Pentamethylcyclopentadienyl halo– and alkyl–alkoxo tantalum(V) complexes. Crystal structure of TaCp*(CH₂SiMe₃)₂{η²-O(2-CH₂-6-MeC₆H₃)}

of $TaCp^*(CH_2SiMe_3)_2\{\eta^2\text{-}O(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)\}$

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Abstract

Reaction of $TaCp^*Cl_4$ with MOR (M = Li, Na) in different molar ratios gives halo alkoxides $TaCp^*Cl_n(OR)_{4-n}$ (n = 3: R = ^tBu 1; $SiPh_3$ 2; $2,6\text{-}Me_2C_6H_3$ 3; n = 2: R = ^tBu 4; $SiPh_3$ 5; $2,6\text{-}Me_2C_6H_3$ 6; n = 1: R = $SiMe_3$ 7) in good yields. The alkylidene complex $TaCp^*(CH_2SiMe_3)_2(CHSiMe_3)$ is hydrolyzed in the presence of traces of water to give the oxo dialkyl derivative $[TaCp^*(CH_2SiMe_3)_2O]_n$ 8, and reacts with 1 equivalent of $2,6\text{-}Me_2C_6H_3NC$ affording a new η^2-iminoacyl compound $TaCp^*(CH_2SiMe_3)(CHSiMe_3)\{\eta^2\text{-}C(CH_2SiMe_3)=N(2,6\text{-}Me_2C_6H_3)\}$ 9. Reactions of $TaCp^*(CH_2SiMe_3)_2(CHSiMe_3)$ with 1 equivalent of C_6H_5OH and $4\text{-}MeC_6H_3(OH)_2$ result in the formation of the alkyl phenoxo $TaCp^*(CH_2SiMe_3)_3(OC_6H_5)$ 10 and 4-methyl pyrocatecholate $TaCp^*(CH_2SiMe_3)_2(O_2C_6H_3Me)$ 11, whereas the related reaction with $2,6\text{-}Me_2C_6H_3OH$ leads to the cyclic alkyl–alkoxo compound $TaCp^*(CH_2SiMe_3)_2\{\eta^2\text{-}O(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)\}$ 12. All the complexes were characterized by IR and NMR (^1H and ^{13}C) spectroscopy. The crystal and molecular structure of 12 has been determined. Crystals of 12 are triclinic, space group $P\bar{1}$ with Z = 2 in a unit cell of dimensions a = 9.151(5) Å, b = 11.835(5) Å, c = 14.045(4) Å, α = 89.35(3)°, β = 72.34(3)° and γ = 88.51(4)°, V = 1449(1) Å³. Final values of R = 0.025 and Rw = 0.0655 were obtained from 5547 reflections measured (5070, > 2σ(I)).

Keywords: Tantalum; Pentamethylcyclopentadienyl derivatives; Halo alkoxides; Alkyl phenoxides; Alkyl alkylidene imino acyl

1. Introduction

Alkoxo and aryloxo ligands have been extensively used to stabilize high oxidation states of early-transition metals and numerous studies have been reported concerning the catalytic activity of their complexes in alkene [1] and methyl methacrylate [2] polymerization, particularly in alkene methathesis [3]. Polinuclear alkoxo niobium and tantalum(V) complexes containing double or triple μ-oxo bridges in coordinatively saturated complexes have been reported [4], where the alkoxo substituent is not especially bulky [5]. However, mononuclear alkoxo complexes of niobium and tantalum containing the cyclopentadienyl group are much less common [6]. Intramolecular activation of the aliphatic C–H

bonds of 2,6-dimethyl substituted phenols [7] involves the coordination of the phenoxo group to d^0 metal centers with alkyl leaving groups, generating stable metallacyclic systems. This transformation has been reported for tantalum(V) complexes containing alkylidene as well as alkyl moieties [8].

In this paper we report the results observed in the reactions of different alkaline alkoxides and phenols with $TaCp^*Cl_4$ and $TaCp^*(CH_2SiMe_3)_2(CHSiMe_3)$, and the X-ray molecular structure of the oxotantalacycle complex $TaCp^*(CH_2SiMe_3)_2\{\eta^2\text{-}O(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)\}$.

