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**Review**

# Structural and chemical aspects of electron deficient pentamethylcyclopentadienyltitanium halides, alkyls, and oxides

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## Introduction

In response to an invitation from the editor to commemorate the 25th anniversary of the Journal of Organometallic Chemistry, we have from our work of the past ten years on the organometallic chemistry of the early transition metals selected for review the chemistry of monopentamethylcyclopentadienyltitanium compounds.

We were interested in electron deficient organotitanium complexes as potential Ziegler–Natta catalysts likely to show particularly interesting structural features and easily accessible low valent oxidation states and so we chose pentamethylcyclopentadienyltitanium trichloride as the starting product for our studies.

## I. Pentamethylcyclopentadienyltitanium trihalides

Although several preparative methods were available in the literature [1,2] none of them seemed to us entirely satisfactory for large scale synthesis, so we had to devise a new one-step method to obtain the pure product in high yield. The route we used was based on the reaction of eq. 1, and gave us almost a quantitative yield.

$$Cp^{\star}SiMe_3 + TiCl_4 \rightarrow \underset{(1)}{Cp^{\star}TiCl_3} + ClSiMe_3 \qquad (1)$$

The synthesis of $Cp^{\star}SiMe_3$ is straightforward, and the procedure is extendable to other titanium halides as well as to the other group 4 metal halides [3].

## II. Pentamethylcyclopentadienyltitanium alkyls and halo-alkyls

Complex **1** can be readily alkylated by use of Grignard or organolithium compounds and careful control of the molar proportion of reagents permits isolation of partially or fully alkylated titanium derivatives. In this way we have prepared a series of di- and tri-alkyls [4] (Scheme 1), and the procedure seems to be extendable to other combinations of halogen and alkyls.

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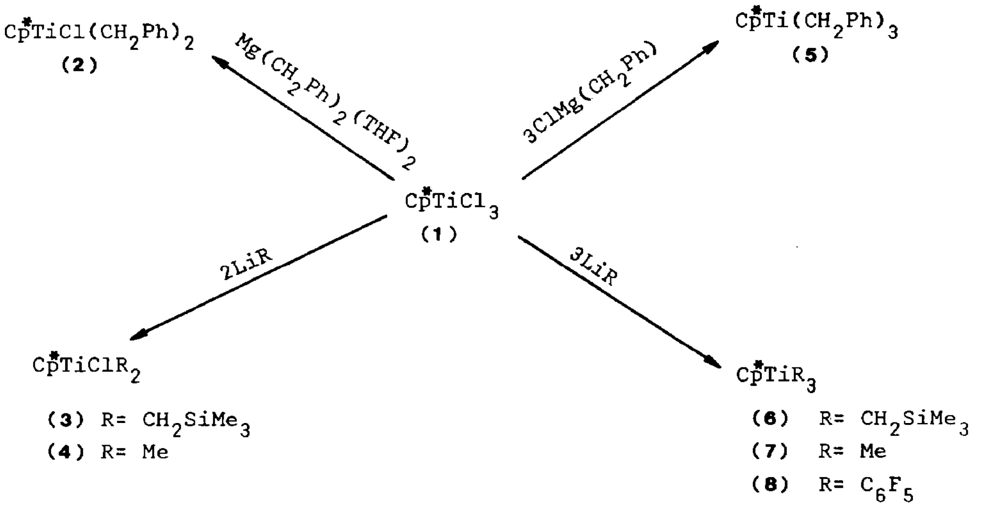


Scheme 1

Except for the pentafluorophenyl compound **8**, the pentamethylcyclopentadienyltitanium di- and tri-alkyls are very thermally stable substances, and differ markedly in this respect from the analogous $C_5H_5$(cp) derivatives. Thus, for instance, $CpTiMe_3$, is reported as an unstable compound that decomposes at 20 ° C [5] whereas $Cp^*TiMe_3$ (**7**) melts at 75–76 ° C without decomposition, and its solution in toluene can even be refluxed for 24 h without noticeable change in the $^1H$ NMR spectrum.

We wondered why these compounds, formally 12 electron species, were so stable. The structure of one of them, **5**, is significant at this respect (Fig. 1); in it one of the benzyl groups is positioned in such a way that its methylene hydrogens lie in the cavity created by the legs of the three-legged piano stool structure, where empty

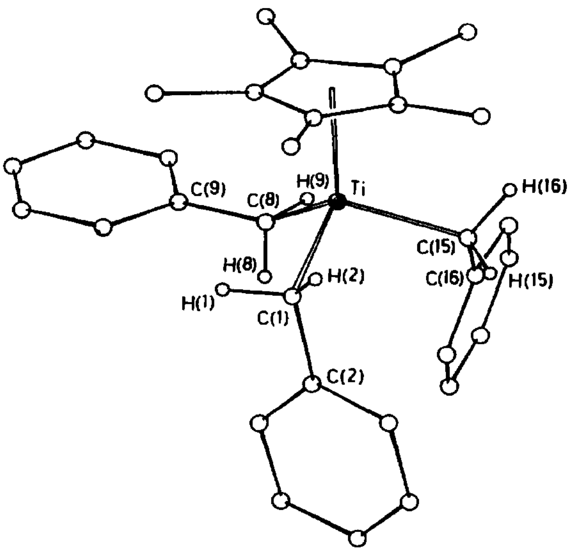


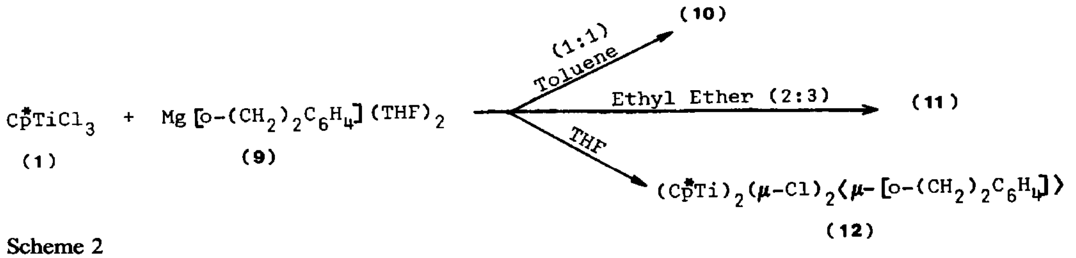
Fig. 1. View of the structure of **5**.

