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Main group metallocenes with substituted cyclopentadienyl ligands: from bonding problems to discotic phases

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Abstract - Metallocenes of main group 1, 2, 3 and 4 elements containing pentamethyl-, pentaphenyl- or pentabenzylcyclopentadienyl ligands demonstrate different behaviours in solution and in the solid state. Single crystal X-ray analyses show monomeric, oligomeric, or polymeric structures, depending on the electronic situation around the different metals and the steric arrangement of the organic groups bond to the cyclopentadienyl anions. From the comparison with some new transition metal and f-element metallocenes containing the same ligands conclusions have been drawn to the bonding situation in the monomeric and polymeric metallocenes. Pentaphenylcyclopentadiene reacts with acyl chlorides to form cyclopentadienes containing five para-substituted phenyl groups. They can be transferred to penta(para-benzoic acid ester)cyclopentadiene derivatives, which are metallated to yield overcrowded metallocenes containing a discotic cyclopentadienyl anion like in some thallium complexes.

INTRODUCTION

Cyclopentadiene, a simple organic compound, found firstly in the volatile parts of coal tar, has become one of the most important compounds used in Organometallic Chemistry of the transition metals. More than 80% of all of their organometallic compounds known, contain the cyclopentadienyl ligand. Organometallic chemistry, which started around 1850 with Frankland's organozink compounds, was stimulated very much by the discovery of ferrocene in 1951 and since, the anion of this hydrocarbon became the top ligand for organometallic coordination compounds of the transition metals.

Not only the organometallic chemistry of the transition metals was enforced by the cyclopentadienyl system, but also main group element chemistry participated in this trend. Organotin compounds are known since the beginning of organometallic chemistry, and up to now more than 50 000 organotin compounds, predominantly derivatives of Sn(IV) are described in the literature. Organotin compounds with the tin atom in the oxidation state +2 which are analogues to the carbenes with a lone pair of electrons and an empty orbital have been known only in few cases.

The first purposive experiment to prepare organotin(II) compounds had been done by E.O. Fischer in 1956 (ref. 1). He reacted $SnCl_2$ and cyclopentadienyl lithium and isolated the first cyclopentadienyl tin(II) compound. X-ray structural analyses showed a bent structure for this stannocene and not the ideal ferrocene-like sandwich arrangement (ref. 2).

However, a compound with a real ferrocene-like sandwich structure, that means with coplanar cyclopentadienyl ligands was obtained 6 years ago, using the reaction of tin dichloride with pentaphenylcyclopentadienyl lithium (ref. 3). The X-ray structure of this decaphenylstannocene clearly demonstrates the steric effect of the bulky pentaphenylcyclopentadienyl ligand by forcing the rings in a perfectly parallel position, obviously leaving no room for the lone-pair of electrons at the carbenoid tin center. The phenyl groups on the staggered cyclopentadienyl rings are canted in an opposite paddlewheel arrangement to give a molecule of S_{10}-symmetry (Fig. 1).

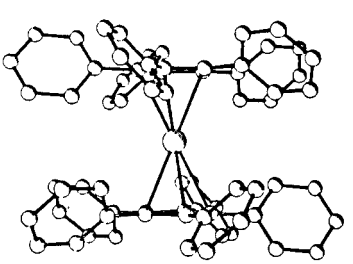


Fig. 1. X-ray structure of Decaphenylstannocene (ref. 3)

The question was: were is the lone pair of electrons? Are they delocalized througout the vast electronic system formed by the 10 phenyl rings? Such a delocalization could be responsible for the intense yellow color of this compound. However, a molecular orbital calculation (ref. 4) negates a possible charge-transfer of tin electron density into the not-antiparallel phenyl groups on the cyclopentadienyl rings.This interesting bonding situation caused us to look for other ligands, qualified for the formation of such compounds.

PENTABENZYLCYCLOPENTADIENYL METAL COMPLEXES

The pentabenzylcyclopentadienyl system is to prepare in a maximum yield of 17% following the route of Hirsch and Bailey (ref. 5). It reacts with butyl lithium in tetrahydrofuran at 0° C within 15 min to give a deep red solution of pentabenzylcyclopentadienyl lithium. The addition of germanium diiodide causes an immediate disappearance of the red color and yellow crystals of bis(pentabenzylcyclopentadienyl)germanium precipitate (ref. 6). Surprisingly, the compound is stable towards

moist air for weeks. It decomposes above 105° C without melting. It is not toxic (LD_{10} > 700 mg/kg rat), but it shows a high antitumor activity with cure rates up to 90 % against special tumors in female mice (ref. 7, 8).

