z(1)	2.05	Ti(1)-Z(2)	2.06
O(1)-C(11)	1.29(2)	O(2)-C(11)	1.20(2)
O(3)-C(13)	1.28(2)	O(4)-C(13)	1.22(2)
Pd(1)-P(1)	2.259(4)	Pd(1)-P(2)	2.276(4)
Pd(1)-Cl(2)	2.341(4)	Pd(1)-Cl(1)	2.347(4)
P(1)-C(15)	1.81(1)	P(1)-C(12)	1.83(1)
P(1)-C(21)	1.83(1)	P(2)-C(33)	1.79(2)
P(2)-C(14)	1.83(1)	P(2)-C(27)	1.85(1)
O(3)-Ti(1)-O(1)	89.4(4)	Z(1)-Ti(1)-Z(2)	131.6
C(11)-O(1)-Ti(1)	142.9(9)	C(13)-O(3)-Ti(1)	142.2(9)
O(1)-C(11)-O(2)	126(1)	O(3)-C(13)-O(4)	127(1)
P(1)-Pd(1)-P(2)	103.9(1)	P(1)-Pd(1)-Cl(2)	170.6(1)
P(2)-Pd(1)-Cl(2)	84.6(1)	P(1)-Pd(1)-Cl(1)	83.1(1)
P(2)-Pd(1)-Cl(1)	172.3(1)	Cl(2)-Pd(1)-Cl(1)	88.1(1)
C(15)-P(1)-C(12)	105.9(7)	C(15)-P(1)-C(21)	103.2(6)
C(12)-P(1)-C(21)	102.1(6)	C(15)-P(1)-Pd(1)	105.9(5)
C(12)-P(1)-Pd(1)	112.9(5)	C(21)-P(1)-Pd(1)	125.1(5)
C(33)-P(2)-C(14)	102.1(7)	C(33)-P(2)-C(27)	101.1(6)
C(14)-P(2)-C(27)	103.0(6)	C(33)-P(2)-Pd(1)	126.4(5)
C(14)-P(2)-Pd(1)	111.7(4)	C(27)-P(2)-Pd(1)	109.9(5)

Z(1) and Z(2) refer to the centres of the cyclopentadienyl rings C(1)-C(5) and C(6)-C(10) respectively.

The palladium atom has a distorted square planar geometry with *cis* tertiary phosphine ligands. The Cl-Pd-Cl angle of 88.11(13)° is almost the ideal 90°. However, the remaining angles around palladium deviate from this with the P-Pd-P angle opening up to 103.94(13)° causing a narrowing of the P-Pd-Cl angles to 84.64(13)° and 83.13(13)°. The two phosphorus and two chlorine atoms around palladium are co-planar with all four atoms within ±0.009Å of the least squares plane. The palladium atom is raised slightly above this plane by 0.064Å.

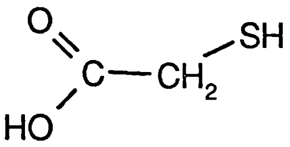
The Pd-P distances [Pd(1)-P(1)=2.259(4)Å, Pd(1)-P(2)=2.276(4)Å] are shorter than those found in the structure of dibromobis(diphenylphosphinoacetic acid)palladium(II) where the phosphorus atoms are *trans* to each other [Pd-P: 2.322(2) Å].[222] In the complex bis(diphenylphosphinoacetate)palladium(II), where two O,P- chelating carboxylates surround each metal atom with the phosphorus atoms in a *cis* arrangement, the phosphorus metal distances [Pd-P: 2.236(2), 2.234(2)Å] are slightly shorter than those in **P10**.3CH_2Cl_2.[226]

Chapter 5.

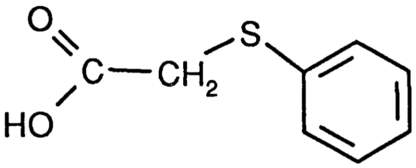
Bis(cyclopentadienyl)titanium(IV) Derivatives of Carboxylic Acids Containing Additional Sulfur Donors.

5.1. Introduction

Following the success of using phosphorus-containing compounds discussed in the preceding chapter, carboxylic acids were chosen in which an alternative soft donor, sulfur was incorporated into secondary functional groups. Two such carboxylic acids were studied, namely mercaptoacetic acid **56** and thiophenoxyacetic acid **57**.



mercaptoacetic acid
(thioglycolic acid)
56



thiophenoxyacetic acid
(phenylthioacetic acid)
57

The sulfur atom of mercaptoacetic acid **56**, has the potential to coordinate to transition metal centres either as a neutral thiol donor or as an anionic thiolate moiety. Examples of the latter behaviour can be found in the structures of $[NH_2\{CH(CH_3)_2\}_2][Ph_3Sn(O_2CCH_2S)]$[240] and $[Et_4N]_4[MoFe_3S_4Cl_3(SCH_2CO_2)]_2$[241] where mercaptoacetic acid is doubly deprotonated.

The triorganotin complex contains a bidentate *O*,*S*-chelating mercaptoacetate which forms a five-membered ring with the tin atom. The mercaptoacetate dianion acts both as a bridging and a chelating ligand in the second complex, where pairs of $MoFe_3S_4$ cubes are linked at the molybdenum apexes *via* bidentate thiolate moieties of the mercaptoacetate. The carboxyl functions are attached to different molybdenum centres in a monodentate fashion, forming five-membered chelate rings as found in the tin complex.

Thiophenoxyacetic acid is the sulfur analogue of diphenylphosphinoacetic acid **54** and is therefore of interest for comparative purposes. It also displays a variety of crystallographically confirmed structural motifs with the carboxyl function acting as a bridging ligand [in $\{Cd(O_2CCH_2SPh)_2H_2O\}_n]$[242] or as a chelating ligand [in $\{Zn(O_2CCH_2SPh)_2(H_2O)_2\}]$,[242] or a combination of the two modes [in $\{Ag(O_2CCH_2SPh)\}_n]$.[243] Examples exist where the sulfur atom is also involved in bonding to metal centres as with the Tl(I) complex $[\{Tl(O_2CCH_2SPh)(HO_2CCH_2SPh)\}_n]$[244] and the Cd(II) and Ag(I) complexes above, or is uncoordinated as in the Zn(II) complex above and the Ba(II) complex $[Ba(O_2CCH_2SPh)_2]$.[245]

5.2. Preparation of the bis(cyclopentadienyl)titanium(IV) carboxylates S1-S3

The complexes S1-S3 were prepared by the methods outlined in Equations 60-62. The products of these reactions were characterised by microanalysis, IR spectroscopy and where possible NMR spectroscopy. In addition, complex S3 was further investigated by mass spectrometry and X-ray crystallography. Tables 41 and 42 contain the analysis and IR data for complexes S1-S3, and listed in Tables 44 and 45 are the ^1H and $^{13}C\{^1H\}$ NMR data for the latter two complexes.

$$Cp_2TiCl_2 + 2NaO_2CCH_2SH \xrightarrow[\text{-2NaCl}]{\text{THF/reflux/4hrs}} \underset{\textbf{S1}}{Cp_2Ti(O_2CCH_2S)} + HO_2CCH_2SH \qquad \text{Eq. 60}$$

$$Cp_2TiMe_2 + 2HO_2CCH_2SH \xrightarrow{CH_2Cl_2/\text{-2MeH}} \underset{\textbf{S2}}{Cp_2Ti(O_2CCH_2SH)_2} \qquad \text{Eq. 61}$$

$$Cp_2TiMe_2 + 2HO_2CCH_2SPh \xrightarrow{CH_2Cl_2/\text{-2MeH}} \underset{\textbf{S3}}{Cp_2Ti(O_2CCH_2SPh)_2} \qquad \text{Eq. 62}$$

Table 41. Microanalysis data for complexes S1-S3. Calculated values for the quoted formulae are given in parentheses.

		%C	%H
$[Cp_2Ti(O_2CCH_2S)]_n$	**S1**	52.6 (53.7)	4.47 (4.51)
$Cp_2Ti(O_2CCH_2SH)_2$	**S2**	45.6 (46.7)	4.46(4.48)
$Cp_2Ti(O_2CCH_2SPh)_2$	**S3**	60.6 (60.9)	4.73 (4.72)

Table 42. IR data for compounds **S1**-**S3**.[a]

		v(C-H)[b]	v(C=C)[b]	δ(C-H)[b]	v(O-C-O)		other
					(asym)	(sym)	
		(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})
$[Cp_2Ti(O_2CCH_2S)]_n$	**S1**	3092	1453	1020	1631	1317	
				830			
$Cp_2Ti(O_2CCH_2SH)_2$[c]	**S2**	3117	1445	1026	1651	1331	2577 [v(SH)]
		3054		828			
$Cp_2Ti(O_2CCH_2SPh)_2$	**S3**	3108	1437	1022	1661	1337	
				824	1632	1302	

a - Further data including relative peak intensities are given in Chapter 7. b - Characteristic cyclopentadienyl vibrations. Spectra recorded as nujol mulls on NaCl except c - recorded as a CH_2Cl_2 solution.

5.2.1. Bis(cyclopentadienyl)(mercaptoacetato)titanium(IV) S1

Reaction of bis(cyclopentadienyl)titanium dichloride with two equivalents of sodium mercaptoacetate in refluxing tetrahydrofuran resulted in a dark red powder which was insoluble in all common solvents. Furthermore, this material was very air and moisture stable and showed no signs of degradation even after washing thoroughly with water.

Due to a complete lack of solubility, characterisation of the product was by microanalysis and IR spectroscopy alone. A comparison of the analytical data of the product with the calculated C, H, S and Ti contents for the mono(mercaptoacetato-*O*,*S*) and bis(mercaptoacetato-*O*) derivatives of bis(cyclopentadienyl)titanium(IV) is given in Table 43.

Table 43. Calculated C, H, S and Ti contents for bis(cyclopentadienyl)mercaptoacetato-titanium(IV) **S1** and bis(cyclopentadienyl)bis(mercaptoacetato)titanium(IV) **S2** and the observed values for the product of Equation 60.

		%C	%H	%S	%Ti
$(C_5H_5)_2Ti(O_2CCH_2S)$	**S1**	53.7	4.51	12.0	17.9
$(C_5H_5)_2Ti(O_2CCH_2SH)_2$	**S2**	46.7	4.48	17.8	13.3
experimental		52.6	4.47	10.8	15.4

The analytical and IR data suggest that there is one doubly deprotonated mercaptoacetate ligand for each metal centre. The carbon and hydrogen content of the product is close to that calculated for a compound of formula $(C_5H_5)_2Ti(O_2CCH_2S)$ and the IR spectrum does not contain a medium strength band at around ν=2500-2600cm^{-1} characteristic of ν(S-H).

A polymeric structure is therefore proposed whereby bis(cyclopentadienyl)titanium moieties are joined by $-SCH_2CO_2-$ units, each metal atom being bonded to an oxygen and a sulphur atom (Fig. 30).

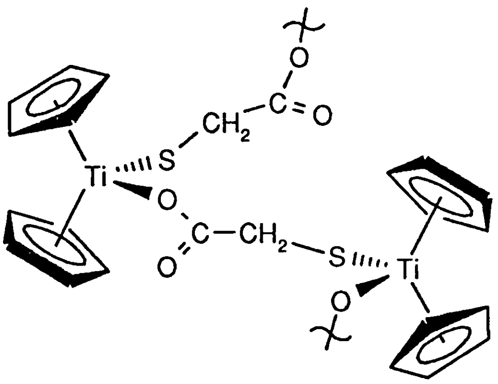


Figure 30. Proposed structure of bis(cyclopentadienyl)(mercaptoacetato)titanium(IV) **S1**.

The IR spectrum displays further bands characteristic of the cyclopentadienyl rings (3092, 1453, 1020 and 830cm^{-1}) and monodentate carboxyl functions (1631and 1317cm^{-1}).

5.2.2. Bis(cyclopentadienyl)bis(mercaptoacetato)titanium(IV) S2

Bis(cyclopentadienyl)bis(mercaptoacetato)titanium(IV) **S2** was prepared by treating mercaptoacetic acid with bis(cyclopentadienyl)bis(methyl)titanium(IV) (Equation 61). It was not possible to isolate the product of this reaction as a solid either by removal of the solvent in high vacuum, or by precipitation with hexanes. In each case a dark maroon oil was produced the analysis of which agrees closely with the calculated values for a compound of formula $(C_5H_5)_2Ti(O_2CCH_2SH)_2$ (Table 41).

Freshly prepared samples of the product were readily soluble in chlorinated solvents and tetrahydrofuran however, after a period of exposure to air the dark maroon oil changed little in appearance but became insoluble. Samples stored under nitrogen remained soluble indefinitely.

The IR spectrum recorded as a dichloromethane solution displays strong bands characteristic of the cyclopentadienyl and carboxylate groups. The asymmetric and symmetric stretches of the carboxyl function appear at 1651cm^{-1} and 1331cm^{-1} which compares with the analogous values of sodium mercaptoacetate at 1578cm^{-1} and 1418cm^{-1}. The increase in frequency difference between the asymmetric and symmetric stretches on going from the sodium salt to the bis(cyclopentadienyl)titanium(IV) derivative suggests monodentate coordination of the carboxyl functions.

The IR spectrum also displays a weak band at v=2577cm^{-1} due to the S-H stretching mode.

Table 44. ^{1}H NMR data for compound S2 and S3.^{a}

		Chemical Shift, δ (ppm)			
		CH_2	C_5H_5	*-SH*	*phenyl*
$Cp_2Ti(O_2CCH_2SH)_2$	S2	3.18^b	6.49	1.96^c	
$Cp_2Ti(O_2CCH_2SPh)_2$	S3	3.61	6.27		7.09, 7.22, 7.35

Solvent $CDCl_3$. a - Further data regarding multiplicities and peak integrals are given in Chapter 7. b - doublet, J=8.06Hz. c - triplet, J=8.06Hz.

The ^{1}H and $^{13}C\{^1H\}$ NMR data for complex S2 (Table 44 and 45) show the expected number of resonances for a compound containing two equivalent cyclopentadienyl rings and two equivalent monodentate mercaptoacetate ligands. The peak integrals in the ^{1}H NMR spectrum are in the approximate ratio of 2:4:10 as expected. Also observed in the proton spectrum is the coupling of the methylene and thiol hydrogen nuclei giving a coupling constant of J=8.06Hz which is identical to that observed in the free acid (J=8.06Hz, $CDCl_3$, 270.1MHz).

Table 45. $^{13}C\{^1H\}$ NMR data for compounds S2 and S3.

		Chemical Shift, δ (ppm)			
		$-CO_2-$	C_5H_5	*$-CH_2-$*	*phenyl*
$Cp_2Ti(O_2CCH_2SH)_2$	S2	175.6	118.8	28.8	
$Cp_2Ti(O_2CCH_2SPh)_2$	S3	174.1	118.5	37.8	125.8, 128.1, 128.8, 136.4

Solvent $CDCl_3$. All signals were observed to be singlets.

5.2.3. Bis(cyclopentadienyl)bis(thiophenoxyacetato)titanium(IV) S3

Treatment of thiophenoxyacetic acid with bis(cyclopentadienyl)bis(methyl)titanium(IV) in tetrahydrofuran resulted in the vigorous evolution of methane and the formation of bis(cyclopentadienyl)bis(thiophenoxyacetato)titanium(IV) S3 in 93% yield. The orange crystalline material produced could be recrystallised from tetrahydrofuran solutions layered with hexane to give large red cube-like crystals.

The analysis of the recrystallised material is in excellent agreement with the calculated values for a compound of formula $(C_5H_5)_2Ti(O_2CCH_2SC_6H_5)_2$ (Table 41). The IR data (Table 42) contain the characteristic bands due to the cyclopentadienyl and carboxyl groups. The separation between the asymmetric and symmetric stretches of the carboxyl functions suggest that these moieties are coordinated to the metal in a monodentate fashion.

The NMR data are also in good agreement with the proposed structure (Tables 44 and 45). The ^{1}H NMR spectrum contains five signals at δ=3.61, 6.27, 7.09, 7.22 and 7.35ppm in the approximate ratio of 4:10:2:4:4. The first two resonances can be assigned to the methylene and cyclopentadienyl protons respectively, with the remaining three peaks arising from the phenyl groups. The $^{13}C\{^1H\}$ NMR spectrum contains the expected seven signals.

Complex S3 was further characterised by FAB mass spectrometry the results of which are summarised in Table 46. The major fragments having positive charges are due to dissociation of the parent ion involving the loss of a carboxylate or cyclopentadienyl ligand.

Table 46. FAB MS data for S3. Relative intensities are given in parentheses.

	m/z (intensity as % of base peak)	
FAB+	447 (7)	$[CpTi(O_2CCH_2SPh)_2]^+$
	345 (100)	$[Cp_2Ti(O_2CCH_2SPh)]^+$
	178 (16)	$[Cp_2Ti]^+$
FAB-	614 (41)	$[CpTi(O_2CCH_2SPh)_3]^{-\cdot}$
	512 (100)	$[Cp_2Ti(O_2CCH_2SPh)_2]^{-\cdot}$
	463 (78)	$[CpTi(O)(O_2CCH_2SPh)_2]^-$
	448 (46)	$[CpTi(H)(O_2CCH_2SPh)_2]^{-\cdot}$
	361 (38)	$[Cp_2Ti(O)(O_2CCH_2SPh)]^-$

The parent ion at m/z=512 is the most abundant ion carrying a negative charge. Further negatively charged ions are observed at m/z values which suggest a degree of intermolecular rearrangement takes place involving exchange of a cyclopentadienyl ring for a carboxylate ligand. The heaviest ion arising from this substitution at m/z=614 is probably due to a species containing one cyclopentadienyl ring and three carboxylate ligands around a titanium atom. Subsequent fragmentation of this species is the likely origin of the peak at m/z=463 and possibly arises from the loss of a neutral fragment $PhSCH_2C{\equiv}O$ with a mass of 151.

The loss of this same fragment with a mass of 151 units is also probably the cause of the peak at m/z=361 (from the parent ion) and the peak at m/z=448 (from an ion of low abundance at m/z=599).

5.2.4. Molecular structure of bis(cyclopentadienyl)bis(mercaptoacetato)titanium(IV) S3

One of the red cube-like crystals of **S3** described earlier was selected for a single crystal X-ray analysis from which the molecular structure displayed in Figure 31 was determined. Selected bond angles and lengths for **S3** are given in Table 47.

The molecular structure shows titanium in the familiar pseudo-tetrahedral environment with the carboxylate ligands bonding solely through the carboxyl functions in a monodentate fashion (Fig. 31). The geometry around titanium involving the centres of the cyclopentadienyl rings and the two oxygen atoms O(1) and O(3) is very similar to other bis(cyclopentadienyl)-titanium(IV) carboxylates. The distances between the metal and the centres of the cyclopentadienyl rings; Ti(1)-Z(1)=2.054Å [for C(17)-C(21)], Ti(1)-Z(2)=2.051Å [for C(22)-C(26)] and the angle between these two vectors (130.67°) fall within the range of previous reports and in particular are similar to those observed in the structure of bis(*o*-methylbenzoato)bis(methylcyclopentadienyl)titanium(IV) [Ti-Z: 2.057, 2.055Å; Z-Ti-Z: 130.1Å, where Z represent the centres of the methylcyclopentadienyl rings].[98]

The O(1)-Ti(1)-O(3) angle of 90.18(9)° and one of the Ti-O distances [Ti(1)-O(1)=1.966(2)Å] are also similar to that found in the above methylbenzoato derivative [∠O-Ti-O=90.5(1)°; Ti-O=1.961(3), 1.979(3)Å]. The other Ti-O distance, Ti(1)-O(3)=1.936(2)Å is slightly shorter and corresponds to the wider Ti-O-C angle [∠Ti(1)-O(3)-C(9)=149.5(2)°, cf. ∠Ti(1)-O(1)-C(1)=137.2(2)°]. As with the diphenylphosphinoacetate derivative **P1** described

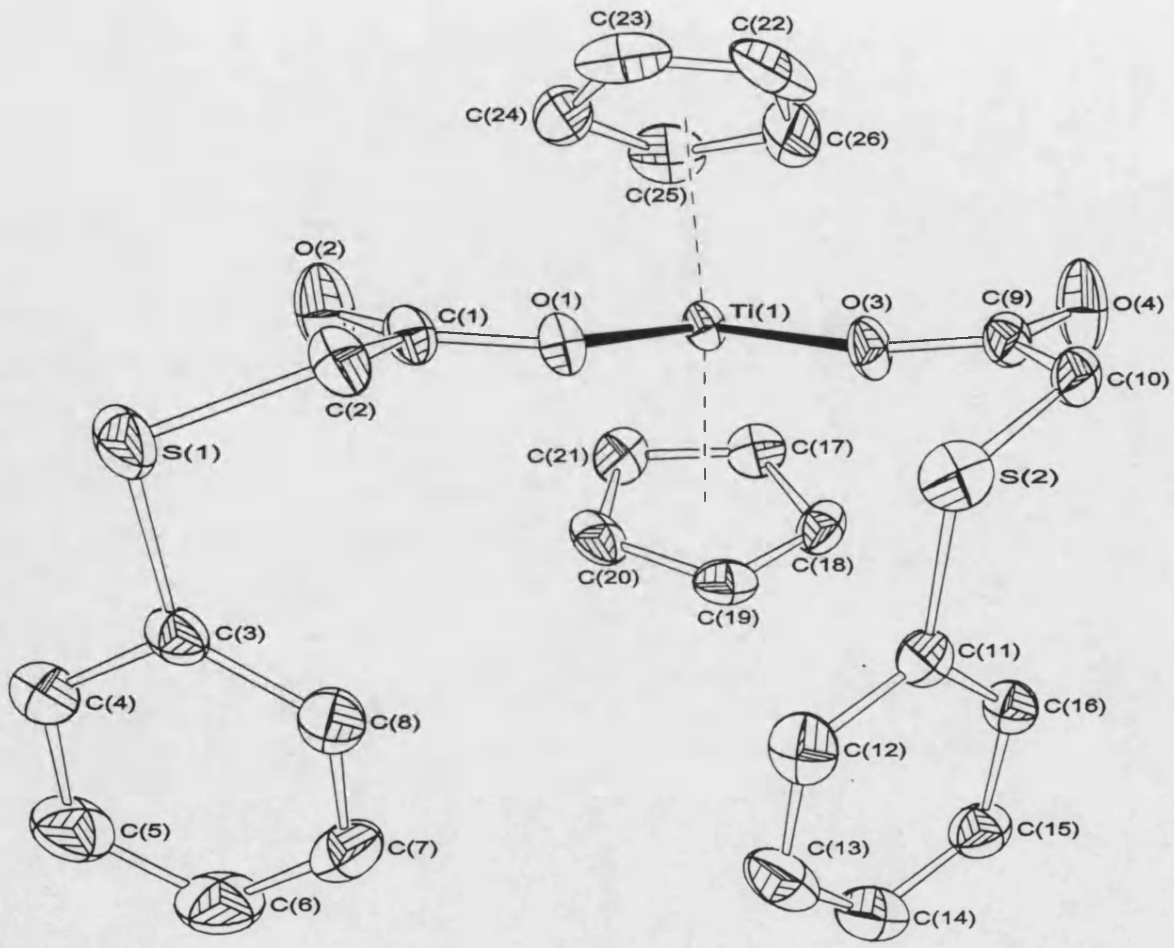


Figure 31. Molecular structure bis(cyclopentadienyl)bis(thiophenoxyacetato)titanium(IV) S3.

earlier, this difference between the two carboxyl moieties could be due to additional charge donation to the metal by one of the oxygen atoms, O(3) in this case.

Table 47. Selected bond lengths (Å) and angles (°) for **S3**.

Ti(1)-O(1)	1.966(2)	Ti(1)-O(3)	1.936(2)
Ti(1)-Z(1)	2.054	Ti(1)-Z(2)	2.051
O(1)-C(1)	1.288(3)	O(3)-C(9)	1.282(4)
O(2)-C(1)	1.207(3)	O(4)-C(9)	1.202(4)
S(1)-C(2)	1.792(3)	S(2)-C(10)	1.793(3)
S(1)-C(3)	1.758(3)	S(2)-C(11)	1.766(3)
O(3)-Ti(1)-O(1)	90.18(9)	Z(1)-Ti(1)-Z(2)	130.67
Ti(1)-O(1)-C(1)	137.2(2)	Ti(1)-O(3)-C(9)	149.5(2)
O(1)-C(1)-O(2)	124.4(3)	O(3)-C(9)-O(4)	125.0(3)
C(2)-S(1)-C(3)	103.9(2)	C(10)-S(2)-C(11)	103.6(2)

Z(1) and Z(2) refer to the centres of the cyclopentadienyl rings, C(17)-C(21) and C(22)-C(26) respectively.

The difference in the C-O bond lengths and the O-C-O angles of the carboxyl functions reflect the monodentate coordination of these groups to titanium [C-O: 1.288(3), 1.282(4), 1.207(3), 1.202(4)Å; O-C-O: 124.4(3), 125.0(3)°]. These values contrast with the corresponding parameters in the zinc(II) and copper(II) complexes $[Zn(O_2CCH_2SPh)_2(H_2O)_2]$[242] and $[Cu_2(O_2CCH_2SPh)_4(py)_2]$[246] (py=pyridine) where the thiophenoxyacetates are bidentate chelating and bidentate bridging respectively [Zn complex; C-O: 1.256(6), 1.245(6)Å; O-C-O: 119.6(4)°; Cu complex; C-O: 1.257(7), 1.262(8), 1.248(6), 1.247(6)Å; O-C-O: 126.8(4), 125.2(5)°].

Excluding the difference in bonding to titanium, the two thiophenoxyacetate ligands are very similar. The bond lengths and angles of the phenyl rings range from 1.358(6)-1.378(5)Å and 118.9(3)-120.4(4)° for ring(1) [C(3)-C(8)] and 1.357(5)-1.382(6)Å and 118.5(3)-121.0(4)° for ring(2) [C(11)-C(16)] with average lengths of 1.372 and 1.373Å respectively. The structure of the free acid displays close similarities with the above [C-C: 1.353(5)-1.394(4)Å, $C\text{-}C_{av}$: 1.376Å; C-C-C: 118.9(2)-121.4(2)°].[242] The C-S-C angles for **S3** [103.9(2) and 103.6(2)°] also resemble the corresponding value in the free acid [103.3(2)°].

5.3. Heterobimetallic complexes

Due to its' lack of solubility and problems in isolating a pure compound, complex **S1** was not investigated for coordination to further transition metal species. Reactions involving the bis(mercaptoacetate) complex **S2** and molybdenum reagents were carried out however, it was not possible to interpret the spectroscopic data of the resulting product mixtures. This work is not reported here.

Preliminary investigations were undertaken involving the reactions of the thiophenoxyacetate **S3** with bicycloheptadiene molybdenum tetracarbonyl or bis(benzonitrile)palladium(II) chloride (Equations 63 and 64). The results obtained in both cases (Tables 48 and 49) are encouraging, but require further studies.

$$\begin{matrix}\mathrm{Cp_2Ti(O_2CCH_2SPh)_2} \\ + \\ \mathrm{C_7H_8Mo(CO)_4}\end{matrix} \xrightarrow[\mathrm{-C_7H_8}]{\mathrm{toluene/20mins}} \mathrm{Cp_2Ti(O_2CCH_2SPh)_2Mo(CO)_4} \qquad \text{Eq. 63}$$

$$\begin{matrix}\mathrm{Cp_2Ti(O_2CCH_2SPh)_2} \\ + \\ \mathrm{(C_6H_5CN)_2PdCl_2}\end{matrix} \xrightarrow[\mathrm{-2C_6H_5CN}]{\mathrm{CH_2Cl_2/24hrs}} \mathrm{Cp_2Ti(O_2CCH_2SPh)_2PdCl_2} \qquad \text{Eq. 64}$$

The product mixture obtained from the reaction described by Equation 63 gave a ^{1}H NMR spectrum containing a large number of resonances (see Chapter 7). Table 48 presents data relating to signals which are postulated to arise from a Ti-Mo species $\mathrm{Cp_2Ti(O_2CCH_2SPh)_2.Mo(CO)_4}$ **58**.

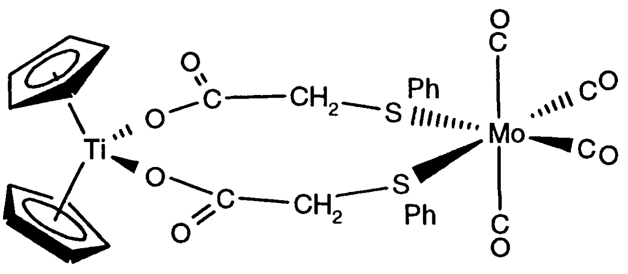


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Table 48. Selected data from the ^1H NMR spectrum of the product mixture from the reaction of **S3** with bicycloheptadiene molybdenum tetracarbonyl. Data for **S3** are included for comparison.

		Chemical Shift δ(ppm)		
		-CH_2-	C_5H_5	phenyl
main component of product mixture		3.68 (s, 4.0H)	6.34 (s, 9.2H)	7.17 (m, 6.5H), 7.29 (m, 7.7H), 7.41 (m, 5.1H)
$Cp_2Ti(O_2CCH_2SPh)_2$	**S3**	3.61 (s, 4.0H)	6.27 (s, 9.3H)	7.09 (m, 2.0H), 7.22 (m, 4.1H), 7.35 (m, 3.8H)

Signal multiplicity and peak integrals are given in parentheses. Additional data are given in Chapter 7.

Assignments in Table 48 are made on the basis of peak integrals and a comparison of the chemical shifts with those of the starting material **S3**. The integrals of the peaks assigned to the phenyl protons are much higher than would be predicted because, unlike the methylene and cyclopentadienyl resonances, it is difficult to separate these signals from signals arising from other species.

The initial analysis of the reaction between complex **S3** and bis(benzonitrile)palladium(II) chloride listed in Table 49, indicates the formation of a bimetallic complex such as **59**.

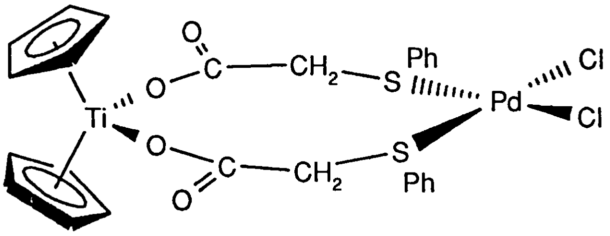

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Table 49. Analytical and IR spectroscopy data for the product of the reaction of **S3** with bis(benzonitrile)palladium(II) chloride.

analysis[a]	%C: 44.2 (45.3); %H: 3.46 (3.51)
IR (cm^{-1})[b]	ν(C-H)$_{Cp}$: 3112, 3060; ν(C=C)$_{Cp}$: 1443; δ(C-H)$_{Cp}$: 1024, 828 ν(O-C-O): 1626, 1350, 1319 ν(Pd-Cl): 358, 324

a - Calculated values for $(C_5H_5)_2Ti(O_2CCH_2SPh)_2.PdCl_2$ are given in parentheses. b - Further data contained in Chapter 7.

The microanalysis is in reasonable agreement with a compound of formula $(C_5H_5)_2Ti(O_2CCH_2SPh)_2.PdCl_2$, and the IR spectrum contains characteristic bands due to the cyclopentadienyl rings and the carboxyl functions. Also shown in the IR spectrum are weak bands at ν=358 and 324cm^{-1} possibly due to Pd-Cl stretches.

Chapter 6.

Conclusion.

A number of bis(cyclopentadienyl)titanium(IV) derivatives of carboxylic acids which contain an additional nitrogen, oxygen, phosphorus or sulfur donor functionality have been synthesised. Various preparative routes to these compounds were utilised as no single method was generally applicable, although the reaction of bis(cyclopentadienyl)bis(methyl)titanium(IV) with the free acids gave satisfactory results in many cases. Most of the complexes were isolated in the solid state and found to be reasonably air stable.

The structures of these compounds were studied by IR and NMR spectroscopy, mass spectrometry and single crystal X-ray crystallography. The molecular structures of four bis(carboxylato)bis(cyclopentadienyl)titanium(IV) compounds were determined crystallographically and in each case the pseudo-tetrahedral titanium atom was observed to be coordinated by two monodentate carboxylates the additional donor functions of which were not bonded to the metal centre. A similar bonding arrangement is suggested for the remaining bis(carboxylato) titanocene complexes from IR spectroscopic data.

The monodentate nature of the carboxylate coordination to the bis(cyclopentadienyl)titanium(IV) moiety observed in this work is in agreement with studies by other researchers. The results presented here also show that despite the presence of additional donor atoms the pseudo-four-coordinate geometry of titanium is preserved. This suggests that previously reported bis(cyclopentadienyl)titanium(IV) carboxylate complexes where the titanium is five-coordinate such as the dipicolinate, are isolated examples which rely upon geometric constraints of the ligand to hold the additional donor atom in close proximity to the metal.

The utility of the bifunctional carboxylic acids to link the bis(cyclopentadienyl)titanium(IV) moiety to late transition metals was investigated and a certain amount of success was achieved using the phosphine containing carboxylic acid, diphenylphosphinoacetic acid. Four Ti-M (M=Pd, Cu, Ag, Au) heterobimetallic compounds were prepared and well characterised. Further complexes (M=Ni, Pt) were also isolated and partially characterised.

Comparison of the crystal structure of the Ti-Pd complex with that of the titanocene carboxylate starting material shows that the environment of the titanium atom is not affected by the presence of the palladium. The titanocene carboxylate moiety acts as a bidentate phosphine ligand, chelating to the palladium with the phosphorus atoms in a *cis* arrangement. The palladium atom adopts a square planar geometry and is situated 4.18Å away from the titanium atom, beyond any reasonable bonding interaction.

In addition to titanocene derivatives, seven *P*-coordinated diphenylphosphinoacetic acid-transition metal complexes were prepared as starting materials for heterometallic compounds. These compounds were characterised by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and FAB mass spectrometry. The solid state structures are expected to show a variety of hydrogen bonding arrangements, which was confirmed by X-ray crystallography for two of the complexes.

Preliminary studies suggest that titanocene derivatives of the sulfur and nitrogen containing acids, thiophenoxyacetic acid (phenylthioacetic acid) and nicotinic acid (pyridine-3-carboxylic acid) can also be used to form Ti-M heterobimetallic complexes (M=Mo, Pd, Pt). Unfortunately, derivatives of carboxylic acids containing additional oxygen donors did not yield titanocene complexes suitable for further coordination studies.

Chapter 7.

Experimental.

7.1. Equipment

Carbon, hydrogen, nitrogen and sulphur microanalyses were carried out on a Carlo Erba Strumentazione E.A. model 1106 Analyser. Titanium content was determined using a Varian AA-275 series atomic absorption spectrometer. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on Jeol GX270 and EX400 spectrometers. ^{1}H and ^{13}C chemical shifts are quoted relative to tetramethylsilane, ^{19}F and ^{31}P reference was internal. Fast atom bombardment mass spectra were recorded on Fisons Instruments V.G. Analytical 7070E and V.G. AutoSpec spectrometers. Infra-red spectra as liquid paraffin or hexachlorobutadiene mulls on NaCl or CsI plates unless otherwise stated, were recorded on a Nicolet Instrument Corporation 510P FT-IR spectrometer with Philips PRO 7CM3209 processor or on a Perkin Elmer 597 spectrometer.

7.2. Reagents

Bromobenzene, diethylphosphite, ethylchloroacetate, ethylorthoformate, methyllithium, potassium hydroxide, potassium metal, sodium ethanoate, sodium hydroxide, tetrahydrothiophene, triphenylphosphine and triethylamine (Aldrich); bicyclo[2.2.1]hepta-2,5-diene (Koch Light Laboratories) were used as supplied.

All operations were carried out in dry nitrogen atmospheres except where mentioned. Toluene, diethyl ether and tetrahydrofuran were dried by distillation over sodium/benzophenone, dichloromethane was distilled from calcium hydride. Pentane, hexane, methylcyclohexane, chloroform, and acetonitrile were stored over 4Å molecular sieves.

7.2.1. Carboxylic acids, sodium and silver(I) carboxylates

β-Alanine, chloroacetic acid, cyanoacetic acid, glycine, mercaptoacetic acid, nicotinic acid, thiophenoxyacetic acid (Aldrich); anthranilic acid and salicylic acid (B.D.H.) were used as supplied.

7.2.1.1. Diphenylphosphinylacetic acid, $Ph_2P(O)CH_2CO_2H$

Diphenylphosphinylacetic acid was synthesised by the method of Grim and Satek.[202] A solution of phenylmagnesium bromide Grignard in diethyl ether was prepared by adding carefully (over 30 minutes) 52.6cm^3 of bromobenzene (0.50mol) in 50cm^3 of diethyl ether to 12.2g of magnesium metal turnings (0.50mol) in 100cm^3 of diethyl ether with a small amount of iodine and allowing to reflux for 2 hours. A further 70cm^3 of diethyl ether was added to the Grignard solution followed by (dropwise) 21.5cm^3 of diethylphosphite (0.17mol) in 80cm^3 of diethyl ether causing a vigorous reaction. After overnight stirring the reaction was quenched with 6M hydrochloric acid in degassed water and the aqueous phase extracted with 4×70cm^3 portions of toluene. The combined organic phases were washed with saturated sodium hydrogen carbonate solution until the organic layer was neutralised, and then dried with magnesium sulphate. Removal of the solvent yielded 32g of a yellow oil (93%).

A portion of this crude oil (5.06g, 25.0mmol) in 15cm^3 of ethanol was rapidly added to a solution of 3.40g of sodium ethanoate (50.0mmol) in 50cm^3 of ethanol. Chloroacetic acid (2.36g, 25.0mmol) was then added followed by a further 50cm^3 of ethanol and the reaction mixture was refluxed for 10 hours. After cooling, the solvent was removed on a rotary evaporator and the residue dissolved in 20cm^3 distilled water. This solution was washed with 2×10cm^3 portions of chloroform. The pH of the aqueous solution was carefully adjusted to 5 with 25% sulfuric acid and extracted with 4×10cm^3 portions of chloroform. Removal of the solvent and recrystallisation of the residue from methylethyl ketone yielded 1.20g (18%) of a white crystalline material. Analysis; Found (calc. $C_{14}H_{13}O_3P$): C 65.3(64.6); H 5.05(5.04)%. NMR (DMSO-d$_6$) ^{1}H (270.1MHz) δ(ppm)=3.68(d, 2.0H, J=13.92Hz, -C*H*$_2$-), 7.47-7.60(m, 6.0H, *phenyl*), 7.82(m, 4.0H, *phenyl*), 12.54(s, 1.0H, -CO$_2$*H*); ^{13}C{^{1}H} (67.8MHz) δ(ppm)=37.8(d, J=62.8Hz, -*C*H$_2$-), 128.6(d, J=11.0Hz, *phenyl*), 130.6(d, J=8.8Hz, *phenyl*), 131.7(d, J=3.3Hz, *phenyl*), 134.2(s, *phenyl*), 167.4(d, J=5.5Hz, -*C*O$_2$H); ^{31}P{^{1}H} (109.3MHz) δ(ppm)=26.3. IR (CsI, liquid paraffin mull), ν(cm^{-1})=2633broad, 1732vs, 1590w,1488w, 1439s, 1410m, 1300s, 1208m, 1157vs, 1127s, 1098s, 1073m, 997m, 914s, 897m, 853s, 801s, 750s, 729s, 694s, 590s, 538s, 523s, 507s, 482m, 388m, 260m. MS FAB+, m/z=521(14), 261(100), 201(28); FAB-, m/z=519(26), 426(55), 412(52), 259(100), 215(76).

Crystals of diphenylphosphinylacetic acid were also isolated as a by-product in the synthesis of diphenylphosphinoacetic acid. This material was spectroscopically identical to the above compound and was used in the single crystal X-ray structure determination. Analysis; Found (calc. $C_{14}H_{13}O_3P$): C 64.7(64.6); H 5.00(5.04)%.