metal orbitals are available [6]. The angles Ti–$C_\alpha$–H (93.6(7) and 96.9(7)°) are much lower than the expected tetrahedral values, indicating that there is an agostic [7] $CH_2$...Ti interaction, by means of which the metallic atom alleviates its electronic deficiency. This interaction results in important distortions in the benzylic skeleton as the phenyl ring is forced to point "upwards", being directed towards the Cp* ring and being almost parallel to it (dihedral angle 7.0(4)°). As a consequence the angle Ti–$C_\alpha$–$C_\beta$ must open and have an unusually high value (139.9(7)°) [8].

The dialkyls **2** and **3** have diastereotopic methylene protons giving rise to two AB doublets in the $^1H$ NMR spectra ($^2J$(H–H) 10.5–11 Hz). Moreover the $^1J$(C–H) coupling constants for the methylene carbons have the same value for **2** (126 Hz), but for **3** they are different: $^1J$(C–H(a)) 105 Hz, $^1J$(C–H(b)) 113 Hz. These NMR spectra remain unchanged up to 80–85°C, at which the compounds start to decompose. There seem to be high barriers to rotation around these Ti–$CH_2$ bonds in these dialkyls.

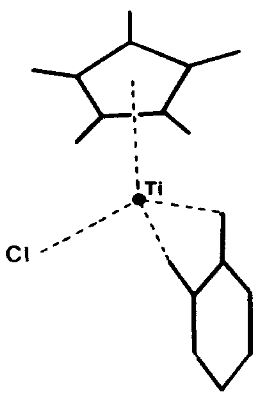
## III. Pentamethylcyclopentadienyltitanium *o*-xylidene complexes

Metallacycles can also be readily prepared from **1** by using the magnesium "*ortho*-xylenediyl" Mg[$o$-$(CH_2)_2C_6H_4$](THF)$_2$ (**9**) described by Lappert et al. [9] as the alkylating agent. The titanacyclopentenes **10** and **11** are obtained adjusting the molar ratio of **1** to **9** to 1/1 or 2/3, respectively.



Scheme 2

The structure of **11** has been determined by X-ray diffraction methods [4] and consists of two Cp*Ti[$o$-$(CH_2)_2C_6H_4$] titanacyclopentene systems bridged by a



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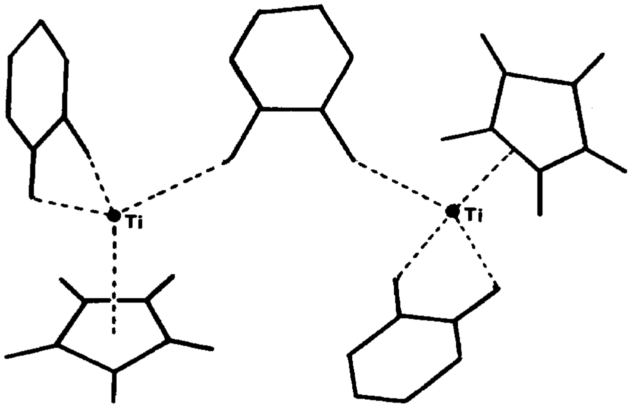


(11)

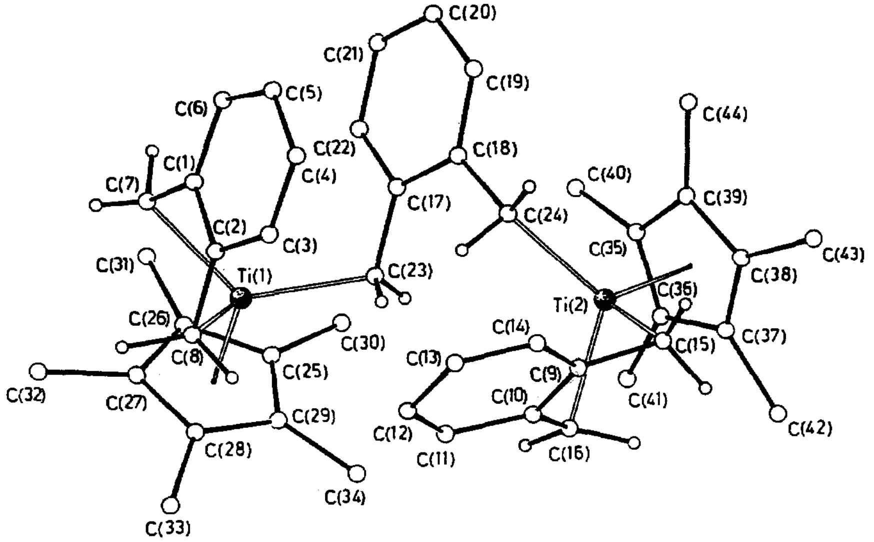


Fig. 2. View of the structure of **11**.

