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Mixed-dicyclopentadienyl niobium and tantalum complexes: synthesis and reactivity

X-ray molecular structures of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2$ and $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}\text{H}_3$

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Abstract

MCp^*Cl_4 , ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) reacts with LiCp ($\text{Cp} = \text{C}_5\text{H}_4(\text{SiMe}_3)$ (Cp'); $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ (Cp'')) and sodium amalgam, in 1:1:1 molar ratio to give the paramagnetic dicyclopentadienyl niobium and tantalum(IV) complexes, $\text{MCp}^*\text{CpCl}_2$, ($\text{M} = \text{Nb}$, $\text{Cp} = \text{Cp}'$ **1**; Cp'' **2**; $\text{M} = \text{Ta}$, $\text{Cp} = \text{Cp}'$ **3**; Cp'' **4**). Reactions of **3** and **4** with 1/2 equivalent of PCl_5 afford the diamagnetic trichloro complexes $\text{TaCp}^*\text{CpCl}_3$, ($\text{Cp} = \text{Cp}'$ **5**; Cp'' **6**), while oxidation with dry O_2 gives the diamagnetic dinuclear complexes $[\text{TaCp}^*\text{CpCl}_2]_2(\mu\text{-O})$, ($\text{Cp} = \text{Cp}'$ **7**; Cp'' **8**), and with air are transformed into the corresponding oxoderivatives $\text{TaCp}^*\text{CpCl}(\text{O})$, ($\text{Cp} = \text{Cp}'$ **9**; Cp'' **10**). Treatment of compounds **3** and **4** with a slight excess of lithium aluminium hydride affords the trihydrido complexes $\text{TaCp}^*\text{CpH}_3$ ($\text{Cp} = \text{Cp}'$ **11**; Cp'' **12**). The trihydrido complex **12** reacts with two-electron donor ligands on heating to yield the hydrido tantalum(III) compounds $\text{TaCp}^*\text{Cp}''\text{H}(\text{L})$ ($\text{L} = \text{CO}$ **13**, C_2H_4 **14**, RNC **15**). All the new complexes were characterized by usual IR and NMR spectroscopic methods. The crystal structures of **3** and **12** were determined by X-ray diffraction studies. Crystals of **3** are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ in a unit cell of dimensions $a = 11.775(5)$ Å, $b = 12.821(1)$ Å, $c = 13.037(7)$ Å. Crystals of **12** are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 7.384(4)$ Å, $b = 10.861(2)$ Å, $c = 16.731(3)$ Å, $\alpha = 75.94(2)^\circ$, $\beta = 84.75(3)^\circ$ and $\gamma = 72.57(4)^\circ$. Both structures were solved from diffractometer data by a combination of direct and Fourier methods and refined by full-matrix least squares fit on the basis of 4088 (**3**) and 4594 (**12**) observed reflections to R and R_w values of 0.040 and 0.064 (**3**) and 0.022 and 0.033 (**12**) respectively.

Keywords: Niobium; Tantalum; Group 5; Oxo-chloro mixed species; Hydrides; Silyl; Cyclopentadienyl

1. Introduction

The chemistry of di-pentamethylcyclopentadienyl complexes of the heavier Group 5 elements niobium and tantalum is receiving growing attention [1] after the dichlorides were made readily accessible in high yields [2]. Such derivatives offer advantages over their $\eta^5\text{-C}_5\text{H}_5$, since they exhibit higher thermal stability. They provide excellent starting materials for the preparation of sufficiently stable complexes in different oxidation states. However, the chemistry of the mixed-ring analogues $\text{MCp}^*\text{CpCl}_2$ [3] has been less extensively studied, and in some cases the complexes are not well characterized and their reactivity scarcely explored.

We herein report a convenient synthesis of mixed-ring dicyclopentadienyl complexes of stoichiometry $\text{MCp}^*\text{-CpCl}_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{M} = \text{Nb}$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)$ (Cp') **1**; $\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$ (Cp'') **2**; $\text{M} = \text{Ta}$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)$ (Cp') **3**; $\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$ (Cp'') **4**), together with studies of their reactivity. We also report the X-ray molecular structures of $\text{TaCp}^*\text{Cp}'\text{Cl}_2$ **3**, and $\text{TaCp}^*\text{Cp}''\text{H}_3$ **12**.

2. Results and discussion

2.1. Dicyclopentadienyl niobium and tantalum(IV) compounds

Treatment of a mixture of the previously described [4,5] compounds MCp^*Cl_4 , ($\text{M} = \text{Nb}$, Ta) and LiCp [6]

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¹ X-ray diffraction studies.

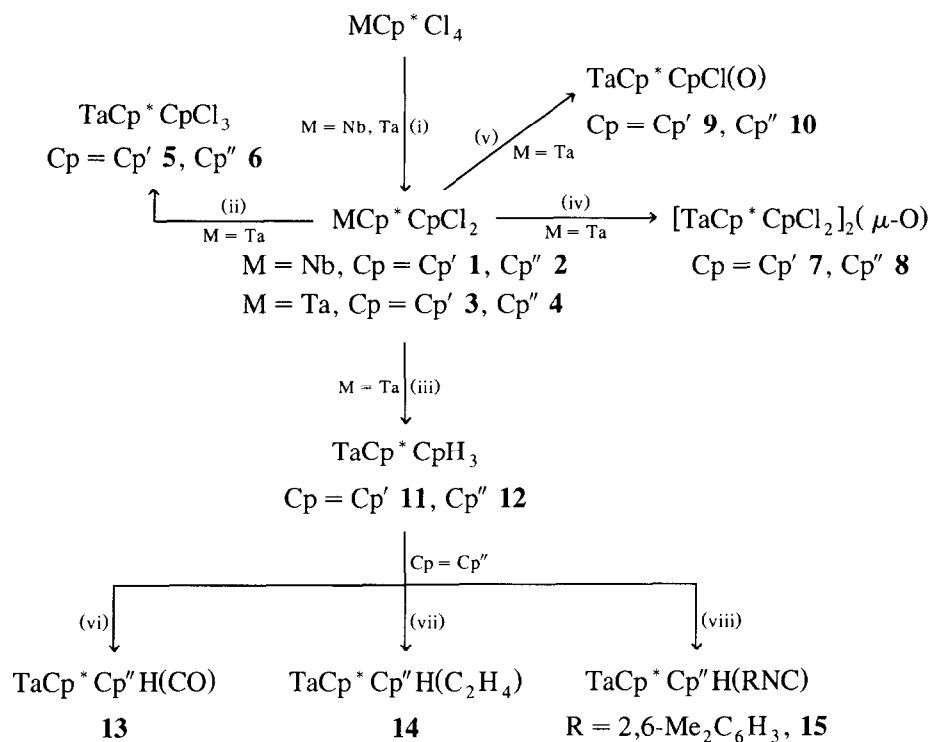
(Cp = C₅H₄(SiMe₃) (Cp'); C₅H₃(SiMe₃)₂ (Cp'')) with 1 equivalent of sodium amalgam in toluene at room temperature affords the paramagnetic mixed-ring dicyclopentadienyl complexes MCp* CpCl₂ (M = Nb, Cp = Cp' **1**; Cp'' **2**; M = Ta, Cp = Cp' **3**; Cp'' **4**) as shown in Scheme 1.

All the complexes are dark-green solids, soluble in aromatic hydrocarbons and less soluble in saturated hydrocarbons and ethyl ether; they are air- and moisture-sensitive, and rigorously dried solvents and handling under dry inert atmosphere were found to be imperative for successful preparations. The analytical and spectroscopic data for compounds **1–4** are consistent with their formulation, and their monomeric nature is supported by their magnetic behaviour and confirmed by the X-ray molecular structure of the tantalum complex **3**.