By the same procedure, but using tin dichloride or lead diacetate instead of germaniumdi-iodide, yellow decabenzylstannocene or orange decabenzylplumbocene were obtained in a 55 or 50% yield, respectively (ref. 9).

$$C_5H_6 + 5\ PhCH_2OH \xrightarrow[\text{Di-isopropylbenzene}]{NaOCH_2Ph} C_5(CH_2Ph)_5H + 5\ H_2O \quad (1)$$

$$C_5(CH_2Ph)_5H + LiC_4H_9 \longrightarrow LiC_5(CH_2Ph)_5 + C_4H_{10} \quad (2)$$

$$+\ GeI_2 \longrightarrow [C_5(CH_2Ph)_5]_2Ge + 2\ LiI \quad (3)$$

$$2\ LiC_5(CH_2Ph)_5 + SnCl_2 \longrightarrow [C_5(CH_2Ph)_5]_2Sn + 2\ LiCl$$

$$+\ Pb(OOCCH_3)_2 \longrightarrow [C_5(CH_2Ph)_5]_2Pb + 2\ LiOOCCH_3 \quad (4)$$

Both compounds show a similar insensibility towards moisture and air like the analogueous germanocene. The nmr spectra of the three derivatives, recorded in benzene at 20°C show only one singlet-signal for the CH_2 protons, thus indicating an equilibration of all benzyl groups in the ligational system. Cooling to -78°C in octadeuterotoluene did not cause any change of the spectra.

The X-ray crystal structure of the germanium derivative shows two pentahapto bonded cyclopentadienyl ligands, which, in contrast to the decaphenylstannocene are not coplanar, but form an angle of 31° (Fig. 2). However, the most interesting feature of this structure is the arrangement of the benzyl groups. Seven of the ten benzyl groups are directed away from the central atom, whereas three of them are orientated towards the germanium atom. The phenyl ring plane of one of those three benzyl groups is intersected by the assumed vector of the lone pair of electrons at the germanium atom. The phenyl rings of the two other benzyl groups flank the space occupied by the lone pair electrons. Such an arrangement of the ligands explains the un- expected high stability of the compound towards moisture and oxygen. The benzyl groups form a protective shield not only for the reactive positions of the cyclopentadienyl rings, but, in particular, for the central germanium atom.

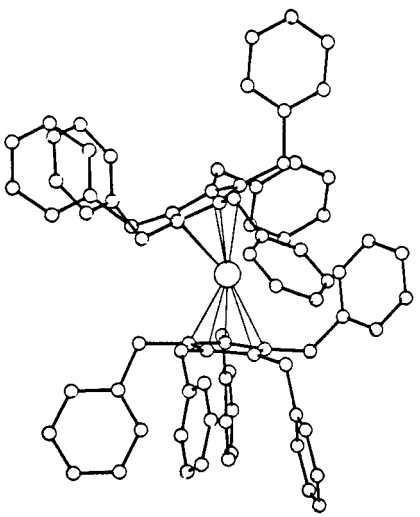


Fig. 2. X-ray structure of decabenzylgermanocene (ref. 6)

The X-ray structure of the homologueous tin compound shows the same situation. Again we have two pentahapto bonded cyclopentadienyl ligands, bent by an angle of now 32.8°, with two benzyl groups from one ligand system and one benzyl group from the opposite ligand system protecting the open site of the metal. Obviously, the increasing mass of the central atom does not effect the structure fundamentally, a fact, which is further proved by the X-ray results of the lead derivative, again demonstrating an isostructural situation.

The distances of the carbon atoms of the phenyl rings, which are orientated towards germanium, tin or lead vary from 3.40 to 5.85 Å. None of the phenyl groups is η^6-orientaded to the metal. That proves that there is no interaction between the π-systems of the aromatic phenyl rings and the lone pair of the elements of group IV in the oxydation state +2.

Asking for the reason for this kind of arrangement in the solid state, electronical and/or only sterical conditions have to be considered.

The first organometallic compounds with pentabenzylcyclopentadienyl ligands, half-sandwich complexes of cobalt, rhodium (ref. 10), manganese and rhenium (ref. 11) of the type $[(PhCH_2)_5C]_5M(CO)_n$, have no lone pairs of electrons. Nevertheless, in all these complexes one of the benzyl groups is turned down to the metal and four are bent away. This fact supports our inten- tion, that sterical reasons will forbid all five benzyl ligands to be on one site of the cyclopentadienyl ring.

The X-ray structural analysis of cyclooctatetraenyl(pentabenzylcyclopentadienyl)lutetium shows a sandwich structure with a small degree of distortion according to an angle of 12.9° between the two ring planes and an angle centroid - lutetium - centroid of 167.7°. And again, one of the five benzyl groups is bent towards the metal atom (ref. 12). In general, organolanthanide compounds of this type contain solvent molecules bonded to the metal, e.g. tetrahydrofurane, what is not possible in this case. One benzyl group of the pentabenzylcyclopentadienyl ligand closes the coordination gap at lutetium, allowing no further coordination of solvent molecules, even when it is crystallized from tetrahydrofurane.

Decabenzylferrocene, an airstable compound (refs. 11, 12, fig. 3), has a parallel and staggered conformation of the cyclopentadienyl rings. All five benzyl groups of each ligand lie on the same side of the cyclopentadienyl ring, directed away from the metal.