2. Results and discussion

Reactions of $TaCp^*Cl_4$ with 1 equivalent of MOR (M = Li or Na) gave solutions from which the
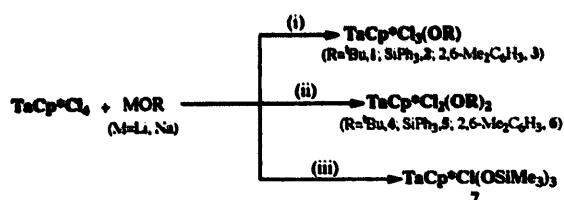
Reagents and conditions:

(i)- 1 equiv LiOR, toluene, 12 h, RT
(ii)- 4 equiv LiOR, toluene, 12 h, RT
(iii)- 4 equiv NaOSiMe₃, toluene, 24 h, RT

Scheme 1.

monoalkoxo complexes $TaCp^*Cl_3(OR)$, (R = ^tBu **1**; $SiPh_3$ **2**; $2,6-Me_2C_6H_3$ **3**) were isolated. Addition of increasing amounts of MOR led to unidentified mixtures, probably containing different halo–alkoxo species. Attempts to synthesize tetrasubstituted derivatives were unsuccessful, probably due to electronic and sterics effects, although $TaCp^*(OPh)_4$ has been reported [6e]. However, when an MOR/Ta molar ratio of 4:1 was

used, partially substi····d $TaCp^*Cl_2(OR)_2$ (R = ^tBu **4**; $SiPh_3$ **5**; $2,6-Me_2C_6H_3$ **6**) and $TaCp^*Cl(OSiMe_3)_3$ **7** were obtained, as shown in Scheme 1.

In contrast to the high reactivity known for alkylidene niobium and tantalum complexes [9], $TaCp^*(CH_2SiMe_3)_2(CHSiMe_3)$ is much more stable due to the presence of the electron acceptor trimethylsilyl substituent and it does not react with unsaturated organic molecules such as $Ph-CHO$, $CH_3-CO-CH_3$, $CH_2=CH_2$, Me_3NO, $Ph-C\equiv CH$ and CH_3-CN under various conditions and proportions. However, it is slowly hydrolyzed to give the oxo dialkyl complex $[TaCp^*(CH_2SiMe_3)_2O]_n$ **8**, identified by its analytical and spectroscopic data, when $TaCp^*(CH_2SiMe_3)_2(CHSiMe_3)$ is stirred in a water saturated benzene solution for 1 week.
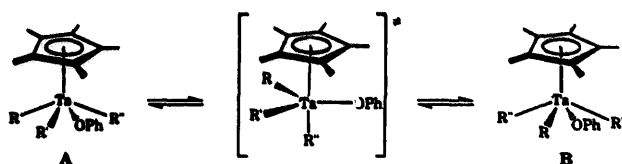
$TaCp^*(CH_2SiMe_3)_2(CHSiMe_3)$ also reacts with CO to give an unidentified mixture of compounds and an instantaneous insertion reaction with $2,6-Me_2C_6H_3NC$ leads to the corresponding η^2-imino acyl derivative **9**, $TaCp^*(CH_2SiMe_3)(CHSiMe_3)\{\eta^2-C(CH_2SiMe_3)=N(2,6-Me_2C_6H_3)\}$. No further reaction is observed when an excess of isocyanide is used.