The IR spectra of complexes **1–4** show the characteristic absorptions (see Experimental section) for the pentamethylcyclopentadienyl [7] ($\nu_{C-C} \sim 1025 \text{ cm}^{-1}$) and mono- or bis-(trimethylsilyl)cyclopentadienyl [8] (ν_{C-H}

$\sim 838 \text{ cm}^{-1}$) rings, for the trimethylsilyl substituents [9] ($\nu_{\delta_s}(\text{CH}_3) \sim 1245 \text{ cm}^{-1}$) and for the M-Cl stretching vibrations [10] ($\nu_{M-Cl} \sim 330 \text{ cm}^{-1}$).

Magnetic susceptibility measurements at room temperature give magnetic moments μ_{eff} of 1.7–1.8 μ_B , similar to those found for the analogous dicyclopentadienyl compounds reported [11]. The ¹H NMR spectra of compounds **3** and **4** were recorded in chloroform-*d*₁, whereas benzene-*d*₆ was required for the niobium derivatives **1** and **2** since they decompose in chloroform-*d*₁. The spectra show broad signals which were assigned to the methyl groups of the pentamethylcyclopentadienyl ring (not observed for compounds **1** and **2**) and to the ring protons of the mono- and bis-trimethylsilylcyclopentadienyl ligands (split for compounds **1** and **2**), according to their relative intensities and the relaxation times obtained (see Experimental section). The resonance due to the SiMe₃ substituents, appears as a much narrower signal at δ 2.3 (**3**, $T_1 = 8.1 \pm 0.04$ ms) and δ 1.8 (**4**, $T_1 = 8 \pm 0.05$ ms). This spectral behaviour can be explained in terms of "contact and



Reagents and conditions:

- (i) 1 equivalent LiCp (Cp = C₅H_{5-x}(SiMe₃)_x, x = 1, 2), 1 equivalent Na–Hg, toluene, 12 h, RT.
- (ii) 1/2 equivalent PCl₅, toluene, 1 h, RT.
- (iii) LiAlH₄ excess, diethyl ether, 12 h, RT; H₂O.
- (iv) Dry O₂ (1 atm), THF, 2–3 h, RT.
- (v) Air, THF, 12 h, RT.
- (vi) CO (1 atm), toluene, 72 h, 120°C.
- (vii) C₂H₄ (1 atm), toluene, 36 h, 120°C.
- (viii) 1 equivalent 2,6-Me₂C₆H₃NC, toluene, 72 h, 120°C.

Scheme 1.

pseudo-contact shifts'' [12], indicating that the unpaired electron is essentially localized on the metal–Cp system, causing a very high downfield shift as observed for the ring proton resonances.

Cooling a toluene solution of the tantalum derivative **3** to -40°C gave crystals suitable for X-ray diffraction studies. An ORTEP drawing of **3** based on the X-ray structural analysis with the atomic labelling scheme is shown in Fig. 1. Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are shown in Table 1. Selected bond distances and angles are given in Table 2.

The molecule has the typical bent-metallocene structure with the tantalum atom in a pseudotetrahedral coordination if the centroids of the cyclopentadienyl rings are considered as occupying one unique coordination site. The molecule is very similar to those reported before for $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Cl}_2$ [13] and NbCp_2Cl_2 , ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ [14a], $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ [14b]), showing only small variations probably derived from the difference between the two Cp rings. The distances from the tantalum atom to the Cp planes are 2.105 and 2.075 Å for Cp* and Cp' respectively, and the mean distance from tantalum to the carbon atoms shows the same trend (2.427 Å for Cp* and 2.402 Å for Cp'). The Ta–Cl distances are also significantly different (Ta–Cl(1) 2.447(3) and Ta–Cl(2) 2.418(3) Å). These values are of the same order as those found in $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Cl}_2$ [13] and shorter than the Cl–Nb distances in NbCp_2Cl_2 [14]. The very short Ta–Cl(2) distance may be related to the differences in the two Cp rings. The Cl(1)–Ta–Cl(2) angle has a value of $85.3(1)^{\circ}$, as expected for d^1 complexes [14].

The angle between the two Cp planes has a typical value of $49.5(3)^{\circ}$, but both Cp planes form different angles with the equatorial plane Cl(1)–Ta–Cl(2) ($23.03(4)^{\circ}$ for Cp* and $26.5(2)^{\circ}$ for Cp'). The SiMe_3 group is out of the Cp plane with the Si atom placed 0.296 Å above this plane. The C–C and Si–C distances have normal values.

2.2. Chloro and oxo dicyclopentadienyl tantalum(V) compounds

Treatment of $\text{TaCp}^*\text{CpCl}_2$ **3** and **4** with the stoichiometric amount of PCl_5 in toluene gave the air-sensitive diamagnetic trichloro derivatives $\text{TaCp}^*\text{CpCl}_3$ ($\text{Cp} = \text{Cp}'$ **5**; Cp'' **6**) as orange solids soluble in most organic solvents.

The mixed-ring tantalum metallocenes **3** and **4** are also oxidized by bubbling dry O_2 through their THF solutions, giving diamagnetic μ -oxo dinuclear complexes $[\text{TaCp}^*\text{CpCl}_2]_2(\mu\text{-O})$, ($\text{Cp} = \text{Cp}'$ **7**; Cp'' **8**). However, when their THF solutions are exposed to air, the mononuclear oxo tantalum(V) derivatives $\text{TaCp}^*\text{-CpCl}(\text{O})$, ($\text{Cp} = \text{Cp}'$ **9**; Cp'' **10**) are obtained. The oxo-

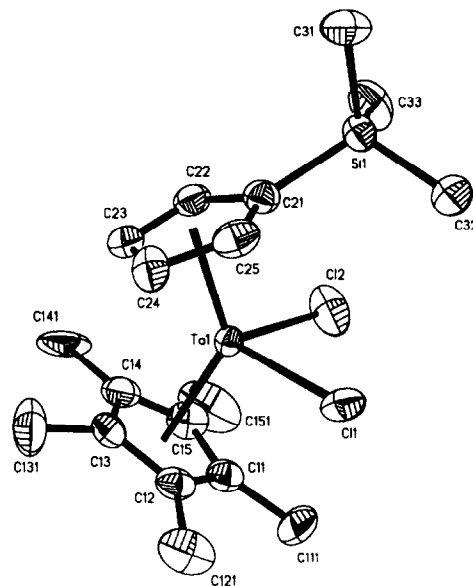


Fig. 1. ORTEP view of the molecular structure of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_3)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2$, **3**, with the atom numbering scheme.

complexes **7–10**, were isolated as air-sensitive solids, insoluble in saturated hydrocarbons, and were analytically and spectroscopically characterized. The IR spectra of complexes **7** and **8** containing μ -oxo bridges show the $\nu_{(\text{Ta}-\text{O}-\text{Ta})}$ [15] at $755\text{--}760\text{ cm}^{-1}$, whereas $\nu_{(\text{Ta}=\text{O})}$ [14,16] absorptions are observed at $901\text{--}910\text{ cm}^{-1}$ for complexes **9** and **10** with terminal oxo lig-

