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Preparation of Ti(IV), Zr(IV) and Sn(IV) metal alkyls containing the $(\text{Pr}^i\text{O})_3\text{SiCH}_2$ fragment

Daniele Cauzzi*, Claudia Graiff, Marianna Marazzi, Giovanni Predieri,
Antonio Tiripicchio

Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Parco Area delle Scienze 17A, Università di Parma, I-43100 Parma, Italy

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract

By reaction of RMgCl ($\text{R} = (\text{Pr}^i\text{O})_3\text{SiCH}_2$) with Cp_2TiCl_2 , Cp_2ZrCl_2 and SnCl_4 , the stable metal alkyls Cp_2TiClR (**1**), Cp_2TiR_2 , Cp_2ZrR_2 and SnR_4 were obtained in high yield and characterized. The reactivity of **1** towards $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (as Cl abstractor) was investigated and compared to previously reported cases. Cp_2TiF_2 was obtained quantitatively. By reaction of **1** with $\text{NaCo}(\text{CO})_4$ the compound $\text{Cp}_2\text{RTi-O-TiClCp}_2$ (**2**) was separated in very low yield. The crystal structures of **1** and **2** were also determined by X-ray diffraction methods.

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1. Introduction

The use of soluble molecular precursors is a very efficient method to obtain well characterized (homogeneous or nanostructured) materials possessing useful properties, the science of organic polymers being the prototype of this approach. For this reason the use of soluble precursors has become one of the routes to obtain also inorganic (oxides) and hybrid inorganic–organic (I–O) materials (e.g. organically functionalized siloxanes) with peculiar characteristics [1]. Beginning from the 50s, hybrid I–O materials are entering the marketplace, finding commercial applications thanks to their unique properties [2].

Most of these materials contain a (mixed) metal oxide structure. The M–O–M linkage can be formed (starting from soluble molecular precursors) using different techniques, the most important being the sol–gel method [3], the non-hydrolytic condensation [4] and

also the thermal decomposition of multi- or single-source molecular precursors [5].

Mixed metal oxides and hybrid materials are often used in heterogeneous and supported-metal catalysis [6]. In the case of heterogeneous catalysis the starting compounds should contain only metal and carbon atoms, in order to have halogen, phosphorus and nitrogen free surfaces. Metal alkyls possess this requisite, but should also contain oxygen atoms along with other elements (e.g. Si) able to build the oxide structure. For instance, if a silica xerogel obtained by sol–gel method is the desired support, metal alkyls should have a metal–carbon bond stable at room temperature and inert towards hydrolysis and contain a siloxane moiety (e.g. $-\text{CH}_2\text{Si}(\text{OR})_3$) [7].

In this paper we report the preparation and the characterization of M(IV) alkyls that could be used for this scope: Cp_2TiClR (**1**), Cp_2TiR_2 , Cp_2ZrR_2 and SnR_4 ($\text{R} = (\text{Pr}^i\text{O})_3\text{SiCH}_2$). These compounds, obtained easily in very high yield and in grams quantity, are very stable at room temperature and contain the $-\text{CH}_2\text{Si}(\text{OPr}^i)_3$ functional group which could be suitable for sol–gel and non-hydrolytic processes [4].

* Corresponding author

E-mail address: cauzzi@unipr.it (D. Cauzzi).

2. Experimental

2.1. Methods and reagents

The solvents were reagent grade and were distilled and dried using standard techniques. The reactions were performed under nitrogen using Schlenk glassware and a standard vacuum line. FTIR spectra were registered using a Nicolet 5PC or Nexus spectrometers. ^1H -, ^{13}C -, ^{29}Si -, ^{119}Sn - and ^{19}F -NMR were recorded on AC100, AC300 and CXP200 Bruker instruments. CHN elemental analyses were performed with a Carlo–Erba EA 1108 automated analyzer. All reagents were pure commercial products except $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ which was prepared as reported in the literature [8].

2.2. Preparation of RMgCl ($R = (\text{Pr}^i\text{O})_3\text{SiCH}_2$)

The procedure for the preparation of the Grignard is the one reported in the literature [9]. $(\text{Pr}^i\text{O})_3\text{SiCH}_2\text{Cl}$ was prepared by alcoholysis of $\text{Cl}_3\text{SiCH}_2\text{Cl}$ in Pr^iOH . When preparing Cp_2TiClR (**1**), Mg was activated with 1,2-dichloroethane in order to avoid the introduction of bromide or iodide anions which do cause halogen scrambling in the final compounds, giving mixtures of Cp_2TiClR and Cp_2TiXR ($X = \text{I}, \text{Br}$). The THF solution of the Grignard was used freshly made and filtered through a cannula.