As shown in Scheme 2, the alkylidene complex is

Table 1
^1H and $^{13}C(^1H)$ NMR data of the new complexes

Compound	^1H NMR	$^{13}C(^1H)$ NMR
1	2.09 (s, C_5Me_5), 1.33 (s, ^tBuO)	125.9 s, 12.3 s (C_5Me_5), 91.4 (s, $OCMe_3$), 28.9 (s, Me_3CO)
2	7.93–7.17 (m, Ph_3SiO), 2.01 (s, C_5Me_5)	136.5s, 136.2 s, 135.4 s, 129.2 s (C_i, C_o, C_p, C_m, Ph_3SiO), 130.5 s, 13.1 s(C_5Me_5)
3	6.86 (d, H_m, $H_3C_6Me_2O$), 6.72(m, H_p, $H_3C_6Me_2O$) 2.56 (s, 2, 6-$Me_2C_6H_3O$), 2.17 (s, C_5Me_5)	164.9 s, 130.1 s, 129.6 s, 129.2 s (C_i, C_o, C_m, C_p, C_6H_3 Me_2O), 124.9 s, 13.7 s (C_5Me_5), 20.9 (s, $2,6-Me_2C_6H_3O$)
4	2.11 (s, C_5Me_5), 1.42 (s, ^tBuO)	124.3 s, 12.5 s (C_5Me_5), 86.9 (s, $OCMe_3$), 30.6 (s, Me_3CO)
5	8.06–7.11 (m, Ph_3SiO), 1.87 (s, C_5Me_5)	136.5 s, 135.9 s, 135.4 s, 129.9 s (C_i, C_o, C_p, C_m, Ph_3SiO), 127.1 s, 12.6 s (C_5Me_5)
6	6.91 (d, H_m, $H_3C_6Me_2O$), 6.75 (t, H_p, $H_3C_6Me_2O$), 2.31 (s, C_5Me_5), 2.12 (s, $2,6-Me_2C_6H_3$)	161.6 s, 135.7 s, 129.2 s, 125.1 s (C_i, C_o, C_m, C_p, C_6H_3 Me_2O), 121.8 s, 12.4 s (C_5Me_5), 19.4 (s, $2,6-Me_2C_6H_3O$)
7	2.01 (s, C_5Me_5), 0.37 s, 0.32 s (Me_3SiO)	122.0 s, 11.9 s (C_5Me_5), 4.8 s, 4.5 s (Me_3SiO)
8	1.77 (s, C_5Me_5), 0.38 (s, Me_3SiCH_2), −1.12 (d, $^2J_{H-H}$ = 12.2 Hz, CH_2SiMe_3)	117.0 s, 11.1 s (C_5Me_5), 57.3 (s, CH_2SiMe_3), 2.4 (s, Me_3SiCH_2)
9	7.00–6.80 (m, $H_3C_6Me_2$), 3.41 (s, $HCSiMe_3$), 2.57d, 2.45d ($^2J_{H-H}$ = 10.6 Hz, CH_2SiMe_3), 2.26 s, 1.54 s ($2,6-Me_2C_6H_3$), 1.97 (s, C_5Me_5), 0.28 (s, Me_3SiCH_2-Ta), 0.27 (s, Me_3SiCH), 0.05 (s, Me_3 $SiCH_2$), −0.33d, −0.71d ($^2J_{H-H}$ = 12.6 Hz, Ta-CH_2 $SiMe_3$)	247.3 (s, CN-$2,6-Me_2C_6H_3$), 222.3 * (s, $CHSiMe_3$), 143.0 s (C_i, $C_6H_3Me_2$), 132.3s, 129.2 s, 128.7 s, 126.2 s (C_6H_3 Me_2), 111.1 s, 12.1 s (C_5Me_5), 57.0 * (Ta-CH_2SiMe_3), 29.8 * (s, CH_2SiMe_3), 19.8 s, 19.4 s ($2,6-Me_2C_6H_3$), 4.5 (s, Me_3SiCH), 3.3 (s, Me_3SiCH_2-Ta), 0.72 (s, Me_3SiCH_2).
10	7.19d, 7.04d, 6.83m (H_o, H_m, H_p, H_3C_6O), 1.82 (s, C_5Me_5), 0.44 (s, CH_2SiMe_3), 0.26 (s, Me_3SiCH_2)	163.8 s (C_i, C_6H_5O), 129.4 s, 122.0 s (C_6H_5O), 120.0 s, 12.3 s (C_5Me_5), 70.1 (s, CH_2SiMe_3), 4.7 (s, Me_3 $SiCH_2$)
11	7.05d, 7.02s, 6.75d ($H_3C_6MeO_2$), 2.32 (s, Me $C_6H_3O_2$), 1.82 (s, C_5Me_5), 1.02d, 0.42d ($^2J_{H-H}$ = 9.6 Hz, CH_2SiMe_3), 0.03 (s, Me_3SiCH_2)	158.5 s, 156.5 s (C_i, $C_6H_3MeO_2$), 120.0 s, 115.4 s, 113.8 s ($C_6H_3MeO_2$), 119.4 s, 11.5 s (C_5Me_5), 70.2 * (s, CH_2Si Me_3), 21.4 (s, $MeC_6H_3O_2$), 3.3 (s, Me_3SiCH_2)
12	7.10d, 7.01 d, 6.89 t ($H_3C_6MeCH_2O$), 2.72 (s, $2-MeC_6H_3CH_2O$), 1.77 (s, $H_2C-C_6H_3MeO$), 1.66 (s, C_5Me_5), 0.52 (s, CH_2SiMe_3), 0.14 (s, Me_3SiCH_2)	167.3 (s, C_i, $C_6H_3MeCH_2O$), 140.9 s, 127.1 s, 125.6 s, 123.5 s, 118.8 s ($C_6H_3MeCH_2O$), 117.4 s, 11.6 s (C_5Me_5), 88.7 * (s, $CH_2C_6H_3MeO$), 72.5 (s, CH_2SiMe_3), 17.3 (s, $2-MeC_6H_3CH_2O$), 3.5 (s, Me_3SiCH_2)

* ^{13}C NMR data: 9, δ 222.3t, $^1J_{C-H}$ = 78.3 Hz; δ 57.0t, $^1J_{C-H}$ = 108.8 Hz; δ 29.8t, $^1J_{C-H}$ = 121.0 Hz; 11, δ 70.2t, $^1J_{C-H}$ = 112.2 Hz; 12, δ 88.7t, $^1J_{C-H}$ = 120.4 Hz; δ 72.5t, $^1J_{C-H}$ = 110.4 Hz.

