DOI: 10.1002/ejic.200600173

(Alkyl)- and (Alkyl)(alkylidene)(pentamethylcyclopentadienyl)tantalum Complexes

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Dedicated to Prof. Victor Riera on the occasion of his 70th birthday

Keywords: Tantalum / Alkyl / Alkylidene / Cyclopentadienyl ligands

Alkylation of [TaCp*Cl_4] (Cp* = η^5-C_5Me_5) with 3 equiv. of $MgCl(CH_2SiMe_3)$ gives the chloridotris(trimethylsilylmethyl) complex [TaCp*$Cl(CH_2SiMe_3)_3$] (**1**). TaCp*Cl_2Me_2 reacts with 2 equiv. of LiR (R = CH_2Ph, CH_2SiMe_3) to give the mixed alkyl derivatives [TaCp*Me_2R_2] (R = CH_2Ph, **2**; CH_2SiMe_3, **3**). The dimethyldineopentyl complex [TaCp*$Me_2(CH_2CMe_3)_2$] (**4**) was obtained by reaction of TaCp*$Cl_2(CH_2CMe_3)_2$ with 2 equiv. of LiMe. The treatment of a toluene solution of TaCp*Cl_2Me_2 with 2 equiv. of neophyllithium in a standard vacuum line gave a mixture of three compounds, [{TaCp*$Me_2(CH_2CMe_2Ph)$}$_2$(**μ**-O)] (**5**), [TaCp*$Me_2(CH_2CMe_2$–*o*-C_6H_4-κ^2*C*,*C*)] (**6**) and [TaCp*$Me(CH_2CMe_2Ph)(CH_2)$] (**7**), which were identified by NMR spectroscopy. However, when the reaction was carried out under rigorously anhydrous conditions, only complexes **6** and **7** were isolated. A chlorido(trimethylsilylmethyl)(trimethylsilylmethylidene) complex [TaCp*$Cl(CH_2SiMe_3)(CHSiMe_3)$] (**8**) was prepared by heating **1** at 60 °C, or by leaving it at room temperature for a long time. A 3:2 (**9**/**10**) mixture of [TaCp*$MeR(CHSiMe_3)$] (R = CH_2SiMe_3, **9**; Me, **10**) was obtained by thermal treatment of **3**, which was accompanied by the evolution of CH_4 and $SiMe_4$. However, irradiation of a [D_6]benzene solution of **3** with a sun lamp gave a mixture of **9** and [TaCp*$(CH_2SiMe_3)R(CH_2)$] (R = Me, **11**; CH_2SiMe_3, **12**) in a 2:1:1 (**9**/**11**/**12**) ratio. When a [D_6]benzene solution of **4** was heated at 60 °C, a mixture of the (alkyl)(neopentylidene) derivatives [TaCp*$MeR(CHCMe_3)$] (R = Me, **13**; CH_2CMe_3, **14**) in a 4:1 (**13**/**14**) ratio was detected by NMR spectroscopy, while irradiation with a sun lamp produced a mixture of alkylidene complexes [TaCp*$(CH_2CMe_3)R(CH_2)$] (R = Me, **15**; CH_2CMe_3, **16**) in a 3:1 (**15**/**16**) ratio. On the other hand, the alkylation of TaCp*$Cl_2(CH_2CMe_3)_2$ with 2 equiv. of $LiCH_2SiMe_3$ gave the (alkyl)(alkylidene) complex [TaCp*$(CH_2CMe_3)(CH_2SiMe_3)(CHCMe_3)$] (**17**) with the elimination of $SiMe_4$, whereas the treatment of TaCp*$Cl_2(CH_2SiMe_3)_2$ with the appropriate reagent gave [TaCp*$(CH_2R)(CH_2SiMe_3)(CHR')$] (R = R′ = Ph, **18**; R = CMe_2Ph, R′ = $SiMe_3$, **19**) with the elimination of $SiMe_4$ and CMe_3Ph, respectively. All compounds were studied by IR and NMR spectroscopy, and the molecular structures of complexes **1**, **4** and **5** were determined by X-ray diffraction methods.

Introduction

The study of early-transition-metal compounds in high oxidation states has been a topic of intense research because of their applications in organic synthesis and in catalysis.[1] In particular, metal alkyls and alkylidenes are among the most studied derivatives. Alkyl derivatives have been extensively used as catalysts for the polymerization of olefins,[1,2] while the importance of alkylidenes is demonstrated by a comprehensive study of the olefin metathesis reactions that they are able to catalyse.[3] Further, in combination with stronger Lewis acids they form highly reactive species that are important as catalysts in other processes involving olefins.[3b,3c,4–6] Additionally, μ-alkylidene complexes have been postulated as intermediates in Fischer–Tropsch, olefin metathesis and Ziegler–Natta catalytic processes.[7]

Preliminary reports from our group have focused on the ability of tetrachlorido(cyclopentadienyl)niobium and -tantalum compounds to coordinate with bulky alkyl substituents. Thus, the crowding of the coordination sphere of the metal by the trimethylsilylmethyl group is the basis for the formation of an alkylidene complex by a spontaneous α-hydrogen-elimination process.[8] On the other hand, we reported[9] that the use of the 2-[(dimethylamino)methyl]-phenyl ligand leads to the synthesis of tantalum(V) complexes that can be transformed into new cyclometalated (alkylidene)tantalum derivatives by the activation of carbon–hydrogen bonds in one of the methylamino groups of

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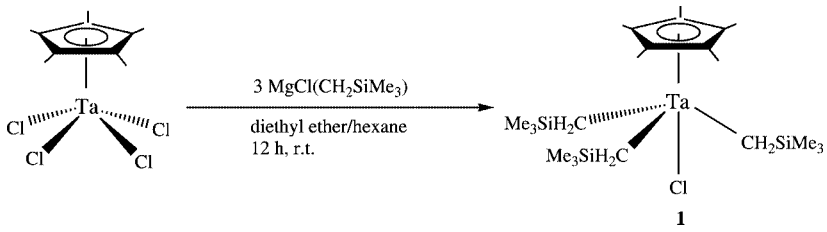


Scheme 1.

the ligand. More recently, the μ-alkylidene complexes $[(TaCp^*Cp')_2(\mu\text{-}CHR)_2]$ (Cp^* = η^5-C_5Me_5, Cp′ = η^5-$C_5H_4SiMe_3$, R = C_6H_5, $SiMe_3$, CMe_3) have been prepared by treatment of the (mixed dicyclopentadienyl)tantalum compound $TaCp^*Cp'Cl_2$ with an appropriate amount of the corresponding alkyllithium.[10]

In this article, we report the preparation of new (alkyl)- and (alkyl)(alkylidene)mono(pentamethylcyclopentadienyl)-tantalum(V) complexes. All compounds were studied by spectroscopic methods. In addition, the molecular structures of complexes **1**, **4** and **5** were determined by X-ray diffraction.

Results and Discussion

$[TaCp^*Cl(CH_2SiMe_3)_3]$ (**1**) was synthesized in good yield by the reaction of $[TaCp^*Cl_4]$ (Cp^* = η^5-C_5Me_5) with 3 equiv. of $MgCl(CH_2SiMe_3)$ (Scheme 1). In contrast, we previously reported[8] the preparation of a dialkyl(alkylidene) derivative $[TaCp^*(CH_2SiMe_3)_2(CHSiMe_3)]$ by the reaction of the tetrachlorido complex with 4 equiv. of an alkylating reagent. Two absorptions bands were observed in the IR spectrum of **1** at $\tilde{\nu}$ = 1026 and 1243 cm^{-1}, which can be assigned to $\nu_{C-C}(Cp^*)$[11] and $\delta_{as}(CH_3)(SiMe_3)$,[11c] respectively. The NMR spectra of this complex are in agreement with a C_{3v} local symmetry around the tantalum atom.

The crystal structure of complex **1** (Figure 1) shows a tantalum atom in a distorted trigonal bipyramidal environment with the three alkyl groups occupying the equatorial positions, and the centroid of the pentamethylcyclopentadienyl ring and the chlorine atom at the apical sites. The tantalum atom is displaced towards the Cp* ring by 0.46 Å from the equatorial plane containing the three carbon (alkyl) atoms.[12] The bond lengths for Ta–Cp*(centroid), Ta–C (average), and Ta–Cl are 2.180, 2.160 and 2.481(1) Å, respectively (Table 1). The Ta–C(alkyl) distance is in the range corresponding to normal values for a Ta–C[11d,13,14] single bond, whereas the Ta–Cl distance is shorter than that for a bridging chlorine[15] and longer than that for a terminal chlorine.[11d,14b,16] The angle Cp*–Ta–Cl is 176.84° and confirms the apical position of the chlorine atom. This pentacoordination is unusual, and to the best of our knowledge, no other group 5 metal (alkyl)chlorido(cyclopentadienyl) derivative has this trigonal bipyramidal configuration; all other examples have a four-legged piano-stool arrangement.[11b–d,17,18] In this case, such an arrangement is very unfavourable because of the important steric requirement of the trimethylsilylmethyl substituent.

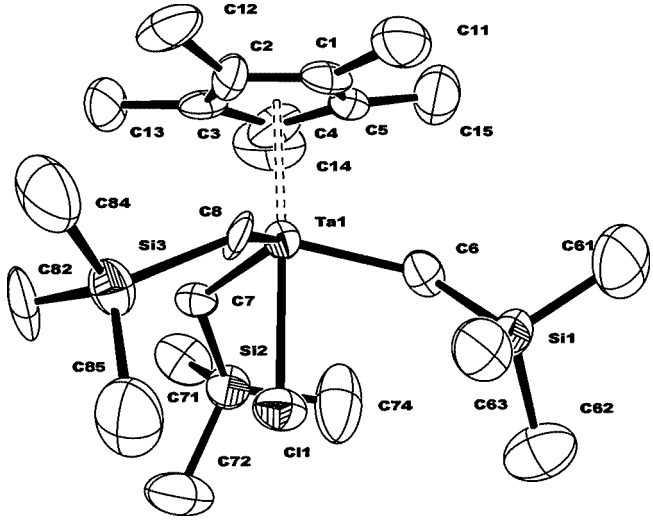


Figure 1. ORTEP drawing of compound **1** with thermal ellipsoids at the 50% probability level.