2.3. Preparation of Cp_2TiClR (**1**)

Cp_2TiCl_2 (5 g, 20 mmol) was dissolved in 100 ml of THF. The dark red solution was cooled to 0 °C and added of 6 g (ca. 5% excess on the 1:1 molar ratio) of RMgCl in 25 ml of THF. The mixture was stirred for 4 h and the colour changed to orange–yellow while a white precipitate formed. The solvent was evaporated under vacuum and the residue extracted and decanted four times with 25 ml of C_6H_{14} . The extracted solution was filtered on celite. The C_6H_{14} was evaporated until a little turbidity appeared and the vessel was kept at –20 °C for 1 day. A crystalline solid formed and was isolated by filtration. Yield: 91%.

M.p. (°C): 82.5, without decomposition.

IR (cm^{-1} , solid, KBr pellet): 3116w, 3094w, 2966s, 2927m, 2891m, 2876m, 1464w, 1448m, 1380s, 1367s, 1354m, 1175s, 1136s, 1120s, 1041vs, 1019vs, 920m, 903m, 864m, 846m, 821s, 779m, 750m.

^1H -NMR (δ , 300 MHz, CDCl_3): 6.4 s (10H, Cp); 4.1 sep (3H, J 6 Hz, $\text{CH}(\text{CH}_3)_3$); 1.8 s (2H, CH_2); 1.2 d (18H, J 6 Hz, $\text{CH}(\text{CH}_3)_3$).

Anal. Calc. for $\text{C}_{20}\text{H}_{33}\text{ClO}_3\text{SiTi}$: C, 55.49; H, 7.68. Found: C, 54.99; H, 7.75%.

2.4. Preparation of Cp_2TiR_2

Cp_2TiCl_2 (3 g, 12 mmol) was dissolved in 80 ml of THF. The dark red solution was cooled to 0 °C and added of 9.2 g (ca. 40% molar excess) of RMgCl in 60 ml of THF. The solution was allowed to reach room temperature (r.t.) and stirred. The colour changed to orange–yellow while a white precipitate formed. The completion of the reaction was monitored by NMR until the complete disappearance of the Cp_2TiCl_2 and Cp_2TiRCl singlets at 6.58 and 6.40 (few ml of the solution were dried, the residue dissolved in 2 ml of CDCl_3 and then filtered with cotton directly into the NMR tube, by using a Pasteur pipette). The THF was then evaporated under vacuum and the solid extracted with C_6H_{14} . The extracted solution was filtered on celite and dried, giving a viscous deep yellow liquid. Yield: 70%.

Anal. Calc. for $\text{C}_{30}\text{H}_{56}\text{O}_6\text{Si}_2\text{Ti}$: C, 58.42; H, 9.15. Found: C, 58.92; H, 9.27%.

^1H -NMR (δ , 100 MHz, CDCl_3): 6.27 s (10H, Cp); 4.12 sep (6H, J 6 Hz, $\text{CH}(\text{CH}_3)_3$); 1.19 d (36H, J 6 Hz, $\text{CH}(\text{CH}_3)_3$), 0.54 s (4H, CH_2).

2.5. Preparation of Cp_2ZrR_2

Cp_2ZrCl_2 (0.6 g, 2.05 mmol) was dissolved in 50 ml of THF. The solution was cooled to 0 °C and added of 1.12 g (4 mmol) of RMgCl in 30 ml of THF. The solution was allowed to reach r.t. and stirred for 7 h. The THF was then evaporated under vacuum and the solid extracted with 3/4 portions of C_6H_{14} . The extracted solutions were filtered on celite and dried, giving a white solid. Yield: 85%.

^1H -NMR (δ , 100 MHz, CDCl_3): 6.3 s (10H, Cp); 4.18 sep (6H, J 6 Hz, $\text{CH}(\text{CH}_3)_3$); 1.18 d (36H, J 6 Hz, $\text{CH}(\text{CH}_3)_3$), 0.11 s (4H, CH_2).

Anal. Calc. for $\text{C}_{30}\text{H}_{56}\text{O}_6\text{Si}_2\text{Zr}$: C, 54.58; H, 8.55. Found: C, 53.92; H, 8.75%.

