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SYNTHESIS, PROPERTIES AND CRYSTAL STRUCTURE OF A DICYCLOPENTADIENYL TANTALUM CYCLOOCTATETRAENE COMPLEX $Cp_2TaC_3H_7 \cdot \eta^2\text{-}C_8H_8$

F. VAN BOLHUIS

Laboratorium voor Chemische Fysica, Rijksuniversiteit Groningen, Nijenborgh 16,
9747 AG Groningen (The Netherlands)

A.H. KLAZINGA * and J.H. TEUBEN

Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16,
9747 AG Groningen (The Netherlands)

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Summary

Reactions of *endo* hydride olefin complexes $Cp_2M(H)L$ (M = Ta, Nb; L = C_3H_6, C_4H_8) with C_8H_8 give the tantalocene and niobocene alkyls $Cp_2MR \cdot C_8H_8$. In solution these complexes partly dissociate giving free cyclooctatetraene and only *endo* hydride olefin complexes. Temperature-dependent ^1H NMR measurements indicate that the C_8H_8 ligand is fluxional on the NMR time scale.

The crystal structure of $Cp_2TaC_3H_7 \cdot C_8H_8$ shows dihapto coordination of the cyclooctatetraene ligand and further reveals the coplanarity of the tantalum atom, the α- and β-carbon atoms of the propyl group and the two coordinated carbon atoms of the C_8H_8 group. In addition there is an unusual planar conformation of the carbon skeleton of the C_8H_8 group.

Introduction

Reactions of tantalocene and niobocene *endo* hydride olefin complexes with π-acceptor molecules (CO, R'NC) lead to the irreversible formation of alkyl species, in which the π-acceptor ligand is "end-on" coordinated [1—3]. The high thermal stability of the products results from a strong metal—ligand interaction.

On the other hand, the formation of $Cp_2NbC_2H_5(C_2H_4)$, with "side-on" coor-

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* Present address: Koninklijke/Shell-Laboratorium, Amsterdam, Badhuisweg 3, Postbus 3003, 1003 AA Amsterdam.

dinated ethylene [4], from $Cp_2Nb(H)C_2H_4$ and C_2H_4, is probably reversible [5]. Depending on the bonding of the unsaturated substrate, the alkyl adducts show substantial differences in behaviour.

For studying the reactions of olefins with hydride olefin complexes, we selected the cyclic polyolefin cyclooctatetraene (C_8H_8), mainly because of the relatively low-lying antibonding π-orbitals in this ligand and its various coordination possibilities. In the case of the coordination of cyclooctatetraene to Cp_2TaR, η^2-coordination is of special interest, because the C_8H_8 behaves as a two-electron donor ligand, giving the metal an 18-electron configuration. Only for $CpMn(CO)_2C_8H_8$ has the dihapto coordination been unequivocally established by X-ray analysis [6]. Preliminary studies on this complex have shown a high lability of the η^2-C_8H_8 ligand, which is readily displaced by phosphines. On the basis of IR data a dihapto coordination of C_8H_8 has also been proposed for the paramagnetic compound $Cp_2NbC_8H_8$, prepared from $C_8H_8NbCl_2 \cdot THF$ and CpNa [7].

In this paper we describe the formation and properties of cyclooctatetraene adducts of Cp_2MR ($M = Ta$, $R = C_3H_7$; $M = Nb$, $R = C_4H_9$) and the molecular structure of the tantalum compound.

Results

Reaction of *endo* $Cp_2Ta(H)C_3H_6$ with an equivalent amount of C_8H_8 in toluene gives $Cp_2TaC_3H_7 \cdot C_8H_8$ in good yield. An analytically pure product is obtained by crystallization from toluene/pentane. The elemental analyses are consistent with the formula $Cp_2TaC_3H_7 \cdot C_8H_8$. The monomeric, dark red crystalline compound is slightly air-sensitive and only moderately soluble in toluene and halogenated solvents.

The IR spectrum of $Cp_2TaC_3H_7 \cdot C_8H_8$ (Figure 1) is closely similar to that of $Cp_2NbC_8H_8$. The absorptions at 1515 and 1595 cm^{-1}, are assigned to the free double bonds of the C_8H_8 ring, and the weak absorption at 1470 cm^{-1} is attributed to the coordinated double bond.

