

Titanium and zirconium chloro, oxo and alkyl derivatives containing silyl-cyclopentadienyl ligands. Synthesis and characterisation

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Abstract

The reaction of the tetramethylcyclopentadiene-silyl substituted derivative $C_5Me_4(SiMe_3)(SiMe_2Cl)$ with MCl_4 afforded the trichloro mono-tetramethylcyclopentadienyl complexes $M(\eta^5-C_5Me_4SiMe_2Cl)Cl_3$ [$M = Ti$ (**1**), Zr (**2**)] with selective elimination of $SiMe_3Cl$. Compound **1** reacts with deoxygenated water in methylene chloride, with the evolution of HCl , to give the dinuclear titanium compound $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl_2\}_2$ (**3**), which was converted into the μ -oxo complex $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl\}_2(\mu-O)$ (**4**) by a further hydrolysis reaction which occurred when a solution of **3** in toluene was refluxed for a long period of time in the air. Depending on the size of the alkyl ligand, reactions of the mononuclear compound **1** with an appropriate alkylating reagent rendered the peralkylated $Ti(\eta^5-C_5Me_4SiMe_2R)R_3$ [$R = Me$ (**5**), CH_2Ph (**6**)] or partially alkylated $\{Ti[(\eta^5-C_5Me_4SiMe_2(CH_2SiMe_3))Cl(CH_2SiMe_3)_2]\}_2$ (**7**) compounds by a salt metathesis route. Attempts to synthesise a partially methylated or benzylated complex were unsuccessful. Treatment of the dinuclear compound **3** with four equivalents of $MgClMe$ yielded the tetramethyl derivative $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Me_2\}_2$ (**8**), while the same reaction carried out with $MgCl(CH_2Ph)$ or $Mg(CH_2Ph)_2 \cdot 2THF$ gave the chloro-benzyl derivative $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl(CH_2Ph)\}_2$ (**9**) as an equimolar mixture of diastereomers, regardless of the molar ratio of the alkylating reagent used. All of the new compounds were characterised by elemental analysis and NMR spectroscopy.

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1. Introduction

Early-transition-metal compounds have provided important classes of precatalyst systems for α -olefin polymerisation and related processes [1]. Derivatives with ancillary cyclopentadienyl ligands have dominated the chemistry as they produce stable complexes with steric and electronic properties that can be easily tailored to perform specific roles by varying the ring substituents [2].

We have recently demonstrated that chlorosilyl-substituted monocyclopentadienyl complexes provide versatile starting compounds for the synthesis of a wide number of organometallic derivatives via reactions at

the Si–Cl bond [3–5]. In view of the synthetic potential of chlorosilyl-substituted monocyclopentadienyl derivatives, research effort in our group was focussed on the stereo and electronic effects that replacing the C_5H_4 ring with C_5Me_4 have on the molecular structure and reactivity of $[M(\eta^5-C_5Me_4SiMe_2Cl)Cl_3]$. We report herein the synthesis of new mono(chlorodimethylsilyl)tetramethylcyclopentadienyl titanium and zirconium compounds $M(\eta^5-C_5Me_4SiMe_2Cl)Cl_3$, together with an investigation into their propensity to undergo hydrolysis and alkylation reactions. The hydrolysis reaction produced dinuclear titanium derivatives containing the ‘ $\eta^5-(C_5Me_4)-Si-O-$ ’ bridge ligand, $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl_2\}_2$ and $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl\}_2(\mu-O)$. Mono- and dinuclear cyclopentadienyl-silyl alkyl titanium complexes were synthesised by reaction of the chloro derivatives with the appropriate alkylating reagent. The results obtained demonstrate that the higher π -donating capacity and larger steric size of the

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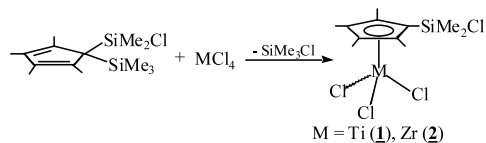
C_5Me_4 ring increases the thermal stability of the compounds generated, and has an influence on reactivity compared with analogous C_5H_4 derivatives.

