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Synthesis and characterisation of (η^5-cyclopentadienyl)(η^5-ring)titanium alkyl (ring = indenyl or $C_5H_4Bu^t$) complexes. Crystal and molecular structure of racemic [Ti(η^5-C_5H_5)(η^5-C_9H_7)(CH_2SiMe_3)Cl]

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New, selective and high-yielding preparations of the mixed-ring complexes [Ti(η^5-C_5H_5)(η^5-C_9H_7)Cl_2] and [Ti(η^5-C_5H_5)(η^5-$C_5H_4Bu^t$)Cl_2] are reported. These have been used to prepare a range of mono- and di-substituted titanium(IV) alkyl and benzenethiolate complexes of the form [Ti(η^5-C_5H_5)(η^5-ring)(CH_2SiMe_3)Cl] and [Ti(η^5-C_5H_5)(η^5-ring)R_2] (ring = indenyl or $C_5H_4Bu^t$; R = Me, CH_2Ph, CH_2SiMe_3 or SPh). While the indenyl ligand in the racemic, chiral-at-metal complex [Ti(η^5-C_5H_5)(η^5-C_9H_7)(CH_2SiMe_3)Cl] is bound in an η^5 fashion, X-ray structural data clearly indicate that there is some 'η^3 ring-slip' character to the bonding. The NMR and nuclear Overhauser effect experiments conducted on [Ti(η^5-C_5H_5)(η^5-$C_5H_4Bu^t$)(CH_2SiMe_3)Cl] demonstrate hindered rotation around the Ti–$C_5H_4Bu^t$ bond and show the geometry to be fixed such that the Bu^t and $SiMe_3$ groups are remote.

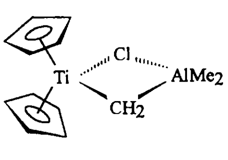
A high level of interest has been maintained in the synthesis of new bent metallocene complexes of the Group 4 metals, because of their great value in a wide range of applications in organic and polymer synthesis (with **A** and **B** striking examples). The Tebbe titanium–methylene complex **A**, identified as a result of investigations into the [Ti(η^5-C_5H_5)$_2$$Cl_2$]–$AlR_3$ ethylene-polymerisation system, shows high and selective reactivity with organic carbonyl compounds, transferring a =CH_2 group and forming terminal alkenes.[1–3] Recent studies have demonstrated that it is also an active alkene-metathesis and ring-opening metathesis polymerisation catalyst.[4,5] While titanocene dichloride-based systems show only moderate activity for alkene polymerisation, they paved the way for the new generation single-component, cationic complexes of Group 4, which are extremely reactive polymerisation catalysts.[6]

The desire to carry out such organic and stereoregular polymer syntheses enantioselectively has necessitated the preparation of bent metallocene complexes of increasing complexity. In this area, *ansa*-metallocenes have proven of value in many asymmetric transformations.[7–11] Compound **B**, which may be prepared enantiomerically pure, has been used both as an asymmetric hydrogenation catalyst and as a stereoregular propylene-polymerisation catalyst.[12–15]

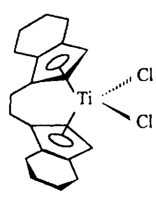
The emphasis of current research in this area lies in the use of chiral ligands to induce the asymmetric reaction desired.[16] A potentially superior approach, however, is to exploit the pseudo-tetrahedral nature of bent metallocene complexes to produce chiral-at-metal reagents; since the reaction of interest usually occurs at the metal, chirality centred here may exert considerably more influence on the stereochemical outcome of the reaction under investigation than ligand-based chirality.[17,18] In this paper we report our preliminary results concerning the synthesis and characterisation of racemic mixed-ring titanocene-based compounds containing chloride, alkyl and benzenethiolate ligands, and describe the solid-state structure of [Ti(η^5-C_5H_5)(η^5-C_9H_7)(CH_2SiMe_3)Cl], the first chiral-at-titanium (alkyl) complex.

Results and Discussion

The use of cyclopentadiene-substituted tin compounds to prepare monocyclopentadienyl transition-metal complexes, first reported by Abel and co-workers,[19] is now an established method for the synthesis of [Ti(η^5-C_5H_5)Cl_3] and related compounds, equation (1).[20–22] We have used the analogous



