

# Synthesis of new chloro methyl niobium and tantalum complexes with silyl-cyclopentadienyl ligands: X-ray crystal structure of $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Cl}_2\text{Me}_2]$

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Received 30 November 2006; received in revised form 31 January 2007; accepted 31 January 2007

Available online 8 February 2007

## Abstract

Trichloro methyl  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiXMe}_2)(\text{SiMe}_3)\}\text{Cl}_3\text{Me}]$  ( $\text{X} = \text{Cl}$ , **2**;  $\text{Me}$ , **3**), dichloro dimethyl  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiXMe}_2)(\text{SiMe}_3)\}\text{Cl}_2\text{Me}_2]$  ( $\text{X} = \text{Cl}$ , **4**;  $\text{Me}$ , **5**) and tetramethyl  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiXMe}_2)(\text{SiMe}_3)\}\text{Me}_4]$  ( $\text{X} = \text{Me}$ , **6**;  $\text{Cl}$ , **7**) niobium complexes were synthesized by treatment of starting tetrachloro derivatives  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiXMe}_2)(\text{SiMe}_3)\}\text{Cl}_4]$  ( $\text{X} = \text{Cl}$ , **1a**;  $\text{Me}$ , **1b**) with dimethyl zinc or chloro methyl magnesium in different proportions and conditions. A mixture of trichloro methyl and dichloro dimethyl tantalum complexes  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Cl}_{4-x}\text{Me}_x]$  ( $x = 1$ , **8**;  $2$ , **9**) in a 2:1 molar ratio was obtained in the reaction of  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Cl}_4]$  (**1c**) with 0.5 equivalents of  $\text{ZnMe}_2$  in toluene at low temperature. **8** could be isolated as single compound when 1 equivalent of **1c** was added to the mixtures of **8** and **9**, while the reaction of **1c** with 1.5 equivalents of dimethyl zinc gave **9** as unitary product. However,  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Cl}_4]$  (**1d**) reacts with 0.5 equivalents of alkylating reagent giving the trichloro methyl compound  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Cl}_3\text{Me}]$  (**10**) in good yield. On the other hand,  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Cl}_4]$  (**1d**) reacts with 2 equivalents of  $\text{MgClMe}$  in hexane at room temperature giving a mixture of dichloro dimethyl and chloro trimethyl complexes  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Cl}_{4-x}\text{Me}_x]$  ( $x = 2$ , **11**;  $3$ , **12**), while the use of 4 equivalents of  $\text{MgClMe}$  converts **1c** into the tetramethyl derivative  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Me}_4]$  (**13**). Finally, a tetramethyl tantalum complex  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Me}_4]$  (**14**) was prepared by reaction of  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiXMe}_2)(\text{SiMe}_3)\}\text{Cl}_4]$  ( $\text{X} = \text{Cl}$ , **1c**;  $\text{Me}$ , **1d**) with 5 ( $\text{X} = \text{Cl}$ ) or 4 ( $\text{X} = \text{Me}$ ) equivalents of  $\text{MgClMe}$  in diethyl ether ( $\text{X} = \text{Cl}$ ) or hexane ( $\text{X} = \text{Me}$ ), respectively, as solvent. All the complexes were studied by IR and NMR spectroscopy and the molecular structure of the complex **11** was determined by X-ray diffraction methods.

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**Keywords:** Niobium; Tantalum; Chloro Methyl; Cyclopentadienyl Complexes

## 1. Introduction

High-valent early transition metal complexes containing different substituted cyclopentadienyl ligands have been intensively studied as efficient precatalyst systems for  $\alpha$ -olefin polymerization [1] and also as versatile reactive intermediates in stoichiometric and catalytic transformations [2]. In particular, niobium and tantalum alkyl complexes have provided relevant synthetic applications mainly related to

the migratory insertion [3] of coordinated unsaturated molecules, such as carbon monoxide and isocyanides, into the metal–carbon bonds and the reactivity of the resulting metal–acyl and metal–iminoacyl functions.

Our earlier studies have been concerned with the ability of tetrachloro monocyclopentadienyl niobium and tantalum compounds to coordinate bulky alkyl substituents. It is very well known that the overpopulation [4] of the coordination sphere of the metal is the basis for the formation of an alkylidene compound by  $\alpha$ -hydrogen elimination and this process was observed in the reactions with trimethylsilylmethyl lithium in which dialkyl alkylidene

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complexes can be isolated with simultaneous elimination of tetramethylsilane [5]. Methyl monocyclopentadienyl complexes  $[\text{MCp}^*\text{Cl}_{4-x}\text{Me}_x]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{M} = \text{Nb}$  [6],  $x = 2, 4$ ;  $\text{M} = \text{Ta}$ ,  $x = 1$  [7], 2 [7], 3 [8], 4 [9]) were prepared by treatment of the corresponding tetrachloro derivatives with the appropriate amount of the alkylating reagent. On the other hand, the chemical behaviour of pseudooctahedral monocyclopentadienyl tantalum complexes containing anionic phosphorous ylide ligands  $[\text{TaCp}^*\text{Cl}_3(\text{CH}_2)_2\text{PRR}']$  [10] ( $\text{R} = \text{R}' = \text{Me}$ ,  $\text{Ph}$ ;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Ph}$ ) with alkylating reagents was studied [11] in order to isolate a trimethyl derivative  $[\text{TaCp}^*\text{Me}_3\{(\text{CH}_2)_2\text{PPh}_2\}]$  which pyrolysis takes place with evolution of methane and leads to the formation of a methylidyne complex  $[\text{TaCp}^*\text{Me}_2(\text{CH})(\text{CH}_2)\text{PPh}_2]$ .