2.6. Preparation of SnR_4

SnCl_4 (10 g, 38.38 mmol) was mixed with 250 ml of cool THF. A white precipitate of THF solvate formed and slowly redissolved. The colourless solution was cooled to 0 °C and added of 44.67 g of RMgCl (ca. 4% molar excess) in 250 ml of THF. The solution was stirred at r.t. for 4 days during which a white precipitate formed. The THF was evaporated under vacuum and the solid extracted with 4/5 portions of C_6H_{14} . The extracted solutions were filtered on celite and dried to give a waxy white solid. Yield: 75%.

^1H -NMR (δ ppm, 300 MHz, CDCl_3): 4.18 sep (12H, J 6 Hz $\text{CH}(\text{CH}_3)_2$); 1.15 d (72H, J 6 Hz $\text{CH}(\text{CH}_3)_2$); 0.12 s (8H, satellites: $^2J(^1\text{H}^{119}\text{Sn})$ 37.8, $^2J(^1\text{H}^{117}\text{Sn})$ 39.3 Hz, CH_2).

^{13}C -NMR (δ ppm, 75 MHz, CDCl_3): 64.4 $\text{CH}(\text{CH}_3)_2$; 25.7 $\text{CH}(\text{CH}_3)_2$; -8.6 CH_2 satellites: $J(^{13}\text{C}-^{119}\text{Sn})$ 116, $J(^{13}\text{C}-^{117}\text{Sn})$ 122 Hz. $^{119}\text{Sn}\{\text{H}\}$ -NMR (δ ppm, 74.5 MHz, CDCl_3): 34 s.

^{119}Sn -NMR (δ ppm, 74.5 MHz, CDCl_3): 34 non $J(^{119}\text{Sn}-^1\text{H})$ 77 Hz. ^{29}Si (δ ppm, 39.7 MHz, CDCl_3): -49.5 s.

Anal. Calc. for $\text{C}_{40}\text{H}_{92}\text{O}_{12}\text{Si}_4\text{Sn}$: C, 48.22; H, 9.31. Found: C, 48.87; H, 9.81%.

2.7. Reaction of Cp_2TiClR with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$

In a Schlenk vessel, 0.3 g (0.69 mmol) of Cp_2TiClR and 0.26 g (0.7 mmol) of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ were degassed and dissolved in 20 ml of CHCl_3 . The mixture was stirred for 3 h and the orange solution changed to yellow with the simultaneous formation of a white precipitate. The solution was dried in vacuum and the vapours collected in a liquid nitrogen trap (in order to collect ^1H -NMR of the condensed liquid, the reaction was repeated using smaller quantities in CDCl_3). The residue was extracted with CHCl_3 and filtered, giving a yellow solution and a white solid with purple nuances. The solution was filtered and dried. The white residue was characterized as CuCl . The yellow solution was dried under vacuum and the yellow solid characterized as pure Cp_2TiF_2 in quantitative yield.

Yellow solid (Cp_2TiF_2): ^1H -NMR (δ ppm, 300 MHz, CDCl_3): 6.44 s. ^{19}F -NMR (δ ppm, 188.3 MHz, CHCl_3): -133 . IR (KBr pellets, cm^{-1}): 3111w, 1444w, 1017w, 824m, 565s, 541m.

Anal. Calc. for $\text{C}_{10}\text{H}_{10}\text{F}_2\text{Ti}$: C, 55.60; H, 4.66. Found: C, 55.37; H, 4.48%.

Condensed liquid: ^1H -NMR (δ ppm, 300 MHz, CDCl_3): 4.9 m, 1.9 s, 1.2 d, 1.5 m. ^{31}P -NMR (δ ppm, 81 MHz, CHCl_3): -3 , -15 , -20 , -21.5 , -33 .

2.8. Reaction of Cp_2TiClR with $\text{NaCo}(\text{CO})_4$

In a Schlenk vessel, excess of Hg-Na amalgam was prepared, added of 40 ml of THF and then of 0.1 g (0.29 mmol) of $\text{Co}_2(\text{CO})_8$. The mixture was vigorously stirred for 1 h at r.t.. In a second vessel, 0.25 g (0.58 mmol) of Cp_2TiClR were dissolved in 20 ml of THF and added of the metalate solution filtered through a cannula. The solution was stirred at r.t. for 2 h and the yellow–orange colour changed to red–brown. The solvent was evaporated under vacuum and the solid extracted with 3/4 portions of C_6H_{14} . The extracted solutions were filtered on celite and dried giving a dark red solid. The residual dark green solid, containing also NaCl , was not characterized due to its instability. The red soluble solid was redissolved in a small quantity of THF and left for 1 month at -20 °C. Orange crystals of **2** separated from the solution in very low yield.