A



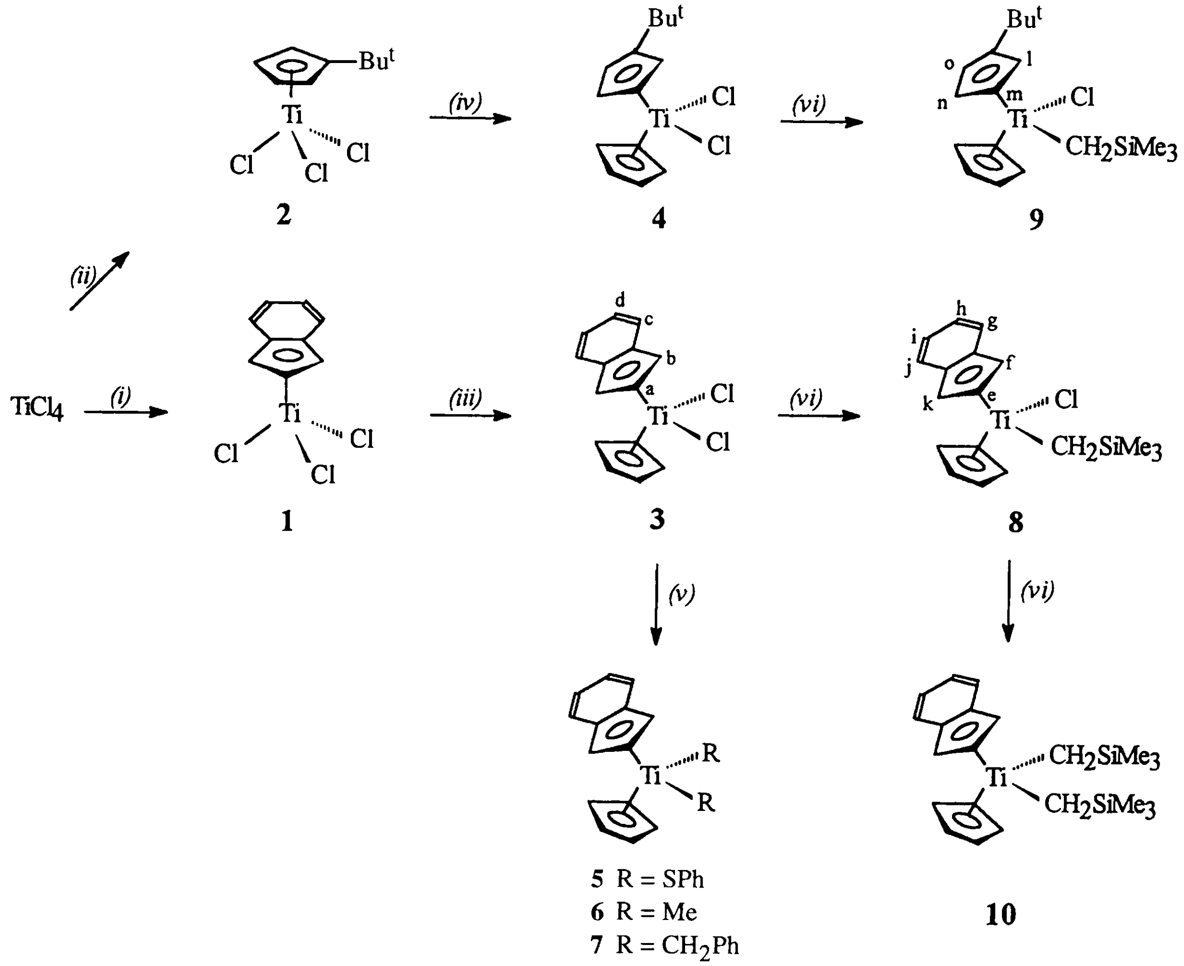
B

$$\mathrm{TiCl_4 + Sn(C_5H_5)Bu_3 \longrightarrow [Ti(\eta^5\text{-}C_5H_5)Cl_3] + SnBu_3Cl} \qquad (1)$$

indene and *tert*-butylcyclopentadiene compounds [Sn(C_9H_7)Bu_3] and [Sn($C_5H_4Bu^t$)Bu_3] to prepare complexes **1** and **2**, (Table 1) Scheme 1.

The solid-state structure of complex **2** has been determined (Fig. 1) and indicates that the molecule adopts a piano-stool conformation, typical of this class of compound.[23–26] Selected bond lengths and angles are given in Table 2. The cyclopentadienyl ring is essentially planar, and very nearly parallel to the Cl(1)–Cl(2)–Cl(3) plane (dihedral plane 2.1°). The *tert*-butyl substituent clearly levers the ring away from the metal centre; the Ti–C(5) bond length of 2.388(5) Å is significantly longer than the other Ti–C bonds, as a result of the steric interactions between the methyl hydrogen and chlorine atoms (closest Cl $\cdots$ H distances 2.89 Å). A similar, though smaller, effect is observed in the structure of the methylcyclopentadienyl analogue, Fig. 2.[26] The structure of [Ti(C_5H_5)Cl_3] has been determined, but with rather lower precision and with some uncertainty as to the correct space group. The Ti–C bond lengths are very similar, given their somewhat large standard deviations.[23]

Reaction of complex **1** or **2** with [Sn(C_5H_5)Bu_3] or LiC_5H_5 respectively, leads to the mixed-ring compounds [Ti(η^5-C_5H_5)(η^5-C_9H_7)Cl_2] **3** and [Ti(η^5-C_5H_5)(η^5-$C_5H_4Bu^t$)Cl_2] **4** in good yield. The mixed cyclopentadienyl–indenyl complex **3** has been prepared previously using lithium indenide; significant quantities of [Ti(C_5H_5)$_2$$Cl_2$] and [Ti($C_9H_7$)$_2$$Cl_2$] were formed as by-products.[3] The use of tin reagents is



Scheme 1 Synthesis of compounds **1**–**10** (*i*) 1 mol equivalent [Sn(C_9H_7)Bu_3], CH_2Cl_2, 0 °C; (*ii*) 1 mol equivalent [Sn($C_5H_4Bu^t$)Bu_3], CH_2Cl_2, 0 °C; (*iii*) 1 mol equivalent [Sn(C_5H_4)Bu_3], CH_2Cl_2, 0 °C; (*iv*) 1 mol equivalent LiC_5H_5, OEt_2, 0 °C; (*v*) 2 mol equivalents LiR (R = SPh) at 0 °C or OEt_2 (R = Me or CH_2Ph) at −40 °C; (*vi*) 1 mol equivalent Me_3SiCH_2MgBr, OEt_2, −40 °C

