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Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Discovery of an "Opened-Envelope" Conformation for the TaC_4 Ring in Tantalacyclopentane Complexes. Crystal and Molecular Structures of $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ and $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$

MELVYN ROWEN CHURCHILL* and WILEY J. YOUNGS

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Structural studies on two tantalacyclopentane complexes have been carried out by using the technique of single-crystal X-ray diffraction. The species $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ crystallizes in the centrosymmetric orthorhombic space group *Pnam*; cell parameters are $a = 10.074$ (2) Å, $b = 11.283$ (2) Å, $c = 13.524$ (2) Å, and $Z = 4$. The structure was solved via Patterson and difference-Fourier methods; least-squares refinement of parameters for all nonhydrogen atoms led to convergence with $R_F = 5.7\%$ and $R_{wF} = 3.9\%$ for all 1850 independent reflections ($4° < 2\theta < 55°$; Mo Kα radiation). The molecule contains an unsubstituted tantalacyclopentane (TaC_4H_8) ring and is bisected by a crystallographic mirror plane. The species $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9.205$ (1) Å, $b = 13.623$ (2) Å, $c = 14.144$ (3) Å, $\beta = 96.63$ (1)°, and $Z = 4$. This structure has been refined to $R_F = 4.4\%$ and $R_{wF} = 3.4\%$ for all 3116 reflections ($4° < 2\theta < 50°$; Mo Kα). All atoms (including hydrogen atoms) were located and refined. The TaC_7H_{12} system defines a tantalabicyclo[3.3.0]octane framework, based upon fused 5-membered rings. The TaC_4H_8 ring in $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ and the $\overline{\text{Ta–CH}_2\text{–CH–CH–CH}_2}$ ring in $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$ each define a saturated system based upon a TaC_4 ring. The TaC_4 rings in the two complexes have an unusual "opened-envelope" conformation (rather than a puckered conformation) in which there are angles of 116.3 and 122.6° between the C(α)–Ta–C(α') plane and the *planar* C(α)–C(β)–C(β')–C(α') system.

Introduction

There have been few crystallographic studies on metallacycloalkane complexes and fewer still on metallacyclo*pentane* complexes. Furthermore, the reported studies involve only the group 8 transition metals. Thus, available structural data provide information on an iridiacyclopentane and a 3,4-dimethyleneiridiacyclopentane complex,[1] a platinacyclopentane complex,[2] a variety of platinacyclobutane derivatives,[3] and a ferracyclobutane (ferretane) complex.[4]

Recently Schrock and co-workers[5,6] have synthesized a variety of tantalacyclopentane derivatives including $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ (prepared as in eq 1) and $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$ (prepared as in eq 2).

$$\begin{aligned}&Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)Cl_3 \xrightarrow{+{}^1/_2ZnEt_2} \\ &\quad Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)(C_2H_5)Cl_2 \xrightarrow{-C(CH_3)_4} \\ &\quad\quad Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2C{=}CH_2)Cl_2 \xrightarrow{+C_2H_4} \\ &\quad\quad\quad Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2 \quad (1)\end{aligned}$$

$$\begin{aligned}&Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}MeCH{=}CH_2)Cl_2 + \\ &\quad CH_2{=}CH(CH_2)_3CH{=}CH_2 \xrightarrow{-MeCH{=}CH_2} \\ &\quad\quad\quad Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2 \quad (2)\end{aligned}$$

We have now completed structural studies on these two tantalacyclopentane derivatives, and our results are reported below. Preliminary results have appeared previously.[7]

Experimental Section

Collection and Treatment of the X-ray Diffraction Data. Crystalline samples of the complexes under study were provided by Professor R. R. Schrock of Massachusetts Institute of Technology. A Syntex P2$_1$ automated four-circle diffractometer was used to collect X-ray diffraction data. The structures were solved with the use of our in-house Syntex XTL system which consists of (i) a Data General Nova 1200 computer (with 24K of 16-bit work memory and with a parallel floating-point processor for 32- or 64-bit arithmetic), (ii) a Diablo moving-head disk unit with a storage capacity of 1.2 million 16-bit words, (iii) a Versatec electrostatic printer/plotter, and (iv) a locally modified version of the XTL conversational crystallographic program package.

1. $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$. A crystal of dimensions 0.15 × 0.15 × 0.22 mm was removed from the provided vial in a modified KSE inert-atmosphere (Ar) drybox and was carefully inserted into a thin-walled glass capillary, which was flame-sealed, set into an aluminum pin with beeswax, and mounted into a eucentric goniometer. Determinations of the crystal class (orthorhombic), the orientation matrix, and accurate unit cell dimensions were carried out as described previously.[8] Both θ–2θ and ω scans were monitored graphically for selected reflections along (and adjacent to) each of the principal reciprocal axes. A rapid survey of data with $20° < 2\theta < 30°$, collected at a scan rate of 29.3°/min, revealed the systematic absences $h0l$ for $h = 2n + 1$ and $0kl$ for $k + l = 2n + 1$; possible space groups are the noncentrosymmetric orthorhombic space group $Pna2_1$ (C_{2v}^9; No. 33) or the centrosymmetric space group *Pnam* (a nonstandard setting of $Pnma\text{-}D_{2h}^{16}$; No. 62).

Collection of intensity data, via the coupled θ–2θ scan technique, was carried out as described before;[8] details appear in Table I. In view of the possibility of the noncentrosymmetric space group $Pna2_1$ (which has a polar c axis), we collected intensity data for the forms hkl and $hk\bar{l}$. Intensity statistics, while rather ambiguous, marginally favored the noncentrosymmetric possibility (see Table II). The structure was, however, successfully solved by using the centrosymmetric space group *Pnam*.

Data were corrected for absorption by an empirical method, based on a series of ψ scans (see Table I), and were converted to unscaled $|F_o|$ values following correction for Lorentz and polarization effects. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$.