Red extract: ^1H -NMR (δ ppm, 300 MHz, CDCl_3): 6.42 s, 6.17 s, 6.15 s d, 4.26 m, 1.24 m.

Green residue: ^1H -NMR (δ ppm, 300 MHz, CDCl_3): 6.27, 4.24, 1.22 (very large peaks).

Crystals of **2**: IR (KBr pellets, cm^{-1}): 3113w, 2969m, 2927w, 2865w, 1441w, 1380m, 1367m, 1173m, 1121s, 1020vs, 809s, 744s, 702vs, 595m.

2.9. X-ray data collection, structure solution and refinement for compounds **1** and **2**

The intensity data of compounds **1** and **2** were collected at 173 K on a Enraf–Nonius CAD4 and at 298 K on a Philips PW1100 single crystal diffractometer, respectively. Crystallographic and experimental details for both structures are summarized in Table 1.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) [10] with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms.

Table 1
Crystal data and structure refinement for compounds **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{20}\text{H}_{33}\text{ClO}_3\text{SiTi}$	$\text{C}_{30}\text{H}_{43}\text{ClO}_4\text{SiTi}_2$
Formula weight	432.90	626.98
Temperature (K)	173(1)	298(1)
Wavelength (Å)	1.54184 (Cu– K_α)	0.71073 (Mo– K_α)
Crystal system	Monoclinic	Monoclinic
Space group	<i>Cc</i>	<i>C2/c</i>
Unit cell dimensions		
<i>a</i> (Å)	14.762(4)	45.083(5)
<i>b</i> (Å)	18.866(5)	8.485(3)
<i>c</i> (Å)	8.211(3)	18.454(4)
β (°)	95.83(3)	113.90(3)
<i>V</i> (Å ³)	2275(1)	6454(3)
<i>Z</i>	4	8
<i>D</i> _{calc} (mg m ⁻³)	1.264	1.291
Absolute coefficient (cm ⁻¹)	48.95	6.46
<i>F</i> (000)	920	2640
Crystal size (mm)	0.18 × 0.32 × 0.37	0.22 × 0.13 × 0.22
θ Range (°)	3.81–69.94	3.30–30.01
Reflections collected	2292	18 197
Independent reflections	2292	9396
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	2258	4676
Max/min transmission factor	1.000, 0.5369	1.000, 0.5585
Data/restraints/parameters	2292/2/244	9396/0/350
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	$R_1 = 0.0697$, $wR_2 = 0.2048$	$R_1 = 0.0465$, $wR_2 = 0.1111$
<i>R</i> indices (all data)	$R_1 = 0.0706$, $wR_2 = 0.2072$	$R_1 = 0.1046$, $wR_2 = 0.1305$
Absolute structure factor	0.088(18)	–

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \frac{[\sum [w(F_c^2 - F_o^2)^2]]^{1/2}}{[\sum w(F_o^2)^2]^{1/2}}$$

The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2 F_o^2(0.1435P)^2 + 10.5476]$ (1), $w = 1/[\sigma^2 F_o^2 + (0.0687)^2]$ (2), where $P = (F_o^2 + 2F_c^2)/3$, was used.

All calculations were carried out on the DIGITAL AlphaStation 255 computers.

3. Discussion

3.1. Preparation and characterization of metal alkyls

The Grignard reagent prepared from RCl is suitable to obtain stable metal alkyls. Once formed, it cannot react with itself, by nucleophilic attack on the Si atom, because of steric hindrance, and it is stable in THF solution [9]. In fact, when analogous trichloro or triethoxy compounds are used, polymeric branched silanes are obtained [11]. For the same reason and the absence of β hydrogens the prepared alkyls are very stable at room temperature.

By reaction with Cp_2TiCl_2 in THF, mono- or disubstitution is easily obtained. The compounds Cp_2TiRCl (1) and Cp_2TiR_2 are, respectively an orange solid and a deep orange liquid and can be obtained in good yields, the first using a 1:1 ratio, the second using an excess of Grignard and longer reaction times. The structure of 1 has been determined by X-ray diffraction methods. No interaction between Ti and O atoms was found in the solid-state and also in CDCl_3 solution at -60°C , as proton NMR did not show any kind of splitting in the methinic CH of the Pr^i group that could suggest the presence of such interaction [12]. By heating 1 in the air, its melting point is reached without decomposition at 82.5°C .