The ^1H NMR spectrum of $Cp_2TaC_3H_7 \cdot C_8H_8$ (Table 1) shows two resonances (at $\delta = 4.55$ and 4.44 ppm) due to the η^5-C_5H_5 groups. At 35°C a broad singlet due to the eight C_8H_8 protons is found at δ 4.88—5.35 ppm. In a rigid confor-

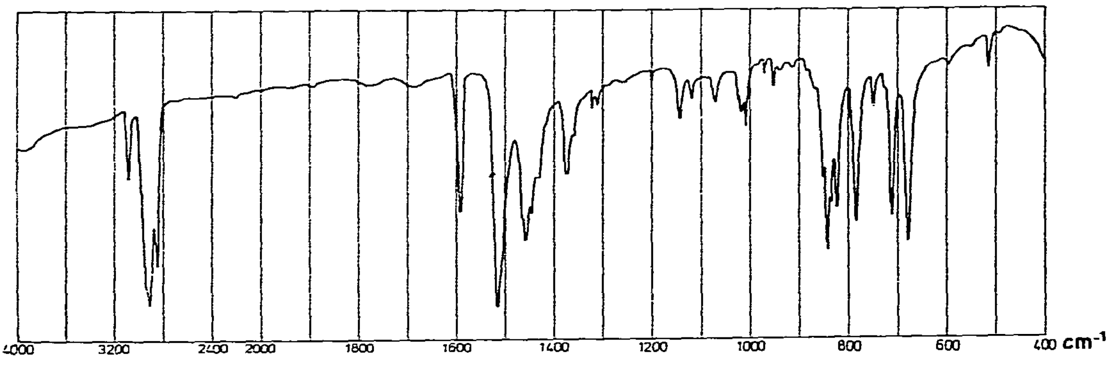

Fig. 1. IR spectrum of $Cp_2TaC_3H_7 \cdot C_8H_8$.

TABLE 1

^{1}H NMR DATA FOR $Cp_2MR.C_8H_8$ [a]

Compound		δCp	δR	δC_8H_8
M	R			
Ta	C_3H_7	4.55, 4.44	0.6—1.5	4.88—5.35
Nb	C_4H_9	4.79, 4.45	0.5—1.9	4.70—5.05

[a] C_6D_6 solution, 35°C, internal standard TMS.

mation however, the protons of the two coordinated carbon atoms are expected to be at higher field, c.f. cyclooctatetraene oxide [8]. The rather broad singlet from the C_8H_8 protons indicates that in contrast with e.g. $CpMn(CO)_2 \cdot C_8H_8$, the ring protons are almost equivalent on the NMR time scale, indicating dynamic behaviour of the C_8H_8 ligand.

The temperature-dependent ^{1}H NMR spectrum of $Cp_2TaC_3H_7 \cdot C_8H_8$ in CD_3COCD_3 shows some interesting features (Figure 2). At room temperature this spectrum consists of two singlets due to the non-equivalent Cp groups (5.12 and 5.62 ppm), a singlet of the C_8H_8 protons at 4.95 ppm and a signal due to the propyl group at higher field (0.8—1.7 ppm). At lower temperatures (—10°C) a broadening of the C_8H_8 resonance is observed. At about —60°C a remarkable change has taken place. The original C_8H_8 signal has completely vanished; instead three new resonances are found at about 6.2 (m, 2 H), 5.35 (m, 4 H) and 2.95 (m, 2 H) ppm. At this temperature the spectrum is very similar to those reported for $CpMn(CO)_2 \cdot C_8H_8$ and cyclooctatetraene oxide [8]. The spectrum does not change on further cooling to —90°C. These observations make it clear that a dihapto coordination of the C_8H_8 ligand is favoured at low temperatures.

The dynamic behaviour of the C_8H_8 ligand in $Cp_2TaC_3H_7 \cdot C_8H_8$ is also illustrated by the ^{13}C NMR spectrum. At room temperature only one signal for the eight-membered ring is found at δ 105.53 ppm (J 178 Hz). In addition, there are one Cp resonance (δ 100.29 ppm, J 176 Hz) and three resonances from the n-propyl group (a quartet at δ 22.50 ppm (J 125 Hz) and two triplets at δ 29.07 ppm (J 123 Hz) and δ 17.74 ppm (J 121 Hz)).