As an extension of our studies we are actually interested in the comparative reactivity of  $\text{M}-\text{Cl}$  and  $\text{Si}-\text{Cl}$  bonds from chloro silylcyclopentadienyl derivatives which may provide convenient sites to introduce functionalities that are useful precursors for supported catalysts [12]. In this paper, we report the chemical behaviour of  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiXMe}_2)(\text{SiMe}_3)\text{Cl}_4]$  ( $\text{M} = \text{Nb}$ ,  $\text{X} = \text{Cl}$ , **1a**;  $\text{Me}$ , **1b**;  $\text{M} = \text{Ta}$ ,  $\text{X} = \text{Cl}$ , **1c**;  $\text{Me}$ , **1d**) in reactions with alkylating reagents and the X-ray crystal structure of one of the dichloro dimethyl compounds isolated.

## 2. Results and discussion

Trichloro methyl and dichloro dimethyl niobium derivatives  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiXMe}_2)(\text{SiMe}_3)\text{Cl}_{4-x}\text{Me}_x]$  ( $x = 1$ ,  $\text{X} = \text{Cl}$ , **2**;  $\text{Me}$ , **3**;  $x = 2$ ,  $\text{X} = \text{Cl}$ , **4**;  $\text{Me}$ , **5**) were prepared by treatment of the corresponding tetrachloro complex **1a** ( $\text{X} = \text{Cl}$ ) or **1b** ( $\text{X} = \text{Me}$ ) with 0.5 ( $x = 1$ ) or 1.5 ( $x = 2$ ) equivalents of  $\text{ZnMe}_2$ , respectively (Scheme 1). In the case of  $\text{X} = \text{Cl}$ , the reactions were carried out at  $-78^\circ\text{C}$  due to the scarce stability of the methyl compounds isolated.

The alkylation of **1a/1b** by using an excess of  $\text{MgClMe}$  leads to the niobium tetramethyl complex  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{Si}$

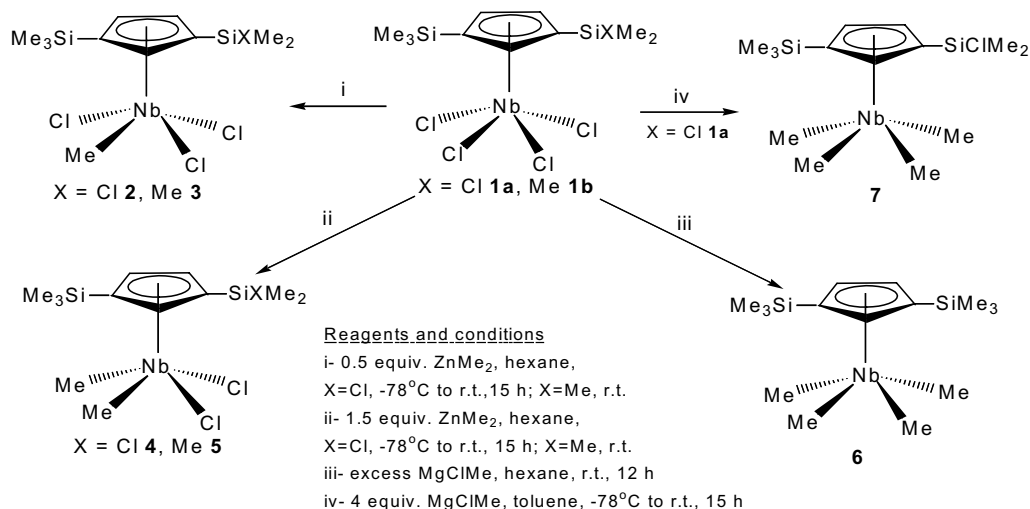
$\text{Me}_3)_2\text{Me}_4]$  (**6**). In this case, the use of an excess of a stronger alkylating reagent produces the total alkylation of the  $\text{Nb}-\text{Cl}$  bonds and also of the relative  $\text{Si}-\text{Cl}$  bond in the chlorodimethyl silyl substituent of the cyclopentadienyl ring in the starting material **1a**. In contrast, when a toluene solution of **1a** was treated at  $-78^\circ\text{C}$  with 4 equivalents of the Grignard reagent, under rigorously anhydrous conditions, the corresponding tetraalkyl compound  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\text{Me}_4]$  (**7**) was isolated as an oily red brown solid, in 40% yield.

On the other hand, a mixture of trichloro methyl and dichloro dimethyl tantalum compounds  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\text{Cl}_{4-x}\text{Me}_x]$  ( $x = 1$ , **8**; 2, **9**) in a 2:1 ratio was obtained by treatment of  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\text{Cl}_4]$  (**1c**) with 0.5 equivalents of  $\text{ZnMe}_2$  in toluene at low temperature (Scheme 2). **8** can be isolated as a single compound by addition of 1 equivalent of **1c** to a benzene- $d_6$  solution of the mixture of the complexes **8** and **9**. Alternatively, solutions of the dichloro dimethyl complex **9** were prepared by alkylation of **1c** with 1.5 equivalents of  $\text{ZnMe}_2$  while, the treatment with 0.5 equivalents of  $\text{ZnMe}_2$  leads to the trichloro methyl derivative  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{Cl}_3\text{Me}]$  (**10**).