Table 1
Positional parameters of **3** with ESDs in parentheses

Atom	x	y	z	B (Å ²)
Ta1	0.17373(3)	0.23314(3)	0.19098(2)	1.936(5)
Cl(1)	0.1992(3)	0.0741(3)	0.2922(2)	4.53(5)
Cl(2)	0.2098(3)	0.3243(3)	0.3501(2)	4.99(7)
Si(1)	-0.0846(2)	0.2632(3)	0.3823(2)	2.87(5)
C(11)	0.3762(8)	0.2228(9)	0.1699(7)	2.8(2)
C(12)	0.3266(8)	0.1582(8)	0.0938(7)	2.8(2)
C(13)	0.2666(7)	0.2211(9)	0.0250(7)	2.9(2)
C(14)	0.2798(9)	0.3278(9)	0.0592(8)	3.4(2)
C(15)	0.3467(9)	0.3283(9)	0.1457(9)	3.5(2)
C(21)	-0.0225(8)	0.2528(8)	0.2500(7)	2.7(2)
C(22)	0.0045(8)	0.3325(8)	0.1783(8)	2.9(2)
C(23)	0.0263(8)	0.2862(9)	0.0808(8)	3.4(2)
C(24)	0.0145(8)	0.1766(9)	0.0919(7)	3.2(2)
C(25)	-0.0174(8)	0.1582(8)	0.1940(9)	3.2(2)
C(31)	-0.240(1)	0.240(1)	0.363(1)	5.2(3)
C(32)	-0.026(1)	0.157(1)	0.4651(9)	4.1(2)
C(33)	-0.063(1)	0.395(1)	0.439(1)	4.9(3)
C(111)	0.455(1)	0.185(1)	0.254(1)	5.1(3)
C(121)	0.350(1)	0.044(1)	0.081(1)	4.6(3)
C(131)	0.217(1)	0.188(1)	-0.0748(8)	5.2(3)
C(141)	0.243(1)	0.423(1)	0.001(1)	5.8(3)
C(151)	0.394(1)	0.423(1)	0.195(1)	6.7(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1, 1) + b^2B(2, 2) + c^2B(3, 3) + ab(\cos \gamma)B(1, 2) + ac(\cos \beta)B(1, 3) + bc(\cos \alpha)B(2, 3)]$.

ands. The ^1H NMR spectra of compounds **5** and **6** show the expected singlets for the methyl groups of the pentamethylcyclopentadienyl ring, and for the SiMe_3 group, and the two multiplets expected for the ring protons of the mono- and di-substituted cyclopentadienyl ligands, consistent [17] with $\text{AA}'\text{BB}'$, and $\text{AA}'\text{B}$ spin systems respectively.

Particularly significant are the observed ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the oxo complex **7** between 20 and 50°C , which show four and five resonances for the silyl-substituted ring protons and carbon atoms respectively. This behaviour indicates that they are magnetically different, due to the absence of a symmetry plane perpendicular to the cyclopentadienyl rings, consistent with a structure in which the μ -oxo system bridges one equatorial side position of at least one of the tantalum atoms. However, the ^1H NMR spectrum of complex **8**, which is also a dinuclear complex, exhibits two resonances for the cyclopentadienyl ring protons ($\text{AA}'\text{B}$ system), consistent with the presence of a plane of symmetry perpendicular to both rings and, therefore, with a structure in which both central positions are involved in the μ -oxo bridging system. The ^{13}C NMR data confirm this proposal.

The oxo-mononuclear complexes **9** and **10** show the NMR behaviour expected for species containing a chiral metal centre.

2.3. Dicyclopentadienyl tantalum hydrides

Treatment of the tantalum(IV) chlorides **3** and **4** with an excess of lithium aluminium hydride in diethyl ether over a period of several hours affords a yellow suspension, containing a mixture of the colourless tantalum(V) hydrides $\text{TaCp}^*\text{CpH}_3$ ($\text{Cp} = \text{Cp}'$, **11**; Cp'' , **12**) and yellow tantalum(III) derivatives, probably similar to the reported [18] niobium complex characterized as the tetrahydridoaluminate compound $\text{Cp}_2\text{NbH}_2\text{AlH}_2$. Addition of water to this mixture of disproportionation products gives the trihydrido complexes **11** and **12** in high yields, as shown in Scheme 1.

Both compounds **11** and **12** are soluble in saturated and aromatic hydrocarbons and decompose in chlorinated solvents.

The IR spectra show the characteristic absorptions for both cyclopentadienyl rings, as well as other internal vibrations of the different substituents. The $\nu_{(\text{Ta}-\text{H})}$ absorption for the trihydrido complexes appears as a broad band at 1778 (**11**) and 1781 (**12**) cm^{-1} , consistent with data reported for similar hydrido derivatives [2c,3a].

The ^1H NMR spectra of both trihydrido compounds **11** and **12** show the expected resonances for the cyclopentadienyl rings along with one doublet and one triplet for the hydride protons, consistent with an AX_2 spin system.

Table 2
Selected bond distances (\AA) and angles (deg) for **3** with ESDs in parentheses

Ta-coordination sphere		Cp^* ring		$\text{C}_5\text{H}_4\text{SiMe}_3$	
<i>Bond distances</i>					
Ta(1)–CE	2.105	C(11)–C(12)	1.42(1)	C(21)–C(22)	1.42(1)
Ta(1)–CE'	2.075	C(11)–C(15)	1.43(2)	C(21)–C(25)	1.42(1)
Ta(1)–Cl(1)	2.447(3)	C(11)–C(111)	1.52(2)	C(22)–C(23)	1.43(1)
Ta(1)–Cl(2)	2.418(3)	C(12)–C(13)	1.40(1)	C(23)–C(24)	1.42(2)
		C(12)–C(121)	1.50(2)	C(24)–C(25)	1.40(1)
		C(13)–C(14)	1.45(2)	Si(1)–C(21)	1.88(1)
		C(13)–C(131)	1.49(1)	Si(1)–C(31)	1.88(1)
		C(14)–C(15)	1.38(2)	Si(1)–C(32)	1.87(1)
		C(14)–C(141)	1.51(2)	Si(1)–C(33)	1.86(1)
		C(15)–C(151)	1.48(2)		
<i>Bond angles</i>					
Cl(1)–Ta(1)–Cl(2)	85.3(1)	C(12)–C(11)–C(15)	107.3(9)	C(22)–C(21)–C(25)	105.5(9)
Cl(1)–Ta(1)–CE	107.5	C(12)–C(11)–C(111)	125.0(1)	C(21)–C(22)–C(23)	109.1(9)
Cl(1)–Ta(1)–CE'	106.0	C(15)–C(11)–C(111)	128.0(1)	C(22)–C(23)–C(24)	107.6(9)
Cl(2)–Ta(1)–CE	106.9	C(11)–C(12)–C(13)	108.7(9)	C(23)–C(24)–C(25)	106.9(9)
Cl(2)–Ta(1)–CE'	108.7	C(11)–C(12)–C(121)	125.1(9)	C(21)–C(25)–C(24)	110.8(9)
CE–Ta(1)–CE'	132.4	C(13)–C(12)–C(121)	125.6(9)	Si(1)–C(21)–C(22)	129.8(7)
		C(12)–C(13)–C(14)	107.0(8)	Si(1)–C(21)–C(25)	123.4(7)
		C(12)–C(13)–C(131)	127.0(1)	C(21)–Si(1)–C(31)	104.2(5)
		C(14)–C(13)–C(131)	125.0(1)	C(21)–Si(1)–C(32)	109.7(5)
		C(13)–C(14)–C(15)	108.6(9)	C(21)–Si(1)–C(33)	111.9(5)
		C(13)–C(14)–C(141)	125.6(9)	C(31)–Si(1)–C(32)	108.8(6)
		C(15)–C(14)–C(141)	125.0(1)	C(31)–Si(1)–C(33)	109.6(7)
		C(11)–C(15)–C(14)	108.0(1)	C(32)–Si(1)–C(33)	112.4(6)
		C(1)–C(15)–C(151)	126.0(1)		
		C(14)–C(15)–C(151)	125.0(1)		

CE is the centroid of the Cp^* ring. CE' is the centroid of the $\text{C}_5\text{H}_4\text{SiMe}_3$ ring.

