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MONOCYCLOPENTADIENYL ALKYL ALKYLIDENE NIOBIUM(V) AND TANTALUM(V) COMPLEXES. X-RAY CRYSTAL STRUCTURE OF $Ta(\eta^5\text{-}Cp')(CH_2SiMe_3)_2(CHSiMe_3)$

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Abstract—Reactions of monocyclopentadienyl complexes $M(\eta^5\text{-}Cp')Cl_4$ with trimethylsilylmethyl lithium leads to the formation of alkylidene derivatives $M(\eta^5\text{-}Cp')(CH_2SiMe_3)_2(CHSiMe_3)$, where M = Nb (**1**); Ta (**2**); Cp′ = C_5Me_5 and M = Ta; Cp′ = $Me_3Si(C_5H_4)$ (**3**), 1,3-$(Me_3Si)_2(C_5H_3)$ (**4**). The new complexes were characterized by ^1H and ^{13}C NMR spectroscopy and the molecular structure of **2** was studied by X-ray diffraction methods.

The chemistry of the alkylidene complexes of the group *5d* and *6d* elements has been well-developed and a vast list of reports account for the isolation, structural characterization and reactivity of these complexes, many of which have found relevant practical applications mainly related to dimerization and metathesis of alkenes. The reader is referred to reports and reviews published by Schrock[1] and to general treatises[2] including references to other authors. We recently reported[3] that $Nb(\eta^5\text{-}C_5Me_5)Cl_4$ can be directly obtained in a crystalline form and high yield using dichloromethane–toluene (3 : 1) as a solvent, by the method previously described,[4] and its hydrolysis to different oxo complexes. A more convenient entry to the selective isolation of these oxo compounds is the hydrolysis of alkyl derivatives. Therefore, we were interested in the ability of tetrachloro-cyclopentadienyl niobium and tantalum compounds to coordinate bulky alkyl substituents. It is very well known[1,5] that "overpopulation" of the coordination sphere of the metal is the basis for the formation of an alkylidene by α-hydrogen elimination, and this process is observed in our reactions with trimethylsilylmethyl lithium. Here we describe the isolation of alkyl alkylidene niobium and tantalum complexes containing differently substituted cyclopentadienyl rings and the X-ray structure of $Ta(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)_2(CHSiMe_3)$.

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RESULTS AND DISCUSSION

The reaction of $M(\eta^5\text{-}Cp')Cl_4$ with four equivalents of $LiCH_2SiMe_3$ in n-hexane or toluene takes place with the simultaneous elimination of $SiMe_4$, giving rise to the alkylidene complexes shown in the following equation:

$$M(\eta^5\text{-}Cp')Cl_4 + 4LiCH_2SiMe_3 \xrightarrow[-TMS]{-4LiCl} M(\eta^5\text{-}Cp')(CH_2SiMe_3)_2(CHSiMe_3)$$

Cp′ = η^5-C_5Me_5; M = Nb (**1**), Ta (**2**)
Cp′ = η^5-$Me_3Si(C_5H_4)$ (**3**),
η^5-1,3-$(Me_3Si)_2(C_5H_3)$ (**4**); M = Ta.

The easy α-hydrogen elimination, which takes place spontaneously, is due[1,5] to bulky trimethylsilylmethyl substituents coordinated to the metal in the presence of bulky cyclopentadienyl rings permethylated or substituted by trimethylsilyl groups.

All the complexes are extremely air- and moisture-sensitive and must be manipulated under a rigorously inert atmosphere. They are soluble in most organic solvents including saturated hydrocarbons.

The IR spectra of all complexes show characteristic absorptions due to the cyclopentadienyl ring at 1023–1025 cm^{-1} and to the $SiMe_3$ groups at 1240–1260 cm^{-1}. Absorptions due to the stretching ν(M—C) frequencies can be observed at 361 and 461–473 cm^{-1}, respectively, for niobium and tantalum derivatives.