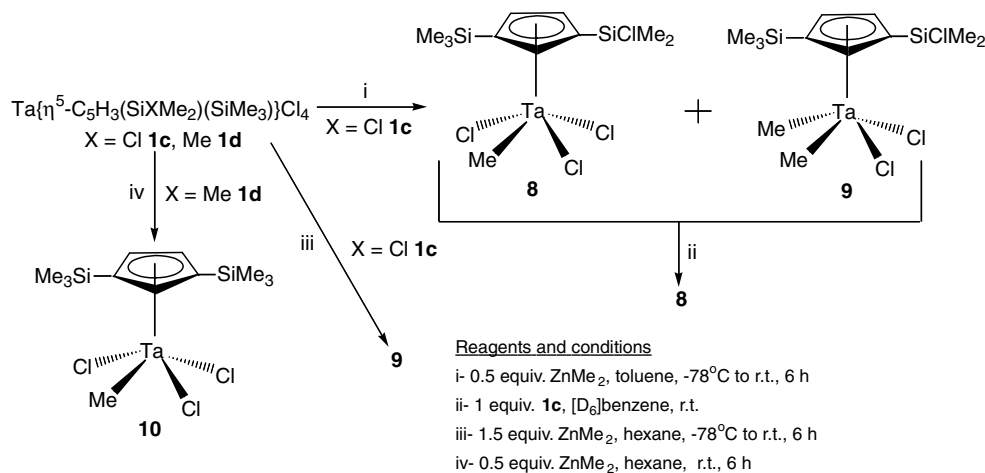
$[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{Cl}_4]$  (**1d**) can also be alkylated and when was treated with 2 equivalents of  $\text{MgClMe}$  gave a mixture of the dichloro dimethyl  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{Cl}_2\text{Me}_2]$  (**11**) and chloro trimethyl  $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{ClMe}_3]$  (**12**) tantalum complexes in a 2:1 ratio (Scheme 3).

Adequate crystals of **11** for X-ray diffraction studies were obtained by recrystallization from a benzene- $d_6$  saturated solution of a **11–12** mixture. The molecular structure and atom-labeling scheme of **11** are shown in Fig. 1, while selected bond distances and angles are summarized in Table 1.

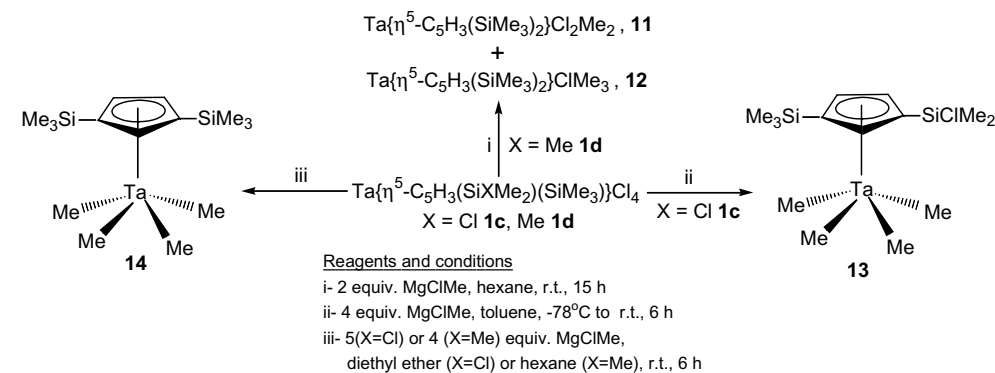
In the asymmetric unit of the unit cell two molecules exist. One of them, molecule A, was solved and refined well as compound **11** and shows a dichlorine dimethyl *cis* system in a four-legged piano-stool environment for the



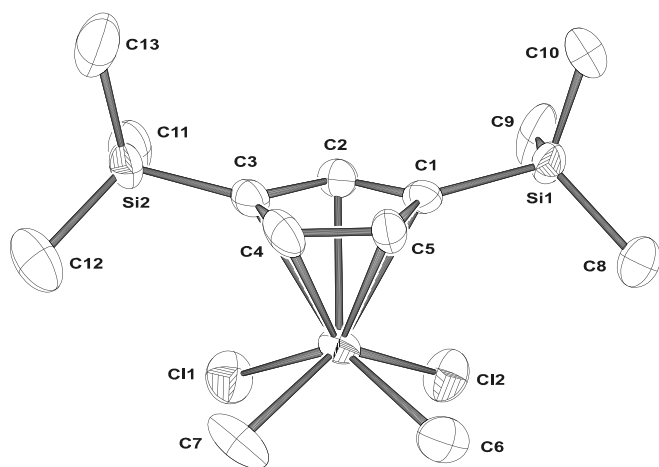
Scheme 1.



Scheme 2.



Scheme 3.

Fig. 1. ORTEP drawing of compound **11** with thermal ellipsoids at the 50% probability level.

tantalum atom. The other, molecule B, shows instead an important disorder in the legs being very difficult to model (see Section 4).

In the molecule A, the bond distances (Ta–Cl 2.367(4) Å; Ta–C(methyl) 2.188(13) Å) are comparable to the values found in other alkyl chlorine complexes reported. However, the only analogous structure previously known is

Table 1  
Selected bond distances (Å) and angles (°) of compound **11** (molecule A)

|                           |                             |
|---------------------------|-----------------------------|
| Ta(1)–Cl(1) 2.370(4)      | Ta(1)–C(6) 2.176(14)        |
| Ta(1)–Cl(2) 2.362(4)      | Ta(1)–C(7) 2.199(13)        |
| Ta(1)–C(1) 2.406(12)      | Ta(1)–C(2) 2.381(12)        |
| Ta(1)–C(3) 2.438(14)      | Ta(1)–C(4) 2.407(14)        |
| Ta(1)–C(5) 2.402(13)      | Ta(1)–Cp(1) 2.083(2)        |
| Si(1)–C(1) 1.891(12)      | Si(2)–C(3) 1.868(15)        |
| Si(1)–C(8) 1.864(15)      | Si(2)–C(11) 1.848(18)       |
| Si(1)–C(9) 1.856(16)      | Si(2)–C(12) 1.856(15)       |
| Si(1)–C(10) 1.854(18)     | Si(2)–C(13) 1.85(2)         |
| C(6)–Ta(1)–C(7) 77.2(7)   | Cl(2)–Ta(1)–Cl(1) 85.39(14) |
| C(7)–Ta(1)–Cl(1) 81.3(5)  | C(6)–Ta(1)–Cl(2) 81.4(4)    |
| C(7)–Ta(1)–Cl(2) 134.4(5) | C(6)–Ta(1)–Cl(1) 133.8(4)   |
| Cp(1)–Ta(1)–Cl(1) 117.11  | Cp(1)–Ta(1)–C(6) 106.20     |
| Cp(1)–Ta(1)–Cl(2) 118.66  | Cp(1)–Ta(1)–C(7) 107.98     |

Cp(1) is the centroid of C1–C5.