Fig. 1. ORTEP view of the molecular structure of $TaCp^*(CH_2SiMe_3)_2\{\eta^2\text{-}O(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)\}$, 12 with the atom numbering scheme.

much more reactive with alcohols. Protonation via 1,2-addition to the Ta=C double bond of the alkylidene group of $TaCp^*(CH_2SiMe_3)_2(CHSiMe_3)$ [10] by C_6H_5OH led to the trialkyl phenoxo complex $TaCp^*(CH_2SiMe_3)_3(OC_6H_5)$ 10, whereas the same reaction with $4\text{-}MeC_6H_3(OH)_2$ proceeds with further elimination of alkane to give the chelated dialkoxo complex $TaCp^*(CH_2SiMe_3)_2(O_2C_6H_3Me)$ 11 (Scheme 2). The analogous reaction of the alkylidene tantalum complex with $2,6\text{-}Me_2C_6H_3(OH)$ also takes place with elimination of alkane, since the protonation is followed by intramolecular C–H bond activation of one of the

methyl substituents of the phenyl group, as has been observed for other high-valent, electron-deficient early-d-block [11], lanthanide [12] and actinide [13] metal compounds. Ultimately the reaction leads to the oxo alkyl tantalacyclic derivative $TaCp^*(CH_2SiMe_3)_2\{\eta^2\text{-}O(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)\}$ 12.

Complexes 1–12 are soluble in aromatic hydrocarbons and moderately soluble in n-hexane. Their toluene solutions are slowly hydrolyzed in air but in the solid state they are indefinitely stable under rigorously anhydrous conditions. They were characterized by IR, ^1H and ^{13}C NMR spectroscopy. Selected NMR data are shown in Table 1.

The IR spectra of all the new complexes reported show characteristic absorptions at 1019–1030 cm^{-1}, (ν_{C-C}) [14]; 1249–929 cm^{-1}, (ν_{C-O}) [5,15] and 596–497 cm^{-1}, (ν_{Ta-O}) [5,16]. IR absorptions at 329–276 cm^{-1} for 1–7 can be assigned to ν_{Ta-Cl} stretching vibrations [17], suggesting the presence of only terminal metal–chlorine bonds, consistent with the observed NMR data and leading to the proposed formulation. Nevertheless, the complexity of the ν_{C-O} and ν_{M-O} stretching vibrations [18] precludes a definitive structural assignment for these absorptions. Complex 12 shows two absorption bands at 2645 and 1573 cm^{-1}, due to the usual $\nu_{C-H\alpha}$ [19] and $\nu_{C=N}$ [20] stretching vibrations of the alkylidene and η^2-imino acyl groups respectively.

The ^1H and ^{13}C NMR spectra of complexes 1–7 shown in Table 1 are in agreement with the proposed structures.

The NMR data for complexes 9, 10 and 12 suggested a pseudo-square-pyramidal geometry, with the pentamethylcyclopentadienyl ring occupying the apical po-

Scheme 2.

Scheme 3.

sition, the X-ray molecular structure of **12** confirmed this geometry (see Fig. 1). The ^{1}H NMR spectra of complexes **9**, **10**, **11** and **12** show AB spin systems for the diastereotopic methylene protons of the trimethylsilyl methyl groups with a geminal coupling of $^2J_{Ha-Hb} = 10$–12 Hz, due to the "prochiral" character of the metal atom, as found for similar tantalum derivatives [9a,21].

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **10** at room temperature show only one signal for the CH_2SiMe_3 group. However, when a $CDCl_3$ solution of **10** is cooled from 293 K to 213 K, the methylene carbon signal of the CH_2SiMe_3 group broadens, and at 213 K is split into two signals centered at δ 69.6 and δ 68.2 in a 1:2 ratio. The same behavior is observed for the signal due to the Me_3SiCH_2 carbon. The kinetic parameters for this process (log $A = 15.0 \pm 0.8$; $E_a = 13.4 \pm 0.8$ kcal mol^{-1}; $\Delta H^{\ddagger} = 12.9 \pm 0.8$ kcal mol^{-1}; $\Delta S^{\ddagger} = 4.5 \pm 3.8$ u.e.; $\Delta G^{\ddagger 298\,K} = 11.5$ kcal mol^{-1}), calculated on the basis of DNMR data by NMR line shape analysis [22], show that this transformation is an intramolecular pseudorotation process (see Scheme 3), similar to that reported [23] for other tantalum(V) monocyclopentadienyl complexes with a four-legged piano stool structure.

The ^{13}C NMR spectra are also in agreement with the proposed structures.

2.1. Description of the crystal structure of TaCp*(CH$_2$ SiMe$_3$)$_2${η^2-O(2-CH$_2$-6-MeC$_6$H$_3$)} 12

Suitable crystals of **12** were obtained from a toluene layered n-hexane solution at -40°C. A view of the molecular structure of this compound is shown in Fig. 1, together with the atom numbering scheme. Selected bond distances and angles are given in Table 2 and atomic coordinates for the non-hydrogen atoms are listed in Table 3.

The compound can be described as a mononuclear tantalum complex with a typical four-legged piano stool coordination around the tantalum atom. The legs are formed by the carbon atoms of the CH_2SiMe_3 groups and the O(1) and C(28) atoms from a five-membered metallacycle. These four legs describe a plane with a maximum deviation of 0.06 Å, the tantalum being located 0.818(3) Å above the plane. This plane is almost parallel to the Cp* plane, with an interplanar angle of 1.6(2)°.