third *o*-xylidene group (Fig. 2). The most remarkable aspect of the structure is found in both titanacyclic systems: the *o*-xylidene groups are bent in such a way that the rings are partially located within the cavity created by the three legs of the three-legged piano stool structures (Fig. 3) so that the electron deficient metal centres can interact with the aromatic systems. The distances Ti–$C_\beta$ (2.45(1) and 2.47(1) Å) are even much shorter than the two "short" Ti–$C_\beta$ distances found in $Ti(CH_2Ph)_4$ (2.61 and 2.81 Å), in which a "benzallyl" type distortion was proposed [11]. This inward bending of the *o*-xylidene group in turn causes the Ti–$C_\alpha$–$C_\beta$ angles to adopt abnormally low values (between 84.6(8) and 85.0(8)°). This distortion is also observed in the $^{13}C$ NMR spectrum, which shows a large $^1J(C–H)$ coupling constant (140 Hz). Almost the same value (144 Hz) is found for **10** and these data suggest that the same type of interaction between the Ti atom and the

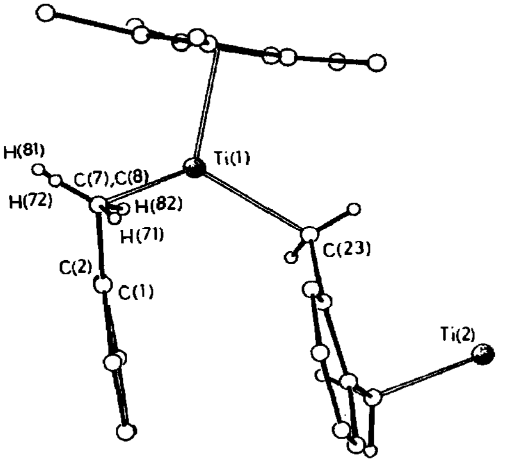


Fig. 3. Projection of a part of the structure of **11** along the line through C(7) and C(8).

*o*-xylidene ring system is present in this compound. The structural behaviour of these electron deficient metallacycles is markedly different from that observed for the 16 electron analogues, such as $Cp_2Ti[o\text{-}(CH_2)_2C_6H_4]$, in which Ti–$C_\beta$ distances are ca. 0.36 Å longer and Ti–$C_\alpha$–$C_\beta$ angles ca. 17° larger than in **11** have been reported [10], and there are no metal–ligand interactions.

This type of metal–ring interaction has been encountered precisely in some electron deficient $d^0$ early transition metal benzyl complexes, and has been confirmed (X-ray) for $M(CH_2Ph)_4$ (M = Ti, Zr, Hf) [11–13], $2,6\text{-}Bu^t_2C_6H_3OZr(CH_2Ph)_3$ [14], $[Cp_2Zr(NCMe)(CH_2Ph)]^+$ [15] and $Cp^*Th(CH_2Ph)_3$ [16]. A similar situation could be expected for **5** instead of the unexpected agostic interaction observed. We do not know for certain what are the reasons for the different ways by which the titanium atom alleviates its electron deficiency in **5** and **11**, namely, Ti...H–C and Ti...C–C interactions, but we suspect that steric as well as electronic effects must be considered.

The reaction between **1** and **9** in an equimolar ratio deserves further comment because it is very solvent-dependent (Scheme 2). When toluene is used, **10** is obtained, whereas if the reaction is carried out in THF overnight, **12** is isolated; when THF and short reaction times are used, a mixture of **1**, **10** and **12** is obtained [17]. The formation of **12** might be thought to take place through **10** by an "*o*-xylidene" elimination process, such as that described for some cobalt complexes [18]. However, after isolation, pure **10** is stable for several days in solution in THF-$d_8$ or benzene-$d_6$, so that additional reaction paths must apparently be involved.

The structure of **12** is unique (Fig. 4); it shows an *o*-xylidene group that has lost its aromatic character and planarity (dihedral angle between the planes C(3)C(4)C(5)C(6) and C(1)C(2)C(3)C(6): 155.0(1.4)°; C(3)–C(4) 1.36(4) Å and C(5)–C(6) 1.31(4) Å, C–C double bond distances; C(4)–C(5) 1.53(5) Å, C–C single bond distance) and is disposed in an asymmetric bridging fashion over a $(Cp^*Ti)_2(\mu\text{-}Cl)_2$ framework. The Ti(1) atom is bonded to the endocyclic *o*-xylidene diene system in a $\eta^4$ mode (mean Ti–C distance 2.36 Å) but the distances between Ti(2) and C(1) and C(2) are notably longer than those to C(7) and C(8) (2.26(3) and 2.24(3) Å); these two latter distances are intermediate between those for a Ti–C($sp^3$) bond (Table 1) and a Ti–C($sp^2$) bond to Ti(1). The structure is thus best described

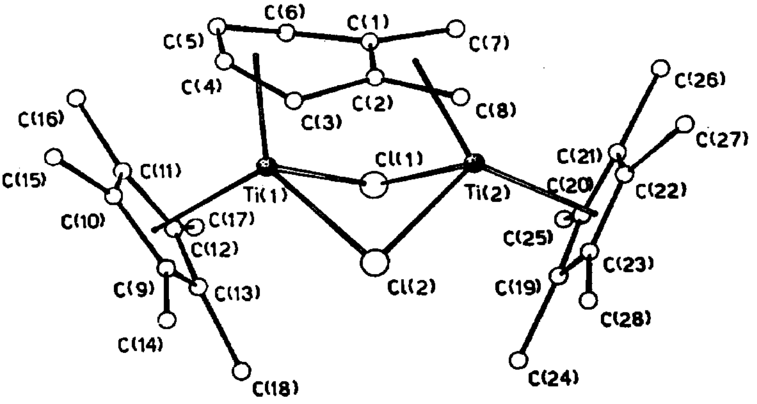


Fig. 4. View of the structure of **12**.