7.2.1.2. Diphenylphosphinoacetic acid, $Ph_2PCH_2CO_2H$

Diphenylphosphinoacetic acid was prepared *via* a variation on the method of Jarolím and Podlahová.[207] A solution of 20.0g of triphenylphosphine (76mmol) in 1,4-dioxane ($100cm^3$) containing 6.0g of potassium metal (153mmol) was refluxed for 5 hours. The cooled reaction mixture was then placed in an ice/water bath and 9.4g of ethylchloroacetate (76mmol) in $20cm^3$ of 1,4-dioxane added dropwise over 30 minutes. Unreacted potassium was removed by filtration, and the resultant orange/brown slurry poured into $400cm^3$ of degassed water. Ethyldiphenylphosphinoacetate was extracted with $4\times100cm^3$ portions of diethyl ether, the combined organic phases were then dried with magnesium sulfate and the solvent removed on a rotary evaporator. The resulting brown oil was distilled at 140°C/0.05mmHg, dissolved in $25cm^3$ of petroleum ether (40-60°C) and treated with a solution of 1.0g sodium hydroxide in $10cm^3$ of ethanol. The sodium salt which precipitated after standing at -20°C overnight was collected by filtration and dissolved in degassed water. Careful addition of 2M hydrochloric acid to the aqueous solution gave a white suspension, which upon filtration and drying gave 4.82g (26%) of an off-white powder. Analysis; Found(calc. $C_{14}H_{13}O_2P$): C 68.9(68.9); H 5.39(5.36)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.11(s, 2.0H, $-CH_2-$), 7.33-7.48(m, 10.0H, *phenyl*), 11.5(v broad, 1.0H, $-CO_2H$); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=35.1(d, J=23.2Hz, $-CH_2-$), 128.4(d, J=6.6Hz, *phenyl*), 129.0(s, *phenyl*), 132.4(d, J=19.9Hz, *phenyl*), 136.7(d, J=14.3Hz, *phenyl*), 177.2(d, J=8.8Hz, $-CO_2H$); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=-15.1. IR (CsI, liquid paraffin mull), $\nu(cm^{-1})$=3080m, 2677w, 1700vs, 1481m, 1470m, 1400m, 1301s, 1291s, 1180w, 1125m, 1070w, 1030w, 1000w, 918w, 795s, 750vs, 699vs, 665w, 590s, 505m, 482m, 478m, 428w, 400w, 310w, 247w. MS FAB+, m/z=396(2), 381(4), 261(15), 245(100), 201(8), 185(11); FAB-, m/z=410(42), 396(56), 341(34), 308(25), 274(18), 257(16), 243(100), 215(23).

The sodium salts of the carboxylic acids were prepared by the reaction of the appropriate acid with sodium hydroxide or sodium ethoxide in distilled water or absolute ethanol respectively, and characterised by carbon, hydrogen and nitrogen microanalyses and IR spectroscopy. Silver salts were prepared by precipitation from an aqueous solution of silver nitrate and the appropriate sodium carboxylate and characterised in a similar manner to the sodium salts. Due to the sensitive nature of silver compounds, light was excluded wherever possible and the compounds were stored in the dark when not in use.

7.2.2. Transition metal-containing starting materials

Bis(cyclopentadienyl)titanium dichloride, bis(cyclopentadienyl)zirconium dichloride, copper(II) perchlorate hexahydrate, copper(II) sulphate pentahydrate, molybdenum hexacarbonyl, palladium(II) chloride, (Aldrich); silver(I) tetrafluoroborate (Avacado); silver(I) nitrate, silver(I) chloride (B.D.H.); hydrated nickel(II)tetrafluoroborate and nickel(II) chloride hexahydrate (Fisons); platinum(II) chloride and sodium tetrachloroaurate(III) (Johnson Mathey) were used as supplied.

Bis(cyclopentadienyl)bis(methyl)titanium(IV) was prepared by the method of Erskine, Wilson and McCowan[247] from bis(cyclopentadienyl)titanium dichloride and methyllithium in diethyl ether. Tetrakis(acetonitrile)copper(I) perchlorate was prepared by the reduction of copper(II) perchlorate hexahydrate by copper metal in refluxing acetonitrile.[248] Copper(I) chloride was prepared by the reduction of copper(II) sulphate in aqueous solution using sulphur dioxide, in the presence of NaCl.[249] Anhydrous nickel(II) chloride was prepared by dehydration of nickel(II) chloride hexahydrate in an oven at 270°C for 3 hours. Hexakis(acetonitrile)nickel(II) tetrafluoroborate was prepared by treating an acetonitrile solution of hydrated nickel(II) tetrafluoroborate with ethylorthoformate.[250] Bis(benzonitrile)palladium(II) chloride and bis(benzonitrile)platinum(II) chloride were prepared by dissolving the metal halides in hot benzonitrile and isolating the crystalline products by filtration of the cooled mixtures. Chloro(tetrahydrothiophene)gold(I) was precipitated from an ethanolic solution of $NaAuCl_4$ by treatment with excess tetrahydrothiophene.[251] Bicycloheptadiene molybdenum tetracarbonyl was prepared from molybdenum hexacarbonyl and bicycloheptadiene in refluxing methylcyclohexane[252].

7.3. Preparations and reactions involving derivatives of carboxylic acids with additional nitrogen donors

7.3.1. Bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) **N1**

Method A: A flame-dried 100cm^3 two-necked round bottomed flask fitted with reflux condenser and magnetic stirring bar was charged with 0.50g (2.0mmol) of bis(cyclopentadienyl)titanium dichloride and 0.56g (5.2mmol) of sodium cyanoacetate. Freshly distilled tetrahydrofuran (25cm^3) was added and the reaction mixture was refluxed under nitrogen for 1 hour. The orange solution produced after cooling and filtration was evaporated to dryness to give 0.46g (66%) of a bright orange solid. Blood red octahedral crystals suitable for X-ray crystallographic analysis were obtained on slow evaporation of a chloroform solution under nitrogen. Analysis; Found (calc. $C_{16}H_{14}N_2O_4Ti$): C 55.4(55.5); H 4.01(4.08); N 7.98(8.09)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.47(s, 4H, -CH_2-), 6.63(s, 10H, η-C_5H_5); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=26.9(s, -CH_2-), 115.2(s, -CN), 116.7, 119.4(s, η-C_5H_5), 167.2(s, -CO_2-). IR (NaCl, hexachlorobutadiene mull), ν(cm^{-1})=3100s, 2961m, 2928m, 2255m, 1670vs, 1446m, 1360vs, 1310vs, 1254vs, 1019m, 826s. MS FAB+, m/z=344(33), 281(9), 262(100), 218(69), 178(45), 149(30), 107(60), 95(48), 81(49); FAB-, m/z=346(23), 297(18), 278(18), 237(12), 212(12), 84(100).

Method B: Bis(cyclopentadienyl)titanium dichloride [0.50g (2.0mmol)] was dissolved in 40cm^3 of degassed, distilled water by stirring for 2 hours. To this orange solution, 1.00g (9.3mmol) of sodium cyanoacetate in 10cm^3 of distilled water was added and the mixture stirred for 1 hour at room temperature. The product was obtained by extraction of the aqueous phase using three 50cm^3 portions of dichloromethane, which were then dried over magnesium sulfate. Slow evaporation of this solution yielded 2.59g (75%) of **N1** as red crystals. Analysis; Found (calc. $C_{16}H_{14}N_2O_4Ti$) C 55.8(55.5); H 4.15(4.08); N 7.55(8.09)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.39(0.5H), 3.45(s, 4H, -CH_2-), 6.36(1.3H), 6.63(s, 10H, η-C_5H_5).

Method C: A 100cm^3 round bottomed flask fitted with a magnetic stirring bar was charged with 0.50g (2.0mmol) of bis(cylopentadienyl)titanium dichloride and 1.15g (6.0mmol) of silver cyanoacetate. After the addition of 40cm^3 of chloroform, the reaction mixture was stirred in the dark for 1 hour at room temperature. Filtration and evaporation of the bright orange chloroform solution gave 0.56g (81%) of a red crystalline solid. Analysis; Found (calc. $C_{16}H_{14}N_2O_4Ti$): C 55.1(55.5); H 4.03(4.08); N 8.20(8.09)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.46(s, 4H, -CH_2-), 6.63(s, 10H, η-C_5H_5).

Method D: A solution of 50mg (0.24mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 3cm^3 of freshly distilled tetrahydrofuran, was added with stirring to a solution of 41mg (0.48mmol) of cyanoacetic acid in 2cm^3 of tetrahydrofuran. Effervescence was observed along with a colour change from yellow/orange to bright orange. Evaporation of the solvent *in vacuo* gave 69mg (83%) of a bright red crystalline solid. Analysis; NMR ($CDCl_3$) ^{1}H (270.1MHz) δ (ppm)=3.45(s, 4H, -CH_2-), 6.62(s, 10H, η-C_5H_5).

Method E: A flame-dried 100cm^3 two-necked round bottomed flask fitted with a magnetic stirring bar was charged with 0.25g (1.0mmol) of bis(cyclopentadienyl)titanium dichloride and 0.39g (2.0mmol) of silver(I) tetrafluoroborate. Acetonitrile (10cm^3) was added and the suspension stirred for 1.5 hours at room temperature. Filtration under dry nitrogen to remove AgCl produced a maroon solution which was added slowly to 0.55g (5.0mmol) of sodium cyanoacetate. This mixture was stirred for 2 hours and then filtered in air to give an orange solution. On evaporation an oil was produced only a small part of which was soluble in dichloromethane. The remaining orange residue was dried *in vacuo* to give an orange/yellow solid, which on leaving in air overnight decomposed to a grey oil. The dichloromethane solution was evaporated and taken into $CDCl_3$ in order to record a ^{1}H NMR spectrum. ($CDCl_3$, 270.1MHz) δ(ppm)=3.47(s, 1H), 3.49(s, 4H, -CH_2-), 3.52(s), 3.57(s), 5.32(s), 6.49, 6.56(s, 2H), 6.59, 6.64(s, 10H, η-C_5H_5), 6.67(s), 7.60(broad, 1H).

7.3.2. Bis(cyanoacetato)bis(cyclopentadienyl)zirconium(IV) N2

A 25cm^3 flask fitted with a magnetic stirring bar was charged with 0.10g (0.34mmol) of bis(cyclopentadienyl)zirconium dichloride and 0.13g (0.68mmol) of silver cyanoacetate. After addition of 10cm^3 of chloroform, this mixture was stirred overnight at room temperature and then filtered to remove AgCl. The colourless solution was evaporated to give 98mg (74%) of a white solid. Analysis; Found (calc. $C_{16}H_{14}N_2O_4Zr$): C 48.8(49.3); H 3.56(3.62); N 7.05(7.19)%. NMR ($CDCl_3$) ^{1}H (270.1MHz) δ(ppm)=3.43(s, 4H, -CH_2-), 6.36(s, 10H, η-C_5H_5); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=26.5(s, -CH_2-), 113.5(s, -CN), 115.0(s, η-C_5H_5), 170.5(s, -CO_2-). IR (NaCl, liquid paraffin mull), v(cm^{-1})=3117m, 3094w, 2265m, 1663s, 1553s, 1456s, 1393s, 1309vs, 1271m, 1019m, 932m, 920w, 827s, 747m, 698m.

7.3.3. Bis(anthranilato)bis(cyclopentadienyl)titanium(IV) N3

Method A: A flame-dried 100cm^3 two-necked round bottomed flask fitted with a magnetic stirring bar was charged with 0.50g (2.0mmol) of bis(cyclopentadienyl)titanium dichloride and

1.25g (8.0mmol) of sodium anthranilate. Freshly distilled toluene (50cm^3) was added and the reaction mixture stirred at 40°C for 2 hours. Filtration and evaporation gave 0.14g of an orange crystalline solid. The residue from the fitration was stirred in warm dichloromethane and filtered, as the product was only partially soluble in toluene. This solution was evaporated to give 71mg of an orange solid. The remainder of the titanium-containing material was extracted by washing the residue with distilled water, filtering and washing with ethanol followed by diethyl ether. This gave a further 0.25g of solid. The three fractions were spectroscopically similar (IR, ^{1}H NMR). Combined yield; 0.46g (51%). Analysis (3rd fraction); Found (calc. $C_{24}H_{22}N_2O_4Ti$): C 63.3(64.0); H 4.82(4.92); N 5.98(6.22)%. NMR ($CDCl_3$) ^{1}H (270.1MHz) δ(ppm)=6.02(very broad, -N*H*$_2$), 6.59(s, 10H, η-C$_5$*H*$_5$), 6.66(m, 6.2H, *phenyl*), 7.24(m, 3.7H, *phenyl/CH*Cl$_3$), 7.85(m, 1.5H, *phenyl*), 7.92(broad). IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3436m, 3326m, 1615s, 1578s, 1539s, 1356s, 1331s, 1298s, 1248vs, 1161s, 1130w, 818m, 801m, 749m.

Method B: Bis(cyclopentadienyl)titanium dichloride [0.50g (2.0mmol)] was dissolved in 30cm^3 of degassed, distilled water by stirring for 2 hours. A solution of 1.25g (8.0mmol) of sodium anthranilate in 20cm^3 of distilled water was added dropwise to give a bright yellow precipitate. The reaction mixture was filtered and the residue washed consecutively with several portions of distilled water, ethanol, and diethyl ether. Yield; 0.46g (51%) of an orange microcrystalline solid. Analysis; Found (calc. $C_{24}H_{22}N_2O_4Ti$): C 64.7(64.0); H 5.03(4.92); N 5.88(6.22)%. NMR ($CDCl_3$) ^{1}H (270.1MHz) δ(ppm)=5.58(very broad, -N*H*$_2$), 6.62(s, 10H, η-C$_5$*H*$_5$), 6.66-6.70(m, 4H, *phenyl*), 7.25(m, 3H, *phenyl/CHCl$_3$*), 7.85(m, 2H, *phenyl*), 7.92(broad). IR (NaCl, nujol mull), ν(cm^{-1})=3440m, 3330m, 1615s, 1578s, 1541s, 1356s, 1331s, 1298s, 1260s, 1161s, 1130w, 1019w, 818m, 801m, 748m; (NaCl, hexachlorobutadiene mull), ν(cm^{-1})=3438m, 3328m, 3110vw. MS FAB+, m/z=385(8), 344(90), 330(7), 314(73), 205(10), 178(15), 149(100); FAB-, m/z=510(40), 447(51), 439(48), 431(28), 339(67), 325(100), 312(87), 289(44), 264(60), 178(18), 135(22).

7.3.4. Bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4

A flame-dried 100cm^3 two-necked round bottomed flask fitted with reflux condenser and magnetic stirring bar was charged with 0.50g (2.0mmol) of bis(cyclopentadienyl)titanium dichloride and 1.00g (6.9mmol) of sodium nicotinate. Freshly distilled tetrahydrofuran (25cm^3) was added and the reaction mixture was refluxed under nitrogen for 1 hour and then allowed to cool. Sodium salts were removed by filtration and the resulting orange solution layered with hexanes. Upon standing at 4°C bright orange-red crystals suitable for single crystal X-ray analysis were formed. Yield; 125mg (15%). Analysis; Found (calc. $C_{22}H_{18}N_2O_4Ti$): C 62.9(62.6); H 4.30(4.30); N 6.66(6.63)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=6.66(s, 9.5H, η-C_5H_5), 7.42(dd, 2.2H, *pyridyl*), 8.28(dt, 2.0H, *pyridyl*), 8.76(dd, 2.0H, *pyridyl*), 9.21(d, 2.0H, *pyridyl*); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=118.8(s, η-C_5H_5), 123.2(s, *pyridyl*), 129.2(s, *pyridyl*), 137.2(s, *pyridyl*), 151.0(s, *pyridyl*), 152.0(s, *pyridyl*), 170.1(s, -CO_2-). IR (NaCl, nujol mull), ν(cm^{-1})=3106s, 3049w, 1634vs, 1588m, 1423m, 1350vs, 1325s, 1306vs, 1154s, 1028m, 866w, 824s, 724m, 694m. MS FAB+, m/z=344(48), 300(100); FAB-, m/z=510(46), 466(64), 447(24), 422(26), 417(38), 373(25), 303(29), 289(24), 275(100), 123(36).

7.3.5. Bis(cyclopentadienyl)bis(glycine)titanium dichloride **N5**

Bis(cyclopentadienyl)bis(glycine)titanium dichloride **N5** was prepared by the method of Klapötke *et al.*[126] Bis(cyclopentadienyl)titanium dichloride (0.50g, 2.0mmol) and glycine (0.30g, 4.0mmol) were stirred in 5cm^3 of methanol at room temperature for 4 hours. The resulting orange precipitate was removed by filtration and dried *in vacuo* to give 0.36g (45%) of a bright orange powder. Analysis; Found (calc. $C_{14}H_{20}Cl_2N_2O_4Ti$): C 41.7(42.1); H 5.10(5.05); N 6.75(7.02)%. ^1H NMR (D_2O, 270.1MHz) δ(ppm)=3.65(s, 5.8H, -CH_2-), 6.57(s, 10.0H, η-C_5H_5).

7.3.6. Attempted preparations of bis(amino acidato)bis(cyclopentadienyl)titanium(IV) complexes

7.3.6.1. Reactions of bis(cyclopentadienyl)titanium dichloride with the sodium salts of glycine and β-alanine

(i) A flame-dried 100cm^3 round bottomed flask fitted with a magnetic stirring bar and reflux condenser was charged with 0.50g (2.0mmol) of bis(cyclopentadienyl)titanium dichloride and 0.97g (10.0mmol) of sodium glycinate. After the addition of 25cm^3 of tetrahydrofuran the reaction mixture was refluxed for two hours. Filtration of the cooled mixture produced 0.96g (after drying) of an off-white solid, and a bright red solution. Evaporation of the solution produced 0.42g of a dull red solid. Analysis; Found (calc. $C_{14}H_{18}N_2O_4Ti$): C 48.2(51.6); H 3.98(5.56); N 0.00(8.59)%. Calculated for $C_{10}H_{10}Cl_2Ti$: C 48.2, H 4.05%. The IR spectrum (CsI, liquid paraffin mull) was identical to that of Cp_2TiCl_2.

(ii) A flame-dried 100cm^3 round bottomed flask fitted with a magnetic stirring bar was charged with 0.50g (2.0mmol) of bis(cyclopentadienyl)titanium dichloride and 0.92g (9.5mmol) of sodium glycinate. After the addition of 25cm^3 of MeCN the reaction mixture was stirred at room temperature. Samples were taken for IR and ^{1}H NMR analysis after 4 hours, 6 hours and after overnight stirring during which period the colour changed from red to yellow. Analysis (after 6 hours); IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3105m, 1653w, 1458m, 1306w, 1017m, 820s. ^{1}H NMR [$(CD_3)_2CO$, 270MHz], δ(ppm)=2.98(s), 6.51(s), 6.61(s), 6.67(s), 6.77(s).

(iii) The above procedure was repeated using sodium β-alaninate in place of sodium glycinate. Stirring overnight at room temperature gave a yellow reaction mixture, which was filtered and evaporated to give an orange solid. Analysis; ^{1}H NMR [$(CD_3)_2CO$, 270MHz], δ(ppm)=1.20(very broad), 1.40(broad), 2.96(s), 6.52(s).

7.3.6.2. Reaction of bis(cyclopentadienyl)titanium dichloride with silver glycinate

A flame-dried 100cm^3 round bottomed flask fitted with a magnetic stirring bar was charged with 0.25g (1.0mmol) of bis(cyclopentadienyl)titanium dichloride and 0.55g (3.0mmol) of silver glycinate. After the addition of 20cm^3 of MeCN the reaction mixture was stirred for 3 hours at room temperature giving a colour change from orange to yellow. Filtration and evaporation yielded an orange solid. Analysis; IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3104m, 1662s, 1526m, 1456m, 1402w, 1306s, 1015s, 810vs. ^{1}H NMR ($CDCl_3$, 270MHz), δ(ppm)=1.25(broad), 1.72(very broad), 6.1-6.6(m).

7.3.6.3. Reaction of bis(cyclopentadienyl)bis(methyl)titanium(IV) with glycine

An orange solution of 50mg (0.24mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in tetrahydrofuran (3cm^3) was added to a suspension of 36mg (0.48mmol) of glycine in tetrahydrofuran (2cm^3) with stirring. After stirring overnight, no colour change was observed and the amount of solid in the reaction mixture remained the same. Tetrahydrofuran was removed *in vacuo* and 5cm^3 of MeCN added. Again after stirring overnight, no change was noted. The reaction mixture was filtered and evaporated to give a light sensitive orange solid. Analysis; IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3108vw, 1653w, 1306w, 1020m, 812vs. ^{1}H NMR ($CDCl_3$, 270MHz), δ(ppm)=-0.14(s, 4H), 0.23(s), 0.84, 3.00, 5.9-6.6(m, weak), 6.07(s, 10H).

7.3.6.4. Reactions of bis(cyclopentadienyl)titanium dichloride with silver(I) tetrafluoroborate and subsequent reactions of these products with sodium glycinate and sodium β-alaninate

(i) A flame-dried 100cm^3 round bottomed flask fitted with a magnetic stirring bar was charged with 0.25g (1.0mmol) of bis(cyclopentadienyl)titanium dichloride and 0.40g (2.0mmol) of silver(I) tetrafluoroborate. After the addition of 10cm^3 of tetrahydrofuran the reaction mixture was stirred at room temperature to give the rapid formation of a grey suspension in an orange solution. Filtration under nitrogen in flame-dried equipment produced a bright orange solution which was added slowly to 0.39g (2.0mmol) of sodium glycinate. Stirring for 3 hours at room temperature and filtration under nitrogen gave a bright red solution and an orange residue. Analysis (red filtrate); IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3106m, 1017m, 822s; (CsI, liquid paraffin mull), ν(cm^{-1})=400m, 360m, 290m, 250w. ^{1}H NMR ($CDCl_3$, 270MHz), δ(ppm)=0.86(m), 1.24(broad), 1.61(m), 3.41(m), 6.51(s), 6.59(s). Analysis (orange residue); ^{1}H NMR [$(CD_3)_2CO$, 270MHz], δ(ppm)=4.08(very broad), 4.30(broad), 4.71, 4.73, 4.95(s), 6.6-7.0(m).

(ii) A flame-dried 100cm^3 round bottomed flask fitted with a magnetic stirring bar was charged with 0.25g (1.0mmol) of bis(cyclopentadienyl)titanium dichloride and 0.40g (2.0mmol) of silver(I) tetrafluoroborate. After the addition of 10cm^3 of acetonitrile the reaction mixture was stirred at room temperature and a dark maroon suspension resulted. Filtration under nitrogen in flame-dried equipment gave a white residue (confirmed to be AgCl by X-ray powder diffraction) and a maroon solution. The solution was added slowly to 0.39g (2.0mmol) of sodium glycinate with a rapid colour change to yellow. Stirring for 3 hours at room temperature and filtration under nitrogen gave an orange solution. A yellow and orange solid was produced on removal of the solvent *in vacuo*. Analysis; ^{1}H NMR (CD_3CN, 270MHz), δ(ppm)=2.79(broad), 3.70(broad), 3.82(s), 6.3-6.7(m).

(iii) The above procedure was repeated using sodium β-alaninate in place of sodium glycinate. Similar results were obtained.

7.3.7. Attempted reactions of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1 with transition metal species

7.3.7.1. Reaction of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1 with silver(I) tetrafluoroborate

A 25cm^3 flame-dried flask fitted with a magnetic stirring bar was charged with 0.10g (0.29mmol) of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1 and 0.12g (0.76mmol) of $AgBF_4$. After the addition of 5cm^3 of freshly distilled tetrahydrofuran the reaction mixture was stirred overnight at room temperature. Filtration and evaporation of the reaction mixture gave a black insoluble solid. Analysis; IR (NaCl, liquid paraffin mull), ν(cm^{-1})=1732m, 1617m, 1225w, 1070m.

7.3.7.2. Reaction of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1 with molybdenum hexacarbonyl

A 100cm^3 flame-dried flask fitted with a magnetic stirring bar was charged with 0.45g (1.7mmol) of molybdenum hexacarbonyl and 10cm^3 of freshly distilled toluene. A solution of 0.25g (0.7mmol) of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1 in toluene (25cm^3) was added to this white suspension and the reaction mixture stirred at room temperature for 4 days. Since no significant change was observed a small sample of the reaction mixture was taken for analysis, while the remainder was heated to 65°C for 5 hours. Analysis (after stirring at room temperature for 4 days); ^{1}H NMR ($CDCl_3$, 270MHz), δ(ppm)=2.80(broad), 3.46(s, 4H), 6.62(s, 10H). IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3096m, 2255m, 1987vs, 1665vs, 1307s, 1254s, 1019m, 826s. Analysis (after additional 5 hours heating); ^{1}H NMR ($CDCl_3$, 270MHz), δ(ppm)=2.35(s), 3.44(s), 3.45(s), 3.47(s, 4H), 3.67(d), 6.36(s), 6.60(s), 6.62(s, 10H), 6.63(s). IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3096m, 2255m, 1987vs, 1663vs, 1306s, 1252s, 1017m, 826s.

7.3.7.3. Reaction of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1 with tetrakis(acetonitrile)copper(I) perchlorate

A 25cm^3 flame-dried flask fitted with a magnetic stirring bar was charged with 0.10g (0.29mmol) of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1 and 0.25g (0.76mmol) of tetrakis(acetonitrile)copper(I) perchlorate. Addition of 10cm^3 of acetonitrile produced an orange solution which after overnight stirring at room temperature, showed no significant change. Evaporation of the reaction mixture gave an non-homogeneous solid containing orange and white particles. Analysis; ^{1}H NMR ($CDCl_3$, 270MHz), δ(ppm)=1.25(s), 2.02(s), 2.19(s), 2.65(s), 3.1(broad), 3.45(s), 6.36(s), 6.62(s).

7.3.7.4. Reaction of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1 with palladium(II) chloride

A 25cm^3 flame-dried flask fitted with a magnetic stirring bar was charged with 0.10g (0.29mmol) of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) **N1** and 0.05g (0.29mmol) of $PdCl_2$. After the addition of 5cm^3 of freshly distilled tetrahydrofuran the reaction mixture was stirred at room temperature for 4 days. Filtration gave a black solid residue and a yellow solution, which after evaporation, yielded an orange solid. Analysis (black residue); IR (CsI, liquid paraffin mull), ν(cm^{-1})=340m [ν(Pd-Cl)]. Analysis (orange filtrate); IR (KBr disc), ν(cm^{-1})=3114w, 2260m, 1736s, 1655sh, 1570vs, 1420s, 1383s, 1277m, 1019m, 836s.

7.3.8. Reaction of bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4 with bis(benzonitrile)palladium(II) chloride and bis(benzonitrile)platinum(II) chloride

7.3.8.1. Bis(cyclopentadienyl)bis(nicotinato)titanium(IV) palladium(II) chloride N6

A solution of 45mg of $(C_6H_5CN)_2PdCl_2$ (0.12mmol) in 5cm^3 of tetrahydrofuran was added dropwise with stirring to a solution of N4 (50mg, 0.12mmol) in 10cm^3 of tetrahydrofuran to give an orange suspension. After stirring for a further 24 hours, the precipitate was removed by filtration and washed with tetrahydrofuran. Yield, 99mg (69%). Analysis; Found (calc. $C_{22}H_{18}Cl_2N_2O_4PdTi$): C 44.0(44.1); H 3.41(3.03); N 4.57(4.67)%. IR (CsI, nujol mull), ν(cm^{-1})=3482(broad), 3108w, 1727m, 1642vs, 1572w, 1462m, 1319vs, 1190w, 1154m, 1113w, 1061w, 1019w, 938vw, 828s, 750s, 704m, 689m, 571m, 436w, 358w, 268w, 252sh, 246w.

7.3.8.2. Bis(cyclopentadienyl)bis(nicotinato)titanium(IV) platinum(II) chloride N7

Solutions of 34mg of $(C_6H_5CN)_2PtCl_2$ (0.07mmol) in 2cm^3 of dichloromethane and N4 (30mg, 0.07mmol) in 3cm^3 of dichloromethane were added together and stirred for a few seconds. The resulting solution was allowed to stand for 48 hours, after which time an orange suspension had formed. The precipitate was removed by filtration and washed with tetrahydrofuran to yield 18mg (37%). Analysis; Found (calc. $C_{22}H_{18}Cl_2N_2O_4PtTi$): C 37.0(38.4); H 2.79(2.64); N 4.40(4.07)%.

7.4. Preparations involving derivatives of carboxylic acids with additional oxygen donors

7.4.1. Bis(cyclopentadienyl)(salicylato)titanium(IV) O1

Bis(cyclopentadienyl)titanium dichloride [0.60g (2.4mmol)] was dissolved in 40cm^3 of degassed, distilled water by stirring for 2 hours. The orange solution was filtered to remove a small amount of undissolved material and 0.34cm^3 (2.4mmol) of triethylamine added. This produced a colour change from orange to dark red. A solution of 0.10g (2.4mmol) of sodium hydroxide and 0.34g (2.4mmol) of salicylic acid in 10cm^3 of distilled water was added dropwise with stirring over a period of 10 minutes. giving a red/brown precipitate, and a maroon solution. The reaction mixture was filtered and the aqueous solution extracted with 2×20cm^3 portions of dichloromethane. The organic phases were combined, washed with 20cm^3 of distilled water and dried over magnesium sulfate. This solution was then evaporated to a smaller volume and hexanes added to precipitate small dark maroon crystals suitable for X-ray crystallography. Yield; 0.20g (27%). The residue precipitated during the reaction was dissolved in dichloromethane, dried over magnesium sulfate and precipitated out of solution by adding hexanes, to give another 0.30g of **O1**. Evaporation of the mother liquor yielded a further 0.14g of the raw product. Combined raw yield = 0.64g (80%). Analysis (1st fraction); Found (calc. $C_{17}H_{14}O_3Ti$): C 64.6(65.0); H 4.42(4.49)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=1.62(broad), 6.40(s, 10H, η-C_5H_5), 6.63(m, 1H, *phenyl*), 6.88(m, 1H, *phenyl*), 7.38(m, 1H, *phenyl*), 8.16(m, 1H, *phenyl*); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=118.5(*phenyl*), 118.6 (η-C_5H_5), 119.3(*phenyl*), 120.5(*phenyl*), 132.3(*phenyl*), 133.3(*phenyl*), 167.3(*phenyl*), 170.3 (-CO_2-). IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3073w, 1622s, 1593m, 1450vs, 1337s, 1136m, 1129sh, 1032w, 1013w, 884m, 820s, 760m. MS FAB+, m/z=344(23), 315(100), 250(7), 205(21), 178(10); FAB-, m/z=314(100), 265(51), 137(50).

7.4.2. Bis(cyclopentadienyl)bis(salicylato)titanium(IV) O2

A flame-dried 100cm^3 two-necked round bottomed flask fitted with a magnetic stirring bar was charged with 0.50g (2.0mmol) of bis(cyclopentadienyl)titanium dichloride and 1.28g (8.0mmol) of sodium salicylate. Freshly distilled toluene (50cm^3) was added and the reaction mixture stirred at 35°C for 6 hours. After filtration, the orange solution was evaporated to approximately one tenth of the initial volume, and stored at 4°C overnight. On filtration this yielded 0.46g (51%) of an orange microcrystalline solid. Analysis; Found (calc. $C_{24}H_{20}O_6Ti$): C 63.6(63.7); H 4.44(4.46)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=6.42[s, η-C_5H_5(monosalicylate)], 6.67(s, 10H η-C_5H_5), 6.89(m, 2.8H, *phenyl*), 7.01(m, 2.5H, *phenyl*), 7.44(m, 2.9H, *phenyl*), 7.83(m, 2H, *phenyl*), 7.94[dd, (salicylic acid)], 8.19[dd, (monosalicylate)], 10.9[very broad, (salicylic acid)], 11.93(broad, 2H, -O*H*).

Carrying out the above reaction in aqueous media, or treating salicylic acid with bis(cyclopentadienyl)bis(methyl)titanium(IV) produced identical results.

7.4.3. Bis(cyclopentadienyl)bis(diphenylphosphinylacetato)titanium(IV) O3

To a suspension of 0.60g (2.3mmol) of diphenyphosphinylacetic acid in 5cm^3 of dichloromethane, a solution of 0.24g (1.1mmol) of bis(cyclopentadienyl)-bis(methyl)titanium(IV) in 1cm^3 of dichloromethane was added dropwise with stirring. An additional 2cm^3 of dichloromethane were added and the reaction stirred at room temperature for a further 5 minutes. Removal of the solvent *in vacuo* resulted in 0.69g (90%) of a bright orange solid. Analysis; Found (calc. $C_{38}H_{34}O_6P_2Ti$): C 63.4(65.5); H 4.90(4.92)%. NMR ($CDCl_3$); ^1H (270.1MHz) δ(ppm)=3.35(d, 4.0H, $^2J(^{31}P-^1H)$=13.7Hz, $-CH_2-$), 6.34(d, 9.2H, J=0.55Hz, η-C_5H_5), 7.53(broad, 12.8H, *phenyl*), 7.89(m, 9.4H, *phenyl*); $^{13}C\{^1H\}$ (100.4MHz) δ(ppm)=40.3(d, J=63.0Hz, $-CH_2-$), 118.6(s, η-C_5H_5), 128.3(d, J=10.1Hz, *phenyl*), 130.6(d, J=10.2Hz, *phenyl*), 131.6(s, *phenyl*), 132.8(d, J=101.7Hz, *phenyl*), 170.0(d, J=4.1Hz, $-CO_2-$); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=28.7(s). IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3054w, 1715m, 1636vs, 1437s, 1294vs, 1190s, 1121s, 1100m, 1071w, 1019m, 826s, 747w, 729m, 694s. MS FAB+, m/z=651(<1), 521(4), 461(<1), 437(10), 344(12), 261(100), 201(32); FAB-, m/z=698(12), 625(16), 606(34), 592(15), 565(18), 510(38), 487(20), 474(32), 460(34), 440(20), 426(53), 412(56), 352(27), 335(33), 322(28), 303(38), 290(28), 275(15), 259(100), 215(60).

7.5. Preparations and reactions involving derivatives of carboxylic acids with additional phosphorus donors

7.5.1.Bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1**

A solution of 0.33g (1.6mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 6cm^3 of dichloromethane was added dropwise to a solution of 0.77g (3.2mmol) of diphenylphosphinoacetic acid in 4cm^3 of dichloromethane. After stirring for 6 hours the solvent was removed on a rotary evaporator to yield 1.01g (95%) of an air-stable brown solid. Recrytallisation from a dichloromethane solution layered with hexanes gave bright orange cubes suitable for a single crystal X-ray diffraction experiment. Analysis; Found (calc. $C_{38}H_{34}O_4P_2Ti$): C 67.6(67.7), 5.13(5.17)%. NMR ($CDCl_3$) ^{1}H (270.1MHz) δ(ppm)=2.96(s, 4H, -C*H*$_2$-), 6.01(s, 10H, η-C$_5$*H*$_5$), 7.10(m, 13H, *phenyl*), 7.29(m, 9H, *phenyl*); ^{13}C{^{1}H} (67.8MHz) δ(ppm)=37.6(d, J=17.6Hz, -*C*H$_2$-), 118.2(s, η-*C*$_5$H$_5$), 128.3(d, J=6.6Hz, *phenyl*), 128.6(s, *phenyl*), 132.6(d, J=19.8Hz, *phenyl*), 138.4(d, J=15.4Hz, *phenyl*), 175.4(d, J=8.8Hz, *phenyl*); ^{31}P{^{1}H} (109.3MHz) δ(ppm)=-17.6. IR (NaCl, liquid paraffin mull) ν(cm^{-1})=3100w, 3056vw, 1649m, 1618s, 1464w, 1433w, 1325s, 1285s, 1271sh, 1167w, 1117m, 1019w, 824m, 741m, 696m. MS FAB+, m/z=665(1), 615(18), 599(4), 522(7), 508(42), 437(36), 421(82), 344(34), 261(26), 245(100), 227(33), 215(22), 201(42), 185(42); FAB-, m/z=682(13), 664(7), 587(15), 396(30), 259(40), 243(100), 215(43), 200(17), 188(30).

7.5.2. Coordination of diphenylphosphinoacetic acid to transistion metal species *via* phosphorus

7.5.2.1. Bis(diphenylphosphinoacetic acid)molybdenum tetracarbonyl **P2**

Bicycloheptadiene molybdenum tetracarbonyl (1.0g, 3.3mmol) and diphenylphosphinoacetic acid (1.6g, 6.7mmol) were dissolved in 20cm^3 of dichloromethane and stirred at room temperature for 18 hours. The resulting precipitate was removed by filtration and washed with dichloromethane yielding 2.2g (96%) of a white powder. Analysis; Found(calc. $C_{32}H_{26}MoO_8P_2$): C 55.1(55.2); H 3.72(3.76)%. NMR [$(CD_3)_2CO$)] ^{1}H (270.1MHz) δ(ppm)=3.25(m, 4.0H, -C*H*$_2$-), 7.39(m, 8.0H, *phenyl*), 7.51(m, 11.4H, *phenyl*); ^{13}C{^{1}H} (67.8MHz) δ(ppm)=37.8(s, -*C*H$_2$-), 129.0(d, J=17.6Hz, *phenyl*), 130.4(s, *phenyl*), 133.1(d, J=12.1Hz, *phenyl*), 137.3(d, J=33.1Hz, *phenyl*), 169.4(s, -*C*O$_2$-), 210.2(d, J=9.9Hz, -*C*O), 216.1(d, J=17.6Hz, -*C*O); ^{31}P{^{1}H} (109.3MHz) δ(ppm)=25.0. IR (CsI, liquid paraffin mull) ν(cm^{-1})=2027s, 1921vs, 1910sh, 1879vs, 1701s, 1435s, 1296m, 1267w, 1176w, 737m, 694m, 611m, 588m, 585m. MS FAB+, m/z=698(5), 670(2), 642(13), 614(1), 586(7), 454(33), 426(17), 342(17), 298(10), 245(100), 201(9), 183(18); FAB-, m/z=697(11), 669(9), 640(8), 612(27), 453(97), 425(100), 243(8).

7.5.2.2. Tetrakis(diphenylphosphinoacetic acid)nickel(II) tetrafluoroborate P3

Hexa(acetonitrile)nickel(II) tetrafluoroborate (0.25g, 0.51mmol) and diphenylphosphinoacetic acid (0.50g, 2.05mmol) were dissolved in 10cm^3 of dichloromethane to give a dark green solution. After stirring for 2 hours the solvent was removed *in vacuo* yielding 0.42g (68%) of a brown solid. On standing in air for several days the colour of the solid changes from brown to green. Analysis; Found(calc. $C_{56}H_{52}B_2F_8NiO_8P_4$): C 54.5(55.6); H 4.37(4.33)%. NMR ($CDCl_3$) ^{1}H (270.1MHz) δ(ppm)=3.16(broad, 8.0H, -CH_2-), 7.29(broad, 45H, *phenyl*); ^{31}P{^{1}H} (109.3MHz) δ(ppm)=-13.0. IR (NaCl, liquid paraffin mull) v(cm^{-1})=3528br, 3462m, 3216br, 3075w, 1700vs, 1635w, 1435m, 1397w, 1287s, 1196w, 1121m, 1069w, 1038w, 999w, 932w, 914w, 793m, 745s, 739s, 693s, 667m. MS FAB+, m/z=847(2), 680(2), 567(20), 545(35), 302(20), 261(70), 245(62), 210(100); FAB-, m\z=619(6), 554(5), 544(5), 467(4), 412(7), 393(6), 359(4), 331(10), 172(10) 259(19), 240(42), 220(31), 197(15), 87(100). Magnetic moment (Evans' NMR method); 2.04B.M.

7.5.2.3. Bis(diphenylphosphinoacetic acid)palladium(II) chloride P4

Bis(benzonitrile)palladium(II) chloride (0.25g, 0.65mmol) was added to a solution of 0.32g (1.30mmol) of diphenylphosphinoacetic acid in 10cm^3 of dichloromethane and stirred for 24 hours. A yellow-green precipitate was isolated by filtration. Yield, 0.40g (92%). Analysis; Found(calc. $C_{28}H_{26}Cl_2O_4P_2Pd$): C 50.1(50.5); H 3.88(3.94); N 0.54(0.00)%. NMR (CD_3CN) ^{1}H (270.1MHz) δ(ppm)=3.71(d, 4.0H, J=12.5Hz, -CH_2-), 7.31(m, 4.3H, *phenyl*), 7.54(m, 14.0H, *phenyl*), 7.83(m, 4.5H, *phenyl*); ^{13}C{^{1}H} (67.8MHz) δ(ppm)=129.6(m, *phenyl*), 132.1(m, *phenyl*), 133.7(s, *phenyl*), 134.6(m, *phenyl*), 141.0. ^{31}P{^{1}H} (109.3MHz) δ(ppm)=12.4. IR (CsI, liquid paraffin mull) v(cm^{-1})=3131m, 1732s, 1707s, 1482w, 1437s, 1350m, 1240w, 1152s, 1123m, 1103m, 851m, 743s, 693s, 552w, 515m, 493w, 461w, 318w, 297w, 262vw. MS FAB+, m/z=1186(10), 942(3), 631(46), 593(100), 549(65), 349(20), 305(32), 245(37); FAB-, m/z=1257(5), 665(8), 628(54), 585(48), 541(24), 473(36), 384(46), 341(65), 188(100).