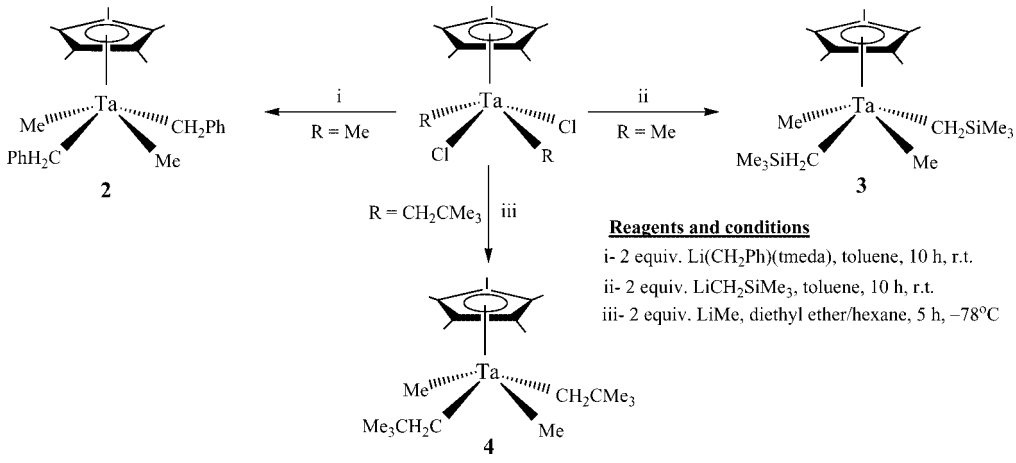
Table 1. Selected bond lengths [Å] and angles [°] for compound **1**.[a]

Ta1–Cl1	2.481(5)	Ta1–Cp1	2.180
Ta1–C6	2.137(16)	Ta1–C7	2.188(14)
Ta1–C8	2.156(16)	Ta1–C1	2.430(16)
Ta1–C2	2.47(2)	Ta1–C3	2.52(2)
Ta1–C4	2.49(2)	Ta1–C5	2.480(19)
Si1–C6	1.911(18)	Si2–C7	1.888(15)
Si3–C8	1.924(15)		
Cp1–Ta1–Cl1	176.84	Cp1–Ta1–C6	103.17
Cp1–Ta1–C7	100.89	Cp1–Ta1–C8	103.25
C6–Ta1–C8	111.7(6)	C6–Ta1–C7	114.4(6)
C8–Ta1–C7	120.3(6)	C6–Ta1–Cl1	79.6(5)
C7–Ta1–Cl1	76.5(4)	C8–Ta1–Cl1	76.9(5)
Si1–C6–Ta1	127.2(9)	Si2–C7–Ta1	126.4(9)
Si3–C8–Ta1	126.9(9)		

[a] Cp1 is the centroid of the C1–C5 ring.

The mixed alkyl complexes $[TaCp^*Me_2R_2]$ (R = CH_2Ph, **2**; CH_2SiMe_3, **3**) were obtained (Scheme 2) at room temperature by treatment of toluene solutions of $TaCp^*Cl_2Me_2$ with stoichiometric amounts of the alkyllithium, LiR, under rigorously anhydrous conditions, while the dimethyldineopentyl complex $[TaCp^*Me_2(CH_2CMe_3)_2]$ (**4**) was synthesized by alkylation, at –78 °C, of the dichloridodineopentyl derivative with 2 equiv. of LiMe in a diethyl ether/hexane mixture.

The mixed alkyl complexes **2**–**4** are extremely air- and moisture-sensitive, are soluble in most organic solvents and were characterised by analytical and spectroscopic methods.



Scheme 2.

Further, the molecular structure of **4** was studied by X-ray diffraction. A view of this molecule is shown in Figure 2, which indicates the atom labelling scheme employed. Selected bond lengths and angles are given in Table 2.

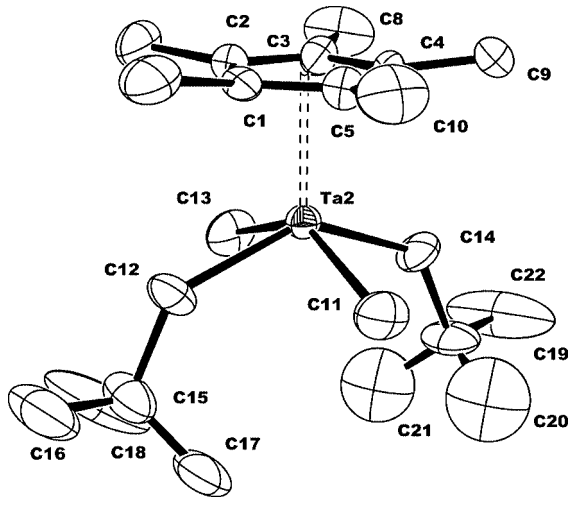


Figure 2. ORTEP drawing of compound **4** with thermal ellipsoids at the 50% probability level.

Table 2. Selected bond lengths [Å] and angles [°] for compound **4**.[a]

Molecule A		Molecule B	
Cp1–Ta1	2.175	Cp2–Ta2	2.175
C1A–Ta1	2.49(2)	C1–Ta2	2.48(2)
C2A–Ta1	2.48(2)	C2–Ta2	2.48(2)
C3A–Ta1	2.50(2)	C3–Ta2	2.46(2)
C4A–Ta1	2.51(2)	C4–Ta2	2.48(2)
C5A–Ta1	2.46(2)	C5–Ta2	2.49(3)
C11A-Ta1	2.20(2)	C11–Ta2	2.19(2)
C12A-Ta1	2.27(2)	C12–Ta2	2.26(2)
C13A-Ta1	2.23(2)	C13–Ta2	2.22(2)
C14A-Ta1	2.245(19)	C14–Ta2	2.20(2)
C12A-C15A	1.49(3)	C12–C15	1.56(4)
C14A-C19A	1.52(3)	C14–C19	1.64(3)
Cp1–Ta1–C11A	109.65	Cp2–Ta2–C11	111.00
Cp1–Ta1–C12A	111.62	Cp2–Ta2–C12	108.17
Cp1–Ta1–C13A	109.72	Cp2–Ta2–C13	108.87
Cp1–Ta1–C14A	108.38	Cp2–Ta2–C14	111.17
C11A–Ta1–C13A	140.6(8)	C11–Ta2–C13	140.1(10)
C11A–Ta1–C14A	83.4(9)	C11–Ta2–C14	84.4(11)
C13A–Ta1–C14A	83.7(10)	C14–Ta2–C13	81.7(10)
C11A–Ta1–C12A	83.3(9)	C11–Ta2–C12	82.1(10)
C13A–Ta1–C12A	83.1(9)	C13–Ta2–C12	85.4(10)
C14A–Ta1–C12A	140.0(8)	C14–Ta2–C12	140.7(9)
C15A-C12A-Ta1	133.5(17)	C15–C12–Ta2	132(2)
C19A-C14A-Ta1	128.5(16)	C19–C14–Ta2	135(2)

[a] Cp1 is the centroid of the C1A–C5A ring and Cp2 is the centroid of the C1–C5 ring.

Complex **4** is a monomer, and if Cp* is considered as occupying the apical coordination site, it has distorted square pyramid geometry. Two independent molecules were found in the asymmetric unit, and their geometrical parameters were essentially coincident. The tantalum atom deviates towards the Cp* ring by 0.75 Å from a plane passing through the atoms C11, C12, C13 and C14, and the two methyl groups and the two neopentyl groups are mutually *trans* in order to separate the sterically demanding groups. This arrangement is usual in five-coordinate cyclopentadienyl complexes.[11b,11c,11d,17,18] All the bond lengths and angles are in the normal ranges.

The ^{1}H NMR spectrum of **4** in [D$_2$]dichloromethane at 298 K shows two sets of signals in a ratio of 14:1. For the major compound, a quintuplet (δ = 0.59 ppm) and a septuplet (δ = 0.20 ppm, $^4J_{H,H}$ = 1.29 Hz) were observed for the Ta–(CH_3)$_2$ and the Ta–(CH_2CMe$_3$)$_2$ moieties, respectively. On the other hand, the minor component, detected in a NOESY1D spectra (Figure 3), shows an AB spin system ($^2J_{H,H}$ = 12.8 Hz) for the Ta–(CH_2CMe$_3$)$_2$ diastereotopic protons.

In contrast to **4**, the Ta–(CH_2SiMe$_3$)$_2$ resonance appears as a broad signal ($\Delta\nu_{1/2}$ = 37 Hz) at δ = –0.25 ppm in the ^{1}H NMR spectrum of **3** at 298 K, while the signal corresponding to Ta–(CH_3)$_2$ was observed as a quintuplet ($^4J_{H,H}$ = 1.31 Hz) at δ = 0.44 ppm.

Further, the variable low temperature spectra of **3** indicate the occurrence of a typical spin exchange process between two very differently populated positions. The minor position (10%) was detected by EXSY1D at 213 K and showed an AB spin system ($^2J_{H,H}$ = 11.6 Hz) at δ_{av} = –0.01 for the Ta–(CH_2SiMe$_3$)$_2$ resonance.