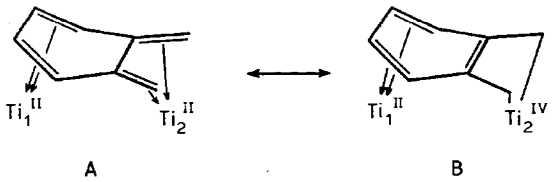
Table 1

Ti–$C_\sigma$ bond distances in some monopentamethylcyclopentadienyltitanium alkyls

| Compound | $d$(Ti–C) (Å) [a] |
|---|---|
| $Cp^{\star}Ti(CH_2Ph)_3$ (**5**) | 2.08(1), 2.14(1), 2.16(1) |
| $\mu$-[$o$-$(CH_2)_2C_6H_4$]{$Cp^{\star}Ti[o$-$(CH_2)_2C_6H_4]$}$_2$ (**11**) | 2.11(1), 2.12(1), 2.13(1) [b] |
| [$Cp^{\star}TiMe(\mu$-$O)]_3$ (**23**) | 2.08(1) [c], 2.10(9) |

[a] Esd in parentheses. [b] Four distances have this value. [c] Two distances have this value.

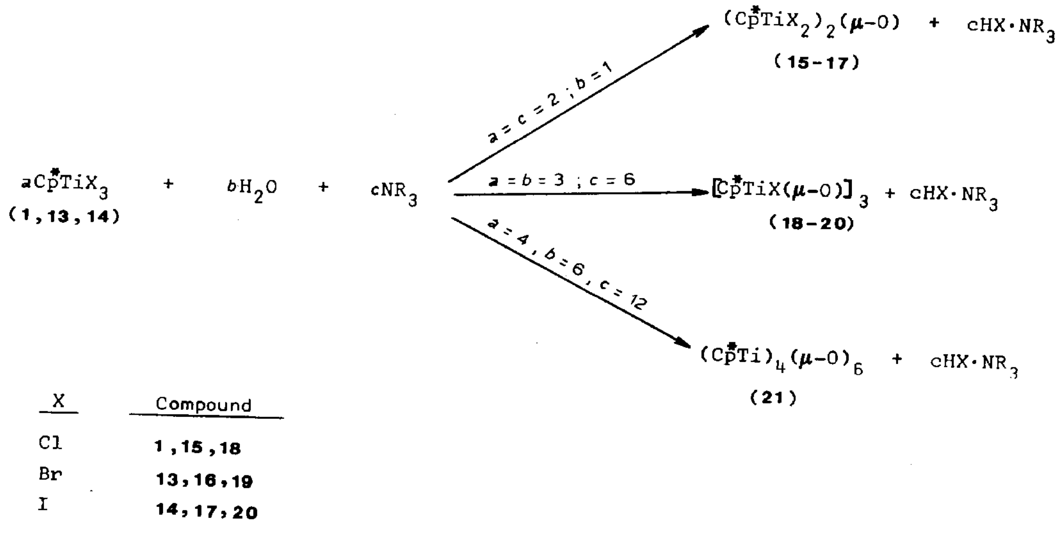
as a resonance hybrid of the two forms depicted in Scheme 3, and the $^1H$ and $^{13}C$ NMR data confirm nicely this description.



Scheme 3

## IV. Pentamethylcyclopentadienyltitanium(IV) oxides

Pentamethylcyclopentadienyltitanium trihalides are relatively stable substances that can be exposed to the air for short periods without noticeable decomposition due to hydrolysis; hydrolysis does take place in solution, however, and is accelerated by the presence of a base such as $NEt_3$ or $NHEt_2$. In this way, under the appropriate reaction conditions dimeric, trimeric and tetrameric species can be obtained (Scheme 4) [19]. The reactions occur increasingly readily in the sequence Cl > Br > I, whereas the Ti–X bond energies and covalent character follow the



| X | Compound |
|---|---|
| Cl | 1, 15, 18 |
| Br | 13, 16, 19 |
| I | 14, 17, 20 |