Recrystallisation from ethanol gave yellow box-like solvated crystals. Analysis; Found(calc. $C_{86}H_{86}Cl_6O_{14}P_6Pd_3$): C 50.1(50.6); H 4.57(4.20)%. IR (CsI, liquid paraffin mull) v(cm^{-1})=1724sh, 1705s, 1694vs, 1462s, 1435s, 1302s, 1272sh, 1188w, 1146w, 1100m, 1028w, 999w, 853m, 746s, 693s, 532m, 522s, 506m, 370w.

7.5.2.4. Bis(diphenylphosphinoacetic acid)platinum(II) chloride P5

A solution of 90mg (0.37mmol) of diphenylphosphinoacetic acid in 1cm^3 of dichloromethane was added to a solution of 87mg (0.18mmol)of bis(benzonitrile)platinum(II) chloride in 2cm^3 of dichloromethane. A further 1cm^3 of solvent was added and the mixture stirred for 10 minutes to give a colourless solution. Allowing the solution to stand for 18 hours produced 103mg (76%) of a white crystalline material. Analysis; Found(calc. $C_{28}H_{26}Cl_2O_4P_2Pt$): C 45.2(44.6); H 3.49(3.47); N 0.26(0.00)%. NMR (CD_3CN) ^{1}H (270.1MHz) δ(ppm)=3.63(d, 4.0H, J=11.7Hz, -CH_2-), 7.28-7.67(m, 25H, *phenyl*); ^{13}C{^{1}H} (67.8MHz) δ(ppm)=33.2(s, -CH$_2$-), 129.4(m, *phenyl*), 132.4(s, *phenyl*), 134.7(m, *phenyl*); ^{31}P{^{1}H} (109.3MHz) δ(ppm)=3.0[^{1}J(^{195}Pt-^{31}P)=3789.5Hz]. IR (CsI, liquid paraffin mull) ν(cm^{-1})=3058vw, 1734sh, 1696s, 1483w, 1437s, 1300m, 1144w, 1101m, 855w, 743m, 693m, 525w, 520w, 332w, 303w, 270sh, 266w.

7.5.2.5. (Diphenylphosphinoacetic acid)copper(I) chloride P6

Copper(I) chloride (0.20g, 2.0mmol) was stirred in a solution of diphenylphosphinoacetic acid (0.50g, 2.0mmol; dichloromethane, 10cm^3) for 24 hours at room temperature. The resulting white suspension was filtered to yield 0.43g (63%) of a white solid. Analysis; Found(calc. $C_{14}H_{13}ClCuO_2P$): C 49.1(49.0); H 3.80(3.82)%. NMR (CD_3CN) ^{1}H (270.1MHz) δ(ppm)=3.42(broad, 2.0H, -CH_2-), 3.66(d, J=13.5Hz), 6.87(broad, 1.2H, -CO$_2H$) 7.46(broad, 7.0H, *phenyl*), 7.68(m, 8.1H, *phenyl*), 7.78-7.83(m, 1.5H); ^{13}C{^{1}H} (67.8MHz) δ(ppm)=34.7(d, J=12.2Hz, -CH$_2$-), 129.6(d, J=8.8Hz, *phenyl*), 131.2(s), 131.6(d, J=9.9Hz, *phenyl*), 133.2(s, *phenyl*), 133.5(d, J=15.4Hz, *phenyl*), 167.4, 170.1(s, -CO$_2$-); ^{31}P{^{1}H} (109.3MHz) δ(ppm)=-13.3(broad). IR (CsI, liquid paraffin mull) ν(cm^{-1})=2664w, 1705vs, 1588w, 1483w, 1437s, 1422m, 1294s, 1181m, 1134m, 1101m, 1071w, 1028w, 999w, 918m, 848m, 743s, 694s, 509s, 490m, 340w, 330w, 300w. MS FAB+, m/z=1336(1), 992(62), 895(2), 857(3), 812(35), 749(16), 651(60), 551(100), 505(20), 462(7), 407(34), 342(10), 263(68), 245(68); FAB-, m/z=1372(2), 1324(2), 1226(2), 1182(2), 1128(6), 1078(3), 1044(2), 1026(4), 980(5), 946(4), 882(24), 838(6), 638(40), 539(86), 443(75), 397(27), 341(80), 297(58), 264(52), 251(40), 233(100).

7.5.2.6. Tris(diphenylphosphinoacetic acid)copper(I) chloride **P7**

Copper(I) chloride (75mg, 0.76mmol) was stirred in a solution of diphenylphosphinoacetic acid (563mg, 2.31mmol; dichloromethane, 10cm^3) for 24 hours at room temperature to give a colourless solution. The solvent was removed *in vacuo* to yield 0.33g (52%) of a white crystalline solid. Analysis; Found(calc. $C_{42}H_{39}ClCuO_6P_3$): C 59.9(60.7); H 4.75(4.73)%. NMR ($CDCl_3$) ^{1}H (270.1MHz) δ(ppm)=3.16(s, 6.0H, -CH_2-), 7.13(broad, 26.9H, *phenyl*) 7.32(broad, 6.6H, *phenyl*), 10.07(broad, 3.5H, -CO_2H); ^{13}C{^{1}H} (67.8MHz) δ(ppm)=33.5(s, -CH_2-), 128.3(d, J=6.6Hz, *phenyl*), 129.8(s, *phenyl*), 131.5(d, J=23.2Hz, *phenyl*), 132.4(d, J=14.4Hz, *phenyl*), 171.9(s, -CO_2-); ^{31}P{^{1}H} (109.3MHz) δ(ppm)=-9.5(s). IR (CsI, liquid paraffin mull) ν(cm^{-1})=3052w, 1725sh, 1700vs, 1588w, 1483w, 1435s, 1290m, 1121m, 1098w, 1073w, 1028w, 1000w, 905m, 849m, 743s, 694s, 567w, 505s, 486m, 440w, 340w, 247vw. MS FAB+, m/z=859(7), 795(2), 651(3), 551(100), 263(50), 245(25); FAB-, m/z=893(3), 793(4), 703(3), 585(12), 549(18), 474(15), 341(75), 297(24), 188(100).

7.5.2.7. (Diphenylphosphinoacetic acid)gold(I) chloride **P8**

A solution of diphenylphosphinoacetic acid (0.15g, 0.6mmol; dichloromethane, 2cm^3) was added to a solution of chloro(tetrahydrothiophene)gold(I) (0.20g, 0.6mmol; dichloromethane, 3cm^3) and stirred overnight to give a yellow solution. The solvent was removed *in vacuo* to yield 0.25g (87%) of a yellow crystalline material which could be recrystallised from dichloromethane. Analysis; Found(calc. $C_{14}H_{13}AuClO_2P$) C 35.2(35.3); H 2.70(2.75)%. NMR ($CDCl_3$) ^{1}H (270.1MHz) δ(ppm)=3.83(d, 2.0H, J=12.46Hz, -CH_2-), 7.62(m, 5.6H, *phenyl*) 7.82(m, 3.8H, *phenyl*); ^{13}C{^{1}H} (67.8MHz) δ(ppm)=35.0(d, J=37.4.0Hz, -CH_2-), 129.9(d, J=61.7Hz, *phenyl*), 130.3(d, J=12.1Hz, *phenyl*), 133.3(s, *phenyl*), 134.2(d, J=14.3Hz, *phenyl*), 168.7(s, -CO_2-); ^{31}P{^{1}H} (109.3MHz) δ(ppm)=25.0(s). IR (CsI, liquid paraffin mull) ν(cm^{-1})=3050w, 2664w, 1700vs, 1588vw, 1485w, 1437m, 1397w, 1300s, 1133m, 1107m, 945br, 916w, 750m, 741m, 694m, 687m, 592m, 517m, 488m, 461w, 440vw, 335m. MS FAB+, m/z=917(22), 685(3), 476(7), 441(100), 244(7); FAB-, m/z=951(25), 914(7), 795(1), 781(5), 642(23), 628(20), 475(45), 431(100).

7.5.3. Heterometallic systems

7.5.3.1. Reaction of P1 with bicycloheptadiene molybdenum tetracarbonyl

Bicycloheptadiene molybdenum tetracarbonyl (0.10g, 0.33mmol) and **P1** (0.20g, 0.33mmol) were stirred at room temperature for 20 hours in 4cm^3 of methylcyclohexane. The resulting orange suspension was removed by filtration and washed with the solvent. Analysis; Found(calc. $C_{42}H_{34}MoO_8P_2$): C 60.2(57.8); H 4.44(3.93)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=0.78(d), 1.18(s), 3.03(broad), 3.06, 3.10(s), 3.43(m), 3.50(m), 3.70(m), 5.81, 5.89, 5.97(m), 5.98(s), 6.03, 6.04(s), 6.05, 6.14(s), 6.18(s), 6.20, 7.24(m), 7.40(m), 7.52(m), 7.72(m); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=-18.2, -17.6, -16.4, 18.2, 24.0, 24.7, 25.6, 28.7, 31.6. IR (CsI, liquid paraffin mull) ν(cm^{-1})=2022m, 1919s, 1902s, 1873s, 1647m, 1622m, 1462vs, 1323m, 1289m, 741m, 694m; (NaCl, hexachlorobutadiene mull) ν(cm^{-1})=3100w, 3090w, 3056w, 2072w, 2022s, 1919vs, 1902vs, 1873vs, 1645s, 1482w, 1433s, 1404w, 1323s, 1267s; (NaCl, dichloromethane solution) ν(cm^{-1})=2022m, 1919s, 1906s, 1879m.

Similar results were obtained when dichloromethane was used as the solvent.

7.5.3.2. Reaction of P2 with bis(cyclopentadienyl)bis(methyl)titanium(IV)

A solution of 0.11g (0.53mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 2cm^3 of dichloromethane was added slowly to a suspension of 0.37g (0.53mmol) of **P2** in 5cm^3 of dichloromethane. The evolution of a gas was noted, and the reaction mixture stirred for an hour or so until a clear maroon solution had formed. Removal of the solvent *in vacuo* gave 0.39g of an orange-brown solid. Analysis; Found(calc. $C_{42}H_{34}MoO_8P_2$): C 56.5(57.8); H 4.21(3.93)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.12(broad), 3.28(broad), 3.69(m, 4.0H), 5.77(m, 11.5H), 5.81(broad, 23.8H), 5.89(s, 9.8H), 5.98(s, 13.1H), 7.25(broad), 7.35(m), 7.52(broad). IR (NaCl, liquid paraffin mull) ν(cm^{-1})=3114vw, 3050w, 2020s, 1984vs, 1960vs, 1920sh, 1717w, 1634s, 1464s, 1433m, 1402vw, 1289s, 1181m, 1125m, 1094w, 1026w, 822s, 741s, 695s, 613m; (NaCl, dichloromethane solution) ν(cm^{-1})=2034m, 1920vs, 1910vs, 1883sh.

7.5.3.3. Reaction of P1 with hexa(acetonitrile)nickel(II) tetrafluoroborate to give P9

A solution of **P1** (0.25g, 0.38mmol; dichloromethane, 2cm^3) was added dropwise to 0.09g of hexa(acetonitrile)nickel(II) tetrafluoroborate in 2cm^3 of dichloromethane and the mixture stirred for 1 hour. Filtration and removal of the solvent on a rotary evaporator gave 0.23g of a dark brown solid. Analysis; Found(calc. $C_{76}H_{68}B_2F_8NiO_8P_4Ti_2$): C 55.1(58.5); H 4.39(4.39)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.07(very broad, 4.0H), 6.26(broad, 6.0H), 6.37(s, 12.1H), 7.27(broad, 27.6H); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=-15.0.

7.5.3.4.Reaction of P3 with bis(cyclopentadienyl)bis(methyl)titanium(IV) to give **P9**

A solution of 0.11g (0.54mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 0.5cm^3 of dichloromethane was added slowly to a solution of 0.33g (0.27mmol) of **P3** in 3cm^3 of dichloromethane. The evolution of a gas was noted. A further 2cm^3 of solvent were added and the reaction mixture stirred for 30 minutes to give a very dark green solution. Removal of the solvent on a rotary evaporator gave 0.36g of a brown solid. Analysis; Found(calc. $C_{76}H_{68}B_2F_8NiO_8P_4Ti_2$): C 57.0(58.5); H 4.59(4.39)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.08(very broad, 4.0H), 6.26(broad, 8.8H), 6.37(s, 11.2H), 7.27(very broad, 26.1H); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=-15.1. IR (NaCl, liquid paraffin mull) ν(cm^{-1})=3450br, 3117w, 3056w, 1719w, 1553br, 1437m, 1396m, 1188w, 1075br, 1057s, 1026sh, 999sh, 828m, 743s, 694s. Magnetic moment (Guoy method) 2.35B.M.

7.5.3.5. Reaction of P1 with bis(benzonitrile)palladium(II) chloride to give P10

P1 was generated *in situ* by reacting 0.19g (0.9mmol) of bis(cyclopentadienyl)bis(methyl)-titanium(IV) and 0.44g (1.8mmol) of diphenyphosphinoacetic acid in 6cm^3 of dichloromethane. A solution of bis(benzonitrile)palladium(II) chloride in 2cm^3 of dichloromethane was added to this reaction mixture with stirring resulting in a red solution. Upon standing, large red solvated crystals formed. Similar crystals also formed rapidly in NMR tubes, hindering the recording of spectra. Yield, 0.43g, (43%, based on three solvent molecules per titanium atom). Analysis; Found(calc. $C_{38}H_{34}Cl_2O_4P_2PdTi$) C 52.1(54.2); H 3.90(4.07)%. NMR (CD_3CN) ^1H (270.1MHz) δ(ppm)=3.74(t, 4.0H, J=4.58Hz, -CH_2-), 6.64(s, 6.9H), 6.99(broad, 6.0H), 7.55(very broad, 25.8H), 8.00(m, 5.6H); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=13.8, 19.0, 21.5. IR (CsI, liquid paraffin mull) ν(cm^{-1})=3087w, 1651vs, 1483m, 1456s, 1435s, 1312vs, 1275vs, 1206w, 1186w, 1159w, 1138m, 1103s, 1071w, 1019m, 999m, 966w, 938w, 852vs, 818s, 743s, 689s, 575w, 509s, 473m, 463s, 438m, 419w, 397w, 339w, 307w, 280sh.

7.5.3.6. Reaction of P4 with bis(cyclopentadienyl)bis(methyl)titanium(IV) to give P10

A solution of 34mg (0.17mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 2cm^3 of dichloromethane was added to a suspension of 110mg (0.17mmol) of **P4** in 2cm^3 of dichloromethane causing slow effervesence of a gas. A further 1cm^3 of solvent was added and the reaction stirred for approximately 2 hours until an orange solution had formed. The solvent was removed *in vacuo* to give an orange solid. Analysis; Found(calc. $C_{38}H_{34}Cl_2O_4P_2PdTi$): C 50.7(54.2); H 3.93(4.07)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.53(t, 4.0H, J=4.40Hz, -CH_2-), 6.30(s, 9.8H), 6.61(broad, 1.8H), 6.84(broad, 1.8H), 7.22(broad, 14.5H), 7.59(m, 7.5H); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=13.5, 21.7. IR (CsI, liquid paraffin mull) ν(cm^{-1})=1622s, 1456s, 1287s, 1140m, 1100m, 1028w, 999w, 943w, 853m, 830s, 741s, 721m, 693s, 581w, 505s, 476w, 451w, 424w, 390sh, 340w.

7.5.3.7. Reaction of P1 with bis(benzonitrile)platinum(II) chloride

P1 was generated *in situ* by reacting 50mg (0.24mmol) of bis(cyclopentadienyl)bis(methyl)-titanium(IV) and 117mg (0.48mmol) of diphenyphosphinoacetic acid in 2cm^3 of dichloromethane. A solution of bis(benzonitrile)platinum(II) chloride in 1cm^3 of dichloromethane was added to this reaction mixture and stirred overnight. A brown oil was isolated upon filtration and removal of the solvent *in vacuo*. Analysis; NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=0.88(t), 1.27(s), 2.01(m), 2.79(m), 2.95(very broad), 3.45(m), 3.76(m), 6.30(m), 6.42(s), 6.53(s), 6.60(s), 6.89(broad), 7.22-7.81(m); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)= -17.9, -10.5, -10.4, -5.3, -1.3, -0.3, 11.3, 14.6, 17.2, 21.7, 22.4, 23.9, 30.5, 41.2, 43.0, 49.0, 49.5.

7.5.3.8. Reaction of P5 with bis(cyclopentadienyl)bis(methyl)titanium(IV)

A solution of 52mg (0.25mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 0.5cm^3 of dichloromethane was added dropwise to a suspension of 166mg (0.25mmol) of **P5** in 6cm^3 of toluene/dichloromethane (5:1 v/v). A further 0.5cm^3 of dichloromethane was added and the reaction stirred for 24 hours to give an orange suspension. The precipitate was removed by filtration and washed with dichloromethane to give 71mg of an orange powder, **P11**. Analysis; Found(calc. $C_{38}H_{34}Cl_2O_4P_2PtTi$): C 48.0(49.1); H 3.60(3.68)%. IR (CsI, liquid paraffin mull) ν(cm^{-1})=3088w, 3052w, 1696m, 1647s, 1593s, 1439s, 1343m, 1312s, 1260m, 1210w, 1186w, 1127w, 1105m, 1028w, 999w, 932w, 903w, 857m, 822w, 795w, 743s, 694s, 532m, 519m, 507m, 490m, 471w, 444w, 424w, 400vw, 375w, 322w, 310w.

The solvent from the orange filtrate was removed *in vacuo* to give 123mg of an orange crystalline solid. Analysis; Found(calc. $C_{38}H_{34}Cl_2O_4P_2PtTi$) C 48.6(49.1); H 3.93(3.68); N 0.14(0.00)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=0.59(s), 0.64(s), 1.04(s), 1.56(broad), 3.27(m), 5.93(s), 6.05(s), 6.22(s), 6.25(s), 6.30(s), 6.32(s), 6.38(s), 6.67(broad), 6.91(m), 7.08(m), 7.26(m), 7.43(m); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=-5.9, -5.8, -1.1, -0.3($^1J^{195}Pt$-^{31}P=3830Hz). IR (CsI, liquid paraffin mull) ν(cm^{-1})=3090w, 3053vw, 1651s, 1437m, 1314s, 1275m, 1129w, 1103w, 1019w, 851m, 822m, 741m, 691m, 507m, 473w, 439w, 400w, 348w.

7.5.3.9. Reaction of **P1** with copper(I) chloride to give **P12**

Copper(I) chloride (0.1g, 1.0mmol) and **P1** (0.34g, 0.5mmol) were stirred for 72 hours in 5cm^3 of dichloromethane to give a dark red solution. Filtration and removal of the solvent *in vacuo* gave 0.40g (93%) of an orange solid. Analysis; Found(calc. $C_{38}H_{34}Cl_2Cu_2O_4P_2Ti$) C 51.5(52.9); H 3.93(3.97)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.42(broad, 4.0H, -C*H*$_2$-), 6.16(broad, 10.3H, η-C$_5$*H*$_5$) 7.33(broad, 18.5H, *phenyl*), 7.61(broad, 14.3H, *phenyl*); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=37.3(s, -*C*H$_2$-), 118.9(s, η-*C*$_5$H$_5$), 128.9(s, *phenyl*), 130.3(s, *phenyl*), 132.2(d, J=15.4Hz, *phenyl*), 132.7(t, J=7.7Hz, *phenyl*), 172.4(s, -*C*O$_2$-); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=-12.3(broad).

7.5.3.10. Reaction of **P6** with bis(cyclopentadienyl)bis(methyl)titanium(IV) to give **P12**

A solution of 61mg (0.29mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 2cm^3 of dichloromethane was added with stirring to a suspension of 200mg (0.58mmol) of **P6** in 2cm^3 of dichloromethane. The evolution of a gas was noted. Stirring was ceased after 20 minutes and the reaction mixture allowed to stand for 72 hours. Filtration and removal of the solvent on a rotary evaporator gave 170mg (68%) of an orange solid. Analysis; Found(calc. $C_{38}H_{34}Cl_2Cu_2O_4P_2Ti$): C 52.4(52.9); H 4.11(3.97)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.48(broad, 4.0H, -C*H*$_2$-), 6.23(s, 9.9H, η-C$_5$*H*$_5$) 7.40(broad, 12.9H, *phenyl*), 7.68(broad, 9.0H, *phenyl*); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=37.3(s, -*C*H$_2$-), 118.9(s, η-*C*$_5$H$_5$), 128.9(s, *phenyl*), 130.3(s, *phenyl*), 132.3(d, J=15.5Hz, *phenyl*), 132.7(t, J=7.7Hz, *phenyl*), 172.5(s, -*C*O$_2$-); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=-12.4(s). IR (CsI, liquid paraffin mull) ν(cm^{-1})=3050w, 1634s, 1435s, 1408w, 1310s, 1283s, 1186w, 1127m, 1100m, 1017w, 941w, 828s, 743s, 694s, 509s, 473w, 446sh, 423w, 254sh, 247m. MS FAB+, m/z=827(15), 762(20), 727(95), 697(15), 662(70), 519(40), 484(5), 454(20), 435(60), 421(47), 344(23), 261(40), 245(15); FAB-, m/z=864(4), 762(25), 441(27), 342(76), 297(38), 288(30), 264(48), 233(97).

7.5.3.11. Reaction of **P7** with bis(cyclopentadienyl)bis(methyl)titanium(IV)

A solution of 28mg (0.14mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 0.5cm^3 of toluene was added with stirring to a suspension of 75mg (0.09mmol) of **P7** in 1.5cm^3 of toluene. The reaction mixture was stirred for 30 minutes and filtered to give 20mg of an orange residue. Analysis; Found(calc. $C_{114}H_{102}Cl_2Cu_2O_{12}P_6Ti_3$): C 58.5(62.5); H 4.65(4.69)%.

The solvent from the filrate was removed on a rotary evaporator to give a brown oil. Analysis; NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=0.83(s), 0.87(s), 2.41(s, 4.9H), 2.95(s, 2.99(m), 3.04(m), 3.34(d, 0.9H, J=14.11Hz), 3.56(broad, 4.0H), 6.06(s, 5.1H), 6.11(s, 5.6H), 6.30(s, 10.7H), 6.53(m, 0.9H), 6.62(m, 0.9H), 7.24(m, 5.5H), 7.32(m, 8.7H), 7.46(m, 17.3H), 7.74(m, 12.7H); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=-17.2(broad), -12.8(s), 22.1(s), 27.3(s).

7.5.3.12. Reaction of **P1** with silver(I) chloride

One equivalent of AgCl.

Silver(I) chloride (11mg, 0.08mmol) and **P1** (50mg, 0.08mmol) were stirred for 72 hours in 4cm^3 of dichloromethane. Filtration and evaporation gave a bright orange crystalline solid. Analysis; Found(calc. $C_{38}H_{34}AgClO_4P_2Ti$): C 53.6(56.5); H 4.17(4.24)%. NMR $^{31}P\{^1H\}$ ($CDCl_3$, 109.3MHz) δ(ppm)=-2.25[$^1J(^{107}Ag-^{31}P)$=439.3Hz, $^1J(^{109}Ag-^{31}P)$=472.7Hz].

The above proceedure was repeated for two and four equivalents of silver(I) chloride.

Two equivalents of AgCl (AgCl, 22mg, 0.15mmol; **P1**, 50mg, 0.08mmol).
Analysis; Found(calc. $C_{38}H_{34}AgClO_4P_2Ti$): C 52.7(56.5); H 4.17(4.24)%. NMR $^{31}P\{^1H\}$ ($CDCl_3$, 109.3MHz) δ(ppm)=-2.27[$^1J(^{107}Ag-^{31}P)$=443.9Hz, $^1J(^{109}Ag-^{31}P)$=503.3Hz].

Four equivalents of AgCl (AgCl, 43mg, 0.30mmol; **P1**, 50mg, 0.08mmol).
Analysis; Found(calc. $C_{38}H_{34}AgClO_4P_2Ti$): C 52.4(56.5); H 4.10(4.24)%. NMR $^{31}P\{^1H\}$ ($CDCl_3$, 109.3MHz) δ(ppm)=-2.23[$^1J(^{107}Ag-^{31}P)$=446.0Hz, $^1J(^{109}Ag-^{31}P)$=499.7Hz].

7.5.3.13. Reaction of silver(I) diphenylphosphinoacetate with bis(cyclopentadienyl)titanium dichloride to give P13

Silver(I) diphenylphosphinoacetate (0.60g, 1.70mmol) and bis(cyclopentadienyl)titanium dichloride (0.21g, 0.85mmol) were stirred in 10cm^3 of dichloromethane for 24 hours. Filtration and removal of the solvent on a rotary evaporator gave 0.16g of a white residue, and 0.53g (77%) of an orange crystalline solid. The white residue was light sensitive. The orange crystalline material could be recrystallised from dichloromethane. Analysis; Found(calc. $C_{38}H_{34}AgClO_4P_2Ti$): C 55.3(56.5); H 4.49(4.24)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.51(s, 4.0H, -C*H*$_2$-), 6.10(s, 9.6H, η-C_5H_5) 7.37(m, 12.5H, *phenyl*), 7.66(m, 8.1H, *phenyl*); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=37.9(t, J=8.3Hz, -CH_2-), 118.9(s, η-C_5H_5), 129.0(t, J=5.0Hz, *phenyl*), 130.5(s, *phenyl*), 131.9(t, J=12.9Hz, *phenyl*), 132.8(t, J=8.3Hz, *phenyl*), 171.7(s, -CO_2-); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=-1.84($J_{^{107}Ag-^{31}P}$=439.3Hz, $J_{^{109}Ag-^{31}P}$=506.4Hz). IR (CsI, liquid paraffin mull) ν(cm^{-1})=3050w, 1723w, 1642vs, 1482m, 1462s, 1435s, 1310sh, 1273vs, 1186w, 1127m, 1100m, 1071w, 1026m, 1017m, 999w, 922m, 828s, 741s, 693s, 644w, 590w, 503s, 471m, 446w, 422w, 395w, 342w, 295w, 260w. MS FAB+, m/z=1093(1), 915(2), 884(<1), 850(1), 808(2), 787(4), 773(52), 743(12), 709(40), 479(18); FAB-, m/z=387(33), 341(68), 310(48), 188(100).

7.5.3.14. Reaction of P1 with chloro(tetrahydrothiophene)gold(I)

Chloro(tetrahydrothiophene)gold(I) (0.19, 0.6mmol) and **P1** (0.20g, 0.3mmol) were stirred for 30 minutes in 5cm^3 of dichloromethane to give a brown solution. The solvent was removed *in vacuo* to give a brown solid. Analysis NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=1.96(d), 2.11(broad), 3.32(broad), 6.18(s), 7.43(m), 7.64(m); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=17.6, 20.8, 24.2, 24.7, 27.6, 30.6, 32.2. IR (NaCl, liquid paraffin mull) ν(cm^{-1})=3041w, 1715w, 1651m, 1588m, 1559m, 1464s, 1437s, 1300m, 1123m, 1069w, 1026w, 997w, 932w, 860w, 804m, 745m, 691s.

7.5.3.15. Reaction of P8 with bis(cyclopentadienyl)bis(methyl)titanium(IV) to give **P14**

A solution of 50mg (0.24mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 1cm^3 of dichloromethane was added slowly with stirring to a suspension of 229mg (0.48mmol) of **P8** in 2cm^3 of dichloromethane. A further 1cm^3 of solvent was added and the reaction mixture stirred overnight. Removal of the solvent *in vacuo* gave 221mg (81%) of an orange-yellow solid. Analysis; Found(calc. $C_{38}H_{34}Cl_2Au_2O_4P_2Ti$): C 40.1(40.4); H 2.92(3.03)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=4.11(d, 4.0H, J=13.37Hz, -CH_2-), 6.24(s, 10.1H, η-C_5H_5) 7.49(m, 12.8H, *phenyl*), 7.84(m, 8.8H, *phenyl*); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=37.8(d, J=33.1Hz, -CH_2-), 119.0(s, η-C_5H_5), 129.1(d, J=11.0Hz, *phenyl*), 129.9(s, *phenyl*), 131.9(s, *phenyl*), 133.3(d, J=14.4Hz, *phenyl*), 170.6(d, J=2.2Hz, -CO_2-); $^{31}P\{^1H\}$ (109.3MHz) δ(ppm)=24.9(s). IR (CsI, liquid paraffin mull) ν(cm^{-1})=3058w, 1634vs, 1458s, 1439s, 1325s, 1292vs, 1190w, 1132m, 1103m, 1017w, 887w, 824s, 747s, 691s, 528s, 484m, 467w, 442w, 422w, 378sh, 335m, 248w. MS FAB+, m/z=1129(3), 1093(13), 1063(3), 102(13), 917(14), 653(27), 594(28), 476(5), 441(100), 344(34); FAB-, m/z=1128(3), 1081(2), 1062(<1), 985(1), 951(15), 475(46), 431(100).

7.6. Preparations and reactions involving derivatives of carboxylic acids with additional sulfur donors

7.6.1 Homometallic carboxylates

7.6.1.1. Bis(cyclopentadienyl)(mercaptoacetato)titanium(IV) S1

A flame-dried 100cm^3 two-necked round bottomed flask fitted with reflux condenser and magnetic stirring bar was charged with 0.50g (2.0mmol) of bis(cyclopentadienyl)titanium dichloride and 0.50g (4.4mmol) of sodium mercaptoacetate. Freshly distilled tetrahydrofuran (25cm^3) was added and the reaction mixture was refluxed under nitrogen for 4 hours. Filtration gave a dark red residue, which was washed consecutively with several portions of distilled water, ethanol, and diethyl ether. IR spectra recorded before and after washing were identical, although the microanalysis was significantly different. This dark red powder was completely insoluble in all common solvents. Analysis; Found (calc. $C_{12}H_{12}SO_2Ti$): C 52.6(53.7); H 4.47(4.51); S 10.8(12.0); Ti 15.4(17.9)%. IR (NaCl, liquid paraffin mull), ν(cm^{-1})=3092m, 1631vs, 1453m, 1317s, 1020m, 830s, 812s.

7.6.1.2. Bis(cyclopentadienyl)bis(mercaptoacetato)titanium(IV) S2

To a solution of 0.21cm^3 (0.27g, 3.0mmol) of mercaptoacetic acid in 13cm^3 of dichloromethane, a solution of 0.31g (1.5mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 2cm^3 of dichloromethane was added dropwise. Methane was evolved rapidly and stirring overnight resulted in a marroon solution. Removal of the solvent *in vacuo* gave an air sensitive, viscous oil. Attempts to precipitate a solid from various solvents were unsuccessful. Analysis; Found (calc. $C_{14}H_{14}O_4S_2Ti$): C 45.6(46.7), H 4.46(4.48)%. NMR ($CDCl_3$); ^1H (270.1MHz) δ(ppm)=1.96(t, 2H, J=8.06Hz, -*SH*), 3.18(d, 4H, J=8.06Hz, -CH_2-), 6.49(s, 10H, η-C_5H_5); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=28.8(s, -CH_2-), 118.8(s, η-C_5H_5), 175.6(s, -CO_2-). IR (NaCl, dichloromethane solution) ν(cm^{-1})=3117w, 3054w, 2685vw, 2577vw, 2305m, 1727m, 1651vs, 1445vw, 1414vw, 1331s, 1211m, 1150w, 1074w, 1026w, 828s.

7.6.1.3. Bis(cyclopentadienyl)bis(thiophenoxyacetato)titanium(IV) S3

A solution of 0.44g (2.1mmol) of bis(cyclopentadienyl)bis(methyl)titanium(IV) in 3cm^3 of tetrahydrofuran was added dropwise to a suspension of 0.71g (4.2mmol) of thiophenoxyacetic acid in 12cm^3 of tetrahydrofuran with vigorous evolution of methane. The reaction mixture was stirred for 1 hour, then the solvent removed *in vacuo*. Yield of bright orange crystalline solid, 1.00g (93%). The solid was recrystallised from a tetrahydrofuran solution layered with hexane to give bright red crystals. Analysis; Found (calc. $C_{26}H_{24}O_4S_2Ti$): C 60.6(60.9), H 4.73(4.72)%. NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=3.61(s, 4H, -CH_2-), 6.27(s, 9.3H, η-C_5H_5), 7.09(m, 2H, *phenyl*), 7.22(m, 4.1H, *phenyl*), 7.35(m, 3.8H, *phenyl*); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=37.8(s, -CH_2-), 118.5(s, η-C_5H_5), 125.8(s, *phenyl*), 128.1(s, *phenyl*), 128.8(s, *phenyl*), 136.4(s, *phenyl*), 174.1(s, -CO_2-). IR (NaCl, liquid paraffin mull) ν(cm^{-1})=3108m, 1661s, 1632vs, 1584m, 1482m, 1437sh, 1399m, 1337s, 1302vs, 1213s, 1165m, 1022m, 1010sh, 870m, 824s, 733s. MS FAB+, m/z=447(7), 431(4), 345(100), 178(16); FAB-, m/z=678(20), 664(11), 614(41), 599(21), 512(100), 463(78), 448(46), 361(38).

7.6.2. Heterometallic systems

7.6.2.1. Reaction of S3 with bicycloheptadiene molybdenum tetracarbonyl

A solution of bicycloheptadiene molybdenum tetracarbonyl (187mg, 0.62mmol) in 5cm^3 of toluene was added dropwise to a solution of 319mg (0.62mmol) of S3 in 5cm^3 of toluene and stirred for 20 minutes at room temperature. The solvent was removed *in vacuo* to give a brown oil. Analysis; ^1H NMR ($CDCl_3$, 270.1MHz) δ(ppm)=1.26, 1.32, 2.34, 3.61(s, 1.3H), 3.68(s, 4H), 3.75(s, 1.4H), 6.22(s, 3.2H), 6.26, 6.28, 6.34(s, 9.2H), 6.43(s, 2.4H), 7.17(m, 6.5H), 7.29(m, 7.7H), 7.41(m, 5.1H).

The above reaction was repeated in dichloromethane with a longer reaction time of 1.5 hours. Analysis; NMR ($CDCl_3$) ^1H (270.1MHz) δ(ppm)=0.88(broad), 1.26(s, 5.0H), 1.33(s, 3.7H), 3.61(s, 1.8H), 3.69(s, 4H), 3.77(broad, 1.7H), 6.27(s, 1.3H), 6.35(s, 9.4H), 6.45(s, 7.1H), 6.58(s, 1.1H), 6.76(s, 1.5H), 7.19(m, 4.2H), 7.30(m, 9.6H), 7.42(m, 7.8H); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=29.5, 34.1, 37.2, 37.8, 48.9, 50.1, 64.8, 78.2, 118.6(m), 119.2(m), 120.0, 125,8, 128.2, 128.4, 128.8, 129.5, 136.5, 143.2, 174.2, 200.8, 208.2, 214.1, 217.9.

7.6.2.2. Reaction of S3 with bis(benzonitrile)palladium(II) chloride

A solution of S3 (89mg, 0.18mmol) in 3cm^3 of dichloromethane was added dropwise to a solution of bis(benzonitrile)palladium(II) chloride (70mg, 0.18mmol) in 5cm^3 of dichloromethane and stirred for 24 hours at room temperature to give a bright orange suspension. The precipitate was removed by filtration and washed with dichloromethane yielding 90mg (72% based on the formation of the S3-$PdCl_2$ 1:1 complex) of an orange powder. Analysis; Found (calc. $C_{26}H_{24}Cl_2O_4PdS_2Ti$): C 44.2(45.3), H 3.46(3.51)%. IR (CsI, liquid paraffin mull) ν(cm^{-1})=3511s, 3460sh, 3112m, 1728w, 1626vs, 1443s, 1350s, 1319vs, 1203w, 1150w, 1024m, 828s, 741s, 687m, 488m, 444w, 425sh, 358w, 324m.

7.7. X-ray crystallography

Data were collected using an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator using MoK_α radiation. Crystal parameters, data collection and structure solution details are listed in the Appendices for each compound studied. Also included in the Appendices are the fractional atomic coordinates and isotropic and anisotropic displacement factors relating to the above structure determinations.

For the compounds **N1**, **N4**, **O1**, **P1**, **P4'**.1/3EtOH.1/3H_2O, **S3** and $HO_2CCH_2P(O)Ph_2$, data were corrected for Lorentz and polarisation effects but not for absorption. For compounds **P8** and **P10**.3CH_2Cl_2, corrections were made for absorption in addition to Lorentz and polarisation effects.[253]

All hydrogen atoms were included at calculated positions except the methylene hydrogens in **N1** and **P8**, and the proton affiliated to the carboxylate group in $HO_2CCH_2P(O)Ph_2$ which were located and positionally refined. The oxygen-bound hydrogen atoms of **P8** and **P4'**.1/3EtOH.1/3H_2O were not located.

All structures were solved using SHELX86[254] and refined using SHELX93[255] except for the structures of **N1** and **O1** which were refined using SHELX76.[256] The graphical representation of the structures were produced using ORTEP[257] (for **N1** and **O1**) or ORTEX[258] (all other structures).

Additional details pertaining to the determination of the structure of silver(I) cyanoacetate are given in Appendix 1.

Chapter 8.

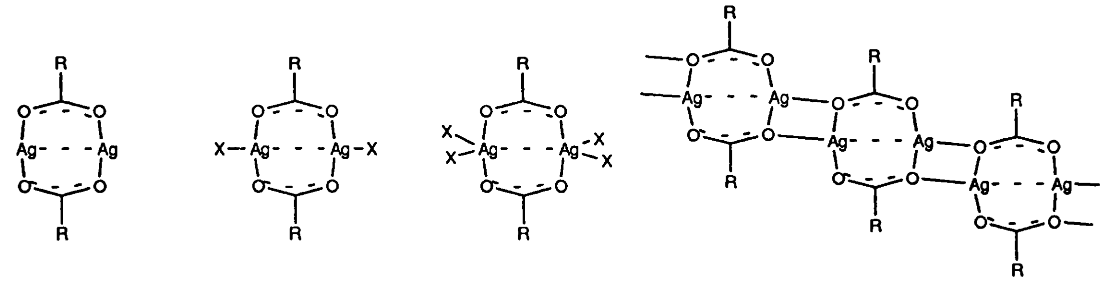
Appendices.

Appendix 1.

Crystal structure determination of silver(I) cyanoacetate and an investigation of the silver-silver interaction by Extended Hückel molecular orbital (EHMO) calculations

In recent years there has been great deal of interest in the solid state structures of silver(I) carboxylates.[259] They display a variety of structural motifs, most of which contain a bis(carboxylato-*O,O'*)disilver(I) dimer. These dimeric arrangements have been classified by Mak *et al.* in to four major catagories (Figure 32).[260] Type (1) has no additional donor atoms at the axial positions of the dimer, e.g. silver(I) (perfluorophenoxy)acetate $[Ag_2(O_2CCH_2OC_6F_5)_2]$.[261] Type (2) has one donor atom at each of the axial positions forming either a polymeric array when the additional donor atom is from a second functional group in the carboxylate ligand, e.g. silver(I) hydrogen maleate $[\{Ag_2(cis\text{-}O_2CCH{=}CHCO_2H)_2\}_n]$,[262] or discrete molecular entities when the axial donors are from separate ligands such as water, e.g. silver(I) *N*-acetylanthranilate dihydrate $[Ag_2(2\text{-}O_2CC_6H_4NHC(O)CH_3)_2(H_2O)_2].2H_2O$.[263]

Type (3) contains two additional donor atoms at the axial positions and is generally polymeric in nature, e.g. silver(I) glycolate hemihydrate $[\{Ag_2(O_2CCH_2OH)_2\}_n.nH_2O]$.[264] Finally structures of type (4) have one or both of the axial sites occupied by carboxyl oxygens of adjacent dimeric units forming step-like polymers, e.g. silver(I) phenoxyacetate $[\{Ag(O_2CCH_2OPh)\}_n]$.[265]



(1) (2) (3) (4)

Figure 32. Structural classification of silver(I) carboxylates containing the bis(carboxylato-*O,O'*)-disilver(I) dimer as conceived by T.C.W. Mak and co-workers (Ref. 260).