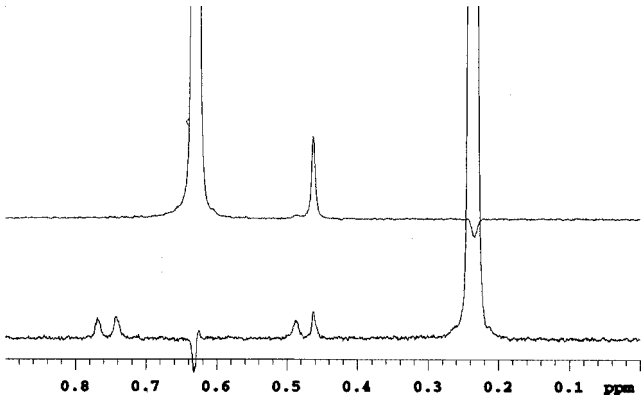


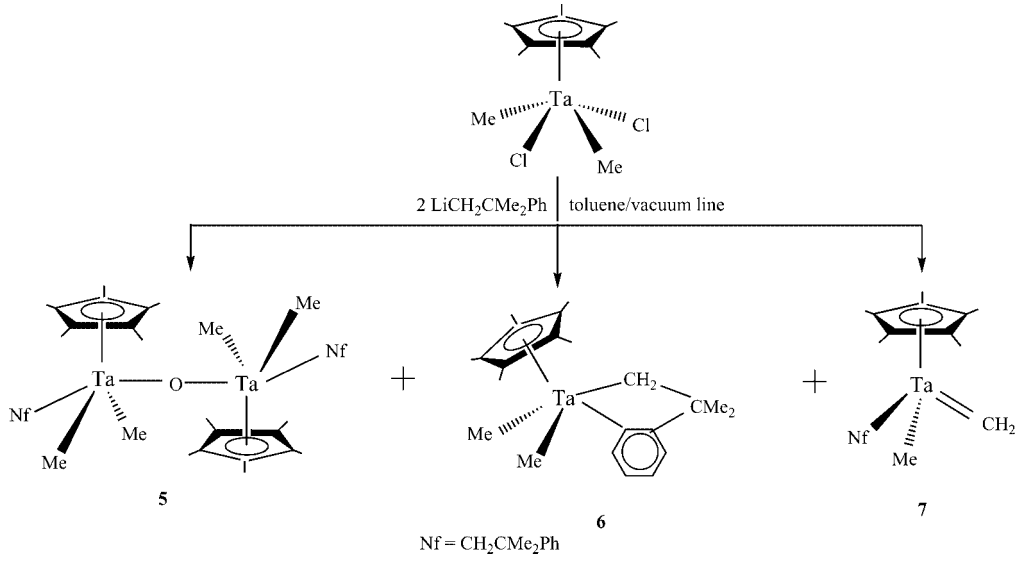
Figure 3. The PFG WFG noesy 1d (mix = 500 ms) proton spectra (spectrum phase = 180°) of complex **4** at 298 K [bottom: Ta–(CH_2CMe_3)$_2$; top: Ta–(CH_3)$_2$ resonances].

This spectral behaviour is in agreement with a *trans* arrangement of the methyl and the alkyl groups (C_{2v} local symmetry) in the major component and a *cis* arrangement of the groups in the minor (C_s symmetry) isomers, which undergo the mutual spin-exchange process known as Berry pseudorotation.[14c,14d,16b,18] We hypothesise that in solution both isomers of the **2**–**4** mixed alkyl complexes exhibit pseudo-square-pyramidal geometry in the ground state and a distorted trigonal bipyramidal environment, similar to that of **1**, in the transition state. Moreover, the isomerization process in complex **3** is faster than that in **4**, this is probably caused by the size of the alkyl group. The ^{13}C NMR spectra of complexes **2**–**4** show all the expected resonances (see Experimental Section).

The addition of 2 equiv. of $LiCH_2CMe_2Ph$ to a toluene solution of $TaCp^*Cl_2Me_2$ by using a standard vacuum line (Scheme 3) gives a mixture of the dimethyl(neophyl)(μ-oxido) complex [{$TaCp^*Me_2(CH_2CMe_2Ph)$}$_2$(μ-O)] (**5**), the dimethyltantalabenzocyclopentene complex [$TaCp^*Me_2$-(CH_2CMe_2-*o*-C_6H_4-κ^2*C*,*C*)] (**6**) and the (methyl)(methylidene)(neophyl) complex [$TaCp^*Me(CH_2CMe_2Ph)(CH_2)$] (**7**), which were observed by NMR spectroscopy. Complexes **5**–**7** can be isolated as pure samples by successive recrystallisations from hexane (see Experimental Section). However, when the same reaction is carried out under rigorously anhydrous conditions (glove box) complex **5** is not formed. We suggest, as a plausible pathway for this alkylation reaction, the initial formation of a mixed alkyl complex "[$TaCp^*Me_2(CH_2CMe_2Ph)_2$]", that, when followed by orthometalation[10,19] of the phenyl ring and by α-hydrogen activation[7e,20] of a methyl group with the elimination of CMe_3Ph, produces complexes **6** and **7**, respectively, while the hydrolysis of this mixed alkyl complex produces the μ-oxido complex **5**.

In the IR spectrum of complex **5** the absorption band observed at 740 cm^{-1} could be assigned to $\nu_{Ta-O-Ta}$,[15,21] while all the NMR spectroscopic data (see Experimental Section) are in agreement with a structural formulation that shows a *trans* arrangement of the methyl groups.

The molecular structure of complex **5** (Figure 4) shows two $TaCp^*Me_2(CH_2CMe_2Ph)$ fragments bonded through a bridging oxygen atom, which acts as an inversion centre. The angle Ta1–O1–Ta2 is 180,° and the bond length Ta–O is 1.9227(6) Å (Table 3). This distance is very short and in agreement with the existence of a π-bonding interaction between the oxygen and tantalum atoms.[14c] Each tantalum atom exhibits the normal four-legged piano-stool geometry[11,17,18] in which the pentamethylcyclopentadienyl ring occupies the apical position and the metal centre is displaced towards the Cp* ring by 0.78 Å from a plane formed by the atoms C21, C6, C8 and O1. The bridging oxygen atom is located in a *trans* position with respect to the bulky ligand. This fact, together with the inversion centre, eliminates steric problems. The distance Ta–C21 [2.294(12) Å] is significantly longer than the bonds between the metal and the methyl groups[18] [Ta–C6 2.208(11) Å and Ta–C8 2.194(12) Å], which is probably a result of the *trans* influence.



Scheme 3.

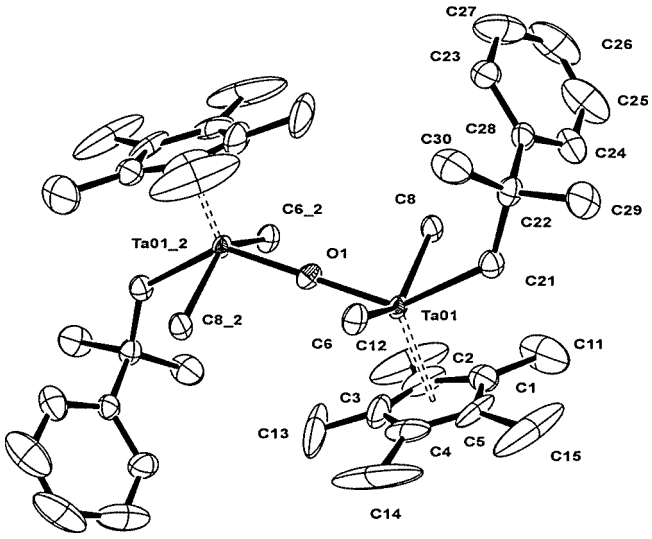


Figure 4. ORTEP drawing of compound **5** with thermal ellipsoids at the 50% probability level.

Table 3. Selected bond lengths [Å] and angles [°] for compound **5**.[a]

Ta1–O1	1.9227(6)	O1–Ta1#1	1.9227(6)
Ta1–Cp1	2.158	Ta1–C6	2.208(11)
Ta1–C8	2.194(10)	Ta1–C21	2.294(12)
Ta1–C1	2.502(12)	Ta1–C2	2.416(14)
Ta1–C3	2.366(16)	Ta1–C4	2.431(13)
Ta1–C5	2.533(11)	C21–C22	1.538(17)
C22–C23	1.529(15)		
Ta1#1–O1–Ta1	180.00(16)	Cp1–Ta1–O1	120.73
Cp1–Ta1–C6	109.88	Cp1–Ta1–C8	109.22
Cp1–Ta1–C21	103.36	O1–Ta1–C6	84.2(3)
C8–Ta1–C6	139.2(5)	O1–Ta1–C21	135.9(3)
O1–Ta1–C8	85.9(3)	C8–Ta1–C21	79.1(4)
C6–Ta1–C21	80.9(4)	C23–C22–C21	112.9(9)
C22–C21–Ta1	134.4(8)		

[a] Cp1 is the centroid of the C1–C5 ring. Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+2$, $-z$.

The NMR spectrum of **6**, which is a monomer species [$D = (11.7 \pm 0.2) \times 10^{-11}$ m^{2}s^{-1}][22] in [D$_2$]dichloromethane [$D = (29.2 \pm 0.5) \times 10^{-11}$ m^{2}s^{-1}] at 298 K, exhibits an ABCD spin system at δ = 8.1, 7.3, 7.2 and 7.12 ppm corresponding to the C_6H_4 moiety, and four singlets for the η^5-C_5Me_5 (δ = 1.94 ppm, 15 H), Ta–CH$_2$C*Me*$_2$Ph (δ = 1.15 ppm, 6 H), Ta–C*H*$_2$CMe$_2$Ph (δ = 0.88 ppm, 2 H, $\Delta\nu_{1/2}$ = 8.7 Hz) and Ta–*Me*$_2$ (δ = 0.27 ppm, 6 H) proton resonances, which justifies the assignment of C_s symmetry to this complex. Unfortunately, the variable temperature spectra did not show any significant changes ($\Delta\nu_{1/2max}$ = 12.7 Hz) to enable the study of any possible fluxional behaviour. NOE data at 203 K indicate short distances between the pentamethylcyclopentadienyl ring and the –CMe$_2$–, Ta–Me$_2$ and Ta–CH$_2$– moieties, and between Ta–Me$_2$ and the phenyl (H2 proton) ring, suggesting an axial position for the phenyl group in the distorted trigonal bipyramidal structure of **6**, as shown in Scheme 3.

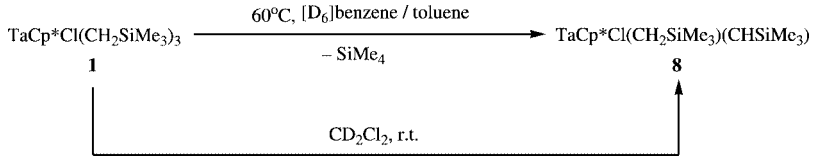
The ^{1}H NMR spectrum of complex **7** in [D$_2$]dichloromethane at 298 K shows a singlet for the Cp* ring (δ = 1.95 ppm), three multiplets for the C_6H_5 group (δ = 7.4, 7.3, 7.13 ppm), two diastereotopic –C*Me*$_2$– (δ = 1.46, 1.40 ppm) groups and an ABC$_3$ spin system at δ = 1.26, 0.04 (AB) and –0.52 (d, $^2J_{H,H}$ = 14.8 Hz, $^4J_{H,H}$ = 1.1 Hz) ppm for the Ta–C*H*$_2$CMe$_2$Ph and Ta–*Me* moieties, respectively. Although **7** contains an asymmetric tantalum(V) central atom, the Ta=CH$_2$ resonance is observed as one singlet (^{1}H NMR, δ = 5.27 ppm; ^{13}C NMR, δ = 205.9 ppm, $^1J_{C,H}$ = 126.1 Hz), which is not like an AB spin system. In the variable temperature ^{1}H NMR study, the maximum broad line ($\Delta\nu_{1/2}$ = 110 Hz) of the methylidene resonance was observed at 173 K, although the multiplicity could not be resolved. We believe that this experimental result could be due to the fast rotation ($\Delta G^{\neq 173\ K} < 32$ kJ mol^{-1}) about the Ta–C vector that accompanies the heterolytic rupture of the double bond, which is in accordance with the reactivity of these complexes. This is known to occur in other methylidene complexes,[18c,23] organic imines[24] and organometallic complexes.[14c,18d]

(Alkyl)(alkylidene)tantalum compounds were obtained by the thermal or photochemical treatment of mixed alkyl derivatives. So, when a toluene or [D$_6$]benzene solution of **1** was heated at 60 °C for 48 h, the (alkyl)(alkylidene)chlorido complex [TaCp*Cl(CH$_2$SiMe$_3$)(CHSiMe$_3$)] (**8**) was formed with the elimination of SiMe$_4$ (Scheme 4). However, complex **1** in [D$_2$]dichloromethane slowly transforms into complex **8** at room temperature.