2. Results and discussion

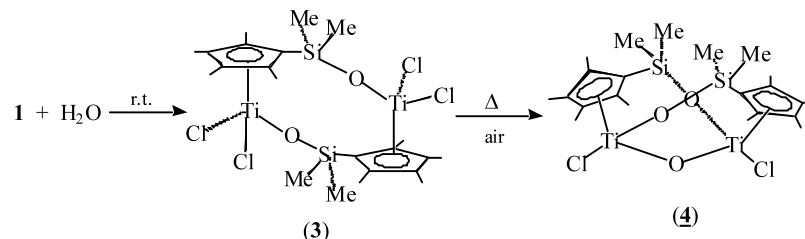
2.1. Chloro cyclopentadienyl complexes

The reaction of $C_5Me_4(SiMe_3)(SiMe_2Cl)$ [6] with an equimolar amount of $TiCl_4$ at $50^\circ C$ in methylene dichloride for 4 days or $ZrCl_4$ at $90^\circ C$ in toluene for 1 day afforded red solutions. After workup, the trichloro mono-tetramethylcyclopentadienyl derivatives $M(\eta^5-C_5Me_4SiMe_2Cl)Cl_3$ [$M = Ti$ (**1**), Zr (**2**)] were isolated (Scheme 1). Complexes **1** and **2** were formed by specific elimination of $SiMe_3Cl$ rather than $SiMe_2Cl_2$, as under these reaction conditions the ‘ $SiMe_2Cl$ ’ group bonded to the cyclopentadiene ring has a lower affinity for the attacking electrophile, probably due to the presence of the more electronegative chloro substituent, although selective $SiMe_3Cl$ elimination is not always observed [7]. Formation of small amounts of the tetramethylcyclopentadienyl titanium complex $Ti(\eta^5-C_5Me_4H)Cl_3$ [8] was always observed in these reactions, its formation will shortly be reported separately [9]. However, its higher solubility in all solvents allowed its ready removal by washing the crude product with cooled hexane. Red crystals of **1** were isolated in 77% yield by cooling its hexane solution to $-30^\circ C$, and **2** was isolated as white crystals in 70% yield following the same procedure.

Compounds **1** and **2** are very moisture sensitive in solution and therefore must be stored under rigorously dry conditions. Both complexes are quite soluble in most of the common solvents. They were characterised by elemental analysis and NMR spectroscopy.



Scheme 1.



Scheme 2.

Spectroscopic and analytical data (see Section 4) support the proposed structures. The 1H and ^{13}C -NMR spectra ($CDCl_3$ at room temperature) for **1** and **2** show the presence of one high field-shifted resonance for the two equivalent methyl groups bonded to silicon and two signals for the methyl-cyclopentadienyl groups. Sharp 1H -NMR signals observed for **2** are similar to those of $[Zr(\eta^5-C_5Me_5)Cl_3]_2$ [10], indicating that a similar dimeric structure can be proposed for this monocyclopentadienyl zirconium compound. We have reported that analogous cyclopentadienyl $M(\eta^5-C_5H_4SiMe_2Cl)Cl_3$ titanium and zirconium derivatives exhibit similar spectroscopic behaviour [3a].

2.2. Oxo complexes

In order to compare the sensitivity of the two types of chloride bond present in the molecule to water, i.e. the chloride bonded to silicon and those bonded to the metal, we investigated compounds **1** and **2** propensity to hydrolyse.

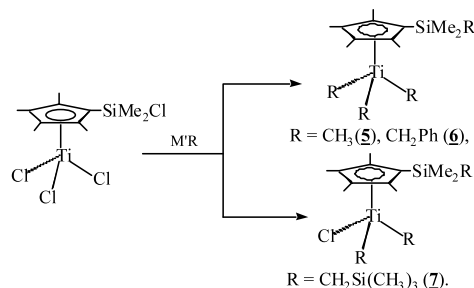
Addition of one equivalent of deoxygenated water to a methylene dichloride or toluene solution of the titanium compound **1** produces the evolution of HCl affording compound **3** in 88% yield, as an orange crystalline solid. Compound **3** was characterised as the dinuclear titanium compound $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl_2\}_2$ (Scheme 2), which shows the oxygen atom bridging the silicon and the titanium atoms forming an eight-membered ring: $(Ti-Cp-Si-O)_2$. A different synthetic route to compound **3** has been reported [11]. However the procedure described herein is more straightforward and produces higher yields.

This behaviour is similar to that reported by our research group for the analogous complex with a C_5H_4 ring [3a]. The formation of the $\{Ti[\mu-(\eta^5-C_5H_4SiMe_2O-\kappa O)]Cl_2\}_2$ compound was proposed as an intermolecular hydrolysis reaction of $Ti(\eta^5-C_5H_4SiMe_2Cl)Cl_3$ and the same process may be proposed in the synthesis of compound **3**. Nevertheless, an intramolecular process cannot be ruled out in either case. Simultaneous intramolecular hydrolysis of both $Si-Cl$ and $Ti-Cl$ bonds with concomitant condensation of the two cyclopentadienyl-oxo-titanium ‘ $CpSiOTi$ ’ units initially formed, would give a dimeric structure analogous

to those isolated for related zirconium complexes [3b,12]. The small size of the titanium atom would cause the four-membered ring 'CpSiOTi' to be too constrained, forcing Ti–O bonds of each mononuclear moiety to open.