Other structural motifs are known, some of which contain the bis(carboxylato-*O,O'*)disilver(I) units having a ligand arrangement that is a combination of types (1)-(4) discussed above. For example, the structure of silver(I) 4-fluorophenoxyacetate hydrate $[\{Ag_2(4\text{-}FC_6H_4OCH_2CO_2)_2(H_2O)_2\}_2]$ consists of pairs of dimers joined together *via* adjacent carboxyl oxygens as in type (4). Each silver atom binds a molecule of water, giving two different silver environments: one is surrounded by three, and the other by four oxygen atoms.[265]

In contrast to dimer units, discrete molecular entities are present in the structure of diammine disilver(I) phthalate $[Ag_2\{C_6H_4(CO_2)_2\}(NH_3)_2]$.[266] The silver atoms adopt an approximately linear two-coordinate geometry bound by one carboxyl oxygen and an ammine nitrogen. The extended structure is held together by intermolecular hydrogen bonds. Linear coordination at the silver atoms is also observed in the structure of silver(I) (4-chloro- 2-methylphenoxy)acetate $[\{Ag(4\text{-}Cl, 2\text{-}MeC_6H_3OCH_2CO_2)\}_n]$.[267] The carboxylate ligands bond to silver solely *via* bidentate bridging *syn, anti* carboxyl functions generating a chain polymer.

Silver(I) cyanoacetate was prepared as a starting material for the synthesis of bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) **N1** and was characterised by microanalysis and IR spectroscopy. The crystal structure was determined to establish the configuration of silver(I) cyanoacetate in the solid state and to provide a basis set for investigating any short silver-silver interactions by molecular orbital calculations.

Experimental

General information concerning equipment, reagents and solvents is contained in Chapter 7.

Preparation of silver(I) cyanoacetate

A solution of silver nitrate (1.91g, 11.3mmol) in water ($10cm^3$) was added dropwise to a stirred solution of cyanoacetic acid (0.96g, 11.3mmol) and sodium hydroxide (0.45g, 11.3mmol) in water ($50cm^3$). After 20 minutes the resulting white precipitate was filtered, washed with portions of water, ethanol and diethyl ether and dried *in vacuo*, all operations being carried out in subdued light with final storage in the dark. Yield 1.56g, 72%. Analysis; Found (calc. $C_3H_2AgNO_2$): C 18.8(18.8), H 1.05(1.05), N 7.40(7.30)%. NMR (D_2O) ^1H (270.1MHz) δ(ppm)=3.47(s, $-CH_2-$); $^{13}C\{^1H\}$ (67.8MHz) δ(ppm)=26.0(s, $-CH_2-$), 117.5(s, CN), 169.3(s, $-CO_2-$). IR (NaCl, liquid paraffin mull) $\nu(cm^{-1})$=2953m, 2923m, 2269m [ν(CN)];1608sh [$\nu(OCO_{asym})$], 1566s [$\nu_{asym}(CO_2)$], 1456s [$\nu(OCO_{sym})$], 1400s [$\nu(OCO_{sym})$], 1366m, 1273m, 1208m, 963m, 928m, 912w, 721m.

Storage of the filtrate from the above reaction in the dark for two months yielded a crop of clear diamond-shaped crystals one of which was selected for the structure determination.

X-ray crystallography

Crystal parameters, data collection and structure solution details are given in Table A1.1. Data were collected at room temperature on a CAD4 automatic four-circle diffractometer using Mo-K_α radiation. The diffraction intensities were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by direct methods using SHELX86 and refined using SHELX93. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were associated with the methylene carbon C(2) were located at calculated positions.

The asymmetric unit is displayed in Figure 33 along with the adopted labeling scheme and an extended view of the structure in Figure 34 illustrates the chain polymer arrangement. Bond lengths and angles are listed in Table 50. Final fractional atomic coordinates, anisotropic temperature factors and hydrogen fractional atomic coordinates and isotropic temperature factors are given at the end of this Appendix in Tables A1.2, A1.3 and A1.4.

Molecular orbital calculations

Calculations on the metal-metal interactions in silver(I) cyanoacetate were of the extended Hückel[268] type using the CACAO suite of programs.[269] The parameters used are given in Table A1.5, the orbital energies and Slater orbital exponents for silver being taken from Reference 270.

Discussion

The solid state structure of silver(I) cyanoacetate exhibits the bis(carboxylato-*O,O'*)disilver Ag_2L_2 dimer typical of silver(I) carboxylates. Using the classification scheme detailed above the cyanoacetate is a new example of the type (2) arrangement (Fig. 33). Infinite polymer chains are formed *via N*-bonded nitrile functions by the linking of adjacent dimers at the axial positions (Fig. 34).

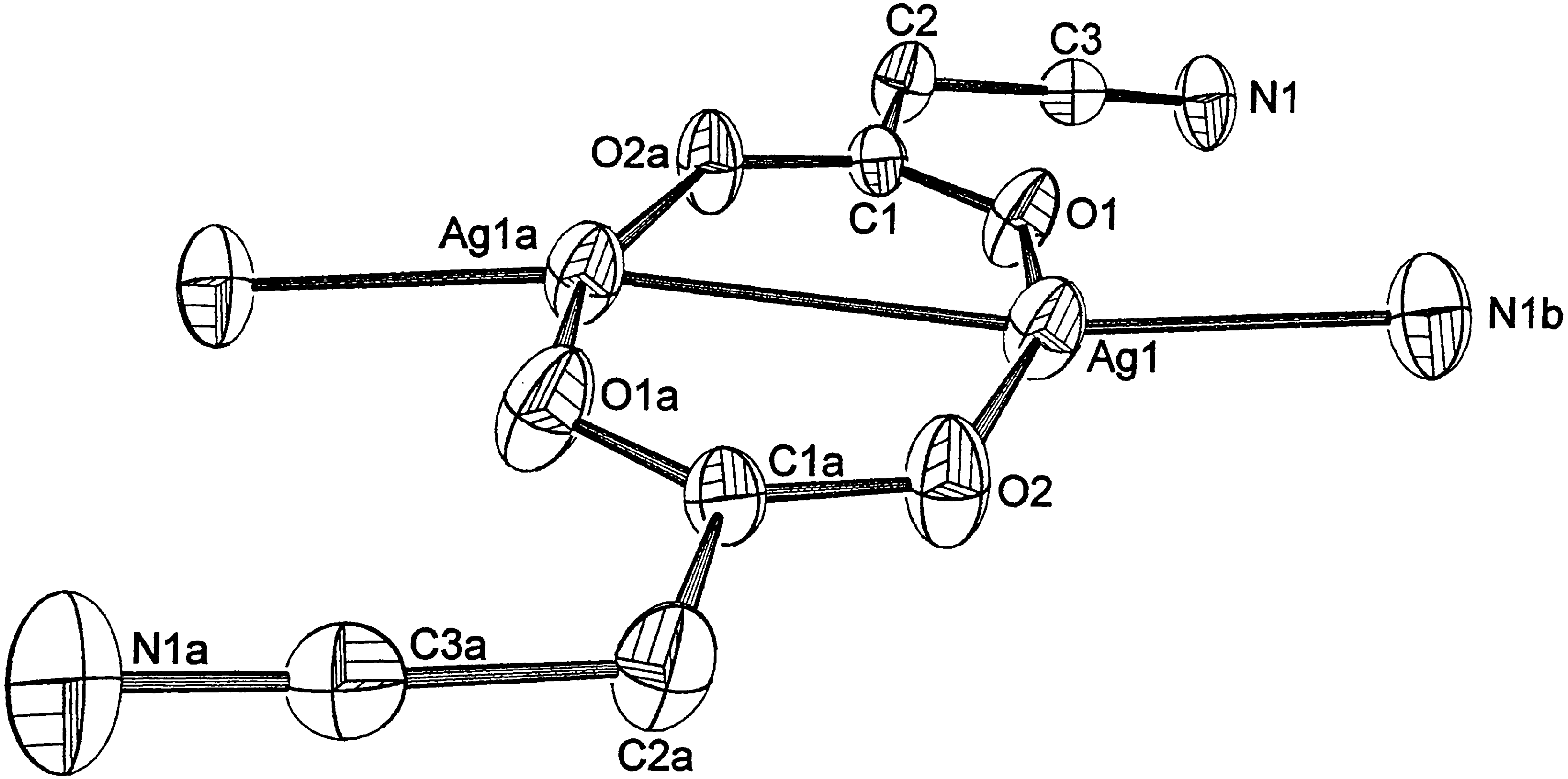


Figure 33. ORTEX plot of a portion of the silver(I) cyanoacetate structure showing the silver dimer and its local coordination environment.

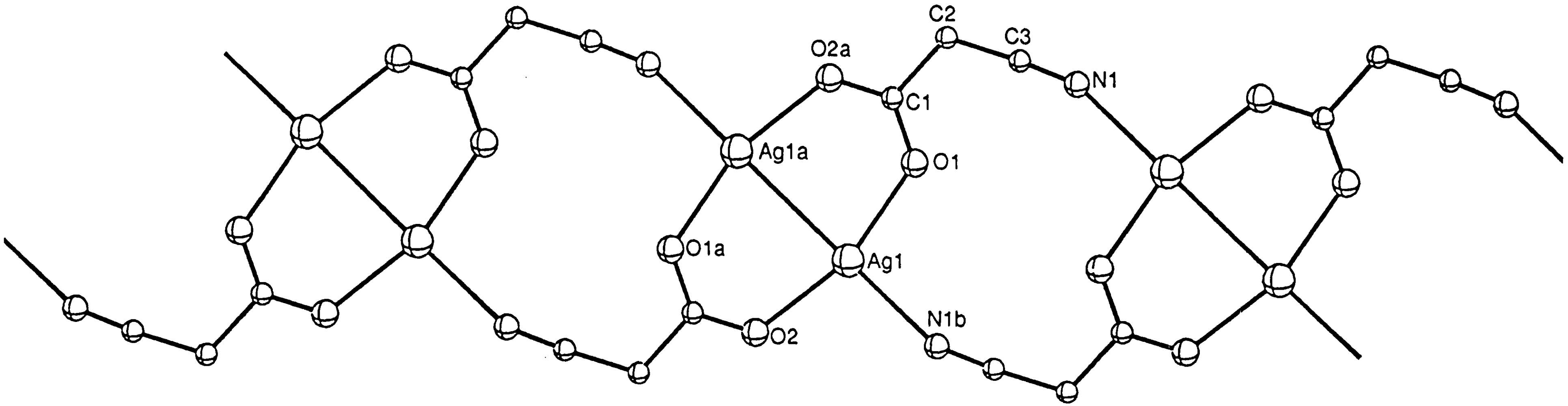


Figure 34. Chain polymer arrangement of silver(I) cyanoacetate.

The shortest Ag-Ag distance [Ag(1)-Ag(1a)] of 2.894(1)Å is the same as that found in the metal itself, and is similar to other silver(I) carboxylates displaying the Ag_2L_2 dimer [e.g. one of the Ag-Ag interactions in silver(I) *o*-nitrobenzoate is 2.892Å(1)[259d] and the hydrogen maleate type (2) structure contains an Ag-Ag separation of 3.000(1)Å].[262] The shortest separation of silver atoms between successive sheets of the polymer chains of 3.273(1) is rather longer than that found in the Ag_2L_2 units and does not suggest the presence of any significant metal-metal interactions in this direction.

TABLE 50. Bond lengths (Å) and angles (°) for silver(I) cyanoacetate.

Ag(1)-O(1)	2.198(5)	Ag(1)-O(2)	2.187(4)
Ag(1)-N(1)#1	2.370(6)	Ag(1)-Ag(1)#2	2.8939(12)
Ag(1)-Ag(1)#3	3.2726(11)	O(1)-C(1)	1.242(8)
O(2)-C(1)#2	1.263(8)	N(1)-C(3)	1.157(10)
N(1)-Ag(1)#1	2.370(6)	C(1)-O(2)#2	1.263(8)
C(1)-C(2)	1.523(8)	C(2)-C(3)	1.426(8)
O(1)-Ag(1)-O(2)	162.6(2)	O(1)-Ag(1)-N(1)#1	97.7(2)
O(2)-Ag(1)-N(1)#1	99.6(2)	O(1)-Ag(1)-Ag(1)#2	81.94(14)
O(1)-Ag(1)-Ag(1)#2	80.97(13)	N(1)#1-Ag(1)-Ag(1)#2	171.2(2)
O(1)-Ag(1)-Ag(1)#3	120.16(13)	O(2)-Ag(1)-Ag(1)#3	59.88(14)
N(1)#1-Ag(1)-Ag(1)#3	88.9(2)	Ag(1)#2-Ag(1)-Ag(1)#3	98.90(3)
C(1)-O(1)-Ag(1)	123.9(5)	C(1)#2-O(2)-Ag(1)	125.4(4)
C(3)-N(1)-Ag(1)#1	154.4(5)	O(1)-C(1)-O(2)#2	127.4(7)
O(1)-C(1)-C(2)	117.2(6)	O(2)#2-C(1)-C(2)	115.4(5)
C(3)-C(2)-C(1)	113.9(5)	N(1)-C(3)-C(2)	117.3(6)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1 #2 -x,-y+1,-z #3 -x+1,-y+1,-z

The immediate coordination sphere of the silver atoms comprises two oxygen atoms and a nitrogen in a T-shaped array. If an additional bond is considered between the two silver atoms of the dimer units [Ag(1)-Ag(1a)], the geometry of the metal atoms can be described as distorted square planar.

The two carboxyl functions and two silver atoms of the Ag_2L_2 dimer form a planar centrosymmetric arrangement. The Ag-O distances [2.187(4), 2.198(5)Å] and O-Ag-O angle [162.6(2)°] are comparable to those of other silver(I) carboxylates where the dimer motif is observed. For example, Ag-O distances range from 2.158(3)Å in the hydrated (*p*-fluorophenoxy)acetate,[265] to 2.387(3)Å in the maleate[262] and O-C-O angles range from 155.8(1)° in the (2-carbamoylphenoxy)acetate,[260] to 171.8(1)° again in the (*p*-fluorophenoxy)-acetate.

Each cyanoacetate ligand bridges three metal centres *via* a *syn*, *syn* bidentate bridging carboxyl function and a monodentate *N*-bonded nitrile group. The nitrile-metal interaction is characterised by an Ag-N bond length of 2.370(6)Å and a C-N-Ag angle of 154.4(5)°. The non-linearity observed with the C-N-M angle is also present in other *N*-bonded cyanoacetate complexes such as the cadmium(II) derivative [$\angle$C-N-Cd=164.3(5)°][183] and the copper(I) triphenylphosphine complexes [$Cu(O_2CCH_2CN)_2H(PPh_3)_2$] [$\angle$C-N-Cu=153.3(3)°][66] and [$Cu(O_2CCH_2CN)(PPh_3)_2$] [$\angle$C-N-Cu=162.0(4)°].[271]

The cyanomethyl moiety is almost linear with a C-C-N angle of 177.3(6)° and contains a C-N bond length of 1.157(10)Å which is very similar to the corresponding distance in the *N*-bonded cyanoacetic acid complex [$W(CO)_5(NCCH_2CO_2H)$] of 1.15(1)Å.[191] The nitrile functions found in the titanocene cyanoacetate described in Chapter 2 are not bound to a metal centre and accordingly have shorter C-N bond lengths [1.137(5), 1.140(5)Å]. However, there is little difference between N-bonded and free cyano bond lengths in cadmium(II) cyanoacetate [1.139(9) and 1.132(10)Å respectively].[183]

The remaining bond lengths and angles of the cyanoacetate ligand are akin to those previously reported in the trimeric Fe(II/III) complex [$Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3$].[182]

Molecular orbital calculations

The short metal-metal separation found in silver carboxylates containing bis(carboxylato-*O,O'*)disilver dimers have often been considered as evidence of a direct interaction between the formally d^{10} metal centres.[259c, 260] Molecular orbital (M.O.) calculations were conducted to enable an estimate of the strength of any bonding interaction to be made and to establish the effect that the ligand set has on such a bond. The approach used is similar to that adopted in the study of metal-metal interactions in copper(I) systems by Hoffmann and co-workers.[272]

The basis set for the EHMO calculation was selected from the structure of silver(I) cyanoacetate descibed above and is shown in Figure 35. It consists of an Ag_2^{2+} core surrounded by four cyanoacetate anions, giving the overall charge for the portion of the structure as -2. Two of the cyanoacetate ligands are *O,O'*-bonded in the *syn, syn* conformation, while the other two are *N*-bonded.

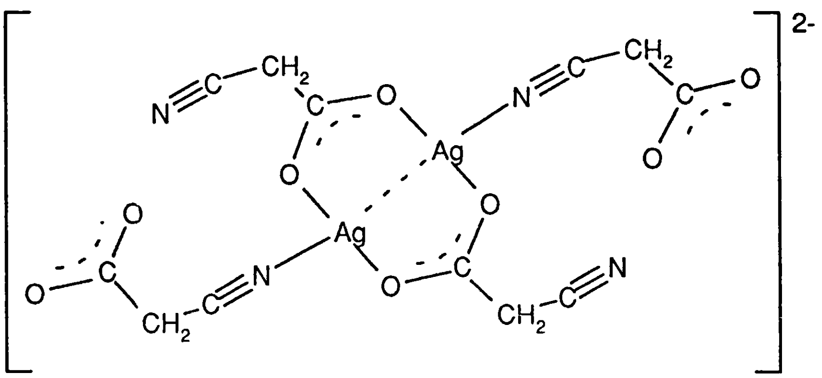


Figure 35. The section of the silver(I) cyanoacetate structure used in the EHMO investigation.

The section of the cyanoacetate structure shown in Figure 35 was treated as two fragments, the Ag_2^{2+} core and the four cyanoacetate ligands, to allow a comparison between an isolated Ag_2^{2+} cation and the whole complex with respect to Ag-Ag bonding. Tables 51 and 52 summarise the results obtained from these calculations. The relative strengths of important bonding interactions expressed as overlap populations are given Table 51 along with the relative binding energies of an Ag_2^{2+} cation using different levels of parameterisation. Table 52 lists the gross atomic orbital populations for the disilver dication and the section of the silver cyanoacetate structure chosen.

Table 51.

	Overlap Population (electrons)				Binding Energy (eV)	
	Ag-Ag		Ag-N	Ag-O		
	4d only	5s, 5p and 4d			4d only	5s, 5p and 4d
Ag_2^{2+} $[Ag\text{-}Ag = 2.894Å]$	-0.001	+0.053			+0.019	-0.163
$[Ag_2(O_2CCH_2CN)_4]^{2-}$		+0.062	+0.220	+0.200		

For the Ag_2^{2+} cation with a separation of 2.894Å between the metal centres, M.O. calculations in which only the 4d orbitals are considered, predicts a slightly repulsive interaction between the silver cations relative to their isolated states, with an overlap population of -0.001 electron and a binding energy of +0.019eV. However, inclusion of the 5s and 5p orbitals gives rise to an attractive interaction with an overlap population of +0.053 electron and a binding energy of -0.163eV. These results are similar to those of Hoffmann for Cu_2^{2+}, who showed that the attractive interaction arose principally from s, p_z and d_{z^2} orbital mixing which lowers the energy of the σ- and σ*-orbitals.[272] This is illustrated in Figure 36 which depicts orbital interaction diagrams for the Ag_2^{2+} fragments where the 5s and 5p orbitals have been omitted (Fig 36a) and included (Fig. 36b) in the M.O. calculations.

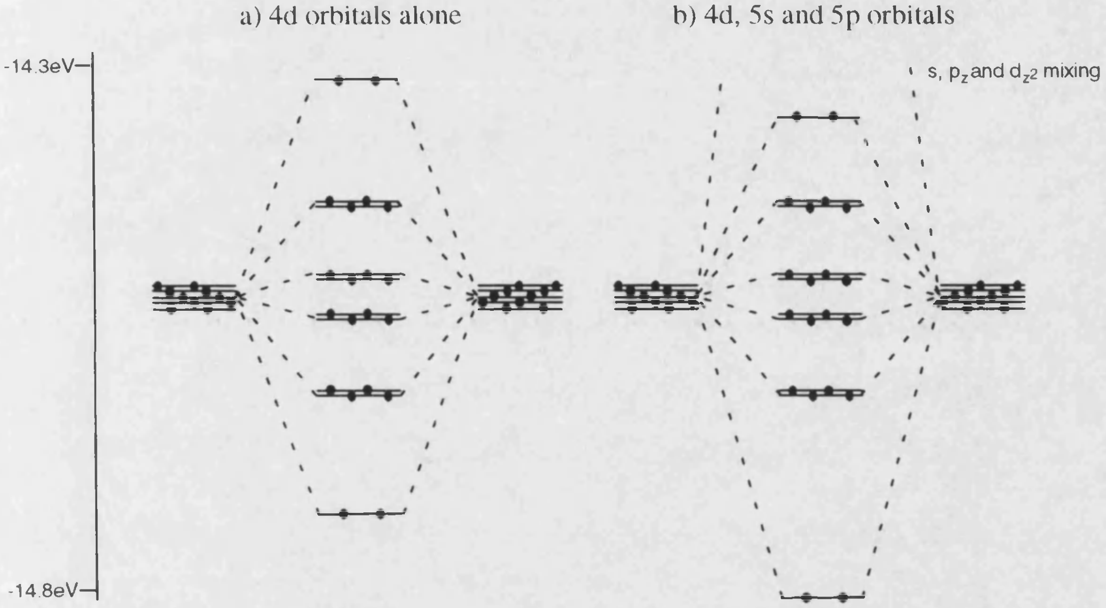


Figure 36. Orbital interaction diagrams for a Ag_2^{2+} cation with a separation of 2.894Å between the metal centres. a) Calculation perfomed considering the 4d orbitals alone. b) Calculation perfomed considering 4d, 5s and 5p orbitals. Energy levels from the 5s and 5p orbitals are omitted for clarity.

Introduction of the ligand set produces a slight enhancement of the Ag-Ag interaction as displayed by the overlap orbital population of +0.062 electron (Table 51). For comparison, the overlap populations of the Ag-O and Ag-N interactions are also given in Table 51 and are similar to that calculated for atomic oxygen absorbed on a metallic silver surface.[270]

A more detailed study of the overlap populations reveals that the d-d overlap actually decreases on going from the isolated dication to the $[Ag_2(O_2CCH_2CN)_4]^{2-}$ species. However, the s and p overlaps more than compensate this decrease, giving a net increase in the combined orbital overlap population. Introduction of the cyanoacetate ligands increases the s, p and d mixing and raises the s and p contributions to the Ag-Ag interaction relative to the isolated Ag_2^{2+}

cation. The silver atoms can be thought of as having moved towards $d^9s^np^{n-1}$ electronic configurations. These results are presented in Table 52.

Table 52. Gross atomic orbital populations.

Orbital	Ag_2^{2+}	$[Ag_2(O_2CCH_2CN)_4]^{2-}$
4d	9.966	9.927
5s	0.026	0.422
5p	0.009	0.297
charge on Ag	+1.000	+0.353

In conclusion, these calculations support the existence of a weak, attractive Ag-Ag interaction which contributes to the stablisation of dinuclear silver(I) carboxylates.

Supplementary data

Table A1.1. Crystal data and structure refinement for silver(I) cyanoacetate.

Empirical formula	$C_3H_2NO_2Ag$
Formula weight	191.9
Temperature	293(2)°K
Wavelength	0.70930Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 4.6920(6)Å alpha = 111.00(2)°
	b = 7.053(1)Å beta = 103.88(2)°
	c = 7.292(1)Å gamma = 94.82(1)°
Volume	214.82(5)Å^3
Z	2
Density (calculated)	2.967 Mg/m^3
Absorption coefficient	4.544mm^{-1}
F(000)	180
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	3.12. to 23.92°
Index ranges	$-5\leq h\leq 0$; $-8\leq k\leq 8$; $-8\leq l\leq 8$
Reflections collected	761
Independent reflections	669 [R(int) = 0.0127]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	669 /0 /67
Goodness-of-fit on F^2	1.285
Final R indices $[I>2\sigma(I)]$	R1 = 0.0490 wR2 = 0.1250
R indices (all data)	R1 = 0.0498 wR2 = 0.1266
Largest diff. peak and hole	2.060 and -2.005eÅ^{-3}
Weighting scheme	calc $w=1/[\sigma^2(F_o^2)+(0.1000P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.1357(195)
Extinction expression	$F_c=kF_c[1+0.001\{F_c^2\lambda^3/\sin(2\theta)\}]^{-1/4}$

TABLE A1.2. Fractional atomic co-ordinates (x10^4) and isotropic displacement parameters (Å^{2}x10^3) for silver(I) cyanoacetate.

	x	*y*	*z*	U(eq)
Ag(1)	2879(1)	5580(1)	1530(1)	42(1)
O(1)	1556(10)	8623(7)	2441(8)	45(1)
O(2)	3015(11)	2346(7)	-173(6)	43(1)
N(1)	2814(16)	13589(9)	5641(10)	52(2)
C(1)	-944(14)	8927(10)	1685(9)	30(1)
C(2)	-1668(12)	11049(8)	2709(8)	35(1)
C(3)	776(14)	12487(9)	4327(9)	34(1)

TABLE A1.3. Anisotropic temperature factors (Å^2 x10^3) for silver(I) cyanoacetate.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag(1)	34(1)	30(1)	48(1)	2(1)	5(1)	5(1)
O(1)	28(3)	33(2)	64(3)	10(2)	9(2)	6(2)
O(2)	41(3)	31(2)	38(2)	2(2)	-4(2)	10(2)
N(1)	49(4)	38(3)	57(4)	19(2)	-4(3)	0(3)
C(1)	27(3)	30(3)	32(3)	13(2)	6(3)	6(2)
C(2)	33(3)	26(3)	38(3)	4(2)	5(2)	8(2)
C(3)	35(3)	26(3)	40(3)	12(3)	11(3)	9(3)

TABLE A1.4. Hydrogen fractional atomic co-ordinates (x10^4) and isotropic temperature factors (Å^2 x10^3) for silver(I) cyanoacetate.

	x	*y*	*z*	U(eq)
H(1)	-2311(12)	11613(8)	1678(8)	66(17)
H(2)	-3323(12)	10889(8)	3255(8)	66(17)

Table A1.5. Orbital energies and Slater orbital exponents used in the molecular orbital calculations.

Orbital	H_{ii} (eV)	Slater Exponents
H 1s	-13.6	1.300
C 2s	-21.4	1.625
C 2p	-11.4	1.625
N 2s	-26.0	1.950
N 2p	-13.4	1.950
O 2s	-32.3	2.275
O 2p	-14.8	2.275
Ag 4d	-14.5	6.070 (0.55908) 2.663 (0.60478)
Ag 5s	-11.1	2.244
Ag 5p	-5.8	2.202

Appendix 2.

Supplementary data for the crystal structure determination of bis(cyanoacetato)-bis(cyclopentadienyl)titanium(IV) N1.

Table A2.1. Crystal parameters, data collection and structure solution details for bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) **N1**.

Identification code	**N1**
Empirical formula	$C_{16}H_{14}N_2O_4Ti$
M	342.2
Space group	$P\bar{1}$
Z	2
a/Å	8.231(1)
b/Å	9.850(1)
c/Å	10.537(2)
α/°	93.46(1)
β/°	108.57(1)
γ/°	99.42(1)
U/Å^3	793.1
D_c/g cm^{-1}	1.43
Crystal dimensions/mm	0.4 × 0.4 × 0.5
μ(Mo-K_α) cm^{-1}	5.30
F(000)	352
Residual densities/eÅ^{-3}	
max., min	0.12, -0.12
Data collected	2658
Unique data	2063
Max. shift/e.s.d.	0.005
No. cycles of least squares	12
R	0.0354
R_w	0.0401
Weighting scheme, *w* =	$2.4649/[\sigma^2(F) + 0.000448(F)^2]$

Table A2.2. Final fractional atomic coordinates (x10^4) for experimentally located atoms of bis(cyanoacetato)bis(cyclopentadienyl)titanium N1.

Atom	*x*	*y*	*z*
Ti(1)	1826(1)	2343	3389
O(1)	115(2)	923(2)	2011(2)
O(2)	-1671(4)	-618(2)	2641(2)
O(3)	2364(2)	3310(2)	1951(2)
O(4)	4662(3)	5009(3)	2382(3)
N(1)	-5255(4)	-2028(3)	-204(4)
N(2)	-367(5)	3120(4)	-1223(3)
C(1)	2977(5)	639(4)	4653(5)
C(2)	3869(5)	1841(5)	5363(3)
C(3)	4758(4)	2492(5)	4649(6)
C(4)	4473(7)	1672(10)	3502(6)
C(5)	3374(8)	512(6)	3504(5)
C(6)	1746(4)	4073(3)	5004(3)
C(7)	607(4)	2861(3)	5066(3)
C(8)	-767(4)	2591(3)	3859(3)
C(9)	-502(4)	3594(3)	3042(3)
C(10)	1039(4)	4528(3)	3755(3)
C(11)	-1225(4)	-43(3)	1799(3)
C(12)	-2241(4)	-414(3)	305(3)
C(13)	-3935(4)	-1315(3)	35(3)
C(14)	3342(4)	4295(3)	1639(3)
C(15)	2689(4)	4555(4)	164(3)
C(16)	980(5)	3749(3)	-613(3)
H(121)	-1541(49)	-842(37)	-51(37)
H(122)	-2403(48)	391(41)	-44(37)
H(151)	3439(51)	4248(37)	-294(37)
H(152)	2739(48)	5507(42)	177(37)

Table A2.3. Bond lengths (Å) for bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1.

Ti(1)-O(1)	1.963(4)	Ti(1)-O(3)	1.966(6)
Ti(1)-C(1)	2.340(5)	Ti(1)-C(2)	2.360(5)
Ti(1)-C(3)	2.330(5)	Ti(1)-C(4)	2.348(6)
Ti(1)-C(5)	2.360(6)	Ti(1)-C(6)	2.358(5)
Ti(1)-C(7)	2.362(5)	Ti(1)-C(8)	2.385(5)
Ti(1)-C(9)	2.389(5)	Ti(1)-C(10)	2.391(5)
O(1)-C(11)	1.282(4)	O(2)-C(11)	1.202(4)
O(3)-C(14)	1.284(4)	O(4)-C(14)	1.195(4)
N(1)-C(13)	1.137(5)	N(2)-C(16)	1.140(5)
C(1)-C(2)	1.326(6)	C(1)-C(3)	2.147(7)
C(1)-C(4)	2.170(8)	C(1)-C(5)	1.355(7)
C(2)-C(3)	1.330(7)	C(2)-C((4)	2.175(8)
C(2)-C(5)	2.174(7)	C(3)-C(4)	1.345(9)

C(3)-C(5)	2.161(9)	C(4)-C(5)	1.336(9)
C(6)-C(7)	1.410(5)	C(6)-C(8)	2.252(6)
C(6)-C(9)	2.254(6)	C(6)-C(10)	1.393(5)
C(7)-C(8)	1.383(5)	C(7)-C(9)	2.250(6)
C(7)-C(10)	2.264(6)	C(8)-C(9)	1.384(5)
C(8)-C(10)	2.250(6)	C(9)-C(10)	1.395(5)
C(11)-C(12)	1.518(6)	C(12)-C(13)	1.457(5)
C(12)-H(121)	0.921(39)	C(12)-H(122)	0.906(40)
C(14)-C(15)	1.527(6)	C(15)-C(16)	1.450(6)
C(15)-H(151)	0.968(40)	C(15)-H(152)	0.931(40)
C(1)-H(11)	0.960	C(2)-H(21)	0.960
C(3)-H(31)	0.960	C(4)-H(41)	0.960
C(5)-H(51)	0.960	C(6)-H(61)	0.960
C(7)-H(71)	0.960	C(8)-H(81)	0.960
C(9)-H(91)	0.960	C(10)-H(101)	0.960

TABLE A2.4. Bond angles (°) for bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) **N1**.

O(3)-Ti(1)-O(1)	89.3(2)	C(1)-Ti(1)-O(1)	91.1(2)
C(1)-Ti(1)-O(3)	133.8(1)	C(2)-Ti(1)-O(1)	123.9(2)
C(2)-Ti(1)-O(3)	126.4(2)	C(2)-Ti(1)-C(1)	32.8(1)
C(3)-Ti(1)-O(1)	132.8(2)	C(3)-Ti(1)-O(3)	93.5(2)
C(3)-Ti(1)-C(1)	54.7(2)	C(3)-Ti(1)-C(2)	32.9(1)
C(4)-Ti(1)-O(1)	102.0(3)	C(4)-Ti(1)-O(3)	79.7(2)
C(4)-Ti(1)-C(1)	55.2(3)	C(4)-Ti(1)-C(2)	55.0(2)
C(4)-Ti(1)-C(3)	33.4(2)	C(5)-Ti(1)-O(1)	78.5(2)
C(5)-Ti(1)-O(3)	102.2(3)	C(5)-Ti(1)-C(1)	33.5(2)
C(5)-Ti(1)-C(2)	54.8(2)	C(5)-Ti(1)-C(3)	54.9(3)
C(5)-Ti(1)-C(4)	33.0(2)	C(6)-Ti(1)-O(1)	136.5(1)
C(6)-Ti(1)-O(3)	106.4(2)	C(6)-Ti(1)-C(1)	104.6(2)
C(6)-Ti(1)-C(2)	78.8(2)	C(6)-Ti(1)-C(3)	87.4(3)
C(6)-Ti(1)-C(4)	120.4(3)	C(6)-Ti(1)-C(5)	133.6(1)
C(7)-Ti(1)-O(1)	108.3(2)	C(7)-Ti(1)-O(3)	135.4(1)
C(7)-Ti(1)-C(1)	87.7(2)	C(7)-Ti(1)-C(2)	77.3(2)
C(7)-Ti(1)-C(3)	102.2(3)	C(7)-Ti(1)-C(4)	132.2(1)
C(7)-Ti(1)-C(5)	121.1(3)	C(7)-Ti(1)-C(6)	34.8(1)
C(8)-Ti(1)-O(1)	80.0(2)	C(8)-Ti(1)-O(3)	118.7(2)
C(8)-Ti(1)-C(1)	106.8(2)	C(8)-Ti(1)-C(2)	108.5(2)
C(8)-Ti(1)-C(3)	136.1(2)	C(8)-Ti(1)-C(4)	161.6(1)
C(8)-Ti(1)-C(5)	133.1(2)	C(8)-Ti(1)-C(6)	56.7(2)
C(8)-Ti(1)-C(7)	33.9(1)	C(9)-Ti(1)-O(1)	85.4(2)
C(9)-Ti(1)-O(3)	85.7(2)	C(9)-Ti(1)-C(1)	140.3(1)
C(9)-Ti(1)-C(2)	132.2(1)	C(9)-Ti(1)-C(3)	141.8(2)
C(9)-Ti(1)-C(4)	163.5(2)	C(9)-Ti(1)-C(5)	161.9(2)
C(9)-Ti(1)-C(6)	56.7(2)	C(9)-Ti(1)-C(7)	56.5(2)
C(9)-Ti(1)-C(8)	33.7(1)	C(10)-Ti(1)-O(1)	118.2(2)

C(10)-Ti(1)-O(3)	78.6(2)	C(10)-Ti(1)-C(1)	138.6(2)
C(10)-Ti(1)-C(2)	111.1(2)	C(10)-Ti(1)-C(3)	108.5(3)
C(10)-Ti(1)-C(4)	133.6(3)	C(10)-Ti(1)-C(5)	163.3(1)
C(10)-Ti(1)-C(6)	34.1(1)	C(10)-Ti(1)-C(7)	56.9(2)
C(10)-Ti(1)-C(8)	56.2(2)	C(10)-Ti(1)-C(9)	33.9(1)
C(11)-O(1)-Ti(1)	143.5(2)	C(14)-O(3)-Ti(1)	147.4(2)
C(2)-C(1)-Ti(1)	74.4(3)	C(3)-C(1)-Ti(1)	62.4(2)
C(3)-C(1)-C(2)	36.1(2)	C(4)-C(1)-Ti(1)	62.6(2)
C(4)-C(1)-C(2)	72.4(4)	C(4)-C(1)-C(3)	36.3(2)
C(5)-C(1)-Ti(1)	74.1(3)	C(5)-C(1)-C(2)	108.3(5)
C(5)-C(1)-C(3)	72.2(4)	C(5)-C(1)-C(4)	36.0(3)
C(1)-C(2)-Ti(1)	72.8(3)	C(3)-C(2)-Ti(1)	72.3(3)
C(3)-C(2)-C(1)	107.9(5)	C(4)-C(2)-Ti(1)	62.2(2)
C(4)-C(2)-C(1)	72.1(4)	C(4)-C(2)-C(3)	35.8(3)
C(5)-C(2)-Ti(1)	62.6(2)	C(5)-C(2)-C(1)	36.3(3)
C(5)-C(2)-C(3)	71.6(4)	C(5)-C(2)-C(4)	35.8(2)
C(1)-C(3)-Ti(1)	62.9(2)	C(2)-C(3)-Ti(1)	74.8(3)
C(2)-C(3)-C(1)	36.0(2)	C(4)-C(3)-Ti(1)	74.0(3)
C(4)-C(3)-C(1)	72.8(4)	C(4)-C(3)-C(2)	108.8(5)
C(5)-C(3)-Ti(1)	63.3(2)	C(5)-C(3)-C(1)	36.7(2)
C(5)-C(3)-C(2)	72.6(4)	C(5)-C(3)-C(4)	36.1(3)
C(1)-C(4)-Ti(1)	62.2(2)	C(2)-C(4)-Ti(1)	62.8(2)
C(2)-C(4)-C(1)	35.5(2)	C(3)-C(4)-Ti(1)	72.6(3)
C(3)-C(4)-C(1)	70.9(4)	C(3)-C(4)-C(2)	35.4(2)
C(5)-C(4)-Ti(1)	74.0(3)	C(5)-C(4)-C(1)	36.5(2)
C(5)-C(4)-C(2)	72.1(4)	C(5)-C(4)-C(3)	107.4(5)
C(1)-C(5)-Ti(1)	72.4(3)	C(2)-C(5)-Ti(1)	62.6(2)
C(2)-C(5)-C(1)	35.4(2)	C(3)-C(5)-Ti(1)	61.8(2)
C(3)-C(5)-C(1)	71.1(4)	C(3)-C(5)-C(2)	35.7(2)
C(4)-C(5)-Ti(1)	73.0(3)	C(4)-C(5)-C(1)	107.5(5)
C(4)-C(5)-C(2)	72.1(4)	C(4)-C(5)-C(3)	36.4(3)
C(7)-C(6)-Ti(1)	72.8(3)	C(8)-C(6)-Ti(1)	62.2(2)
C(8)-C(6)-C(7)	35.8(2)	C(9)-C(6)-Ti(1)	62.3(2)
C(9)-C(6)-C(7)	71.6(3)	C(9)-C(6)-C(8)	35.8(1)
C(10)-C(6)-Ti(1)	74.2(3)	C(10)-C(6)-C(7)	107.7(4)
C(10)-C(6)-C(8)	71.9(3)	C(10)-C(6)-C(9)	36.1(2)
C(6)-C(7)-Ti(1)	72.5(3)	C(8)-C(7)-Ti(1)	74.0(3)
C(8)-C(7)-C(6)	107.5(4)	C(9)-C(7)-Ti(1)	62.3(2)
C(9)-C(7)-C(6)	71.9(3)	C(9)-C(7)-C(8)	35.6(2)
C(10)-C(7)-Ti(1)	62.2(2)	C(10)-C(7)-C(6)	35.9(2)
C(10)-C(7)-C(8)	71.6(3)	C(10)-C(7)-C(9)	36.0(1)
C(6)-C(8)-Ti(1)	61.1(2)	C(7)-C(8)-Ti(1)	72.2(3)
C(7)-C(8)-C(6)	36.7(2)	C(9)-C(8)-Ti(1)	73.3(3)
C(9)-C(8)-C(6)	72.2(3)	C(9)-C(8)-C(7)	108.8(4)
C(10)-C(8)-Ti(1)	62.0(2)	C(10)-C(8)-C(6)	36.0(1)
C(10)-C(8)-C(7)	72.7(3)	C(10)-C(8)-C(9)	36.1(2)