Pure $Cp_2TaC_3H_7 \cdot C_8H_8$ decomposes above 171°C (m.p. 161°C). In solution, however, $Cp_2TaC_3H_7 \cdot C_8H_8$ partly dissociates above 70°C, giving free cyclooctatetraene and *endo* $Cp_2Ta(H)C_3H_6$ only. The exclusive formation of *endo* $Cp_2Ta(H)C_3H_6$ from $Cp_2Ta\text{n-}C_3H_7 \cdot \eta^2\text{-}C_8H_8$ strongly supports the view that *endo* hydride olefin complexes are formed from Cp_2TaCl_2 and n-alkyl Grignard reagents [9]. Furthermore, this behaviour indicates that the ligand C_8H_8 is "side-on" coordinated in $Cp_2TaC_3H_7(C_8H_8)$, comparable with the ethylene molecule in $Cp_2NbC_2H_5(C_2H_4)$ [4].

The niobium complex $Cp_2Nb(C_4H_9)C_8H_8$ is very similar to the tantalum compound. It was prepared from *endo* $Cp_2Nb(H)C_4H_8$ and after crystallization was identified by IR spectroscopy (free double bonds at 1515 and 1595 cm^{-1}; coordinated double bond at 1480 cm^{-1}), and ^{1}H NMR (Table 1) spectra.

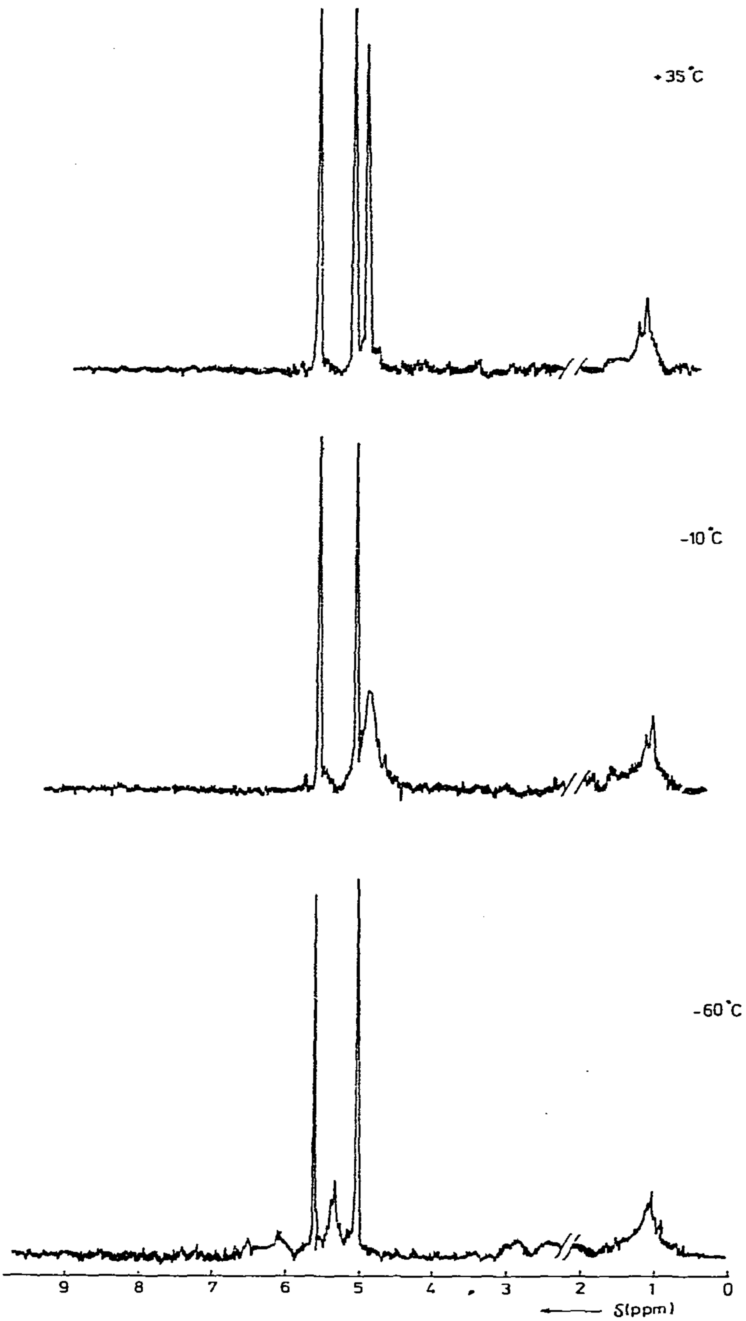

Fig. 2. ^{1}H-NMR spectrum of $Cp_2TaC_3H_7 \cdot C_8H_8$ at various temperatures (resonances due to the solvent, acetone-d_6, are omitted).