However, the product of a further hydrolysis reaction is strongly dependent on the steric requirements of the cyclopentadienyl ligand. When a solution of **3** in toluene was refluxed over a long period in the air, compound **3** was slowly transformed into a unique compound which was isolated in 80% yield as a yellow crystalline solid and identified as the μ -oxo complex $\{\text{Ti}[\mu-(\eta^5\text{-C}_5\text{Me}_4\text{-SiMe}_2\text{O-}\kappa\text{O})\text{Cl}]_2(\mu\text{-O})\}$ (**4**) (Scheme 2). By contrast, the similar complex $\{\text{Ti}[\mu-(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{O-}\kappa\text{O})\text{Cl}]_2\}_2$ reacts in toluene by further addition of water to give a mixture of compounds from which only the mononuclear $\{\text{Ti}[\mu-(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{OSiMe}_2\text{O-}\kappa\text{O})\text{Cl}]_2\}_2$ compound was isolated and identified [3a]. Complex **4** resulted from the intramolecular hydrolysis of two Ti–Cl bonds, one on each metal atom, forming a 'Ti–O–Ti' bridge, thus maintaining the dinuclear system. Compound **4** shows a folded structure, which allows the two titanium atoms to approach each other to generate the oxo bridge group. This molecular disposition is reminiscent of those reported for related dinuclear cationic complexes $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{O-}\kappa\text{O})(\text{CH}_2\text{Ph})\}_2(\mu\text{-X})]$ ($\text{X} = \text{Cl}, \text{CH}_2\text{Ph}$) [13].

The NMR spectroscopic behaviour of complex **3** at room temperature is relatively simple. The ^1H -NMR spectrum (CDCl_3 at room temperature) exhibits the resonances from the methyl groups attached to the silicon atom and the methyl cyclopentadienyl protons expected for a C_{2h} -symmetric compound. Such spectroscopic features contrast with the C_i symmetry shown by **3** in the solid state [11], suggesting fluxional behaviour in solution resulting in enantiomeric conformational metallacycle interconversion. The ^1H and ^{13}C -NMR (CDCl_3 at room temperature) spectra of compound **4** display resonances consistent with a C_2 -symmetric compound, static on the NMR time scale, since the presence of the μ -oxo bridge generates a chiral arrangement around each titanium centre. As a result, the distal and proximal methyl groups of the cyclopentadienyl ligand form no equivalent pairs, appearing as four different signals along with two singlets for the silicon-bound diastereotopic methyl groups. To justify such spectroscopic behaviour, it is necessary to assume that the central core of **4** bends with respect to the Ti–Ti axis, adopting a folded conformation to accommodate the linear Ti–O–Si systems bridging the two titanium atoms. This compound can be described as a dinuclear species formed by two 'Ti(C₅Me₄SiMe₂)Cl' fragments connected by three oxygen bridges, and related by the C_2 axis perpendicular to the Ti–Ti line and passing through the bridging oxygen Ti–O–Ti.



Scheme 3.

2.3. Alkyl complexes

Compounds **1** and **2** have two different types of chlorine atom, the chlorine bonded to silicon and those bonded to the metal centre, which also may be involved in substitution reactions. Complex **1** was readily converted to the fully alkylated compounds $\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{-SiMe}_2\text{R})\text{R}_3$ [$\text{R} = \text{Me}$ (**5**), CH_2Ph (**6**)] by a salt metathesis route. Treatment of **1** with four equivalents of MgClMe or MgClBz or two equivalents of $\text{MgBz}_2 \cdot 2\text{THF}$ reagents in diethyl ether or hexane at -78°C yielded the corresponding peralkylated derivatives in good yield (Scheme 3).

Compound **5** was recently synthesised in a similar way [9]. Compounds **5** and **6** were isolated as a yellow solid and a red oil, respectively, together with non-coordinated diethyl ether. Both compounds are moisture sensitive and very soluble in the usual solvents. However, **5** is more thermally stable than **6**. Thus, while **5** may be stored for weeks at room temperature the benzyl derivative slowly decomposes at room temperature even in the solid state.

