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Preliminary communication

Synthesis of sandwich and half-sandwich complexes of Ti, Zr and Hf containing η^5-$C_5H_4SiMe_2Cl$ ligand. Molecular structure of $[TiCl_2(\mu\text{-}OSiMe_2\text{-}\eta^5\text{-}C_5H_4)]_2$

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Abstract

Reactions of $(C_5H_4SiMe_3)SiMe_2Cl$ (**1**) and $(\mu\text{-}SiMe_2C_5H_4)_2$ (**2**) with Ti, Zr and Hf tetrachlorides lead to the complexes $M(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ (M = Ti, **3a**; Zr, **3b**; Hf, **3c**). Treatment of **3a** with cyclopentadienyl thallium affords $Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_2$ (**4**). Dimeric oxo-derivative $[TiCl_2(\mu\text{-}OSiMe_2\text{-}\eta^5\text{-}C_5H_4)]_2$ (**5**) was prepared by slow hydrolysis of **3a**. Structure of **5** was determined by X-ray diffraction.

Keywords: Titanium; Zirconium; Hafnium; Silicon

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1. Introduction

Over the last few years a great number of early transition metal complexes containing functionalized cyclopentadienyl ligands have been prepared [1–7]. Most attention has been paid to ligands with π-donating groups (such as $CpPR_2$ [3], Cp_2PR [4], η^5-indenyl [5], $Cp\text{-}SiMe_2\text{-}C_5H_4\text{-}SnMe_2Cl$ [6], and so on) that can be modified easily just inside the transition metal complexes. However, there are only few examples of these complexes with substituents bearing an active halogen atom [7].

Electrophilic substitution in monosilylated cyclopentadienes is a well-known preparative method for half-sandwich complexes of Ti and Zr [8]. Here we report some reactions of disilylated cyclopentadienes **1** and **2** with MCl_4 (M = Ti, Zr, Hf) as an efficient synthetic route to $M(C_5H_4SiMe_2Cl)Cl_3$ and $M(C_5H_5)(C_5H_4SiMe_2Cl)Cl_2$ species.

2. Results and discussion

Compound $(C_5H_4SiMe_2Cl)SiMe_3$ (**1**) possesses two different Si–Cp bonds, these bonds can be attacked by various electrophilic reagents. Compound **1** could be expected to form two products under the action of $TiCl_4$ (Scheme 1); however, treatment of **1** with $TiCl_4$ (molar ratio 1:1) in toluene at 50°C produced the observable product **3a** exclusively [9] (shown by ^1H NMR spectroscopy of the reaction mixture [10]).

If pentane is employed as a solvent, complex **3a** is isolated by low temperature crystallization as a yellow moisture-sensitive powder in 90% yield. The extraordinary immobility of the $SiMe_2Cl$ group is of great importance for the following examination.

Compound **2** is an intramolecularly disilylated biscyclopentadiene with silicon atoms linked to the allyl and vinyl positions of the rings simultaneously [11]. It is suggested that consecutive cleavage of the Si–Cp bonds in **2** can lead to the mono- and bi-metallic products shown in Scheme 2. It should be noted that intermediate **6** contains a moeity similar in nature to **1**; so, cleavage of the RMe_2Si–Cp bond rather than that of $ClMe_2Si$–Cp is strongly preferred. Really, treatment of **2** with $TiCl_4$ (molar ratio 1:1) in toluene or pentane at 50–60°C affords **3a** in a good yield (76%), but this reaction requires significantly more time (5–10 h) than a similar reaction involving **1**.

The alternative products, structure **7** [12], **8** or **9**, were not observed under these conditions (^1H NMR spectroscopy data for the reaction mixtures). However,

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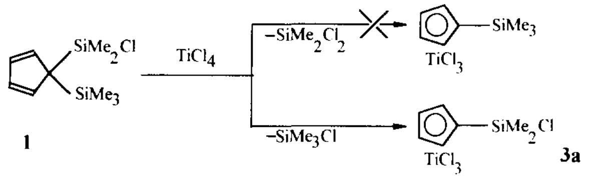
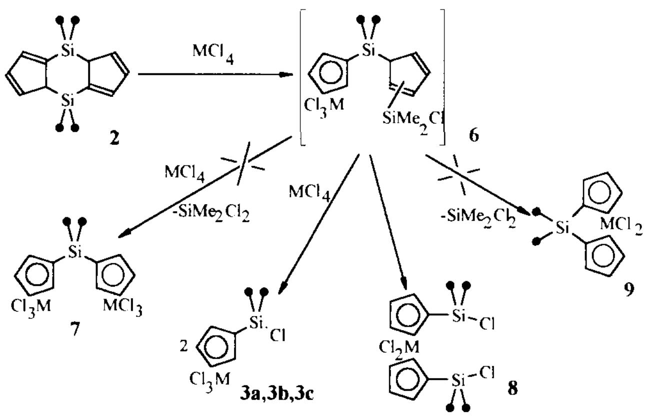


Scheme 1.



Scheme 2.

treatment of **2** with $ZrCl_4$ in warm toluene produces a mixture of **3b** [13] and $Zr(C_5H_4SiMe_2Cl)_2Cl_2$ (**8**) [14] in molar ratio 3:2. Complex **8** is the product of RMe_2Si–Cp bond cleavage; probably cleavage of intramolecular type. The different solubilities of **3b** and **8** in hot hexane allows the separation of **3b** as a colourless crystalline solid (45%). Analogous procedures using $HfCl_4$ produce **3c** [15] in 56% yield.