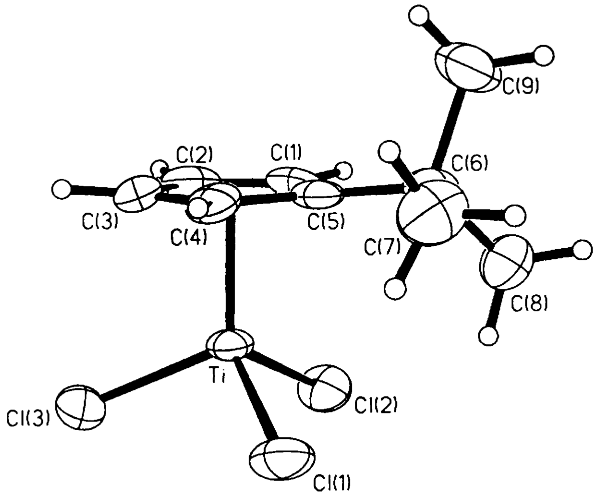


Fig. 1 Molecular structure of compound **2** (50% thermal ellipsoids)

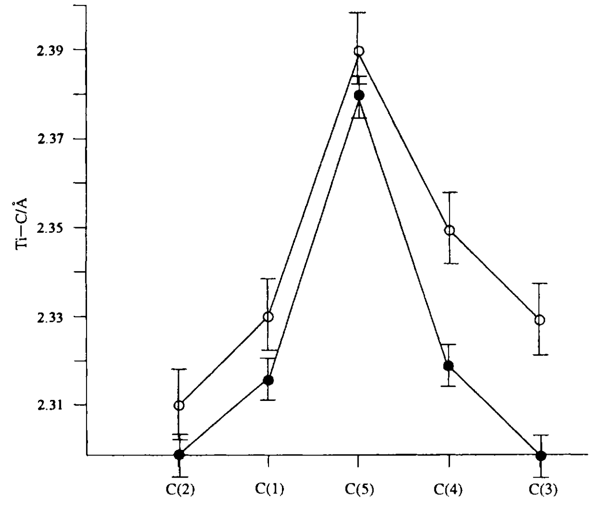


Fig. 2 Variation in Ti–C bond lengths in the monocyclopentadienyltitanium complexes **2** (open circles) and [Ti(η^5-C_5H_4Me)Cl_3] (solid circles). Error bars denote 2.7 estimated standard deviations

superior in this respect; we have no evidence of such ring-exchange reactions.

We have investigated the reactions of complexes **3** and **4** with a range of lithium and magnesium reagents, and shown that nucleophilic displacement of both chloride ligands is possible. Thus reaction of **3** with 2 mol equivalents of lithium benzenethiolate leads to the formation of red-purple crystals of [Ti(η^5-C_5H_5)(η^5-C_9H_7)$(SPh)_2$] **5** in high yield. The related bis(cyclopentadienyl) analogue [Ti(η^5-C_5H_5)$_2$$(SPh)_2$] has been reported previously.[27] In a similar fashion, the new methyl and benzyl complexes [Ti(η^5-C_5H_5)(η^5-C_9H_7)R_2] (R = Me **6** or CH_2Ph **7**) may be prepared by reaction of **3** with 2 mol equivalents of the appropriate Grignard reagent, as pale yellow and dark brown powders respectively. The products of these reactions are solvent dependent; intractable solids and oils are obtained from reactions carried out in thf. Diethyl ether is the solvent of choice. The low symmetry of complex **7** renders the benzylic CH_2 groups diastereotopic. Accordingly, two doublets are present in the ^1H NMR spectrum at δ 1.55 and 1.35

Table 1 Analytical and spectroscopic data

Complex	Analysis[a] (%)	^{1}H NMR[b]	^{13}C NMR
1	C, 41.95 (42.40); H, 3.00 (3.20)	7.81 (2 H, m, C_6H_4) 7.55 (2 H, m, C_6H_4) 7.20 [2 H, d, $J(H_aH_b)$ = 3.4, H_b] 7.12 (1 H, t, H_a)	130.8 (C_q) 129.9 (C_6H_4) 127.1 (C_6H_4) 123.3 (C_c) 116.9 (C_d)
2	C, 39.55 (39.25); H, 4.85 (4.75)	7.26 (2 H, m, C_5H_4) 7.04 (2 H, m, C_5H_4) 1.39 (9 H, s, CMe_3)	156.1 (C_q) 123.7 (C_5H_4) 120.9 (C_5H_4) 34.3 ($\mathit{C}Me_3$) 30.7 [$C(\mathit{C}H_3)_3$]
3	C, 56.30 (56.20); H, 3.85 (4.05)	7.69 (2 H, m, C_6H_4) 7.38 (2 H, m, C_6H_4) 6.89 [2 H, d, $J(H_aH_b)$ = 3.4, H_b] 6.68 (1 H, t, H_a) 6.21 (5 H, s, C_5H_5)	128.6 (C_q) 128.2 (C_6H_4) 126.2 (C_6H_4) 126.1 (C_c) 110.4 (C_d) 120.8 (C_5H_5)
4		6.60 (2 H, m, C_5H_4) 6.55 (2 H, m, C_5H_4) 6.47 (5 H, s, C_5H_5) 1.29 (9 H, s, CMe_3)	149.4 (C_q) 120.0 (C_5H_5) 119.0 (C_5H_4) 118.4 (C_5H_4) 34.3 ($\mathit{C}Me_3$) 30.9 [$C(\mathit{C}H_3)_3$]
8	C, 60.75 (61.65); H, 7.10 (6.60)	7.57 [1 H, dd, $J(H_eH_f)$ = $J(H_eH_g)$ = 4.3, H_e] 7.16 [1 H, d, $J(H_hH_g)$ = 3.9, H_h] 6.95 (2 H, overlapping m, H_g + H_f) 6.74 [1 H, dd, $J(H_iH_j)$ = $J(H_iH_k)$ = 2.6, H_i] 6.28 [1 H, dd, $J(H_jH_k)$ = 3.4, H_j] 5.66 (1 H, dd, H_k) 5.72 (5 H, s, C_5H_5) 2.02 [1 H, d, J(HH) = 10.0, CH_2] 1.46 (1 H, d, CH_2) 0.12 (9 H, s, $SiMe_3$)	134.0 (C_q of C_6H_4) 132.4 (C_q of C_6H_4) 126.8 (C_6H_4) 126.4 (C_6H_4) 126.2 (C_6H_4) 125.3 (C_6H_4) 120.3 (C_5H_3) 111.1 (C_5H_3) 103.3 (C_5H_3) 116.1 (C_5H_5) 78.3 (CH_2) 1.4 ($SiMe_3$)
9	C, 60.35 (60.60); H, 8.10 (8.20)	6.90 (1 H, m, H_m) 6.77 (1 H, m, H_l) 6.00 (5 H, m, C_5H_5) 5.13 (1 H, m, H_o) 4.85 (1 H, m, H_n) 2.34 [d, J(HH) = 9.8, CH_2] 2.06 [dd, J(HH) = 1.0, CH_2] 1.25 (9 H, s, Bu^t) 0.09 (9 H, s, $SiMe_3$)	145.9 (C_q) 119.9 (C_5H_4) 118.8 (C_5H_4) 115.1 (C_5H_5) 107.7 (C_5H_4) 106.2 (C_5H_4) 71.5 (CH_2) 33.2 ($\mathit{C}Me_3$) 30.9 [$C(\mathit{C}H_3)_3$] 2.6 ($SiMe_3$)