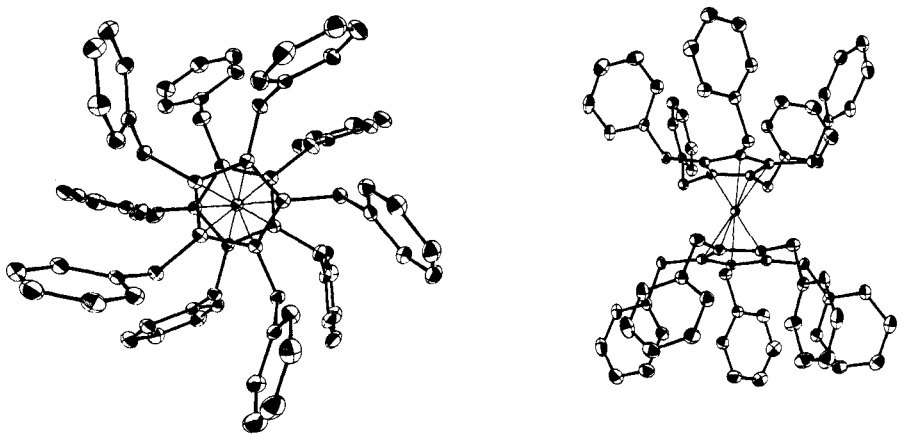


Fig. 3. Crystal structure of Decabenzylferrocene (refs. 11, 12)

However, this orientation can not be attributed to a missing iron - phenyl π-interaction, but follows from the steric situation caused by the opposite spacefully pentabenzylcyclopentadienyl moieties in connection with the small size of the iron atom in-between. The distance between both cyclopentadienyl centroids is only 3.3 Å compared to 4.4 Å in decabenzylgermanocene or 5 Å in decabenzylplumbocene. Molecular model studies clearely demonstrate the inability of a benzyl group to rotate around the cyclopentadienyl - methylene - carbon - bond or to be orientated towards the iron, owing to lack of space. The repulsion and the steric crowding by the methylene groups of the opposite pentabenzylcyclopentadienyl rings are in their turn a consequence of the smallness of the iron center. Thus the observed ordering of the five benzyl groups will be the optimum resolution for the molecule to minimize steric constraints.

Because of the small distance of only 3.3 Å between the cyclopentadienyl ring centroids in ferrocenes, the formation of a decaphenylferrocene is not possible (ref. 13). Five phenyl rings can not be arranged all planar around a cyclopentadienyl system. They have to be canted like in decaphenylstannocene. But that is no more possible with iron as a central atom. As a consequence, the system rearranges to a more stable zwitterionic complex with the iron bound to one pentaphenylcyclopentadienyl ligand and one phenyl of the second pentaphenylcyclopentadienyl group, yielding a $[Ph_5C_5]Fe[C_6H_5\text{-}C_5Ph_4]$.

Besides the germanium, tin and lead derivatives, only one other main group element pentabenzylcyclopentadienyl complex has been investigated by X-ray structural analysis, pentabenzylcyclopentadienyl potassium (ref. 14). It is a monomer in the solid state, containing three tetrahydrofurane molecules, coordinated to the potassium opposite to the cyclopentadienyl ring. The kind of ligand arrangement again clearly demonstrates, that , if there is enough space around the central metal atom, some of the five phenyl groups, in this case two of them, bend down towards the metal, thus relaxing the sterical situation around the cyclopentadienyl ring and resulting in a piano-chair conformation of the complex.

Another interesting metal is gold, which is on the borderline between the main group and the transition metals. Pentabenzylcyclopentadienyl triphenylphosphine gold(I) can be isolated from the reaction of chloro triphenylphosphine gold(I) with pentabenzylcyclopentadienyl lithium. The compound is air stable, but sensitive to light, thus leaving a golden flask after the preparation (ref. 15). Its nmr spectrum, recorded in chloroform in the temperature range of 20° down to -78° shows only one singlet for the methylene protons, thus giving the idea of a cyclopentadienyl system η^5-bonded to gold. However, the X-ray structural analysis (fig. 4) indicates a linearely coordinated gold with the phosphorus on the one side and a η^1-bonded cyclopentadienyl ring on the other. The gold atom is bonded to the sp^3-carbon of the cyclopentadiene system with a distance of 2.12 Å, which is a little bit shorter than the sum of the covalent radii. A close contact also exists between gold and the carbons C2 and C5, what can be interpreted with a slip distortion, a week dynamic interference between a η^1- and an allylic η^3-coordination of the cyclopentadienyl ring to gold. And finally, there is again a relaxed arrangement of the pentabenzylcyclopentadienyl moiety with four phenyl groups directed away from the gold, and one orientated towards the metal.