In order to establish the exact coordination of the cyclooctatetraene ligand and to check the arrangement of the ligands around the metal atom the structure of $Cp_2TaC_3H_7 \cdot C_8H_8$ was studied by X-ray diffraction.

Crystal structure of $Cp_2TaC_3H_7 \cdot C_8H_8$

The observed molecular structure of $Cp_2TaC_3H_7 \cdot C_8H_8$ is shown in Figure 3. The bond lengths and angles are given in Table 2; best least squares planes and dihedral angles are given in Table 2. From Figure 3 and Table 2 it can be inferred that both cyclopentadienyl rings are π-bonded to the metal; they are approximately staggered. The distances of the tantalum atom to the centroids RC(III) and RC(IV) of the two rings are 2.06 and 2.04 Å, respectively, whereas the average distances from tantalum to the carbon atoms of the two rings are 2.38 and 2.35 Å, respectively (Table 3). The rings are planar and the dihedral angle between the two ring planes is 50.1°. Mean C—C distances of 1.40 and 1.39 Å in the C_5H_5 rings are normal values for this type of compound.

The crystal structure unequivocally shows the dihapto coordination of the cyclooctatetraene ligand.

The Ta—C(11) and Ta—C(12) bond lengths of 2.32 and 2.33(2) Å, respectively, are comparable with the Nb—C (olefin) distances in $Cp_2NbC_2H_5(C_2H_4)$ [4]. A remarkably large value of 1.45(2) Å is found for the C(11)—C(12) distance of the coordinated double bond of the C_8H_8 ring. This distance is considerably longer than that in the complexes $CpMn(CO)_2C_8H_8$ (1.398(2) Å) [6] and $(C_8H_8CuCl)_n$ (1.392(11) Å) [10], which also have a η^2-C_8H_8 ligand, and also exceeds the ethylene C—C distance of 1.406(13) Å in $Cp_2NbC_2H_5(C_2H_4)$.

Apart from the extraordinarily long C—C distance of the coordinated double bond, a regular alternation of longer and shorter C—C distances is found in the eight-membered ring. Despite the dihapto coordination of the cyclooctatetraene ligand and the alternating double bonds, the carbon skeleton of this ligand is planar; within 0.02 Å all eight atoms lie in a plane (II) (Table 3). Further-

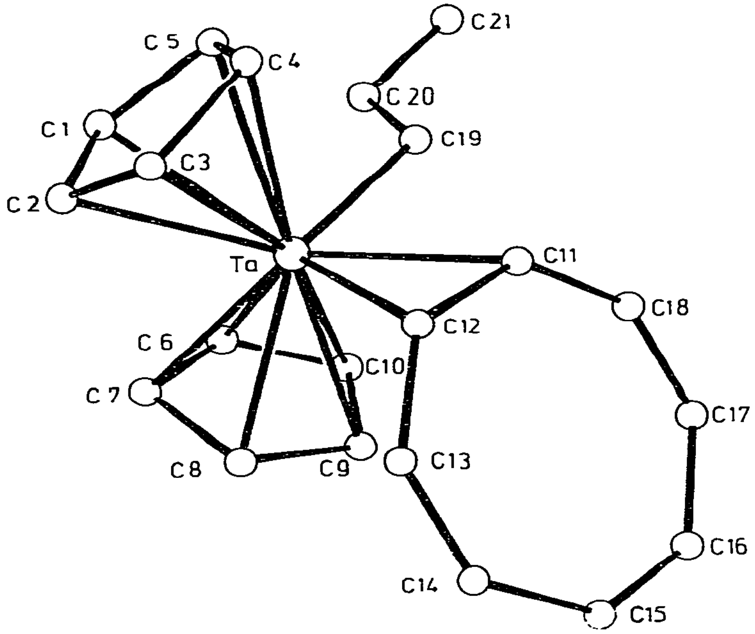

Fig. 3. Structure of $Cp_2TaC_3H_7 \cdot \eta^2$-$C_8H_8$.