Similarly, by reaction with Cp_2ZrCl_2 , Cp_2ZrR_2 has been prepared. Tentatives of preparing the pure mono-substituted Cp_2ZrClR , using a 1:1 ratio, failed and a mixture of starting reagent, mono- and disubstituted products was always obtained.

By reacting RMgCl with SnCl_4 the compound SnR_4 was obtained as a white wax, in one passage in good yield, although long reaction times were required (up to 4 days, depending on the quantity of reagent). Less substituted compounds obtained with shorter reaction times, are liquids and have not been isolated. This compound has been characterized by multinuclear (^1H , ^{13}C , ^{119}Sn , ^{29}Si)-NMR and the presence of a nonet in the Sn spectra confirms the complete tetra substitution.

Similar compounds of Ti, Zr and Hf were previously reported, and some of them structurally characterized, using the $-\text{CH}_2\text{SiMe}_3$ [13], $-\text{CH}_2\text{SiMe}_2\text{OSiMe}_3$ [14] and $-\text{CH}_2\text{SiMe}_2(\text{OR})$ [15] substituents but, to our knowledge, none with a $-\text{CH}_2\text{Si}(\text{OR})_3$ siloxane group.

In the case of tin, mono- and disubstituted alkyl ($-\text{CH}_2\text{Si}(\text{OR})_3$, R = Me, Et) compounds were prepared [16].

3.2. Reactivity of Cp_2TiRCl versus Cl abstraction

The reactivity of the compound $\text{Cp}_2\text{TiCl}\{\text{CH}_2\text{Si}(\text{Me}_2)\text{O}^i\text{Bu}^t\}$ towards Cl abstraction with Ag^+ salts, with the aim of obtaining a Si–O–Ti bond formation, has been investigated and reported in the literature [15]. By reacting with Ag^+ salts in diethyl ether, it was found that: (a) AgBF_4 leads to decomposition and substitution of the O^iBu^t group on Si by a F atom; (b) AgCF_3SO_3 leads to the formation of a Si–O–Si linkage by elimination of C_4H_8 ; (c) AgCF_3CO_2 leads to the formation of $\text{Cp}_2\text{Ti}\{\text{CH}_2\text{Si}(\text{Me}_2)\text{O}^i\text{Bu}^t\}\text{CF}_3\text{CO}_2$ where the trifluoroacetate is coordinated by the Ti atom. We wanted to see if 1 could react in similar ways using Cu^+ instead of Ag^+ and if the presence of three –OR groups could afford the stabilization of the cation. By reacting Cp_2TiClR with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ in the non-coordinating chloroform solvent, a white precipitate and a yellow solution were obtained. The dried solution gave a yellow solid product, which was characterized as Cp_2TiF_2 by ^1H -, ^{19}F -NMR, FTIR and elemental analysis. The proton chemical shift of the Cp group is identical to the one reported in the literature [17]. The fluorine chemical shift was found at -133.4 ppm with respect to CFCl_3 . The formation of a Ti–O–Ti bond was excluded by the absence of the typical strong band at ca. 720 cm^{-1} [18]. In this case the fluoride ion attacked directly and quantitatively the Ti atom. In the evaporated solution phosphorus species were found by NMR, but not characterized. Also, the alkyl fragment was found in the same solution. The same reaction took place when reacting $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ with a sample of $\text{Cp}_2\text{TiClCH}_2\text{SiMe}_3$ prepared and reacted in the same manner as 1, starting from $\text{ClCH}_2\text{SiMe}_3$. We can conclude that this reactivity is independent on the presence of oxygen atoms.