2. $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$. A crystal of dimensions 0.23 × 0.28 × 0.31 mm was mounted, centered, and oriented as described for the previous complex. The C_{2h} Laue symmetry and systematic absences ($h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$) indicate uniquely the centrosymmetric monoclinic space group $P2_1/n$ (a nonstandard

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Table I. Details of Data Collection for $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ and $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$

	$Ta(\eta^5\text{-}C_5Me_5)\cdot(C_4H_8)Cl_2$	$Ta(\eta^5\text{-}C_5Me_5)\cdot(C_7H_{12})Cl_2$
	(A) Crystal Parameters	
cryst system	orthorhombic	monoclinic
space group	*Pnam*	$P2_1/n$
a, Å	10.0736 (18)[a]	9.2051 (13)[a]
b, Å	11.2834 (20)	13.6233 (24)
c, Å	13.5239 (24)	14.1436 (26)
β, deg		96.631 (13)
V, $Å^3$	1537.2 (5)	1761.8 (5)
Z	4	4
mol wt	443.19	483.25
ρ(calcd), g cm^{-3}	1.91	1.82
temp, °C	24	25
	(B) Collection of Intensity Data	
diffractometer	syntex $P2_1$	
radiation	Mo Kα ($\bar{\lambda}$ = 0.710 730 Å)	
monochromator	highly oriented graphite; equatorial geometry; $2\theta_{mono} = 12.2°$	
reflctns measd	$+h, +k, \pm l$ (two forms)	$\pm h, +k, +l$ (one form)
2θ range, deg	4.0–55.0	4.0–50.0
scan type	coupled θ(crystal)–2θ(counter)	
scan speed, deg/min in 2θ	4.0	3.0
scan range, deg	$2\theta(Mo\ K\alpha_1) - 0.9 \rightarrow 2\theta(Mo\ K\alpha_2) + 0.9$	$2\theta(Mo\ K\alpha_1) - 1.0 \rightarrow 2\theta(Mo\ K\alpha_2) + 0.9$
bgd measmt	stationary crystal–stationary counter at beginning and end of 2θ scan; each for one-fourth of total scan time	
stds	3 every 97 reflections: no significant decay	
reflctns collected	3654 total, yielding 1850 independent	3585 total, yielding 3116 independent
data averaging	*R*(*I*) = 2.76% for 1701 pairs of averaged reflections	*R*(*I*) = 2.52% for 295 pairs of averaged reflections
abs coeff, cm^{-1}	78.6	68.6
reflctns used for empirical abs cor: *hkl*, 2θ, $T_{max}:T_{min}$	$\bar{2}23$, 14.11°, 1.164:1 $\bar{2}25$, 18.59°, 1.149:1 $\bar{3}35$, 22.25°, 1.134:1 $\bar{3}37$, 26.81°, 1.179:1 $\bar{4}46$, 28.45°, 1.193:1 $\bar{5}58$, 36.81°, 1.189:1	$2\bar{2}4$, 16.56°, 1.422:1 $3\bar{3}5$, 22.77°, 1.425:1 $4\bar{3}6$, 28.00°, 1.381:1

[a] Based on 24 reflections with 2θ = 20–30°.

Table II. Intensity Statistics for $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$

		theoret	
	obsd	centric	acentric
$\langle\lvert E\rvert\rangle$	0.831	0.798	0.886
$\langle\lvert E^2\rvert\rangle$	1.000	1.000	1.000
$\langle\lvert E^2 - 1\rvert\rangle$	0.871	0.968	0.736
$\lvert E\rvert > 1.0$	37.24%	31.73%	36.78%
$\lvert E\rvert > 2.0$	1.95%	4.55%	1.89%
$\lvert E\rvert > 3.0$	0.00%	0.27%	0.01%

setting of $P2_1/c\text{-}C_{2h}^5$; No. 14). Experimental details appear in Table I.

Solution and Refinement of the Structures. Scattering factors for neutral tantalum, carbon, and hydrogen were used in their analytical forms;[9a] the contributions of all nonhydrogen atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[9b] The function minimized during the least-squares process was $\sum w(|F_o| - |F_c|)^2$; the weights used (w) are the stochastic $\sigma(|F_o|)$ values modified by an "ignorance factor" (p) as shown in eq 3.

$$w = [[\sigma(|F_o|)]^2 + (p|F_o|)^2]^{-1} \tag{3}$$

1. $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$. Data were converted to an approximately absolute scale by means of a Wilson plot. The positions of the tantalum and chlorine atoms were determined from a three-dimensional Patterson synthesis. These results suggested that the molecule belonged to the centrosymmetric space group *Pnam* (rather than $Pna2_1$) with a mirror plane relating the two chloride atoms and bisecting the tantalum atom. All subsequent calculations were therefore performed by using the space group *Pnam*.

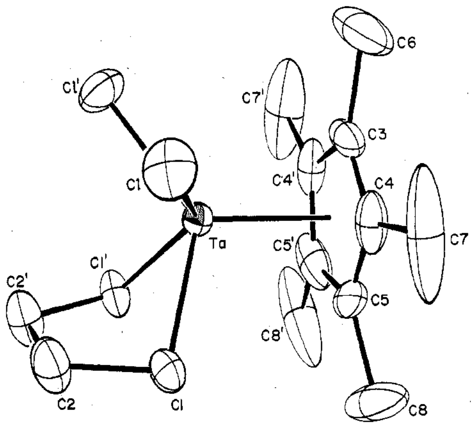

Figure 1. Labeling diagram for $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$ (ORTEP-II; 30% ellipsoids).

Full-matrix least-squares refinement of positional and isotropic thermal parameters for the heavy atoms (Ta and Cl) led to R_F = 11.7% and R_{wF} = 17.5%. A difference-Fourier synthesis led to the unambiguous location of all carbon atoms. Continued full-matrix least-squares refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms (with appropriate restraints on parameters for atoms Ta, C(3), and C(6)—which lie on the crystallographic mirror plane) led to convergence with R_F = 5.7%, R_{wF} = 3.9%, and GOF = 1.35 for all 1850 independent reflections (none rejected). It may be noted that discrepancy indices for those 1461 reflections with $|F_o| > 3\sigma(|F_o|)$ were R_F = 3.8%, R_{wF} = 3.7%, and GOF = 1.46. The NO:NV ratio was 1850:82 or ~22.6:1.[10]

Attempts to ascertain the positions of the hydrogen atoms from a difference-Fourier synthesis were only partially successful, probably due to the large thermal motions of the pentamethylcyclopentadienyl ligand. This aspect of the structure was not further pursued.