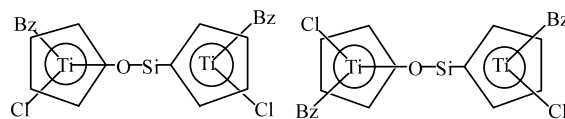
Attempts to prepare the partially substituted methyl or benzyl derivatives by reaction of **1** with an appropriate amount of the respective alkylating reagent were unsuccessful, always leading to intractable mixtures from which pure substances could not be isolated, and indicating that the Si–Cl and Ti–Cl bonds show no selectivity towards nucleophiles of this type. This behaviour resembles that observed for the analogous silyl-cyclopentadienyl zirconium derivative $\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})\}\text{Cl}_3$ [14], but contrasts with that observed for the titanium derivative $\text{Ti}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})\}\text{Cl}_3$, from which the compound $\text{Ti}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})\}\text{Bz}_3$ was exclusively obtained, even when an excess of alkylating reagent was used [3a].

Nevertheless, the use of a large bulky alkyl group permits partially alkylated products to be prepared. Treatment of **1** with four equivalents of $\text{MgCl}(\text{CH}_2\text{SiMe}_3)$ in diethyl ether at -78°C yielded the trisubstituted derivative $\text{Ti}[\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2(\text{CH}_2\text{SiMe}_3)]\text{Cl}(\text{CH}_2\text{SiMe}_3)_2$ (**7**), isolated as a yellow oil in good yield. Compounds **5**, **6** and **7** were characterised by elemental analysis and NMR spectroscopy.

The ^1H spectra (C_6D_6 at room temperature) of compounds **5–7** show the expected AA'BB' spin system for ring-methyl groups and a high field-shifted singlet corresponding to methyl-silicon groups. Furthermore, the ^1H -NMR spectrum of **5** shows a singlet assigned to the methyl groups attached to titanium. The ^1H -NMR spectrum of **6** shows two singlets assigned to the equivalent methylene protons of the two different benzyl ligands (TiCH_2Ph and SiCH_2Ph) contained in the molecule. In complex **7** the diastereotopic protons of the metal-bound methylene groups, $\text{Ti}-\text{CH}_2\text{SiMe}_3$, appear as two doublets ($J_{\text{H-H}} = 11.2$ Hz) confirming the prochiral character of the metal centre. The ^{13}C -NMR spectra are consistent with the proposed structures.

Part of our current research interest is focused on the synthesis of alkyl dinuclear derivatives of group four metals in order to evaluate their behaviour compared with related mononuclear compounds [13,15,16]. Consequently, we studied the reaction of **3** with different alkylating reagents. Reaction of **3** with four equivalents of MgClMe in hexane at -78°C produced the tetramethyl derivative $\{\text{Ti}[\mu-(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{O-}\kappa\text{O})]\text{Me}_2\}_2$ (**8**) (Scheme 4), which was isolated as a yellow solid in high yield. Compound **8** is thermally stable and can be stored under inert conditions without appreciable decomposition, results that contrast with those previously observed for the analogous compound containing the C_5H_4 ligand [3a].

When a bulkier alkyl group was used the related tetraalkyl derivative was never obtained, regardless of the molar ratio of the alkylating reagent used. The addition of an excess of either MgClBz or $\text{MgBz}_2 \cdot 2\text{THF}$ to a suspension of **3** in hexane at -78°C afforded a red solution from which the crystalline dibenzyl derivative $\{\text{Ti}[\mu-(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{O-}\kappa\text{O})]\text{Cl}(\text{CH}_2\text{Ph})\}_2$ (**9**) was obtained in good yield, as an equimolar mixture of diastereomers. The presence of two chiral titanium atoms in the molecule gives rise to two pairs of diastereomers as a consequence of the *cis*- and *trans*-disposition of the benzyl groups with respect to the molecular plane, at the same or at opposite faces, respectively (Scheme 5). Attempts to separate this

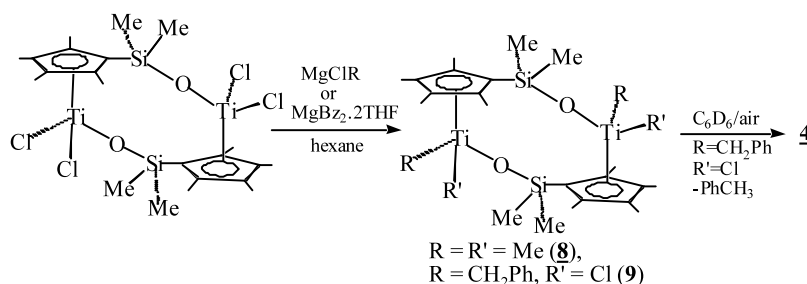


Scheme 5.

mixture by repeated recrystallisation from toluene–hexane solutions were unsuccessful.