The protons of the cyclopentadienyl ring give

two triplets in the ^{1}H NMR spectrum of **3** corresponding to an AA'BB' spin system, whereas **4** shows one multiplet, and one singlet due to the methyl ring protons is observed for **1** and **2**. The methyl protons of the $SiMe_3$ groups bonded to the rings give one singlet at 0.24 ppm for both **3** and **4**, and the CH_2SiMe_3 groups also give one singlet but at higher fields between 0.19 and 0.33 ppm, those of the alkylidene group, $=CHSiMe_3$, appear as one singlet at a slightly lower field between 0.18 and 0.31 ppm. The alkylidene proton is remarkably shifted to lower field giving one singlet between 4.39 and 6.30 ppm. This proton is very sensitive to changes due to different metal centres or to different cyclopentadienyl rings. It is possible to conclude that tantalum behaves less as an electron donor than niobium, whereas $SiMe_3$-substituted rings are more electron accepting than the permethylated ring. The presence of two $SiMe_3$ groups in the ring compensate each other in such a way that the disubstituted ring is less of an electron acceptor than the monosubstituted one. This effect has been previously explained on the basis of the 1,3-$C_5H_3(SiMe_3)_2$ ligand being sterically more demanding than C_5Me_5.[6]

The methylene protons $—CH_2SiMe_3$ are diastereotopic giving rise to two doublets with a geminal coupling of ^2J(Ha—Hb) = 11–12 Hz and chemical shifts following the same general pattern as that discussed for the methylene proton. However, only one doublet is observed for **3** and **4** because the other is overlapped by different more intense resonances, corresponding to n-hexane which was used as a solvent.

The ^{13}C NMR spectra of complexes **1** and **2** show one singlet for the methyl ring carbon atoms, whereas complexes **3** and **4** show three resonances for the three different types of carbon atoms (one *ipso* C_1, two *ortho* $C_{2,5}$ and two *meta* $C_{3,4}$ for **3** and two *ipso* $C_{1,3}$, one C_2 and two $C_{4,5}$). Their chemical shifts are sensitive to the nature of the metal and other substituents, but the differences are small. Each of the methylsilyl carbon atoms gives one singlet and their comparative chemical shifts vary always in the order $Me_3SiCH=$ > Me_3SiCH_2 > Me_3Si-ring (ppm), as could be expected. The methylene carbon atom of the CH_2SiMe_3 group gives one singlet between 50.25 and 56.31 ppm depending on the metal and the ring. The alkylidene C_α resonance is found at low field between 223.94 and 270.97 ppm, characteristic of transition-metal–carbon double bonds and confirms the presence of the alkylidene group.[5] The difference in chemical shifts for niobium **1** and tantalum **2** complexes is significant, but the effect of different rings is very small.

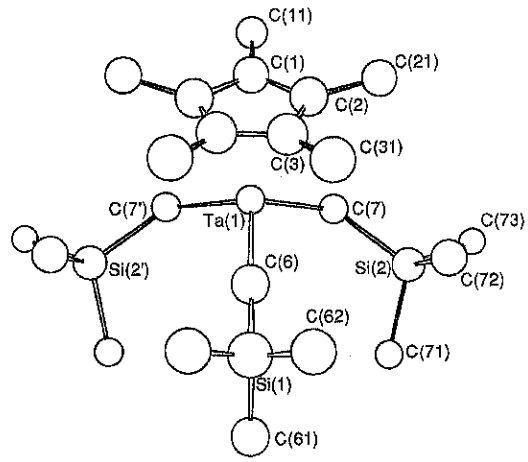

Fig. 1. The molecular structure of Ta(η^5-C_5Me_5) (CH_2SiMe_3)$_2$($CHSiMe_3$).

The molecular structure of **2** has been determined by an X-ray diffraction study. A view of this molecule is shown in Fig. 1 with the labelling scheme employed. Selected bond distances and angles are given in Table 1.