The function $\sum w(|F_o| - |F_c|)^2$ showed no major trends as a function of $|F_o|$, $(\sin\theta)/\lambda$, sequence number, parity, or identity of crystallographic indices. The weighting scheme is therefore acceptable.

The reasonableness of the structure indicates that *Pnam* is the appropriate space group. Final positional and thermal parameters are collected in Table III.

2. $Ta(\eta^5\text{-}C_5Me_5)(C_7H_{12})Cl_2$. The position of the tantalum atom was determined from a Patterson synthesis; the remaining chlorine and carbon atoms were located on a difference-Fourier map. Refinement of positional and isotropic thermal parameters for all nonhydrogen atoms converged with R_F = 6.8%, R_{wF} = 7.2%, and GOF = 2.87. Continued refinement, now using anisotropic thermal parameters for all nonhydrogen atoms, converged with R_F = 5.1%, R_{wF} = 4.6%, and GOF = 1.77.

A second difference-Fourier map now revealed the positions of all 27 hydrogen atoms in the structure. Inclusion of their contributions and refinement of their positional and isotropic thermal parameters led to final convergence with R_F = 4.4%, R_{wF} = 3.4%, and GOF = 1.33 for all 3116 reflections; discrepancy indices for those 2603 reflections with $|F_o| > 3\sigma(|F_o|)$ were R_F = 3.2%, R_{wF} = 3.2%, and GOF = 1.39. The "overdetermination ratio" NO:NV was 3116:289 or ~10.8:1.

The usual tests (vide supra) indicated that the weighting scheme was satisfactory and that the structure was complete. Final positional and thermal parameters are collected in Table IV.

Description of the Molecular Structures

1. $Ta(\eta^5\text{-}C_5Me_5)(C_4H_8)Cl_2$. This complex crystallizes in the centrosymmetric space group *Pnam* with the molecule being bisected by a crystallographic mirror plane which includes atoms Ta, C(3), and C(6). The atomic numbering scheme is shown in Figures 1 and 2. Atoms in the basic

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(9) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

(10) NO = number of observations; NV = number of variables.

Table III. Positional and Anisotropic Thermal Parameters[a] (Å^2) for Ta(η^5-C_5Me_5)(C_4H_8)Cl_2

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta	0.10176 (4)	0.02869 (3)	0.25000 (0)[b]	2.546 (16)	2.445 (15)	3.045 (16)	0.283 (16)	0.0000 (0)	0.0000 (0)
Cl	0.11927 (24)	0.17705 (18)	0.37296 (18)	6.93 (13)	4.75 (9)	6.41 (12)	0.48 (9)	−1.18 (11)	−2.42 (9)
C(1)	−0.0608 (7)	−0.0351 (7)	0.3469 (7)	3.1 (3)	5.0 (4)	5.5 (4)	1.4 (3)	1.1 (3)	0.7 (4)
C(2)	−0.1716 (8)	0.0480 (7)	0.3074 (7)	4.4 (4)	8.2 (6)	4.7 (4)	2.4 (4)	0.5 (3)	0.5 (4)
C(3)	0.3297 (10)	−0.0237 (10)	0.25000 (0)[b]	2.3 (4)	3.0 (4)	10.4 (10)	0.4 (4)	0.0000 (0)	0.0000 (0)
C(4)	0.2737 (9)	−0.0768 (8)	0.3333 (6)	5.4 (4)	7.5 (5)	2.9 (3)	4.1 (4)	−0.2 (3)	−0.5 (4)
C(5)	0.1859 (8)	−0.1632 (7)	0.3016 (8)	3.8 (3)	4.0 (3)	11.2 (7)	1.8 (3)	1.9 (4)	3.6 (4)
C(6)	0.4366 (14)	0.0725 (13)	0.25000 (0)[b]	3.6 (7)	4.8 (7)	34.0 (32)	−0.8 (5)	0.0000 (0)	0.0000 (0)
C(7)	0.3066 (17)	−0.0554 (17)	0.4418 (9)	17.5 (12)	27.3 (18)	5.8 (7)	17.7 (13)	−6.3 (8)	−5.8 (9)
C(8)	0.1178 (11)	−0.2563 (11)	0.3590 (16)	9.5 (7)	9.2 (7)	35.2 (23)	5.8 (6)	13.2 (11)	13.7 (11)

[a] The form of the thermal parameter is $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$. [b] Atom on special positions. Atom occupancy = 0.5 for structure factor calculations.

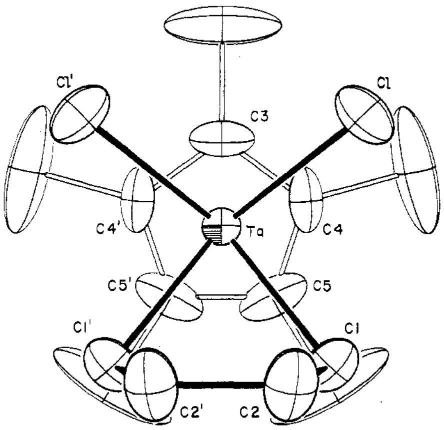

Figure 2. Relative orientation of η^5-C_5Me_5 ligand and the remainder of the Ta(η^5-C_5Me_5)(C_4H_8)Cl_2 molecule. Note the substantial libration of the η^5-C_5Me_5 ligand about the Ta···Cp axis.

asymmetric unit are labeled normally. Those related by the transformation (x, y, $^1/_2 - z$) are labeled with a prime. Distances and angles for this molecule are collected in Table V, while important planes are listed in Table VI.