[a] Analytical data given as found (required). Mass spectra, with molecular ions showing the appropriate isotope distribution, were obtained for **1**–**4**. [b] In $CDCl_3$ (compounds **1**–**4**) or C_6D_6 (**5**–**9**) solution (295 K). Data given as: chemical shift (δ) (relative intensity, multiplicity, J Hz, assignment). Labels refer to Scheme 1; C_q refers to quaternary carbon centre. Assignments made using NOE, homo- and hetero-nuclear correlation spectroscopy.

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Ti–Cl(1)	2.232(3)	Ti–C(2)	2.312(6)
Ti–Cl(2)	2.230(3)	Ti–C(3)	2.329(6)
Ti–Cl(3)	2.233(3)	Ti–C(4)	2.348(6)
Ti–C(1)	2.331(6)	Ti–C(5)	2.388(5)
Cl(1)–Ti–Cl(2)	102.67(10)	Cent–Ti–Cl(1)	116.0
Cl(1)–Ti–Cl(3)	102.87(13)	Cent–Ti–Cl(2)	116.1
Cl(2)–Ti–Cl(3)	101.74(12)	Cent–Ti–Cl(3)	115.4

(geminal coupling constant $^1J_{HH}$ = 8.9 Hz). The analogous methylene groups in $[Ti(\eta^5\text{-}C_5H_5)_2(CH_2Ph)_2]$ are present as a singlet at δ 1.90.[28]

Reaction of complex **3** with 1 mol equivalent of these nucleophiles does not lead to the chiral-at-titanium products $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)(R)Cl]$ (R = SPh, CH_2Ph or Me). This is in marked contrast to reports in the literature, where several $[Ti(\eta^5\text{-}C_5H_5)_2(R')Cl]$ complexes (R′ = various alkyl groups) are described.[29–31] In related studies, Lappert and co-workers[31,32] have successfully used bulky CH_2SiMe_3 and $CH(SiMe_3)_2$ groups to stabilise a wide range of metal–alkyl complexes, including the homoleptic $[M(CH_2SiMe_3)_4]$ and bis(cyclopentadienyl) $[M(\eta^5\text{-}C_5H_5)_2(CH_2SiMe_3)_2]$ (M = Ti, Zr or Hf) complexes. Notably, monosubstituted products $[M(\eta^5\text{-}C_5H_5)_2(CH_2SiMe_3)Cl]$ (M = Zr or Nb) were accessible. Accordingly, we carried out the reaction of **3** with 1 mol equivalent of Me_3SiCH_2MgCl in diethyl ether. Upon work-up, beautiful deep red crystals of $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)(CH_2SiMe_3)Cl]$ **8** were obtained. The low-temperature crystal structure has been determined, and shows that complex **8** crystallises in the centred monoclinic space group *C*2/*c*. The molecular structure is shown in Fig. 3 and selected bond lengths and angles are given in Table 3. Complex **8** is the first structurally characterised example of a simple titanocene alkyl chloride. The titanium atom is a pseudo-tetrahedral centre bound to four different ligands, and as such is chiral. The complex crystallises from toluene–light petroleum (b.p. 40–60 °C) mixtures as a racemate such that the *R* and *S* enantiomers are equally present in the crystal, related to each other by crystallographically imposed elements of symmetry (*c* glide plane, C_2 axis and centre of inversion). The Ti–Cl and Ti–C bond lengths and the C–Ti–Cl angles of some related compounds are summarised in Table 4. There is a remarkable constancy in these structural parameters, regardless of the steric bulk of the alkyl group or the electronic effect of the electronegative chloride ligands. However, the rather open Ti–C(15)–Si and C(15)–Si–C(18) angles of 130.9(2) and 115.1(2)° are an indicator of the large steric requirements of the trimethylsilylmethyl group.