The angles between adjacent legs ranged from 85.9 to 74.8°, this latter being the internal O(1)–Ta–C(28) angle of the metallacycle. The Ta(1), O(1), C(21), C(26) and C(28) atoms form a five-membered ring, puckered by the O(1) and C(28) atoms, causing the phenyl ring connected to Ta to be displaced. These C(28) and O(1) atoms are in the phenyl ring plane.

The Ta–Cp* (centroid) distance is 2.134 Å, similar to that found in TaCp*(CH$_2$SiMe$_3$)$_2$(CHSiMe$_3$) [10] and the Cp* (centroid)–leg angles ranged from 109.0 to 116.7°.

The Ta–C(31) and Ta–C(41) distances are 2.216(4) and 2.175(5) Å respectively, which are normal values for Ta(V)–C(sp^3), and are slightly shorter than the

Table 2
Selected bond distances (Å) and angles (°) with ESDs in parentheses for **12**

Bond distances			
Ta(1)–O(1)	1.971(3)	Si(2)–C(41)	1.861(5)
Ta(1)–C(28)	2.249(4)	Si(2)–C(42)	1.861(7)
Ta(1)–C(31)	2.216(4)	Si(2)–C(43)	1.869(7)
Ta(1)–C(41)	2.175(5)	Si(2)–C(44)	1.848(7)
Ta(1)–CE	2.134	O(1)–C(21)	1.372(5)
Si(1)–C(31)	1.866(5)	C(21)–C(26)	1.385(7)
Si(1)–C(32)	1.862(6)	C(22)–C(27)	1.499(8)
Si(1)–C(33)	1.871(8)	C(26)–C(28)	1.491(6)
Si(1)–C(34)	1.858(7)		
Bond angles			
Ta(1)–O(1)–C(21)	123.5(3)	C(31)–Ta(1)–C(28)	79.2(2)
Ta(1)–C(28)–C(26)	109.4(3)	C(41)–Ta(1)–O(1)	85.9(2)
O(1)–Ta(1)–C(28)	74.8(2)	Si(1)–C(31)–Ta(1)	125.6(2)
O(1)–C(21)–C(26)	115.0(4)	Si(2)–C(41)–Ta(1)	129.6(2)
O(1)–C(21)–C(22)	120.9(4)	CE–Ta(1)–O(1)	114.1
C(21)–C(26)–C(28)	113.9(4)	CE–Ta(1)–C(28)	110.3
C(21)–C(22)–C(27)	122.3(4)	CE–Ta(1)–C(31)	109.0
C(31)–Ta(1)–C(41)	85.8(2)	CE–Ta(1)–C(41)	116.7

CE is the centroid of the Cp* ring.

Table 3

Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for 12

Atom	x	y	z	U_{eq}
Ta(1)	2101(1)	7045(1)	2730(1)	37(1)
Si(1)	1648(2)	4226(1)	1874(1)	58(1)
Si(2)	2266(2)	8066(2)	234(1)	66(1)
O(1)	439(3)	8096(3)	2644(2)	47(1)
C(11)	2560(6)	7974(5)	4164(4)	60(1)
C(12)	3437(7)	6956(4)	4022(4)	65(2)
C(13)	4571(6)	7036(5)	3093(5)	68(2)
C(14)	4373(7)	8058(6)	2663(4)	70(2)
C(15)	3162(7)	8644(4)	3312(5)	66(2)
C(16)	1333(8)	8351(9)	5066(6)	123(4)
C(17)	3294(11)	6023(7)	4774(7)	126(4)
C(18)	5869(8)	6218(8)	2687(8)	141(4)
C(19)	5487(9)	8518(9)	1711(6)	136(4)
C(20)	2648(12)	9846(5)	3179(8)	129(4)
C(21)	−963(5)	8174(4)	3362(3)	44(1)
C(22)	−1970(5)	9078(4)	3371(4)	53(1)
C(23)	−3354(6)	9065(5)	4145(5)	66(2)
C(24)	−3674(6)	8232(5)	4861(5)	72(2)
C(25)	−2640(5)	7356(5)	4835(4)	61(1)
C(26)	−1253(5)	7315(4)	4067(3)	47(1)
C(27)	−1584(7)	10012(5)	2614(5)	70(2)
C(28)	−23(5)	6418(4)	3872(4)	51(1)
C(31)	2514(5)	5193(4)	2583(4)	49(1)
C(32)	2848(7)	4090(6)	546(4)	81(2)
C(33)	1582(12)	2774(6)	2423(7)	126(3)
C(34)	−344(8)	4608(8)	1895(7)	131(4)
C(41)	2846(6)	7081(4)	1105(3)	51(1)
C(42)	3498(11)	7767(9)	−1063(5)	135(4)
C(43)	2429(9)	9603(6)	464(6)	94(2)
C(44)	254(8)	7825(7)	294(6)	100(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Ta–C(28) distance (2,249(4) Å) in the cycle, similar to other tantalacycles previously described [7a,24].