TABLE 2

BOND LENGTHS [a] AND ANGLES

	Å		Degrees
Ta—C(11)	2.32(2)	C(11)—Ta—C(12)	36(1)
Ta—C(12)	2.33(2)	Ta—C(11)—C(12)	72(1)
Ta—C(19)	2.29(1)	Ta—C(12)—C(11)	71(1)
		Ta—C(11)—C(18)	120(1)
Ta—C(1)	2.37(2)	Ta—C(12)—C(13)	121(1)
Ta—C(2)	2.36(1)	C(11)—Ta—C(19)	77(1)
Ta—C(3)	2.41(2)	Ta—C(19)—C(20)	123(1)
Ta—C(4)	2.39(2)	C(19)—C(20)—C(21)	115(1)
Ta—C(5)	2.39(2)		
		C(1)—C(2)—C(3)	108(2)
Ta—C(6)	2.35(2)	C(2)—C(3)—C(4)	106(2)
Ta—C(7)	2.34(2)	C(3)—C(4)—C(5)	111(2)
Ta—C(8)	2.31(2)	C(4)—C(5)—C(1)	108(2)
Ta—C(9)	2.37(2)	C(5)—C(1)—C(2)	107(2)
Ta—C(10)	2.37(2)		
		C(6)—C(7)—C(8)	105(2)
C(1)—C(2)	1.39(3)	C(7)—C(8)—C(9)	108(2)
C(2)—C(3)	1.42(3)	C(8)—C(9)—C(10)	111(2)
C(3)—C(4)	1.41(2)	C(9)—C(10)—C(6)	106(2)
C(4)—C(5)	1.34(3)	C(10)—C(6)—C(7)	111(2)
C(5)—C(1)	1.45(3)		
		C(11)—C(12)—C(13)	134(1)
C(6)—C(7)	1.39(3)	C(12)—C(13)—C(14)	136(2)
C(7)—C(8)	1.45(3)	C(13)—C(14)—C(15)	136(2)
C(8)—C(9)	1.33(3)	C(14)—C(15)—C(16)	135(2)
C(9)—C(10)	1.39(3)	C(15)—C(16)—C(17)	133(2)
C(10)—C(6)	1.37(3)	C(16)—C(17)—C(18)	137(2)
		C(17)—C(18)—C(11)	136(2)
C(11)—C(12)	1.45(2)	C(18)—C(11)—C(12)	134(2)
C(12)—C(13)	1.43(2)		
C(13)—C(14)	1.36(3)		
C(14)—C(15)	1.46(3)		
C(15)—C(16)	1.40(3)		
C(16)—C(17)	1.46(3)		
C(17)—C(18)	1.36(3)		
C(18)—C(11)	1.43(2)		
C(19)—C(20)	1.50(3)		
C(20)—C(21)	1.53(3)		
Ta—RC(III)	2.06		
Ta—RC(IV)	2.04		

[a] Standard deviations (in parentheses) are in units of the last decimal place; RC(III) = C(1)—C(5) ring centroid, RC(IV) = C(6)—C(10) ring centroid.

more, the structure confirms the presence of a n-propyl group. The Ta—C (n-propyl) bond length is 2.29(1) Å, which lies in the range observed for other Ta—C (sp^3) distances [11,12]. The tantalum atom, the carbon atoms C(11) and C(12) of the C_8H_8 ligand and the α-carbon atom C(19) of the n-propyl group are almost coplanar (plane I). As in $Cp_2NbC_2H_5(C_2H_4)$ the β-carbon atom, C(20), of the alkyl group also lies in this plane. The dihedral angle between this plane and the C_8H_8 ring is 62.1°. There are no intermolecular C—C contacts less than 3.60 Å in the crystal structure.

Discussion

The crystal structure of $Cp_2TaC_3H_7 \cdot C_8H_8$ (Figure 3) clearly shows the dihapto coordination of the C_8H_8 group and therefore the bonding in this molecule is comparable with that in $Cp_2NbC_2H_5(C_2H_4)$. In both structures the metal atom, the two carbon atoms of the coordinated double bond and the α- and β-carbon atoms of the alkyl group lie in one plane, corresponding with the yz-plane in the Lauher and Hoffman model for bent Cp_2M systems [13]. For hydride olefin or related complexes a maximum overlap between the metal $1a_1$ and olefin π^* orbitals is expected if the olefin plane is perpendicular to this yz-plane. However, back donation of electrons from the metal into the olefin π^* orbitals leads to a non-planar olefin with the substituents on the double bond bent away from the metal. Particularly for strong electron-withdrawing substituents (e.g. CN, F) a large distortion of the planar geometry is observed. At the same time the double bond becomes weaker and, therefore, longer.