C(6)-C(9)-Ti(1)	61.0(2)	C(7)-C(9)-Ti(1)	61.1(2)
C(7)-C(9)-C(6)	36.5(1)	C(8)-C(9)-Ti(1)	73.0(3)
C(8)-C(9)-C(6)	72.1(3)	C(8)-C(9)-C(7)	35.6(2)
C(10)-C(9)-Ti(1)	73.1(3)	C(10)-C(9)-C(6)	36.0(2)
C(10)-C(9)-C(7)	72.5(3)	C(10)-C(9)-C(8)	108.1(3)
C(6)-C(10)-Ti(1)	71.7(3)	C(7)-C(10)-Ti(1)	60.9(2)
C(7)-C(10)-C(6)	36.4(2)	C(8)-C(10)-Ti(1)	61.8(2)
C(8)-C(10)-C(6)	72.1(3)	C(8)-C(10)-C(7)	35.7(1)
C(9)-C(10)-Ti(1)	72.9(3)	C(9)-C(10)-C(6)	107.9(4)
C(9)-C(10)-C(7)	71.5(3)	C(9)-C(10)-C(8)	35.8(2)
O(2)-C(11)-O(1)	126.4(4)	C(12)-C(11)-O(1)	111.7(3)
C(12)-C(11)-O(2)	121.9(3)	C(13)-C(12)-C(11)	113.1(3)
C(12)-C(13)-N(1)	178.4(4)	O(4)-C(14)-O(3)	126.6(4)
C(15)-C(14)-O(3)	114.6(3)	C(15)-C(14)-O(4)	118.8(4)
C(16)-C(15)-C(14)	114.4(3)	C(15)-C(16)-N(2)	179.7(2)
H(11)-C(1)-Ti(1)	117.6(2)	C(2)-C(1)-H(11)	125.9(4)
C(3)-C(1)-H(11)	161.9(3)	C(4)-C(1)-H(11)	161.7(3)
C(5)-C(1)-H(11)	125.8(5)	H(21)-C(2)-Ti(1)	120.6(2)
H(21)-C(2)-C(1)	126.2(4)	C(3)-C(2)-H(21)	126.0(4)
C(4)-C(2)-H(21)	161.8(3)	C(5)-C(2)-H(21)	162.3(3)
H(31)-C(3)-Ti(1)	117.7(2)	H(31)-C(3)-C(1)	161.5(3)
H(31)-C(3)-C(2)	125.6(4)	C(4)-C(3)-H(31)	125.6(5)
C(5)-C(3)-H(31)	161.8(3)	H(41)-C(4)-Ti(1)	118.9(2)
H(41)-C(4)-C(1)	163.1(3)	H(41)-C(4)-C(2)	161.4(3)
H(41)-C(4)-C(3)	126.0(5)	C(5)-C(4)-H(41)	126.6(5)
H(51)-C(5)-Ti(1)	120.3(2)	H(51)-C(5)-C(1)	126.5(5)
H(51)-C(5)-C(2)	161.8(3)	H(51)-C(5)-C(3)	162.4(3)
H(51)-C(5)-C(4)	126.0(5)	H(61)-C(6)-Ti(1)	118.8(2)
C(7)-C(6)-H(61)	126.1(3)	C(8)-C(6)-H(61)	161.9(1)
C(9)-C(6)-H(61)	162.3(1)	C(10)-C(6)-H(61)	126.2(3)
H(71)-C(7)-Ti(1)	119.3(2)	H(71)-C(7)-C(6)	126.2(3)
C(8)-C(7)-H(71)	126.3(3)	C(9)-C(7)-H(71)	161.9(1)
C(10)-C(7)-H(71)	162.1(1)	H(81)-C(8)-Ti(1)	120.7(2)
H(81)-C(8)-C(6)	162.2(1)	H(81)-C(8)-C(7)	125.5(3)
C(9)-C(8)-H(81)	125.7(3)	C(10)-C(8)-H(81)	161.8(1)
H(91)-C(9)-Ti(1)	119.7(2)	H(91)-C(9)-C(6)	162.0(1)
H(91)-C(9)-C(7)	161.5(1)	H(91)-C(9)-C(8)	125.9(3)
C(10)-C(9)-H(91)	126.0(3)	H(101)-C(10)-Ti(1)	121.1(2)
H(101)-C(10)-C(6)	126.0(3)	H(101)-C(10)-C(7)	162.4(1)
H(101)-C(10)-C(8)	161.9(1)	H(101)-C(10)-C(9)	126.1(3)
H(121)-C(12)-C(11)	105.8(24)	H(121)-C(12)-C(13)	110.8(23)
H(122)-C(12)-C(11)	107.1(24)	H(122)-C(12)-C(13)	109.2(24)
H(122)-C(12)-H(121)	110.8(34)	H(151)-C(15)-C(14)	109.4(23)
H(151)-C(15)-C(16)	103.0(23)	H(152)-C(15)-C(14)	105.8(24)
H(152)-C(15)-C(16)	113.0(24)	H(152)-C(15)-H(151)	111.2(32)

TABLE A2.5. Anisotropic displacement factors (Å x10^3) for bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) **N1.** The anisotropic displacement factor exponent takes the form: -2 (U .h .a* + ... +2U .h.k.a*.b*)

	U11	U22	U33	U23	U13	U12
Ti(1)	33	44	0	8	8	9
O(1)	41(1)	55(1)	0(1)	-5(1)	13(1)	1(1)
O(2)	102(2)	78(2)	0(1)	17(1)	34(1)	-6(1)
O(3)	55(1)	61(1)	0(1)	18(1)	18(1)	9(1)
O(4)	82(2)	85(2)	0(2)	21(1)	-16(1)	-26(1)
N(1)	52(2)	78(2)	0(3)	-11(2)	27(2)	-11(2)
N(2)	80(2)	98(2)	0(2)	7(2)	-9(2)	8(2)
C(1)	58(2)	84(3)	0(3)	63(3)	18(2)	26(2)
C(2)	80(2)	112(3)	0(2)	11(2)	-3(2)	57(2)
C(3)	36(2)	94(3)	0(5)	64(3)	-19(2)	0(2)
C(4)	86(3)	285(8)	0(3)	110(5)	61(3)	122(5)
C(5)	126(4)	126(4)	0(3)	-31(3)	-27(3)	102(3)
C(6)	55(2)	66(2)	0(2)	-11(1)	6(1)	19(1)
C(7)	78(2)	67(2)	0(2)	17(1)	37(2)	34(2)
C(8)	45(2)	61(2)	0(2)	0(1)	27(1)	13(1)
C(9)	48(2)	64(2)	0(2)	3(1)	9(1)	27(1)
C(10)	65(2)	46(1)	0(2)	8(1)	23(1)	19(1)
C(11)	46(1)	47(1)	0(1)	5(1)	17(1)	9(1)
C(12)	41(1)	53(2)	0(2)	-1(1)	16(1)	-2(1)
C(13)	53(2)	55(2)	0(2)	-6(1)	20(1)	8(1)
C(14)	51(2)	48(1)	0(2)	12(1)	10(1)	8(1)
C(15)	59(2)	63(2)	0(2)	23(1)	19(1)	9(2)
C(16)	68(2)	66(2)	0(2)	18(1)	16(2)	22(2)

Table A2.6. Cyclopentadienyl hydrogen fractional atomic coordinates (x10^4) and isotropic temperature factors (Å^{2}x10^3) for bis(cyanoacetato)bis(cyclopentadienyl)titanium(IV) N1.

	x	*y*	*z*	U
H(11)	2185(5)	-27(4)	4909(5)	90(3)
H(21)	3872(5)	2182(5)	6237(3)	90(3)
H(31)	5486(4)	3398(5)	4911(6)	90(3)
H(41)	4967(7)	1887(10)	2810(6)	90(3)
H(51)	2949(8)	-268(6)	2816(5)	90(3)
H(61)	2816(4)	4505(3)	5698(3)	90(3)
H(71)	757(4)	2324(3)	5811(3)	90(3)
H(81)	-1743(4)	1831(3)	3626(3)	90(3)
H(91)	-1247(4)	3638(3)	2142(3)	90(3)
H(101)	1526(4)	5341(3)	3442(3)	90(3)

Appendix 3.

Supplementary data for the crystal structure determination of bis(cyclopentadienyl)-bis(nicotinato)titanium(IV) N4.

Table A3.1. Crystal parameters, data collection and structure solution detalis for bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4.

Identification code	N4
Empirical formula	$C_{22}H_{18}N_2O_4Ti$
Formula weight	422.28
Temperature	293(2)°K
Wavelength	0.70930 Å
Crystal system	Triclinic
Space group	P-1(No.2)
Unit cell dimensions	a = 7.830(2)Å alpha = 87.46(2)°
	b = 10.593(2)Å beta = 82.86(2)°
	c = 12.046(3)Å gamma = 79.34(2)°
Volume	974.0(4) $Å^3$
Z	2
Density (calculated)	1.440 Mg/m^3
Absorption coefficient	0.471 mm^{-1}
F(000)	436
Crystal size	0.25 x 0.25 x 0.25 mm
Theta range for data collection	2.56 to 23.92°
Index ranges	-8<=h<=0; -12<=k<=11; -13<=l<=13
Reflections collected	3291
Independent reflections	3041 [R(int) = 0.0131]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3036 / 0 / 263
Goodness-of-fit on F^2	1.049
Final R indices [I>2σ(I)]	R1 = 0.0364 wR2 = 0.0881
R indices (all data)	R1 = 0.0637 wR2 = 0.1032
Largest diff. peak and hole	0.248 and -0.202 e.A-3
Weighting scheme	calc $w=1/[\sigma^2(Fo\text{^}2\text{^})+(0.0466P)^2+0.5031P]$ where $P=(Fo^2+2Fc^2)/3$
Extinction coefficient	0.0132(19)
Extinction expression	$Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Table A3.2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ti(1)	3368(1)	6020(1)	2517(1)	44(1)
N(1)	-2672(3)	9456(3)	-254(3)	69(1)
N(2)	-2942(3)	8958(3)	4908(2)	71(1)
O(1)	1865(3)	6961(2)	3738(2)	68(1)
O(2)	2716(3)	6689(3)	5433(2)	97(1)
O(3)	2031(3)	7010(2)	1438(2)	76(1)
O(4)	1810(4)	6651(3)	-315(2)	99(1)
C(1)	2243(6)	4369(3)	1731(4)	83(1)
C(2)	1282(5)	4638(4)	2746(5)	93(1)
C(3)	2363(8)	4309(4)	3565(4)	98(1)
C(4)	3992(6)	3842(3)	3051(4)	92(1)
C(5)	3930(5)	3893(3)	1908(4)	82(1)
C(6)	5002(5)	7712(4)	2152(4)	76(1)
C(7)	5285(4)	7239(4)	3174(3)	74(1)
C(8)	6109(4)	5978(4)	3095(4)	83(1)
C(9)	6389(4)	5703(4)	1938(5)	98(2)
C(10)	5662(5)	6813(5)	1396(3)	89(1)
C(11)	1666(4)	7148(3)	4806(3)	58(1)
C(12)	-26(3)	7979(2)	5230(2)	46(1)
C(13)	-341(4)	8415(3)	6307(3)	62(1)
C(14)	-1959(4)	9127(3)	6672(3)	71(1)
C(15)	-3193(4)	9368(3)	5946(3)	70(1)
C(16)	-1380(4)	8272(3)	4576(2)	58(1)
C(17)	1303(4)	7221(3)	538(3)	57(1)
C(18)	-267(3)	8285(3)	630(2)	46(1)
C(19)	-763(4)	9038(3)	1554(3)	57(1)
C(20)	-2219(4)	9993(3)	1576(3)	67(1)
C(21)	-3112(4)	10153(3)	656(3)	70(1)
C(22)	-1267(4)	8540(3)	-250(3)	57(1)

Table A3.3. Bond lengths (Å) and angles (°) for bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4.

Ti(1)-O(3)	1.922(2)	C(9)-Ti(1)-C(7)	56.40(13)
Ti(1)-O(1)	1.951(2)	C(5)-Ti(1)-C(7)	129.70(14)
Ti(1)-C(8)	2.330(3)	C(3)-Ti(1)-C(7)	122.9(2)
Ti(1)-C(4)	2.346(3)	C(10)-Ti(1)-C(7)	54.73(14)
Ti(1)-C(9)	2.348(3)	C(2)-Ti(1)-C(7)	154.0(2)
Ti(1)-C(5)	2.347(3)	O(3)-Ti(1)-C(1)	79.83(12)
Ti(1)-C(3)	2.361(4)	O(1)-Ti(1)-C(1)	116.38(14)
Ti(1)-C(10)	2.369(4)	C(8)-Ti(1)-C(1)	129.7(2)
Ti(1)-C(2)	2.371(3)	C(4)-Ti(1)-C(1)	55.85(13)
Ti(1)-C(7)	2.377(3)	C(9)-Ti(1)-C(1)	107.5(2)
Ti(1)-C(1)	2.379(3)	C(5)-Ti(1)-C(1)	33.55(13)
Ti(1)-C(6)	2.383(3)	C(3)-Ti(1)-C(1)	55.9(2)
N(1)-C(21)	1.323(4)	C(10)-Ti(1)-C(1)	116.2(2)
N(1)-C(22)	1.325(4)	C(2)-Ti(1)-C(1)	33.43(14)
N(2)-C(15)	1.322(4)	C(7)-Ti(1)-C(1)	162.97(14)
N(2)-C(16)	1.327(4)	O(3)-Ti(1)-C(6)	80.71(13)
O(1)-C(11)	1.296(4)	O(1)-Ti(1)-C(6)	91.51(12)
O(2)-C(11)	1.207(4)	C(8)-Ti(1)-C(6)	55.91(13)
O(3)-C(17)	1.279(3)	C(4)-Ti(1)-C(6)	135.7(2)
O(4)-C(17)	1.201(4)	C(9)-Ti(1)-C(6)	55.77(14)
C(1)-C(5)	1.364(5)	C(5)-Ti(1)-C(6)	131.33(14)
C(1)-C(2)	1.366(6)	C(3)-Ti(1)-C(6)	155.5(2)
C(2)-C(3)	1.370(6)	C(10)-Ti(1)-C(6)	32.62(13)
C(3)-C(4)	1.361(6)	C(2)-Ti(1)-C(6)	168.53(14)
C(4)-C(5)	1.382(6)	C(7)-Ti(1)-C(6)	32.63(12)
C(6)-C(10)	1.334(5)	C(1)-Ti(1)-C(6)	145.9(2)
C(6)-C(7)	1.337(5)	C(21)-N(1)-C(22)	116.2(3)
C(7)-C(8)	1.373(5)	C(15)-N(2)-C(16)	116.4(3)
C(8)-C(9)	1.418(6)	C(11)-O(1)-Ti(1)	144.3(2)
C(9)-C(10)	1.381(6)	C(17)-O(3)-Ti(1)	156.6(2)
C(11)-C(12)	1.494(4)	C(5)-C(1)-C(2)	108.1(4)
C(12)-C(13)	1.375(4)	C(5)-C(1)-Ti(1)	72.0(2)
C(12)-C(16)	1.380(4)	C(2)-C(1)-Ti(1)	73.0(2)
C(13)-C(14)	1.380(4)	C(1)-C(2)-C(3)	108.5(4)
C(14)-C(15)	1.365(4)	C(1)-C(2)-Ti(1)	73.6(2)
C(17)-C(18)	1.503(4)	C(3)-C(2)-Ti(1)	72.8(2)
C(18)-C(19)	1.372(4)	C(4)-C(3)-C(2)	107.5(4)
C(18)-C(22)	1.383(4)	C(4)-C(3)-Ti(1)	72.6(2)
C(19)-C(20)	1.376(4)	C(2)-C(3)-Ti(1)	73.6(2)
C(20)-C(21)	1.370(5)	C(3)-C(4)-C(5)	108.5(4)
		C(3)-C(4)-Ti(1)	73.8(2)
O(3)-Ti(1)-O(1)	90.71(10)	C(5)-C(4)-Ti(1)	72.9(2)
O(3)-Ti(1)-C(8)	135.14(13)	C(1)-C(5)-C(4)	107.4(4)
O(1)-Ti(1)-C(8)	100.40(14)	C(1)-C(5)-Ti(1)	74.5(2)
O(3)-Ti(1)-C(4)	135.66(12)	C(4)-C(5)-Ti(1)	72.8(2)
O(1)-Ti(1)-C(4)	108.6(2)	C(10)-C(6)-C(7)	109.5(4)

C(8)-Ti(1)-C(4)	81.37(14)	C(10)-C(6)-Ti(1)	73.1(2)
O(3)-Ti(1)-C(9)	112.2(2)	C(7)-C(6)-Ti(1)	73.4(2)
O(1)-Ti(1)-C(9)	133.46(13)	C(6)-C(7)-C(8)	109.2(4)
C(8)-Ti(1)-C(9)	35.29(14)	C(6)-C(7)-Ti(1)	73.9(2)
C(4)-Ti(1)-C(9)	83.2(2)	C(8)-C(7)-Ti(1)	71.1(2)
O(3)-Ti(1)-C(5)	105.83(13)	C(7)-C(8)-C(9)	106.2(3)
O(1)-Ti(1)-C(5)	135.45(13)	C(7)-C(8)-Ti(1)	74.9(2)
C(8)-Ti(1)-C(5)	96.2(2)	C(9)-C(8)-Ti(1)	73.0(2)
C(4)-Ti(1)-C(5)	34.24(14)	C(10)-C(9)-C(8)	105.9(3)
C(9)-Ti(1)-C(5)	78.24(14)	C(10)-C(9)-Ti(1)	73.8(2)
O(3)-Ti(1)-C(3)	121.8(2)	C(8)-C(9)-Ti(1)	71.7(2)
O(1)-Ti(1)-C(3)	79.57(14)	C(6)-C(10)-C(9)	109.1(4)
C(8)-Ti(1)-C(3)	103.0(2)	C(6)-C(10)-Ti(1)	74.3(2)
C(4)-Ti(1)-C(3)	33.6(2)	C(9)-C(10)-Ti(1)	72.1(2)
C(9)-Ti(1)-C(3)	115.7(2)	O(2)-C(11)-O(1)	124.5(3)
C(5)-Ti(1)-C(3)	56.4(2)	O(2)-C(11)-C(12)	121.1(3)
O(3)-Ti(1)-C(10)	80.96(14)	O(1)-C(11)-C(12)	114.3(3)
O(1)-Ti(1)-C(10)	124.11(14)	C(13)-C(12)-C(16)	117.2(3)
C(8)-Ti(1)-C(10)	56.8(2)	C(13)-C(12)-C(11)	121.6(3)
C(4)-Ti(1)-C(10)	115.5(2)	C(16)-C(12)-C(11)	121.1(3)
C(9)-Ti(1)-C(10)	34.1(2)	C(12)-C(13)-C(14)	119.2(3)
C(5)-Ti(1)-C(10)	99.5(2)	C(15)-C(14)-C(13)	118.5(3)
C(3)-Ti(1)-C(10)	149.0(2)	N(2)-C(15)-C(14)	124.1(3)
O(3)-Ti(1)-C(2)	88.66(14)	N(2)-C(16)-C(12)	124.7(3)
O(1)-Ti(1)-C(2)	84.26(14)	O(4)-C(17)-O(3)	124.5(3)
C(8)-Ti(1)-C(2)	135.4(2)	O(4)-C(17)-C(18)	121.9(3)
C(4)-Ti(1)-C(2)	55.67(14)	O(3)-C(17)-C(18)	113.6(3)
C(9)-Ti(1)-C(2)	133.61(14)	C(19)-C(18)-C(22)	117.6(3)
C(5)-Ti(1)-C(2)	55.88(14)	C(19)-C(18)-C(17)	122.9(2)
C(3)-Ti(1)-C(2)	33.7(2)	C(22)-C(18)-C(17)	119.5(3)
C(10)-Ti(1)-C(2)	149.6(2)	C(18)-C(19)-C(20)	119.5(3)
O(3)-Ti(1)-C(7)	110.33(13)	C(21)-C(20)-C(19)	117.8(3)
O(1)-Ti(1)-C(7)	78.04(11)	N(1)-C(21)-C(20)	124.7(3)
C(8)-Ti(1)-C(7)	33.91(13)	N(1)-C(22)-C(18)	124.3(3)
C(4)-Ti(1)-C(7)	112.52(14)		

Table A3.4. Anisotropic displacement parameters (Å^2 x 10^3) for bis(cyclopentadienyl)bis(nicotinato)titanium(IV) **N4**. The anisotropic displacement factor exponent takes the form: -2pi^2[h^{2}a*2U11 + ... + 2hka*b*U12]

Atom	U11	U22	U33	U23	U13	U12
Ti(1)	35(1)	44(1)	52(1)	-3(1)	-12(1)	-1(1)
N(1)	46(2)	80(2)	81(2)	14(2)	-23(1)	-7(1)
N(2)	56(2)	86(2)	67(2)	-14(2)	-19(1)	11(1)
O(1)	53(1)	79(2)	66(2)	-21(1)	2(1)	-1(1)
O(2)	66(2)	127(2)	79(2)	9(2)	-16(1)	33(2)
O(3)	80(2)	64(1)	88(2)	6(1)	-48(1)	3(1)
O(4)	105(2)	100(2)	72(2)	-16(2)	-14(2)	38(2)
C(1)	109(3)	61(2)	94(3)	0(2)	-51(3)	-33(2)
C(2)	56(2)	72(2)	156(4)	-4(3)	-14(3)	-27(2)
C(3)	139(4)	79(3)	84(3)	12(2)	-6(3)	-52(3)
C(4)	110(3)	45(2)	136(4)	18(2)	-75(3)	-17(2)
C(5)	80(3)	55(2)	110(3)	-24(2)	-8(2)	-9(2)
C(6)	71(2)	64(2)	98(3)	3(2)	-5(2)	-28(2)
C(7)	59(2)	90(3)	83(3)	-24(2)	-7(2)	-32(2)
C(8)	46(2)	91(3)	121(3)	29(3)	-41(2)	-21(2)
C(9)	38(2)	82(3)	171(5)	-60(3)	17(2)	-8(2)
C(10)	74(3)	126(4)	71(2)	-6(3)	9(2)	-42(3)
C(11)	48(2)	58(2)	64(2)	1(2)	-4(2)	-1(1)
C(12)	45(2)	45(2)	48(2)	1(1)	-6(1)	-7(1)
C(13)	61(2)	67(2)	58(2)	-10(2)	-20(2)	-1(2)
C(14)	76(2)	71(2)	60(2)	-27(2)	-10(2)	6(2)
C(15)	59(2)	65(2)	80(2)	-17(2)	-14(2)	11(2)
C(16)	54(2)	70(2)	47(2)	-5(1)	-8(1)	-3(2)
C(17)	53(2)	56(2)	63(2)	8(2)	-17(2)	-6(1)
C(18)	40(1)	50(2)	48(2)	9(1)	-11(1)	-12(1)
C(19)	51(2)	67(2)	56(2)	5(2)	-13(1)	-17(2)
C(20)	52(2)	68(2)	80(2)	-11(2)	5(2)	-13(2)
C(21)	37(2)	63(2)	106(3)	14(2)	-10(2)	-5(1)
C(22)	48(2)	66(2)	57(2)	5(1)	-13(1)	-9(2)

Table A3.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for bis(cyclopentadienyl)bis(nicotinato)titanium(IV) N4.

Atom	*x*	*y*	*z*	U(eq)
H(1)	1819(6)	4488(3)	1038(4)	99
H(2)	95(5)	4987(4)	2862(5)	111
H(3)	2041(8)	4391(4)	4331(4)	117
H(4)	4979(6)	3540(3)	3408(4)	110
H(5)	4867(5)	3647(3)	1361(4)	98
H(6)	4433(5)	8539(4)	1992(4)	92
H(7)	4972(4)	7692(4)	3834(3)	89
H(8)	6421(4)	5418(4)	3682(4)	100
H(9)	6947(4)	4933(4)	1611(5)	118
H(10)	5637(5)	6917(5)	627(3)	106
H(13)	525(4)	8233(3)	6783(3)	74
H(14)	-2202(4)	9435(3)	7397(3)	85
H(15)	-4279(4)	9852(3)	6198(3)	84
H(16)	-1183(4)	7968(3)	3850(2)	69
H(19)	-119(4)	8903(3)	2161(3)	68
H(20)	-2586(4)	10512(3)	2194(3)	80
H(21)	-4097(4)	10798(3)	672(3)	83
H(22)	-932(4)	8036(3)	-881(3)	68

Appendix 4.

Supplementary data for the crystal structure determination of bis(cyclopentadienyl)-(salicylato)titanium(IV) O1.

Table A4.1. Crystal parameters, data collection and structure solution details for bis(cyclopentadienyl)(salcylato)titanium(IV) **O1**.

Identification code	O1
Empirical formula	$C_{17}H_{14}O_3Ti$
M	314.2
Space group	$P2_1/c$
Z	4
a/Å	12.088(3)
b/Å	7.855(3)
c/Å	15.621(4)
α/°	
β/°	107.33(2)
γ/°	
U/Å^3	1415.9
D_c/g cm^{-1}	1.47
Crystal dimensions/mm	0.15 × 0.15 × 0.1
μ(Mo-K_α) cm^{-1}	5.8
F(000)	648
Residual densities/eÅ^{-3}	max., min
	0.13, -0.16
Data collected	2509
Unique data	989
Max. shift/e.s.d.	0.002
No. cycles of least squares	10
R	0.0570
R_w	0.0393
Weighting scheme, *w* =	$2.8942/[\sigma^2(F) + 0.000045(F)^2]$

TABLE A4.2. Fractional atomic co-ordinates (x10^4) for bis(cyclopentadienyl)(salicylato)titanium(IV) **O1**

	x	*y*	*z*
Ti(1)	2904(1)	2068(2)	1105(1)
O(1)	1524(4)	857(6)	1076(3)
O(2)	3482(4)	1595(6)	2380(3)
O(3)	3847(4)	169(6)	3635(3)
C(1)	1380(6)	-331(9)	1632(5)
C(2)	2140(6)	-572(9)	2499(5)
C(3)	3229(7)	414(10)	2871(5)
C(4)	362(6)	-1305(9)	1361(5)
C(5)	100(7)	-2446(9)	1937(7)
C(6)	852(9)	-2653(10)	2793(6)
C(7)	1858(7)	-1756(10)	3058(5)
C(8)	3185(12)	931(21)	-189(7)
C(9)	4161(12)	1843(11)	210(10)
C(10)	4704(7)	1097(16)	990(8)
C(11)	4109(13)	-317(15)	1082(8)
C(12)	3175(11)	-450(14)	348(11)
C(13)	1757(15)	4356(14)	1340(16)
C(14)	2811(21)	4790(13)	1738(8)
C(15)	3393(10)	4969(12)	1147(18)
C(16)	2583(24)	4649(16)	319(11)
C(17)	1601(13)	4288(13)	492(13)

TABLE A4.3. Bond lengths (Å) for bis(cyclopentadienyl)(salicylato)titanium(IV) O1.

O(1)-Ti(1)	1.909(6)	O(2)-Ti(1)	1.940(7)
C(8)-Ti(1)	2.325(11)	C(9)-Ti(1)	2.358(10)
C(10)-Ti(1)	2.362(10)	C(11)-Ti(1)	2.379(10)
C(12)-Ti(1)	2.377(10)	C(13)-Ti(1)	2.364(12)
C(14)-Ti(1)	2.372(12)	C(15)-Ti(1)	2.350(12)
C(16)-Ti(1)	2.342(12)	C(17)-Ti(1)	2.353(11)
C(1)-O(1)	1.321(8)	C(3)-O(2)	1.297(8)
C(3)-O(3)	1.221(8)	C(2)-C(1)	1.405(9)
C(4)-C(1)	1.403(9)	C(3)-C(2)	1.488(9)
C(7)-C(2)	1.385(9)	C(5)-C(4)	1.373(9)
C(6)-C(5)	1.385(10)	C(7)-C(6)	1.359(9)
C(9)-C(8)	1.362(12)	C(10)-C(8)	2.183(16)
C(11)-C(8)	2.197(16)	C(12)-C(8)	1.374(12)
C(10)-C(9)	1.335(11)	C(11)-C(9)	2.188(14)
C(12)-C(9)	2.206(16)	C(11)-C(10)	1.354(11)
C(12)-C(10)	2.190(16)	C(12)-C(11)	1.352(12)
C(14)-C(13)	1.287(13)	C(15)-C(13)	2.142(18)
C(16)-C(13)	2.131(18)	C(17)-C(13)	1.282(13)
C(15)-C(14)	1.324(15)	C(16)-C(14)	2.154(20)
C(17)-C(14)	2.095(17)	C(16)-C(15)	1.393(15)
C(17)-C(15)	2.169(19)	C(17)-C(16)	1.325(14)
H(51)-C(4)	0.960	H(51)-C(5)	0.960
H(61)-C(6)	0.960	H(71)-C(7)	0.960
H(81)-C(8)	0.960	H(91)-C(9)	0.960
H(101)-C(10)	0.960	H(111)-C(11)	0.960
H(121)-C(12)	0.960	H(131)-C(13)	0.960
H(141)-C(14)	0.960	H(151)-C(15)	0.960
H(161)-C(16)	0.960	H(171)-C(17)	0.960

TABLE A4.4. Bond angles (°) for bis(cyclopentadienyl)(salicylato)titanium(IV) O1.

O(2)-Ti(1)-O(1)	88.5(3)	C(8)-Ti(1)-O(1)	98.1(6)
C(8)-Ti(1)-O(2)	135.9(3)	C(9)-Ti(1)-O(1)	131.4(4)
C(9)-Ti(1)-O(2)	119.7(5)	C(9)-Ti(1)-C(8)	33.8(3)
C(10)-Ti(1)-O(1)	130.9(3)	C(10)-Ti(1)-O(2)	87.6(5)
C(10)-Ti(1)-C(8)	55.5(4)	C(10)-Ti(1)-C(9)	32.9(3)
C(11)-Ti(1)-O(1)	98.1(5)	C(11)-Ti(1)-O(2)	80.2(4)
C(11)-Ti(1)-C(8)	55.7(4)	C(11)-Ti(1)-C(9)	55.0(4)
C(11)-Ti(1)-C(10)	33.2(3)	C(12)-Ti(1)-O(1)	79.8(4)
C(12)-Ti(1)-O(2)	106.9(6)	C(12)-Ti(1)-C(8)	33.9(3)
C(12)-Ti(1)-C(9)	55.5(4)	C(12)-Ti(1)-C(10)	55.0(4)
C(12)-Ti(1)-C(11)	33.0(3)	C(13)-Ti(1)-O(1)	80.4(5)
C(13)-Ti(1)-O(2)	92.0(7)	C(13)-Ti(1)-C(8)	132.1(6)
C(13)-Ti(1)-C(9)	131.3(4)	C(13)-Ti(1)-C(10)	148.6(5)
C(13)-Ti(1)-C(11)	172.1(6)	C(13)-Ti(1)-C(12)	152.1(7)

C(14)-Ti(1)-O(1)	108.0(8)	C(14)-Ti(1)-O(2)	78.0(4)
C(14)-Ti(1)-C(8)	138.2(6)	C(14)-Ti(1)-C(9)	115.7(8)
C(14)-Ti(1)-C(10)	118.8(8)	C(14)-Ti(1)-C(11)	145.2(6)
C(14)-Ti(1)-C(12)	171.2(7)	C(14)-Ti(1)-C(13)	31.5(3)
C(15)-Ti(1)-O(1)	134.0(3)	C(15)-Ti(1)-O(2)	98.4(8)
C(15)-Ti(1)-C(8)	107.2(9)	C(15)-Ti(1)-C(9)	83.6(7)
C(15)-Ti(1)-C(10)	94.9(6)	C(15)-Ti(1)-C(11)	127.9(6)
C(15)-Ti(1)-C(12)	138.6(7)	C(15)-Ti(1)-C(13)	54.0(5)
C(15)-Ti(1)-C(14)	32.6(3)	C(16)-Ti(1)-O(1)	114.3(8)
C(16)-Ti(1)-O(2)	131.1(5)	C(16)-Ti(1)-C(8)	85.5(6)
C(16)-Ti(1)-C(9)	77.8(6)	C(16)-Ti(1)-C(10)	104.6(8)
C(16)-Ti(1)-C(11)	132.8(5)	C(16)-Ti(1)-C(12)	119.0(6)
C(16)-Ti(1)-C(13)	53.9(5)	C(16)-Ti(1)-C(14)	54.4(5)
C(16)-Ti(1)-C(15)	34.6(4)	C(17)-Ti(1)-O(1)	83.4(6)
C(17)-Ti(1)-O(2)	123.5(7)	C(17)-Ti(1)-C(8)	100.6(7)
C(17)-Ti(1)-C(9)	106.6(8)	C(17)-Ti(1)-C(10)	136.8(7)
C(17)-Ti(1)-C(11)	156.3(6)	C(17)-Ti(1)-C(12)	126.1(7)
C(17)-Ti(1)-C(13)	31.5(3)	C(17)-Ti(1)-C(14)	52.6(5)
C(17)-Ti(1)-C(15)	54.9(5)	C(17)-Ti(1)-C(16)	32.8(3)
C(2)-C(1)-O(1)	123.5(8)	C(4)-C(1)-O(1)	117.6(8)
C(4)-C(1)-C(2)	118.7(8)	C(3)-C(2)-C(1)	123.7(7)
C(7)-C(2)-C(1)	119.0(8)	C(7)-C(2)-C(3)	117.3(8)
O(3)-C(3)-O(2)	120.5(8)	C(2)-C(3)-O(2)	118.6(7)
C(2)-C(3)-O(3)	120.8(8)	C(5)-C(4)-C(1)	120.8(8)
C(6)-C(5)-C(4)	119.7(8)	C(7)-C(6)-C(5)	120.3(8)
C(6)-C(7)-C(2)	121.5(8)	C(10)-C(8)-C(9)	35.6(5)
C(11)-C(8)-C(9)	71.5(7)	C(11)-C(8)-C(10)	36.0(3)
C(12)-C(8)-C(9)	107.5(11)	C(12)-C(8)-C(10)	72.0(8)
C(12)-C(8)-C(11)	36.0(6)	C(10)-C(9)-C(8)	108.1(11)
C(11)-C(9)-C(8)	72.3(8)	C(11)-C(9)-C(10)	35.8(5)
C(12)-C(9)-C(8)	36.4(6)	C(12)-C(9)-C(10)	71.7(7)
C(12)-C(9)-C(11)	35.8(3)	C(9)-C(10)-C(8)	36.4(6)
C(11)-C(10)-C(8)	72.5(7)	C(11)-C(10)-C(9)	108.9(11)
C(12)-C(10)-C(8)	36.6(3)	C(12)-C(10)-C(9)	73.0(8)
C(12)-C(10)-C(11)	35.9(5)	C(9)-C(11)-C(8)	36.2(3)
C(10)-C(11)-C(8)	71.4(7)	C(10)-C(11)-C(9)	35.3(5)
C(12)-C(11)-C(8)	36.6(6)	C(12)-C(11)-C(9)	72.8(8)
C(12)-C(11)-C(10)	108.1(11)	C(9)-C(12)-C(8)	36.1(6)
C(10)-C(12)-C(8)	71.4(8)	C(10)-C(12)-C(9)	35.4(3)
C(11)-C(12)-C(8)	107.4(12)	C(11)-C(12)-C(9)	71.4(8)
C(11)-C(12)-C(10)	36.0(6)	C(15)-C(13)-C(14)	35.5(8)
C(16)-C(13)-C(14)	73.5(9)	C(16)-C(13)-C(15)	38.1(4)
C(17)-C(13)-C(14)	109.3(14)	C(17)-C(13)-C(15)	73.9(9)
C(17)-C(13)-C(16)	35.8(8)	C(15)-C(14)-C(13)	110.2(15)
C(16)-C(14)-C(13)	71.5(9)	C(16)-C(14)-C(15)	38.7(8)
C(17)-C(14)-C(13)	35.3(7)	C(17)-C(14)-C(15)	75.0(10)

C(17)-C(14)-C(16)	36.3(4)	C(14)-C(15)-C(13)	34.3(7)
C(16)-C(15)-C(13)	70.6(9)	C(16)-C(15)-C(14)	104.9(13)
C(17)-C(15)-C(13)	34.6(3)	C(17)-C(15)-C(14)	68.9(9)
C(17)-C(15)-C(16)	36.0(7)	C(14)-C(16)-C(13)	34.9(3)
C(15)-C(16)-C(13)	71.4(9)	C(15)-C(16)-C(14)	36.4(7)
C(17)-C(16)-C(13)	34.5(7)	C(17)-C(16)-C(14)	69.4(9)
C(17)-C(16)-C(15)	105.9(14)	C(14)-C(17)-C(13)	35.4(7)
C(15)-C(17)-C(13)	71.5(9)	C(15)-C(17)-C(14)	36.1(4)
C(16)-C(17)-C(13)	109.7(14)	C(16)-C(17)-C(14)	74.3(10)
C(16)-C(17)-C(15)	38.2(8)	H(51)-C(4)-C(1)	119.6(5)
C(5)-C(4)-H(51)	119.6(6)	H(51)-C(5)-C(4)	120.1(6)
C(6)-C(5)-H(51)	120.1(6)	H(61)-C(6)-C(5)	119.9(6)
C(7)-C(6)-H(61)	119.9(6)	H(71)-C(7)-C(2)	119.2(6)
H(71)-C(7)-C(6)	119.3(6)	C(9)-C(8)-H(81)	126.2(11)
C(10)-C(8)-H(81)	161.6(8)	C(11)-C(8)-H(81)	162.2(8)
C(12)-C(8)-H(81)	126.3(12)	H(91)-C(9)-C(8)	126.0(11)
C(10)-C(9)-H(91)	125.9(10)	C(11)-C(9)-H(91)	161.7(8)
C(12)-C(9)-H(91)	162.3(8)	H(101)-C(10)-C(8)	161.9(8)
H(101)-C(10)-C(9)	125.6(10)	C(11)-C(10)-H(101)	125.5(10)
C(12)-C(10)-H(101)	161.4(8)	H(111)-C(11)-C(8)	162.5(8)
H(111)-C(11)-C(9)	161.3(8)	H(111)-C(11)-C(10)	126.0(10)
C(12)-C(11)-H(111)	125.9(10)	H(121)-C(12)-C(8)	126.3(11)
H(121)-C(12)-C(9)	162.2(8)	H(121)-C(12)-C(10)	162.3(8)
H(121)-C(12)-C(11)	126.3(10)	C(14)-C(13)-H(131)	125.0(16)
C(15)-C(13)-H(131)	160.4(13)	C(16)-C(13)-H(131)	161.5(13)
C(17)-C(13)-H(131)	125.7(15)	H(141)-C(14)-C(13)	125.2(16)
C(15)-C(14)-H(141)	124.6(16)	C(16)-C(14)-H(141)	163.2(14)
C(17)-C(14)-H(141)	160.4(13)	H(151)-C(15)-C(13)	162.2(13)
H(151)-C(15)-C(14)	127.9(16)	C(16)-C(15)-H(151)	127.2(16)
C(17)-C(15)-H(151)	163.2(13)	H(161)-C(16)-C(13)	161.2(13)
H(161)-C(16)-C(14)	163.8(14)	H(161)-C(16)-C(15)	127.4(16)
C(17)-C(16)-H(161)	126.8(16)	H(171)-C(17)-C(13)	124.9(15)
H(171)-C(17)-C(14)	160.3(13)	H(171)-C(17)-C(15)	163.6(13)
H(171)-C(17)-C(16)	125.4(16)		

TABLE A4.5. Anisotropic displacement factors (Å x10^{3}) for bis(cyclopentadienyl)(salicylato)titanium(IV) **O1**.