The ^{1}H NMR spectrum of **8** ($D = 13.0 \times 10^{-10}$ m^{2}s^{-1})[22] shows signals at δ = 5.54 (1 H) and 0.065 ppm (9 H) for Ta=C*H*Si*Me*$_3$ (^{29}Si NMR, δ = –8.2 ppm), an AB spin system at δ = 0.053 and 0.23 ppm ($^2J_{H,H}$ = 12.65 Hz, 2 H) and one singlet at δ = 0.12 ppm (9 H) for the Ta–C*H*$_2$Si*Me*$_3$ moiety, and also a resonance for the Cp* ring at δ = 2.15 ppm. Further, free SiMe$_4$ ($D = 24.5 \times 10^{-10}$ m^{2}s^{-1}) that was eliminated from **1** during the reaction was also observed in the solution. The assignment of the trimethylsilyl resonances and the determination of the ^{29}Si NMR chemical shifts were based on CIGAR data (Figure 5).

When a [D$_6$]benzene solution of **3** was heated at 60 °C for 20 h, a mixture of the dialkyl(alkylidene) compounds [TaCp*MeR(CHSiMe$_3$)] (R = CH$_2$SiMe$_3$, **9**; Me, **10**) was generated in a 3:2 ratio; this mixture was identified by NMR spectroscopy. The reaction occurred with the elimination of CH$_4$ and SiMe$_4$ (Scheme 5). On the other hand, the irradiation of a [D$_6$]benzene solution of **3** with a sun lamp gave a mixture of **9** and [TaCp*(CH$_2$SiMe$_3$)R(CH$_2$)] (R = Me, **11**; CH$_2$SiMe$_3$, **12**) in a 2:1:1 ratio. Both processes, thermal and photochemical, take place by C–Hα activation of the CH$_2$SiMe$_3$ or Me groups. Complex **9** is the major product that results from the preferential elimination of CH$_4$.

In addition, [D$_6$]benzene solutions of the mixed tetraalkyl complex **4** slowly decomposed at room temperature when exposed to a sun lamp, yielding a mixture of the alkylidenes **13**–**16**. When solutions of **4** were heated at 60 °C, the decomposition was faster, and a mixture of (alkyl)(neo-



Scheme 4.

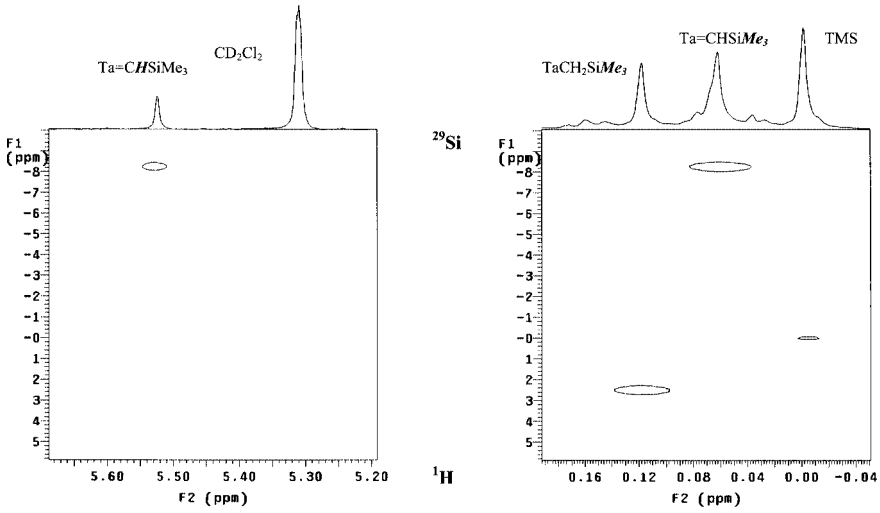
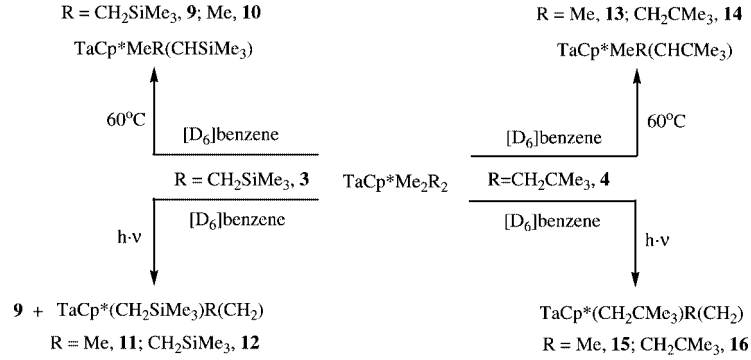


Figure 5. PFG Accord HMBC (CIGAR) ^{1}H-{^{29}Si} spectra of **8** acquired over a period of 20 minutes in a Mercury VX spectrometer with PFG-Z VT 5 mm ATB NMR probe. All parameters were optimized for the ^{1}H–^{29}Si geminal spin coupling.

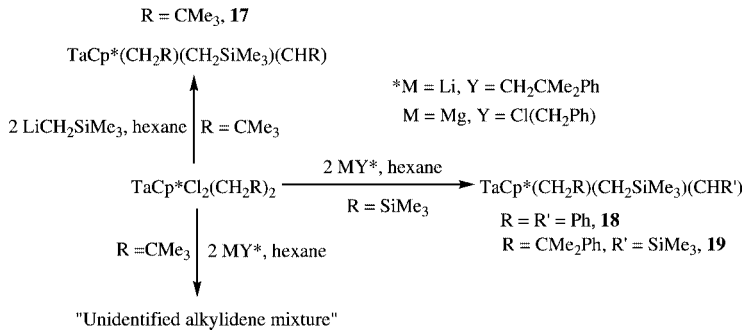


Scheme 5.

pentylidene) derivatives [TaCp*MeR(CHCMe$_3$)] (R = Me, **13**; CH_2CMe_3, **14**) in a 4:1 ratio was produced and identified by NMR spectroscopy. Further, a mixture of the (alkyl)(methylidene) complexes [TaCp*(CH_2CMe_3)R(CH_2)] (R = Me, **15**; CH_2CMe_3, **16**) in a 3:1 ratio was obtained from the irradiation of a [D_6]benzene solution of **4** with a sun lamp. These results indicate that a C–Hα bond is activated by thermal (–CH_2CMe_3) and photochemical (–CH_3) processes, but in both cases the elimination of neopentane is preferential.

A spontaneous α-hydrogen-abstraction process takes place in unstable mixed tetraalkyl intermediates formed by the reaction of complexes [TaCp*Cl_2(CH_2R)$_2$] (R = CMe_3, $SiMe_3$) with an alkylating reagent. So, the reaction of [TaCp*Cl_2(CH_2CMe_3)$_2$] with 2 equiv. of $LiCH_2SiMe_3$ gave the (alkyl)(alkylidene) complex [TaCp*(CH_2CMe_3)(CH_2SiMe_3)(CHCMe$_3$)] (**17**) with the selective elimination of $SiMe_4$ (Scheme 6). The use of neophyllithium or benzylmagnesium chloride leads to an unidentified mixture of alkylidene derivatives. However, new (alkyl)(alkylidene) derivatives [TaCp*(CH_2R)(CH_2SiMe_3)(CHR′)] (R = R′ = Ph, **18**; R = CMe_2Ph, R′ = $SiMe_3$, **19**) were prepared by treatment of [TaCp*Cl_2(CH_2SiMe_3)$_2$] with 2 equiv. of the appropriate alkylating reagent; these reactions occur with the elimination of $SiMe_4$ and CMe_3Ph, respectively.

For some reported coordinatively unsaturated alkylidene complexes,[8,25] the stretching frequency corresponding to the C–H bond in the IR spectrum was assigned to absorp-



Scheme 6.

tion bands localized in the 2700–2350 cm^{-1} region, which are at a lower wavenumber than those for normal C–H stretches probably as a result of the observed increase in the length of the C–H bond. In the case of (alkyl)(alkylidene) compounds **7** and **17**–**19**, the absorption band localized at $\tilde{\nu}_{average}$ = 2553 cm^{-1} can be assigned to ν_{C-H}.

In accordance with all the NMR spectroscopic data (see Experimental Section) the alkylidene complexes **7**–**19** are monomeric species with the expected three-legged piano-stool geometry.[8,26,27] A large degree of deshielding is observed for the alkylidene carbon resonances ($\delta > 200$ ppm). The direct proton–carbon coupling constants for the Ta=*CH*R signals for complexes **7**, **11**, **12**, **15** and **16** are smaller than the $^1J_{C,H}$ values resulting from coupling involving an sp^3 carbon (Ta–*CH*$_2$R groups) and are comparable to other d^0 terminal (alkylidene)niobium and -tantalum complexes.[26,27] For the rest of the complexes, we found similar values for the isostructural alkylmethylidene moiety.