Moreover, we reacted Cp_2TiRCl with the nucleophilic carbonylmetalate species $\text{NaFe}(\text{CO})_2\text{Cp}$ and $\text{NaCo}(\text{CO})_4$ that were also used with the hope of substituting the Cl atom to obtain binuclear Ti–Co or Ti–Fe compounds, but none was isolated. In particular, by reacting Cp_2TiRCl with $\text{NaCo}(\text{CO})_4$ two main fractions were obtained in low yield, together with unreacted Cp_2TiRCl . From the crude reaction residue, by extracting with hexane, a red–orange solid separated. Its ^1H -NMR showed the presence of three Cp resonances, one assigned to unreacted Cp_2TiClR and other two minor peaks of equal integral area at 6.17 and 6.15 ppm. By crystallization from a concentrated THF solution, crystals of $\text{Cp}_2\text{RTi–O–TiClCp}_2$ (2) were obtained in very low yield. In the non-soluble green fraction, which

contained NaCl, Co was present, but no stable compounds could be isolated.

Compound **2** was characterized by FTIR in which the presence of a Ti–O–Ti group was evidenced from the very strong band at 702 cm^{-1} ; moreover its structure was fully elucidated by X-ray diffraction. To our knowledge (searching in the Cambridge crystallographic data base) **2** is the first asymmetric compound of the kind $\text{Cp}_2\text{XM–O–MRCp}_2$, where $\text{M} = \text{Ti, Zr, Hf}$, $\text{X} = \text{F, Cl, Br, I}$, $\text{R} = \text{alkyl fragment}$. The carbonylmetalate $\text{NaFe}(\text{CO})_2\text{Cp}$ did not show any reactivity towards Cp_2TiClR . Compound **2** can derive from the decomposition or hydrolysis of an unstable intermediate obtained by nucleophilic attack of the metalate on the Ti atom.

From our tentative and those made by other groups [15] of abstracting the Cl atom from compounds containing the $\text{Cp}_2\text{TiClCH}_2\text{Si–OR}$ moiety, these remarks can be pointed out: non-coordinating counterions with mobile fluorides (BF_4^- and PF_6^-) tend to react with Ti or Si. Once the cation is formed after the precipitation of MX ($\text{M} = \text{Ag or Cu}$), it decomposes or by reaction of F^- with Si or by reaction with Ti. When a coordinating anion is used, the cation is stable enough to be isolated. If a non-coordinating anion is present, then a coordinating solvent can occupy the vacant coordination site. In the literature $[(\text{C}_5\text{Me}_5)_2\text{Zr}(\text{THF})\text{CH}_2\text{SiMe}_3][\text{BPh}_4]$ was prepared by protonation of the 1-sila-3-metallacyclobutane $(\text{C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_2\text{SiMe}_2\text{CH}_2)$ with $[\text{Bu}_3\text{NH}][\text{BPh}_4]$ in THF [19] and tentative of isolating a THF-free cation failed. Last, the formation of Si–O–Si or Ti–O–Ti bonds can be induced by elimination of the alkoxy or alkyl groups bound, respectively to Si or Ti atoms. A general reaction pathway is difficult to propose with such reactivity. We can just conclude that the oxygen(s) bound to the Si atom seems not able to stabilize the formed cation through a Si–O–Ti interaction.

3.3. Crystal structure determination of compounds **1** and **2**

The molecular structure of compound **1** is shown in Fig. 1. Selected bond distances and angles are given in Table 2.

The Ti atom exhibits a distorted tetrahedral coordination, involving the Cl1 atom, the C10 carbon atom of the $\text{CH}_2\text{Si}(\text{OPr}^t)_3$ group and the centroids of the two η^5 -coordinated cyclopentadienyl ligands. The Ti1–C10 bond distance, $2.167(8)\text{ \AA}$, is shorter than those generally found with sp^3 -hybridized carbon atoms as in $(\eta^5\text{-C}_9\text{H}_7)_2\text{TiMe}_2$ [$2.21(2)\text{ \AA}$] [20] and in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_2\text{Ph})_2$ [$2.239(6), 2.210(5)\text{ \AA}$] [21], but it is well comparable with that found in the analogous compound $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiClCH}_2\text{SiMe}_3$ [$2.166(3)\text{ \AA}$] [22]. The O3, Si1, C10, Ti1, Cl1 atoms are nearly coplanar

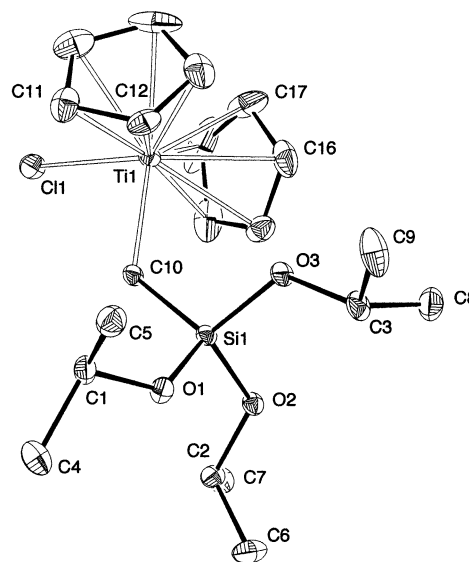


Fig. 1. Perspective view of the complex **1** with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