Previous results [1,2] have shown that Cp_2TaR (R = alkyl) is an excellent π-donor species and so strong back donation into the π^* orbitals of C_8H_8 is also expected. The large C—C distance of the coordinated double bond and the large deviation of the dihedral angle between the yz-plane and the C_8-plane, from 90° support this idea, although steric hindrance between the C_8H_8 ligand and one of the C_5H_5 ligands will also contribute to the latter deviation.

Another important feature of this structure is the presence of a planar carbon skeleton of the C_8H_8 ligand. Free cyclooctatetraene exists in a non-planar tub form, with a deviation (α) (Fig. 4) from planar geometry of about 43° [14]. Upon coordination to $CpMn(CO)_2$ the tub conformation still persists ($\alpha \approx 35°$), but it is less pronounced than in free C_8H_8. In $Cp_2TaC_3H_7 \cdot C_8H_8$ the eight-membered ring is virtually planar ($\alpha \approx 0°$).

On going from C_8H_8 via $CpMn(CO)_2 \cdot C_8H_8$ to $Cp_2TaC_3H_7 \cdot C_8H_8$ the stronger back donation induces a higher electron density on the C_8H_8 ligand, which probably causes the planarity of the eight-membered ring. Another possible explanation for this unusual conformation of the cyclooctatetraene ligand may lie in the crystal packing forces.

The cyclooctatetraene adducts $Cp_2MR \cdot L$ are rather stable, they dissociate only in solution, and then only partially. No insertion of the olefin into the metal—alkyl bond is observed, in contrast to the reaction observed for complexes of lower, less sterically hindered olefins being studied at present.

Experimental

All experiments were performed under nitrogen. Solvents were distilled from benzophenoneketylsodium. The *endo* isomers of $Cp_2Ta(H)C_3H_6$ and $Cp_2Nb(H)$-

Fig. 4. C_8H_8 tub conformation.

TABLE 3

LEAST SQUARES PLANES [a]

Atoms	Plane	P	Q	R	S
a) Equations of the planes					
Ta, C(11), C(12), C(19)	I	0.2035	0.8384	0.5057	7.1347
C(11)—C(18)	II	−0.5830	0.2306	0.7791	6.4048
C(1)—C(5)	III	0.6219	0.6982	0.3547	8.2176
C(6)—C(10)	IV	−0.1934	0.8128	0.5495	4.6045
RC(III), Ta, RC(IV)	V	0.1360	−0.5437	0.8282	1.8525

Atom	Plane I	Atom	Plane II	Atom	Plane III	Atom	Plane IV	Atom	Plane V
b) Distances of some atoms from the respective planes (in Å)									
Ta	−0.058	C(11)	0.020	C(1)	0.004	C(6)	−0.006	C(1)	−0.800
C(11)	−0.080	C(12)	0.007	C(2)	−0.001	C(7)	−0.004	C(2)	0.587
C(12)	0.086	C(13)	−0.014	C(3)	−0.002	C(8)	0.014	C(3)	1.196
C(19)	0.053	C(14)	−0.017	C(4)	0.005	C(9)	−0.018	C(4)	0.103
C(20)	−0.009	C(15)	0.024	C(5)	−0.006	C(10)	0.014	C(5)	−1.086
C(21)	0.264	C(16)	0.012	Ta	−2.058	Ta	2.035	C(6)	−1.014
C(13)	−0.703	C(17)	−0.027					C(7)	0.239
C(14)	−1.885	C(18)	−0.005					C(8)	1.170
C(15)	−2.904							C(9)	0.490
C(16)	−3.077							C(10)	−0.884
C(17)	−2.305								
C(18)	−1.109								

c) Dihedral angles (deg.)

I $\wedge$ II	62.1	I $\wedge$ V	89.5
I $\wedge$ III	27.0	II $\wedge$ V	63.9
I $\wedge$ IV	23.1	III $\wedge$ IV	50.1

[a] The equations of the planes are $PI + QJ + RK = S$ in orthogonal Ångstrom space where P, Q and R are direction cosines, referred to orthogonal unit axes I, J and K with $I//a$, $J//b$ and $K//c^*$.