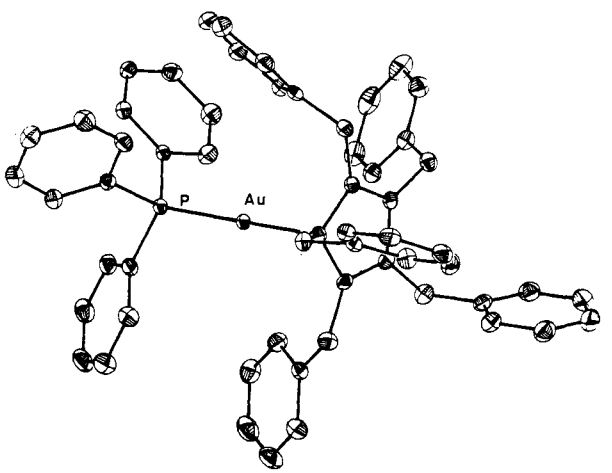


Fig. 4. Crystal structure of $Ph_3P\text{-}Au\text{-}C_5(CH_2Ph)_5$

To increase the knowledge of pentabenzylcyclopentadienyl complexes of main group elements, we investigated the derivatives of group 3 in their lower oxidation state +1. The addition of thallium ethoxide to pentabenzylcyclopentadiene in toluene resulted in the formation of pentabenzylcyclopentadienyl thallium(I), an air- and light-stable compound (ref. 16). According to molecular weight determinations and nmr results (only one doublet for the methylene protons), it is a monomer in benzene solution with a pentahapto bonded cyclopentadienyl system, bearing equal benzyl groups. The splitting of the signal by 10.7 Hz is caused by the thallium atom. However, on crystallization, two reversibly interconvertible modifications are formed. During evaporation of the solvent, tiny yellowish needles precipitate very rapidly, whereas on standing of the solution over night, slowly crystallizing, thermodynamically more stable parallelepipeds are formed. After separate redissolution, both modifi- cations are to obtain from both solutions.

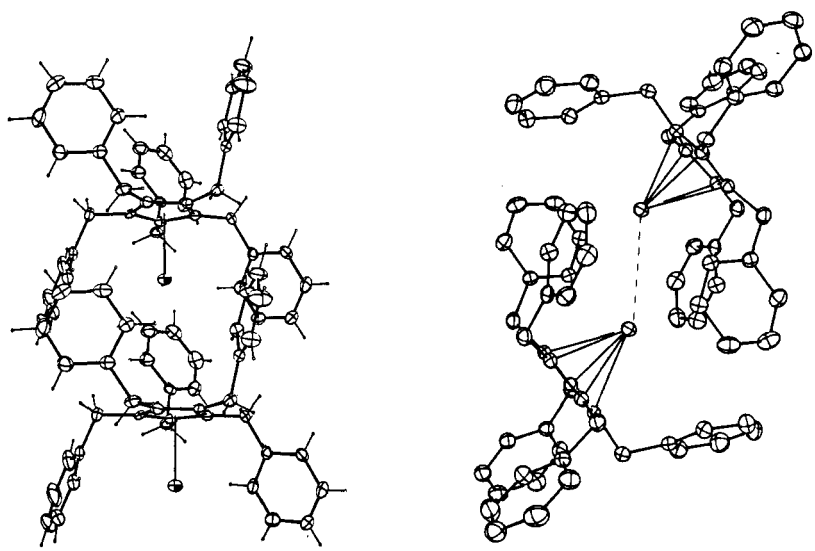
The X-ray crystal structure of the tiny needles (ref. 17, fig. 5a) furnished the expected result, enriched with some new features:

1.) In contrast to all known cyclopentadienylthallium derivatives which form a chain structure, bent at the thallium atom, this is the first compound with a linear arrangement with a thallium - centroid - thallium angle of 176°.

2.) It is only a pseudo-polymer and built up by monomers, held together by only weak connections via the benzyl groups of the pentabenzylcyclopentadienyl ligands. The distance thallium to the centre of its pentahapto bonded cyclopentadienyl ring is 2.49 Å, but the distance to the center of the opposite cyclopentadienyl ring is nearly twice as long, it is 4.87 Å.

3.) There is again an interesting arrangement of the phenyl rings, two of them coming down to the thallium atom, and three of them bent away from it. The result is an arrangement in which five benzyl groups are orientated towards one thallium atom, two of its own pentabenzylcyclopentadienyl ligand and three belonging to the next ligand in the chain. The contacts between the thallium atom and the carbon atoms of the phenyl groups do not differ with respect to own or foreign benzyl ligands. This distances range from 3.4 to 4.1 Å, and correspond with those found for decabenzylstannocene.

$$C_5(CH_2Ph)_5H + TlOC_2H_5 \longrightarrow Tl[C_5(CH_2Ph)_5] + C_2H_5OH \qquad (5)$$



a b

Fig. 5. Crystal structure of $Tl[C_5(CH_2Ph)_5]$: 5a: needle modification, 5b: parallelepiped modification

The second modification, the parallelepipeds have an even more interesting structure(ref. 16, fig. 5b). They are set up from dimers. Like in the first modification, each basic unit contains a thallium pentahapto bonded to the cyclopentadienyl ring with two of the benzyl groups orientated towards the thallium and three of the benzyl groups orientated away from the thallium. But now, these units are arranged in such a manner, that two thallium atoms face each other. The result is a dimer with a thallium - thallium separation of 3.6 Å, certainly too large for a conventional bond. The distance of the thallium to the centroid of the cyclopentadienyl ring is 2.49 Å, exactly the same as the closest contact in the linear polymer. The dimer will be kept together by those six benzyl groups, enveloppping the two thallium atoms.