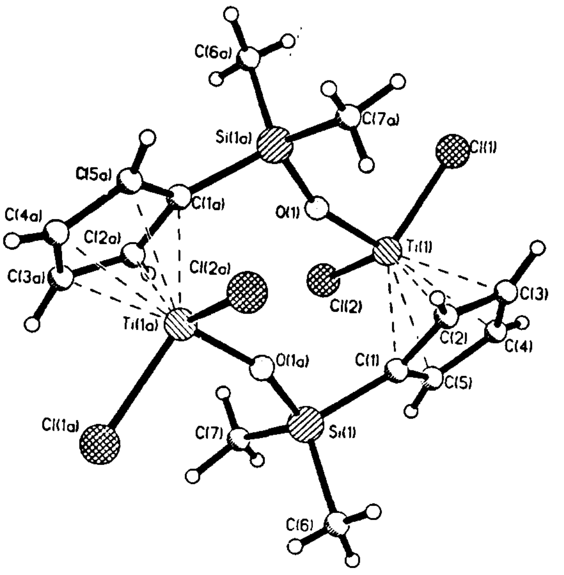


Fig. 1. Important bond lengths (Å) and angles (°) are Ti(1)–C(11) 2.256(1), Ti(1)–C(12) 2.238(1), Ti(1)–O(1) 1.771(2), Si(1)–C(1) 1.862(3), Si(1)–O(1a) 1.646(2), C(11)–Ti(1)–C(12) 101.48(4), C(11)–Ti(1)–O(1) 101.71(8), C(12)–Ti(1)–O(1) 103.90(8), C(1)–Si(1)–O(1a) 106.2(1), Ti(1)–O(1)–Si(1a) 159.9(2).

Complexes **3a–c** possess two types of element–halogen bond: metal–Cl and Si–Cl. The two types of bond show differing levels of reactivity with several nucleophiles. For example, the reaction of **3a** with C_5H_5Tl in THF at room temperature yields $Ti(C_5H_5)(C_5H_4SiMe_2Cl)Cl_2$ (**4**) [16] as brick-red crystalline powder (94%). However, moisture destroys both types of element–halogen bond: slow hydrolysis of a toluene solution of **3a** results in crystallization of the bi-metallic oxo-complex $[TiCl_2(\mu\text{-}OSiMe_2\text{-}\eta^5\text{-}C_5H_4)]_2$ (**5**). The structure of **5** was determined by X-ray diffraction (Fig. 1) [17].

3. Experimental details

All reactions were carried out in sealed evacuated Schlenk-type vessels. Solvents were dried by standard methods ^1H and ^{13}C NMR spectra were recorded on Varian VXR-300 and VXR-400 instruments at 30°C.

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[9] ^1H NMR (300 MHz, C_6D_6): δ 0.56 (s, 6H, Me), 6.20 (t, 2H, Cp), 6.59 (t, 2H, Cp). $^{13}C\{^1H\}$ NMR: δ 2.1 (Me), 126.5 (*C*(Cp)-H), 129.2 (*C*(Cp)-H), 134.8 (*C*(Cp)-Si).

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[13] ^1H NMR (300 MHz, C_6D_6): δ 0.70 (s, 6H, Me), 5.88 (t, 2H, Cp), 6.42 (t, 2H, Cp). $^{13}C\{^1H\}$ NMR: δ 3.0 (Me), 116.0 (*C*(Cp)-H), 126.2 (*C*(Cp)-H), 122.6 (*C*(Cp)-Si).

[14] ^1H NMR (400 MHz, THF-d_8): δ 0.82 (s, 12H, Me), 6.63 (t, 4H, Cp), 6.78 (t, 4H, Cp).

[15] ^1H NMR (300 MHz, PhMe-d_8): δ 0.47 (s, 6H, Me), 6.05 (t, 2H, Cp), 6.21 (t, 2H, Cp). $^{13}C\{^1H\}$ NMR: δ −2.0 (Me), 120.9 (*C*(Cp)-H), 123.9 (*C*(Cp)-H), 126.2 (*C*(Cp)-Si).

[16] ^1H NMR (300 MHz, THF-d_8): δ 0.77 (s, 6H, Me), 6.60 (s, 5H, Cp), 6.72 (t, 2H, Cp), 6.85 (t, 2H, Cp). $^{13}C\{^1H\}$ NMR: δ 3.3 (Me), 119.3 (*C*(Cp)-H), 121.0 (*C*(Cp)-H), 121.4 (*C*(Cp)-H), 129.4 (*C*(Cp)-Si).

[17] Enraf-Nonius CAD4 diffractometer (2θ-θ scan mode, graphite-monochromated MoKα radiation, $\lambda = 0.71069$ Å). Monoclinic, space group $P2_1/n$, $a = 9.447(7)$, $b = 10.920(2)$, $c = 10.494(3)$ Å, $\beta = 95.92(5)°$; $V = 1077.6(9)$ Å^3; $Z = 2$; $D_c = 1.584$ g cm^{-3}; $\mu = 1.35$ cm^{-1}; $2 < \theta < 36°$; $R(Rw) = 0.0321$ (0.0358) for 2249 reflections with $F > 2\sigma(F)$ (unique data: 2260). The structure was solved by direct method (SHELXS) and refined by full-matrix least squares. All non-hydrogen atoms were determined using a difference Fourier map and refined anisotropically. Detailed crystallographic results are available from the authors.