The geometry of the indenyl group is summarised in Fig. 4. It is clear that the titanium atom is much closer to carbons C(7)–C(9), while the Ti–C(6) and Ti–C(10) bond lengths are significantly longer. It is also noteworthy that the C(11)–C(12) and C(13)–C(14) bonds are shorter than the other bonds in the C_6 ring. While the reported structure of $[Ti(\eta^5\text{-}C_9H_7)_2Me_2]$ is too imprecise to draw a meaningful comparison, the zirconium analogue $[Zr(\eta^5\text{-}C_9H_7)_2Me_2]$ shows very similar features.[33d]

The bonding in complex **8** may be represented by either of the structures **C** or **D**. The data in Fig. 4 clearly indicate that while the ring-slipped structure **D** makes a significant contribution, **C** is a better representation of the ground state of the molecule. Certainly, we imagine that the η^5–η^3 ring slip will play an important role in the chemistry of **8**, and therefore by implication of the other indenyl complexes reported here.

The preparation of the related compound $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Bu^t)(CH_2SiMe_3)Cl]$ **9** may be achieved using the same synthetic procedure. The titanium-centred chirality is clearly shown in the ^1H NMR spectrum by the presence of four resonances attributable to the ring hydrogens of the $\eta^5\text{-}C_5H_4Bu^t$ ring. In contrast, the prochiral precursor **4** shows only two resonances. It is also noteworthy that both **8** and **9** show two resonances for the diastereotopic CH_2 group. Restricted rotation around the the $Ti\text{-}C_5H_4Bu^t$ bond in **9** might be expected. As the ^1H NMR spectrum showed only one set of sharp resonances the rate of this rotation might be either very fast or negligible. The NMR experiments indicate that there is no nuclear Overhauser enhancement (NOE) between the Bu^t and $SiMe_3$ groups of **9**. 'Nearest neighbour' NOE allows the assignment of the indenyl and *tert*-butylcyclopentadienyl ligands in **8** and **9** (for example, a strong enhancement between the CH_2 group and H_m, and a weaker enhancement between CH_2 and H_n and H_l, between the CH_2 and C_5H_5 groups, between the Bu^t group and H_o and H_l, between the $SiMe_3$ group and H_m, *etc.*). We conclude that the rate of rotation about the $Ti\text{-}C_5H_4Bu^t$ bond is at most slow, and that the geometries of complexes **8** and **9** are fixed so that the ring substituents and the CH_2SiMe_3 group are as far from each other as possible, such that the complexes exist as rotational isomers of structure **E** and **F**. While the barrier to rotation about the $M\text{-}C_5H_5$ bond is usually small, restricted rotation in complexes containing substituted cyclopentadienyl ligands has been noted previously.[34]

The disubstituted compound $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)(CH_2SiMe_3)_2]$ **10** may be prepared by reaction of **3** with 2 mole equivalents of Me_3SiCH_2MgCl in diethyl ether, in an

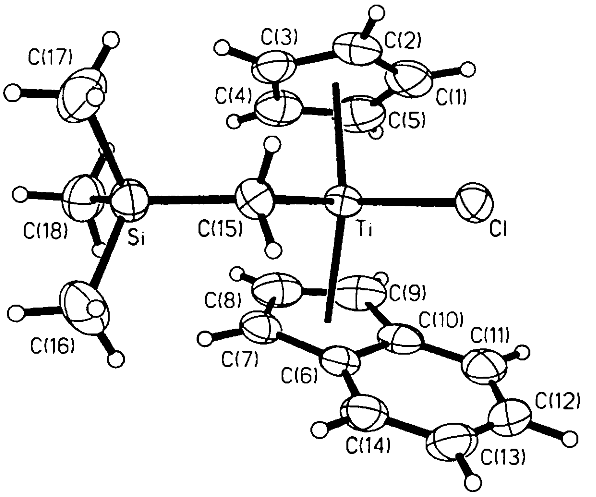


Fig. 3 Molecular structure of compound **8** (50% thermal ellipsoids)

Table 3 Selected bond lengths (Å) and angles (°) for complex **8**

Ti–Cl	2.337(2)	Ti–C(5)	2.373(4)
Ti–C(15)	2.162(3)	Ti–C(6)	2.533(3)
Ti–C(1)	2.381(4)	Ti–C(7)	2.401(4)
Ti–C(2)	2.377(4)	Ti–C(8)	2.335(3)
Ti–C(3)	2.387(3)	Ti–C(9)	2.364(3)
Ti–C(4)	2.368(3)	Ti–C(10)	2.531(3)
C(15)–Ti–Cl	92.53(11)	C(9)–C(10)–C(11)	133.1(3)
Si–C(15)–Ti	130.9(2)	C(6)–C(10)–C(11)	119.2(3)
C(7)–C(6)–C(14)	132.6(3)	C(6)–C(10)–C(9)	107.6(3)
C(10)–C(6)–C(14)	120.2(3)	C(10)–C(11)–C(12)	118.8(3)
C(7)–C(6)–C(10)	107.2(3)	C(11)–C(12)–C(13)	122.1(3)
C(6)–C(7)–C(8)	107.6(3)	C(12)–C(13)–C(14)	120.8(4)
C(7)–C(8)–C(9)	109.8(3)	C(13)–C(14)–C(6)	119.0(3)
C(8)–C(9)–C(10)	107.5(3)		

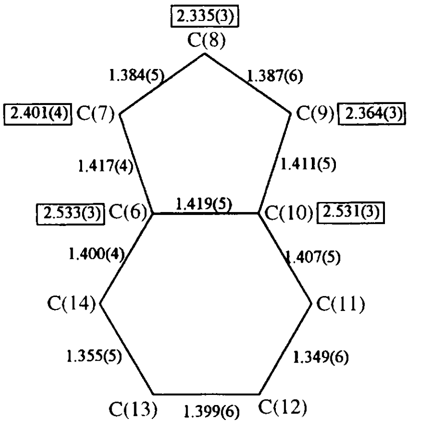
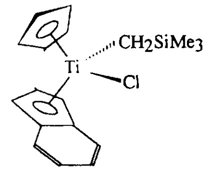