Features of interest in the molecule include the following. (i) The tantalacyclopentane ring has an unusual "opened-envelope" conformation, the dihedral angle between the strictly planar C(1)–Ta–Cl(1′) and C(1)–C(2)–C(2′)–C(1′) systems being 116.26° (see Figure 3). This is in strict contrast to the puckered (δ or λ) conformation found in other saturated systems—e.g., M(en)$_x$ complexes. (ii) The C(1)–C(2)–C(2′)–C(1′) system is almost at right angles (strictly, 92.50°) to the η^5-cyclopentadienyl system. (iii) The C(1)–Ta–C(1′) angle is surprisingly acute (72.45 (28)°); other angles within the tantalacyclopentane ring are Ta–C(1)–C(2) = Ta–C(1′)–C(2′) = 97.57 (48)° and C(1)–C(2)–C(2′) = C(1)′–C(2′)–C(2) = 110.12 (67)°. (iv) The tantalum-carbon σ-bond distance is Ta–C(1) = Ta–Ca(1′) = 2.217 (8) Å; the β-carbon atoms are quite close to the metal atom, with Ta···C(2) = Ta···C(2′) = Ta···C(2′) = 2.869 (8) Å. (v) The Ta–C(cyclopentadienyl) distances range from 2.371 (10) to 2.428 (8) Å and the methyl groups are displaced from the carbocyclic ring by amounts ranging from −0.065 (14) to −0.206 (11) Å. (The negative sign here indicates that the displacement is *away from* the tantalum atom.) (vi) The tantalum–chlorine distances are each 2.366 (2) Å, and the C(1)–Ta–C(1′) angle is 89.30 (8)°.

The substantial librational motion observed for the η^5-C_5Me_5 ligand, coupled with a persistent worry that the crystallographically imposed mirror plane might mask some fine (but important) aspect of the molecular geometry, provided the impetus for a structural study of a second tantalacyclopentane complex. The results of our study of Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2, in which none of the aforementioned troublesome features remain, appear below.

2. Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2. The atomic numbering scheme is shown in Figures 4 and 5, and a stereoscopic view of the molecule appears as Figure 6. There are no crystallographically imposed constraints upon the molecular geometry, no abnormally large thermal motions are observed, and all hydrogen atoms were located. Interatomic distances and angles are collected in Tables VII and VIII; important planes are listed in Table IX.

The TaC_7H_{12} system defines a tantalabicyclo[3.3.0]octane framework, consisting of two fused five-membered rings. The bicyclic system has an exo,cis-exo configuration relative to the tantalum atom. Although there is no crystallographically dictated symmetry, the molecule possesses approximate C_s symmetry (see, especially, Figure 5). The tantalacyclopentane ring again has the "opened-envelope" conformation. The C(11)–C(12)–C(16)–C(17) system is close to planar, the root-mean-square deviation from planarity being only 0.038 Å. The dihedral angle between the strictly planar C(11)–Ta–C(17) system and the approximately planar C(11)–C(12)–C(16)–C(17) system is 122.64°.

The Cl(1)–Ta–Cl(2) and C(11)–Ta–C(17) planes make angles of 142.52 and 155.31° with the η^5-cyclopentadienyl ligand; the C(11)–C(12)–C(16)–C(17) system lies almost perpendicular to the cyclopentadienyl ring, the dihedral angle between the two planes being 97.95°.

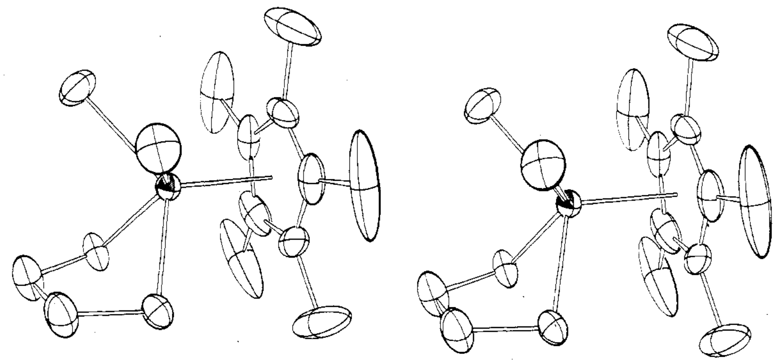

Figure 3. Stereoscopic view of the Ta(η^5-C_5Me_5)(C_4H_8)Cl_2 molecule.

Table IV. Final Positional and Thermal Parameters for Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2