TaCp\*Cl<sub>2</sub>Me<sub>2</sub> [7] that exhibits a disorder between the chlorine and methyl positions with intermediate values of the distances that preclude any posterior analysis.

The C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub> ring is bound to the tantalum in a η<sup>5</sup>-coordination with the Ta–C distances ranging from 2.381(12) to 2.438(14) Å. The distance Ta–Cp(1) ring is 2.083(2) Å and the silicon atoms bonded to the cyclopentadienyl ring are located 0.28 Å above the ring plane.

The tantalum atom is displayed 0.8832(2) Å above the plane formed by two carbon and the two chlorine atoms, which is almost parallel to the Cp ring, being the dihedral angle between them 8.4°.

In the molecule **B**, no position of the basal substituents could be well defined. This result precludes a posterior analysis of these distances. However, the C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub> ring and the tantalum atom are well defined with the corresponding geometrical parameters comparable to the molecule **A**: Ta–C(Cp ring) ranged from 2.364(11) to 2.418(13) Å, Ta–Cp(1) plane distance is 2.067 Å and the silicon atoms are 0.37 and 0.33 Å above the cyclopentadienyl ring plane.

The addition of 4 equivalents of MgClMe to toluene solutions of **1c** gives the tetramethyl tantalum derivative [Ta{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiClMe<sub>2</sub>)(SiMe<sub>3</sub>)<sub>2</sub>}Me<sub>4</sub>] (**13**), while the tetramethyl bistrimethylsilylcyclopentadienyl tantalum complex [Ta{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>}Me<sub>4</sub>] (**14**) can be synthesized by alkylation of **1c** or **1d** with 5 or 4 equivalents of MgClMe in diethyl ether (X = Cl) or hexane (X = Me), respectively (Scheme 3). Therefore, the alkylation reaction of the Ta–Cl and Si–Cl bonds in the starting tetrachloro complex **1c** leads to the completely alkylated tetramethyl compound **14**.

All of the complexes **2–14** are soluble in most organic solvents. They are extremely air- and moisture-sensitive and rigorously dried solvents and handling under dry atmosphere were found to be imperative for successful preparations.

All of the compounds were characterized by analytic and spectroscopic methods and the data (see Section 4) are in agreement with the proposed structures. The IR spectra show the characteristic absorptions for cyclopentadienyl ring ( $\bar{\nu}_{\text{C-H}} \approx 850 \text{ cm}^{-1}$ ) [13] and the silyl substituent ( $\bar{\nu}_{\text{as}}(\text{CH}_3) \approx 1257 \text{ cm}^{-1}$ ) [3g,3h,13a] whereas the absorption due to the M–C stretching vibrations [6,14] is observed at  $\bar{\nu} \approx 464 \text{ cm}^{-1}$ .

The NMR data of the complexes **2–14** are consistent with the expected four-legged piano-stool geometry similar to that observed for analogous group 5 metal monocyclopentadienyl derivatives [7,15]. The <sup>1</sup>H NMR spectra of the mixed silylcyclopentadienyl niobium (**2**, **4**, **7**) and tantalum (**8**, **9**, **13**) complexes show an ABC spin system for the protons of the Cp ring, whereas the <sup>13</sup>C{<sup>1</sup>H} NMR spectra show five resonances for the same group, in accordance with a C<sub>1</sub> symmetry. On the other hand, the <sup>1</sup>H NMR spectra of the bistrimethylsilylcyclopentadienyl niobium (**3**, **5**, **6**) and tantalum (**10**, **11**, **12**, **14**) complexes show an A<sub>2</sub>B spin system for the Cp ring protons and consistently, three ring carbon resonances appear in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra.

The resonance corresponding to the M–Me protons is shifted to higher field as the number of methyl groups increases. Further, in the case of the niobium complexes, the <sup>13</sup>C{<sup>1</sup>H} NMR spectra show broad signals for all carbon atoms directly bonding to the metal center due to the quadrupole moment interaction [3j,16] with the <sup>93</sup>Nb nucleus.

### 3. Conclusions

By conventional alkylation processes, monomethyl [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiXMe<sub>2</sub>)(SiMe<sub>3</sub>)}Cl<sub>3</sub>Me] (X = Cl, **2**; Me, **3**), dimethyl [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiXMe<sub>2</sub>)(SiMe<sub>3</sub>)}Cl<sub>2</sub>Me<sub>2</sub>] (X = Cl, **4**; Me, **5**) and tetramethyl [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiXMe<sub>2</sub>)(SiMe<sub>3</sub>)}Me<sub>4</sub>] (X = Me, **6**; Cl, **7**) niobium compounds have been isolated from starting tetrachloro bisilylcyclopentadienyl [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiXMe<sub>2</sub>)(SiMe<sub>3</sub>)}Cl<sub>4</sub>] (X = Cl, **1a**; Me, **1b**) complexes. In the case of tetrachloro tantalum derivatives, the alkylation of [Ta{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiClMe<sub>2</sub>)(SiMe<sub>3</sub>)}Cl<sub>4</sub>] (**1c**) with 0.5 equivalents of ZnMe<sub>2</sub> leads to a mixture of monomethyl and dimethyl species [Ta{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiClMe<sub>2</sub>)(SiMe<sub>3</sub>)}Cl<sub>4-x</sub>Me<sub>x</sub>] (x = 1, **8**; 2, **9**) while, the use of 1.5 equivalents of alkylating reagent give the dimethyl complex as unitary product. On the other hand, monomethyl, dimethyl and trimethyl tantalum derivatives [Ta{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>}Cl<sub>4-x</sub>Me<sub>x</sub>] (x = 1, **10**; 2, **11**; 3, **12**) were prepared by treatment of the corresponding tetrachloro complex with the appropriate reagent. Finally, the tetramethyl derivatives [Ta{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiClMe<sub>2</sub>)(SiMe<sub>3</sub>)}Me<sub>4</sub>] (**13**) and [Ta{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>}Me<sub>4</sub>] (**14**) were isolated by total alkylation of the starting tetrachloro complexes.