Fig. 4 The Ti–C (boxed) and C–C bond lengths (Å) within the indenyl ligand of complex **8**

Table 4 Selected bond lengths (Å) and angles (°) for complex **8** and related complexes

Complex	Ti–Cl/Å	Ti–C/Å	Angle at Ti[a]/°	Ref.
$[Ti(\eta^5\text{-}C_5H_5)_2Me(thf)]^+$	—	1.988(10)	88.9(3)	33(*a*)
$[Ti(\eta^5\text{-}C_5H_5)_2Me_2]$	—	2.170(2) 2.181(2)	91.2(1)	33(*b*)
$[Ti(\eta^5\text{-}C_9H_7)_2Me_2]$	—	2.21(2)	92.8(12)	33(*c*)
$[Ti\{\eta^{10}\text{-}(C_5H_4)_2SiMe_2\}(CH_2SiMe_3)_2]$	—	2.177(2) 2.179(2)	91.7(1)	33(*d*)
$[Ti(\eta^5\text{-}C_5H_4Bu^t)_2Cl_2]$	2.370(2)	—	92.5(5)	33(*e*)
8	2.337(2)	2.162(3)	92.5(1)	This work
$[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}L^1)\{OC_6H_3Me_2\text{-}2,6\}Cl]$[b]	2.38(2)	—	97	33(*f*)
$[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}L^1)\{OC_6H_3Me_2\text{-}2,6\}(NCS)]$	—	—	95	33(*g*)
$[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}L^2)\{OC_6H_3Me_2\text{-}2,6\}Cl]$[c]	2.374(2)	—	98.5(2)	33(*h*)

[a] Angle subtended at titanium by non-cyclopentadienyl ligands. [b] L^1 = 1-Methyl-3-propylcyclopentadienyl. [c] L^2 = 1-[Dimethyl(phenyl)methyl]-3-methylcyclopentadienyl.



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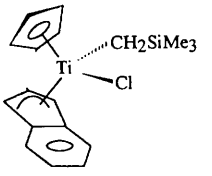

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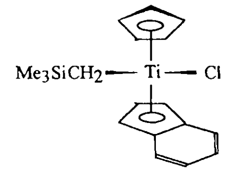

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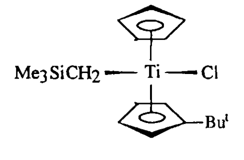

F

analogous fashion to **5**–**7**. Indeed, **10** is often present in samples of **8**, unless the stoichiometry of the reaction is strictly controlled. In contrast, $[Ti(\eta^5-C_5H_5)(\eta^5-C_5H_4Bu^t)(CH_2SiMe_3)_2]$ is not easily accessible from **3** and Me_3SiCH_2MgCl as a pure compound, even when the Grignard is present in large excess. Samples are always contaminated by large quantities of **9**. This is attributable to the steric demands of the *tert*-butyl and trimethylsilyl groups, as exemplified by the lack of rotation about the $Ti–C_5H_4Bu^t$ bond in compound **9** and the rather long $Ti–CBu^t$ bond length in **2**.

The early work of Tirouflet and co-workers[35] identified several chiral alkoxide complexes based upon symmetrical titanocene fragments; structurally characterised examples are included in Table 4. Compound **8** is the first structurally characterised chiral-at-metal titanocene complex containing a simple alkyl ligand, and as such is of significance in the fields of Ziegler–Natta polymerisation and early transition-metal alkylidene chemistry described in the Introduction. It is noteworthy that early experiments indicate that mixtures of **9** and methylaluminoxane $\{[Al(Me)O]_n\}$ are highly effective ethylene-polymerisation catalysts, and our work is continuing in this area.

Experimental

All manipulations of air- and moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques under an atmosphere of argon, or in a dry-box under an atmosphere of nitrogen. All solvents were purified and dried by refluxing over a suitable drying agent, followed by distillation under a nitrogen atmosphere. Toluene was dried over molten sodium, light petroleum (b.p. 40–60 °C) and diethyl ether over sodium–potassium alloy ($NaK_{2.2}$), tetrahydrofuran over molten potassium and dichloromethane over calcium hydride. The compounds $[Sn(C_5H_5)Bu_3]$ and $[Ti(\eta^5-C_5H_5)Cl_3]$ were prepared according to literature methods,[36,37] $[Sn(C_9H_7)Bu_3]$ and $[Sn(C_5H_4Bu^t)Bu_3]$ using appropriate modifications of the synthesis of $[Sn(C_5H_5)Bu_3]$.

Nuclear magnetic resonance spectra were recorded using Bruker AC-250 and AC-400 spectrometers. Spectra were referenced using the resonances of residual protons in the deuteriated solvents. Microanalyses were obtained using a Leeman Labs CE440 analyser.

Preparations

$[Ti(\eta^5-C_9H_7)Cl_3]$ 1. To a solution of $TiCl_4$ (1.27 g, 0.03 mol) in CH_2Cl_2 (30 cm^3) at 0 °C was added $[Sn(C_9H_7)Bu_3]$ (12.12 g, 0.03 mol), dropwise with stirring. The mixture was warmed to room temperature and stirred for 12 h. The resulting red solution was concentrated and cooled to -30 °C to give 7.04 g (87%) of deep purple crystals of **1** [m.p. 112 °C (decomp.)], which were washed with toluene (3 x 20 cm^3) and dried *in vacuo*.