A. Positional and Isotropic Thermal Parameters

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Ta	0.31164 (2)	0.25630 (1)	0.07610 (2)		H(17A)	0.368 (7)	0.286 (5)	−0.103 (4)	4.2 (14)
Cl(1)	0.40307 (26)	0.16374 (14)	0.21238 (13)		H(17B)	0.221 (9)	0.234 (5)	−0.116 (6)	5.1 (19)
Cl(2)	0.55435 (19)	0.30335 (14)	0.05932 (17)		H(6A)	0.332 (7)	0.549 (5)	0.143 (5)	3.9 (17)
C(1)	0.2574 (7)	0.4226 (4)	0.1091 (4)		H(6B)	0.418 (10)	0.527 (7)	0.053 (6)	11.0 (30)
C(2)	0.1705 (6)	0.4009 (4)	0.0217 (4)		H(6C)	0.449 (8)	0.486 (6)	0.166 (5)	5.6 (20)
C(3)	0.0660 (6)	0.3296 (4)	0.0410 (4)		H(7A)	0.125 (8)	0.505 (6)	−0.081 (5)	5.1 (18)
C(4)	0.0886 (7)	0.3061 (4)	0.1389 (4)		H(7B)	0.164 (9)	0.414 (6)	−0.117 (6)	5.6 (23)
C(5)	0.2047 (6)	0.3637 (4)	0.1815 (4)		H(7C)	0.263 (8)	0.478 (6)	−0.073 (5)	5.6 (21)
C(6)	0.3711 (9)	0.5013 (6)	0.1256 (6)		H(8A)	−0.125 (9)	0.330 (6)	−0.028 (6)	6.7 (24)
C(7)	0.1769 (11)	0.4515 (6)	−0.0722 (6)		H(8B)	−0.080 (11)	0.234 (7)	−0.025 (7)	7.0 (28)
C(8)	−0.0580 (8)	0.2937 (6)	−0.0289 (6)		H(8C)	−0.040 (11)	0.309 (7)	−0.085 (7)	8.6 (30)
C(9)	−0.0035 (11)	0.2359 (6)	0.1892 (7)		H(9A)	−0.084 (9)	0.264 (5)	0.199 (6)	5.3 (20)
C(10)	0.2560 (11)	0.3711 (6)	0.2861 (5)		H(9B)	0.045 (14)	0.215 (9)	0.236 (9)	11.6 (44)
C(11)	0.1938 (8)	0.1187 (4)	0.0421 (5)		H(9C)	−0.052 (11)	0.193 (8)	0.157 (7)	9.3 (34)
C(12)	0.3048 (7)	0.0611 (4)	−0.0082 (5)		H(10A)	0.217 (9)	0.423 (6)	0.309 (5)	5.6 (20)
C(13)	0.2439 (10)	−0.0309 (5)	−0.0608 (6)		H(10B)	0.375 (14)	0.401 (9)	0.297 (8)	13.6 (38)
C(14)	0.2028 (12)	0.0018 (7)	−0.1602 (6)		H(10C)	0.214 (11)	0.315 (8)	0.322 (7)	10.3 (29)
C(15)	0.3148 (12)	0.0741 (6)	−0.1805 (6)		H(13A)	0.179 (8)	−0.067 (6)	−0.021 (5)	6.1 (19)
C(16)	0.3600 (7)	0.1272 (4)	−0.0869 (5)		H(13B)	0.318 (8)	−0.085 (6)	−0.077 (5)	6.2 (19)
C(17)	0.2989 (8)	0.2315 (5)	−0.0783 (5)		H(14A)	0.097 (11)	0.045 (8)	−0.156 (7)	11.1 (35)
H(11A)	0.108 (8)	0.125 (5)	−0.004 (5)	4.9 (17)	H(14B)	0.205 (7)	−0.056 (4)	−0.214 (4)	4.1 (14)
H(11B)	0.166 (6)	0.084 (4)	0.099 (4)	3.4 (13)	H(15A)	0.290 (9)	0.115 (6)	−0.231 (6)	6.7 (23)
H(12)	0.375 (7)	0.045 (4)	0.033 (4)	2.8 (13)	H(15B)	0.399 (15)	0.051 (10)	−0.214 (9)	16.4 (50)
H(16)	0.454 (7)	0.139 (5)	−0.077 (5)	4.5 (16)					

B. Anisotropic Thermal Parameters[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta	2.351 (10)	2.380 (10)	2.691 (11)	0.300 (8)	0.320 (7)	−0.044 (9)
Cl(1)	9.05 (14)	5.22 (9)	3.59 (8)	2.85 (9)	−1.17 (8)	0.21 (7)
Cl(2)	2.73 (7)	5.10 (9)	9.94 (14)	−0.68 (6)	1.54 (8)	−1.21 (9)
C(1)	3.05 (27)	2.39 (22)	3.36 (27)	0.31 (19)	−0.17 (21)	−0.26 (19)
C(2)	2.80 (27)	2.84 (23)	2.70 (25)	0.62 (19)	−0.13 (20)	−0.11 (19)
C(3)	2.53 (25)	2.73 (23)	3.44 (27)	0.63 (19)	0.26 (20)	−0.78 (20)
C(4)	3.3 (3)	3.23 (25)	2.95 (26)	0.45 (21)	0.92 (21)	−0.54 (20)
C(5)	3.3 (3)	3.00 (23)	2.56 (25)	0.33 (20)	0.26 (20)	−0.32 (19)
C(6)	3.3 (3)	3.2 (3)	6.2 (5)	−0.19 (25)	−0.0 (3)	−1.1 (3)
C(7)	5.5 (5)	3.6 (3)	3.7 (4)	1.0 (3)	0.6 (3)	0.9 (3)
C(8)	3.0 (3)	4.0 (3)	4.8 (4)	0.22 (27)	−0.22 (27)	−0.6 (3)
C(9)	4.6 (4)	4.3 (3)	4.7 (4)	0.0 (3)	2.2 (3)	−0.4 (3)
C(10)	6.6 (5)	4.4 (3)	2.8 (3)	0.6 (3)	−0.3 (3)	−0.87 (27)
C(11)	3.3 (3)	2.83 (24)	3.7 (3)	−0.33 (21)	1.28 (26)	−0.11 (22)
C(12)	3.3 (3)	3.25 (26)	3.3 (3)	0.35 (22)	0.70 (24)	−0.52 (22)
C(13)	6.1 (4)	3.0 (3)	5.0 (4)	−0.5 (3)	1.1 (3)	−0.71 (27)
C(14)	8.5 (6)	5.3 (4)	4.9 (4)	−2.1 (4)	−0.7 (4)	−0.9 (3)
C(15)	8.2 (6)	4.3 (4)	4.2 (4)	−0.6 (4)	2.0 (4)	−0.9 (3)
C(16)	2.9 (3)	3.11 (26)	4.9 (3)	−0.22 (22)	1.17 (25)	−0.91 (23)
C(17)	4.0 (3)	3.6 (3)	2.74 (25)	0.02 (24)	1.13 (23)	−0.19 (22)

[a] The form of the thermal parameter is $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

The C(11)–Ta–C(17) angle is markedly acute (71.47 (2)°); the Ta–C(11)–C(12) and Ta–C(17)–C(16) angles are also reduced slightly from the regular tetrahedral value, with values of 101.6 (4) and 104.0 (4)°, respectively. The other angles within the metallacyclopentane ring are quite normal, with C(11)–C(12)–C(16) = 109.0 (5)° and C(17)–C(16)–C(12) = 108.9 (5)°.

The tantalum–carbon σ-bond lengths are 2.191 (6) and 2.200 (6) Å (average = 2.196 [6] Å[11]). These are consistent with the Ta–C distances found in Ta(η^5-C_5Me_5)(C_4H_8)Cl_2 (2.217 (8) Å—see above) and the other reported tantalum–alkyl distances, viz., 2.175 [8] Å in Ta(η^5-C_5Me_5)(η^2-C_6H_4)Me_2,[12] 2.246 (12) Å in Ta(η^5-C_5H_5)$_2$(=CH_2)Me,[13] 2.30 (1) Å in Ta(η^5-C_5H_5)$_2$(=CHPh)(CH_2Ph),[14] and 2.23 [5] Å in Ta(CH_2CMe_3)$_3$(≡$CCMe_3$)Li(dmp).[15]

The tantalum–(β-carbon) distances, Ta···C(12) = 2.912 (12) Å and Ta···C(16) = 2.974 (7) Å, are relatively short for nonbonded contacts.