### 4. Experimental

#### 4.1. Materials and procedures

All reactions and manipulations were carried out under argon using standard Schlenk-tube and glove-box techniques. Solvents were refluxed in the presence of an appropriate drying agent and distilled and degassed prior use: benzene-*d*<sub>6</sub> and hexane (Na/K alloy), diethyl ether (Na/benzophenone) and toluene (Na). Starting tetrachloro compounds [M{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiXMe<sub>2</sub>)(SiMe<sub>3</sub>)}Cl<sub>4</sub>] (M = Nb, X = Cl, **1a**; Me, **1b**; M = Ta, X = Cl, **1c**; Me, **1d**) [13b] were prepared as described previously. Reagent grade were purchased from commercial sources and used without further purification as follows: ZnMe<sub>2</sub> (2 M in toluene) and MgClMe (3 M in tetrahydrofuran, Aldrich). Infrared spectra were recorded with a Perkin–Elmer Spectrum 2000 spectrophotometer (4000–400 cm<sup>-1</sup>) with samples prepared as KBr pellets or as Nujol mulls between CsI plates. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded with an “Unity 300” and “Mercury VX 300” (Varian NMR Systems) spectrometers; chemical shifts were referenced to the <sup>13</sup>C (δ = 128) and <sup>1</sup>H (δ = 7.15) residual resonances of the benzene-*d*<sub>6</sub> solvent. Microanalyses (C, H) were performed in a LECO CHNS 932 microanalyzer.

#### 4.2. Synthesis of [Nb{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiXMe<sub>2</sub>)(SiMe<sub>3</sub>)}Cl<sub>3</sub>Me] (X = Cl, **2**; Me, **3**)

2. A 2 M solution of ZnMe<sub>2</sub> in toluene (0.30 mL, 0.60 mmol) was added to a solution of **1a** (0.56 g, 1.20 mmol) in hexane (40 mL) at –78 °C. The solution was stirred for 15 h and allowed to warm slowly to room

temperature. The solution was filtered, concentrated to ca. 10 mL and cooled to  $-20^{\circ}\text{C}$  to give the trichloro methyl derivative **2** as a dark red microcrystalline solid. Yield 0.25 g (50%). IR (KBr):  $\bar{\nu}$  3088  $\text{cm}^{-1}$  (m), 1400 (m), 1265 (vs), 1094 (s), 927 (s), 910 (s), 839 (vs), 650 (m), 487 (s), 456 (m), 408 (s).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.66 (t, 1H,  $^3J_{\text{H-H}} = 2.4$  Hz), 6.46 [d, 2H,  $^3J_{\text{H-H}} = 2.4$  Hz,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 2.12 (br, 3H, Nb-Me), 0.57 (s, 3H), 0.55 [s, 3H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 0.09 [s, 9H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  139.8, 133.9, 130.2, 129.8, 126.2 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 76.6 (Nb-Me), 1.88, 1.58 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ],  $-0.81$  [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ]. Anal. Calc. for  $\text{C}_{11}\text{H}_{21}\text{Cl}_4\text{NbSi}_2$  (444.18): C, 29.74; H, 4.76. Found: C, 30.35; H, 4.43%.

3. A 2 M solution of  $\text{ZnMe}_2$  in toluene (0.10 mL, 0.22 mmol) was slowly added at room temperature to a stirred freshly prepared suspension of **1b** (0.20 g, 0.45 mmol) in 40 mL of hexane. The mixture was stirred for 15 h and then filtered. The resulting solution was evaporated to dryness and the oily dark red solid washed with cold hexane (2 x 5 mL), dried in vacuo and identified as **3**. Yield 0.11 g (60%). IR (KBr):  $\bar{\nu}$  3089  $\text{cm}^{-1}$  (m), 1409 (m), 1262 (vs), 1086 (vs), 839 (vs), 466 (m), 409 (s).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.60 (br, 2H), 6.44 [br, 1H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 2.19 (br, 3H, Nb-Me), 0.18 [s, 18H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  139.5, 130.6, 127 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 75.8 (Nb-Me),  $-0.43$  [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ]. Anal. Calc. for  $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{NbSi}_2$  (423.76): C, 34.01; H, 5.71. Found: C, 34.37; H, 5.95%.