Janiak and Hoffmann deduce from the results of molecular orbital calculations a real thallium - thallium bond for the dimeric complex (ref. 18). They analyzed the simplified model H-Tl-Tl-H and focused on the significant role of the angle ligand - Thallium - Thallium. The surprising result was, that the overlap population between the Thallium atoms increases dramatically upon bending, and comes to a substantial maximum at a H - Tl - Tl angle of about 120°, followed by a decline going towards the bridging geometry. For the more realistic ligand C_5H_5, the maximum Tl - Tl - overlap population is only a little bit less at a bonding angle of 131°, just the angle which is found in the dimeric pentabenzylcyclopentadienyl thallium.

The analogueous indium(I) compound, pentabenzylcyclopentadienyl indium(I) forms only one modification in the solid state, the isostructural, dimeric parallelepipeds (ref. 19). The distance of 3.63 Å between both indium atoms is exactly the same like in the thallium complex. We never could isolate crystals with a pseudo polymeric chain structure. The unit cell of the indium complex contains four basic units. The organic ligand systems fill the inside of the cell, whereas the indium atoms lie on the periphery of the cell, each facing the indium atom of the neighbouring basic unit.

Recent MO calculations of Budzelaar and Boersma (ref. 20) for the dimeric pentabenzylcyclopentadienyl indium revealed that a linear approach of the metal atoms would result in a strong repulsion between the filled lone pair orbitals, whereas in the bent form weak metal - metal bonds exist. They compared these compounds with Lapperts stannylene dimers, containing a strongly trans-bent metal - metal bond (ref. 21).

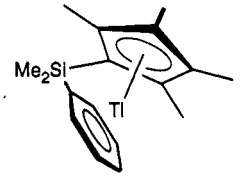
In-In distances of 3.9 Å could be found in hexameric pentamethylcyclopentadienylindium (ref.22). In this compound six indium atoms form an octahedron, envelopped by six C_5Me_5 groups. The vectors from the indium atoms to the centroids of the cyclopentadienyl rings are not directed to the center of the octahedron. Are there real In-In bonds in this compound, or is there an In_6 cluster, a little piece of indium metal, coated and kept together by the surrounding organic material ?

CYCLOPENTADIENYL THALLIUM COMPLEXES WITH OTHER BULKY CYCLOPENTADIENYL LIGANDS

Dimethyl(phenyl)silyl-tetramethylcyclopentadiene results from the reaction of dimethyl(phenyl)chlorosilane with tetramethylcyclopentadienyl lithium. It reacts with thalliumethoxide to give dimethyl(phenyl)silyl-tetramethylcyclopentadienylthallium(I). Dimethyl(benzyl)silyl-tetramethylcyclopentadienylthallium(I), which has the phenyl group separeted from the cyclopentadienyl ligand by the silicon atom and a methylene bridge, is made similarly, starting with dimethyl(benzyl)chlorosilane (ref. 23).

$$Me_2(C_6H_5)SiCl + LiC_5Me_4H \longrightarrow Me_2(C_6H_5)SiC_5Me_4H + LiCl \quad (6)$$

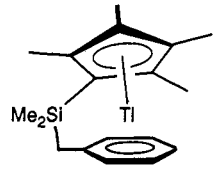
$$Me_2(C_6H_5)SiC_5Me_4H + TlOC_2H_5 \longrightarrow$$



$$+ C_2H_5OH \quad (7)$$

$$Me_2(C_6H_5CH_2)SiCl + LiC_5Me_4H \longrightarrow Me_2(C_6H_5CH_2)SiC_5Me_4H + LiCl \quad (8)$$

$$Me_2(C_6H_5CH_2)SiC_5Me_4H + TlOC_2H_5 \longrightarrow$$



$$+ C_2H_5OH \quad (9)$$

Both compounds are soluble in aromatic hydrocarbons. Molecular weight determinations show them to be monomeric. The ^{13}C-NMR spectrum of the benzyl derivative shows a coupling constant J(TlC) of 20 Hz for all six phenyl carbon atoms, a fact which supports that in solution the phenyl group is coordinated to thallium in a way that all six carbon atoms have the same distance from thallium.

The solid state structures of both compounds show another arrangement. In the basic unit of dimethyl(phenyl)silyl-tetramethylcyclopentadienyl thallium(I) the phenyl group is orientated towards the thallium atom. The phenyl ring has no other possibility of orientation, because the compound is not a monomer, but forms zig-zag-chains of cyclopentadienyl thallium units with angles cyclopentadienyl centroid - thallium - cyclopentadienyl centroid of 142° and thallium - cyclopentadienyl centroid - thallium of 173°. With distances of 2.63 and 2.86 Å, the thallium atoms are not equidistant between the cyclopentadienyl rings. The distances phenyl carbon - thallium vary from 3.9 to 5.7 Å, and are too long, to speak in favour of π-interaction between the phenyl ring and the thallium atom (fig. 6).