The tantalum atom is in a formal oxidation state of +5 (d^0) and is associated with 14 outer valence electrons; the coordination geometry about tantalum is that of a four-legged piano stool. Angles from "Cp" (the centroid of the carbocylic ring in the η^5-C_5Me_5 ligand) to the monodentate ligands are Cp–Ta–Cl(1) = 115.72°, Cp–Ta–Cl(2) = 119.26°, Cp–Ta–C(11) = 107.96°, and Cp–Ta–C(17) = 107.35°. Angles between the monodentate ligands include Cl(1)–Ta–Cl(2) = 88.57 (7)°, Cl(1)–Ta–C(11) = 81.03 (18)°, Cl(2)–Ta–C(17) = 83.38 (18)°, Cl(1)–Ta–C(17) = 134.24 (18)°, and Cl(2)–Ta–C(11) = 131.30 (18)°.

The tantalum atom lies +2.0939 (2) Å from the plane of the cyclopentadienyl system. The methyl groups of the η^5-C_5Me_5 ligand are all displaced from this plane in a direction *away from* the tantalum atom. Individual deviations vary

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(11) The esd of an average distance is shown in square brackets and is calculated by the expression $[\sigma] = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$.

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Table V. Intramolecular Distances (Å) and Angles (Deg), with Esd's, for Ta(η^5-C_5Me_5)(C_4H_8)Cl_2

A. Distances from Tantalum Atom

Ta–Cl	2.366 (2)	Ta–C(3)	2.371 (10)
Ta–C(1)	2.217 (8)	Ta–C(4)	2.385 (9)
Ta···C(2)	2.869 (8)	Ta–C(5)	2.428 (8)
Ta–Cp[a]	2.088 (–)		

B. C–C Distances within the TaC_4 Ring

C(1)–C(2)	1.552 (11)	C(2)–C(2′)	1.553 (12)

C. C–C Distances within the η^5-C_5Me_5 System

C(3)–C(4)	1.395 (10)	C(3)–C(6)	1.529 (18)
C(4)–C(5)	1.384 (12)	C(4)–C(7)	1.524 (15)
C(5)–C(5′)	1.397 (15)	C(5)–C(8)	1.474 (18)

D. Angles around the Tantalum Atom

Cl–Ta–Cl′	89.30 (8)	Cp–Ta–Cl[a]	116.22 (–)
Cl–Ta–C(1)	82.49 (21)	Cp–Ta–C(1)	107.49 (–)
Cl–Ta–C(1′)	134.43 (21)	C(1)–Ta–C(1′)	72.45 (28)

E. Angles within the TaC_4 Ring

C(1)–Ta–C(1′)	72.45 (28)	C(1)–C(2)–C(2′)	110.12 (67)
Ta–C(1)–C(2)	97.57 (48)		

F. Angles within the η^5-C_5Me_5 System

C(4′)–C(3)–C(4)	107.6 (8)	C(3)–C(4)–C(7)	128.4 (10)
C(3)–C(4)–C(5)	108.2 (8)	C(5)–C(4)–C(7)	123.3 (9)
C(4)–C(5)–C(5′)	108.0 (8)	C(4)–C(5)–C(8)	129.5 (10)
C(4)–C(3)–C(6)	126.2 (8)	C(5′)–C(5)–C(8)	121.7 (10)

[a] Cp is the centroid of the pentaatomic cyclopentadienyl ring.

Table VI

Important Planes[a] and Atomic Deviations Therefrom (Å) for Ta(η^5-C_5Me_5)(C_4H_8)Cl_2

(A) C(1)–C(2)–C(2′)–C(1′) Plane (Precisely Planar)

$$-0.6430X - 0.7659Y - 0.6970 = 0$$

dev: Ta, –1.6041 (4); Cl, –3.000 (2)

(B) C(1)–Ta–C(1′) Plane (Precisely Planar)

$$0.4023X - 0.9155Y - 0.1161 = 0$$

dev: C(2), –1.307 (8); Cl, –1.462 (2)

(C) Cl–Ta–Cl′ Plane (Precisely Planar)

$$0.9945X - 0.1048Y - 0.9855 = 0$$

(D) Cyclopentadienyl Plane

$$-0.7371X + 0.6758Y + 2.6233 = 0$$

dev: C(3),[b] –0.006 (10); C(4),[b] 0.005 (9); C(5),[b] –0.002 (8); C(4′),[b] 0.005 (9); C(5′),[b] –0.002 (8); Ta, 2.0864 (4); C(6), –0.065 (14); C(7), –0.076 (18); C(8), –0.206 (11); C(7′), –0.076 (18); C(6), –0.065 (14); C(1), 2.807 (7); C(2), 4.263 (8); C(2′), 4.263 (8); C(1′), 2.807 (7)

Interplanar Angles (Deg) for Ta(η^5-C_5Me_5)(C_4H_8)Cl_2

A/B	116.26	B/C	119.74
A/D	92.50	B/D	156.24
C/D	143.50		

[a] Orthonormal coordinates. [b] These atoms used in defining the plane.

considerably, being –0.136 (8) Å for C(6), –0.113 (9) Å for C(7), –0.157 (8) Å for C(8), –0.050 (9) Å for C(9), and –0.145 (9) Å for C(10).

The tantalum–carbon bond distances for the η^5-C_5Me_5 ligand range from 2.378 (6) to 2.469 (6) Å; the longest distance involves atom C(3), which lies *under* (relative to Figure 5) the tantalacyclopentane system. Carbon–carbon distances within the cyclopentadienyl system are all equivalent, ranging from 1.405 (8) to 1.428 (8) Å [average = 1.417 [9] Å], while C–Me distances range from 1.498 (10) to 1.509 (11) Å [average = 1.504 [4] Å].