#### 4.3. Synthesis of $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiXMe}_2)(\text{SiMe}_3)\}\text{Cl}_2\text{Me}_2]$ ( $X = \text{Cl}$ , **4**; $\text{Me}$ , **5**)

4. To a solution of **1a** (0.325 g, 0.70 mmol) in hexane (50 mL) at  $-78^{\circ}\text{C}$  was added by syringe 0.50 mL of a 2 M solution of  $\text{ZnMe}_2$  (1.00 mmol) in toluene. The mixture was allowed to warm to room temperature and stirred for 15 h. Concentration and cooling of the filtrate produced **4** as a red solid. Yield 0.15 g (50%). IR (KBr):  $\nu$  3088  $\text{cm}^{-1}$  (m), 1400 (m), 1265 (vs), 1085 (s), 839 (vs), 494 (vs), 460 (m), 408 (s).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.52 (t, 1H,  $^3J_{\text{H-H}} = 1.8$  Hz), 6.34 (t, 1H,  $^3J_{\text{H-H}} = 1.8$  Hz), 6.07 [t, 1H,  $^3J_{\text{H-H}} = 1.8$  Hz,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 1.68 (s, 6H, Nb-Me), 0.50 (s, 3H), 0.45 [s, 3H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 0.07 [s, 9H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  134.1, 128.3, 126.3, 126.1, 121.3 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 69.6 (Nb-Me), 1.93, 1.76 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ],  $-0.72$  [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ]. Anal. Calc. for  $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{NbSi}_2$  (423.76): C, 34.01; H, 5.71. Found: C, 33.79; H, 5.65%.

5. A suspension of **1b** (0.18 g, 0.40 mmol) in hexane (40 mL) was treated at room temperature with 1 equivalent of  $\text{ZnMe}_2$  (2 M in toluene, 0.20 mL, 0.40 mmol) and the mixture was stirred for 15 h. The resulting suspension was filtered, the solution was concentrated to ca. 10 mL and cooled to  $-20^{\circ}\text{C}$  to yield **5** as a dark red microcrystalline solid. Yield 0.12 g (65%). IR (KBr):  $\bar{\nu}$  3084  $\text{cm}^{-1}$  (m),

1408 (vs), 1251 (vs), 1085 (vs), 893 (vs), 470 (m), 410 (m).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.41 (br, 2H), 6.05 [br, 1H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 1.72 (s, 6H, Nb-Me), 0.12 [s, 18H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  133.2, 126.3, 121.7 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 65.6 (Nb-Me),  $-0.6$  [s, 18H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ]. Anal. Calc. for  $\text{C}_{13}\text{H}_{27}\text{Cl}_2\text{NbSi}_2$  (403.34): C, 38.71; H, 6.75. Found: C, 38.57; H, 6.79%.

#### 4.4. Synthesis of $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Me}_4]$ (**6**)

A suspension of **1a** (0.28 g, 0.60 mmol) in hexane (50 mL) was treated with excess of a 3 M solution of  $\text{MgClMe}$  (1.20 mL, 3.60 mmol) in tetrahydrofuran. The mixture was stirred to room temperature for 12 h. The suspension obtained was filtered, the solvent evaporated to dryness and the dark brown oil residue characterized by NMR spectroscopy as **6**. Yield 0.18 g (80%).

**6** can be also prepared from **1b** (0.16 g, 0.37 mmol) following the same procedure. Yield 0.11 (60%). IR (KBr):  $\bar{\nu}$  3085  $\text{cm}^{-1}$  (m), 1455 (s), 1252 (vs), 1088 (s), 838 (vs), 420 (s).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.17 (br, 1H), 5.71 [br, 2H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 1.55 (br, 12H, Nb-Me), 0.08 [s, 18H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  119.5, 117.5 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 60.1 (Nb-Me), 0.15 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ]. Repeated attempts to obtain a satisfactory microanalysis on this material were unsuccessful.

#### 4.5. Synthesis of $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Me}_4]$ (**7**)

A toluene (40 mL) solution of **1a** (0.38 g, 0.82 mmol) was treated at  $-78^{\circ}\text{C}$  with 3 equivalents of a 3 M solution of  $\text{MgClMe}$  (1.10 mL, 3.28 mmol) in tetrahydrofuran. The mixture was allowed to warm to room temperature and stirred for 15 h. The suspension obtained was filtered, the solvent evaporated to dryness and the red brown residue extracted with hexane (2 x 15 mL). The resulting suspension was filtered, the solution was concentrated to ca. 10 mL and cooled to  $-20^{\circ}\text{C}$  yielding **7** as an oily red brown microcrystalline solid. Yield 0.12 (40%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.28 (m, 1H), 5.74 (m, 1H), 5.66 [m, 1H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 1.52 (br, 12H, Nb-Me), 0.36 (s, 3H), 0.31 [s, 3H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 0.04 [s, 9H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  137.4, 134.9, 129.3, 119.8, 118.9 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 60.7 (Nb-Me), 3.53, 3.48 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 0.03 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ]. Anal. Calc. for  $\text{C}_{14}\text{H}_{30}\text{ClNbSi}_2$  (382.92): C, 43.91; H, 7.90. Found: C, 43.75; H, 7.85%.

#### 4.6. Synthesis of $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiXMe}_2)(\text{SiMe}_3)\}\text{-Cl}_{4-x}\text{Me}_x]$ ( $X = \text{Cl}$ , $x = 1$ , **8**; $2$ , **9**; $X = \text{Me}$ , $x = 1$ , **10**)

8.  $\text{ZnMe}_2$  (2 M in toluene, 0.20 mL, 0.44 mmol) was added to a solution of **1c** (0.44 g, 0.80 mmol) in 50 mL of toluene at  $-78^{\circ}\text{C}$ . The reaction mixture was slowly warmed to room temperature and stirred for 6 h. After filtration the resulting solution was concentrated to dryness



to give a yellow oil characterized as a mixture of complexes **8** and **9** in a 2:1 molar ratio (**8** 0.12 g, 66%; **9** 0.06 g, 33%). However, the addition of 1 equivalent of **1c** to the mixture of complexes **8** and **9** permits to isolate **8** as single compound with quantitative yield (**8** 0.21 g, 40%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.58 (m, 1H), 6.49 (m, 1H), 6.39 [m, 1H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 1.73 (s, 3H, Ta-Me), 0.60 (s, 3H), 0.58 [s, 3H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 0.12 [s, 9H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  137.4, 131.7, 125.4,  $\text{C}_i$  not observed [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 78.4 (Ta-Me), 1.84, 1.52 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], -0.6 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ]. Anal. Calc. for  $\text{C}_{11}\text{H}_{21}\text{Cl}_4\text{TaSi}_2$  (532.22): C, 24.82; H, 3.98. Found: C, 24.87; H, 3.88%.