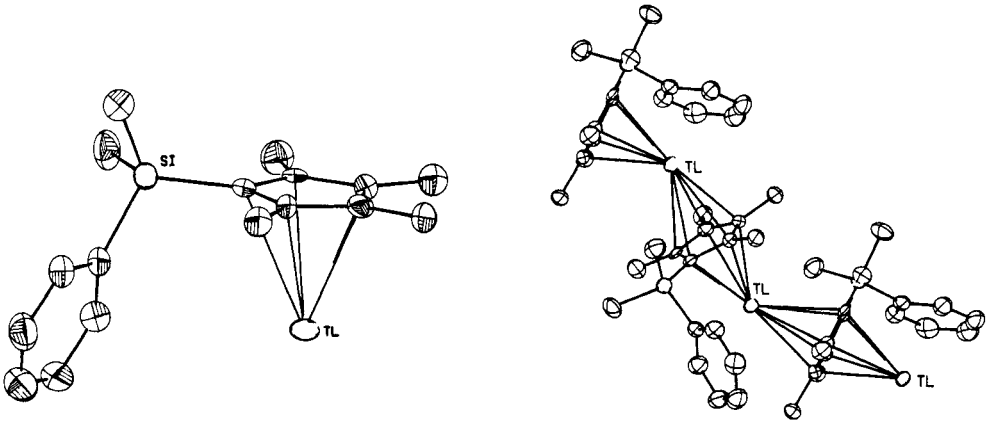


Fig. 6. The crystal structure of $Me_2(C_6H_5)SiC_5Me_4Tl$ as a molecule and in the polymeric chain

In the basic unit of benzyl(dimethyl)silyl-tetramethylcyclopentadienyl thallium(I) the phenyl group is bent away from the thallium atom, although, from steric reasons, the ring plane could face the thallium atom. But the basic unit is only a cut-out of a polymer structure, build up by zig-zag chains with also an 175° angle at the cyclopentadienyl centroid and an 147° angle at the thallium atoms, but now the distances thallium - cyclopentadienyl centroid are equal with 2.74 Å each (fig. 7). There is no contact between the thallium atoms and the phenyl groups. Obviously the polymerisation of the unsaturated monomer via the π-system of the neighbouring cyclopentadienyl system is preferred to an intra- or intermolecular π-interaction with the phenyl groups.

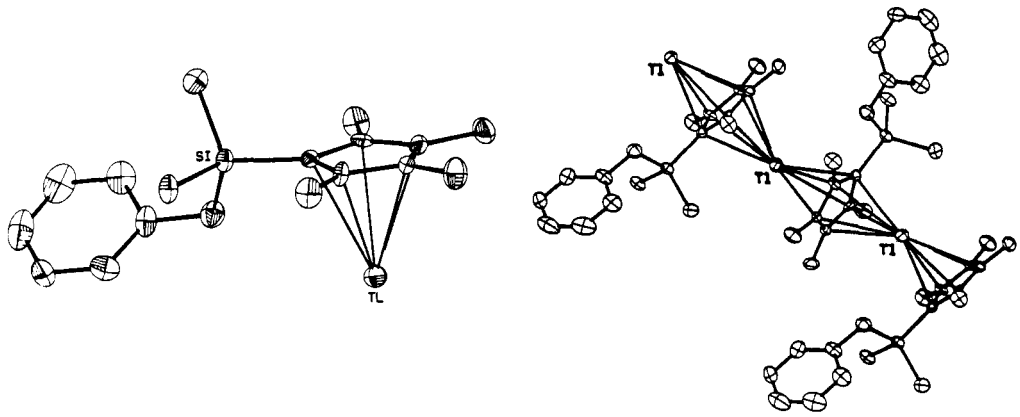


Fig. 7. The crystal structure of $Me_2(C_6H_5CH_2)SiC_5Me_4Tl$ as a molecule and in the polymeric chain

The first really monomeric cyclopentadienyl thallium(I) derivative is diphenylphosphino(tetramethyl)cyclopentadienyl thallium(I), prepared from diphenylphosphino(tetramethyl)cyclopentadiene and thalliumethoxide (ref. 24). The X-ray structure of this compound shows the same arrangement like the dimethylsilyl derivatives mentioned above, but the cell plot shows chains, in which the single molecules are separated by the bulky diphenylphosphine groups, which do not allow an interaction of the molecules, neither via the cyclopentadienyl π-system of the next monomer, nor by a contact between two thallium atoms (fig. 8).