The sterically more demanding C_5Me_4 ligand prevents the titanium atom from being doubly alkylated, a result that contrasts with that found for $\{\text{Ti}[\mu-(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{O-}\kappa\text{O})]\text{Cl}_2\}_2$ which was fully benzylated [3a]. Moreover, the formation of both diastereomers in a molar ratio of 1:1 indicates that in the starting compound **3**, the ‘ CpTiCl_2O ’ moieties are placed so far away from each other that their chemical behaviour must be independent. Thus, once the first benzyl ligand coordinates to one of the titanium centres, the second benzyl ligand is equally free to coordinate to the other titanium atom on the same or the opposite face.

The NMR spectroscopic studies of **8** and **9** confirm the proposed structures. The ^1H -NMR and ^{13}C spectra of **8** (C_6D_6 at room temperature) are comparable with that recorded for **3**, indicating that **8** adopts an analogous open conformation. The ^1H -NMR spectrum shows two singlets for the cyclopentadienyl methyl groups, one signal for the SiMe_2 methyl protons, and one resonance assigned to the methyl groups bonded to titanium. Resonances corresponding to 12 methyl groups were observed in the ^1H -NMR spectrum (C_6D_6 at room temperature) of compound **9** due to the presence of two diastereomers. The formation of these in a 1:1 molar ratio does not allow the resonances corresponding to one diastereomer to be distinguished from the other. The eight resonances found in the region between 1.8 and 2.1 ppm were assigned to the C_5Me_4 methyl protons, while the methyl groups attached to silicon atom appear as three signals, one of which overlaps and represents two methyl groups. The methylene protons of the benzyl groups exhibit an AB spin system due to the chiral character of the metal centres. Moreover, the resonance due to *ipso*-carbons of the phenyl rings and the values of $^2J_{\text{H-H}}$ (≈ 11 Hz) indicate



Scheme 4.

the presence of an undistorted η^1 -bonded benzyl ligand [17].

The dinuclear titanium chloro-benzyl complex $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{-}\kappa\text{O})\text{ClBz}]_2$ is thermally unstable and extremely moisture sensitive in solution. When a solution of **9** in C_6D_6 was left in the air the compound spontaneously hydrolysed with elimination of two equivalents of toluene, as evidenced by $^1\text{H-NMR}$ spectroscopy, affording the μ -oxo complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{-}\kappa\text{O})\text{Cl}\}_2(\mu\text{-O})]$ (**4**), therefore supporting the proposed structure.

3. Conclusions

The synthesis and characterisation of new trichloro monocyclopentadienyl titanium and zirconium compounds containing the tetramethylcyclopentadienyl-chlorotrimethyl-silyl ligand is described. The influence of the bulky C_5Me_4 ligand on the reactivity of $\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Cl})\text{Cl}_3$ with water and alkylating reagents, and on the thermal stability of their alkyl derivatives has been investigated. Simultaneous hydrolysis of both Si–Cl and Ti–Cl bonds in $\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Cl})\text{Cl}_3$ gave one dinuclear titanium derivative with the ‘ $\text{C}_5\text{Me}_4\text{-SiMe}_2\text{-O}$ ’ bridge unit. A further hydrolysis selectively proceeds with reaction of the second Ti–Cl bond with the formation of a new ‘Ti–O–Ti’ bridge. In the treatment of $\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Cl})\text{Cl}_3$ with different alkylating reagents, the nature of the resulting alkyl derivative was strongly dependent on the steric requirements of the alkyl group introduced. The reaction with four equivalents of MgClR gave the tetra alkyl derivatives $\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{R})\text{R}_3$ for $\text{R} = \text{Me}, \text{Bz}$, while when $\text{R} = \text{CH}_2\text{SiMe}_3$ only two Ti–Cl and the Si–Cl bonds reacted for steric reasons. These results indicate the reactivity of the Si–Cl and Ti–Cl bonds in $\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Cl})\text{Cl}_3$ towards nucleophiles is not selective. The tetramethyl dinuclear titanium complex $\{\text{Ti}[\mu\text{-}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{O-}\kappa\text{O})]\text{Me}_2\}_2$ can be readily synthesised from methylating reactions of $\{\text{Ti}[\mu\text{-}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{O-}\kappa\text{O})]\text{Cl}_2\}_2$. However, when a bulkier alkyl group is used (benzyl) only partial alkylation can be achieved, affording the chloro-benzyl compound $\{\text{Ti}[\mu\text{-}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{O-}\kappa\text{O})]\text{Cl}(\text{CH}_2\text{Ph})\}_2$ as a mixture of diastereoisomers.