**9.** A 2 M solution of  $\text{ZnMe}_2$  in toluene (0.60 mL, 1.20 mmol) at  $-78^\circ\text{C}$  was added to a solution of **1c** (0.44 g, 0.80 mmol) in toluene (50 mL). The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvent was removed in vacuo and the residue extracted into hexane ( $3 \times 15$  mL). The solution was filtered, concentrated to dryness and the dark yellow oil identified as **9** by NMR spectroscopy. Yield 0.20 g (50%). IR (KBr):  $\bar{\nu}$  3089  $\text{cm}^{-1}$  (m), 1405 (vs), 1259 (vs), 1088 (s), 496 (s), 458 (m), 380 (s).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.45 (t, 1H,  $^3J_{\text{H-H}} = 2.4$  Hz), 6.29 (t, 1H,  $^3J_{\text{H-H}} = 2.4$  Hz), 6.16 [t, 1H,  $^3J_{\text{H-H}} = 2.4$  Hz,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 1.35 (s, 6H, Ta-Me), 0.52 (s, 3H), 0.49 [s, 3H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 0.10 [s, 9H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  133.3, 129.3, 125.5, 125.3, 121.6 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 73.2 (Ta-Me), 1.9, 1.6 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], -0.8 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ]. Repeated attempts to obtain a satisfactory microanalysis on this material were unsuccessful.

**10.** A 2 M in toluene solution of  $\text{ZnMe}_2$  (0.45 mL, 0.90 mmol) was added to a solution of **1d** (1.02 g, 1.80 mmol) in hexane (60 mL) at room temperature and the mixture stirred for 6 h. The resulting suspension was evaporated to dryness and the residue extracted into hexane ( $2 \times 10$  mL). The solution was evaporated to dryness and the yellow oily solid identified as **10**. Yield 0.51 g (50%). IR (CsI):  $\bar{\nu}$  3084  $\text{cm}^{-1}$  (m), 1418 (vs), 1261 (vs), 1090 (s), 803 (vs), 466 (m), 386 (s).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.51 (br, 1H), 6.42 [br, 2H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 1.79 (s, 3H, Ta-Me), 0.18 [s, 18H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  141.3, 136.8, 130.9, 126.7, 125.8 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 77.8 (Ta-Me), -0.59 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].

#### 4.7. Synthesis of [ $\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Cl}_{4-x}\text{Me}_x$ ] ( $x=2$ , **11**; 3, **12**)

A 3 M solution of  $\text{MgClMe}$  (0.40 mL, 1.20 mmol) in tetrahydrofuran was added at room temperature to a suspension of **1d** (0.32 g, 0.60 mmol) in hexane (50 mL). The reaction mixture was stirred for 15 h and then filtered. The yellow solution was evaporated to ca. 20 mL and cooled to  $-20^\circ\text{C}$  to give an oily yellow solid identified as a mixture of **11** and **12** in a 2:1 ratio (**11** 0.10 g, 30%; **12** 0.05 g, 18 %). However, adequate yellow crystals of **11**

for X-ray diffraction studies were prepared from a saturated solution of that mixture in benzene- $d_6$ .

The data for **11** follow.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.39 (br, 2H), 6.12 [br, 1H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 1.38 (s, 6H, Ta-Me), 0.14 [s, 18H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  132.5, 125.5, 122.9 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 73.2 (Ta-Me), -0.5 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].

The data for **12** follow.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.19 (br, 2H), 6.07 [br, 1H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 1.20 (s, 9H, Ta-Me), 0.14 [s, 18H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  132.6, 121.8, 121 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 71.3 (Ta-Me), -0.52 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].

#### 4.8. Synthesis of [ $\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Me}_4$ ] (**13**)

A toluene (60 mL) solution of **1c** (0.17 g, 0.30 mmol) was treated at  $-78^\circ\text{C}$  with  $\text{MgClMe}$  (3 M in tetrahydrofuran, 0.40 mL, 1.20 mmol). The reaction mixture was slowly warmed to room temperature and stirred for 6 h and then, the white precipitate filtered off. The resulting yellow solution was evaporated to dryness and the residue extracted with hexane ( $2 \times 5$  mL). The solvent was again removed to give a yellow oil identified as **13**. Yield 0.05 g (35%). IR (KBr):  $\bar{\nu}$  2958  $\text{cm}^{-1}$  (m), 1409 (m), 1259 (vs), 1087 (vs), 841 (vs), 498 (m), 415 (m).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.35 (m, 1H), 5.86 (m, 1H), 5.77 [m, 1H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 1.03 (s, 12H, Ta-Me), 0.38 (s, 3H), 0.35 [s, 3H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 0.06 [s, 9H,  $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  129.3, 127.8, 120.6, 120.5, 120 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], 71.7 (Ta-Me), 3.2, 3.1 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ], -0.12 [ $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$ ]. Anal. Calc. for  $\text{C}_{14}\text{H}_{30}\text{ClTaSi}_2$  (470.96): C, 35.70; H, 6.42. Found: C, 35.62; H, 6.35%.

#### 4.9. Synthesis of [ $\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{Me}_4$ ] (**14**)

The complex **14** can be prepared by two synthetic methods.