The molecular structure shows a typical three-legged piano-stool coordination around the tantalum atom. A symmetrical plane divides the molecule in two crystallographic equivalent moieties. This plane is defined by tantalum, alkylidene-C and the C_5Me_5 centroid.

The most relevant features of this structure are the distances Ta—C(6) and Ta—C(7) with the values 1.920(6) and 2.165(7) Å, respectively, and the angles Ta—C(6)—Si(1) and Ta—C(7)—Si(2) with values of 169.6(5)° and 126.9(3)°, respectively.

These values clearly tell us about the different bond order in the alkyl and alkylidene carbon atoms. The Ta—C(6) distance is significantly short and the Ta—C—Si angle is very large for a C(sp^2) atom, but they are in good agreement with those

Table 1. Selected bond distances (Å) and angles (°)

Ta(1)—C(6)	1.920(6)
Ta(1)—C(7)	2.165(7)
Si(1)—C(6)	1.857(7)
Si(1)—C(61)	1.786(15)
Si(1)—C(62)	1.719(21)
Si(2)—C(7)	1.871(7)
Si(2)—C(71)	1.824(9)
Si(2)—C(72)	1.852(12)
Si(2)—C(73)	1.860(12)
C(6)—Ta(1)—C(7)	104.6(2)
Ta(1)—C(6)—Si(1)	169.6(5)
Ta(1)—C(7)—Si(2)	126.9(3)

found by Schrock[7] *et al.* in Ta(η^5-C_5Me_5)(CHPh)$_2$ (CHPh).

The Ta—C(alkyl) distances and angles are normal compared with those found in $(Me_2SiCH_2)_2Ta(\mu$-$CSiMe_3)_2Ta(CH_2SiMe_3)(OAr$-2,6$Me_2)$,[8] which are in the range 2.14–2.16 Å and Ta—C—Si angles between 125–127°, but very short compared with those in $TaCp_2(CO)(CH_2SiHBu^t_2)$,[9] which shows a Ta—C(alkyl) distance of 2.321(4) Å.

These values confirm that the electron deficient metal atom attracts electron density from the CH_α bond.

The bond distance C—Si ranges from 1.82 to 1.87 Å for Si(2) and is 1.857(7) Å in Si(1)—C(6). These values are normal[9] while the Si(1)—C(61) and Si(1)—C(62) distances are very short, probably due to a disorder problem. The C—C distances between ring carbon atoms are normal.

The three silicon atoms define a plane fairly parallel to the C_5Me_5-ring best plane, with an angle of 4° between both planes.

The distance from tantalum to the C_5Me_5-ring best plane is 2.138(1) Å.

EXPERIMENTAL

All the operations were performed under an inert atmosphere using Schlenk techniques or in a vacuum atmospheres glove-box equipped with a HE-63-P Dri Train. Solvents were dried over prescribed drying agents, freshly distilled and degassed prior to use. M(η^5-Cp′)Cl_4 starting materials were prepared using reported methods [M = Nb, Cp′ = C_5Me_5;[3] M = Ta, Cp′ = C_5Me_5,[10] $C_5H_4SiMe_3$,[11] 1,3-$C_5H_3(SiMe_3)_2$[12]]. $LiCH_2SiMe_3$ was prepared and isolated as already described.[13]

Spectral measurements

IR spectra were recorded as Nujol mulls (4000–200 cm^{-1}) between polyethylene films on a Perkin–Elmer 583 spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Varian Unix 300 MHz instrument. Chemical shifts are reported in δ units (positive chemical shifts to a higher frequency) relative to tetramethylsilane, TMS.