The reactivity of neutral alkyl derivatives of this type to generate cationic species is being studied and work to test their activity as precursors for olefin polymerisation is in process.

4. Experimental

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or in a glove-

box model HE-63. The solvents were purified by distillation under argon before use by employing the appropriate drying/deoxygenated agent. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. TiCl_4 , ZrCl_4 , MgClMe , MgClBz and $\text{MgCl}(\text{CH}_2\text{SiMe}_3)$ were purchased from commercial sources (Aldrich) and used as received. $\text{C}_5\text{Me}_4(\text{SiMe}_3)(\text{SiMe}_2\text{Cl})$ [6] and $\text{MgBz}_2 \cdot 2\text{THF}$ [18] were prepared by known procedures. C and H microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus CHN-O-Rapid microanalyser. The analytical data found for **9** deviated from expected values as the product was an oil and residual magnesium species could not be completely removed. NMR spectra, measured at 25 °C, were recorded on a Varian Unity 300 (^1H at 300 MHz and ^{13}C at 75 MHz) spectrometer, and chemical shifts are referenced to residual protons and carbon signals of the solvent.

4.1. Synthesis of $\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Cl})\text{Cl}_3$ (**1**)

TiCl_4 (0.58 ml, 5.27 mmol) was injected into a solution containing 1.76 ml of $\text{C}_5\text{Me}_4(\text{SiMe}_3)(\text{SiMe}_2\text{Cl})$ (5.27 mmol) in 50 ml of dichloromethane. The reaction mixture was maintained at 50 °C for 4 days giving a red solution and an oily red residue. After filtration the solvent was removed under vacuum and the resulting solid was washed with hexane (2×10 ml) and dried under vacuum to give a red solid. Recrystallisation from toluene/hexane afforded **1** as a microcrystalline red solid (1.5 g, 4.08 mmol, 77% yield). Anal. Calc. for $\text{C}_{11}\text{H}_{18}\text{Cl}_4\text{SiTi}$: C, 35.90; H, 4.94. Found: C, 36.57; H, 4.99%. $^1\text{H-NMR}$ (CDCl_3): δ 0.91 (s, 6H, SiMe_2); 2.34, 2.56 (s, $2 \times 6\text{H}$, C_5Me_4). $^{13}\text{C-NMR}$ (CDCl_3): δ 5.1 (SiMe_2); 14.2, 17.6 (C_5Me_4); 132.8, 141.9, 144.4 (C_5Me_4).

4.2. Synthesis of $\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Cl})\text{Cl}_3$ (**2**)

1.43 ml of $\text{C}_5\text{Me}_4(\text{SiMe}_3)(\text{SiMe}_2\text{Cl})$ (4.29 mmol) was added via syringe to a suspension of ZrCl_4 (1 g, 4.29 mmol) in 40 ml of toluene at room temperature (r.t.). The reaction mixture was warmed to 90 °C and vigorously stirred for 1 day. The final red solution was filtrated and concentrated under vacuum to give a pale pink product. Recrystallisation from toluene/hexane gave **2** as a microcrystalline white solid (1.24 g, 3.01 mmol, 70% yield). Anal. Calc. for $\text{C}_{11}\text{H}_{18}\text{Cl}_4\text{SiZr}$: C, 32.11; H, 4.42. Found: C, 32.83; H, 4.69%. $^1\text{H-NMR}$ (CDCl_3): δ 0.85 (s, 6H, SiMe_2); 2.20, 2.42 (s, $2 \times 6\text{H}$, C_5Me_4). $^{13}\text{C-NMR}$ (CDCl_3): δ 5.2 (SiMe_2); 12.8, 15.9 (C_5Me_4); 123.6, 135.6, 137.3 (C_5Me_4).

4.3. Synthesis of $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl_2\}_2$ (**3**)

Deoxygenated water (49×10^{-3} ml, 2.72 mmol) was added, at r.t., to a solution of $Ti(\eta^5-C_5Me_4SiMe_2Cl)Cl_3$ (1 g, 2.72 mmol) in 30 ml of dichloromethane. The reaction mixture was stirred for 24 h. After filtration the solvent was evaporated under vacuum to give an orange solid which was washed with hexane (2×10 ml), and dried under vacuum to afford **3** as a crystalline orange solid (0.75 g, 1.2 mmol, 88% yield). Anal. Calc. for $C_{22}H_{36}Cl_4O_2Si_2Ti_2$: C, 42.19; H, 5.80. Found: C, 42.27; H, 5.76%. 1H -NMR ($CDCl_3$): δ 0.49 (s, 12H, SiMe₂); 2.25, 2.37 (s, 2×12 H, C₅Me₄). ^{13}C -NMR ($CDCl_3$): δ 2.4 (SiMe₂); 13.1, 16.4 (C₅Me₄); 129.4, 139.4, 140.2 (C₅Me₄).