$[Ti(\eta^5-C_5H_4Bu^t)Cl_3]$ 2. To a solution of $TiCl_4$ (5.2 g, 27.5 mmol) in CH_2Cl_2 (30 cm^3) at 0 °C was added $[Sn(C_5H_4Bu^t)Bu_3]$ (11.37 g, 27.5 mmol). After stirring for 12 h the solvent was removed *in vacuo* and the residue extracted with light petroleum (100 cm^3). After filtering the solution was cooled to -30 °C to give 2.64 g (35%) of orange crystals of **2** (m.p. 80–81 °C).

$[Ti(\eta^5-C_5H_5)(\eta^5-C_9H_7)Cl_2]$ 3. To a solution of complex **1** (1.42 g, 5.3 mmol) in CH_2Cl_2 (30 cm^3) at 0 °C was added $[Sn(C_5H_5)Bu_3]$ (1.80 g, 5.3 mmol). Work-up as described for **1** yielded 1.26 g (81%) of a brown powder of **3** [m.p. 128 °C (decomp.)].

$[Ti(\eta^5-C_5H_5)(\eta^5-C_5H_4Bu^t)Cl_2]$ 4. To a solution of complex **2** (4.00 g, 14.4 mmol) in diethyl ether (100 cm^3) at 0 °C was added LiC_5H_5 (1.04 g, 14.4 mmol). After stirring for 12 h the solvent was removed *in vacuo* and the residue extracted with CH_2Cl_2 (50 cm^3). After filtering the solution was concentrated and light petroleum added to precipitate 3.56 g (81%) of a red powder of **4** [m.p. 179 °C (decomp.)]. In spite of repeated attempts we were unable to obtain satisfactory microanalytical data for **4**, which always suggested a major deficiency in carbon content. We attribute this to incomplete combustion of the sample during the analysis.

$[Ti(\eta^5-C_5H_5)(\eta^5-C_9H_7)(SPh)_2]$ 5. To a solution of complex **3** (0.1 g, 0.33 mmol) in thf (30 cm^3) at -40 °C was added LiSPh (0.66 cm^3 of 1 mol dm^{-3} solution), dropwise with stirring. The mixture was stirred for 5 h, allowed to warm to room temperature and the solvent removed *in vacuo*. The resulting pinky red residue was extracted with toluene (15 cm^3) and filtered. After concentrating the solution and cooling to -30 °C, *ca.* 0.12 g (80%) of red crystals of **5** [m.p. 83 °C (decomp.)] were isolated. NMR (C_6D_6): ^1H, δ 7.96 (4 H, m, C_6H_5), 7.2 (6 H, m, C_6H_5 + C_6H_4), 7.00 (2 H, tt, J = 7.4, 1.3, C_6H_5), 6.72 (3 H, m, C_6H_4 + H_a), 6.34 [2 H, d, $J(H_aH_b)$ = 3.4 Hz, H_b] and 5.45 (5 H, s, C_5H_5); ^{13}C, δ 149.6 [quaternary C (C_q) of C_6H_5], 132.3 (C_6H_5), 128.6 (C_6H_5), 126.0 (C_6H_5), 125.6 (C_6H_4), 125.4 (C_6H_4), 123.9 (C_b), 123.6 (C_q of C_6H_4), 115.1 (C_5H_5) and 104.3 (C_a).

$[Ti(\eta^5-C_5H_5)(\eta^5-C_9H_7)Me_2]$ 6. To a solution of complex **3** (0.1 g, 0.33 mmol) in ether (30 cm^3) at -40 °C was added MgMeBr (0.66 cm^3 of 1 mol dm^{-3} solution), dropwise with stirring. Work-up as above yielded *ca.* 0.06 g (68%) of yellow crystals of **6** [m.p. 94 °C (decomp.)]. NMR (C_6D_6): ^1H, δ 7.33 (2 H, m, C_6H_4), 7.03 (2 H, m, C_6H_4), 5.95 [2 H, d, $J(H_aH_b)$ = 3.3 Hz, H_b], 5.60 (5 H, s, C_5H_5), 5.57 (1 H, t, H_a) and -0.24 (6 H, s, Me); ^{13}C, δ 125.9 (C_q), 125.5 (C_6H_4), 115.7 (C_b), 113.6 (C_5H_5), 103.9 (C_a) and 48.7 (Me).

$[Ti(\eta^5-C_5H_5)(\eta^5-C_9H_7)(CH_2Ph)_2]$ 7. To a solution of complex **3** (0.1 g, 0.33 mmol) in ether (30 cm^3) at -40 °C was added $PhCH_2MgBr$ (0.66 cm^3 of 1 mol dm^{-3} solution), dropwise with stirring. Work-up as above yielded *ca.* 0.07 g (50%) of a brown powder of **7** [m.p. 85 °C (decomp.)] [Found: (Calc.) C, 81.60 (81.95); H, 6.30 (6.40)%] NMR (C_6D_6): ^1H, δ 7.24 (4 H, m, C_6H_5), 7.13 (2 H, m, C_6H_4), 6.96 (2 H, m, C_6H_5), 6.92 (2 H, m, C_6H_4), 6.82 (4 H, m, C_6H_5), 6.09 [2 H, d, $J(H_aH_b)$ = 3.3, H_b], 5.90 (1 H, t, H_a), 5.40 (5 H, s, C_5H_5), 1.55 (2 H, d, J = 8.9 Hz, CH_2) and 1.35 (2 H, d, CH_2); ^{13}C, δ 153.8 (C_q of C_6H_5), 126.3 (C_6H_5), 122.0 (C_6H_5), 119.2 (C_6H_5), 126.4 (C_q of C_6H_4), 126.0 (C_6H_4), 125.3 (C_6H_4), 113.5 (C_a), 106.2 (C_b), 116.7 (C_5H_5) and 77.2 (CH_2).