X-ray diffraction studies

Single crystals of **2** suitable for X-ray study were obtained by crystallization at −40°C from a solution of toluene/n-hexane. A single crystal of **2** was sealed in a Lindemann glass capillary under dry argon and used for data collection. Crystallographic data are collected in Table 2. Data were collected at room temperature (22°C) on an

Table 2. Crystal data, experimental data and structure refinement procedures for **2**

Formula	$C_{22}H_{47}TaSi_3$
Cryst. habit	Prismatic
Cryst. size (mm)	0.2 × 0.15 × 0.2
Symmetry	Monoclinic, $P2_1/m$
Unit cell determn	Least-squares fit from 25 reflections
Unit cell dimensions	
a (Å)	8.432(1)
b (Å)	18.119(4)
c (Å)	9.605(3)
α (°)	90
β (°)	99.31(1)
γ (°)	90
Packing (V Å^3); Z	1448(1); 2
D_{calc} (g cm^{-3})	1.323
M_w	576.824
F(000)	588
μ (cm^{-1})	38.8
Technique	Four-circle diffractometer Enraf–Nonius CAD-4; bisecting geometry, graphite oriented monochromator, Mo-K_α $\omega/2\theta$ scans θ_{max} = 30.0
No. of reflections measured	4769
Independent observations	3529, 3$\sigma(I)$ criterium
Range of hkl	−11–11; 0–25; 0–13
Standard reflections	2 reflections every 120 min. No variation
R_1	0.050
R_w	0.062

Enraf–Nonius CAD-4 diffractometer. Intensities were corrected for Lorentz and polarization effects. No absorption or extinction corrections were made. The structure was solved by a combination of direct methods and Fourier synthesis and refined (on F) by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. In the latter stages of refinement hydrogen atoms were included from geometric calculations with fixed positions and thermal parameters.

Final values of $R = 0.050$ and $R_w = 0.062$ with $R_w = [\Sigma w||F_o|-|F_c||^2 \Sigma w|F_o|^2]^{1/2}$ and $w = 4F_o^2/[\sigma F_o^2]^2$ were obtained. Anomalous dispersion corrections and atomic scattering factors were taken from ref. 14. Calculations were performed with the SDP Enraf–Nonius package,[15] MULTAN[16] and DIRDIF[17] on a MICROVAX II computer.

Preparation of M(η^5-Cp′)(CH_2SiMe_3)$_2$($CHSiMe_3$) **1–4**

In a typical experiment, n-hexane or toluene (40 cm^3) was added to a stirred mixture of solids M(η^5-Cp′)Cl_4 (2.20 mmol) and $LiCH_2SiMe_3$ (0.81 g, 8.60 mmol) at room temperature. After 6 h the suspension was filtered and evaporated to dryness *in vacuo*. The residue was extracted with n-hexane (3×15 cm^3) and the solution was reduced in volume to *ca* 20 cm^3 and then cooled to -40°C to give orange crystals of **2** and yellow–brown solids of **1**, **3** and **4**.

1: yield 1.08 g (85%); IR (ν, Nujol mull): 1440(m), 1337(m), 1243(vs), 1025(s), 932(vs), 841(vs), 750(s), 681(s) and 361(m) cm^{-1}. ^{1}H NMR (δ ppm in benzene-d_6): 5.96 (s, 1H, =C*H*—$SiMe_3$), 1.76 (s, 15H, C_5Me_5), 0.32 (s, 18H, CH_2SiMe_3), 0.30 (s, 9H, =$CHSiMe_3$), 0.44 [d, 2H, ^2J(Ha—Hb) = 12 Hz, CH_2SiMe_3], -0.94 [d, 2H, ^2J(Ha—Hb) = 12 Hz, CH_2SiMe_3]. $^{13}C\{^1H\}$ NMR (δ ppm in benzene-d_6): 270.97 (s, =*C*$HSiMe_3$), 114.45 (s, C_5Me_5), 50.25 (s, *C*H_2SiMe_3), 11.92 (s, C_5Me_5), 2.49 (s, $CHSiMe_3$), 2.30 (s, CH_2SiMe_3).