The hydrogen atoms of the η^5-C_5Me_5 system were all located and refined (C–H(av) = 0.90 Å, as compared to the expected "X-ray-determined" distance of 0.95 Å).[16] The rotational conformation taken up by the methyl groups is such that one hydrogen atom of each methyl group (the "A" hydrogen in each case) lies the plane of the cyclopentadienyl ligand (by about 0.9 Å) pointing directly away from the tantalum atom (see Figures 4–6 and Table IX, section D).

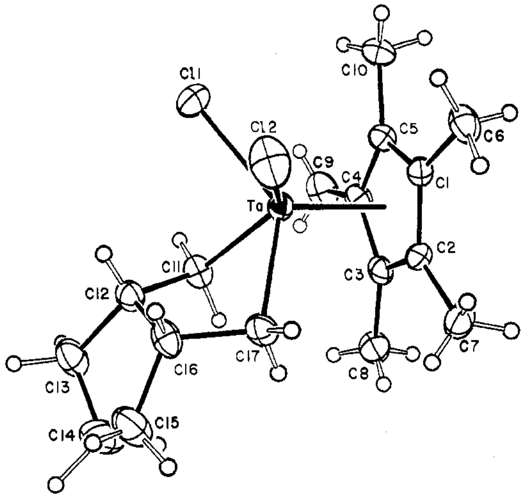

Figure 4. Labeling diagram for the Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2 molecule (ORTEP-II diagram; 30% ellipsoids, with hydrogen atom shown as reduced spheres).

Table VII. Interatomic Distances (Å) for Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2

(A) Distances from the Tantalum Atom

Ta–Cl(1)	2.375 (2)	Ta–C(1)	2.378 (5)
Ta–Cl(2)	2.362 (2)	Ta–C(2)	2.435 (6)
Ta–C(11)	2.191 (6)	Ta–C(3)	2.469 (6)
Ta–C(17)	2.200 (6)	Ta–C(4)	2.426 (6)
Ta···C(12)	2.912 (12)	Ta–C(5)	2.381 (6)
Ta···C(16)	2.974 (7)	Ta···Cp	2.096 (–)

(B) C–C Distances within C_7H_{12} Ligand

C(11)–C(12)	1.528 (9)	C(14)–C(15)	1.478 (14)
C(12)–C(13)	1.530 (10)	C(15)–C(16)	1.523 (11)
C(12)–C(16)	1.562 (9)	C(16)–C(17)	1.539 (9)
C(13)–C(14)	1.481 (12)		

(C) C–H Distances within C_7H_{12} Ligand

C(11)–H(11A)	0.97 (7)	C(14)–H(14B)	1.10 (6)
C(11)–H(11B)	0.99 (6)	C(15)–H(15A)	0.90 (8)
C(12)–H(12)	0.85 (6)	C(15)–H(15B)	1.00 (14)
C(13)–H(13A)	0.99 (8)	C(16)–H(16)	0.88 (7)
C(13)–H(13B)	1.05 (8)	C(17)–H(17A)	1.07 (7)
C(14)–H(14A)	1.14 (11)	C(17)–H(17B)	0.84 (8)

(D) C–C Distances within η^5-C_5Me_5 System

C(1)–C(2)	1.424 (8)	C(1)–C(6)	1.498 (10)
C(2)–C(3)	1.416 (8)	C(2)–C(7)	1.504 (10)
C(3)–C(4)	1.412 (8)	C(3)–C(8)	1.504 (10)
C(4)–C(5)	1.405 (8)	C(4)–C(9)	1.509 (11)
C(5)–C(1)	1.428 (8)	C(5)–C(10)	1.504 (9)

(E) C–H Distances within η^5-C_5Me_5 System

C(6)–H(6A)	0.79 (7)	C(8)–H(8C)	0.86 (10)
C(6)–H(6B)	1.22 (9)	C(9)–H(9A)	0.87 (8)
C(6)–H(6C)	0.89 (7)	C(9)–H(9B)	0.81 (12)
C(7)–H(7A)	0.88 (8)	C(9)–H(9C)	0.84 (11)
C(7)–H(7B)	0.81 (8)	C(10)–H(10A)	0.87 (8)
C(7)–H(7C)	0.87 (8)	C(10)–H(10B)	1.16 (13)
C(8)–H(8A)	0.79 (8)	C(10)–H(10C)	1.02 (10)
C(8)–H(8B)	0.85 (9)		

Discussion

The "opened-envelope" conformation is preferred over the puckered (δ or λ) conformation for two tantalacyclopentane

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Table VIII. Selected Interatomic Angles (Deg) for Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2