4.4. Synthesis of $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl\}_2(\mu-O)$ (**4**)

A Schlenk flask charged with a solution of **3** (1 g, 1.6 mmol) in 80 ml of toluene was connected to a condenser and refluxed for 5 days in the air. The solvent was completely removed to give a yellow solid which was recrystallised from diethyl ether to afford **4** as a crystalline yellow solid (0.84 g, 1.47 mmol, 92% yield). Anal. Calc. for $C_{22}H_{36}Cl_2O_3Si_2Ti_2$: C, 46.25; H, 6.36. Found: C, 46.31; H, 6.75%. 1H -NMR ($CDCl_3$): δ 0.44, 0.55 (s, 2×6 H, SiMe₂); 1.92, 2.00, 2.17, 2.33 (s, 4×6 H, C₅Me₄). ^{13}C -NMR ($CDCl_3$): δ 3.0, 4.7 (SiMe₂); 12.1, 12.5, 15.3, 15.6 (C₅Me₄); 128.9, 133.1, 133.7, 134.4, 135.9 (C₅Me₄).

4.5. Synthesis of $Ti(\eta^5-C_5Me_4SiMe_3)Me_3$ (**5**)

3.63 ml of a 3 M solution of MgClMe (10.88 mmol) in THF was injected into a solution of $Ti(\eta^5-C_5Me_4SiMe_2Cl)Cl_3$ (1 g, 2.72 mmol) in 50 ml of diethyl ether at $-78^\circ C$. The cooling bath was removed and the reaction mixture was allowed to warm to r.t. and stirred for 2 h. After filtration, the solvent was pumped off and the residue extracted into hexane (2×10 ml). The filtrate was concentrated and left to crystallise at $-40^\circ C$ to give **5** as a yellow oily solid (0.5 g, 1.75 mmol, 64% yield). Anal. Calc. for $C_{15}H_{30}SiTi$: C, 62.91; H, 10.56. Found: C, 62.50; H, 10.69. 1H -NMR (C_6D_6): δ 0.24 (s, 9H, SiMe₃); 1.14 (s, 9H, TiMe); 1.68, 1.95 (s, 2×6 H, C₅Me₄). ^{13}C -NMR (C_6D_6): δ 1.9 (SiMe₃); 12.1, 15.1 (C₅Me₄); 62.6 (TiMe); C₅Me₄ overlap by C_6D_6 signal.

4.6. Synthesis of $Ti[(\eta^5-C_5Me_4SiMe_2(CH_2Ph)](CH_2Ph)_3$ (**6**)

5.44 ml of a 2 M solution of MgClBz (10.9 mmol) in THF was injected into a solution of $Ti(\eta^5-C_5Me_4SiMe_2Cl)Cl_3$ (1 g, 2.72 mmol) in 50 ml of hexane at

$-78^\circ C$. The cooling bath was removed and the reaction mixture was allowed to warm to r.t. and stirred for 2 h. After filtration, the solvent was removed, and the dark oily residue extracted into hexane. The solvent was completely removed to give **6** as a red oil (0.9 g, 1.52 mmol, 56% yield). Anal. Calc. for $C_{39}H_{46}SiTi$: C, 79.30; H 7.86. Found: C, 79.0; H, 8.01%. 1H -NMR (C_6D_6): δ 0.26 (s, 6 H, SiMe₂); 1.51, 1.83 (s, 2×6 H, C₅Me₄); 2.22 (s, 2 H, SiCH₂Ph); 2.89 (s, 6H, TiCH₂Ph); 6.6–7.2 (m, 20H, Ph). ^{13}C -NMR (C_6D_6): δ -0.5 (SiMe₂); 11.9, 15.4 (C₅Me₄); 27.6 (SiCH₂Ph); 96.6 (TiCH₂Ph); 122–130 (Ph and C₅Me₄); 139.6, 150.5 (C_{ipso} , PhCH₂Si and PhCH₂Ti).