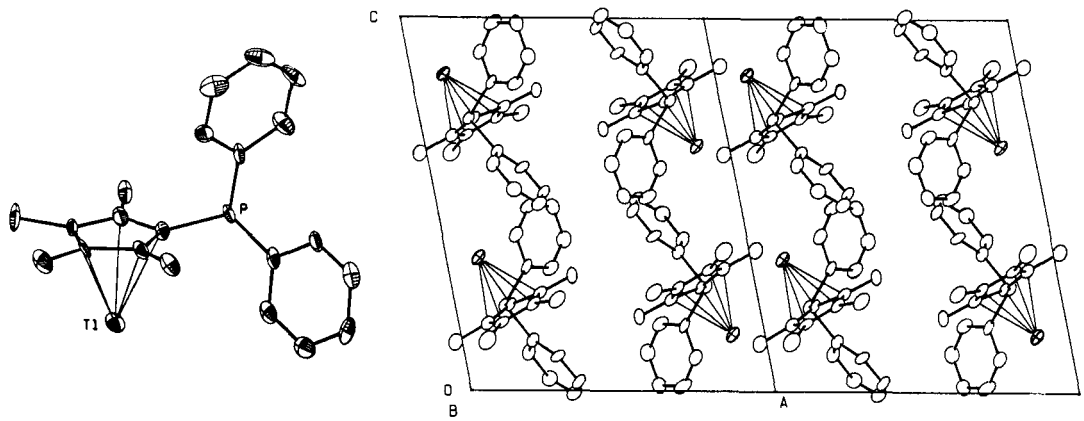


Fig. 8. The crystal structure of $(C_6H_5)_2PC_5Me_4Tl$

The shortest thallium - thallium distance in this arrangement is 5.77 Å, the shortest thallium - phosphorus distance is 3.62 Å, the last being also an intermolecular distance. Provided that an additional coordination should be responsible for that structure, it could be this coordination of phosphorus to thallium.

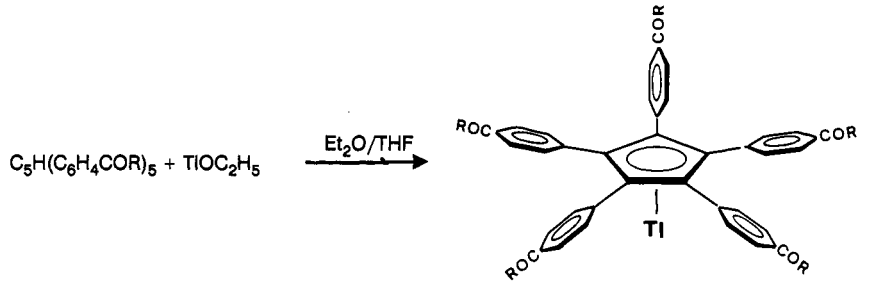
As result of all these structure investigations one has to come to the conviction that neither a coordination by an electron pair - empty orbital interaction nor an interaction between the π-systems and the metal, nor a metal - metal contact causes the respective molecular arrangements. The achievement of an optimum crystal packing will be the driving force.

DISCOTIC METALLOCENES

If crystal packing effects caused by the bulkyness of very voluminous ligands are responsible for the molecular arrangement of the organometallic compounds described above, the development of discotic metallocenes should be possible, which may show an anisotropic, liquid crystalline behaviour.

Pentaphenylcyclopentadiene reacts with acyl chlorides, RCOCl, in dichloroethane and in the presence of aluminum chloride with acylation of all five phenyl rings only in the para-position. The reaction products could be isolated in yields between 60 and 85% as solids for R = methyl and propyl, and as viscous oils in the case of long-chain acyl chlorides. The products are pure after several steps of column chromatography using hexane/ether for eluation. They react with thallium ethoxide in tetrahydrofurane at room temperature within 24 hours to form the corresponding thallium(I) complexes in yields up to 90 %, which are solids at room temperature. They decompose between 160°C (C7-chain) and 250°C (C3 chain), but do not melt before decomposition.