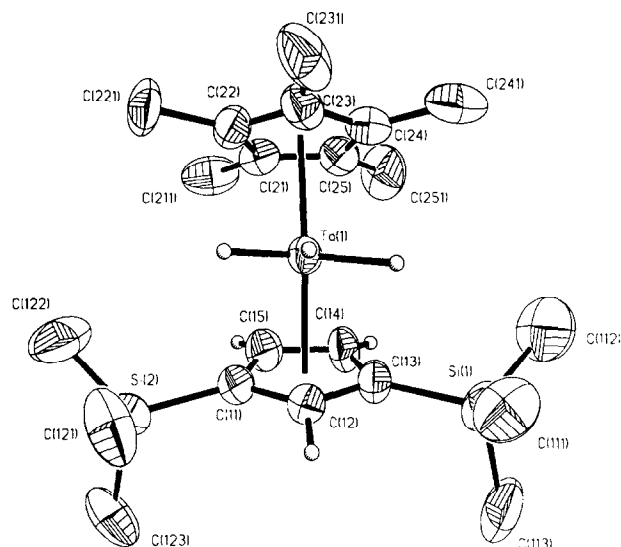


Fig. 2. ORTEP view of the molecular structure of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)\text{H}_3$, **12**, with the atom numbering scheme.

The molecular structure of **12** obtained by X-ray diffraction studies with the atomic numbering scheme is shown in Fig. 2. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are displayed in Table 3. Selected bond distances and angles are given in Table 4. The molecular structure is that of a typical bent metallocene similar to $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_3$, ($\text{M} = \text{Nb}, \text{Ta}$) [19]. The position of the hydrogen atoms found in the difference Fourier map could not be refined, but the Ta–H(1) and Ta–H(2) distances (1.77 and 1.75 Å) have normal values, whereas the Ta–H(3) distance (1.51 Å) is shorter than expected; however, the apparent differences may not be real.

The angle between the two cyclopentadienyl planes has a value of $37.9(1)^\circ$ and Ta–centroid distances have similar values (Ta–Cp'' 2.064 Å and Ta–Cp' 2.078 Å),

Table 3

Positional parameters for **12** with ESDs in parentheses

Atom	x	y	z	B (Å ²)
Ta(1)	0.19438(1)	0.17888(1)	0.20886(1)	2.912(3)
Si(1)	0.4122(2)	−0.1971(1)	0.26473(8)	5.40(3)
Si(2)	0.1796(2)	0.2521(1)	0.42252(6)	5.28(3)
C(11)	0.1664(5)	0.1384(3)	0.3574(2)	4.14(7)
C(12)	0.3252(5)	0.0372(3)	0.3351(2)	3.96(7)
C(13)	0.2584(5)	−0.0426(3)	0.2936(2)	4.15(7)
C(14)	0.0585(5)	0.0136(3)	0.2881(2)	4.42(8)
C(15)	0.0015(5)	0.1231(4)	0.3265(2)	4.41(8)
C(111)	0.6594(8)	−0.1875(5)	0.2424(4)	7.4(1)
C(112)	0.316(1)	−0.2223(5)	0.1720(4)	9.0(2)
C(113)	0.406(1)	−0.3379(5)	0.3543(4)	10.8(2)
C(121)	0.4282(8)	0.2747(5)	0.4132(4)	8.6(1)
C(122)	−0.008(1)	0.4137(5)	0.3951(3)	9.4(2)
C(123)	0.139(1)	0.1702(7)	0.5315(3)	9.4(2)
C(21)	−0.0911(4)	0.3286(3)	0.1455(2)	3.72(7)
C(22)	0.0473(5)	0.3961(3)	0.1255(2)	4.19(7)
C(23)	0.1920(5)	0.3265(4)	0.0756(2)	4.20(7)
C(24)	0.1326(5)	0.2189(3)	0.0642(2)	4.00(7)
C(25)	−0.0386(4)	0.2196(3)	0.1073(2)	3.86(7)
C(211)	−0.2786(6)	0.3758(5)	0.1911(3)	6.0(1)
C(221)	0.0365(8)	0.5271(4)	0.1432(3)	7.7(1)
C(231)	0.3536(6)	0.3729(5)	0.0325(3)	7.4(1)
C(251)	−0.1618(6)	0.1306(4)	0.1051(3)	6.5(1)
C(241)	0.2251(8)	0.1291(5)	0.0062(3)	7.1(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1, 1) + b^2B(2, 2) + c^2B(3, 3) + ab(\cos \gamma)B(1, 2) + ac(\cos \beta)B(1, 3) + bc(\cos \alpha)B(2, 3)]$.

both features are comparable with that found for TaCp_2H_3 .

The two cyclopentadienyl rings are eclipsed and their substituents are moved away from the metal to minimize their mutual repulsion. The silicon atoms are 0.193(1) Å out of the Cp plane, and the methyl carbon atoms C(221) and C(241), eclipsed by the SiMe₃ groups,

Table 4

Selected bond distances (Å) and angles (deg) for **12** with ESDs in parentheses

Bond distances					
Ta(1)–C(11)	2.417(3)	Si(1)–C(111)	1.858(6)	C(14)–C(15)	1.423(6)
Ta(1)–C(12)	2.380(3)	Si(1)–C(112)	1.875(7)	C(21)–C(22)	1.400(5)
Ta(1)–C(13)	2.409(3)	Si(1)–C(113)	1.872(6)	C(21)–C(25)	1.416(5)
Ta(1)–C(14)	2.380(4)	Si(2)–C(11)	1.863(4)	C(21)–C(211)	1.527(5)
Ta(1)–C(15)	2.386(4)	Si(2)–C(121)	1.912(7)	C(22)–C(23)	1.439(5)
Ta(1)–C(21)	2.394(3)	Si(2)–C(122)	1.864(5)	C(22)–C(221)	1.501(6)
Ta(1)–C(22)	2.415(3)	Si(2)–C(123)	1.864(5)	C(23)–C(24)	1.423(6)
Ta(1)–C(23)	2.408(3)	C(11)–C(12)	1.438(4)	C(23)–C(231)	1.491(6)
Ta(1)–C(24)	2.414(3)	C(11)–C(15)	1.433(6)	C(24)–C(25)	1.396(5)
Ta(1)–C(25)	2.399(3)	C(12)–C(13)	1.444(6)	C(24)–C(241)	1.515(6)
Si(1)–C(13)	1.869(3)	C(13)–C(14)	1.420(5)	C(25)–C(251)	1.521(6)
Ta(1)–CE	2.083	Ta(1)–CE'	2.063		
Bond angles					
CE–Ta(1)–CE'	142.6	C(13)–Si(1)–C(111)	110.5(2)		
C(13)–Si(1)–C(112)	110.0(2)	C(13)–Si(1)–C(113)	106.9(2)		
C(11)–Si(2)–C(121)	109.7(2)	C(11)–Si(2)–C(122)	111.2(2)		
C(11)–Si(2)–C(123)	107.1(3)				

CE is the centroid of the Cp' ring. CE' is the centroid of the C₅H₃(SiMe₃)₂.

show an even more important deviation with respect to the Cp* plane (0.194(5) and 0.188(5) Å).

A comparison between the two molecular structures of **3** and **12** containing mono- and di-silyl-substituted rings shows that the angle formed by the two cyclopentadienyl rings is smaller for complex **12** which contains the more substituted ring.

Simple adducts may be prepared by thermolysis of **12** in toluene in the presence of two-electron donor ligands. When TaCp* Cp''H₃, **12**, is heated at 120°C under atmosphere of CO, C₂H₄ or in the presence of 2,6-Me₂C₆H₃NC, hydrogen is displaced to give the hydrido tantalum(III) complexes TaCp* CpH(L) (L = CO, **13**; C₂H₄, **14**; 2,6-Me₂C₆H₃NC, **15**), which are obtained in good yields, as shown in Scheme 1.