4.7. Synthesis of $Ti[(\eta^5-C_5Me_4SiMe_2(CH_2SiMe_3)]Cl(CH_2SiMe_3)_2$ (**7**)

Compound **7** was prepared from $Ti(\eta^5-C_5Me_4SiMe_2Cl)Cl_3$ (1 g, 2.72 mmol) following the method given for **5**, using 11 ml of a 1 M solution of MgCl(CH₂SiMe₃) in THF, and obtained as a yellow oil (1.07 g, 2.04 mmol, 75% yield). Anal. Calc. for $C_{23}H_{51}ClSi_4Ti$: C 52.7; H, 9.84. Found: C, 52.45; H, 9.72%. 1H -NMR (C_6D_6): δ -0.04 (s, 2H, SiCH₂SiMe₃); 0.02 (s, 9H, SiCH₂SiMe₃); 0.27 (s, 6H, SiMe₂); 0.34 (s, 18H, TiCH₂SiMe₃); 1.44, 1.92 (d, $J_{H-H} = 11.17$ Hz, 2×2 H, TiCH₂SiMe₃); 1.80, 2.07 (s, 2×6 H, C₅Me₄). ^{13}C -NMR (C_6D_6): 0.00 (SiCH₂SiMe₃); 1.4 (SiCH₂SiMe₃); 2.6 (TiCH₂SiMe₃); 2.8 (SiMe₂); 12.9, 16.3 (C₅Me₄); 91.9 (TiCH₂Si); 122.0, 130.3, 132.0 (C₅Me₄).

4.8. Synthesis of $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Me_2\}_2$ (**8**)

2.14 ml of a 3 M a solution of MgClMe (6.4 mmol) in THF was injected into a suspension of $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl_2\}_2$ (1 g, 1.60 mmol) in 50 ml of hexane at $-78^\circ C$. The reaction mixture was allowed to warm to r.t. and stirred for 3 h. After filtration, the solvent was evaporated in vacuo to yield a yellow solid. Recrystallisation from toluene/hexane gave **8** as a microcrystalline yellow solid (0.60 g, 1.1 mmol, 69% yield). Anal. Calc. for $C_{26}H_{48}O_2Si_2Ti_2$: C, 57.35; H, 8.9. Found: C, 56.90; H, 8.81%. 1H -NMR (C_6D_6): δ 0.54, 0.56 (s, 2×12 H, SiMe₂, TiMe); 1.94, 2.02 (s, 2×12 H, C₅Me₄). ^{13}C -NMR (C_6D_6): δ 0.7 (SiMe₂); 8.9, 11.5 (C₅Me₄); 49.6 (TiMe); C₅Me₄ overlap by C_6D_6 signals.

4.9. Synthesis of $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2O-\kappa O)]Cl(CH_2Ph)\}_2$ (**9**)

A suspension of **3** (1 g, 1.6 mmol) in hexane (50 ml) was cooled to $-78^\circ C$ and treated drop wise with a solution of MgBz₂·2THF (1.13 g, 3.2 mmol) in 30 ml of toluene. The reaction mixture was warmed to r.t. and stirred for 3 h. After filtration, volatiles were removed

under vacuum and the brownish solid was extracted into hexane. The red filtrate was concentrated and cooled at $-20\text{ }^{\circ}\text{C}$ to afford **9** as a brownish-red solid (0.5 g, 0.68 mmol, 43%). Anal. Calc. for $\text{C}_{36}\text{H}_{50}\text{Cl}_2\text{O}_2\text{Si}_2\text{Ti}_2$: C, 58.61; H, 6.84. Found: C, 56.37; H, 6.38%. The isolated solid consisted mainly of **9**, but it contained a small irremovable amount of MgCl_2 which prevented us from obtaining a correct elemental analysis, although satisfactory spectroscopy data were obtained. $^1\text{H-NMR}$ (C_6D_6): (mixture of diastereomers) δ 0.16, 0.18, 0.26 (s, 6, 6, 12H, SiMe); 1.82, 1.84, 1.89, 1.92, 1.94, 1.95, 1.96, 2.08 (s, $8 \times 6\text{H}$, C_5Me_4); 1.88, 2.25 (d, $J_{\text{H-H}} = 10.8\text{ Hz}$, $2 \times 2\text{H}$, TiCH_2Ph); 2.37, 2.47 (d, $J_{\text{H-H}} = 11.1\text{ Hz}$, $2 \times 2\text{H}$, TiCH_2Ph); 6.9, 7.20 (m, 12H, 8H, TiCH_2Ph). $^{13}\text{C-NMR}$ (C_6D_6): δ 2.3, 3.8, 4.1 (SiMe); 11.9, 12.0, 12.2, 12.4, 15.2, 15.4, 15.5, 16.0 (C_5Me_4); 85.4, 88.0 (TiCH_2Ph); 149.4, 151.0 ($\text{C}_{\text{ipso-PhCH}_2\text{Ti}}$); C_5Me_4 and PhCH_2Ti resonances overlap by C_6D_6 signals.

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