The Ta–O(1) distance is 1.971(3) Å, in the normal range for this type of compound, and is longer than found in normal aryloxo derivatives (mean value 1.898 Å) [24].

The C–Si distances range from 1.848 to 1.871 Å and C–C distances have typical values. The methyl groups in the pentamethylcyclopentadienyl ring are located above the ring plane, with a mean deviation of 0.14 Å.

This structure is related to $NbAr_2\{OC_6H_3{}^iPr-\eta^2-C(MeO=CH_2)\}(THF)$ and $NbAr_2\{OC_6H_3{}^iPr-C(Me)-CH_2-C(Ph)=CPh\}$ (Ar = 2,6-${}^iPr_2C_6H_3O)$ [24b], both niobium compounds with five-membered metallacycle rings, but to our knowledge complex 12 is the first five-membered tantalacycle ring.

3. Experimental

All reactions and manipulations were carried out under an argon atmosphere using conventional Schlenk and dry-box techniques. The solvents were carefully

dried by standard methods (n-hexane over Na/K alloy and toluene over sodium), distilled under argon and deoxygenated prior to use. Reagent grade chemicals Li^nBu (1.6 M in hexane, Aldrich), $NaOSiMe_3$ (Fluka), $HOSiPh_3$ (Ventron), HO^tBu (Panreac), HOC_6H_5 (Panreac), $HOC_6H_3Me_2$ (Panreac), $4\text{-MeC}_6H_3(OH)_2$ (Fluka) were purchased from commercial sources and used without further purification. Lithium reagents LiOR (R = ^tBu, $SiPh_3$, $C_6H_3Me_2$) were prepared by treating the appropriate HOR with 1 equivalent of Li^nBu. Starting materials $TaCp^*Cl_4$ [25], $TaCp^*(CH_2SiMe_3)_2(CH-SiMe_3)$ [10] and $2,6\text{-Me}_2C_6H_3NC$ [26] were prepared as previously described.

Infrared spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000–200 cm^{-1}) as Nujol mulls between CsI windows. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity-300 instrument. ^1H and ^{13}C NMR shifts were measured relative to residual ^1H and ^{13}C resonances in the deuterated solvents: $C_6D_6(\delta\ 7.15)$, $CDCl_3(\delta\ 7.24)$ and $C_6D_6(\delta\ 128)$, $CDCl_3(\delta\ 77)$ respectively.

A DNMR5 program [27] was used for evaluation of kinetic parameters. C, H and N analyses were carried out with a Perkin-Elmer 240C microanalyzer.

3.1. Preparation of TaCp* Cl$_3$(OR) (R = ^tBu 1; SiPh$_3$ 2; 2,6-Me$_2$C$_6$H$_3$ 3)

Toluene (75 ml) was added to a mixture of $TaCp^*Cl_4$ (1.17 g, 2.55 mmol) and LiOR (2.55 mmol). After stirring over night at room temperature the suspension was decanted and filtered off through Celite. The filtrate was concentrated to ca. 25 ml and cooled to −40°C to give 1–3 as yellow (1, 2) or orange (3) crystals.

The data for the complexes are as follows.

1. Yield 75% (0.95 g). Anal. Found: C, 33.82; H, 4.92. $C_{14}H_{24}Cl_3OTa$ (495.63). Calc. C 33.92; H, 4.88%. IR: 1242 m, 1160 m, 1022 m, 976 s, 548 m, 497 m, 276 m cm^{-1}.

2. Yield 80% (1.42 g). Anal. Found: C, 48.13; H, 4.34. $C_{28}H_{30}Cl_3OSiTa$ (697.91). Calc.: C, 48.00; H, 4.33%. IR: 1114 s, 1024 m, 929 s, 540 m, 512 s, 299 s cm^{-1}.

3. Yield 80% (1.11 g). Anal. Found: C, 39.85; H. 4.50. $C_{18}H_{24}Cl_3OTa$ (543.67). Calc.: C, 39.76; H, 4.45%. IR: 1199 s, 1097 m, 1019 m, 895 s, 568 m, 331 m, 302 m cm^{-1}.

3.2. Preparation of TaCp* Cl$_2$(OR)$_2$(R = ^tBu 4; SiPh$_3$ 5; 2,6-Me$_2$C$_6$H$_3$ 6)

A suspension of $TaCp^*Cl_4$ (1.00 g, 2.18 mmol) and LiOR (8.72 mmol) in toluene (100 ml) was stirred at room temperature for 12 h. The resulting suspension was decanted and filtered off through Celite. The filtrate

was concentrated to ca. 10 ml, n-hexane was added (2 ml) followed by cooling to −40°C to give microcrystalline solids identified as **4** (pale yellow), **5** (uncolored) or **6** (yellow–green).