TABLE 4

CRYSTALLOGRAPHIC DATA AND DETAILS OF EXPERIMENTAL METHODS

Data	Experimental details
Monoclinic	Weissenberg photographs of zero and higher layer lines
Space group $P2_1/n$	
a = 9.57(0.7) Å	Least squares refinement based on $\sin^2\theta$ values of 15 reflections from counter data;
b = 15.19(1) Å	λ(Cu—K_α) = 1.5418 Å
c = 11.60(1) Å	
β = 97.05(15)°	
Z = 4	
D_{calc} = 1.82 g cm^{-3}	D_{exp} = 1.80 (floating method)
μ(Cu) = 123.4 cm^{-1}	Dimensions crystal: 0.25 × 0.50 × 0.15 mm^3
3564 intensities	Automatic Nonius CAD-4 diffractometer, Ni-filtered Cu radiation; ω-scan, $\sin\theta/\lambda \leqslant 0.636$ Å^{-1}.
	Reflections with I (net) $\leqslant 0$ were discarded.
3286 independent $\|F(hkl)\|$ values with $\|F\| > 3\sigma(\|F\|)$	Corrections for L.P. factors and absorption [15]

TABLE 5

FINAL PARAMETERS

a) Coordinates for the non-hydrogen atoms

Atom	*x/a*	*y/b*	*z/c*
Ta	0.2102(1)	0.3252(1)	0.4567(1)
C(1)	0.3971(19)	0.4225(12)	0.4312(16)
C(2)	0.4427(14)	0.3684(12)	0.5253(16)
C(3)	0.3619(18)	0.3887(12)	0.6167(16)
C(4)	0.2639(17)	0.4536(10)	0.5729(15)
C(5)	0.2825(20)	0.4755(10)	0.4639(16)
C(6)	0.2648(28)	0.2609(12)	0.2836(15)
C(7)	0.3569(21)	0.2264(13)	0.3742(22)
C(8)	0.2681(23)	0.1779(10)	0.4441(16)
C(9)	0.1363(21)	0.1828(10)	0.3927(17)
C(10)	0.1288(22)	0.2361(12)	0.2942(15)
C(11)	0.0064(15)	0.3159(10)	0.5462(14)
C(12)	0.1206(17)	0.2784(11)	0.6245(12)
C(13)	0.1496(18)	0.1916(10)	0.6700(15)
C(14)	0.8401(22)	0.1123(14)	0.6603(17)
C(15)	—0.0482(23)	0.0786(12)	0.6001(18)
C(16)	—0.1587(22)	0.1142(13)	0.5245(17)
C(17)	—0.1848(19)	0.2017(13)	0.4742(16)
C(18)	—0.1200(16)	0.2812(12)	0.4833(14)
C(19)	0.5429(16)	0.4093(10)	0.3377(13)
C(20)	0.8831(19)	0.4482(13)	0.2254(16)
C(21)	—0.0232(20)	0.5116(12)	0.1671(15)

b) Parameters U_{ij} (in 10^{-3} Å^2) of the temperature factor $\exp[-2\pi^2(h^2(a^*)^2U_{11} + \ldots 2ha^*kb^*U_{12} \ldots)]$ of the non-hydrogen atoms