Table 2
Selected bond lengths (\AA) and angles ($^\circ$) for **1**

Bond lengths			
Ti(1)–Cl(1)	2.368(3)	Si(1)–O(3)	1.636(6)
Ti(1)–C(10)	2.167(8)	Si(1)–C(10)	1.831(7)
Ti(1)–CE(1)	2.090(8)	O(1)–C(1)	1.428(11)
Ti(1)–CE(2)	2.077(8)	O(2)–C(2)	1.442(10)
Si(1)–O(1)	1.635(6)	O(3)–C(3)	1.451(10)
Si(1)–O(2)	1.639(6)		
Bond angles			
C(10)–Ti(1)–CE(1)	104.7(1)	O(2)–Si(1)–O(3)	105.4(3)
C(10)–Ti(1)–CE(2)	104.9(2)	O(1)–Si(1)–C(10)	113.6(3)
C(10)–Ti(1)–Cl(1)	92.9(2)	O(2)–Si(1)–C(10)	111.8(3)
Cl(1)–Ti(1)–CE(1)	106.6(1)	O(3)–Si(1)–C(10)	110.1(3)
Cl(1)–Ti(1)–CE(2)	107.6(1)	C(1)–O(1)–Si(1)	129.5(5)
CE(1)–Ti(1)–CE(2)	132.9(2)	C(2)–O(2)–Si(1)	121.9(5)
O(1)–Si(1)–O(2)	105.1(3)	C(3)–O(3)–Si(1)	123.0(5)
O(1)–Si(1)–O(3)	110.4(3)	Si(1)–C(10)–Ti(1)	127.9(4)

CE(1) and CE(2) are the centroid of the Cp rings defined by C11–C15 and C16–C20, respectively.

(maximum deviation from the mean plane defined by the five atoms for O3 $0.16(1)\text{ \AA}$) and the Si1–C10–Ti1 bond angle is $127.9(4)^\circ$ which is narrower than the one found in $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiClCH}_2\text{SiMe}_3$ ($136.9(1)^\circ$). This narrow angle and the coplanarity of the O3, Si1, C10, Ti1, Cl1 atoms allow the O3 to point towards Ti1 (the Ti1···O3 separation is of $3.75(1)\text{ \AA}$). The Ti1–Cl1, and the Ti1–M ($\text{M} = \text{centroid of the Cp ring}$) bond distances [$2.368(3), 2.090(8)$ and $2.077(8)\text{ \AA}$] are in good agreement with those found in other reported titanocene chloride complexes [23].

A view of the structure of compound **2** is shown in Fig. 2. Selected bond distances and angles are given in Table 3.