##### 4.9.1. Method A

A 3 M solution of  $\text{MgClMe}$  in THF (0.50 mL, 1.50 mmol) was added at room temperature to a green solution of **1c** (0.18 g, 0.30 mmol) in diethyl ether (50 mL) and the mixture was stirred for 6 h. The solvent was removed in vacuo and the residue extracted in hexane ( $3 \times 10$  mL). The solution was filtered, concentrated to ca. 10 mL and cooled to  $-20^\circ\text{C}$  to give the tetramethyl complex **14** as an oily yellow solid. Yield 0.09 g (70 %).

##### 4.9.2. Method B

A hexane (50 mL) suspension of **1d** (0.13 g, 0.25 mmol) was treated at room temperature with  $\text{MgClMe}$  (3 M in THF, 0.33 mL, 1.00 mmol) and the mixture stirred for 6 h. After removal of the solvent, the resultant solid was extracted with hexane ( $2 \times 15$  mL) to give a bright yellow solution and a white precipitate of magnesium chloride.

Concentration of the filtrate to dryness produce **14** as an oily yellow solid. Yield 0.09 g (70 %). IR (KBr):  $\bar{\nu}$  3081  $\text{cm}^{-1}$  (m), 1408 (s), 1250 (vs), 1086 (vs), 877 (vs), 471 (s), 405 (m).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.24 (br, 1H), 5.86 [br, 2H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 1.04 (s, 12H, Ta- $\text{Me}_4$ ), 0.10 [s, 18H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  128.3, 127.2, 120.4 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 71.2 (Ta- $\text{Me}_4$ ), 0.14 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ]. Anal. Calc. for  $\text{C}_{15}\text{H}_{33}\text{TaSi}_2$  (450.55): C, 39.99; H, 7.38. Found: C, 40.52; H, 7.56%.

#### 4.10. X-ray crystallographic studies

Crystallographic and experimental details of the crystal structure determination is given in Table 2. Suitable crystals of the complex **11** were covered with mineral oil and mounted in the  $\text{N}_2$  stream of a Bruker-Nonius Kappa CCD diffractometer and data were collected using graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data collections were performed at low temperature (see Table 2) with an exposure time of 38 s per frame (4 sets; 298 frames). Raw data were corrected for Lorentz and polarization effects. A empirical absorption correction was made.

The structure was solved by direct methods, completed by the subsequent difference Fourier techniques and refined by full-matrix least squares on  $F^2$  (SHELXL-97) [17]. In the asymmetric unit of the unit cell exist two different molecules. The molecule A is well refined and anisotropic thermal parameters were used in the last cycles of refinement

Table 2  
Crystal data and structure refinement for compound **11**

|   |   |
|---|---|
| Chemical formula                                    | $\text{C}_{13}\text{H}_{27}\text{Cl}_2\text{Si}_2\text{Ta}$           |
| Formula weigh                                       | 491.38  |
| $T$ (K)   | 150(2)  |
| $\lambda$ (Mo $\text{K}\alpha$ ) ( $\text{Å}$ )     | 0.71073   |
| Crystal system                                      | Monoclinic  |
| Space group   | $P2_1/n$  |
| $a$ ( $\text{Å}$ )                                  | 16.037(3)   |
| $b$ ( $\text{Å}$ ); $\beta$ ( $^\circ$ )            | 13.3948(8); 112.59(1)   |
| $c$ ( $\text{Å}$ )                                  | 19.508(3)   |
| $V$ ( $\text{Å}^3$ )                                | 3868.8(10)  |
| $Z$   | 8   |
| $\rho_{\text{calc}}$ ( $\text{g cm}^{-3}$ )         | 1.687   |
| $\mu$ ( $\text{mm}^{-1}$ )                          | 6.067   |
| $F(000)$  | 1920  |
| Crystal size (mm)                                   | $0.25 \times 0.2 \times 0.2$  |
| $\theta$ Range ( $^\circ$ )                         | 5.02–27.52  |
| Index ranges  | $-20 \leq h \leq 20$ , $-17 \leq k \leq 17$ ,<br>$-25 \leq l \leq 25$ |
| No. of data collected                               | 73864   |
| No. of unique observed data<br>[ $I > 2\sigma(I)$ ] | 8837 [ $R_{\text{int}} = 0.2901$ ]                                    |
| Absorption correction                               | Empirical   |
| Max. and min. transmission                          | 0.4719 and 0.0496   |
| Parameters refined                                  | 326   |
| Goodness-of-fit on $F^2$                            | 1.086   |
| Final $R$ indices [ $I > 2\sigma(I)$ ]              | $R_1 = 0.0754$ , $wR_2 = 0.1582$                                      |
| $R$ indices (all data)                              | $R_1 = 0.1223$ , $wR_2 = 0.1857$                                      |
| Largest diff. peak and hole ( $\text{e \AA}^{-3}$ ) | 2.131 and $-3.033$  |

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

for the non-hydrogen atoms. The hydrogen atoms were included from geometrical calculations and refined using a riding model. But in the molecule B, no position of the basal substituents could be well refined. After numerous attempts with different disorder schemes, no good results were obtained. The best situation consists in modeling three positions for two methyl carbon atoms, one of them with an occupancy factor equal to 1 and the other with 0.6 and 0.4 and, five positions for the two chlorine atoms, one of them with an occupancy factor 0.75. This disorder is probably produced by the existence of small quantities of the chlorine trimethyl tantalum complex **12**, superimposed in some position with the compound **11**. All the calculations were made using the WINGX system [18].

#### 5. Supplementary material

CCDC 625113 contains the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

#### Acknowledgments

We thank to the MEC (Project CTQ 2006-04540/BQU), to the CAM (Project S-0505/PPQ/0328-02) and to Universidad de Alcalá (Project GC 2005/94) its financial support for this research.

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