Conclusions

New trialkylchlorido and dialkyldimethyl(pentamethylcyclopentadienyl)tantalum complexes [TaCp*$Cl_xMe_yR_z$] (x = 1, y = 0, z = 3, R = CH_2SiMe_3, **1**; x = 0, y = z = 2, R = CH_2Ph, **2**; CH_2SiMe_3, **3**; CH_2CMe_3, **4**) have been prepared by the direct reaction of tetrachlorido or dialkyldichlorido derivatives [TaCp*$Cl_{4-x}R_x$] (x = 0; x = 2, R = Me, CH_2CMe_3) with the appropriate alkylating reagent. However, when lithium neophyl is used as the reagent under standard conditions, a different sequence of reactions takes place, which leads to a mixture from which [{TaCp*$Me_2(CH_2CMe_2Ph)$}$_2$(μ-O)] (**5**), [TaCp*Me_2-(CH_2CMe_2–o-C_6H_4-κ^2*C*,*C*)] (**6**) and [TaCp*Me-(CH_2CMe_2Ph)(CH_2)] (**7**) were isolated and identified by NMR spectroscopy. Thermal treatment of toluene or [D_6]-benzene solutions of **1** leads to an intramolecular C–Hα bond activation in an alkyl group, giving the (alkyl)(alkylidene)chlorido complex [TaCp*Cl(CH_2SiMe_3)($CHSiMe_3$)] (**8**) with the evolution of $SiMe_4$. A mixture of dialkyl(alkylidene) derivatives [TaCp*MeR($CHSiMe_3$)] (R = CH_2SiMe_3, **9**; Me, **10**) was produced when **3** was heated at 60 °C in [D_6]benzene; the mixture was identified by NMR measurements. Further, the direct irradiation of a [D_6]benzene solution of **3** gave a mixture of **9** and [TaCp*(CH_2SiMe_3)-R(CH_2)] (R = Me, **11**; CH_2SiMe_3, **12**). On the other hand, [D_6]benzene solutions of **4** slowly decompose at room temperature, giving a mixture of alkylidenes [TaCp*MeR($CHCMe_3$)] (R = Me, **13**; CH_2CMe_3, **14**) and [TaCp*(CH_2CMe_3)R(CH_2)] (R = Me, **15**; CH_2CMe_3, **16**), but the decomposition is faster when activated thermally or photochemically, leading to a mixture of **13**–**14** and **15**–**16**, respectively. Finally, a spontaneous α-hydrogen-abstraction process occurs during the alkylation reaction of TaCp*$Cl_2(CH_2CMe_3)_2$ with $LiCH_2SiMe_3$, which gives [TaCp*(CH_2CMe_3)(CH_2SiMe_3)($CHCMe_3$)] (**17**) with selective elimination of $SiMe_4$. However, new (alkyl)(alkylidene) complexes [TaCp*(CH_2R)(CH_2SiMe_3)(CHR′)] (R = R′ = Ph, **18**; R = CMe_2Ph, R′ = $SiMe_3$, **19**) were obtained by treatment of TaCp*$Cl_2(CH_2SiMe_3)_2$ with 2 equiv. of the appropriate alkylating reagent; these reactions occurred with the elimination of $SiMe_4$ and CMe_3Ph, respectively.

Experimental Section

All operations were carried out under a dry argon atmosphere, by using standard Schlenk tube and cannula techniques, or in a conventional argon-filled glove-box. Solvents were refluxed over an appropriate drying agent, distilled and degassed prior to use: [D_6]-benzene and hexane (Na/K alloy), and toluene (Na). Starting materials Ta(η^5-C_5Me_5)Cl_4,[28] Ta(η^5-C_5Me_5)Cl_2Me_2,[13] Ta(η^5-C_5Me_5)-$Cl_2(CH_2CMe_3)_2$[26a,29] and the alkylating reagents LiR (R = CH_2SiMe_3, CH_2CMe_2Ph)[30] and Li($CH_2C_6H_5$)(tmeda)[31] were prepared as previously described. Reagent grade LiMe (1.5 M in diethyl ether, Aldrich) and MgCl(CH_2SiMe_3) (1 M in diethyl ether, Aldrich) were purchased from commercial sources and were used without further purification.

Samples for infrared spectroscopy were prepared as KBr pellets or as Nujol mulls between CsI plates, and the spectra were recorded with a Perkin–Elmer Spectrum 2000 spectrophotometer (4000–400 cm^{-1}). The NMR spectra were recorded with Unity 300, Mercury VX 300 and Unity ^{Plus} 500 (Varian NMR Systems) spectrometers; chemical shifts were referenced to the ^{13}C- and residual ^{1}H resonances of the deuterated solvents. Microanalyses (C, H) were performed with a LECO CHNS 932 microanalyser.

[TaCp*Cl(CH_2SiMe_3)$_3$] (1): A solution of MgCl(CH_2SiMe_3) [6.90 mL, 1 M, 6.60 mmol] in diethyl ether was added, at room temperature, to a suspension of TaCp*Cl_4 (1.00 g, 2.20 mmol) in hexane (25 mL), and the mixture was stirred for 12 h. The resulting

suspension was filtered through Celite and then concentrated to ca. 10 mL, the solution was cooled to –20 °C to give **1** as a yellow microcrystalline solid. Yield 0.90 g (68%). IR (KBr): $\tilde{\nu}$ = 2917 (vs), 1494 (m), 1441 (m), 1380 (s), 1243 (vs), 1105 (s), 1026 (s), 845 (vs), 749 (s), 678 (s), 470 (m), 407 (m) cm^{-1}. ^1H NMR (300 MHz, [D_6]-benzene, 25 °C): δ = 1.78 (s, 15 H, C_5Me_5), 0.65 (s, 6 H, CH_2SiMe_3), 0.35 (s, 27 H, CH_2SiMe_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene, 25 °C): δ = 121.5 (C_5Me_5), 88.0 (CH_2SiMe_3), 12.8 (C_5Me_5), 4.2 (CH_2SiMe_3) ppm. $C_{22}H_{48}ClSi_3Ta$ (613.28): calcd. C 43.08, H 7.89; found C 43.31, H 7.78.

[TaCp*Me$_2$(CH$_2$C$_6$H$_5$)$_2$] (2): This reaction was carried out in a dry box by using darkened glassware designed for photosensitive materials. A solution of Li(CH_2Ph)(tmeda) (0.31 g, 1.44 mmol) in toluene (20 mL) was added to a solution of TaCp*Cl_2Me_2 (0.30 g, 0.72 mmol) in toluene (30 mL) at room temperature, and the mixture was stirred for 10 h. The suspension was concentrated to dryness and the residue extracted with hexane (3 × 20 mL). The solution was filtered, concentrated to ca. 10 mL, and cooled to give **2** as a red microcrystalline solid. Yield 0.29 g (80%). IR (KBr): $\tilde{\nu}$ = 2916 (s), 1591 (m), 1484 (vs), 1450 (m), 1379 (s), 1203 (s), 1150 (m), 1062 (s), 1025 (s), 807 (m), 750 (vs), 698 (vs), 601 (m), 529 (m), 443 (w) cm^{-1}. ^1H NMR (300 MHz, [D_6]benzene, 25 °C): δ = 7.21 (m, 2 H), 7.11 (m, 2 H), 6.85 (m, 1 H, $H_5C_6CH_2$–Ta), 1.67 (br., 4 H, Ta–CH_2Ph), 1.60 (s, 15 H, C_5Me_5), 0.86 (br., 6 H, Ta–Me_2) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene, 25 °C): δ = not detected (C_i), 127.9 (C_m), 127.3 (C_o), 123.2 (C_p, $C_6H_5CH_2$–Ta), 119.5 (C_5Me_5), 94.8 (Ta–$CH_2C_6H_5$), 81.3 (Ta–Me_2), 11.4 (C_5Me_5) ppm. $C_{26}H_{35}Ta$ (528.51): calcd. C 59.08, H 6.67; found C 58.98, H 6.70.

[TaCp*Me$_2$(CH$_2$SiMe$_3$)$_2$] (3): A stirred suspension of TaCp*Cl_2Me_2 (0.50 g, 1.20 mmol) in toluene (30 mL) was treated with a solution of $LiCH_2SiMe_3$ (0.23 g, 2.40 mmol) in toluene (20 mL). The reaction mixture was stirred for 10 h at room temperature, and the resulting suspension was decanted and filtered. The solution was concentrated to dryness and the residue extracted with hexane (3 × 15 mL). The solution was filtered, concentrated to ca. 10 mL, and cooled to –40 °C to give **3** as a yellow microcrystalline solid. Yield 0.35 g (74%). IR (KBr): $\tilde{\nu}$ = 2947 (vs), 1490 (m), 1432 (s), 1380 (m), 1295 (w), 1241 (s), 1160 (m), 1026 (m), 947 (s), 856 (vs), 823 (vs), 744 (m), 718 (s), 676 (m), 612 (m), 521 (w), 442 (m) cm^{-1}. ^1H NMR (500 MHz, [D_2]dichloromethane, 25 °C): δ = 2.00 (s, 15 H, C_5Me_5), 0.40 (quint, $^4J_{H,H}$ = 1.1 Hz, 6 H, Ta–Me_2), 0.06 (s, 18 H, Ta–CH_2SiMe_3), –0.30 (m, 4 H, Ta–CH_2SiMe_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene, 25 °C): δ = 118.9 (C_5Me_5), 83.6 (Ta–CH_2SiMe_3), 71.7 (Ta–Me_2), 11.7 (C_5Me_5), 3.8 (CH_2SiMe_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, [D_2]dichloromethane, 25 °C): δ = 118.9 (C_5Me_5), 83.2 (Ta–CH_2SiMe_3), 70.7 (Ta–Me_2), 11.1 (C_5Me_5), 3.5 (CH_2SiMe_3) ppm. $C_{20}H_{43}Si_2Ta$ (520.68): calcd. C 46.12, H 8.32; found C 45.90, H 8.02.