The IR spectrum of TaCp* Cp''H(CO) **13**, displays the characteristic ν_{CO} stretching frequency at 1880 cm⁻¹ consistent with considerable back-donation from tantalum to carbon monoxide. This value is expectedly higher than that observed for TaCp₂H(CO), (ν_{CO} = 1865 cm⁻¹) [3a] and is similar to that found for TaCp₂H(CO), (ν_{CO} = 1885 cm⁻¹) [20], indicating that the increased electron density of the metal centre due to the C₅Me₅ ring is alleviated by the negative mesomeric effect [21] of the silyl groups in the disubstituted C₅H₃(SiMe₃)₂ ligand.

The $\nu_{\text{C=N}}$ absorption of the coordinated isocyanide ligand in complex **15** appears at 1860 cm⁻¹, a displacement of 258 cm⁻¹ to lower frequency with respect to the value observed for the free ligand (2,6-Me₂C₆H₃NC, ν = 2118 cm⁻¹), as a consequence of the π -electron donation to the antibonding ligand orbitals, which decreases the C–N bond order [21].

The η^2 -olefin compound TaCp* Cp''H(C₂H₄), **14**, is formed in a quantitative yield and is thermally stable, with evolution of ethane only being observed by prolonged heating of **12** (3 days at 120°C) under an excess of ethylene.

The NMR (¹H and ¹³C) behaviour of complexes **13**–**15** is as expected for chiral complexes (see Experimental section). The ¹H NMR spectrum of **14** reveals a small coupling (³J_{H–H_{endo}} = 2.40 Hz) between the endo ethylenic hydrogens and the metal-bound hydrogen atom. The upfield ¹³C NMR shifts for the ethylenic carbons at δ 10.99 and δ 9.77 are indicative of a significant π -back donation, consistent with a significant contribution of a tantalacyclopropane system [22].

3. Experimental section

3.1. General considerations

All manipulations of air- and/or moisture-sensitive materials were carried out on a conventional vacuum

line, using standard Schlenk or cannula techniques, or in a drybox under an atmosphere of argon.

Solvents were dried and purified by prolonged reflux under appropriate drying agent (*n*-hexane over Na–K alloy; toluene, THF and diethyl ether over sodium) and distilled under an argon atmosphere before use. Reagent-grade chemicals purchased from commercial sources and used without further purification were as follows: sodium and mercury (Panreac), phosphorus pentachloride (Fluka), lithium aluminium hydride (Aldrich), carbon monoxide and ethylene (SEO), MCp* Cl₄ (M = Nb [4], Ta [5]), LiCp (Cp = C₅H_{5–x}(SiMe₃)_x, x = 1, 2) [6] and 2,6-Me₂C₆H₃NC [23] were prepared by published methods.

IR spectra were recorded on a Perkin–Elmer 583 spectrophotometer (4000–200 cm⁻¹) using Nujol mulls between CsI pellets. ¹H and ¹³C{¹H} NMR spectra were recorded on a Varian VXR Unity-300 and 500 MHz spectrometer. Chemical shifts are reported in δ units (positive chemical shifts to a higher frequency), relative to a TMS standard. Magnetic susceptibilities were measured by the Faraday method using a Bruker B-E 15 magnetic balance with a temperature control unit. C, H and N analyses were performed with a Perkin–Elmer 240C microanalyser.

3.2. Synthesis of MCp* CpCl₂, (M = Nb, Cp = Cp' **1**; Cp'' **2**; M = Ta, Cp = Cp' **3**; Cp'' **4**)

A toluene (75 ml) suspension of MCp* Cl₄ (M = Nb, 0.80 g; Ta, 1.00 g; 2.16 mmol) and LiCp (Cp = Cp', 0.31 g, 2.16 mmol or Cp'', 0.47 g, 2.16 mmol) was added to 10% sodium amalgam (0.052 g, 2.16 mmol). The mixture was stirred for 12 h at room temperature. The dark-green suspension was filtered through Celite and after concentration to ca. 20 ml, the solution was cooled to –40°C to give green crystals of **1**–**4**.

The data for **1** follow. Yield 0.47 g (50%). IR (Nujol mull, ν cm⁻¹): 1246(s), 1166(m), 1080(w), 1022(s), 900(w), 836(vs), 756(w), 725(w), 631(w), 430(w), 392(m), 330(m). ¹H NMR (δ ppm, in benzene-*d*₆): 14.3(br, 1H, H₄C₅SiMe₃), 12.2(br, 2H, H₄C₅SiMe₃), 10.0(br, 1H, H₄C₅SiMe₃), 1.3(s, 9H, Me₃SiC₅H₄). Anal. Found: C, 47.61; H, 6.50. C₁₈H₂₈Cl₂NbSi. Calc.: C, 47.56; H, 6.47%.

The data for **2** follow. Yield 0.55 g (50%). IR (Nujol mull, ν cm⁻¹): 1251(s), 1160(w), 1080(w), 1021(m), 980(w), 836(vs), 756(m), 728(m), 691(w), 632(w), 392(m,br). ¹H NMR (δ ppm, in benzene-*d*₆): 14.28(br, 1H, H₃C₅(SiMe₃)₂), 12.14(br, 2H, H₃C₅(SiMe₃)₂). Anal. Found: C, 49.67; H, 7.20. C₂₁H₃₆Cl₂NbSi₂. Calc.: C, 49.60; H, 7.10%.

The data for **3** follow. Yield 0.56 g (70%). IR (Nujol mull, ν cm⁻¹): 1245(vs), 1190(w), 1169(s), 1087(s), 1027(s), 903(s), 839(s,br), 756(m), 695(m), 632(m), 479(m), 360(s), 301(s), 270(s). ¹H NMR (δ ppm, in

chloroform- d_1): 26.00(br, 15H, C_5Me_5), 20.17(br, 4H, $H_4C_5SiMe_3$), 2.30(br, 9H, $Me_3SiC_5H_4$). Anal. Found: C, 40.98; H, 5.29. $C_{18}H_{28}Cl_2SiTa$. Calc.: C, 41.23; H, 5.38%.

The data for **4** follow. Yield 0.63 g (70%). IR (Nujol mull, ν cm^{-1}): 1264(m), 1241(s), 1190(w), 1088(m), 1060(w), 1020(m), 920(m), 903(m), 875(m), 840(vs), 753(m), 720(w), 695(w), 625(w), 377(w), 296(m). 1H NMR (δ ppm, in chloroform- d_1): 26.00(br, 15H, C_5Me_5), 23.00(br, 3H, $H_3C_5(SiMe_3)_2$), 1.80(s, 18H, $(Me_3Si)_2C_5H_3$). Anal. Found: C, 42.30; H, 5.96. $C_{21}H_{36}Cl_2Si_2Ta$. Calc.: C, 42.28; H, 6.00%.

3.3. Synthesis of $TaCp^*CpCl_3$ ($Cp = Cp'$ **5**; Cp'' **6**)

PCl_5 ($Cp = Cp'$, 0.10 g, 0.47 mmol; $Cp = Cp''$, 0.09 g, 0.42 mmol) was added to a toluene (50 ml) suspension of $TaCp^*CpCl_2$ ($Cp = Cp'$, 0.50 g, 0.95 mmol; $Cp = Cp''$, 0.50 g, 0.83 mmol). The mixture was stirred for 1 h at room temperature and then the resultant orange suspension was decanted and filtered. The residual orange solid was washed with *n*-hexane (2×5 ml), dried in vacuo and identified as complexes **5** and **6**.