	U11	U22	U33	U23	U13	U12
Ti(1)	54(1)	51(1)	53(1)	4(1)	14(1)	-5(1)
O(1)	57(3)	94(4)	54(3)	16(3)	-1(3)	-27(3)
O(2)	77(4)	105(4)	53(3)	15(3)	1(3)	-34(3)
O(3)	80(4)	102(4)	45(3)	10(3)	8(3)	2(3)
C(1)	52(5)	48(5)	62(6)	5(5)	27(5)	-2(4)
C(2)	58(5)	41(4)	44(5)	2(4)	27(4)	4(4)
C(3)	69(6)	62(5)	45(5)	3(5)	26(5)	9(5)
C(4)	55(5)	53(5)	86(6)	-9(5)	28(5)	-11(4)
C(5)	80(6)	55(7)	121(7)	-14(6)	56(6)	-25(5)
C(6)	124(8)	62(6)	89(7)	13(6)	55(6)	-14(6)
C(7)	87(6)	61(6)	61(5)	-6(5)	34(5)	-3(5)
C(8)	115(10)	130(12)	74(7)	-20(8)	17(7)	52(9)
C(9)	125(9)	63(7)	130(9)	34(8)	92(8)	39(8)
C(10)	79(7)	65(7)	132(10)	-14(7)	35(7)	9(6)
C(11)	150(11)	46(8)	119(10)	19(7)	32(9)	34(7)
C(12)	126(11)	57(8)	159(12)	-55(9)	57(9)	-18(7)
C(13)	121(13)	84(8)	190(17)	-43(10)	101(12)	-15(8)
C(14)	195(16)	60(7)	101(10)	-33(7)	-9(12)	-36(9)
C(15)	58(7)	39(6)	300(22)	39(11)	56(12)	-8(6)
C(16)	249(19)	82(9)	132(13)	66(9)	136(14)	103(12)
C(17)	119(12)	76(7)	120(12)	-34(9)	-31(10)	50(8)

TABLE A4.6. Hydrogen fractional atomic co-ordinates (x10^{4}) and isotropic temperature factors (Å^{2} x10^{3}) for bis(cyclopentadienyl)(salicylato)titanium(IV) O1.

	x	*y*	*z*	U
H(51)	-157(6)	-1172(9)	766(5)	121(8)
H(51)	-603(7)	-3099(9)	1747(7)	121(8)
H(61)	663(9)	-3434(10)	3201(6)	121(8)
H(71)	2385(7)	-1945(10)	3645(5)	121(8)
H(81)	2610(12)	1206(21)	-744(7)	121(8)
H(91)	4415(12)	2847(11)	-27(10)	121(8)
H(101)	5403(7)	1496(16)	1417(8)	121(8)
H(111)	4313(13)	-1090(15)	1580(8)	121(8)
H(121)	2609(11)	-1346(14)	224(11)	121(8)
H(131)	1181(15)	4122(14)	1635(16)	121(8)
H(141)	3135(21)	4959(13)	2373(8)	121(8)
H(151)	4195(10)	5259(12)	1260(18)	121(8)
H(161)	2707(24)	4681(16)	-260(11)	121(8)
H(171)	880(13)	4016(13)	52(13)	121(8)

Appendix 5.

Supplementary data for the crystal structure determination of diphenylphosphinylacetic acid, $HO_2CCH_2P(O)Ph_2$.

Table A5.1. Crystal parameters, data collection and structure solution details for diphenylphosphinylacetic acid, $HO_2CCH_2P(O)Ph_2$.

Identification code	$HO_2CCH_2P(O)Ph_2$
Empirical formula	$C_{14}H_{13}O_3P$
Formula weight	260.21
Temperature	293(2)° K
Wavelength	0.70930 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 5.6875(7)Å
	b = 17.049(4)Å beta = 93.36(1)°
	c = 13.471(2)Å
Volume	1304.0(4) $Å^3$
Z	4
Density (calculated)	1.325 Mg/m^3
Absorption coefficient	0.208 mm^{-1}
F(000)	544
Crystal size	0.3 x 0.2 x 0.2 mm
Theta range for data collection	2.38 to 23.92°
Index ranges	-6<=h<=0; -19<=k<=0; -15<=l<=15
Reflections collected	2282
Independent reflections	2057 [R(int) = 0.0181]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2054 / 0 / 213
Goodness-of-fit on F^2	1.033
Final R indices [$I>2\sigma(I)$]	R1 = 0.0531 wR2 = 0.1210
R indices (all data)	R1 = 0.1153 wR2 = 0.1656
Largest diff. peak and hole	0.323 and -0.286 $eÅ^{-3}$
Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0636P)^2+2.0525P]$ where $P=(Fo^2+2Fc^2)/3$
Extinction coefficient	0.0063(25)
Extinction expression	$Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Table A5.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for diphenylphosphinylacetic acid, $HO_2CCH_2P(O)Ph_2$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	U(eq)
P(1)	-238(2)	355(1)	7962(1)	42(1)
O(1)	2239(4)	410(2)	8383(2)	54(1)
O(2)	-4851(6)	1196(2)	9538(3)	65(1)
O(3)	-1102(6)	1231(2)	9993(3)	70(1)
C(1)	-1103(7)	1221(3)	7284(3)	48(1)
C(2)	426(10)	1813(3)	7168(5)	91(2)
C(3)	-121(12)	2462(4)	6594(6)	103(2)
C(4)	-2200(11)	2542(4)	6152(5)	82(2)
C(5)	-3766(12)	1987(6)	6262(7)	156(4)
C(6)	-3248(11)	1318(5)	6820(6)	138(4)
C(7)	-608(8)	-465(3)	7134(4)	60(1)
C(8)	-119(26)	-1128(7)	7317(9)	78(3)
C(8A)	-2709(23)	-915(7)	7035(7)	82(4)
C(9)	-472(41)	-1757(8)	6674(13)	85(4)
C(9A)	-2859(38)	-1564(10)	6448(13)	114(7)
C(10)	-1272(35)	-1703(18)	5736(17)	77(7)
C(10A)	-804(93)	-1801(26)	6069(25)	155(22)
C(11)	-1801(34)	-916(9)	5437(10)	133(7)
C(11A)	1218(38)	-1486(10)	6239(15)	115(6)
C(12)	-1464(29)	-280(8)	6064(9)	114(5)
C(12A)	1404(24)	-835(8)	6841(10)	82(3)
C(13)	-2349(6)	204(2)	8893(3)	40(1)
C(14)	-2697(7)	916(2)	9523(3)	44(1)

Table A5.3. Bond lengths (Å) and angles (°) for diphenylphosphinylacetic acid, $HO_2CCH_2P(O)Ph_2$.

P(1)-O(1)	1.490(3)	H(2)-O(1)#1	1.653(7)
P(1)-C(1)	1.790(4)	P(1)-C(7)	1.793(5)
P(1)-C(13)	1.804(4)	O(2)-C(14)	1.316(5)
O(3)-C(14)	1.202(5)	C(1)-C(2)	1.347(7)
C(1)-C(6)	1.348(7)	C(2)-C(3)	1.375(8)
C(3)-C(4)	1.300(8)	C(4)-C(5)	1.314(9)
C(5)-C(6)	1.389(9)	C(7)-C(8)	1.187(12)
C(7)-C(12A)	1.384(13)	C(7)-C(8A)	1.420(12)
C(7)-C(12)	1.526(13)	C(8)-C(9)	1.38(2)
C(8A)-C(9A)	1.36(2)	C(9)-C(10)	1.32(3)
C(9A)-C(10A)	1.36(5)	C(10)-C(11)	1.43(3)
C(10A)-C(11A)	1.28(5)	C(11)-C(12)	1.38(2)
C(11A)-C(12A)	1.37(2)	C(13)-C(14)	1.501(6)
O(1)-P(1)-C(1)	111.6(2)	O(1)-P(1)-C(7)	111.1(2)
C(1)-P(1)-C(7)	107.9(2)	O(1)-P(1)-C(13)	113.4(2)
O(2)-H(2)-O(1)#1	176(6)	C(1)-P(1)-C(13)	107.3(2)
C(7)-P(1)-C(13)	105.2(2)	C(2)-C(1)-C(6)	115.3(5)
C(2)-C(1)-P(1)	121.1(3)	C(6)-C(1)-P(1)	123.5(4)
C(1)-C(2)-C(3)	122.8(5)	C(4)-C(3)-C(2)	120.8(6)
C(3)-C(4)-C(5)	118.5(6)	C(4)-C(5)-C(6)	122.0(6)
C(1)-C(6)-C(5)	120.6(6)	C(8)-C(7)-C(12A)	55.8(8)
C(8)-C(7)-C(8A)	72.0(9)	C(12A)-C(7)-C(8A)	115.6(9)
C(8)-C(7)-C(12)	116.8(8)	C(12A)-C(7)-C(12)	92.8(9)
C(8A)-C(7)-C(12)	78.6(8)	C(8)-C(7)-P(1)	126.6(7)
C(12A)-C(7)-P(1)	117.6(6)	C(8A)-C(7)-P(1)	123.2(6)
C(12)-C(7)-P(1)	116.5(6)	C(7)-C(8)-C(9)	125.7(11)
C(9A)-C(8A)-C(7)	121.2(13)	C(10)-C(9)-C(8)	125(2)
C(8A)-C(9A)-C(10A)	116(2)	C(9)-C(10)-C(11)	113(2)
C(11A)-C(10A)-C(9A)	126(3)	C(12)-C(11)-C(10)	123.1(14)
C(10A)-C(11A)-C(12A)	119(3)	C(11)-C(12)-C(7)	116.1(11)
C(11A)-C(12A)-C(7)	120.0(14)	C(14)-C(13)-P(1)	113.2(3)
O(3)-C(14)-O(2)	120.3(4)	O(3)-C(14)-C(13)	122.6(4)
O(2)-C(14)-C(13)	117.1(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-1+x, y, z$

Table A5.4. Anisotropic displacement parameters (A^2 x 10^3) for diphenylphosphinylacetic acid, $HO_2CCH_2P(O)Ph_2$. The anisotropic displacement factor exponent takes the form:

$-2 pi^2 [h^2 a^* 2 U11 + ... + 2 h k a^* b^* U12]$

Atom	U11	U22	U33	U23	U13	U12
P(1)	27(1)	46(1)	53(1)	-2(1)	-4(1)	2(1)
O(1)	26(1)	61(2)	74(2)	-3(2)	-8(1)	1(1)
O(2)	47(2)	69(2)	78(2)	-32(2)	4(2)	6(2)
O(3)	57(2)	75(2)	77(2)	-22(2)	-19(2)	-10(2)
C(1)	32(2)	65(3)	48(3)	9(2)	8(2)	9(2)
C(2)	73(4)	58(3)	136(5)	27(4)	-36(4)	-10(3)
C(3)	92(5)	65(4)	149(7)	31(4)	-20(5)	-7(3)
C(4)	77(4)	91(4)	81(4)	37(3)	28(3)	23(3)
C(5)	64(4)	201(9)	197(9)	143(8)	-34(5)	-8(5)
C(6)	57(4)	174(8)	178(8)	129(7)	-42(4)	-34(4)
C(7)	47(3)	66(4)	68(3)	-20(3)	4(2)	1(2)
C(8)	112(11)	62(8)	56(7)	-9(6)	-25(7)	10(7)
C(8A)	110(9)	90(8)	49(6)	-26(6)	15(6)	-45(7)
C(9)	132(16)	43(7)	80(12)	-3(9)	7(11)	7(8)
C(9A)	174(19)	113(13)	55(9)	-25(9)	6(11)	-62(13)
C(10)	80(9)	89(15)	62(15)	-52(12)	10(8)	-1(8)
C(10A)	319(61)	91(18)	55(21)	-31(16)	8(23)	-42(25)
C(11)	229(20)	95(11)	71(9)	-30(8)	-32(10)	40(12)
C(11A)	169(18)	94(12)	83(11)	-31(11)	16(14)	53(12)
C(12)	196(16)	74(9)	66(8)	-3(7)	-40(9)	26(9)
C(12A)	84(9)	82(9)	80(9)	-17(8)	-1(7)	29(7)
C(13)	30(2)	39(2)	51(2)	4(2)	-8(2)	1(2)
C(14)	42(2)	46(3)	44(2)	2(2)	-2(2)	-2(2)

Table A5.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for diphenylphosphinylacetic acid, $HO_2CCH_2P(O)Ph_2$.

Atom	*x*	*y*	*z*	U(eq)
H(2)	-5845(118)	893(39)	9122(52)	122(24)
H(2)	1915(10)	1781(3)	7490(5)	109
H(3)	1012(12)	2848(4)	6520(6)	124
H(4)	-2571(11)	2983(4)	5767(5)	98
H(5)	-5266(12)	2045(6)	5958(7)	187
H(6)	-4392(11)	932(5)	6874(6)	165
H(8)	561(26)	-1235(7)	7947(9)	93
H(8A)	-4007(23)	-763(7)	7377(7)	99
H(9)	-119(41)	-2255(8)	6922(13)	102
H(9A)	-4271(38)	-1829(10)	6314(13)	137
H(10)	-1469(35)	-2133(18)	5315(17)	92
H(10A)	-881(93)	-2233(26)	5647(25)	186
H(11)	-2400(34)	-828(9)	4790(10)	160
H(11A)	2541(38)	-1693(10)	5959(15)	138
H(12)	-1743(29)	231(8)	5848(9)	137
H(12A)	2881(24)	-644(8)	7051(10)	98
H(13A)	-3849(6)	57(2)	8566(3)	48
H(13B)	-1822(6)	-227(2)	9319(3)	48

Appendix 6.

Supplementary data for the crystal structure determination of bis(cyclopentadienyl)-bis(diphenylphosphinoacetato)titanium(IV) P1.

Table A6.1. Crystal parameters, data collection and structure solution details for bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1**.

Identification code	**P1**
Empirical formula	$C_{38}H_{34}O_4P_2Ti$
Formula weight	664.49
Temperature	293(2)°K
Wavelength	0.70930 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.664(3)Å alpha = 95.09(2)°
	b = 11.847(3)Å beta = 101.18(3)°
	c = 14.191(4)Å gamma = 117.33(2)°
Volume	1673.1(8) Å^3
Z	2
Density (calculated)	1.319 Mg/m^3
Absorption coefficient	0.391 mm^{-1}
F(000)	692
Crystal size	0.2 x 0.2 x 0.3 mm
Theta range for data collection	2.03 to 22.00 deg.
Index ranges	-13<=h<=0; -12<=k<=13; -15<=l<=16
Reflections collected	4374
Independent reflections	4123 [R(int) = 0.0360]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3967 / 0 / 404
Goodness-of-fit on F2	1.042
Final R indices [I>2σ(I)]	R1 = 0.0656 wR2 = 0.1310
R indices (all data)	R1 = 0.1505 wR2 = 0.1775
Largest diff. peak and hole	0.601 and -0.267 e.A-3
Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0610P)^2+2.5766P]$ where $P=(Fo^2+2Fc^2)/3$
Extinction coefficient	0.0000(8)
Extinction expression	$Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Table A6.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	U(eq)
Ti(1)	2334(1)	1887(1)	4219(1)	47(1)
P(1)	5616(2)	3940(2)	1754(1)	59(1)
P(2)	-535(2)	-2306(2)	1270(1)	65(1)
O(1)	2944(4)	2434(4)	3053(3)	55(1)
O(2)	4556(6)	4485(5)	3459(4)	96(2)
O(3)	974(5)	205(4)	3457(3)	59(1)
O(4)	-1206(5)	-808(6)	2862(4)	92(2)
C(1)	2993(8)	415(8)	4863(6)	65(2)
C(2)	3154(9)	1319(9)	5635(5)	70(2)
C(3)	4171(8)	2520(8)	5564(6)	70(2)
C(4)	4595(8)	2334(9)	4750(6)	74(2)
C(5)	3871(8)	1052(9)	4320(6)	71(2)
C(6)	535(11)	2351(12)	3927(8)	99(3)
C(7)	628(12)	2001(10)	4792(12)	111(4)
C(8)	1789(15)	2923(14)	5398(8)	109(4)
C(9)	2472(7)	3821(6)	4946(6)	100(4)
C(10)	1610(7)	3445(6)	3920(6)	99(3)
C(11)	3801(8)	3482(8)	2860(6)	60(2)
C(12)	3866(6)	3401(7)	1801(5)	55(2)
C(13)	5417(7)	3574(6)	434(5)	54(2)
C(14)	4296(7)	3246(7)	-304(6)	65(2)
C(15)	4289(8)	3042(7)	-1276(5)	72(2)
C(16)	5386(9)	3148(7)	-1535(6)	72(2)
C(17)	6517(9)	3470(8)	-818(6)	79(2)
C(18)	6535(8)	3684(7)	156(6)	71(2)
C(19)	5761(7)	2542(8)	2108(5)	62(2)
C(20)	5081(8)	1317(8)	1510(7)	82(2)
C(21)	5253(10)	309(9)	1802(8)	101(3)
C(22)	6096(13)	516(13)	2690(9)	114(4)
C(23)	6785(11)	1703(14)	3281(8)	108(4)
C(24)	6628(8)	2744(9)	2999(6)	81(2)
C(25)	-115(8)	-384(7)	2742(5)	55(2)
C(26)	130(7)	-579(7)	1755(5)	61(2)
C(27)	479(8)	-2683(7)	2224(5)	59(2)
C(28)	1831(9)	-2177(8)	2420(6)	76(2)
C(29)	2531(9)	-2478(9)	3161(6)	86(3)
C(30)	1861(12)	-3329(10)	3701(7)	90(3)
C(31)	499(12)	-3862(9)	3524(7)	97(3)
C(32)	-202(8)	-3550(7)	2761(6)	75(2)
C(33)	261(8)	-2243(9)	264(5)	66(2)
C(34)	-207(10)	-3402(10)	-347(7)	102(3)
C(35)	248(12)	-3514(13)	-1162(9)	119(4)
C(36)	1193(14)	-2449(18)	-1354(8)	118(5)

C(37)	1683(11)	-1274(14)	-774(9)	116(4)
C(38)	1215(10)	-1192(10)	22(6)	93(3)

Table A6.3. Bond lengths (Å) and angles (°) for bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1**.

Ti(1)-O(3)	1.925(5)	Ti(1)-O(1)	1.972(4)
Ti(1)-C(7)	2.343(9)	Ti(1)-C(8)	2.340(9)
Ti(1)-C(3)	2.341(7)	Ti(1)-C(2)	2.344(7)
Ti(1)-C(9)	2.349(6)	Ti(1)-C(6)	2.374(9)
Ti(1)-C(4)	2.384(8)	Ti(1)-C(1)	2.390(7)
Ti(1)-C(10)	2.394(6)	Ti(1)-C(5)	2.402(7)
P(1)-C(13)	1.830(7)	P(1)-C(19)	1.842(7)
P(1)-C(12)	1.856(6)	P(2)-C(26)	1.830(7)
P(2)-C(33)	1.837(8)	P(2)-C(27)	1.845(7)
O(1)-C(11)	1.282(8)	O(2)-C(11)	1.216(8)
O(3)-C(25)	1.300(7)	O(4)-C(25)	1.189(8)
C(1)-C(2)	1.383(10)	C(1)-C(5)	1.383(10)
C(2)-C(3)	1.402(10)	C(3)-C(4)	1.380(10)
C(4)-C(5)	1.360(10)	C(6)-C(7)	1.331(13)
C(6)-C(10)	1.329(13)	C(7)-C(8)	1.338(14)
C(8)-C(9)	1.310(12)	C(9)-C(10)	1.50
C(11)-C(12)	1.516(9)	C(13)-C(14)	1.374(9)
C(13)-C(18)	1.388(9)	C(14)-C(15)	1.376(10)
C(15)-C(16)	1.353(10)	C(16)-C(17)	1.367(10)
C(17)-C(18)	1.377(10)	C(19)-C(24)	1.380(10)
C(19)-C(20)	1.386(10)	C(20)-C(21)	1.383(11)
C(21)-C(22)	1.363(13)	C(22)-C(23)	1.348(14)
C(23)-C(24)	1.408(12)	C(25)-C(26)	1.502(9)
C(27)-C(28)	1.362(10)	C(27)-C(32)	1.375(10)
C(28)-C(29)	1.379(10)	C(29)-C(30)	1.364(11)
C(30)-C(31)	1.372(12)	C(31)-C(32)	1.408(11)
C(33)-C(34)	1.360(11)	C(33)-C(38)	1.363(11)
C(34)-C(35)	1.383(13)	C(35)-C(36)	1.335(14)
C(36)-C(37)	1.351(14)	C(37)-C(38)	1.362(12)
O(3)-Ti(1)-O(1)	91.5(2)	O(3)-Ti(1)-C(7)	86.5(3)
O(1)-Ti(1)-C(7)	128.9(4)	O(3)-Ti(1)-C(8)	118.3(4)
O(1)-Ti(1)-C(8)	130.4(3)	C(7)-Ti(1)-C(8)	33.2(3)
O(3)-Ti(1)-C(3)	131.8(2)	O(1)-Ti(1)-C(3)	110.3(3)
C(7)-Ti(1)-C(3)	108.5(5)	C(8)-Ti(1)-C(3)	79.7(4)
O(3)-Ti(1)-C(2)	100.9(3)	O(1)-Ti(1)-C(2)	136.1(2)
C(7)-Ti(1)-C(2)	94.0(4)	C(8)-Ti(1)-C(2)	79.4(3)
C(3)-Ti(1)-C(2)	34.8(3)	O(3)-Ti(1)-C(9)	138.1(2)
O(1)-Ti(1)-C(9)	98.9(2)	C(7)-Ti(1)-C(9)	55.7(3)

C(8)-Ti(1)-C(9)	32.5(3)	C(3)-Ti(1)-C(9)	81.9(3)
C(2)-Ti(1)-C(9)	99.1(3)	O(3)-Ti(1)-C(6)	82.8(3)
O(1)-Ti(1)-C(6)	96.4(3)	C(7)-Ti(1)-C(6)	32.8(3)
C(8)-Ti(1)-C(6)	54.2(4)	C(3)-Ti(1)-C(6)	133.3(3)
C(2)-Ti(1)-C(6)	126.7(4)	C(9)-Ti(1)-C(6)	55.9(3)
O(3)-Ti(1)-C(4)	119.9(3)	O(1)-Ti(1)-C(4)	80.3(2)
C(7)-Ti(1)-C(4)	142.2(5)	C(8)-Ti(1)-C(4)	111.2(4)
C(3)-Ti(1)-C(4)	33.9(2)	C(2)-Ti(1)-C(4)	57.0(3)
C(9)-Ti(1)-C(4)	101.9(3)	C(6)-Ti(1)-C(4)	157.0(4)
O(3)-Ti(1)-C(1)	75.7(2)	O(1)-Ti(1)-C(1)	114.3(3)
C(7)-Ti(1)-C(1)	114.4(4)	C(8)-Ti(1)-C(1)	111.2(3)
C(3)-Ti(1)-C(1)	56.3(3)	C(2)-Ti(1)-C(1)	34.0(2)
C(9)-Ti(1)-C(1)	132.9(3)	C(6)-Ti(1)-C(1)	142.5(4)
C(4)-Ti(1)-C(1)	55.6(3)	O(3)-Ti(1)-C(10)	109.2(2)
O(1)-Ti(1)-C(10)	77.4(2)	C(7)-Ti(1)-C(10)	55.7(3)
C(8)-Ti(1)-C(10)	56.4(3)	C(3)-Ti(1)-C(10)	117.1(3)
C(2)-Ti(1)-C(10)	134.3(3)	C(9)-Ti(1)-C(10)	36.74(8)
C(6)-Ti(1)-C(10)	32.4(3)	C(4)-Ti(1)-C(10)	126.1(3)
C(1)-Ti(1)-C(10)	167.6(3)	O(3)-Ti(1)-C(5)	87.0(3)
O(1)-Ti(1)-C(5)	82.8(2)	C(7)-Ti(1)-C(5)	147.7(4)
C(8)-Ti(1)-C(5)	133.2(3)	C(3)-Ti(1)-C(5)	55.7(3)
C(2)-Ti(1)-C(5)	56.4(3)	C(9)-Ti(1)-C(5)	134.4(3)
C(6)-Ti(1)-C(5)	169.7(4)	C(4)-Ti(1)-C(5)	33.0(2)
C(1)-Ti(1)-C(5)	33.5(2)	C(10)-Ti(1)-C(5)	154.6(3)
C(13)-P(1)-C(19)	99.8(3)	C(13)-P(1)-C(12)	101.8(3)
C(19)-P(1)-C(12)	98.8(3)	C(26)-P(2)-C(33)	101.4(4)
C(26)-P(2)-C(27)	100.2(3)	C(33)-P(2)-C(27)	101.9(3)
C(11)-O(1)-Ti(1)	136.1(5)	C(25)-O(3)-Ti(1)	143.4(4)
C(2)-C(1)-C(5)	108.4(7)	C(2)-C(1)-Ti(1)	71.2(4)
C(5)-C(1)-Ti(1)	73.7(4)	C(1)-C(2)-C(3)	106.5(7)
C(1)-C(2)-Ti(1)	74.8(4)	C(3)-C(2)-Ti(1)	72.5(4)
C(4)-C(3)-C(2)	108.3(7)	C(4)-C(3)-Ti(1)	74.7(4)
C(2)-C(3)-Ti(1)	72.7(4)	C(5)-C(4)-C(3)	108.1(8)
C(5)-C(4)-Ti(1)	74.2(4)	C(3)-C(4)-Ti(1)	71.3(4)
C(4)-C(5)-C(1)	108.7(8)	C(4)-C(5)-Ti(1)	72.8(5)
C(1)-C(5)-Ti(1)	72.7(4)	C(7)-C(6)-C(10)	112.6(9)
C(7)-C(6)-Ti(1)	72.3(5)	C(10)-C(6)-Ti(1)	74.6(5)
C(6)-C(7)-C(8)	107.2(10)	C(6)-C(7)-Ti(1)	74.9(6)
C(8)-C(7)-Ti(1)	73.3(6)	C(9)-C(8)-C(7)	111.6(10)
C(9)-C(8)-Ti(1)	74.2(5)	C(7)-C(8)-Ti(1)	73.5(6)
C(8)-C(9)-C(10)	105.5(8)	C(8)-C(9)-Ti(1)	73.4(5)
C(10)-C(9)-Ti(1)	73.2(2)	C(6)-C(10)-C(9)	103.1(6)
C(6)-C(10)-Ti(1)	73.0(5)	C(9)-C(10)-Ti(1)	70.0(2)
O(2)-C(11)-O(1)	125.0(7)	O(2)-C(11)-C(12)	119.8(7)
O(1)-C(11)-C(12)	115.2(7)	C(11)-C(12)-P(1)	109.5(5)
C(14)-C(13)-C(18)	117.1(7)	C(14)-C(13)-P(1)	126.8(6)

C(18)-C(13)-P(1)	116.1(5)	C(13)-C(14)-C(15)	121.3(7)
C(16)-C(15)-C(14)	120.9(7)	C(15)-C(16)-C(17)	119.3(7)
C(16)-C(17)-C(18)	120.2(8)	C(17)-C(18)-C(13)	121.3(7)
C(24)-C(19)-C(20)	118.8(7)	C(24)-C(19)-P(1)	118.0(7)
C(20)-C(19)-P(1)	123.2(5)	C(21)-C(20)-C(19)	120.8(8)
C(22)-C(21)-C(20)	119.9(10)	C(23)-C(22)-C(21)	120.6(10)
C(22)-C(23)-C(24)	120.5(10)	C(19)-C(24)-C(23)	119.4(9)
O(4)-C(25)-O(3)	123.3(7)	O(4)-C(25)-C(26)	122.9(7)
O(3)-C(25)-C(26)	113.6(6)	C(25)-C(26)-P(2)	110.4(5)
C(28)-C(27)-C(32)	118.8(7)	C(28)-C(27)-P(2)	124.7(6)
C(32)-C(27)-P(2)	116.5(6)	C(27)-C(28)-C(29)	121.6(8)
C(30)-C(29)-C(28)	119.8(9)	C(29)-C(30)-C(31)	120.2(9)
C(30)-C(31)-C(32)	119.3(8)	C(27)-C(32)-C(31)	120.3(8)
C(34)-C(33)-C(38)	115.6(8)	C(34)-C(33)-P(2)	115.4(7)
C(38)-C(33)-P(2)	129.0(7)	C(33)-C(34)-C(35)	122.6(10)
C(36)-C(35)-C(34)	119.0(11)	C(35)-C(36)-C(37)	120.8(12)
C(36)-C(37)-C(38)	119.0(11)	C(37)-C(38)-C(33)	123.1(10)

Table A6.4. Anisotropic displacement parameters (Å^2 x 10^3) for bis(cyclopentadienyl)bis-(diphenylphosphinoacetato)titanium(IV) **P1**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a* 2 U11 + ... + 2 h k a* b* U12]

Atom	U11	U22	U33	U23	U13	U12
Ti(1)	47(1)	50(1)	45(1)	9(1)	11(1)	25(1)
P(1)	54(1)	59(1)	56(1)	17(1)	8(1)	23(1)
P(2)	57(1)	79(2)	57(1)	2(1)	11(1)	34(1)
O(1)	58(3)	55(3)	53(3)	21(2)	19(2)	26(3)
O(2)	111(5)	65(4)	69(4)	-4(3)	31(4)	9(4)
O(3)	59(3)	54(3)	53(3)	5(2)	10(3)	22(3)
O(4)	50(4)	113(5)	78(4)	-16(3)	19(3)	16(3)
C(1)	67(5)	66(5)	77(6)	28(5)	12(5)	44(4)
C(2)	96(7)	94(7)	51(5)	26(5)	22(4)	68(6)
C(3)	74(6)	64(6)	63(6)	-2(4)	-18(5)	41(5)
C(4)	55(5)	92(7)	70(6)	26(5)	6(5)	34(5)
C(5)	68(6)	96(7)	71(5)	18(5)	18(5)	58(6)
C(6)	111(8)	134(10)	85(7)	7(7)	0(6)	99(8)
C(7)	90(8)	70(7)	210(14)	40(8)	96(9)	46(6)
C(8)	186(13)	156(12)	77(7)	53(8)	76(8)	137(11)
C(9)	69(6)	63(6)	144(9)	-52(6)	-7(7)	40(5)
C(10)	154(10)	95(8)	132(9)	68(7)	90(8)	102(8)
C(11)	59(5)	60(5)	62(5)	12(4)	16(4)	30(4)
C(12)	48(4)	61(5)	57(5)	20(4)	13(3)	26(4)
C(13)	51(5)	50(4)	56(5)	19(3)	13(4)	21(4)
C(14)	58(5)	78(5)	63(5)	22(4)	10(4)	36(4)
C(15)	64(6)	93(6)	50(5)	15(4)	2(4)	37(5)
C(16)	92(7)	64(5)	53(5)	11(4)	16(5)	33(5)
C(17)	74(6)	95(7)	72(6)	18(5)	30(5)	39(5)
C(18)	59(5)	84(6)	61(5)	19(4)	6(4)	32(5)
C(19)	58(5)	86(6)	50(5)	34(4)	12(4)	40(5)
C(20)	84(6)	72(6)	95(6)	43(6)	26(5)	38(5)
C(21)	129(9)	83(7)	126(9)	57(6)	60(7)	64(7)
C(22)	154(11)	157(12)	119(10)	92(9)	75(9)	123(10)
C(23)	116(9)	189(12)	92(8)	77(8)	47(7)	117(10)
C(24)	83(6)	124(7)	67(6)	42(5)	35(5)	67(6)
C(25)	52(5)	50(5)	50(5)	2(4)	6(4)	19(4)
C(26)	72(5)	75(5)	49(4)	20(4)	20(4)	43(4)
C(27)	68(6)	60(5)	57(5)	3(4)	16(4)	38(4)
C(28)	74(6)	80(6)	72(6)	11(5)	21(5)	36(5)
C(29)	87(7)	108(8)	85(7)	14(6)	17(6)	69(6)
C(30)	116(9)	91(7)	86(7)	22(6)	13(6)	74(7)
C(31)	133(9)	100(7)	77(6)	49(6)	52(6)	57(7)
C(32)	71(6)	68(6)	75(6)	6(5)	27(5)	25(5)
C(33)	66(5)	100(7)	38(4)	6(5)	6(4)	50(5)
C(34)	111(8)	107(8)	83(7)	-8(6)	38(6)	49(7)
C(35)	127(10)	139(11)	94(9)	-22(7)	22(7)	78(9)
C(36)	148(12)	225(16)	59(7)	42(9)	41(7)	148(13)

C(37)	122(9)	173(12)	116(9)	62(9)	79(8)	101(9)
C(38)	107(8)	110(8)	80(7)	22(6)	44(6)	61(7)

Table A6.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for bis(cyclopentadienyl)bis(diphenylphosphinoacetato)titanium(IV) **P1**.

Atom	*x*	*y*	*z*	U(eq)
H(1)	2396(8)	-471(8)	4731(6)	78
H(2)	2680(9)	1161(9)	6109(5)	84
H(3)	4503(8)	3308(8)	5991(6)	84
H(4)	5261(8)	2973(9)	4533(6)	89
H(5)	3954(8)	668(9)	3755(6)	85
H(6)	-202(11)	1882(12)	3387(8)	119
H(7)	4(12)	1255(10)	4946(12)	133
H(8)	2076(15)	2927(14)	6057(8)	131
H(9)	3315(7)	4541(6)	5209(6)	120
H(10)	1784(7)	3872(6)	3403(6)	119
H(12A)	3554(6)	3949(7)	1500(5)	66
H(12B)	3290(6)	2515(7)	1439(5)	66
H(14)	3528(7)	3162(7)	-144(6)	78
H(15)	3519(8)	2827(7)	-1761(5)	86
H(16)	5370(9)	3003(7)	-2193(6)	87
H(17)	7276(9)	3545(8)	-989(6)	95
H(18)	7312(8)	3906(7)	637(6)	85
H(20)	4502(8)	1170(8)	904(7)	98
H(21)	4793(10)	-509(9)	1394(8)	121
H(22)	6198(13)	-167(13)	2890(9)	136
H(23)	7369(11)	1835(14)	3880(8)	130
H(24)	7103(8)	3561(9)	3410(6)	97
H(26A)	1084(7)	-115(7)	1814(5)	74
H(26B)	-298(7)	-230(7)	1305(5)	74
H(28)	2293(9)	-1614(8)	2043(6)	91
H(29)	3457(9)	-2101(9)	3293(6)	103
H(30)	2330(12)	-3549(10)	4191(7)	108
H(31)	43(12)	-4423(9)	3904(7)	117
H(32)	-1129(8)	-3931(7)	2620(6)	89
H(34)	-859(10)	-4147(10)	-212(7)	122
H(35)	-98(12)	-4318(13)	-1570(9)	143
H(36)	1518(14)	-2516(18)	-1893(8)	142
H(37)	2331(11)	-532(14)	-916(9)	139
H(38)	1561(10)	-380(10)	420(6)	111

Appendix 7.

Supplementary data for the crystal structure determination of bis(diphenylphosphinoacetic acid)gold(I) chloride P8.

Table A7.1. Crystal parameters, data collection and structure solution details for bis(diphenylphosphinoacetic acid)gold(I) chloride **P8**.

Identification code	**P8**
Empirical formula	$C_{14} H_{13} Au Cl O_2 P$
Formula weight	476.63
Temperature	293(2)° K
Wavelength	0.70930 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 9.296(1)Å
	b = 9.479(1)Å beta = 97.05(1)°
	c = 17.534(2)Å
Volume	1533.4(3) $Å^3$
Z	4
Density (calculated)	2.065 Mg/m^3
Absorption coefficient	9.866 mm^{-1}
F(000)	896
Crystal size	0.2 x 0.2 x 0.25 mm
Theta range for data collection	2.34 to 23.92 deg.
Index ranges	-10<=h<=10; 0<=k<=10; 0<=l<=20
Reflections collected	2396
Independent reflections	2396 [R(int) = 0.0000]
Absorption correction	DIFABS
Max. and min. transmission	1.000 and 0.230
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2396 / 0 / 173
Goodness-of-fit on F^2	1.099
Final R indices [$I>2\sigma(I)$]	R1 = 0.0338 wR2 = 0.0801
R indices (all data)	R1 = 0.0641 wR2 = 0.0948
Largest diff. peak and hole	1.330 and -1.044 $eÅ^{-3}$
Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0511P)^2+5.0094P]$ where $P=(Fo^2+2Fc^2)/3$
Extinction coefficient	0.0026(3)
Extinction expression	$Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Table A7.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for bis(diphenylphosphinoacetic acid)gold(I) chloride **P8**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	U(eq)
Au(1)	419(1)	2659(1)	9472(1)	47(1)
Cl(1)	-638(4)	3125(3)	8261(2)	82(1)
P(1)	1475(2)	2238(2)	10655(1)	35(1)
O(1)	4903(7)	4149(7)	10826(4)	61(2)
O(2)	3122(7)	4902(8)	9987(4)	70(2)
C(1)	2728(9)	772(8)	10730(5)	37(2)
C(2)	2685(10)	-175(10)	10131(5)	50(2)
C(3)	3602(12)	-1337(10)	10192(7)	67(3)
C(4)	4540(11)	-1537(12)	10816(7)	72(3)
C(5)	4607(12)	-607(11)	11417(6)	72(3)
C(6)	3706(11)	557(11)	11370(5)	61(3)
C(7)	205(8)	1904(8)	11332(4)	35(2)
C(8)	281(11)	759(11)	11809(6)	62(3)
C(9)	-768(13)	563(15)	12289(7)	86(4)
C(10)	-1856(12)	1453(15)	12339(6)	72(3)
C(11)	-1978(11)	2585(13)	11867(7)	79(4)
C(12)	-946(11)	2868(11)	11351(6)	60(3)
C(13)	2473(10)	3747(8)	11095(5)	47(2)
C(14)	3594(10)	4301(9)	10613(5)	45(2)

Table A7.3. Bond lengths (Å) and angles (°) for bis(diphenylphosphinoacetic acid)gold(I) chloride P8.

Au(1)-P(1)	2.220(2)	Au(1)-Cl(1)	2.270(3)
P(1)-C(7)	1.803(8)	P(1)-C(1)	1.808(8)
P(1)-C(13)	1.824(9)	O(1)-C(14)	1.237(10)
O(2)-C(14)	1.265(11)	C(1)-C(6)	1.371(12)
C(1)-C(2)	1.378(11)	C(2)-C(3)	1.389(13)
C(3)-C(4)	1.33(2)	C(4)-C(5)	1.370(14)
C(5)-C(6)	1.382(13)	C(7)-C(8)	1.367(12)
C(7)-C(12)	1.410(13)	C(8)-C(9)	1.375(13)
C(9)-C(10)	1.33(2)	C(10)-C(11)	1.35(2)
C(11)-C(12)	1.42(2)	C(13)-C(14)	1.514(12)
P(1)-Au(1)-Cl(1)	179.01(11)	C(7)-P(1)-C(1)	106.6(4)
C(7)-P(1)-C(13)	101.5(4)	C(1)-P(1)-C(13)	106.4(4)
C(7)-P(1)-Au(1)	113.4(3)	C(1)-P(1)-Au(1)	114.4(3)
C(13)-P(1)-Au(1)	113.5(3)	C(6)-C(1)-C(2)	118.8(8)
C(6)-C(1)-P(1)	122.0(7)	C(2)-C(1)-P(1)	119.2(7)
C(1)-C(2)-C(3)	119.8(9)	C(4)-C(3)-C(2)	120.8(10)
C(3)-C(4)-C(5)	120.4(10)	C(4)-C(5)-C(6)	119.9(10)
C(1)-C(6)-C(5)	120.2(9)	C(8)-C(7)-C(12)	118.8(8)
C(8)-C(7)-P(1)	123.6(7)	C(12)-C(7)-P(1)	117.5(7)
C(7)-C(8)-C(9)	119.6(10)	C(10)-C(9)-C(8)	123.9(11)
C(9)-C(10)-C(11)	118.1(10)	C(10)-C(11)-C(12)	121.8(10)
C(7)-C(12)-C(11)	117.7(10)	C(14)-C(13)-P(1)	112.6(6)
O(1)-C(14)-O(2)	122.5(8)	O(1)-C(14)-C(13)	120.6(8)
O(2)-C(14)-C(13)	116.8(8)		

Table A7.4. Anisotropic displacement parameters ($Å^2$ x 10^3) for bis(diphenylphosphinoacetic acid)gold(I) chloride **P8**. The anisotropic displacement factor exponent takes the form:

$-2 pi^2 [h^2 a^* 2 U11 + ... + 2 h k a^* b^* U12]$

Atom	U11	U22	U33	U23	U13	U12
Au(1)	48(1)	48(1)	45(1)	9(1)	7(1)	8(1)
Cl(1)	117(3)	75(2)	51(1)	11(1)	-3(2)	32(2)
P(1)	25(1)	34(1)	45(1)	2(1)	7(1)	0(1)
O(1)	32(4)	75(5)	75(4)	13(4)	8(3)	0(3)
O(2)	35(4)	83(5)	92(5)	40(4)	1(4)	-5(4)
C(1)	26(5)	41(5)	45(5)	-2(3)	10(4)	2(4)
C(2)	41(6)	55(6)	51(5)	-9(4)	-2(4)	3(4)
C(3)	64(7)	47(6)	87(8)	-23(5)	1(6)	13(5)
C(4)	47(7)	55(7)	111(9)	-12(6)	0(6)	15(5)
C(5)	58(7)	69(7)	81(8)	0(6)	-23(6)	26(6)
C(6)	60(7)	65(6)	54(6)	-14(5)	-12(5)	19(5)
C(7)	16(4)	41(4)	49(4)	-5(4)	3(3)	2(3)
C(8)	43(6)	66(6)	80(7)	28(5)	26(5)	9(5)
C(9)	63(8)	111(10)	90(9)	47(7)	32(7)	0(8)
C(10)	47(7)	107(10)	66(7)	13(7)	28(5)	-15(7)
C(11)	31(6)	110(11)	97(9)	-39(8)	11(6)	6(6)
C(12)	50(6)	61(6)	71(6)	-1(5)	17(5)	7(5)
C(13)	49(6)	31(4)	64(6)	-5(4)	21(5)	-3(4)
C(14)	32(6)	35(4)	70(6)	-1(4)	8(5)	1(4)

Table A7.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for bis(diphenylphosphinoacetic acid)gold(I) chloride P8.