[TaCp*Me$_2$(CH$_2$CMe$_3$)$_2$] (4): A solution of LiMe in diethyl ether (1.30 mL, 1.5 M, 1.95 mmol) was added to a solution of TaCp*$Cl_2(CH_2CMe_3)_2$ (0.40 g, 0.75 mmol) in hexane (40 mL) at –78 °C, and the mixture was stirred for 5 h. The suspension was then warmed to room temperature and LiCl filtered off. The solution was concentrated to ca. 10 mL and cooled to –40 °C to give a yellow microcrystalline solid identified as **4**. Yield 0.30 g (81%). IR (KBr): $\tilde{\nu}$ = 2940 (vs), 1431 (m), 1379 (s), 1205 (s), 1157 (m), 1023 (m), 804 (w), 746 (m), 601 (m), 522 (m), 455 (m) cm^{-1}. ^1H NMR (300 MHz, [D_6]benzene, 25 °C): δ = 1.66 (s, 15 H, C_5Me_5), 1.40 (s, 18 H, Ta–CH_2CMe_3), 0.92 (6 H, Ta–Me_2), 0.34 (4 H, Ta–CH_2CMe_3) ppm. ^1H NMR (500 MHz, [D_2]dichloromethane, 25 °C): δ = 1.96 (s, 15 H, C_5Me_5), 1.07 (s, 18 H, Ta–CH_2CMe_3), 0.59 (quint, $^4J_{H,H}$ = 1.3 Hz, 6 H, Ta–Me_2), 0.20 (sept, $^4J_{H,H}$ = 1.3 Hz, 4 H, Ta–CH_2CMe_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]-benzene, 25 °C): δ = 118.6 (C_5Me_5), 111.2 (Ta–CH_2CMe_3), 76.6 (Ta–Me_2), not detected (Ta–CH_2CMe_3), 36.3 (Ta–CH_2CMe_3), 11.7 (C_5Me_5) ppm. $C_{22}H_{43}Ta$ (488.53): calcd. C 54.09, H 8.87; found C 53.95, H 8.72.

[{TaCp*Me$_2$(CH$_2$CMe$_2$Ph)}$_2$(μ-O)] (5): Complex **5** was isolated together with complexes **6** and **7** by using a standard vacuum line and Schlenk techniques. A mixture of TaCp*Cl_2Me_2 (0.50 g, 1.20 mmol) and $LiCH_2CMe_2Ph$ (0.34 g, 2.40 mmol) was stirred in toluene (30 mL) at room temperature for 15 h. LiCl was filtered off, and the resulting solution was concentrated to dryness. The brown residue was extracted with hexane (3 × 10 mL), concentrated to ca. 10 mL, and then cooled to –40 °C to give **5**. The filtrate was cooled to –78 °C to give **6** as a yellow microcrystalline solid, and the final solution was concentrated to dryness to give **7** as a brown oil. IR (KBr): $\tilde{\nu}$ = 2912 (s), 1599 (w), 1491 (m), 1436 (s), 1378 (s), 1203 (w), 1157 (m), 1027 (m), 740 (vs), 709 (s), 650 (m), 555 (w), 466 (m) cm^{-1}. ^1H NMR (300 MHz, [D_6]benzene, 25 °C): δ = 7.62 (m, 4 H), 7.33 (m, 4 H), 7.12 (m, 2 H, $H_5C_6Me_2C$–CH_2–Ta), 1.79 (s, 12 H, Ta–CH_2CMe_2Ph), 1.68 (s, 30 H, C_5Me_5), 1.04 (s, 4 H, Ta–CH_2CMe_2Ph), 0.68 (s, 12 H, Ta–Me_2) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene, 25 °C): δ = 157.3 (C_i), 127.9, 126.3, 124.8 ($H_5C_6Me_2C$–CH_2), 117.8 (C_5Me_5), 88.3 (Ta–CH_2CMe_2Ph), 61.4 (Ta–Me_2), 43.7 (Ta–CH_2CMe_2Ph), 35.2 (Ta–CH_2CMe_2Ph), 11.4 (C_5Me_5) ppm.

[TaCp*Me$_2$(CH$_2$CMe$_2$-*o*-C$_6$H$_4$-κ^2*C*,*C*)] (6) and [TaCp*Me(CH$_2$CMe$_2$Ph)(CH$_2$)] (7): Under rigorously anhydrous conditions (glove box), a solution of TaCp*Cl_2Me_2 (0.50 g, 1.20 mmol) in toluene (30 mL) was treated with a solution of $LiCH_2CMe_2Ph$ (0.34 g, 2.40 mmol) in toluene (10 mL), and the mixture was stirred at room temperature for 15 h. The resulting suspension was concentrated to dryness, and the residue extracted with hexane (2 × 15 mL). The solution was filtered, concentrated to ca. 10 mL and cooled to –78 °C over a period of several minutes to give a pale brown microcrystalline solid identified as **6**. Compound **6** was then filtered off, and the solution was concentrated to dryness to give **7** as a sticky brown solid.

Data for **6**: Yield 0.18 g (32%). IR (KBr): $\tilde{\nu}$ = 2909 (vs), 1654 (w), 1574 (w), 1492 (m), 1438 (s), 1377 (s), 1238 (m), 1102 (m), 1024 (m), 762 (s), 731 (vs), 560 (m), 460 (m), 411 (m) cm^{-1}. ^1H NMR (500 MHz, [D_2]dichloromethane, –40 °C): δ = 8.05 (m, 1 H, H_4C_6–*o*-CMe_2–CH_2–Ta), 7.27 (m, 1 H, H_4C_6–*o*-CMe_2–CH_2–Ta), 7.20 (m, 1 H, H_4C_6–*o*-CMe_2–CH_2–Ta), 7.10 (m, 1 H, H_4C_6–*o*-CMe_2–CH_2–Ta), 1.89 (s, 15 H, C_5Me_5), 1.07 (s, 6 H, H_4C_6–*o*-CMe_2–CH_2–Ta), 0.77 (s, 2 H, H_4C_6–*o*-CMe_2–CH_2–Ta), 0.18 (s, 6 H, Ta–Me_2) ppm. ^{13}C NMR[32] (125 MHz, [D_2]dichloromethane, 25 °C): δ = 219.1 (C_i–Ta), 137.1, 124.0, 123.8, 123.2, 160.3 ppm (H_4C_6–*o*-CMe_2–CH_2–Ta), 115.9 (C_5Me_5), 112.4 (H_4C_6–*o*-CMe_2–CH_2–Ta), 67.4 (Ta–Me_2), 49.5 (H_4C_6–*o*-CMe_2–CH_2–Ta), 34.0 (H_4C_6–*o*-CMe_2–CH_2–Ta), 10.2 (C_5Me_5) ppm. $C_{22}H_{33}Ta$ (478.45): calcd. C 55.23, H 6.95; found C 55.10, H 6.75.

Data for **7**: Yield 0.32 g (56%). ^1H NMR (500 MHz, [D_2]dichloromethane, 25 °C): δ = 7.41, 7.28, 7.13 ($H_5C_6Me_2C$–CH_2–Ta), 5.27 (s, 2 H, Ta=CH_2), 1.95 (s, 15 H, C_5Me_5), 1.46 (s, 3 H), 1.40 (s, 3 H, $H_5C_6Me_2C$–CH_2–Ta), 1.26 (d), 0.04 (q, AB, $^2J_{H,H}$ = 14.8 Hz, 2 H, $H_5C_6Me_2C$–CH_2–Ta), –0.52 (d, $^4J_{H,H}$ = 1.1 Hz, 3 H, Ta–*Me*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene, 25 °C): δ = 205.9 (t, $^1J_{C,H}$ = 126.1 Hz, Ta=CH_2), 153.5–125.4 ($H_5C_6Me_2C$–CH_2–Ta), 113.6 (C_5Me_5), 94.8 (t, $^1J_{C,H}$ = 105.6 Hz, $H_5C_6Me_2C$–CH_2–Ta), 44 (Ta–*Me*), 40 ($H_5C_6Me_2C$–CH_2–Ta), 31.4, 32 ($H_5C_6Me_2C$–CH_2–Ta), 11.3 (C_5Me_5) ppm.

[TaCp*Cl(CH_2SiMe_3)($CHSiMe_3$)] (8): A solution of **1** (0.15 g, 0.24 mmol) in toluene (20 mL) was placed in an ampoule under rigorously anhydrous conditions and then sealed. The solution was heated to 60 °C for 2 days. After the ampoule was opened, the solution was concentrated to dryness, and the brown oil residue was identified as **8**. Yield 0.10 g (80%). IR (KBr): $\tilde{\nu}$ = 2913 (s), 2578 (w), 1584 (m), 1488 (m), 1432 (m), 1378 (m), 1244 (vs), 1097 (m), 1026 (s), 941 (s), 841 (vs), 750 (s), 682 (s), 483 (m), 437 (w) cm^{-1}. ^1H NMR (500 MHz, [D$_2$]dichloromethane, 25 °C): δ = 5.54 (s, 1 H, Ta=C*H*SiMe$_3$), 2.15 (s, 15 H, C$_5$*Me*$_5$), 0.23 (AB, $^2J_{H,H}$ = 12.7 Hz, 1 H, Ta–CH*H*SiMe$_3$), 0.12 (s, 9 H, Ta–CH$_2$Si*Me*$_3$), 0.07 (s, 9 H, Ta=CHSi*Me*$_3$), 0.053 (AB, $^2J_{H,H}$ = 12.7 Hz, 1 H, Ta–CH*H*SiMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, [D$_6$]benzene, 25 °C): δ = 231.5 (d, $^1J_{C,H}$ = 89.0 Hz, Ta=*C*HSiMe$_3$), 116.5 (*C*$_5$Me$_5$), 50.6 (Ta–*C*H$_2$SiMe$_3$), 11.9 (C$_5$*Me*$_5$), 3.4 (Ta–CH$_2$Si*Me*$_3$), 2.5 (Ta=CHSi*Me*$_3$) ppm. $C_{18}H_{36}ClSi_2Ta$ (524.879): calcd. C 41.15, H 6.91; found C 41.18, H 6.81.

[TaCp*MeR(CHSiMe$_3$)] (R = CH$_2$SiMe$_3$, 9; Me, 10): A solution of **3** (0.07 g, 0.13 mmol) in [D$_6$]benzene (0.70 mL) was placed into an NMR tube with a valve, and this tube was heated to 60 °C. The reaction was monitored by NMR spectroscopy, and after 20 h the formation of a mixture of the (alkyl)(alkylidene) derivatives **9** and **10** in a 3:2 ratio was confirmed.