The data for **5** follow. Yield 0.43 g (80%). IR (Nujol mull, ν cm^{-1}): 1250(s), 1176(m), 1075(w), 1027(m), 904(m), 838(vs), 759(m), 727(m), 635(m), 447(vs), 348(s), 325(m), 293(w). 1H NMR (δ ppm, in chloroform- d_1): 7.19 (m, 2H, $H_4C_5SiMe_3$), 6.83(m, 2H, $H_4C_5SiMe_3$), 2.53(s, 15H, C_5Me_5), 0.35(s, 9H, $Me_3SiC_5H_4$). $^{13}C\{^1H\}$ NMR (δ ppm, in chloroform- d_1): 148.73(s, C_1 , $C_5H_4SiMe_3$), 133.53(s, $C_{2,5}$, $C_5H_4SiMe_3$), 129.82(s, C_5Me_5), 115.68(s, $C_{3,4}$, $C_5H_4SiMe_3$), 13.24(s, Me_5C_5), -0.16 (s, $Me_3SiC_5H_4$). Anal. Found: C, 38.56; H, 5.09. $C_{18}H_{28}Cl_3SiTa$. Calc.: C, 38.62; H, 5.04%.

The data for **6** follow. Yield 0.42 g (80%). IR (Nujol mull, ν cm^{-1}): 1243(s), 1097(m), 1023(m), 935(m), 911(m), 839(vs), 760(m), 726(m), 635(w), 450(s), 380(m), 334(s). 1H NMR (δ ppm, in chloroform- d_1): 7.20(m, 2H, $H_3C_5(SiMe_3)_2$), 6.77(m, 1H, $H_3C_5(SiMe_3)_2$), 2.56(s, 15H, C_5Me_5), 0.28(s, 18H, $(Me_3Si)_2C_5H_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in chloroform- d_1): 151.98(s, $C_{1,3}$, $C_5H_3(SiMe_3)_2$), 130.54(s, C_5Me_5), 127.48(s, C_2 , $C_5H_3(SiMe_3)_2$), 121.53(s, $C_{4,5}$, $C_5H_3(SiMe_3)_2$), 13.5(s, Me_5C_5), -0.17 (s, $(Me_3Si)_2C_5H_3$). Anal. Found: C, 39.98; H, 5.70. $C_{21}H_{36}Cl_3Si_2Ta$. Calc.: C, 39.90; H, 5.74%.

3.4. Synthesis of $[TaCp^*CpCl_2]_2$ ($\mu-O$), ($Cp = Cp'$ **7**; Cp'' **8**)

A Schlenk tube containing a solution of **3** ($Cp = Cp'$, 0.70 g, 1.33 mmol) or **4** ($Cp = Cp''$, 0.70 g, 1.17 mmol) in THF (70 ml) was sealed under 1 atm of dry O_2 . The resulting orange solution was stirred for 2 or 3 h at room temperature, filtered and concentrated to ca. 15 ml. Yellow or orange crystals of **7** or **8** were obtained by cooling to $-40^\circ C$ overnight.

The data for **7** follow. Yield 0.56 g (40%). IR (Nujol mull, ν cm^{-1}): 1243(vs), 1170(m), 1089(m), 1028(s), 960(m), 845(vs), 630(m), 415(m), 350(s), 330(s). 1H NMR (δ ppm, in chloroform- d_1): 7.05(m, 1H, $H_4C_5SiMe_3$), 6.43(m, 1H, $H_4C_5SiMe_3$), 6.35(m, 1H, $H_4C_5SiMe_3$), 5.80(m, 1H, $H_4C_5SiMe_3$), 2.54(s, 15H, C_5Me_5), 0.30(s, 9H, $Me_3SiC_5H_4$). $^{13}C\{^1H\}$ NMR (δ ppm, in chloroform- d_1): 131.80(s, C_1 , $C_5H_4SiMe_3$), 124.73(s, C_5 , $C_5H_4SiMe_3$), 121.93(s, C_2 , $C_5H_4SiMe_3$), 119.61(s, C_5Me_5), 114.02(s, C_4 , $C_5H_4SiMe_3$), 110.31(s, C_3 , $C_5H_4SiMe_3$), 14.27(s, Me_5C_5), -0.14 (s, $Me_3SiC_5H_4$). Anal. Found: C, 40.70; H, 5.32. $C_{36}H_{46}Cl_4OSi_2Ta_2$. Calc.: C, 40.61; H, 5.30%.

The data for **8** follow. Yield 0.57 g (40%). IR (Nujol mull, ν cm^{-1}): 1248(vs), 1097(s), 1068(s), 1024(s), 937(m), 839(vs), 887(w), 760(m), 724(s), 635(m), 397(s), 332(s), 246(m). 1H NMR (δ ppm, in chloroform- d_1): 7.41(m, 2H, $H_3C_5(SiMe_3)_2$), 6.75(m, 1H, $H_3C_5(SiMe_3)_2$), 2.56(s, 15H, C_5Me_5), 0.26(s, 18H, $(Me_3Si)_2C_5H_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in chloroform- d_1): 151.98(s, $C_{1,3}$, $C_5H_3(SiMe_3)_2$), 130.47(s, C_5Me_5), 127.57(s, C_2 , $C_5H_3(SiMe_3)_2$), 121.77(s, $C_{4,5}$, $C_5H_3(SiMe_3)_2$), 13.45(s, Me_5C_5), -0.19 (s, $(Me_3Si)_2C_5H_3$). Anal. Found: C, 41.80; H, 5.95. $C_{42}H_{72}Cl_4OSi_4Ta_2$. Calc.: C, 41.72; H, 6.00%.

3.5. Synthesis of $TaCp^*CpCl(O)$, ($Cp = Cp'$ **9**; Cp'' **10**)

Solutions of **3** (0.70 g, 1.33 mmol) or **4** (0.70 g, 1.17 mmol) in THF (70 ml) were stirred in air for 12 h (**3**) or 2–3 days (**4**). The resulting orange suspension was filtered, the solid washed with cold *n*-hexane (2×5 ml), dried in vacuo and identified as **9** or **10**.

The data for **9** follow. Yield 0.27 g (40%). IR (Nujol mull, ν cm^{-1}): 1246(vs), 1171(m), 1088(m), 1032(s), 962(m), 901(s), 840(vs), 630(m), 417(m), 368(s), 327(s), 283(m). 1H NMR (δ ppm, in chloroform- d_1): 7.84(m, 1H, $H_4C_5SiMe_3$), 6.57(m, 1H, $H_4C_5SiMe_3$), 6.22(m, 1H, $H_4C_5SiMe_3$), 5.90(m, 1H, $H_4C_5SiMe_3$), 2.18(s, 15H, C_5Me_5), 0.32(s, 9H, $Me_3SiC_5H_4$). $^{13}C\{^1H\}$ NMR (δ ppm, in chloroform- d_1): 133.86(s, C_1 , $C_5H_4SiMe_3$), 127.49(s, C_5 , $C_5H_4SiMe_3$), 124.87(s, C_2 , $C_5H_4SiMe_3$), 124.75(s, C_5Me_5), 112.79(s, C_4 , $C_5H_4SiMe_3$), 119.19(s, C_3 , $C_5H_4SiMe_3$), 12.11(s, Me_5C_5), -0.11 (s, $Me_3SiC_5H_4$). Anal. Found: C, 42.60; H, 5.49. Calcd. for $C_{18}H_{28}ClOSiTa$. Calc.: C, 42.81; H, 5.59%.