Atom	*x*	*y*	*z*	U(eq)
H(2)	2043(10)	-37(10)	9687(5)	60
H(3)	3558(12)	-1983(10)	9790(7)	80
H(4)	5157(11)	-2314(12)	10845(7)	86
H(5)	5257(12)	-760(11)	11856(6)	87
H(6)	3763(11)	1197(11)	11775(5)	74
H(8)	1037(11)	117(11)	11810(6)	74
H(9)	-711(13)	-240(15)	12596(7)	103
H(10)	-2516(12)	1300(15)	12689(6)	86
H(11)	-2758(11)	3195(13)	11880(7)	95
H(12)	-1027(11)	3662(11)	11038(6)	72
H(13A)	1795(10)	4497(8)	11171(5)	56
H(13B)	2953(10)	3474(8)	11596(5)	56

Appendix 8.

Supplementary data for the crystal structure determination of *trans*-bis(diphenylphosphinoacetic acid)palladium(II) chloride.1/3EtOH.1/3H_2O, P4'.1/3EtOH.1/3H_2O.

Table A8.1. Crystal parameters, data collection and structure solution details for *trans*-bis(diphenylphosphinoacetic acid)palladium(II) chloride.1/3EtOH.1/3H_2O P4'.1/3EtOH.1/3H_2O.

Identification code	**P4'**.1/3EtOH.1/3H_2O
Empirical formula	$C_{43} H_{43} Cl_3 O_7 P_3 Pd_{1.50}$
Formula weight	1030.63
Temperature	293(2)°K
Wavelength	0.70930 Å
Crystal system	Triclinic
Space group	P-1(No.2)
Unit cell dimensions	a = 9.881(4)Å alpha = 87.27°
	b = 15.674(2)Å beta = 79.610(10)°
	c = 15.716(2)Å gamma = 85.78°
Volume	2386.1(11) $Å^3$
Z	2
Density (calculated)	1.434 Mg/m^3
Absorption coefficient	0.885 mm^{-1}
F(000)	1044
Crystal size	0.3 x 0.3 x 0.25 mm
Theta range for data collection	2.10 to 23.93 °.
Index ranges	0<=h<=11; -17<=k<=17; -17<=l<=17
Reflections collected	7952
Independent reflections	7461 [R(int) = 0.0146]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7440 / 0 / 542
Goodness-of-fit on F^2	1.117
Final R indices [I>2σ(I)]	R1 = 0.0353 wR2 = 0.1014
R indices (all data)	R1 = 0.0645 wR2 = 0.1327
Largest diff. peak and hole	0.846 and -0.420 $eÅ^{-3}$
Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0605P)^2+3.2051P]$ where $P=(Fo^2+2Fc^2)/3$

Table 2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for *trans*-bis(diphenylphosphinoacetic acid)palladium(II) chloride.1/3EtOH.1/3H$_2$O P4'.1/3EtOH.1/3H$_2$O. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd(1)	0	5000	0	29(1)
Pd(2)	5000	0	0	32(1)
Pd(3)	5000	5000	5000	37(1)
Cl(1)	-481(1)	6351(1)	543(1)	46(1)
Cl(2)	4417(2)	-98(1)	-1344(1)	54(1)
Cl(3)	4739(2)	5018(1)	3578(1)	53(1)
P(1)	1290(1)	5501(1)	-1289(1)	30(1)
P(2)	3919(1)	1358(1)	21(1)	33(1)
P(3)	4911(1)	6495(1)	4929(1)	43(1)
O(1)	5099(4)	5085(3)	-1100(2)	60(1)
O(2)	3321(4)	4870(3)	-61(2)	68(1)
O(3)	1347(4)	351(2)	359(3)	55(1)
O(4)	528(4)	820(3)	-813(3)	72(1)
O(5)	7041(5)	8073(3)	5415(3)	86(2)
O(6)	4852(7)	8418(4)	5877(5)	124(2)
C(1)	496(5)	5322(3)	-2219(3)	32(1)
C(2)	-812(5)	5020(3)	-2102(3)	41(1)
C(3)	-1452(6)	4930(3)	-2806(4)	50(1)
C(4)	-808(7)	5140(4)	-3613(4)	56(2)
C(5)	501(7)	5441(4)	-3749(3)	55(2)
C(6)	1146(6)	5530(4)	-3054(3)	48(1)
C(7)	1705(5)	6612(3)	-1476(3)	34(1)
C(8)	623(5)	7236(3)	-1440(4)	47(1)
C(9)	864(6)	8079(4)	-1617(4)	57(2)
C(10)	2201(6)	8323(4)	-1849(4)	59(2)
C(11)	3284(6)	7717(4)	-1885(4)	55(2)
C(12)	3044(5)	6867(3)	-1696(3)	47(1)
C(13)	2967(5)	4888(3)	-1519(3)	35(1)
C(14)	3847(5)	4960(3)	-851(3)	38(1)
C(15)	3347(5)	1880(3)	1037(3)	40(1)
C(16)	2743(6)	1420(4)	1761(3)	50(1)
C(17)	2264(6)	1823(5)	2533(4)	63(2)
C(18)	2410(6)	2687(4)	2589(4)	62(2)
C(19)	3030(6)	3141(4)	1888(4)	60(2)
C(20)	3505(6)	2748(3)	1109(4)	52(1)
C(21)	5168(5)	2047(3)	-593(3)	40(1)
C(22)	6468(6)	1974(4)	-380(4)	60(2)
C(23)	7489(7)	2488(5)	-805(5)	81(2)
C(24)	7223(8)	3024(5)	-1470(5)	81(2)
C(25)	5938(8)	3110(4)	-1689(4)	71(2)
C(26)	4893(6)	2618(4)	-1254(4)	55(1)
C(27)	2415(5)	1493(3)	-514(3)	42(1)
C(28)	1396(5)	834(3)	-273(3)	43(1)

C(29)	5979(5)	6963(4)	3993(3)	45(1)
C(30)	7216(6)	6519(4)	3646(4)	56(2)
C(31)	8154(6)	6878(5)	3013(4)	66(2)
C(32)	7898(7)	7700(5)	2717(4)	73(2)
C(33)	6657(8)	8146(5)	3042(4)	76(2)
C(34)	5708(7)	7779(4)	3668(4)	62(2)
C(35)	3174(6)	6954(4)	4947(4)	54(1)
C(36)	2410(7)	7345(4)	5672(5)	76(2)
C(37)	1041(9)	7639(6)	5657(7)	105(3)
C(38)	448(9)	7553(6)	4969(9)	113(4)
C(39)	1194(9)	7156(6)	4254(7)	109(3)
C(40)	2576(7)	6861(5)	4229(5)	78(2)
C(41)	5557(7)	6958(4)	5826(4)	63(2)
C(42)	5813(9)	7892(5)	5701(5)	76(2)
O(7)	6697(15)	10456(9)	6963(8)	124(5)
C(43)	7521(35)	10997(13)	7254(18)	164(12)
C(44)	8875(39)	10777(18)	7249(28)	255(25)
O(8)	7433(19)	9746(11)	5248(12)	193(9)

Table A8.3. Bond lengths (Å) and angles (°) for *trans*-bis(diphenylphosphinoacetic acid)palladium(II) chloride.1/3EtOH.1/3H_2O **P4'**.1/3EtOH.1/3H_2O.

Pd(1)-Cl(1)	2.3051(12)	Pd(1)-Cl(1)#1	2.3051(12)
Pd(1)-P(1)	2.3259(12)	Pd(1)-P(1)#1	2.3259(12)
Pd(2)-Cl(2)#2	2.3025(13)	Pd(2)-Cl(2)	2.3025(13)
Pd(2)-P(2)#2	2.3091(12)	Pd(2)-P(2)	2.3091(12)
Pd(3)-Cl(3)#3	2.2945(13)	Pd(3)-Cl(3)	2.2945(13)
Pd(3)-P(3)#3	2.337(2)	Pd(3)-P(3)	2.337(2)
P(1)-C(7)	1.816(5)	P(1)-C(1)	1.821(4)
P(1)-C(13)	1.839(5)	P(2)-C(15)	1.807(5)
P(2)-C(21)	1.814(5)	P(2)-C(27)	1.830(5)
P(3)-C(35)	1.808(6)	P(3)-C(29)	1.807(5)
P(3)-C(41)	1.847(6)	O(1)-C(14)	1.255(6)
O(2)-C(14)	1.262(6)	O(3)-C(28)	1.215(6)
O(4)-C(28)	1.314(6)	O(5)-C(42)	1.264(9)
O(6)-C(42)	1.212(9)	C(1)-C(2)	1.387(6)
C(1)-C(6)	1.388(7)	C(2)-C(3)	1.388(7)
C(3)-C(4)	1.350(8)	C(4)-C(5)	1.386(8)
C(5)-C(6)	1.378(7)	C(7)-C(8)	1.390(7)
C(7)-C(12)	1.389(7)	C(8)-C(9)	1.368(8)
C(9)-C(10)	1.383(8)	C(10)-C(11)	1.373(8)
C(11)-C(12)	1.380(8)	C(13)-C(14)	1.491(6)
C(15)-C(16)	1.382(7)	C(15)-C(20)	1.394(7)
C(16)-C(17)	1.384(8)	C(17)-C(18)	1.381(9)
C(18)-C(19)	1.357(9)	C(19)-C(20)	1.385(8)
C(21)-C(22)	1.380(8)	C(21)-C(26)	1.390(7)
C(22)-C(23)	1.392(8)	C(23)-C(24)	1.360(10)
C(24)-C(25)	1.370(10)	C(25)-C(26)	1.393(8)
C(27)-C(28)	1.484(7)	C(29)-C(34)	1.380(8)
C(29)-C(30)	1.396(8)	C(30)-C(31)	1.362(8)
C(31)-C(32)	1.370(10)	C(32)-C(33)	1.391(10)
C(33)-C(34)	1.367(9)	C(35)-C(40)	1.382(9)
C(35)-C(36)	1.389(8)	C(36)-C(37)	1.401(11)
C(37)-C(38)	1.336(13)	C(38)-C(39)	1.376(13)
C(39)-C(40)	1.404(10)	C(41)-C(42)	1.501(9)
O(7)-C(43)	1.36(3)	C(43)-C(44)	1.36(4)
Cl(1)-Pd(1)-Cl(1)#1	180.0	Cl(1)-Pd(1)-P(1)	93.24(4)
Cl(1)#1-Pd(1)-P(1)	86.76(4)	Cl(1)-Pd(1)-P(1)#1	86.76(4)
Cl(1)#1-Pd(1)-P(1)#1	93.24(4)	P(1)-Pd(1)-P(1)#1	180.0
Cl(2)#2-Pd(2)-Cl(2)	180.0	Cl(2)#2-Pd(2)-P(2)#2	86.45(5)
Cl(2)-Pd(2)-P(2)#2	93.55(5)	Cl(2)#2-Pd(2)-P(2)	93.55(5)
Cl(2)-Pd(2)-P(2)	86.45(5)	P(2)#2-Pd(2)-P(2)	180.0
Cl(3)#3-Pd(3)-Cl(3)	180.0	Cl(3)#3-Pd(3)-P(3)#3	89.10(5)
Cl(3)#3-Pd(3)-P(3)	90.90(5)	Cl(3)-Pd(3)-P(3)#3	90.90(5)
Cl(3)-Pd(3)-P(3)	89.10(5)	P(3)#3-Pd(3)-P(3)	180.0
C(7)-P(1)-C(1)	101.8(2)	C(7)-P(1)-C(13)	104.5(2)

C(1)-P(1)-C(13)	103.8(2)	C(7)-P(1)-Pd(1)	122.6(2)
C(1)-P(1)-Pd(1)	112.1(2)	C(13)-P(1)-Pd(1)	110.3(2)
C(15)-P(2)-C(21)	104.6(2)	C(15)-P(2)-C(27)	103.8(2)
C(21)-P(2)-C(27)	105.3(2)	C(15)-P(2)-Pd(2)	120.2(2)
C(21)-P(2)-Pd(2)	106.0(2)	C(27)-P(2)-Pd(2)	115.7(2)
C(35)-P(3)-C(29)	106.9(3)	C(35)-P(3)-C(41)	107.0(3)
C(29)-P(3)-C(41)	101.8(3)	C(35)-P(3)-Pd(3)	111.8(2)
C(29)-P(3)-Pd(3)	115.3(2)	C(41)-P(3)-Pd(3)	113.4(2)
C(2)-C(1)-C(6)	118.6(4)	C(2)-C(1)-P(1)	120.4(3)
C(6)-C(1)-P(1)	121.0(4)	C(1)-C(2)-C(3)	120.4(5)
C(4)-C(3)-C(2)	120.2(5)	C(3)-C(4)-C(5)	120.5(5)
C(6)-C(5)-C(4)	119.6(5)	C(5)-C(6)-C(1)	120.6(5)
C(8)-C(7)-C(12)	118.3(5)	C(8)-C(7)-P(1)	118.2(4)
C(12)-C(7)-P(1)	123.5(4)	C(9)-C(8)-C(7)	121.1(5)
C(8)-C(9)-C(10)	120.1(5)	C(11)-C(10)-C(9)	119.7(5)
C(10)-C(11)-C(12)	120.3(5)	C(11)-C(12)-C(7)	120.5(5)
C(14)-C(13)-P(1)	114.0(3)	O(1)-C(14)-O(2)	122.4(4)
O(1)-C(14)-C(13)	118.4(4)	O(2)-C(14)-C(13)	119.2(4)
C(16)-C(15)-C(20)	118.6(5)	C(16)-C(15)-P(2)	120.3(4)
C(20)-C(15)-P(2)	121.1(4)	C(15)-C(16)-C(17)	120.5(5)
C(18)-C(17)-C(16)	120.1(6)	C(19)-C(18)-C(17)	120.0(5)
C(18)-C(19)-C(20)	120.6(6)	C(19)-C(20)-C(15)	120.3(6)
C(22)-C(21)-C(26)	119.6(5)	C(22)-C(21)-P(2)	116.2(4)
C(26)-C(21)-P(2)	124.2(4)	C(21)-C(22)-C(23)	120.3(6)
C(24)-C(23)-C(22)	119.5(6)	C(23)-C(24)-C(25)	121.1(6)
C(24)-C(25)-C(26)	120.1(6)	C(25)-C(26)-C(21)	119.2(6)
C(28)-C(27)-P(2)	115.1(4)	O(3)-C(28)-O(4)	122.4(5)
O(3)-C(28)-C(27)	124.5(5)	O(4)-C(28)-C(27)	113.1(5)
C(34)-C(29)-C(30)	118.3(5)	C(34)-C(29)-P(3)	123.0(4)
C(30)-C(29)-P(3)	118.3(4)	C(31)-C(30)-C(29)	121.5(6)
C(30)-C(31)-C(32)	119.7(6)	C(31)-C(32)-C(33)	119.5(6)
C(34)-C(33)-C(32)	120.6(7)	C(33)-C(34)-C(29)	120.2(6)
C(40)-C(35)-C(36)	119.8(6)	C(40)-C(35)-P(3)	118.0(5)
C(36)-C(35)-P(3)	122.1(5)	C(35)-C(36)-C(37)	118.9(8)
C(38)-C(37)-C(36)	122.0(8)	C(37)-C(38)-C(39)	119.3(8)
C(38)-C(39)-C(40)	121.0(9)	C(35)-C(40)-C(39)	119.0(7)
C(42)-C(41)-P(3)	114.8(5)	O(6)-C(42)-O(5)	124.4(7)
O(6)-C(42)-C(41)	119.0(7)	O(5)-C(42)-C(41)	116.6(7)
C(44)-C(43)-O(7)	121(2)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z
#2 -x+1,-y,-z
#3 -x+1,-y+1,-z+1

Table A8.4. Anisotropic displacement parameters (Å^2 x 10^3) for *trans*-bis(diphenylphosphinoacetic acid)palladium(II) chloride.1/3EtOH.1/3H$_2$O P4'.1/3EtOH.1/3H$_2$O. The anisotropic displacement factor exponent takes the form: -2 pi2 [h2 a* 2 U11 + ... + 2 h k a* b* U12]

Atom	U11	U22	U33	U23	U13	U12
Pd(1)	25(1)	34(1)	28(1)	-2(1)	-5(1)	-5(1)
Pd(2)	30(1)	29(1)	38(1)	-1(1)	-8(1)	-5(1)
Pd(3)	30(1)	54(1)	28(1)	-3(1)	-5(1)	-3(1)
Cl(1)	53(1)	37(1)	47(1)	-6(1)	0(1)	-5(1)
Cl(2)	63(1)	53(1)	50(1)	-10(1)	-24(1)	5(1)
Cl(3)	58(1)	73(1)	32(1)	-3(1)	-13(1)	-8(1)
P(1)	23(1)	39(1)	28(1)	0(1)	-6(1)	-5(1)
P(2)	31(1)	29(1)	41(1)	0(1)	-8(1)	-5(1)
P(3)	38(1)	55(1)	37(1)	-5(1)	-5(1)	-3(1)
O(1)	30(2)	105(3)	48(2)	10(2)	-9(2)	-17(2)
O(2)	35(2)	134(4)	37(2)	2(2)	-9(2)	-12(2)
O(3)	48(2)	59(2)	63(2)	9(2)	-19(2)	-23(2)
O(4)	59(3)	90(3)	80(3)	24(2)	-41(2)	-32(2)
O(5)	74(3)	98(4)	85(3)	-10(3)	-1(3)	-34(3)
O(6)	92(4)	72(4)	203(7)	-46(4)	7(4)	-17(3)
C(1)	29(2)	37(3)	30(2)	-1(2)	-8(2)	-2(2)
C(2)	33(3)	47(3)	45(3)	0(2)	-15(2)	-5(2)
C(3)	43(3)	53(3)	59(4)	-2(3)	-23(3)	-11(3)
C(4)	74(4)	55(3)	49(3)	-7(3)	-35(3)	-4(3)
C(5)	72(4)	68(4)	28(3)	-4(3)	-13(3)	-6(3)
C(6)	47(3)	65(4)	34(3)	-3(2)	-10(2)	-12(3)
C(7)	35(3)	40(3)	30(2)	0(2)	-6(2)	-10(2)
C(8)	34(3)	48(3)	60(3)	0(3)	-11(2)	-3(2)
C(9)	53(4)	44(3)	77(4)	-3(3)	-18(3)	3(3)
C(10)	65(4)	48(3)	70(4)	7(3)	-26(3)	-22(3)
C(11)	42(3)	55(3)	73(4)	10(3)	-20(3)	-22(3)
C(12)	35(3)	53(3)	54(3)	4(3)	-12(2)	-9(2)
C(13)	27(2)	44(3)	35(3)	0(2)	-5(2)	-3(2)
C(14)	28(3)	47(3)	39(3)	2(2)	-7(2)	2(2)
C(15)	31(3)	43(3)	46(3)	-6(2)	-10(2)	1(2)
C(16)	47(3)	53(3)	50(3)	-3(3)	-6(3)	-3(3)
C(17)	51(4)	90(5)	46(3)	-3(3)	-1(3)	3(3)
C(18)	47(3)	82(5)	59(4)	-33(3)	-10(3)	7(3)
C(19)	48(3)	55(4)	77(4)	-31(3)	-11(3)	4(3)
C(20)	45(3)	46(3)	64(4)	-12(3)	-7(3)	-1(2)
C(21)	39(3)	36(3)	45(3)	-4(2)	-6(2)	-8(2)
C(22)	48(3)	64(4)	72(4)	14(3)	-16(3)	-21(3)
C(23)	51(4)	85(5)	112(6)	20(5)	-18(4)	-29(4)
C(24)	71(5)	67(4)	100(6)	21(4)	4(4)	-31(4)
C(25)	88(5)	59(4)	63(4)	18(3)	-5(4)	-22(4)
C(26)	58(4)	47(3)	60(4)	5(3)	-12(3)	-10(3)
C(27)	36(3)	38(3)	53(3)	3(2)	-14(2)	-5(2)
C(28)	34(3)	47(3)	49(3)	-4(3)	-10(2)	-3(2)

C(29)	39(3)	59(3)	36(3)	-4(2)	-9(2)	-5(2)
C(30)	46(3)	60(4)	62(4)	-3(3)	-7(3)	-5(3)
C(31)	41(3)	94(5)	59(4)	-6(4)	2(3)	-9(3)
C(32)	58(4)	107(6)	53(4)	10(4)	-5(3)	-24(4)
C(33)	89(5)	73(5)	66(4)	15(4)	-17(4)	-19(4)
C(34)	63(4)	70(4)	52(4)	3(3)	-8(3)	4(3)
C(35)	37(3)	58(4)	62(4)	-1(3)	2(3)	0(3)
C(36)	59(4)	74(5)	85(5)	-10(4)	15(4)	-6(4)
C(37)	59(5)	95(6)	145(9)	-31(6)	30(5)	3(5)
C(38)	47(5)	83(6)	198(12)	-8(7)	0(6)	16(4)
C(39)	63(5)	118(7)	153(9)	13(7)	-50(6)	9(5)
C(40)	50(4)	96(5)	90(5)	-11(4)	-26(4)	18(4)
C(41)	71(4)	77(4)	46(3)	-11(3)	-14(3)	-19(3)
C(42)	86(6)	75(5)	68(4)	-19(4)	-10(4)	-17(4)
O(7)	142(12)	110(10)	105(9)	15(8)	15(8)	-1(9)
C(43)	270(37)	66(13)	169(23)	-36(14)	-43(24)	-66(19)
C(44)	286(45)	117(21)	437(61)	87(28)	-263(47)	-91(26)
O(8)	200(17)	161(14)	221(18)	-89(13)	20(14)	-116(14)

Table A8.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for *trans*-bis(diphenylphosphinoacetic acid)palladium(II) chloride.1/3EtOH.1/3H_2O P4'.1/3EtOH.1/3H_2O.

Atom	*x*	*y*	*z*	U(eq)
H(2)	-1263(5)	4876(3)	-1547(3)	49
H(3)	-2326(6)	4723(3)	-2722(4)	60
H(4)	-1246(7)	5083(4)	-4082(4)	67
H(5)	941(7)	5583(4)	-4307(3)	66
H(6)	2025(6)	5730(4)	-3144(3)	58
H(8)	-280(5)	7077(3)	-1294(4)	57
H(9)	128(6)	8489(4)	-1581(4)	69
H(10)	2366(6)	8895(4)	-1980(4)	71
H(11)	4184(6)	7880(4)	-2038(4)	66
H(12)	3784(5)	6462(3)	-1715(3)	56
H(13A)	2809(5)	4289(3)	-1564(3)	42
H(13B)	3462(5)	5085(3)	-2074(3)	42
H(16)	2657(6)	836(4)	1729(3)	60
H(17)	1843(6)	1511(5)	3014(4)	76
H(18)	2083(6)	2958(4)	3107(4)	75
H(19)	3137(6)	3721(4)	1930(4)	71
H(20)	3930(6)	3065(3)	633(4)	62
H(22)	6663(6)	1580(4)	50(4)	72
H(23)	8347(7)	2464(5)	-637(5)	98
H(24)	7924(8)	3338(5)	-1780(5)	97
H(25)	5764(8)	3497(4)	-2130(4)	85
H(26)	4021(6)	2672(4)	-1404(4)	66
H(27A)	1952(5)	2051(3)	-379(3)	50
H(27B)	2732(5)	1490(3)	-1135(3)	50
H(30)	7405(6)	5964(4)	3852(4)	68
H(31)	8964(6)	6567(5)	2783(4)	79
H(32)	8549(7)	7957(5)	2302(4)	87
H(33)	6471(8)	8698(5)	2832(4)	91
H(34)	4877(7)	8081(4)	3875(4)	75
H(36)	2802(7)	7410(4)	6159(5)	91
H(37)	529(9)	7902(6)	6141(7)	126
H(38)	-460(9)	7759(6)	4973(9)	136
H(39)	776(9)	7083(6)	3779(7)	131
H(40)	3081(7)	6606(5)	3739(5)	94
H(41A)	4893(7)	6879(4)	6354(4)	76
H(41B)	6410(7)	6642(4)	5903(4)	76
H(43A)	7471(35)	11529(13)	6916(18)	197
H(43B)	7105(35)	11122(13)	7845(18)	197
H(44A)	9290(98)	11238(99)	7463(230)	382
H(44B)	9329(88)	10664(233)	6668(46)	382
H(44C)	8964(40)	10273(143)	7612(196)	382

Appendix 9.

Supplementary data for the crystal structure determination of $[(\eta^5\text{-}C_5H_5)_2Ti(O_2CCH_2PPh_2)_2PdCl_2].3CH_2Cl_2$, $P10.3CH_2Cl_2$.

Table A9.1. Crystal parameters, data collection and structure solution details for $[(\eta^5\text{-}C_5H_5)_2Ti(O_2CCH_2PPh_2)_2PdCl_2].3CH_2Cl_2$, **P10**.$3CH_2Cl_2$.

Identification code	**P10**.$3CH_2Cl_2$
Empirical formula	$C_{41}\,H_{40}\,Cl_8\,O_4\,P_2\,Pd\,Ti$
Formula weight	1096.57
Temperature	170(2)° K
Wavelength	0.70930 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 12.350(3)Å
	b = 22.037(4)Å β= 102.04(2)°
	c = 16.770(5)Å
Volume	4464(2) $Å^3$
Z	4
Density (calculated)	1.632 Mg/m^3
Absorption coefficient	1.173 mm^{-1}
F(000)	2208
Crystal size	0.4 x 0.35 x 0.2 mm
Theta range for data collection	2.09 to 21.95°
Index ranges	-13<=h<=12; 0<=k<=23; 0<=l<=17
Reflections collected	5448
Independent reflections	5448 [R(int) = 0.0000]
Absorption correction	DIFABS
Max. and min. transmission	1.00 and 0.733
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5426 / 0 / 461
Goodness-of-fit on F^2	1.135
Final R indices [I>2sigma(I)]	R1 = 0.0788 wR2 = 0.1345
R indices (all data)	R1 = 0.1609 wR2 = 0.1790
Largest diff. peak and hole	1.280 and -0.883 $eÅ^{-3}$
Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0000P)^2+75.0648P]$ where $P=(Fo^2+2Fc^2)/3$
Extinction coefficient	0.00000(14)

Table A9.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[(\eta^5\text{-}C_5H_5)_2Ti(O_2CCH_2PPh_2)_2PdCl_2].3CH_2Cl_2$, **P10**.$3CH_2Cl_2$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Pd(1)	2280(1)	1656(1)	1836(1)	14(1)
Ti(1)	4448(2)	1766(1)	4107(1)	15(1)
P(1)	1201(3)	1040(2)	2415(2)	16(1)
P(2)	3544(3)	1016(2)	1476(2)	15(1)
O(1)	2900(7)	1492(4)	3792(5)	16(2)
O(2)	1905(8)	1501(5)	4747(6)	38(3)
O(3)	4686(7)	1515(4)	3035(5)	17(2)
O(4)	6286(8)	1792(5)	2718(6)	36(3)
Cl(1)	1029(3)	2403(2)	2072(2)	23(1)
Cl(2)	3147(3)	2399(2)	1192(2)	26(1)
C(1)	3584(15)	2705(8)	3640(11)	46(5)
C(2)	4591(14)	2709(8)	3465(11)	46(5)
C(3)	5338(15)	2697(7)	4151(10)	43(5)
C(4)	4836(15)	2690(8)	4809(11)	46(5)
C(5)	3683(15)	2688(8)	4483(11)	52(5)
C(6)	5971(14)	1107(8)	4531(10)	38(5)
C(7)	5998(13)	1523(7)	5130(10)	36(5)
C(8)	5031(15)	1438(7)	5460(9)	36(5)
C(9)	4470(11)	946(6)	5034(9)	21(4)
C(10)	5058(12)	754(7)	4484(9)	25(4)
C(11)	1999(11)	1437(6)	4056(9)	17(3)
C(12)	962(12)	1333(6)	3385(8)	24(4)
C(13)	5357(11)	1578(6)	2549(8)	18(3)
C(14)	4935(11)	1347(6)	1686(8)	18(3)
C(15)	-142(11)	1033(6)	1726(9)	19(4)
C(16)	-202(13)	840(7)	913(9)	30(4)
C(17)	-1167(13)	819(7)	362(10)	36(4)
C(18)	-2149(14)	998(8)	586(10)	42(5)
C(19)	-2093(13)	1199(8)	1372(10)	37(4)
C(20)	-1107(13)	1217(7)	1942(9)	32(4)
C(21)	1472(12)	234(6)	2646(8)	19(4)
C(22)	2430(12)	89(7)	3219(9)	25(4)
C(23)	2651(14)	-499(7)	3456(9)	32(4)
C(24)	1922(15)	-961(8)	3155(10)	41(5)
C(25)	944(13)	-807(7)	2591(11)	42(5)
C(26)	738(12)	-211(7)	2347(9)	29(4)
C(27)	3244(12)	915(6)	356(8)	16(3)
C(28)	4019(12)	637(7)	-1(9)	28(4)
C(29)	3815(13)	562(7)	-838(9)	32(4)
C(30)	2816(16)	755(7)	-1302(10)	46(5)
C(31)	2091(16)	1038(7)	-940(9)	44(5)
C(32)	2251(13)	1112(6)	-94(9)	28(4)
C(33)	3815(12)	249(7)	1815(8)	21(4)

C(34)	4737(12)	76(7)	2408(8)	21(4)
C(35)	4951(13)	-531(7)	2622(8)	29(4)
C(36)	4252(12)	-977(7)	2237(9)	24(4)
C(37)	3329(12)	-829(7)	1669(9)	24(4)
C(38)	3120(12)	-217(6)	1466(8)	21(4)
C(39)	7957(15)	-2162(8)	3457(11)	53(6)
Cl(3)	6720(4)	-1856(3)	3008(4)	89(2)
Cl(4)	9071(4)	-1736(3)	3294(3)	81(2)
C(40)	1418(16)	278(10)	5870(10)	62(6)
Cl(5)	1976(5)	-136(3)	6728(3)	82(2)
Cl(6)	1570(5)	-55(3)	4990(3)	88(2)
C(41)	9566(16)	2309(12)	4666(11)	85(8)
Cl(7)	10318(5)	2897(2)	4374(4)	80(2)
Cl(8)	8410(4)	2110(3)	3931(3)	63(2)

Table A9.3. Bond lengths (Å) and angles (°) for $[(\eta^5\text{-}C_5H_5)_2Ti(O_2CCH_2PPh_2)_2PdCl_2].3CH_2Cl_2$, **P10**.$3CH_2Cl_2$.

Pd(1)-P(1)	2.259(4)	Pd(1)-P(2)	2.276(4)
Pd(1)-Cl(2)	2.341(4)	Pd(1)-Cl(1)	2.347(4)
Ti(1)-O(3)	1.961(9)	Ti(1)-O(1)	1.969(8)
Ti(1)-C(3)	2.32(2)	Ti(1)-C(8)	2.346(14)
Ti(1)-C(7)	2.350(14)	Ti(1)-C(4)	2.35(2)
Ti(1)-C(2)	2.36(2)	Ti(1)-C(6)	2.36(2)
Ti(1)-C(9)	2.380(14)	Ti(1)-C(5)	2.38(2)
Ti(1)-C(1)	2.39(2)	Ti(1)-C(10)	2.39(2)
P(1)-C(15)	1.813(13)	P(1)-C(12)	1.831(14)
P(1)-C(21)	1.834(14)	P(2)-C(33)	1.79(2)
P(2)-C(14)	1.831(14)	P(2)-C(27)	1.850(13)
O(1)-C(11)	1.29(2)	O(2)-C(11)	1.20(2)
O(3)-C(13)	1.28(2)	O(4)-C(13)	1.22(2)
C(1)-C(2)	1.34(2)	C(1)-C(5)	1.39(2)
C(2)-C(3)	1.32(2)	C(3)-C(4)	1.37(2)
C(4)-C(5)	1.41(2)	C(6)-C(7)	1.35(2)
C(6)-C(10)	1.36(2)	C(7)-C(8)	1.43(2)
C(8)-C(9)	1.40(2)	C(9)-C(10)	1.35(2)
C(11)-C(12)	1.53(2)	C(13)-C(14)	1.52(2)
C(15)-C(20)	1.38(2)	C(15)-C(16)	1.42(2)
C(16)-C(17)	1.35(2)	C(17)-C(18)	1.40(2)
C(18)-C(19)	1.38(2)	C(19)-C(20)	1.38(2)
C(21)-C(26)	1.36(2)	C(21)-C(22)	1.40(2)
C(22)-C(23)	1.37(2)	C(23)-C(24)	1.38(2)
C(24)-C(25)	1.41(2)	C(25)-C(26)	1.38(2)
C(27)-C(32)	1.37(2)	C(27)-C(28)	1.38(2)
C(28)-C(29)	1.38(2)	C(29)-C(30)	1.38(2)
C(30)-C(31)	1.34(2)	C(31)-C(32)	1.40(2)
C(33)-C(38)	1.39(2)	C(33)-C(34)	1.40(2)

C(34)-C(35)	1.40(2)	C(35)-C(36)	1.38(2)
C(36)-C(37)	1.36(2)	C(37)-C(38)	1.40(2)
C(39)-Cl(3)	1.70(2)	C(39)-Cl(4)	1.73(2)
C(40)-Cl(6)	1.69(2)	C(40)-Cl(5)	1.72(2)
C(41)-Cl(7)	1.72(2)	C(41)-Cl(8)	1.74(2)
P(1)-Pd(1)-P(2)	103.94(13)	P(1)-Pd(1)-Cl(2)	170.61(14)
P(2)-Pd(1)-Cl(2)	84.64(13)	P(1)-Pd(1)-Cl(1)	83.13(13)
P(2)-Pd(1)-Cl(1)	172.33(14)	Cl(2)-Pd(1)-Cl(1)	88.11(13)
O(3)-Ti(1)-O(1)	89.4(4)	O(3)-Ti(1)-C(3)	96.8(5)
O(1)-Ti(1)-C(3)	134.9(5)	O(3)-Ti(1)-C(8)	136.5(5)
O(1)-Ti(1)-C(8)	104.5(5)	C(3)-Ti(1)-C(8)	101.2(6)
O(3)-Ti(1)-C(7)	110.5(6)	O(1)-Ti(1)-C(7)	136.4(5)
C(3)-Ti(1)-C(7)	82.5(6)	C(8)-Ti(1)-C(7)	35.5(5)
O(3)-Ti(1)-C(4)	130.5(5)	O(1)-Ti(1)-C(4)	119.0(5)
C(3)-Ti(1)-C(4)	34.2(5)	C(8)-Ti(1)-C(4)	78.1(6)
C(7)-Ti(1)-C(4)	77.4(6)	O(3)-Ti(1)-C(2)	77.9(5)
O(1)-Ti(1)-C(2)	107.9(5)	C(3)-Ti(1)-C(2)	32.6(5)
C(8)-Ti(1)-C(2)	132.4(6)	C(7)-Ti(1)-C(2)	113.9(6)
C(4)-Ti(1)-C(2)	55.9(6)	O(3)-Ti(1)-C(6)	80.9(5)
O(1)-Ti(1)-C(6)	124.0(5)	C(3)-Ti(1)-C(6)	101.0(6)
C(8)-Ti(1)-C(6)	57.0(6)	C(7)-Ti(1)-C(6)	33.4(5)
C(4)-Ti(1)-C(6)	108.4(6)	C(2)-Ti(1)-C(6)	123.1(6)
O(3)-Ti(1)-C(9)	113.7(4)	O(1)-Ti(1)-C(9)	79.7(4)
C(3)-Ti(1)-C(9)	135.2(6)	C(8)-Ti(1)-C(9)	34.4(5)
C(7)-Ti(1)-C(9)	56.9(5)	C(4)-Ti(1)-C(9)	110.9(6)
C(2)-Ti(1)-C(9)	166.7(6)	C(6)-Ti(1)-C(9)	55.8(5)
O(3)-Ti(1)-C(5)	128.8(5)	O(1)-Ti(1)-C(5)	85.2(5)
C(3)-Ti(1)-C(5)	56.5(6)	C(8)-Ti(1)-C(5)	93.8(6)
C(7)-Ti(1)-C(5)	108.0(6)	C(4)-Ti(1)-C(5)	34.8(6)
C(2)-Ti(1)-C(5)	56.1(6)	C(6)-Ti(1)-C(5)	141.1(6)
C(9)-Ti(1)-C(5)	115.2(6)	O(3)-Ti(1)-C(1)	94.9(5)
O(1)-Ti(1)-C(1)	80.5(5)	C(3)-Ti(1)-C(1)	54.5(6)
C(8)-Ti(1)-C(1)	127.6(6)	C(7)-Ti(1)-C(1)	132.7(6)
C(4)-Ti(1)-C(1)	56.1(6)	C(2)-Ti(1)-C(1)	32.7(5)
C(6)-Ti(1)-C(1)	154.8(6)	C(9)-Ti(1)-C(1)	144.7(5)
C(5)-Ti(1)-C(1)	34.0(5)	O(3)-Ti(1)-C(10)	83.2(4)
O(1)-Ti(1)-C(10)	91.1(4)	C(3)-Ti(1)-C(10)	133.9(6)
C(8)-Ti(1)-C(10)	56.1(5)	C(7)-Ti(1)-C(10)	55.4(5)
C(4)-Ti(1)-C(10)	130.9(6)	C(2)-Ti(1)-C(10)	152.8(6)
C(6)-Ti(1)-C(10)	33.2(5)	C(9)-Ti(1)-C(10)	33.0(4)
C(5)-Ti(1)-C(10)	147.6(6)	C(1)-Ti(1)-C(10)	171.4(6)
C(15)-P(1)-C(12)	105.9(7)	C(15)-P(1)-C(21)	103.2(6)
C(12)-P(1)-C(21)	102.1(6)	C(15)-P(1)-Pd(1)	105.9(5)
C(12)-P(1)-Pd(1)	112.9(5)	C(21)-P(1)-Pd(1)	125.1(5)
C(33)-P(2)-C(14)	102.1(7)	C(33)-P(2)-C(27)	101.1(6)