Atom	U_{11}	U_{22}	U_{33}	2 U_{12}	2 U_{13}	2 U_{23}
Ta	42.9(3)	46.6(3)	49.5(4)	—1.8(3)	8.3(3)	—4.1(3)
C(1)	50(9)	65(11)	69(11)	—39(9)	17(9)	—13(9)
C(2)	15(6)	80(12)	71(12)	—14(7)	—5(7)	—12(10)
C(3)	58(10)	65(11)	55(11)	—11(9)	—16(8)	—19(9)
C(4)	50(9)	40(8)	61(10)	—7(7)	—1(8)	—21(7)
C(5)	72(12)	30(7)	65(11)	—9(8)	—4(9)	—10(8)
C(6)	142(21)	57(10)	33(9)	—21(12)	55(12)	—24(8)
C(7)	59(12)	59(11)	108(17)	18(9)	30(12)	—32(12)
C(8)	96(14)	28(7)	64(11)	15(9)	11(10)	—5(8)
C(9)	77(12)	35(8)	72(12)	—14(8)	43(10)	—32(8)
C(10)	86(14)	57(10)	44(9)	—13(9)	5(9)	—31(8)
C(11)	29(7)	56(9)	54(9)	—6(7)	20(6)	3(8)
C(12)	46(9)	61(10)	28(7)	1(7)	18(6)	8(7)
C(13)	53(10)	48(9)	53(9)	11(7)	22(8)	7(7)
C(14)	78(14)	71(12)	64(12)	25(11)	32(11)	17(10)
C(15)	77(14)	55(10)	69(13)	—11(10)	37(11)	—4(9)
C(16)	74(13)	61(11)	67(12)	—19(10)	38(10)	—17(9)
C(17)	50(10)	81(13)	50(10)	—6(9)	11(8)	—12(9)
C(18)	33(8)	65(10)	46(9)	—6(7)	14(7)	0(8)
C(19)	44(8)	50(8)	42(8)	24(7)	—3(7)	18(7)
C(20)	50(10)	75(12)	63(11)	—1(9)	15(9)	3(9)
C(21)	70(12)	62(11)	53(10)	13(9)	15(9)	16(8)

Standard deviations (in units of the last decimal place) are given in parentheses.

C_4H_8 were prepared according to published procedures [9,3]. IR spectra were recorded on a Jasco IRA-2 spectrophotometer with Nujol mulls between KBr discs. ^1H NMR spectra were run on a Jeol 60 HL instrument; the ^{13}C NMR spectrum of $Cp_2TaC_3H_7 \cdot C_8H_8$ was recorded on a Varian XL 100 instrument by drs. D.M. Kok. Elemental analyses were performed at the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga.

Preparation of $Cp_2TaC_3H_7 \cdot C_8H_8$

A solution of *endo* $Cp_2Ta(H)C_3H_6$ (540 mg, 1.52 mmol) and C_8H_8 (184 mg, 1.77 mmol) in 10 ml of toluene was stirred for 32 h at 60° C. The dark red mixture was evaporated and the residue washed with n-pentane. After drying in vacuo the product was isolated. Yield: 470 mg $Cp_2TaC_3H_7 \cdot C_8H_8$ (67%). The compound was purified by crystallization from toluene. After filtration of a saturated solution of $Cp_2TaC_3H_7 \cdot C_8H_8$ in 10 ml of toluene, 15 ml of pentane was slowly (3—4 days) distilled onto the dark red solution at room temperature. Dark red crystals were formed. The mother liquor was decanted and the crystals were washed with pentane, dried in vacuo, and sealed in ampoules. Single crystals satisfactory for an X-ray determination were obtained. Analysis. Found: C, 54.83; H, 5.49; Ta, 39.46. $C_{21}H_{25}Ta$ calcd.: C, 55.03; H, 5.50; Ta, 39.47%. Molecular weight (in benzene): 430 (calcd. 458).

The preparation of the cyclooctatetraene adduct of $Cp_2NbC_4H_9$ proceeds much more readily and under milder conditions ($t = 15$ h, $T = 25°$C).

A few suitable crystals were selected for the X-ray study. These crystals were sealed in thin-walled capillaries under nitrogen and mounted with vaseline. Crystallographic data and experimental details are listed in Table 4.

The positions of the tantalum and some of the carbon atoms were found by direct methods with the Multon program [16] of the X-ray 1976 system of crystallographic Programs [17], and were used to solve the structure by the heavy-atom method. All non-hydrogen atoms were readily found and their positional and thermal parameters were refined by anisotropic least-squares techniques. The quantity $Q = \Sigma w(H)[F_0(H) - F_c(H)]^2$ with $w(H) = 1/\sigma^2[|F|]$ was minimized. Scattering factors were taken from Cromer and Mann [18].

The refinement index $R \equiv [\Sigma(\Delta F)^2/\Sigma(F_0)^2]^{1/2}$ decreased to 0.099 for 3286 reflections. The final parameters are listed in Table 5. A list of observed and calculated structure factors is available on request.

The final difference map shows a few maxima ($\sim 1.7\ e\text{Å}^{-3}$) between Ta and the Cp rings, which are thought to be due to incomplete correction for absorption [19] since a refinement with $|F|$ values which are not corrected for absorption gives still higher maxima.

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