The data for **10** follow. Yield 0.34 g (45%). IR (Nujol mull, ν cm^{-1}): 1250(vs), 1027(s), 935(s), 910(s), 840(vs), 760(s), 635(m), 369(s), 330(s), 246(m). 1H NMR (δ ppm, in chloroform- d_1): 7.19(m, 1H, $H_3C_5(SiMe_3)_2$), 6.23(m, 1H, $H_3C_5(SiMe_3)_2$), 5.80(m, 1H, $H_3C_5(SiMe_3)_2$), 2.28(s, 15H, C_5Me_5), 0.32(s, 9H, $(Me_3Si)_2C_5H_3$), 0.24(s, 9H, $(Me_3Si)_2C_5H_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in chloroform- d_1): 129.27s, 128.76s($C_{1,3}$, $C_5H_3(SiMe_3)_2$), 127.65(s, C_5 , $C_5H_3(SiMe_3)_2$), 125.62(s, C_5Me_5), 117.1(s, C_4 , $C_5H_3(SiMe_3)_2$),

116.73(s, C_2 , $C_5H_3(SiMe_3)_2$), 17.14(s, Me_5C_5), 2.10(s, $(Me_3Si)_2C_5H_3$), 0.17(s, $(Me_3Si)_2C_5H_3$). Anal. Found: C, 43.57; H, 6.19. Calcd. for $C_{21}H_{36}ClOSi_2Ta$. Calc.: C, 43.70; H, 6.29%.

3.6. Synthesis of $TaCp^*CpH_3$ ($Cp = Cp'$ **11**; Cp'' **12**)

Stirred solutions of **3** ($Cp = Cp'$, 1.00 g, 1.90 mmol) or **4** ($Cp = Cp''$, 1.00 g, 1.67 mmol) and $LiAlH_4$ ($Cp = Cp'$, 0.43 g, 11.44 mmol; $Cp = Cp''$, 0.38 g, 10.06 mmol) in diethyl ether (50 ml) at $-78^\circ C$ were slowly warmed to room temperature. After 12 h, the resulting yellow suspension was cooled to $0^\circ C$ and treated dropwise with degassed H_2O (1.0 ml). The solvent was then removed under reduced pressure and the residue was dried in vacuo. Extraction into *n*-hexane (2×30 ml) followed by concentration and cooling to $-78^\circ C$ afforded colourless crystals of **11** and **12**.

The data for **11** follow. Yield 0.61 g (70%). IR (Nujol mull, ν cm^{-1}): 1778(s), 1248(s), 1084(m), 1028(m), 947(m), 908(m), 837(vs), 760(m), 726(m), 635(w), 450(s). 1H NMR (δ ppm, in benzene- d_6): 4.85(t, 2H, $^3J_{H-H} = 2.58$ Hz, $H_4C_5SiMe_3$), 4.63(t, 2H, $^3J_{H-H} = 2.22$ Hz, $H_4C_5SiMe_3$), 1.97(s, 15H, C_5Me_5), 0.28(s, 9H, $Me_3SiC_5H_4$), -0.23 (t, 1H, $^2J_{H-H} = 11.35$ Hz, Ta-H), -1.69 (d, 2H, $^2J_{H-H} = 11.35$ Hz, Ta-H). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene- d_6): 102.54(s, C_5Me_5), 98.01(s, C_1 , $C_5H_4SiMe_3$), 92.9(s, $C_{3,4}$, $C_5H_4SiMe_3$), 92.8(s, $C_{2,5}$, $C_5H_4SiMe_3$), 12.77(s, Me_5C_5), 0.63(s, $Me_3SiC_5H_4$). Anal. Found: C, 47.46; H, 6.90. $C_{18}H_{31}SiTa$. Calc.: C, 47.36; H, 6.85%.

The data for **12** follow. Yield 0.62 g (70%). IR (Nujol mull, ν cm^{-1}): 1781(s), 1246(s), 1176(m), 1075(w), 1029(m), 904(m), 837(vs), 759(m), 727(m), 632(m), 447(vs). 1H NMR (δ ppm, in benzene- d_6): 4.21(m, 2H, $H_3C_5(SiMe_3)_2$), 4.14(m, 1H, $H_3C_5(SiMe_3)_2$), 1.98(s, 15H, C_5Me_5), 0.34(s, 18H, $(Me_3Si)_2C_5H_3$), -0.68 (t, 1H, $^2J_{H-H} = 9.9$ Hz, Ta-H), -2.03 (d, 2H, $^2J_{H-H} = 9.9$ Hz, Ta-H). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene- d_6): 103.62(s, $C_{1,3}$, $C_5H_3(SiMe_3)_2$), 101.55(s, C_5Me_5), 97.40(s, $C_{4,5}$, $C_5H_3(SiMe_3)_2$), 89.24(s, C_2 , $C_5H_3(SiMe_3)_2$), 12.56(s, Me_5C_5), 0.54(s, $(Me_3Si)_2C_5H_3$). Anal. Found: C, 47.80; H, 7.50. $C_{21}H_{39}Si_2Ta$. Calc.: C, 47.71; H, 7.44%.

3.7. Synthesis of $TaCp^*Cp''H(CO)$, **13**

A Schlenk tube containing a solution of **12** (0.50 g, 0.94 mmol) in toluene (20 ml) was sealed under 1 atm of CO. The mixture was stirred at $120^\circ C$ for 72 h to give a purple solution which was filtered and dried in vacuo. Extraction of the residue into *n*-hexane (2×5 ml) gave a purple solution which was filtered and cooled to $-40^\circ C$ to give purple crystals of **13**. Yield 0.40 g (70%).

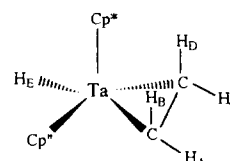
The data for **13** follow. IR (Nujol mull, ν cm^{-1}): 3730(w), 2955(vs), 2905(vs), 1880(vs), 1777(m),

1404(m), 1378(vs), 1247(vs), 1183(m), 1082(vs), 1029(m), 976(s), 920(s), 836(vs), 753(s), 689(m), 633(m), 496(w), 463(w), 372(w). 1H NMR (δ ppm, in benzene- d_6): 4.01m, 3.95m, 3.90m(3H, $H_3C_5(SiMe_3)_2$), 1.85(s, 15H, C_5Me_5), 0.29(s, 9H, $(Me_3Si)_2C_5H_3$), 0.25(s, 9H, $(Me_3Si)_2C_5H_3$), -6.20 (s, 1H, Ta-H). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene- d_6): 268.63(s, CO), 107.4s, 86.93s($C_{1,3}$, $C_5H_3(SiMe_3)_2$), 97.73s, 95.95s, 87.87s($C_{2,4,5}$, $C_5H_3(SiMe_3)_2$), 98.16(s, C_5Me_5), 12.33(s, Me_5C_5), 0.92s, 0.67s($(Me_3Si)_2C_5H_3$). Anal. Found: C, 47.12; H, 6.59. $C_{22}H_{37}OSi_2Ta$. Calc.: C, 47.64; H, 6.72%.

3.8. Synthesis of $TaCp^*Cp''H(C_2H_4)$, **14**

In a manner analogous to **13**, a solution of $TaCp^*Cp''H_3$ (0.50 g, 0.94 mmol) in toluene (20 ml) was saturated with ethylene (1 atm). The mixture was stirred at $120^\circ C$ for 36 h to give a yellow solution. Volatiles were removed in vacuo and the residue was extracted into *n*-hexane (2×10 ml). The resulting yellow solution was filtered and cooled to $-40^\circ C$ to afford yellow microcrystals of **14**. Yield 0.45 g(86%).