Scheme 4

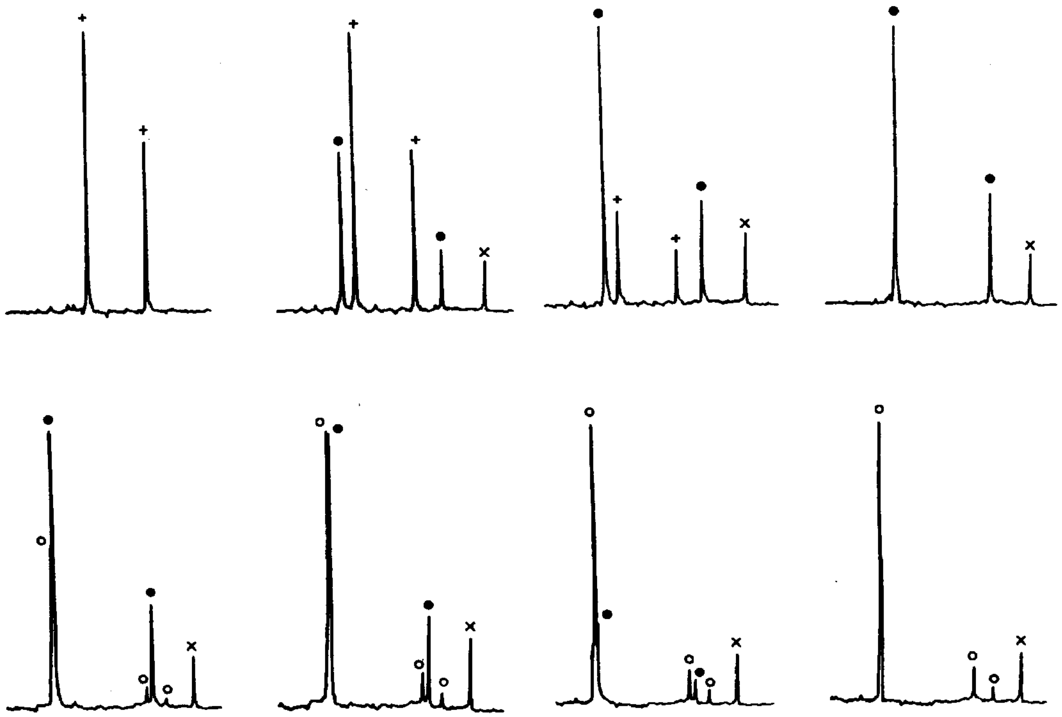


Fig. 5. $^1$H-NMR ($C_6D_6$) sequential study corresponding to Scheme 5 $^+$ 7; $^\bullet$ 22; $^\circ$ 23; $^\times CH_4$.

opposite trend. The observed order is probably determined by steric factors; that is, the initial step, which must be the attack by the $H_2O$ molecule on the relatively small Ti atom, is hindered by the bulkier halogen atoms.

A similar hydrolysis process, but in this case easily monitored by $^1$H NMR spectroscopy (Fig. 5), is observed in the case of 7 (Scheme 5). This sequence, in

$$\underset{(7)}{Cp^*TiMe_3} \xrightarrow[-CH_4]{H_2O} \underset{(22)}{(Cp^*TiMe_2)_2(\mu\text{-}O)} \xrightarrow[-CH_4]{H_2O} \underset{(23)}{[Cp^*TiMe(\mu\text{-}O)]_3}$$

Scheme 5

which no other intermediate products are detected, constrasts with that reported for $CpTiCl_3$ [20] and $MeCpTiCl_3$ [2] (Scheme 6) in which the cyclic tetramers **26**

$$\underset{(24)}{CpTiCl_3} \xrightarrow{H_2O} \underset{(25)}{(CpTiCl_2)_2(\mu\text{-}O)} \xrightarrow{H_2O} \underset{(26)}{(CpTiCl)_4(\mu\text{-}O)_4}$$

Scheme 6

are suggested to be formed by a pairwise combination of dimers **25**. In the case of our pentamethylcyclopentadienyl analogues **23** is clearly formed from **22**, and presumably **18–20** from **15–17**, and these conversions must involve Ti–O bond breaking and remaking, so that more complex mechanism must be involved. The structure of **23** (Fig. 6) can be viewed as based on an almost equilateral triangle of Ti atoms whose hypothetical edges are bridged by three oxygens to form a nearly planar $Ti_3O_3$ ring, in which the O(1) atom nevertheless is 0.332(6) Å below (Fig. 7)

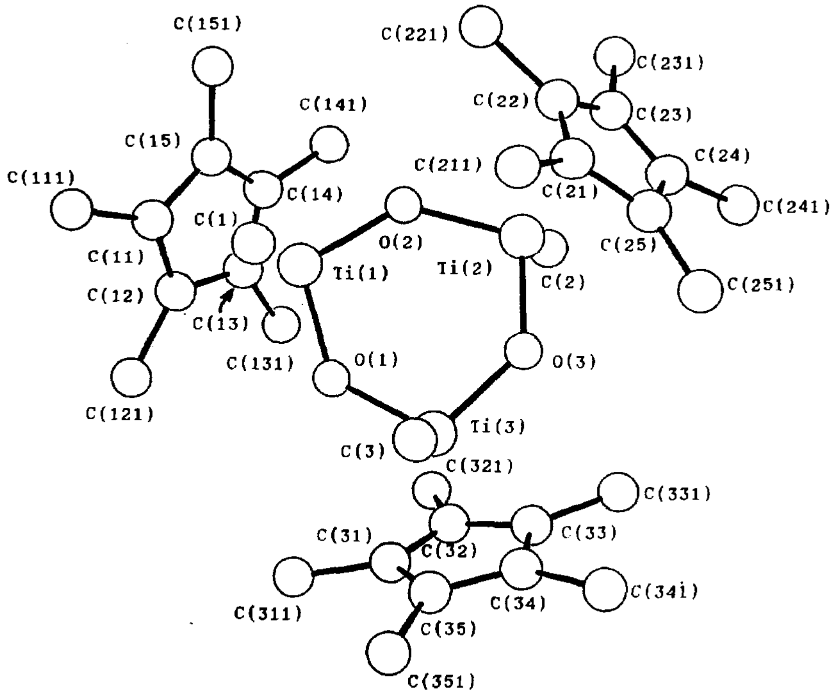


Fig. 6. View of the structure of 23.

[22]. As a consequence of the six-membered ring structure the Ti–O–Ti angles are rather acute, ranging from 131.6(3) to 133.5(3)°. Two Cp* rings and one titanium-bonded methyl group are situated below the $Ti_3O_3$ pseudoplane, while the other two methyls and Cp* completing the pseudotetrahedral Ti environement lie above that plane.