Data for **9**: ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 4.80 (s, 1 H, Ta=C*H*SiMe$_3$), 1.82 (s, 15 H, C$_5$*Me*$_5$), 0.32 (s, 9 H, Ta–CH$_2$Si*Me*$_3$), 0.28 (s, 9 H, Ta=CHSi*Me*$_3$), 0.06 (s, 3 H, Ta–*Me*), –0.06 (AB, $^2J_{H,H}$ = 12.4 Hz, 1 H, Ta–CH*H*SiMe$_3$), –0.93 (AB, $^2J_{H,H}$ = 12.4 Hz, 1 H, Ta–CH*H*SiMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 223.3 (d, $^1J_{C,H}$ = 76.9 Hz, Ta=*C*HSiMe$_3$), 114.8 (*C*$_5$Me$_5$), 59.9 (t, $^1J_{C,H}$ = 105.3 Hz, Ta–*C*H$_2$SiMe$_3$), 42.2 (Ta–*Me*), 11.8 (C$_5$*Me*$_5$), 3.7 (Ta–CH$_2$Si*Me*$_3$), 2.8 (Ta=CHSi*Me*$_3$) ppm.

Data for **10**: ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 5.81 (s, 1 H, Ta=C*H*SiMe$_3$), 1.79 (s, 15 H, C$_5$*Me*$_5$), 0.37 (s, 9 H, Ta=CHSi*Me*$_3$), 0.13 (s, 6 H, Ta–*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 222.8 (d, $^1J_{C,H}$ = 75.7 Hz, Ta=*C*HSiMe$_3$), 114.7 (*C*$_5$Me$_5$), 47.9 (Ta–*Me*$_2$), 11.6 (C$_5$*Me*$_5$), 3.9 (Ta=CHSi*Me*$_3$) ppm.

[TaCp*(CH$_2$SiMe$_3$)R(CH$_2$)] (R = Me, 11; CH$_2$SiMe$_3$, 12): In a standard experiment, a solution of **3** (0.07 g, 0.13 mmol) in [D$_6$]benzene (0.60 mL) was transferred to a valved NMR tube and then irradiated with a sun lamp for 2 h. A mixture of the (alkyl)(alkylidene) compounds **9**, **11** and **12**, in a ratio 2:1:1, together with the elimination products CH_4 and $SiMe_4$, was identified in the NMR spectrum of the resulting solution.

Data for **11**: ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 6.06 (s, 2 H, Ta=C*H*$_2$), 1.77 (s, 15 H, C$_5$*Me*$_5$), 0.34 (s, 9 H, Ta–CH$_2$Si*Me*$_3$), 0.11 (s, 3 H, Ta–*Me*), –0.14 (AB, $^2J_{H,H}$ = 12.5 Hz, 1 H, Ta–CH*H*SiMe$_3$), –0.69 (AB, $^2J_{H,H}$ = 12.5 Hz, 1 H, Ta–CH*H*SiMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 207.0 (t, $^1J_{C,H}$ = 125.8 Hz, Ta=*C*H$_2$), 113.3 (*C*$_5$Me$_5$), 60 (Ta–*C*H$_2$SiMe$_3$), 43.1 (Ta–*Me*), 11.3 (C$_5$*Me*$_5$), 2.5 (Ta–CH$_2$Si*Me*$_3$) ppm.

Data for **12**: ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 5.89 (s, 2 H, Ta=C*H*$_2$), 1.79 (s, 15 H, C$_5$*Me*$_5$), 0.31 (s, 18 H, Ta–CH$_2$Si*Me*$_3$), 0.06 (AB, $^2J_{H,H}$ = 11.9 Hz, 1 H, Ta–CH*H*SiMe$_3$), –1.05 (AB, $^2J_{H,H}$ = 11.9 Hz, 1 H, Ta–CH*H*SiMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 205.5 (t, $^1J_{C,H}$ = 126.6 Hz, Ta=*C*H$_2$), 113.2 (*C*$_5$Me$_5$), 56.8 (Ta–*C*H$_2$SiMe$_3$), 11.5 (C$_5$*Me*$_5$), 2.6 (Ta–CH$_2$Si*Me*$_3$) ppm.

[TaCp*MeR(CHCMe$_3$)] (R = Me, 13; CH$_2$CMe$_3$, 14): A solution of **4** (0.04 g, 0.08 mmol) in [D$_6$]benzene (0.60 mL) was placed into a sealed NMR tube and then heated to 60 °C for 4 h. The reaction was monitored by NMR, and a mixture of (alkyl)(alkylidene) compounds **13** and **14**, in a 4:1 ratio, together with the organic elimination products CMe_4 (δ = 0.9 ppm) and CH_4 (δ = 0.15 ppm), was identified by NMR spectroscopy.

Data for **13**: ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 3.38 (s, 1 H, Ta=C*H*CMe$_3$), 1.84 (s, 15 H, C$_5$*Me*$_5$), 1.30 (s, 9 H, Ta=CHC*Me*$_3$), 0.07 (s, 6 H, Ta–*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 224.2 (d, $^1J_{C,H}$ = 80.3 Hz, Ta=*C*HCMe$_3$), 114.3 (*C*$_5$Me$_5$), 40.9 (Ta–*Me*$_2$), 34.9 (Ta=CH*C*Me$_3$), 33.9 (Ta=CHC*Me*$_3$), 11.3 (C$_5$*Me*$_5$) ppm.

Data for **14**: ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 3.26 (s, 1 H, Ta=C*H*CMe$_3$), 1.83 (s, 15 H, C$_5$*Me*$_5$), 1.34 (s, 9 H, Ta=CHC*Me*$_3$), 1.34 (s, 9 H, Ta–CH$_2$C*Me*$_3$), 1.08 (AB, $^2J_{H,H}$ = 14.2 Hz, 1 H, Ta–CH*H*CMe$_3$), –0.07 (s, 3 H, Ta–*Me*), –0.71 (AB, $^2J_{H,H}$ = 14.2 Hz, 1 H, Ta–CH*H*CMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 226.1 (d, $^1J_{C,H}$ = 78.1 Hz, Ta=*C*HCMe$_3$), 113.9 (*C*$_5$Me$_5$), 94.2 (t, $^1J_{C,H}$ = 102.1 Hz, Ta–*C*H$_2$CMe$_3$), 47.1, 37 (Ta–*Me*), 35.2, 34.0 (Ta=CHC*Me*$_3$, Ta–CH$_2$C*Me*$_3$), 33.7 (Ta=CH*C*Me$_3$, Ta–CH$_2$*C*Me$_3$), 11.6 (C$_5$*Me*$_5$) ppm.

[TaCp*(CH$_2$CMe$_3$)R(CH$_2$)] (R = Me, 15; CH$_2$CMe$_3$, 16): In a typical experiment, a yellow solution of **4** (0.04 g, 0.08 mmol) in [D$_6$]-benzene (0.60 mL) was transferred to a valved NMR tube and then irradiated with a sun lamp for 3 h. The (alkyl)(alkylidene) complexes **15** and **16**, in a ratio of 3:1, and the organic elimination products CMe_4 and CH_4 were identified in the NMR spectrum.

Data for **15**: ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 5.92 (s, 2 H, Ta=C*H*$_2$), 1.75 (s, 15 H, C$_5$*Me*$_5$), 1.28 (s, 9 H, Ta–CH$_2$C*Me*$_3$), 1.06 (AB, $^2J_{H,H}$ = 14.4 Hz, 1 H, Ta–CH*H*CMe$_3$), 0.032 (s, 3 H, Ta–*Me*), –0.30 (AB, $^2J_{H,H}$ = 14.4 Hz, 1 H, Ta–CH*H*CMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 205.5 (t, Ta=*C*H$_2$, $^1J_{C,H}$ = 125.3 Hz), 113.2 (*C*$_5$Me$_5$), 96 (t, Ta–*C*H$_2$CMe$_3$, $^1J_{C,H}$ = 117.2 Hz), 42.9 (Ta–*Me*), 34.8 (Ta–CH$_2$C*Me*$_3$), 32.8 (Ta–CH$_2$*C*Me$_3$), 11.2 (C$_5$*Me*$_5$).

Data for **16**: ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 5.80 (s, 2 H, Ta=C*H*$_2$), 1.77 (s, 15 H, C$_5$*Me*$_5$), 1.34 (s, 18 H, Ta–CH$_2$C*Me*$_3$), 1.20 (AB, $^2J_{H,H}$ = 13.0 Hz, 1 H, Ta–CH*H*CMe$_3$), –0.40 (AB, $^2J_{H,H}$ = 13.0 Hz, 1 H, Ta–CH*H*CMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 209.4 (t, $^1J_{C,H}$ = 126.1 Hz, Ta=*C*H$_2$), 112.8 (C$_5$*Me*$_5$), 92.4 (t, $^1J_{C,H}$ = 110.9 Hz, Ta–*C*H$_2$CMe$_3$), 35 (Ta–CH$_2$C*Me*$_3$), 34 (Ta–CH$_2$*C*Me$_3$), 11.6 (C$_5$*Me*$_5$) ppm.

[TaCp*(CH$_2$CMe$_3$)(CH$_2$SiMe$_3$)(CHCMe$_3$)] (17): TaCp*Cl$_2$-(CH$_2$CMe$_3$)$_2$ (0.70 g, 1.30 mmol) and LiCH$_2$SiMe$_3$ (0.25 g, 2.60 mmol) were stirred in hexane (45 mL) at room temperature for 10 h. The resulting suspension was filtered and concentrated to ca. 5 mL and cooled overnight to –40 °C to give **17** as an orange microcrystalline solid. Yield 0.44 (61%). IR (CsI): $\tilde{\nu}$ = 2940 (vs), 2430 (m), 1459 (s), 1434 (m), 1353 (s), 1243 (vs), 1024 (m), 950 (s), 853 (vs), 827 (s), 744 (m), 720 (m), 684 (m), 573 (w), 508 (m), 417 (m) cm^{-1}. ^1H NMR (500 MHz, [D$_6$]benzene, 25 °C): δ = 3.10 (s, 1 H, Ta=C*H*CMe$_3$), 1.84 (s, 15 H, C$_5$*Me*$_5$), 1.38 (s, 9 H) and 1.35 (s, 9 H) (Ta=CHC*Me*$_3$ and Ta–CH$_2$C*Me*$_3$), 1.03 (AB, $^2J_{H,H}$ = 13.8 Hz, 1 H, Ta–CH*H*CMe$_3$), 0.32 (s, 9 H, Ta–CH$_2$Si*Me*$_3$), 0.11 (AB, $^2J_{H,H}$ = 12.0 Hz, 1 H, Ta–CH*H*SiMe$_3$), –0.38 (AB, $^2J_{H,H}$ = 13.8 Hz, 1 H, Ta–CH*H*CMe$_3$), –1.44 (AB, $^2J_{H,H}$ = 12.0 Hz, 1 H, Ta–CH*H*SiMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, [D$_6$]benzene, 25 °C): δ = 226.4 (d, $^1J_{C,H}$ = 77.4 Hz, Ta=*C*HSiMe$_3$), 114 (*C*$_5$Me$_5$), 88.7 (Ta–*C*H$_2$CMe$_3$), 53.7 (Ta–*C*H$_2$SiMe$_3$), 47.6, 35.4, 34.2 (Ta–CH$_2$C*Me*$_3$, Ta=CHC*Me*$_3$), 34.1 (Ta–CH$_2$*C*Me$_3$, Ta=CH*C*Me$_3$), 12.0 (C$_5$*Me*$_5$), 3.2 (Ta–CH$_2$Si*Me*$_3$) ppm. $C_{24}H_{47}SiTa$ (544.663): calcd. C 52.92, H 8.69; found C 52.67, H 8.97.