C(14)-P(2)-C(27)	103.0(6)	C(33)-P(2)-Pd(1)	126.4(5)
C(14)-P(2)-Pd(1)	111.7(4)	C(27)-P(2)-Pd(1)	109.9(5)
C(11)-O(1)-Ti(1)	142.9(9)	C(13)-O(3)-Ti(1)	142.2(9)
C(2)-C(1)-C(5)	110(2)	C(2)-C(1)-Ti(1)	72.7(11)
C(5)-C(1)-Ti(1)	72.8(11)	C(3)-C(2)-C(1)	109(2)
C(3)-C(2)-Ti(1)	72.0(11)	C(1)-C(2)-Ti(1)	74.6(11)
C(2)-C(3)-C(4)	111(2)	C(2)-C(3)-Ti(1)	75.4(11)
C(4)-C(3)-Ti(1)	74.1(11)	C(3)-C(4)-C(5)	106(2)
C(3)-C(4)-Ti(1)	71.7(10)	C(5)-C(4)-Ti(1)	73.7(10)
C(1)-C(5)-C(4)	105(2)	C(1)-C(5)-Ti(1)	73.2(11)
C(4)-C(5)-Ti(1)	71.5(10)	C(7)-C(6)-C(10)	109(2)
C(7)-C(6)-Ti(1)	72.7(9)	C(10)-C(6)-Ti(1)	74.7(9)
C(6)-C(7)-C(8)	108(2)	C(6)-C(7)-Ti(1)	73.9(9)
C(8)-C(7)-Ti(1)	72.1(8)	C(9)-C(8)-C(7)	105.6(14)
C(9)-C(8)-Ti(1)	74.1(8)	C(7)-C(8)-Ti(1)	72.4(8)
C(10)-C(9)-C(8)	108.1(14)	C(10)-C(9)-Ti(1)	74.1(8)
C(8)-C(9)-Ti(1)	71.5(8)	C(9)-C(10)-C(6)	110(2)
C(9)-C(10)-Ti(1)	72.9(8)	C(6)-C(10)-Ti(1)	72.2(9)
O(2)-C(11)-O(1)	126.0(13)	O(2)-C(11)-C(12)	119.5(13)
O(1)-C(11)-C(12)	114.3(12)	C(11)-C(12)-P(1)	116.1(10)
O(4)-C(13)-O(3)	126.5(13)	O(4)-C(13)-C(14)	118.1(12)
O(3)-C(13)-C(14)	115.4(12)	C(13)-C(14)-P(2)	116.0(10)
C(20)-C(15)-C(16)	117.9(13)	C(20)-C(15)-P(1)	123.9(12)
C(16)-C(15)-P(1)	118.2(11)	C(17)-C(16)-C(15)	122(2)
C(16)-C(17)-C(18)	120(2)	C(19)-C(18)-C(17)	118(2)
C(18)-C(19)-C(20)	122(2)	C(15)-C(20)-C(19)	120(2)
C(26)-C(21)-C(22)	119.5(14)	C(26)-C(21)-P(1)	122.9(12)
C(22)-C(21)-P(1)	117.3(11)	C(23)-C(22)-C(21)	120.4(14)
C(22)-C(23)-C(24)	121(2)	C(23)-C(24)-C(25)	118(2)
C(26)-C(25)-C(24)	120(2)	C(21)-C(26)-C(25)	121(2)
C(32)-C(27)-C(28)	121.7(13)	C(32)-C(27)-P(2)	119.2(11)
C(28)-C(27)-P(2)	119.1(11)	C(27)-C(28)-C(29)	120.0(14)
C(30)-C(29)-C(28)	119(2)	C(31)-C(30)-C(29)	120(2)
C(30)-C(31)-C(32)	123(2)	C(27)-C(32)-C(31)	116(2)
C(38)-C(33)-C(34)	116.0(14)	C(38)-C(33)-P(2)	120.4(11)
C(34)-C(33)-P(2)	123.5(11)	C(35)-C(34)-C(33)	121.7(14)
C(36)-C(35)-C(34)	119.8(14)	C(37)-C(36)-C(35)	120.5(14)
C(36)-C(37)-C(38)	119.0(14)	C(33)-C(38)-C(37)	123.0(14)
Cl(3)-C(39)-Cl(4)	112.7(10)	Cl(6)-C(40)-Cl(5)	113.7(12)
Cl(7)-C(41)-Cl(8)	113.6(12)		

Table A9.4. Anisotropic displacement parameters (Å^2 x 10^3) for [(η^5-C_5H_5)$_2$Ti($O_2CCH_2PPh_2$)$_2$PdCl_2].3CH_2Cl_2, **P10.3CH_2Cl_2**. The anisotropic displacement factor exponent takes the form:

$-2\ pi^2\ [\ h^2 a^*\ 2\ U11 + \ldots + 2\ h\ k\ a^*\ b^*\ U12\ ]$

Atom	U11	U22	U33	U23	U13	U12
Pd(1)	15(1)	11(1)	14(1)	0(1)	3(1)	0(1)
Ti(1)	17(2)	13(2)	14(1)	0(1)	-1(1)	-2(1)
P(1)	11(2)	15(2)	21(2)	0(2)	1(2)	2(2)
P(2)	16(2)	14(2)	18(2)	0(2)	7(2)	2(2)
O(1)	12(5)	24(6)	14(5)	-2(4)	5(4)	-9(4)
O(2)	26(6)	62(9)	27(6)	0(6)	5(5)	-5(6)
O(3)	25(6)	18(6)	12(5)	5(4)	11(4)	-6(4)
O(4)	27(6)	50(8)	30(6)	-9(6)	5(5)	-16(6)
Cl(1)	24(2)	19(2)	28(2)	1(2)	9(2)	7(2)
Cl(2)	32(2)	17(2)	31(2)	6(2)	13(2)	1(2)
C(6)	41(12)	45(12)	32(11)	19(10)	17(9)	15(9)
C(7)	29(10)	22(10)	43(11)	20(9)	-24(9)	-1(8)
C(8)	60(13)	29(10)	12(9)	-2(7)	-10(9)	30(9)
C(9)	11(8)	26(9)	30(9)	13(8)	14(7)	10(7)
C(12)	31(10)	13(8)	22(9)	4(7)	-6(7)	11(7)
C(14)	24(9)	13(8)	19(8)	-5(6)	9(7)	4(7)
C(15)	6(8)	13(8)	31(9)	-2(7)	-9(7)	0(6)
C(16)	25(10)	36(10)	30(10)	-8(8)	4(8)	-11(8)
C(17)	22(10)	43(11)	37(11)	-8(9)	-8(9)	-10(8)
C(18)	31(11)	53(12)	32(11)	11(9)	-17(9)	1(9)
C(19)	17(10)	53(12)	39(11)	1(9)	2(8)	-6(8)
C(20)	30(11)	39(11)	25(10)	-5(8)	-1(8)	5(8)
C(21)	28(9)	19(9)	12(8)	-1(7)	10(7)	-10(7)
C(22)	29(10)	21(9)	22(9)	3(7)	1(8)	1(7)
C(23)	49(11)	20(9)	22(9)	4(7)	-6(8)	6(9)
C(24)	57(13)	30(11)	42(11)	11(9)	21(10)	-2(10)
C(25)	20(10)	32(11)	71(14)	3(10)	5(10)	-7(8)
C(26)	15(9)	29(10)	42(11)	16(8)	6(8)	-2(8)
C(27)	27(9)	7(7)	13(8)	2(6)	4(7)	5(7)
C(28)	26(10)	39(10)	22(9)	-2(8)	9(8)	6(8)
C(30)	78(15)	23(10)	30(11)	-9(8)	-3(10)	10(10)
C(31)	75(14)	25(10)	22(10)	-4(8)	-12(10)	21(10)
C(32)	32(10)	20(9)	25(9)	-3(7)	-5(8)	9(8)
C(33)	16(9)	30(9)	17(8)	-6(7)	3(7)	13(7)
C(34)	23(9)	25(9)	18(8)	-10(7)	12(7)	5(7)
C(35)	33(10)	44(11)	10(8)	2(8)	1(7)	25(9)
C(38)	19(9)	28(9)	16(8)	0(7)	3(7)	-3(7)
C(39)	73(15)	47(12)	50(13)	24(10)	37(11)	12(11)
Cl(3)	40(3)	149(7)	76(4)	-12(4)	4(3)	32(4)
Cl(4)	50(3)	132(6)	68(4)	-29(4)	29(3)	-31(4)
C(40)	59(14)	86(17)	43(12)	4(11)	16(10)	7(12)
Cl(5)	116(5)	83(4)	41(3)	-7(3)	3(3)	-10(4)
Cl(6)	110(5)	115(5)	43(3)	-6(3)	23(3)	42(4)

C(41)	41(13)	177(27)	39(13)	-28(15)	9(10)	1(15)
Cl(7)	59(4)	55(4)	121(5)	-14(4)	7(4)	0(3)
Cl(8)	39(3)	100(4)	51(3)	-27(3)	9(3)	-1(3)

Table A9.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for $[(\eta^5\text{-}C_5H_5)_2Ti(O_2CCH_2PPh_2)_2PdCl_2].3CH_2Cl_2$, **P10**.$3CH_2Cl_2$.

Atom	*x*	*y*	*z*	U(eq)
H(1)	2919(15)	2714(8)	3258(11)	55
H(2)	4740(14)	2717(8)	2944(11)	55
H(3)	6100(15)	2694(7)	4185(10)	52
H(4)	5183(15)	2688(8)	5357(11)	55
H(5)	3114(15)	2677(8)	4769(11)	62
H(6)	6492(14)	1069(8)	4206(10)	46
H(7)	6548(13)	1812(7)	5296(10)	43
H(8)	4819(15)	1662(7)	5871(9)	43
H(9)	3809(11)	779(6)	5115(9)	25
H(10)	4865(12)	430(7)	4128(9)	29
H(12A)	568(12)	1715(6)	3281(8)	29
H(12B)	482(12)	1051(6)	3591(8)	29
H(14A)	5449(11)	1043(6)	1569(8)	22
H(14B)	4942(11)	1682(6)	1312(8)	22
H(16)	445(13)	723(7)	754(9)	36
H(17)	-1180(13)	687(7)	-166(10)	43
H(18)	-2822(14)	982(8)	214(10)	50
H(19)	-2739(13)	1326(8)	1524(10)	44
H(20)	-1096(13)	1353(7)	2469(9)	39
H(22)	2922(12)	395(7)	3440(9)	29
H(23)	3302(14)	-590(7)	3826(9)	39
H(24)	2071(15)	-1361(8)	3319(10)	49
H(25)	435(13)	-1108(7)	2382(11)	50
H(26)	92(12)	-114(7)	1974(9)	34
H(28)	4681(12)	499(7)	320(9)	34
H(29)	4344(13)	385(7)	-1086(9)	39
H(30)	2649(16)	687(7)	-1862(10)	55
H(31)	1449(16)	1194(7)	-1267(9)	53
H(32)	1713(13)	1285(6)	149(9)	33
H(34)	5220(12)	374(7)	2666(8)	25
H(35)	5565(13)	-633(7)	3023(8)	35
H(36)	4410(12)	-1382(7)	2365(9)	29
H(37)	2845(12)	-1129(7)	1420(9)	28
H(38)	2487(12)	-119(6)	1081(8)	25
H(39A)	8008(15)	-2568(8)	3245(11)	64
H(39B)	7995(15)	-2195(8)	4039(11)	64
H(40A)	635(16)	339(10)	5852(10)	74
H(40B)	1768(16)	674(10)	5912(10)	74
H(41A)	9329(16)	2425(12)	5161(11)	103
H(41B)	10043(16)	1957(12)	4791(11)	103

Appendix 10.

Supplementary data for the crystal structure determination of bis(cyclopentadienyl)-bis(thiophenoxyacetato)titanium(IV) S3.

Table A10.1. Crystal data and structure refinement for bis(cyclopentadienyl)bis(thiophenoxyacetato)titanium(IV) S3.

Identification code	S3
Empirical formula	$C_{26}H_{24}O_4S_2Ti$
Formula weight	512.47
Temperature	293(2)°K
Wavelength	0.70930 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.011(2)Å α= 104.39(2)°
	b = 10.693(3)Å β= 102.84(2)°
	c = 12.011(3)Å γ= 90.09(2)°
Volume	1212.1(5) $Å^3$
Z	2
Density (calculated)	1.404 Mg/m^3
Absorption coefficient	0.556 mm^{-1}
F(000)	532
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	2.09 to 21.93°
Index ranges	-10<=h<=0; -11<=k<=11; -12<=l<=12
Reflections collected	3183
Independent reflections	2972 [R(int) = 0.0158]
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	2963 / 0 / 299
Goodness-of-fit on F^2	1.095
Final R indices [I>2σ(I)]	R1 = 0.0313 wR2 = 0.0664
R indices (all data)	R1 = 0.0591 wR2 = 0.0799
Largest diff. peak and hole	0.169 and -0.204 $eÅ^{-3}$
Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0273P)^2+0.8713P]$ where $P=(Fo^2+2Fc^2)/3$
Extinction coefficient	0.0119(10)
Extinction expression	$Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Table A10.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for bis(cyclopentadienyl)bis(thiophenoxyacetato)titanium(IV) S3. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	U(eq)
Ti(1)	1477(1)	9370(1)	7547(1)	33(1)
S(1)	4036(1)	8452(1)	12046(1)	61(1)
S(2)	5565(1)	7842(1)	6834(1)	59(1)
O(1)	2784(2)	9151(2)	8962(2)	41(1)
O(2)	1829(3)	9568(3)	10495(2)	72(1)
O(3)	2886(2)	9027(2)	6657(2)	46(1)
O(4)	2647(3)	9346(3)	4882(2)	84(1)
C(1)	2794(3)	9262(3)	10057(3)	41(1)
C(2)	4156(3)	8976(3)	10763(3)	46(1)
C(3)	3066(3)	6967(3)	11467(3)	47(1)
C(4)	2402(4)	6564(3)	12216(3)	58(1)
C(5)	1675(4)	5383(4)	11860(4)	80(1)
C(6)	1591(5)	4611(4)	10759(5)	91(1)
C(7)	2216(5)	5015(4)	9995(4)	85(1)
C(8)	2961(4)	6185(4)	10346(3)	68(1)
C(9)	3307(3)	9035(3)	5725(3)	42(1)
C(10)	4753(3)	8614(3)	5715(3)	47(1)
C(11)	4551(3)	6387(3)	6507(3)	47(1)
C(12)	4694(4)	5728(4)	7376(3)	66(1)
C(13)	3960(5)	4564(4)	7162(4)	80(1)
C(14)	3076(5)	4057(4)	6099(4)	78(1)
C(15)	2938(4)	4698(4)	5240(4)	66(1)
C(16)	3666(3)	5857(3)	5431(3)	52(1)
C(17)	-609(3)	8318(3)	6364(3)	56(1)
C(18)	413(3)	7532(3)	6036(3)	55(1)
C(19)	1056(3)	7080(3)	6996(3)	54(1)
C(20)	421(4)	7558(3)	7913(3)	56(1)
C(21)	-602(3)	8331(3)	7534(3)	56(1)
C(22)	2055(6)	11469(4)	7428(7)	95(2)
C(23)	2087(4)	11548(3)	8588(5)	77(1)
C(24)	780(4)	11277(3)	8678(4)	63(1)
C(25)	-45(4)	11061(4)	7599(4)	69(1)
C(26)	712(7)	11138(4)	6814(4)	84(2)

Table A10.3. Bond lengths (Å) and angles (°) for bis(cyclopentadienyl)bis(thiophenoxyacetato)titanium(IV) S3.

Ti(1)-O(3)	1.936(2)	Ti(1)-O(1)	1.966(2)
Ti(1)-C(26)	2.338(4)	Ti(1)-C(17)	2.350(3)
Ti(1)-C(21)	2.353(3)	Ti(1)-C(24)	2.353(3)
Ti(1)-C(23)	2.359(4)	Ti(1)-C(22)	2.363(4)
Ti(1)-C(25)	2.364(3)	Ti(1)-C(18)	2.377(3)
Ti(1)-C(19)	2.383(3)	Ti(1)-C(20)	2.385(3)
S(1)-C(3)	1.758(3)	S(1)-C(2)	1.792(3)
S(2)-C(11)	1.766(3)	S(2)-C(10)	1.793(3)
O(1)-C(1)	1.288(3)	O(2)-C(1)	1.207(3)
O(3)-C(9)	1.282(4)	O(4)-C(9)	1.202(4)
C(1)-C(2)	1.513(4)	C(3)-C(4)	1.376(5)
C(3)-C(8)	1.378(5)	C(4)-C(5)	1.377(5)
C(5)-C(6)	1.358(6)	C(6)-C(7)	1.369(6)
C(7)-C(8)	1.376(5)	C(9)-C(10)	1.518(4)
C(11)-C(16)	1.379(4)	C(11)-C(12)	1.380(5)
C(12)-C(13)	1.382(6)	C(13)-C(14)	1.363(6)
C(14)-C(15)	1.357(5)	C(15)-C(16)	1.379(5)
C(17)-C(18)	1.388(5)	C(17)-C(21)	1.400(5)
C(18)-C(19)	1.389(5)	C(19)-C(20)	1.383(5)
C(20)-C(21)	1.386(5)	C(22)-C(23)	1.369(6)
C(22)-C(26)	1.380(6)	C(23)-C(24)	1.372(5)
C(24)-C(25)	1.337(5)	C(25)-C(26)	1.351(6)
O(3)-Ti(1)-O(1)	90.18(9)	O(3)-Ti(1)-C(26)	94.1(2)
O(1)-Ti(1)-C(26)	135.0(2)	O(3)-Ti(1)-C(17)	109.15(11)
O(1)-Ti(1)-C(17)	135.36(11)	C(26)-Ti(1)-C(17)	84.8(2)
O(3)-Ti(1)-C(21)	136.38(11)	O(1)-Ti(1)-C(21)	105.40(11)
C(26)-Ti(1)-C(21)	101.9(2)	C(17)-Ti(1)-C(21)	34.65(12)
O(3)-Ti(1)-C(24)	133.17(12)	O(1)-Ti(1)-C(24)	90.01(13)
C(26)-Ti(1)-C(24)	55.71(14)	C(17)-Ti(1)-C(24)	103.08(14)
C(21)-Ti(1)-C(24)	88.16(14)	O(3)-Ti(1)-C(23)	100.7(2)
O(1)-Ti(1)-C(23)	79.20(13)	C(26)-Ti(1)-C(23)	56.0(2)
C(17)-Ti(1)-C(23)	132.10(13)	C(21)-Ti(1)-C(23)	121.9(2)
C(24)-Ti(1)-C(23)	33.86(14)	O(3)-Ti(1)-C(22)	78.55(12)
O(1)-Ti(1)-C(22)	104.3(2)	C(26)-Ti(1)-C(22)	34.1(2)
C(17)-Ti(1)-C(22)	118.5(2)	C(21)-Ti(1)-C(22)	132.9(2)
C(24)-Ti(1)-C(22)	56.2(2)	C(23)-Ti(1)-C(22)	33.7(2)
O(3)-Ti(1)-C(25)	127.42(14)	O(1)-Ti(1)-C(25)	122.81(14)
C(26)-Ti(1)-C(25)	33.4(2)	C(17)-Ti(1)-C(25)	76.84(14)
C(21)-Ti(1)-C(25)	77.43(14)	C(24)-Ti(1)-C(25)	32.94(13)
C(23)-Ti(1)-C(25)	55.26(14)	C(22)-Ti(1)-C(25)	55.8(2)
O(3)-Ti(1)-C(18)	80.09(11)	O(1)-Ti(1)-C(18)	120.33(11)
C(26)-Ti(1)-C(18)	104.5(2)	C(17)-Ti(1)-C(18)	34.13(11)
C(21)-Ti(1)-C(18)	56.73(12)	C(24)-Ti(1)-C(18)	137.20(14)
C(23)-Ti(1)-C(18)	160.5(2)	C(22)-Ti(1)-C(18)	130.1(2)
C(25)-Ti(1)-C(18)	108.67(14)	O(3)-Ti(1)-C(19)	84.84(11)

O(1)-Ti(1)-C(19)	86.93(11)	C(26)-Ti(1)-C(19)	138.1(2)
C(17)-Ti(1)-C(19)	56.70(12)	C(21)-Ti(1)-C(19)	56.44(12)
C(24)-Ti(1)-C(19)	141.91(13)	C(23)-Ti(1)-C(19)	165.0(2)
C(22)-Ti(1)-C(19)	159.8(2)	C(25)-Ti(1)-C(19)	131.27(13)
C(18)-Ti(1)-C(19)	33.92(12)	O(3)-Ti(1)-C(20)	117.20(12)
O(1)-Ti(1)-C(20)	78.47(11)	C(26)-Ti(1)-C(20)	135.9(2)
C(17)-Ti(1)-C(20)	56.89(13)	C(21)-Ti(1)-C(20)	34.01(12)
C(24)-Ti(1)-C(20)	108.68(14)	C(23)-Ti(1)-C(20)	135.6(2)
C(22)-Ti(1)-C(20)	164.18(14)	C(25)-Ti(1)-C(20)	109.39(14)
C(18)-Ti(1)-C(20)	56.30(13)	C(19)-Ti(1)-C(20)	33.71(11)
C(3)-S(1)-C(2)	103.9(2)	C(11)-S(2)-C(10)	103.6(2)
C(1)-O(1)-Ti(1)	137.2(2)	C(9)-O(3)-Ti(1)	149.5(2)
O(2)-C(1)-O(1)	124.4(3)	O(2)-C(1)-C(2)	122.4(3)
O(1)-C(1)-C(2)	113.2(3)	C(1)-C(2)-S(1)	114.1(2)
C(4)-C(3)-C(8)	118.9(3)	C(4)-C(3)-S(1)	116.3(3)
C(8)-C(3)-S(1)	124.8(3)	C(3)-C(4)-C(5)	120.4(4)
C(6)-C(5)-C(4)	120.3(4)	C(5)-C(6)-C(7)	119.8(4)
C(6)-C(7)-C(8)	120.4(4)	C(7)-C(8)-C(3)	120.2(4)
O(4)-C(9)-O(3)	125.0(3)	O(4)-C(9)-C(10)	119.0(3)
O(3)-C(9)-C(10)	116.0(3)	C(9)-C(10)-S(2)	117.4(2)
C(16)-C(11)-C(12)	118.5(3)	C(16)-C(11)-S(2)	124.0(3)
C(12)-C(11)-S(2)	117.4(3)	C(11)-C(12)-C(13)	120.2(4)
C(14)-C(13)-C(12)	120.7(4)	C(15)-C(14)-C(13)	119.3(4)
C(14)-C(15)-C(16)	121.0(4)	C(15)-C(16)-C(11)	120.2(3)
C(18)-C(17)-C(21)	107.4(3)	C(18)-C(17)-Ti(1)	74.0(2)
C(21)-C(17)-Ti(1)	72.8(2)	C(17)-C(18)-C(19)	108.1(3)
C(17)-C(18)-Ti(1)	71.9(2)	C(19)-C(18)-Ti(1)	73.3(2)
C(20)-C(19)-C(18)	108.3(3)	C(20)-C(19)-Ti(1)	73.2(2)
C(18)-C(19)-Ti(1)	72.8(2)	C(19)-C(20)-C(21)	108.0(3)
C(19)-C(20)-Ti(1)	73.1(2)	C(21)-C(20)-Ti(1)	71.7(2)
C(20)-C(21)-C(17)	108.1(3)	C(20)-C(21)-Ti(1)	74.3(2)
C(17)-C(21)-Ti(1)	72.6(2)	C(23)-C(22)-C(26)	106.6(4)
C(23)-C(22)-Ti(1)	73.0(2)	C(26)-C(22)-Ti(1)	71.9(2)
C(22)-C(23)-C(24)	108.2(4)	C(22)-C(23)-Ti(1)	73.3(2)
C(24)-C(23)-Ti(1)	72.8(2)	C(25)-C(24)-C(23)	107.9(4)
C(25)-C(24)-Ti(1)	74.0(2)	C(23)-C(24)-Ti(1)	73.3(2)
C(24)-C(25)-C(26)	109.2(4)	C(24)-C(25)-Ti(1)	73.1(2)
C(26)-C(25)-Ti(1)	72.2(2)	C(25)-C(26)-C(22)	108.1(4)
C(25)-C(26)-Ti(1)	74.4(2)	C(22)-C(26)-Ti(1)	73.9(2)

Table A10.4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for bis(cyclopentadienyl)bis-(thiophenoxyacetato)titanium(IV) S3. The anisotropic displacement factor exponent takes the form: $-2 pi^2 [h^2 a^* 2 U11 + ... + 2 h k a^* b^* U12]$

Atom	U11	U22	U33	U23	U13	U12
Ti(1)	27(1)	38(1)	36(1)	12(1)	11(1)	4(1)
S(1)	74(1)	64(1)	38(1)	19(1)	-6(1)	-20(1)
S(2)	36(1)	61(1)	70(1)	8(1)	3(1)	0(1)
O(1)	38(1)	54(1)	36(1)	17(1)	9(1)	3(1)
O(2)	58(2)	111(2)	59(2)	30(2)	31(1)	29(2)
O(3)	41(1)	60(2)	49(1)	22(1)	26(1)	11(1)
O(4)	70(2)	142(3)	52(2)	46(2)	17(1)	30(2)
C(1)	37(2)	46(2)	42(2)	14(2)	14(2)	0(2)
C(2)	37(2)	58(2)	43(2)	19(2)	4(2)	-4(2)
C(3)	46(2)	47(2)	47(2)	18(2)	4(2)	4(2)
C(4)	63(2)	55(2)	58(2)	18(2)	15(2)	5(2)
C(5)	86(3)	70(3)	96(4)	32(3)	36(3)	-3(3)
C(6)	101(4)	57(3)	113(4)	13(3)	31(3)	-22(3)
C(7)	113(4)	56(3)	74(3)	-8(2)	25(3)	-8(3)
C(8)	80(3)	62(3)	63(3)	11(2)	21(2)	-8(2)
C(9)	38(2)	46(2)	43(2)	9(2)	13(2)	-3(2)
C(10)	42(2)	49(2)	53(2)	4(2)	24(2)	-5(2)
C(11)	37(2)	50(2)	54(2)	12(2)	14(2)	12(2)
C(12)	54(2)	79(3)	65(3)	25(2)	5(2)	15(2)
C(13)	85(3)	73(3)	101(4)	53(3)	26(3)	19(3)
C(14)	82(3)	53(3)	101(4)	25(3)	23(3)	3(2)
C(15)	69(3)	53(2)	70(3)	4(2)	16(2)	-4(2)
C(16)	54(2)	48(2)	55(2)	12(2)	14(2)	0(2)
C(17)	38(2)	57(2)	62(2)	9(2)	-2(2)	-4(2)
C(18)	54(2)	55(2)	48(2)	-5(2)	14(2)	-9(2)
C(19)	44(2)	37(2)	80(3)	10(2)	15(2)	-2(2)
C(20)	51(2)	56(2)	64(2)	22(2)	14(2)	-16(2)
C(21)	38(2)	61(2)	66(3)	1(2)	23(2)	-9(2)
C(22)	101(4)	43(3)	184(6)	49(3)	102(4)	22(3)
C(23)	53(3)	33(2)	117(4)	-2(2)	-15(3)	3(2)
C(24)	81(3)	46(2)	67(3)	8(2)	34(2)	20(2)
C(25)	44(2)	52(2)	105(4)	17(2)	8(3)	20(2)
C(26)	141(5)	62(3)	62(3)	37(2)	27(3)	44(3)

Table A10.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for bis(cyclopentadienyl)bis(thiophenoxyacetato)titanium(IV) S3.

Atom	*x*	*y*	*z*	U(eq)
H(2A)	4765(3)	9750(3)	11009(3)	55
H(2B)	4564(3)	8311(3)	10256(3)	55
H(4)	2445(4)	7093(3)	12967(3)	69
H(5)	1240(4)	5114(4)	12376(4)	96
H(6)	1110(5)	3809(4)	10526(5)	109
H(7)	2138(5)	4496(4)	9234(4)	102
H(8)	3395(4)	6448(4)	9826(3)	82
H(10A)	5328(3)	9371(3)	5780(3)	57
H(10B)	4730(3)	8025(3)	4952(3)	57
H(12)	5286(4)	6069(4)	8108(3)	79
H(13)	4070(5)	4121(4)	7749(4)	96
H(14)	2574(5)	3280(4)	5964(4)	93
H(15)	2342(4)	4351(4)	4512(4)	79
H(16)	3561(3)	6282(3)	4832(3)	63
H(17)	-1192(3)	8757(3)	5894(3)	67
H(18)	629(3)	7342(3)	5300(3)	66
H(19)	1789(3)	6546(3)	7019(3)	65
H(20)	641(4)	7391(3)	8654(3)	67
H(21)	-1183(3)	8779(3)	7979(3)	67
H(22)	2795(6)	11610(4)	7114(7)	113
H(23)	2860(4)	11750(3)	9209(5)	92
H(24)	515(4)	11248(3)	9366(4)	76
H(25)	-990(4)	10886(4)	7418(4)	82
H(26)	385(7)	10994(4)	6002(4)	101

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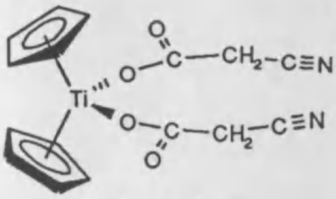

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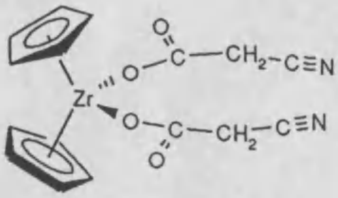

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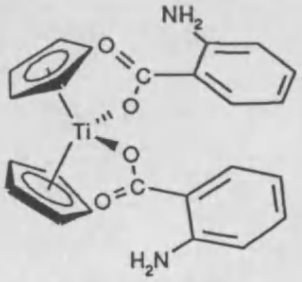
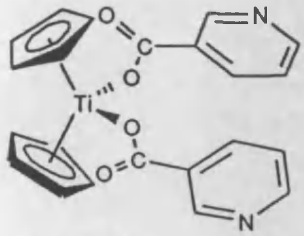


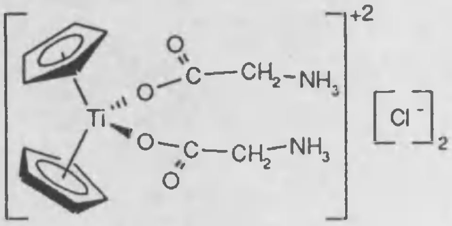
$Cp_2Ti(O_2CC_6H_4NH_2)_2$

N3



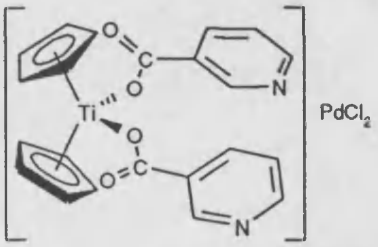
$Cp_2Ti(O_2CC_5H_4N)_2$

N4



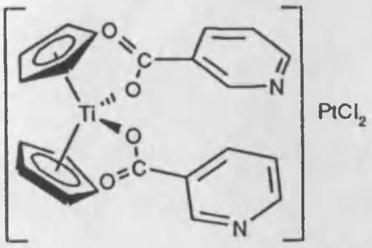
$[Cp_2Ti(O_2CCH_2NH_3)_2][Cl]_2$

N5



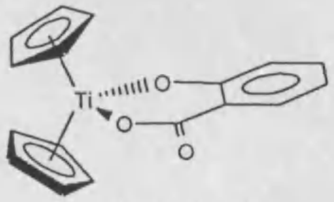
$Cp_2Ti(O_2CC_5H_4N)_2.PdCl_2$

N6



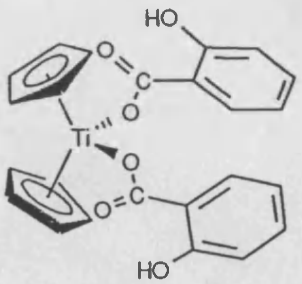
$Cp_2Ti(O_2CC_5H_4N)_2.PtCl_2$

N7



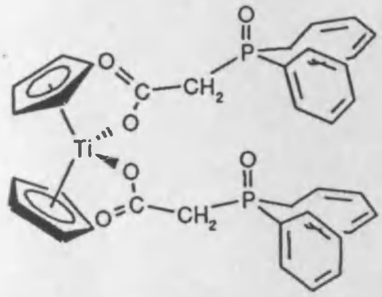
$Cp_2Ti(O_2CC_6H_4O)$

O1



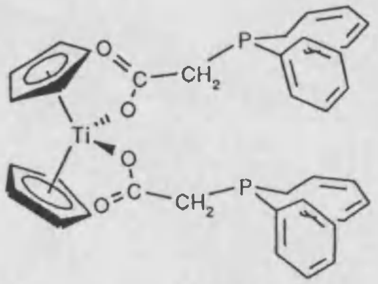
$Cp_2Ti(O_2CC_6H_4OH)_2$

O2



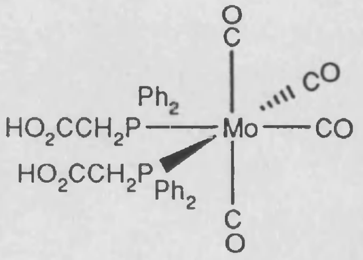
$Cp_2Ti(O_2CCH_2P(O)Ph_2)_2$

O3



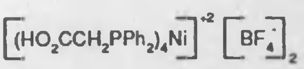
$Cp_2Ti(O_2CCH_2PPh_2)_2$

P1



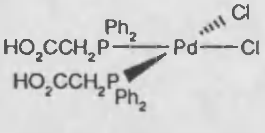
$(HO_2CCH_2PPh_2)_2Mo(CO)_4$

P2



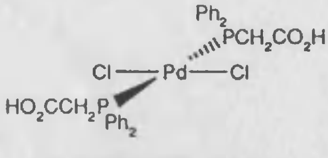
$[(HO_2CCH_2PPh_2)_4Ni][BF_4]_2$

P3



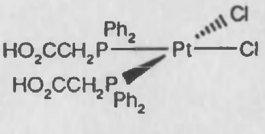
$(HO_2CCH_2PPh_2)_2PdCl_2$

P4



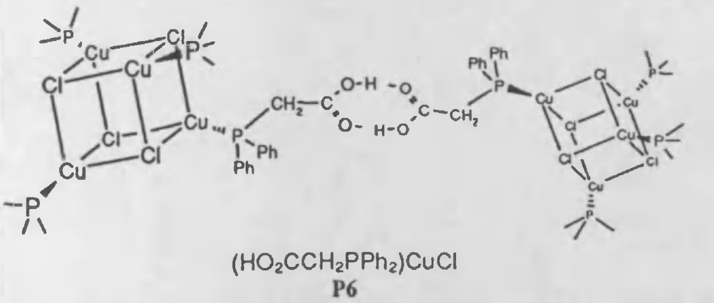
$(HO_2CCH_2PPh_2)_2PdCl_2$

P4'



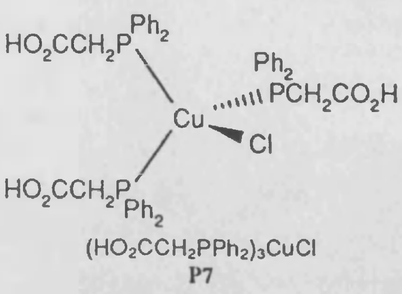
$(HO_2CCH_2PPh_2)_2PtCl_2$

P5



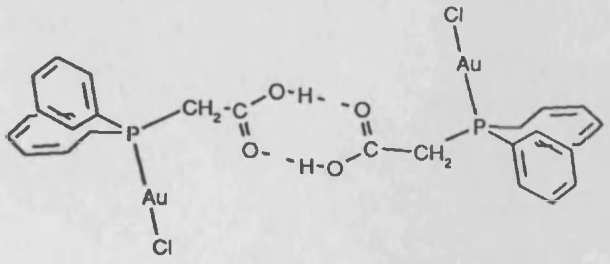
$(HO_2CCH_2PPh_2)CuCl$

P6



$(HO_2CCH_2PPh_2)_3CuCl$

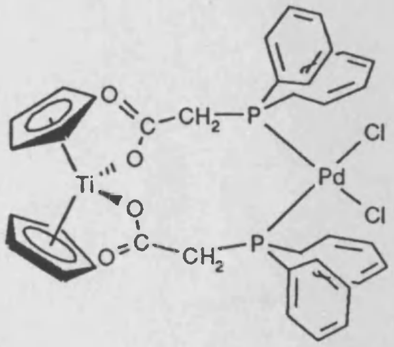
P7



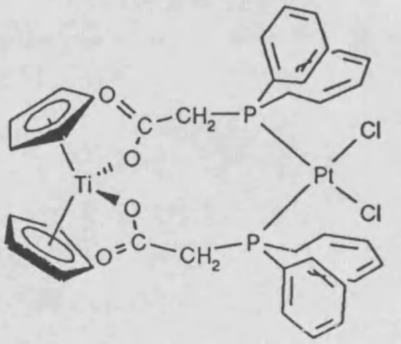
$(HO_2CCH_2PPh_2)AuCl$
P8

$$\left[\{Cp_2Ti(O_2CCH_2PPh_2)_2\}_2Ni\right]^{+2}\left[BF_4^-\right]_2$$

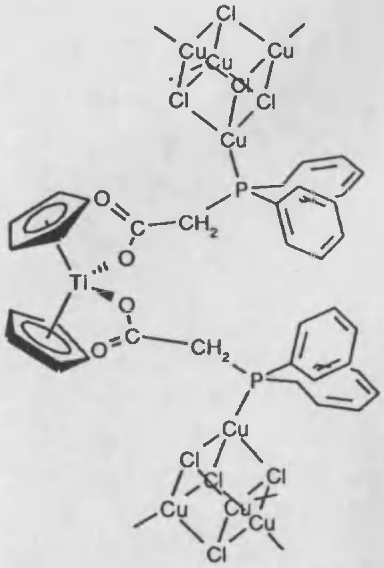
$[\{Cp_2Ti(O_2CCH_2PPh_2)_2\}_2Ni][BF_4]_2$
P9



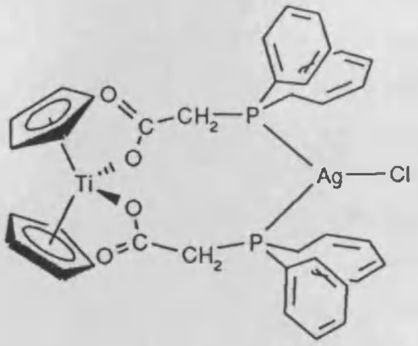
$Cp_2Ti(O_2CCH_2PPh_2)_2PdCl_2$
P10



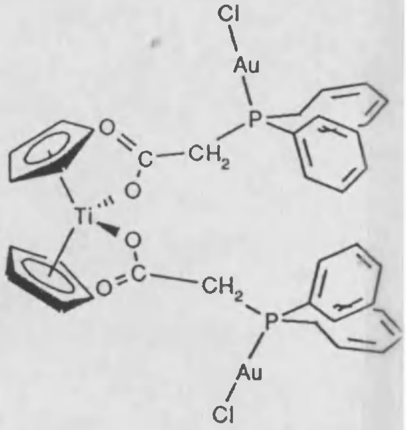
$Cp_2Ti(O_2CCH_2PPh_2)_2PtCl_2$
P11



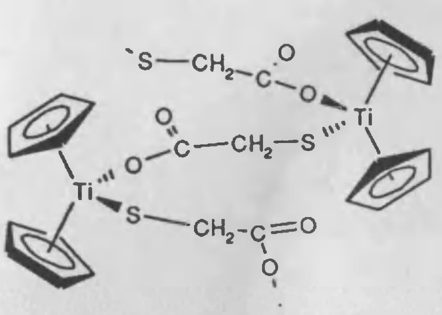
$Cp_2Ti(O_2CCH_2PPh_2)_2.2CuCl$
P12



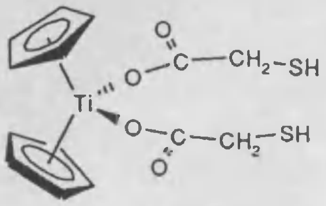
$Cp_2Ti(O_2CCH_2PPh_2)_2.AgCl$
P13



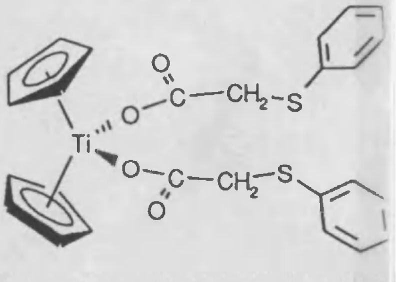
$Cp_2Ti(O_2CCH_2PPh_2)_2.2AuCl$
P14



$Cp_2Ti(O_2CCH_2S)$
S1



$Cp_2Ti(O_2CCH_2SH)_2$
S2



$Cp_2Ti(O_2CCH_2SPh)_2$
S3