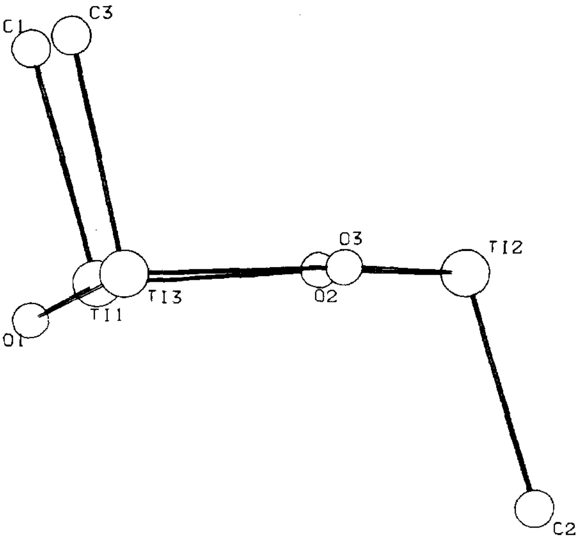


Fig. 7. Perspective of the $Ti_3O_3$ core of 23 (Cp* rings omitted for clarity).

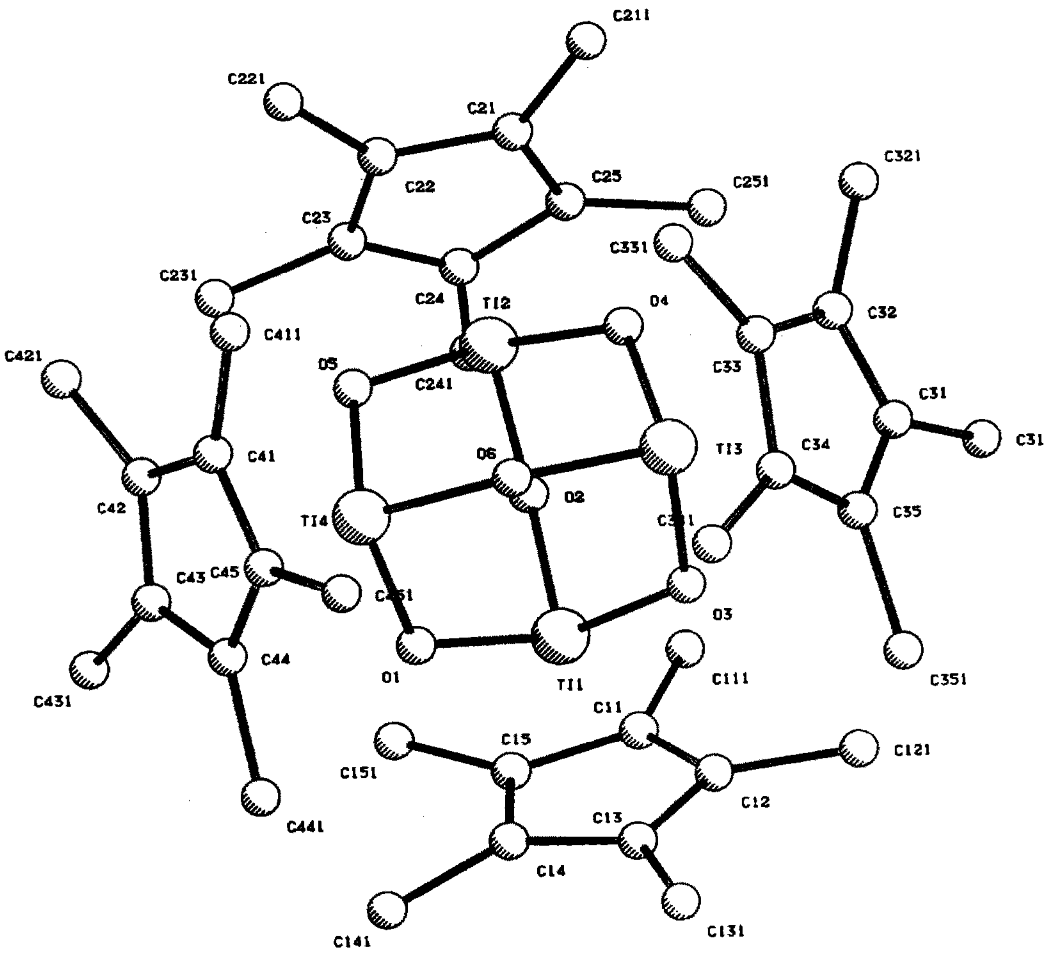


Fig. 8. View of the structure of **21**.

Hydrolysis of other pentamethylcyclopentadienyl titanium trialkyls does not lead to isolable analogues of **22** or **23**. In the case of **6** for example, **21** can be easily obtained (eq. 2) and no intermediate species are detected by $^1$H NMR.

$$\underset{(\mathbf{6})}{\mathrm{Cp^{*}Ti(CH_3SiMe_3)_3}} + 6\mathrm{H_2O} \rightarrow \underset{(\mathbf{21})}{\mathrm{(Cp^{*}Ti)_4O_6}} + 12\mathrm{SiMe_4} \qquad (2)$$