[TaCp*(CH$_2$Ph)(CH$_2$SiMe$_3$)(CHPh)] (18): This reaction was carried out in a glove box in darkened glassware designed for photosensitive materials. A 1 M solution of MgCl(CH$_2$Ph) in diethyl ether (1.50 mL, 1.45 mmol) was added to a solution of TaCp*Cl$_2$-(CH$_2$SiMe$_3$)$_2$ (0.40 g, 1.71 mmol) in hexane (30 mL), and the mixture was stirred for 14 h. The resulting suspension was decanted and filtered through Celite. The red solution was concentrated to ca. 5 mL and cooled to –40 °C overnight to give **18** as a red microcrystalline solid. Yield 0.27 g (65%). IR (CsI): $\tilde{\nu}$ = 2914 (vs), 2494 (w), 1856 (w), 1592 (m), 1485 (vs), 1449 (s), 1378 (m), 1242 (s), 1199 (m), 1054 (m), 1027 (s), 950 (m), 850 (vs), 750 (vs), 695 (s), 536 (m), 438 (w) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 7.29–6.86 (several phenyl, $H_5C_6CH_2$–Ta, H_5C_6CH=Ta), 5.45 (s, 1 H, Ta=C*H*Ph), 1.79 (s, 15 H, C$_5$*Me*$_5$), 1.68 (AB, $^2J_{H,H}$ = 12.3 Hz, 1 H, Ta–CH*H*Ph), 1.61 (AB, $^2J_{H,H}$ = 12.3 Hz, 1 H, Ta–CH*H*Ph), 0.88 (AB, $^2J_{H,H}$ = 12.1 Hz, 2 H, Ta–CH*H*Ph , Ta–CH*H*SiMe$_3$), 0.09 (s, 9 H, Ta–CH$_2$Si*Me*$_3$), –1.29 (AB, $^2J_{H,H}$ = 12.1 Hz, 2 H, Ta–CH*H*Ph, Ta–CH*H*SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 216.7 (d, $^1J_{C,H}$ = 82.6 Hz, Ta=*C*HPh), 151.1–122.9 (several phenyl, $H_5C_6CH_2$–Ta, H_5C_6CH=Ta), 114.5 (*C*$_5$Me$_5$), 69.1 (t, $^1J_{C,H}$ = 119.4 Hz, Ta–*C*H$_2$Ph), 64.1 (t, $^1J_{C,H}$ = 104.2 Hz, Ta–*C*H$_2$SiMe$_3$), 11.3 (C$_5$*Me*$_5$), 2.7 (Ta–CH$_2$Si*Me*$_3$) ppm. $C_{28}H_{39}SiTa$ (584.65): calcd. C 57.52, H 6.72; found C 57.48, H 6.75.

[TaCp*(CH$_2$CMe$_2$Ph)(CH$_2$SiMe$_3$)(CHSiMe$_3$)] (19): TaCp*Cl$_2$-(CH$_2$SiMe$_3$)$_2$ (0.30 g, 0.53 mmol) and Li(CH$_2$CMe$_2$Ph) (0.16 g, 1.20 mmol) were stirred in toluene (40 mL) at room temperature for 15 h. The volatiles were removed under reduced pressure, and the residual solid was extracted with hexane (2 × 15 mL). The solution was filtered and concentrated to dryness to give **19** as a pale brown oil. Yield 0.26 g (81%). IR (CsI): $\tilde{\nu}$ = 2910 (vs), 2564 (w), 1599 (w), 1492 (m), 1442 (s), 1379 (s), 1242 (vs), 1169 (m), 1028 (m), 945 (vs), 847 (vs), 762 (s), 702 (s), 626 (w), 552 (m), 434 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 7.44 (m, 2 H, $H_5C_6Me_2CCH_2$–Ta), 7.26 (m, 2 H, $H_5C_6Me_2CCH_2$–Ta), 7.09 (m, 1 H, $H_5C_6Me_2CCH_2$–Ta), 4.17(s, 1 H, Ta=C*H*SiMe$_3$), 1.79 (s, 15 H, C$_5$*Me*$_5$), 1.70 (s, 3 H), 1.57 (s, 3 H, Ta–CH$_2$C*Me*$_2$Ph), 1.01 (AB, $^2J_{H,H}$ = 14.4 Hz, 1 H), not detected (AB, $^2J_{H,H}$ = 14.4 Hz, 1 H), 0.40 (AB, $^2J_{H,H}$ = 11.7 Hz, 2 H, Ta–CH*H*CMe$_2$Ph, Ta–CH*H*SiMe$_3$), 0.28 (s, 9 H), 0.14 (s, 9 H, Ta–CH$_2$Si*Me*$_3$, Ta=CHSi-*Me*$_3$), –2.05 (AB, $^2J_{H,H}$ = 11.7 Hz, 2 H, Ta–CH*H*CMe$_2$Ph, Ta–CH*H*SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): δ = 226.8 (d, $^1J_{C,H}$ = 76.6 Hz, Ta=*C*HSiMe$_3$), 153.6 (C$_i$), 128.5 (C$_o$), 126.4 (C$_m$), 125.5 (C$_p$, $H_5C_6Me_2CCH_2$–Ta), 114.4 (*C*$_5$Me$_5$), 86.7 (t, $^1J_{C,H}$ = 109.5 Hz, Ta–*C*H$_2$CMe$_2$Ph), 64.0 (t, $^1J_{C,H}$ = 103.4 Hz Ta–*C*H$_2$SiMe$_3$), 40.1 (Ta–CH$_2$*C*Me$_2$Ph), 36.9, 31.9 (Ta–CH$_2$C*Me*$_2$Ph), 11.9 (C$_5$*Me*$_5$), 3.6, 2.8 (Ta–CH$_2$Si*Me*$_3$, TaCHSi-*Me*$_3$).

Crystal Structure Determination for Compounds 1, 4 and 5: Crystallographic and experimental details of the crystal structure determinations are given in Table 4. Suitably sized crystals were sealed under argon in a Lindemann capillary tube and mounted on an Enraf Nonius CAD 4 automatic four circle diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensities were collected at room temperature and corrected for Lorenz and polarization effects in the usual manner. No extinction corrections were made. Empirical absorption corrections (DIFABS)[33] were made to the data for **1** and **4**, and the data for **5** were corrected with ψ

Table 4. Crystal data and structure refinement details for **1**, **4** and **5**.[a]

	1	**4**	**5**
Chemical formula	$C_{22}H_{48}ClSi_3Ta$	$C_{22}H_{43}Ta$	$C_{44}H_{68}OTa_2$
Formula weight	613.27	488.529	974.8
T [K]	293(2)	293(2)	293(2)
λ (Mo-K_α) [Å]	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
a [Å]; α [°]	15.401(1); 90.00	9.230(1); 90.00	8.639(2); 101.7(2)
b [Å]; β [°]	10.945(1); 91.09(2)	31.913(1); 99.06(5)	10.278(2); 98.77(2)
c [Å]; γ [°]	17.721(1); 90.00	16.087(1); 90.00	12.159(4); 100.71(2)
V [Å]^3	2986.6(4)	4679.4(6)	1018.3(5)
Z	4	8	1
ρ_{calcd} [g cm^{-3}]	1.364	1.3804	1.590
μ [mm^{-1}]	3.896	4.698	5.399
F(000)	1248	1984	486
Crystal size [mm^3]	0.27 × 0.30 × 0.33	0.35 × 0.30 × 0.20	0.35 × 0.35 × 0.10
θ range [°]	1.32 to 22.97	1.28 to 22.93	2.08 to 25.11
Index ranges	–16 ≤h≤ 16	–9 ≤h≤ 0	–10 ≤h≤ 0
	–12 ≤k≤ 0	–34 ≤k≤ 0	–12 ≤k≤ 12
	0 ≤l≤ 19	–16 ≤l≤ 16	–14 ≤l≤ 14
Number of data collected	4366	6144	3873
Number of unique data	4134 [R(int) = 0.0661]	5711 [R(int) = 0.1381]	3612 [R(int) = 0.0172]
Number of observed reflections [I>2σ(I)]	1669	2531	3368
Absorption correction	Empirical (DIFABS)	Empirical (DIFABS)	ψ-scan
Max. and min. transmission	0.702, 0.243	0.638, 0.166	0.5815, 0.0942
Number of refined parameters	244	390	214
Goodness-of-fit on F^2	0.926	0.951	1.105
Final R indices [I>2σ(I)]	R_1 = 0.0628	R_1 = 0.0677	R_1 = 0.0710
	wR_2 = 0.1079	wR_2 = 0.1421	wR_2 = 0.1764
R indices (all data)	R_1 = 0.2540	R_1 = 0.2431	R_1 = 0.0744
	wR_2 = 0.1469	wR_2 = 0.1870	wR_2 = 0.1802
Largest diff. peak and hole [e Å^{-3}]	0.857 and –1.422	0.917 and –1.605	5.664 and –5.187 (near Ta)

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

scan methods. Structures were initially solved by direct methods, completed by the subsequent difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL-97).[34] Anisotropic thermal parameters were included in the last cycles of refinement for the non-hydrogen atoms, except for five carbon atoms in compound **5** that remained isotropic. The hydrogen atoms were included from geometrical calculations and refined by using a riding model. All the calculations were performed with the WINGX system.[35]

CCDC-299683(**1**), 299684(**4**) and 299685(**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra of complexes **9-16**.

Acknowledgments

We thank the MCYT (Project BQU 2002–03754) and Universidad de Alcalá (Project GC 2005/94) for their financial support for this research.

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Received: February 27, 2006
Published Online: September 14, 2006