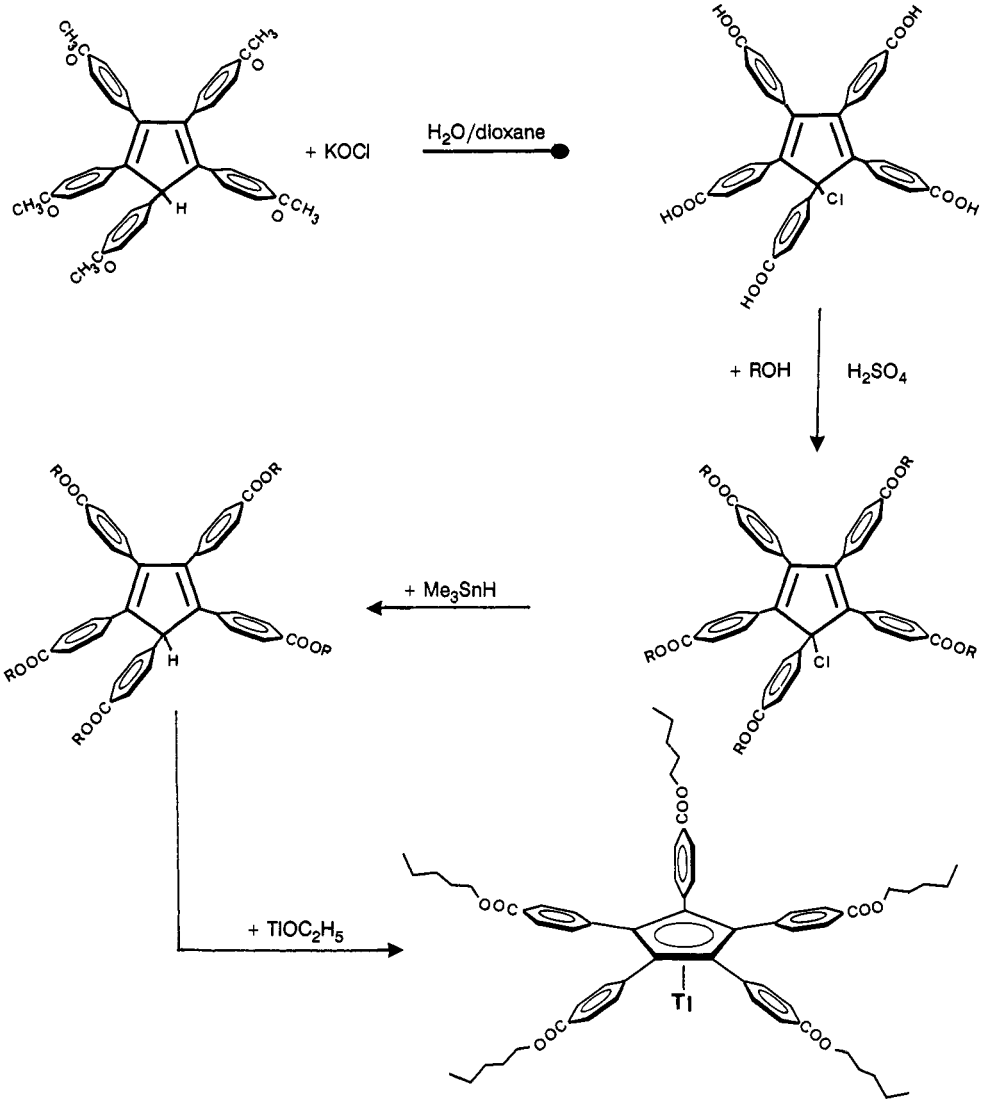
$$C_5H(C_6H_5)_5 + 5\,RCOCl \xrightarrow[ClCH_2CH_2Cl]{AlCl_3} C_5H(C_6H_4COR)_5 + 5\,HCl \qquad (10)$$



(11)

R = CH_3, C_3H_7, C_5H_{11}, C_7H_{15}

The first discotic cyclopentadienyl derivative was prepared starting from [(1,3-cyclopentadiene-1,2,3,4,5-pentayl)pentakis-(4,1-phenylene)]pentakis(1-ethanone), which reacts with potassium hypochloride in water/dioxane at 0°C with oxidation of the acetyl groups and substitution of the hydrogen by chlorine, thus yielding (5-chloro-1,3-cyclopentadiene-1,2,3,4,5-pentayl)-pentakis(benzoic acid). In its turn, this acid reacts with ethanol or pentanol in diluted sulfuric acid to give the appropriate penta ester which can be transferred into the chlorine free cyclopentadiene derivative using trimethyltin hydride. Both products could be isolated in a 90 % yield. The ethyl derivative is a solid, melting at 160°C, the amyl derivative is a viscous oil, which did not solidify. Both cyclopentadienes react with thallium ethoxide to give solid thallium(I) complexes. They melt without decomposition, the ethyl derivative at 250°C, the amyl derivative at 180°C. The amyl derivative is a real mesogene, forming a viscous oily melt, which resolidifies at 176°C and shows a phase transition at 164°C.



(12)

The temperature region of this phase transition is too high to investigate the liquid crystalline behaviour more intensively. To come down till to the region of room temperature, the preparation of derivatives of this type with longer alkyl chains or with other para substituents at the pentaphenylcyclopentadienyl system is in progress (ref. 25).

CONCLUSIONS

Pentaphenylcyclopentadiene and Pentabenzylcyclopentadiene are very interesting ligands in organometallic chemistry. The bulkyness of the pentabenzylcyclopentadienyl anion is responsible for a kind of packing of the molecules in the solid state which in some cases is inconsistant with the general rules of chemical bonding. Decaphenylstannocene for instants, has coplanar cyclopentadienyl rings, thus leaving no room for the lone pair of electrons, but which is also not delocalized over the organic system. Decabenzylmetallocenes of germanium, tin and lead posess the respected bent metallocene structure with space for the electron pair, but the phenyl groups of the ligand show an unexpected arrangement. Pentabenzylcyclopentadienylindium(I) and -thallium(I) have solid state structures, which demonstrate, that crystal packing forces can overrule the principles of electron bonding. The molecules are connected by a "new type of bonding" best nameed as weak ligand - ligand interactions, which envelop the heavy elements in a type of skin made up from the organic ligands. The knowledge about such weak forces and especially about the related second effects like liquid crystalline properties will cause in the near future the synthesis of compounds, which may be important not only for scientists, but also for industrial use.

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