The data for the complexes are as follows.

4. Yield 70% (0.81 g). Anal. Found: C, 40.51 H, 6.20. $C_{18}H_{33}Cl_2O_2Ta$ (533.29). Calc.: C, 40.54; H, 6.23%. IR: 1235 m, 1166 m, 1022 m, 947 s, 547 w, 501 w, 329 m, 303 m cm^{-1}.

5. Yield 82% (1.68 g). Anal. Found: C, 59.00; H, 4.92 $C_{46}H_{45}Cl_2O_2Si_2Ta$ (937.85). Calc.: C, 58.90; H, 4.84%. IR: 1113 s, 1027 m, 967 s, 536 m, 511 s, 279 m cm^{-1}.

6. Yield 78% (1.07 g). Anal. Found: C, 49.53; H, 5.40. $C_{26}H_{33}Cl_2O_2Ta$ (629.37). Calc.: C, 49.61; H, 5.28: IR: 1196 s, 1104 m, 1029 m, 982 s, 569 w, 547 m, 249 m cm^{-1}.

3.3. Preparation of TaCp* Cl(OSiMe₃)₃ 7

Toluene (70 ml) was added to a mixture of TaCp* Cl₄ (0.51 g, 1.11 mmol) and NaOSiMe₃ (0.50 g, 4.44 mmol). The mixture was stirred for 24 h at room temperature. The resulting suspension was decanted, filtered through Celite and the filtrate was evaporated to dryness. The residue was extracted into n-hexane (2 ×

10 ml), concentrated to ca. 10 ml and cooled to −40°C to give **7** as a colorless microcrystalline solid. Yield 87% (0.60 g). Anal. Found: C, 36.76; H, 6.89. $C_{19}H_{42}ClO_3Si_3Ta$ (619.19). Calc.: C, 36.85; H, 6.84%. IR: 1057 s, 1030 m, 595 m, 245 m, 223 m cm^{-1}.

3.4. Preparation of [TaCp*(CH₂SiMe₃)₂O]ₙ 8

Water saturated C_6H_6 (0.5 ml) was added to a solution of TaCp*(CH₂SiMe₃)₂(CHSiMe₃) (0.28 g, 0.48 mmol) in toluene (20 ml) and the mixture was stirred for 1 week. The yellow solution obtained was evaporated to dryness and the unstable oil residue was tentatively characterized on the basis of its ¹H and ¹³C NMR spectral data as **8**.

3.5. Preparation of TaCp*(CH₂SiMe₃)(CHSiMe₃){η²-C(CH₂SiMe₃)= N(2,6-Me₂C₆H₃)} 9

A solution of 2,6-Me₂C₆H₃NC (0.11 g, 0.86 mmol) in toluene (20 ml) was added at room temperature to a solution of TaCp*(CH₂SiMe₃)₂(CHSiMe₃) (0.50 g, 0.86 mmol) in toluene (30 ml) and stirred for 12 h. The color of the mixture quickly changed from orange-brown to yellow. The solution obtained was evaporated to dryness and the residue extracted into n-hexane

Table 4
Crystal data, experimental data and structure refinement procedures for compound 12

Formula	$C_{26}H_{45}OSi_2Ta$
Crystal habit	Prismatic
Color	Yellow
Crystal size	$0.35 \times 0.31 \times 0.26$ mm^3
Symmetry	Triclinic $P\bar{1}$
Unit cell determination	Least-squares fit from 25 reflections
Unit cell dimensions	
a, b, c (Å)	9.151(5), 11.835(5), 14.045(4)
α, β, γ (°)	89.35(3), 72.34(3), 88.51(4)
V (Å^3)	1449(1)
Z	2
D_{cal} (g cm^{-3})	1.400
Mw	610.75
$F(000)$	620
μ (cm^{-1})	38.90
Scan mode	$\omega/2\theta$ scans; $\theta_{max} = 50°$
Index ranges	$0 < H < 10, -14 < K < 14, -16 < L < 16$
Temperature	293(2) K
No. reflections measured	5547
No. independent reflections observed	$5070 I > 2\sigma(I)$ criterion
Range of h, k, l	$-19 \leqslant h \leqslant 19; 0 \leqslant k \leqslant 12; 0 \leqslant l \leqslant 21$
No. standard reflections	2 every 120 mins, no variation
Absorption correction	ψ scan
Max. and min. transmission	0.963 and 0.364
$R [I > 2\sigma(I)]$	$R_1 = 0.0252, wR_2 = 0.0655$
R (all data)	$R_1 = 0.0468, wR_2 = 0.1485$
Weighting scheme	Calc $w = 1/[\sigma^2(F_o^2) + (0.0420P)^2 + 1.71P]$ where $P = (F_o^2 + 2F_c^2)/3$
Max. peak in final difference map (e Å^{-3})	1.214
Min. peak in final difference map (e Å^{-3})	−0.866

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

(2 × 15 ml). The solution, which was filtered, concentrated to ca. 10 ml and cooled to −40°C, gave **9** as yellow crystals. Yield 85% (0.52 g). Anal. Found: C, 52.69; H, 7.91; N, 1.99. $C_{31}H_{56}NSi_3Ta$ (708). Calc.: C, 52.59; H, 7.97; N, 1.98%. IR: 2645 w, 1573 s, 1240 s, 1025 m, 918 s, 852 s, 676 m, 459 w, 349 w cm^{-1}.