The data for **14** follow. IR (Nujol mull, ν cm^{-1}): 1807(m), 1246(vs), 1204(m), 1126(s), 1088(s), 1027(m), 925(s), 836(vs), 755(s), 691(m), 634(s), 492(m), 376(m). 1H NMR (δ ppm, in benzene- d_6): 4.53dd, 4.01dd, 3.17dd(3H, $^3J_{H-H} = ^4J_{H-H} = 2.5$ Hz, $H_3C_6(SiMe_3)_2$), 1.65(s, 15H, C_5Me_5), 0.98(m, H_D , $^3J_{D-E} = 2.40$ Hz, H_4C_2), 0.85(m, H_C , $^2J_{C-D} = 11.30$ Hz, H_4C_2), 0.65(m, H_B , $^3J_{B-C} = 11.30$ Hz, $^3J_{B-D} = 7.10$ Hz, $^3J_{B-E} = 2.40$ Hz, H_4C_2), -0.67 (m, H_A , $^2J_{A-B} = 10.95$ Hz, $^3J_{A-C} = 5.90$ Hz, $^3J_{A-D} = 10.90$ Hz, H_3C_2), -3.38 (t, $^3J_{B-E} = ^3J_{D-E} = 2.40$ Hz, Ta- H_E). $^{13}C\{^1H\}$ NMR (δ ppm, in benzene- d_6): 109.3s, 99.71s($C_{1,3}$, $C_5H_3(SiMe_3)_2$), 107.23(s, C_5Me_5), 100.78s, 100.71s, 92.51s($C_{2,4,5}$, $C_5H_3(SiMe_3)_2$), 11.97(s, Me_5C_5), 10.99s, 9.77s(C_2H_4), 1.30s, 0.63s($(Me_3Si)_2C_5H_3$). Anal. Found: C, 48.98; H, 7.31. $C_{23}H_{41}Si_2Ta$. Calc.: C, 49.80; H, 7.45%.



3.9. Synthesis of $TaCp^*Cp''H(CNR)$, **15**

$TaCp^*Cp''H_3$ (0.50 g, 0.94 mmol) and 2,6- $Me_2C_6H_3NC$ (0.12 g, 0.94 mmol) were stirred in toluene (20 ml) at $120^\circ C$ for 3 days. The resulting dark-green solution was evaporated to dryness and the residue extracted into *n*-hexane (2×15 ml). The resulting solution was filtered, concentrated to ca. 10 ml and

cooled to -40°C overnight to give **15** as green microcrystalline solid. Yield 0.50 g (81%).

The data for **15** follow. IR (Nujol mull, ν cm^{-1}): 2357(w), 1860(m), 1783(vs), 1586(s), 1288(w), 1243(vs), 1188(s), 1085(s), 1027(m), 921(s), 837(vs), 761(s), 691(w), 630(s), 577(s), 499(s), 382(m). ^1H NMR (δ ppm, in benzene- d_6): 6.94m, 6.92m, 6.86m(3H, $\text{H}_3\text{C}_6\text{Me}_2\text{-NC}$), 4.26m, 4.19m, 4.03m(3H, $\text{H}_3\text{C}_5(\text{SiMe}_3)_2$), 2.75(s, 6H, $\text{Me}_2\text{C}_6\text{H}_3\text{-NC}$), 1.95(s, 15H, C_5Me_5), 0.35(s, 9H, $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$), 0.30(s, 9H, $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$), -4.45 (m, 1H, Ta-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ ppm, in benzene- d_6): 274.72(s, $\text{CN-C}_6\text{H}_3\text{Me}_2$), 137.30s, 134.19s, 128.92s, 125.52s (C_i , C_o , C_m , C_p , $\text{C}_6\text{H}_3\text{Me}_2\text{-NC}$), 106.83s, 92.16s($\text{C}_{1,3}$, $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$), 100.05s, 99.03s, 92.69s($\text{C}_{2,4,5}$, $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$), 99.90s, C_5Me_5), 21.54(s, $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$), 12.54(s, Me_5C_5), 1.07s, 0.86s($(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$). Anal. Found: C, 53.85; H, 6.94; N, 2.12. $\text{C}_{30}\text{H}_{46}\text{NSi}_2\text{Ta}$. Calc.: C, 54.78; H, 7.04; N, 2.13%.

3.10. X-ray data collection, structure determination and refinement for compounds **3** and **12**

Crystallographic and experimental details of X-ray crystal structure determination for compounds **3** and **12** are given in Table 5. Suitable crystals of **3** and **12** were sealed in Lindeman tubes under argon and mounted on

an Enraf-Nonius CAD-4 automatic four circle diffractometer with bisecting geometric and using a graphite-oriented monochromator, with Mo $\text{K}\alpha$ radiation ($\lambda_{\text{Mo K}\alpha} = 0.71073 \text{ \AA}$). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No extinction corrections were made. The structures were solved by a combination of direct methods and Fourier synthesis and refined (on F) by full matrix least squares calculations. Absorption correction was made using DIFABS methods [24].

All the non-hydrogen atoms were refined anisotropically. In the last cycle of refinement the hydrogen atoms were introduced from geometric calculation, refined for one cycle isotropically and then fixed, except for the hydride atoms and the hydrogen bonded to C(12), C(14) and C(15) in **12** that were found in the difference Fourier synthesis map, and then fixed.

Final values of $R = 0.040$ and $R_w = 0.064$ were obtained for **3** and $R = 0.022$ and $R_w = 0.033$ for **12**, with $R_w[\sum w \|F_o - |F_c|\|^2 / w \|F_o\|^2]^{1/2}$ and $w = 4F_o^2 / [\sigma |F_o|]^2$.

Anomalous dispersion corrections and atomic scattering factors were taken from *International Tables for X-Ray Crystallography* [25]. Calculations were performed with the SDP package [26], and the programs MULTAN [27] and DIRDIF [28] on a MicroVax II computer.

Table 5
Crystal and experimental data and structure refinement procedures for compounds **3** and **12**

	3	12
Formula	$\text{C}_{18}\text{H}_{28}\text{Cl}_2\text{Si}_1\text{Ta}$	$\text{C}_{21}\text{H}_{39}\text{Si}_2\text{Ta}$
Crystal habit	prismatic	prismatic
Colour	green	yellow
Crystal size (mm^3)	$0.40 \times 0.22 \times 0.30$	$0.2 \times 0.20 \times 0.3$
Symmetry	orthorhombic $P2_12_12_1$	triclinic $P\bar{1}$
Unit cell determination	least squares fit from 25 reflections	
Unit cell dimensions:		
a, b, c (\AA)	11.775(5), 12.821(1), 13.037(7)	7.384(4), 10.861(2), 16.731(3)
α, β, γ (deg)		75.94(2), 84.75(3), 72.57(4)
V (\AA^3)	1968.1(6)	1241.6(9)
Z	4	2
D_{cal} (g cm^{-3})	1.756	1.414
Mw	524.36	528.65
$F(000)$	1012	532
μ (cm^{-1})	58.49	44.71
Scan mode	$\omega-2\theta$ scans; $\theta_{\text{max}} = 30^{\circ}$	$\omega-2\theta$ scans; $\theta_{\text{max}} = 26^{\circ}$
N° reflections:		
measured	4675	5045
independent observed	4088 $I > 2\sigma(I)$ criterion	4594 $I > 2\sigma(I)$ criterion
Range of hkl	$h - 15$ to 15 ; $k 0$ to 16 ; $l 0$ to 16	$h - 9$ to 9 ; $k - 13$ to 13 ; $l 0$ to 20
Standard reflections	2 reflections every 120 min, no variation	
R	0.040	0.022
R_w	0.064	0.033
Max. peak in final diff. map (e \AA^{-3})	1.290	1.041
Min. peak in final diff. map (e \AA^{-3})	-1.143	-0.687
Goodness of fit indicator	2.549	1.3665
Largest parameter shift/error	0.03	0.03

4. Supplementary material available

Tables of positional parameters of hydrogen atoms (Table S1-3, 1 page; Table S1-12, 2 pages), general displacement parameter expressions (Table S2-3, 1 page; Table S2-12, 1 page), complete bond distances and angles (Table S3-3, 3 pages; Table S3-12, 9 pages) and structure factors (Table S4-3, 21 pages; Table S4-12, 23 pages) for complexes **3** and **12** are available. Ordering information is given on any current masthead page.

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