2: yield 0.96 g (77%); IR (ν, Nujol mull): 2555(m), 1431(m), 1312(m), 1240(vs), 1166(s), 1067(w), 1023(m), 939(b, vs), 839(b, vs), 749(vs), 700(s), 681(vs), 631(w), 544(m), 461(vs), 432(m), 387(m), 355(vs) and 335(m) cm^{-1}. ^{1}H NMR (δ ppm in benzene-d_6): 4.39 (s, 1H, =C*H*$SiMe_3$), 1.82 (s, 15H, C_5Me_5), 0.31 (s, 9H, =$CHSiMe_3$), 0.33 (s, 18H, CH_2SiMe_3), -0.02 [d, 2H, ^2J(Ha—Hb) = 12.09 Hz, CH_2SiMe_3], -1.14 [d, 2H, ^2J(Ha—Hb) = 12.09 Hz, CH_2SiMe_3]. $^{13}C\{^1H\}$ NMR (δ ppm in benzene-d_6), 223.94 (s, =*C*$HSiMe_3$), 115.01 (s, C_5Me_5), 56.31 (s, *C*H_2SiMe_3), 12.30 (s, C_5Me_5), 4.03 (s, =$CHSiMe_3$), 3.07 (s, CH_2SiMe_3).

3: yield 1.08 g (85%); IR (ν, Nujol mull): 1460(m), 1420(m), 1260(vs), 1180(m), 1100(b, vs), 1020(vs), 810(vs), 700(m), 640(w), 473(m) and 405(s) cm^{-1}. ^{1}H NMR (δ ppm in benzene-d_6): 6.03 (t, 2H, $C_5H_4SiMe_3$), 5.61 (t, 2H, $C_5H_4SiMe_3$), 6.30 (s, 1H, =C*H*$SiMe_3$), 0.24 (s, 9H, $C_5H_4SiMe_3$), 0.19 (s, 18H, CH_2SiMe_3), 0.18 (s, =$CHSiMe_3$), -0.46 [d, 2H, ^2J(Ha—Hb) = 10.98 Hz, CH_2SiMe_3]. $^{13}C\{^1H\}$ NMR (δ ppm in benzene-d_6): 228.59 (s, =$CHSiMe_3$), 115.27 (s, C^1, $C_5H_4SiMe_3$), 110.46 (s, $C^{2,5}$, $C_5H_4SiMe_3$), 115.27 (s, $C^{3,4}$, $C_5H_4SiMe_3$), 55.27 (s, *C*H_2SiMe_3), 3.10 (s, =$CHSiMe_3$), 2.12 (s, CH_2SiMe_3), -0.43 (s, $C_5H_4SiMe_3$).

4: yield 1.0 g (82%); IR (δ, Nujol mull): 1445(m), 1420(m), 1320(w), 1250(vs), 1090(m), 940(vs), 845(vs), 750(m), 690(m), 630(m) and 472(w) cm^{-1}. ^{1}H NMR (δ ppm in benzene-d_6): 6.03 [m, 3H, $C_5H_3(SiMe_3)_2$], 5.58 (s, 1H, =C*H*$SiMe_3$), 0.24 [s, 18H, $C_5H_3(SiMe_3)_2$], 0.28 (s, 18H, CH_2SiMe_3), 0.30 (s, 9H, =$CHSiMe_3$), -0.53 [d, 2H, ^2J(Ha—Hb) = 11.96 Hz, CH_2SiMe_3]. $^{13}C\{^1H\}$ NMR (δ ppm in benzene-d_6): 227.94 (s, =*C*$HSiMe_3$), 123.37 [s, $C^{1,3}$, $C_5H_3(SiMe_3)_2$], 120.25 [s, C^2, $C_5H_3(SiMe_3)_2$], 111.86 [s, $C^{4,5}$, $C_5H_3(SiMe_3)_2$], 55.54 (s, *C*H_2SiMe_3), 3.88 (s, =$CHSiMe_3$), 2.88 (s, CH_2SiMe_3), 0.80 [s, $C_5H_3(SiMe_3)_2$].

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