3.6. Preparation of TaCp*(CH₂SiMe₃)₃(OC₆H₅) 10

C_6H_5OH (0.10 g, 1.09 mmol) was added to a solution of TaCp*$(CH_2SiMe_3)_2$(CHSiMe₃) (0.63 g, 1.09 mmol) in toluene (50 ml) and the mixture was stirred for 12 h at room temperature. The resulting yellow solution was concentrated to ca. 10 ml and cooled to −40°C, yielding **10** as yellow crystals. Yield 74% (0.54 g). Anal. Found: C, 50.20; H 7.89. $C_{28}H_{53}OSi_3Ta$ (670.92). Calc.: C, 50.12; H, 7.96%. IR: 1587 m, 1259 s, 1162 m, 1023 m, 993 s, 968 s, 505 m cm^{-1}.

3.7. Preparation of TaCp*(CH₂SiMe₃)₂[O₂(4-MeC₆H₃)] 11

A toluene (40 ml) solution of 4-MeC₆H₃(OH)₂ (0.18 g, 1.42 mmol) was slowly added at room temperature to a stirring, freshly prepared solution of TaCp*$(CH_2SiMe_3)_2$(CHSiMe₃) (0.82 g, 1.42 mmol) in toluene (60 ml). The stirring was continued for 3 h, when the solution was concentrated to ca. 10 ml, n-hexane was added (10 ml) followed by cooling to −40°C to give **11** as an orange microcrystalline solid. Yield 82% (0.71 g). Anal. Found: C, 48.94; H, 6.98. $C_{25}H_{43}O_2Si_2Ta$ (612.72). Calc.: C, 49.00; H, 7.07%. IR: 1584 w, 1259 s, 1115 w, 1024 m, 969 m, 943 m, 596 m, 564 m cm^{-1}.

3.8. Preparation of TaCp*(CH₂SiMe₃)₂{η²-O(2-CH₂-6-MeC₆H₃)} 12

A stirred orange–brown solution of TaCp*$(CH_2Si-Me_3)_2$(CHSiMe₃) (0.71 g, 1.23 mmol) in toluene (50 ml) was treated with 2,6-Me₂C₆H₃OH (0.15 g, 1.23 mmol) under rigorously anhydrous conditions for 12 h. During this time, the mixture quickly became bright orange. The solution was concentrated to ca. 10 ml, n-hexane (10 ml) was added and the solution was cooled to −40°C to give **12** as orange crystals. Yield 77% (0.58 g). Anal. Found: C, 51.02; H, 7.32. $C_{26}H_{45}OSi_2Ta$ (610.75). Calc.: C, 51.13; H, 7.42%. IR: 1576 m, 1240 s, 1107 w, 1021 m, 969 m, 927 m, 563 w, 541 w cm^{-1}.

3.9. X-ray data collection, structure determination and refinement for compound 12

Crystallographic and experimental details of the X-ray crystal structure determination of complex **12** are given in Table 4. A suitable crystal of **10** was sealed in a Lindeman tube under argon and mounted on an Enraf-Nonius CAD-4 automatic four circle diffractometer with bisecting geometry and using a graphite monochromator with Mo Kα radiation (λ(Mo Kα) = 0.71073 Å). Data were collected at room temperature. Intensities were corrected for Lorentz and polarisation effects in the usual manner. No extinction correction was made. Absorption was corrected by ψ-scan method.

The structure was solved by a combination of direct methods and Fourier synthesis and refined (on F^2) by full-matrix least-squares calculations. All the non-hydrogen atoms were refined anisotropically. In the last cycle of refinement the hydrogen atoms were introduced from geometrical calculation and refined using a riding model with a fixed thermal parameter ($U = 0.08$ Å^2). Final values of $R_1 = 0.0252$ and $Rw = 0.0655$ were obtained. Anomalous dispersion corrections and atomic scattering factors were taken from *International Tables for X-ray Crystallography* [28]. Calculations were performed with the SHELXS-90 [29] and SHELXL-93 [30] programs on an Alpha AXP digital workstation.

4. Supplementary material available

Tables of hydrogen atom coordinates and isotropic displacement parameters (Table S1, 1 page), anisotropic displacement parameters (Table S2, 1 page), structure factors (Table S3, 12 pages) and complete bond distances and angles (Table S4, 1 page) for complex **12**. Ordering information is given on any current masthead page.

Acknowledgments

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