Table 5 Crystal data for complexes **2** and **8**[a]

	2	**8**
(*a*) Crystal parameters		
Formula	$C_9H_{13}Cl_3Ti$	$C_{18}H_{23}ClSiTi$
M	275.44	350.80
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	9.351(10)	28.749(25)
b/Å	12.551(10)	6.650(5)
c/Å	10.318(10)	20.894(12)
β/°	98.80(13)	120.68(6)
U/Å^3	1197	3435
Z	4	8
Crystal dimensions/mm	0.64 × 0.31 × 0.19	0.54 × 0.50 × 0.50
Colour	Red-orange	Red
D_c/g cm^{-3}	1.529	1.357
μ(Mo-Kα)/mm^{-1}	1.34	0.72
(*b*) Data collection		
Data collected (h, k, l)	11, 14, ±12	34, 7, ±24
Reflections collected	2248	3100
Independent reflections	2113	3039
Independent observed reflections [$F_o \geqslant 4\sigma(F_o)$]	1739	2585
Variation in standards (%)	3	< 1
(*c*) Refinement		
R^b	0.088	0.046
$wR2^c$	0.245	0.149
Δ/σ_{max}	0.001	0.001
ρ/Å e^{-3}	1.51	0.63
$N_o/N_v{}^d$	17.4	15.6
S	1.064	1.057
Weighting scheme, $w^{-1\,e}$	$\sigma^2(F_o{}^2) + 0.187P^2 + 0.661P$	$\sigma^2(F_o{}^2) + 0.089P^2 + 5.213P$

[a] Data collected at 200 K on a Siemens R3m diffractometer, uncorrected for absorption; graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), $2\theta_{max}$ = 50°, three standards every 197 reflections. Anisotropic thermal parameters were used for all non-H atoms. [b] $R = \Sigma|F_o - F_c|/\Sigma F_o$ for $F_o \geqslant 4\sigma(F_o)$. [c] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{\frac{1}{2}}$ for all data. [d] N_o = Number of observations, N_v = number of variables. [e] $P = [\max(F_o{}^2,0) + 2F_c{}^2]/3$, where $\max(F_o{}^2,0)$ indicates that the larger of $F_o{}^2$ or 0 is taken.

[Ti(η^5-C_5H_5)(η^5-C_9H_7)(CH_2SiMe_3)Cl] 8. To a solution of complex **2** (0.1 g, 0.33 mmol) in ether (30 cm^3) at −40 °C was added Me_3SiCH_2MgBr (0.24 cm^3 of 1.4 mol dm^{-3} solution), dropwise with stirring. Work-up as above yielded red crystals of **8** [m.p. 103 °C (decomp.)].

[Ti(η^5-C_5H_5)(η^5-$C_5H_4Bu^t$)(CH_2SiMe_3)Cl] 9. To a solution of complex **4** (0.1 g, 0.33 mmol) in ether (30 cm^3) at −40 °C was added Me_3SiCH_2MgBr (0.24 cm^3 of 1.4 mol dm^{-3} solution), dropwise with stirring. Work-up as above yielded *ca.* 0.06 g (55%) of an orange powder of **9** [m.p. 144 °C (decomp.)].

[Ti(η^5-C_5H_5)(η^5-C_9H_7)(CH_2SiMe_3)$_2$] 10. To a solution of complex **3** (0.1 g, 0.33 mmol) in ether (30 cm^3) at −40 °C was added Me_3SiCH_2MgBr (0.48 cm^3 of 1.4 mol dm^{-3} solution), dropwise with stirring. The mixture was stirred for 5 h, allowed to warm to room temperature and the solvent removed *in vacuo*. The residue was extracted with light petroleum (15 cm^3) and filtered. After concentrating the solution and cooling to −30 °C, *ca.* 0.07 g (56%) of yellow crystals of **10** [m.p. 202 °C (decomp.)] were isolated [Found (Calc.): C, 63.45 (65.65); H, 9.05 (8.50)%]. NMR (C_6D_6): ^{1}H, δ 7.48 (2 H, m, C_6H_4), 7.09 (2 H, m, C_6H_4), 6.07 [2 H, d, $J(H_aH_b)$ = 3.2 Hz, H_b], 5.22 (1 H, t, H_a), 0.15 (2 H, s, CH_2), 0.14 (2 H, s, CH_2) and 0.11 (18 H, s, $SiMe_3$); ^{13}C, δ 134.0 (C_q of C_6H_4), 125.9 (C_6H_4), 125.2 (C_6H_4), 113.0 (C_a), 101.8 (C_b), 112.4 (C_5H_5), 67.3 (CH_2) and 3.6 ($SiMe_3$).

Crystallography

Crystallographic data for complexes **2** and **8** are summarised in Table 5. Suitable single crystals were quickly glued to quartz fibres, coated in Nujol and cooled in the cold nitrogen gas stream of the diffractometer. Encasing the crystal in frozen oil prevented aerial oxidation for the duration of the data collection. The structures were solved by direct methods. Hydrogen atoms were placed in calculated positions and refined, with fixed isotropic thermal parameters, U = 0.08 Å^2, riding on the supporting carbon atom. The structure solutions were carried out using SHELXTL PLUS[38] software on a DEC Microvax-II computer. Refinements (on F^2) were carried out with SHELXL 93[39] software on an Elonex 486DX computer, minimising the weighted R factor $wR2$.

Atomic coordinates, thermal parameters, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/88.

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