The structure of **21** [19], which was simultaneously and independently published by Babook, Day and Klemperer [23], is remarkable (Fig. 8): it consists of a nearly perfect tetrahedron array of Ti atoms (Ti...Ti contacts ranging from 3.221(1) to 3.231(1) Å) whose edges are bridged by six oxygen atoms to form an adamantane-like structure (Fig. 9). Viewed in another way, the $\mathrm{Ti_4O_6}$ core is formed from four fused $\mathrm{Ti_3O_3}$ rings, but in contrast to **23** they have a chair conformation with no centre of symmetry because the two angles defined by the three planes (Fig. 10) are unequal; the $\alpha$ angles range from 137.7(1) to 138.1(1)° while the $\beta$ angles have values between 128.4(2) and 129.3(1)°. In accord with this different conformation of the $\mathrm{Ti_3O_3}$ rings in **21** and **23**, the internal angles are more acute in the chair rings than in the planar ring [(mean angles: around Ti, 101.9(1) in **21** and 105.3(2)° in **23**;

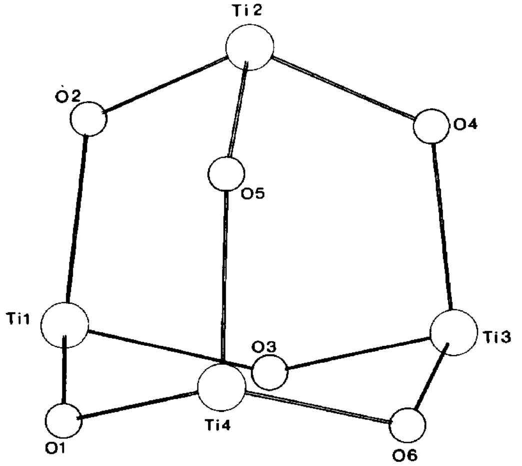


Fig. 9. Drawing of the $Ti_4O_6$ core of **21** (Cp* rings omitted for clarity).

around O, 122.9(2) in **21** and 132.9(3)° in **23**)]. An alternative description of the structure of **21** is one based on three-legged piano stool $Cp^{\star}Ti(\mu\text{-}O)_3$ fragments, sharing O atoms. The four fragments are very similar and rather regular, and the Cp* ring planes are parallel to the planes defined by the three O atoms and also to the planes defined by the other three Ti atoms. The electron impact mass spectrum gives the $Ti_4O_6^+$ ion as one of the ions of high relative abundance, giving an idea of the robustness of the metal-oxide core.

## V. Chemical behaviour of alkyltitanium oxides

In addition to having unusual structural features, these organotitanium oxides also show an unusual and interesting chemistry. The reaction of the dimer **22** with diphenyldiazomethane is evidence for the high acidic character of the metallic centers, and proceeds with successive insertion of $N_2CPh_2$ molecules into Ti–$CH_3$ bonds to give $\eta^2$-hydrazonato(1 − ) ligands, namely the dimers **27** and **28**, whereas the trimer **23** undergoes insertion of only one diazoalkane molecule, probably for steric reasons [24] (Scheme 7).

Carbon monoxide also reacts with the dimer, and the overall result is the transfer of one methyl group from each titanium to the carbonyl C to form $\mu$-$\eta^2$-acetone

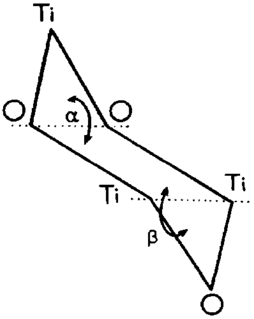
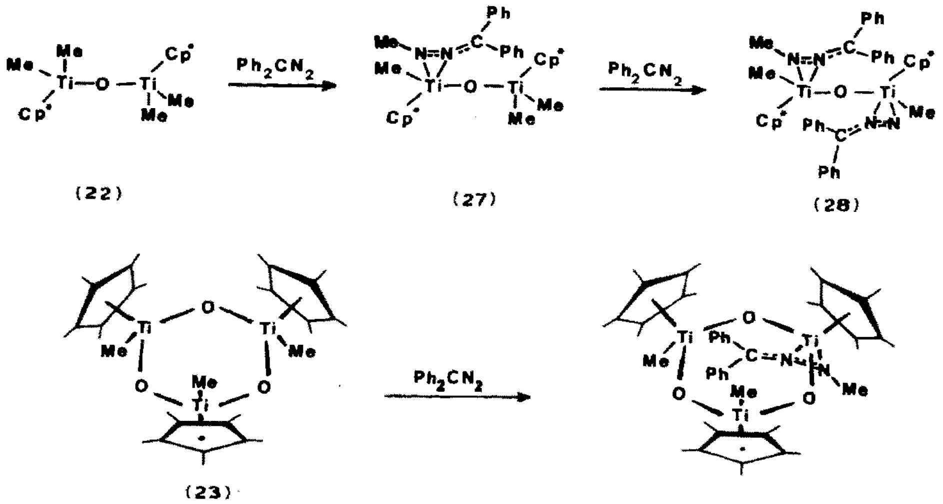
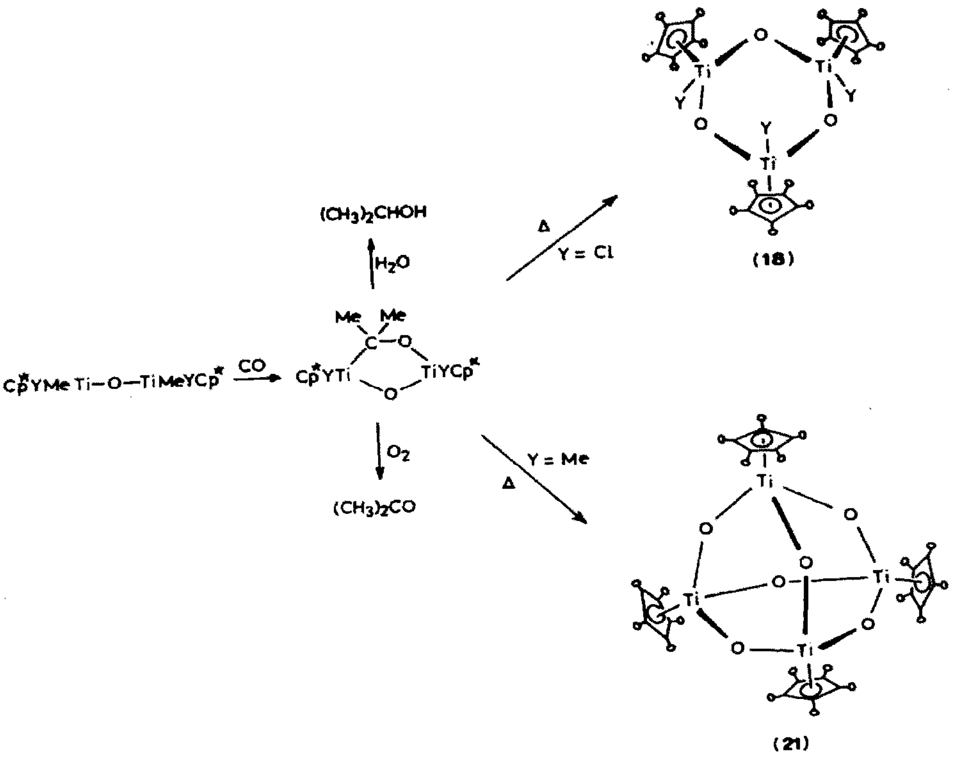