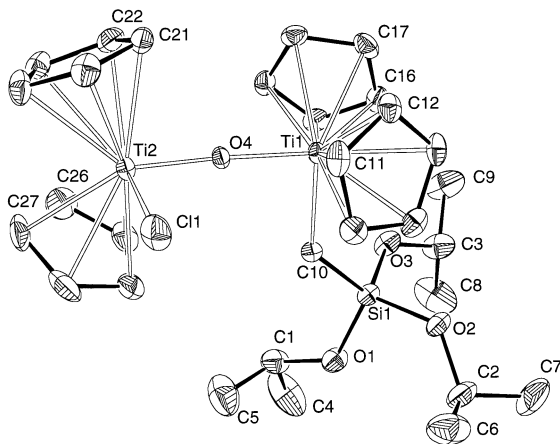


Fig. 2. Perspective view of the compound **2** with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Ti(2)–Cl(1)	2.429(1)	O(3)–C(3)	1.426(4)
Ti(1)–C(10)	2.214(2)	Si(1)–C(10)	1.833(2)
Ti(1)–CE(1)	2.091(8)	Si(1)–O(1)	1.643(2)
Ti(1)–CE(2)	2.100(7)	Si(1)–O(2)	1.628(2)
Ti(2)–CE(3)	2.114(8)	Si(1)–O(3)	1.633(2)
Ti(2)–CE(4)	2.102(8)	Ti(2)–O(4)	1.820(1)
O(1)–C(1)	1.432(4)	Ti(1)–O(4)	1.873(1)
O(2)–C(2)	1.441(4)		
Bond angles			
C(10)–Ti(1)–CE(1)	104.8(1)	O(2)–Si(1)–O(3)	108.80(11)
C(10)–Ti(1)–CE(2)	105.3(2)	O(2)–Si(1)–O(1)	103.33(10)
C(10)–Ti(1)–O(4)	94.10(8)	O(3)–Si(1)–O(1)	110.14(11)
O(4)–Ti(1)–CE(1)	108.1(1)	O(2)–Si(1)–C(10)	113.90(11)
O(4)–Ti(1)–CE(2)	108.5(1)	O(3)–Si(1)–C(10)	108.18(11)
M(1)–Ti(1)–CE(2)	129.9(2)	O(1)–Si(1)–C(10)	112.38(11)
O(4)–Ti(2)–CE(3)	109.3(1)	C(1)–O(1)–Si(1)	126.8(2)
O(4)–Ti(2)–CE(4)	107.4(1)	C(2)–O(2)–Si(1)	128.1(2)
O(4)–Ti(2)–Cl(1)	94.93(6)	C(3)–O(3)–Si(1)	128.7(2)
Cl(1)–Ti(2)–CE(3)	105.4(1)	Si(1)–C(10)–Ti(1)	135.01(13)
Cl(1)–Ti(2)–CE(4)	105.0(1)	Ti(2)–O(4)–Ti(1)	174.96(9)
CE(3)–Ti(2)–CE(4)	129.2(2)		

CE(1), CE(2), CE(3) and CE(4) are the centroid of the Cp rings defined by C11–C15, C16–C20, C21–C25 and C26–C30 atoms, respectively.

The two Ti atoms are slightly asymmetrically bridged by the O4 atom, the Ti1–O4 and Ti2–O4 bond distances being of 1.820(1) and 1.873(1) Å. Both Ti atoms exhibit distorted tetrahedral coordinations, involving the centroids of the two η^5 -coordinated cyclopentadienyl ligands and the μ -O4 atom, the coordination being completed by the C11 atom for Ti1 and by the C10 atom of the $\text{CH}_2\text{Si}(\text{OPr}^i)_3$ group for Ti2. The Ti1–C10 bond distance of 2.214(2) Å is in good agreement with the bond lengths involving sp^3 -hybridized carbon atoms [20,21] as well as the Ti–M (M = centroid of the Cp ring) bond distances [2.091(8),

2.100(7), 2.114(8) and 2.102(8) Å] are comparable with those found in other reported titanocene chloride complexes [23]. The dihedral angle between the mean planes defined by C11, Ti2, O4, Ti1 and Ti2, O4, Ti1, C10 is 87.36(5)°. The μ -oxo bridge is practically linear, the Ti1–O4–Ti2 bond angle being of 179.9(1)°, much larger than the ones observed in the related compound (μ -O)[Ti(C₅Me₅)(CH₂SiMe₃)₂]₂ (155.9(1)°) [24].

4. Conclusions

By reacting the Grignard reagent (Pr^iO)₃SiCH₂MgCl (RMgCl) with Cp₂MCl₂ (M = Ti, Zr) and SnCl₄, the stable metal alkyls Cp₂TiClR, Cp₂TiR₂, Cp₂ZrR₂ and SnR₄ were obtained in high yields. In particular, the reactivity of Cp₂TiClR towards Cl abstraction was investigated and by comparison with the results reported in literature it is possible to conclude that the reactivity is strongly dependent on the counterion of the Cl abstractor which can react with the newly formed cation, stabilizing it, or form Ti–O–Ti or Si–O–Si linkages. The molecular structures of two new Ti alkyls, compounds **1** and **2**, were determined by X-ray diffraction. The prepared metal alkyls are among the few containing a sol–gel processable Si(OR)₃ group. We plan to prepare xerogels and mixed metal-oxides by sol–gel process or direct non-hydrolytic condensation.

5. Supplementary material

The supplementary material for the structures includes the lists of atomic coordinates for the non-H atoms, of calculated coordinates for the hydrogen atoms, of anisotropic thermal parameters and complete lists of bond lengths and angles. The details of the crystal structure investigations are deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 188840–188841 for compounds **1** and **2**. Copies of this data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (int. code) +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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