Fig. 10. $Ti_3O_3$ chair ring of **21** showing the $\alpha$ and $\beta$ angles.



Scheme 7



Scheme 8

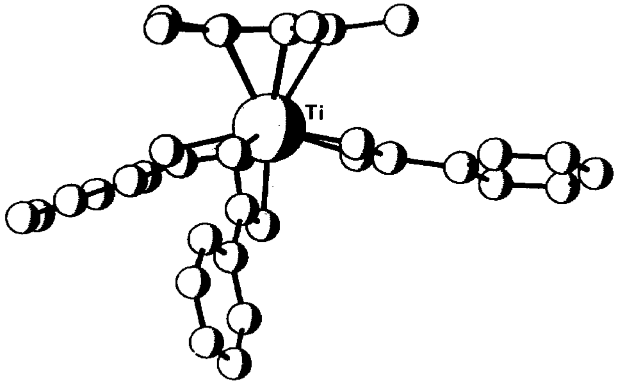


Fig. 11. View of the structure of **29**.

complexes ($\nu$(C–O) 1190 $cm^{-1}$; $\delta(^{13}C)$ 121.2 and 127.6 ppm; $^{1}J$(C–C) 36.3 Hz). This compound liberates $Me_2CO$ upon treatment with oxygen and isopropanol upon hydrolysis. Thermolysis leads to loss of the organic fragments except for the Cp* rings, and rearrangement of the metal-oxide fragments in such a way that **21** or **18** are isolated; the formation of **18** proceeds smoothly and mainly by propene extrusion, in which the central carbon atom is that originally in CO, as demonstrated by isotopic labeling [25] (Scheme 8).

We conclude with the formation of an 18 electron complex in order to demonstrate that the pentamethylcyclopentadienyltitanium(IV) fragment is also stable in the 18 electron configuration when appropriate substituents are present. The tris-benzoate derivative **29** is readily obtained by the reaction shown in eq. 3 (Fig. 11).

$$Cp^{\star}TiMe_3 + 3PhCOOH \rightarrow \underset{\mathbf{(29)}}{Cp^{\star}Ti(OOCPh)_3} + 3\,CH_4 \qquad (3)$$

The structure, depicted in Fig. 11, shows one benzoate group roughly perpendicular to the other two, so that O(3) can interact with the empty $d_{z^2}$ titanium orbital [26]. Alternatively we could speak of a distorted pentagonal bipyramidal environment for titanium. There are several noteworthy differences between this structure and the electron deficient structures mentioned above: the Ti-centroid distance is the longest (Table 2), the centroid Ti–O angles are the smallest (between 100.3(2) and 105.9(2)° compared with the 110–120° usual range), and the Ti–O distances

Table 2

Ti–Cp* centroid distances in some monopentamethylcyclopentadienyltitanium(IV) compounds

| Compound | $d$(Ti–cent.) (Å) [a] |
|---|---|
| $Cp^{\star}Ti(CH_2Ph)_3$ (**5**) | 2.04(1) |
| $\mu$-[$o$-$(CH_2)_2C_6H_4$]{$Cp^{\star}Ti$[$o$-$(CH_2)_2C_6H_4$]}$_2$ (**11**) | 2.06(1) |
| $\mu$-[$o$-$(CH_2)_2C_6H_4$]($\mu$-Cl)$_2$($Cp^{\star}Ti$)$_2$ (**12**) | 2.05(2), 2.07(2) |
| [$Cp^{\star}TiMe(\mu$-O)]$_3$ (**23**) | 2.041(1), 2.059(1) |
| $(Cp^{\star}Ti)_4(\mu\text{-}O)_6$ (**21**) | 2.06(1), 2.07(1) |
| $Cp^{\star}Ti(OOCPh)_3$ (**29**) | 2.103(1) |

[a] Esd values in parentheses.

(between 2.095(7) and 2.206(6) Å) are notably longer than those in **21** (1.816(6) to 1.830(6) Å) and **23** (1.830(3) to 1.841(3) Å), in which O to Ti $\pi$-donation must be involved.

## Acknowledgements

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