(A) Angles around the Tantalum Atom					
Cl(1)-Ta-Cl(2)	88.57 (7)	Cl(2)-Ta-C(11)	131.30 (18)	Cp-Ta-Cl(1)	115.72
Cl(1)-Ta-C(11)	81.03 (18)	Cl(2)-Ta-C(17)	83.38 (18)	Cp-Ta-Cl(2)	119.26
Cl(1)-Ta-C(17)	134.24 (18)	C(11)-Ta-C(17)	71.47 (25)	Cp-Ta-C(11)	107.96
				Cp-Ta-C(17)	107.35
(B) Ta-C-C and C-C-C Angles within TaC_7H_{12} Moiety					
Ta-C(11)-C(12)	101.6 (4)	C(13)-C(12)-C(16)	104.9 (6)	C(17)-C(16)-C(12)	108.9 (5)
Ta-C(17)-C(16)	104.0 (4)	C(12)-C(13)-C(14)	104.7 (7)	C(15)-C(16)-C(12)	105.5 (6)
C(11)-C(12)-C(13)	114.8 (6)	C(13)-C(14)-C(15)	106.2 (8)	C(14)-C(15)-C(16)	105.9 (7)
C(11)-C(12)-C(16)	109.0 (5)	C(17)-C(16)-C(15)	116.2 (6)		
(C) Angles Involving Hydrogen Atoms in TaC_7H_{12} Moiety					
Ta-C(11)-H(11A)	114 (4)	C(12)-C(13)-H(13B)	119 (4)	C(17)-C(16)-H(16)	100 (4)
Ta-C(11)-H(11B)	113 (3)	C(14)-C(13)-H(13A)	125 (4)	C(12)-C(16)-H(16)	113 (4)
Ta-C(17)-H(17A)	105 (3)	C(14)-C(13)-H(13B)	96 (4)	C(15)-C(16)-H(16)	113 (4)
Ta-C(17)-H(17B)	124 (5)	H(13A)-C(13)-H(13B)	102 (6)	C(16)-C(15)-H(15A)	114 (5)
C(12)-C(11)-H(11A)	105 (4)	C(13)-C(14)-H(14A)	103 (5)	C(16)-C(15)-H(15B)	114 (8)
C(12)-C(11)-H(11B)	113 (3)	C(13)-C(14)-H(14B)	115 (3)	C(14)-C(15)-H(15A)	116 (5)
H(11A)-C(11)-H(11B)	109 (5)	H(14A)-C(14)-H(14B)	119 (6)	C(14)-C(15)-H(15B)	119 (8)
C(11)-C(12)-H(12)	108 (4)	C(16)-C(17)-H(17B)	112 (3)	H(15A)-C(15)-H(15B)	87 (9)
C(16)-C(12)-H(12)	111 (4)	C(16)-C(17)-H(17B)	106 (5)	C(15)-C(14)-H(14A)	107 (5)
C(13)-C(12)-H(12)	110 (4)	H(17A)-C(17)-H(17B)	105 (6)	C(15)-C(14)-H(14B)	106 (3)
C(12)-C(13)-H(13A)	110 (4)				
(D) Internal C-C-C Angles of η^5-C_5Me_5 Ligand					
C(5)-C(1)-C(2)	107.6 (5)	C(2)-C(3)-C(4)	108.6 (5)	C(4)-C(5)-C(1)	108.1 (5)
C(1)-C(2)-C(3)	107.5 (5)	C(3)-C(4)-C(5)	108.2 (5)		
(E) External C-C-C Angles for η^5-C_5Me_5 Ligand					
C(5)-C(1)-C(6)	125.4 (6)	C(2)-C(3)-C(8)	125.2 (6)	C(5)-C(4)-C(9)	126.3 (6)
C(2)-C(1)-C(6)	126.6 (6)	C(4)-C(3)-C(8)	125.9 (6)	C(4)-C(5)-C(10)	126.6 (6)
C(1)-C(2)-C(7)	126.7 (6)	C(3)-C(4)-C(9)	125.3 (6)	C(1)-C(5)-C(10)	125.0 (6)
C(3)-C(2)-C(7)	125.6 (6)				

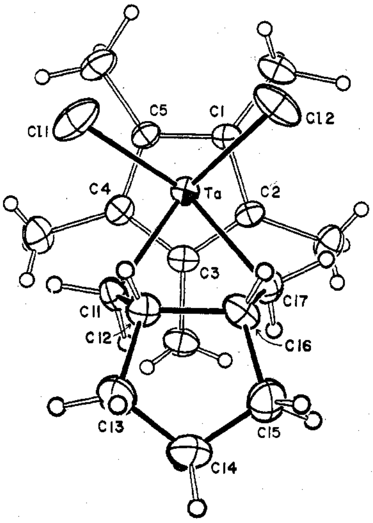
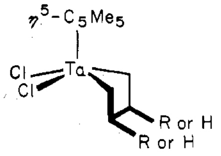


Figure 5. The Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2 molecule projected onto the plane of the η^5-cyclopentadienyl ligand. Note the approximate C_s symmetry of the molecule.

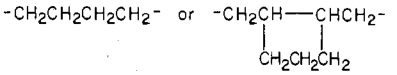
derivatives of type I. We expect it to be general for such species.



I

The causes of such an arrangement include a number of interrelated factors, and it is not easy to identify a single dominant factor which causes all of the observed features. Factors which must be considered include the following.

(i) There is a limited "cone angle" of space available to the



$$-CH_2CH_2CH_2CH_2- \text{ or } -CH_2\underset{|}{C}H\text{—}\underset{|}{C}HCH_2- \quad (CH_2CH_2CH_2)$$

ligand at the tantalum atom center. If the puckered conformation were to occur, there would be considerably more interaction between the metallacyclopentane ring and the η^5-C_5Me_5 ligand.

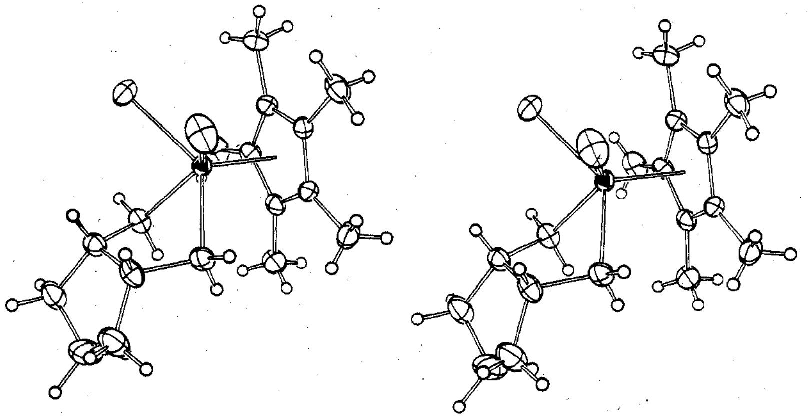


Figure 6. Stereoscopic view of the Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2 molecule.

Table IX. Important Planes[a] and Atomic Deviations Therefrom (Å), for Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2

(A) C(11)-C(12)-C(16)-C(17) Plane

$$-0.6827X - 0.2654Y - 0.6808Z + 2.0278 = 0$$

dev: C(11),[b] 0.025 (7); C(12),[b] −0.039 (7); C(16),[b] 0.040 (7); C(17),[b] −0.026 (7); Ta, −1.5003 (2); C(13), 1.121 (9); C(15), 1.307 (10); C(14), 2.100 (10)

(B) C(11)-Ta-C(17) Plane (Exact)

$$-0.8545X + 0.5027Y - 0.1312Z + 0.7301 = 0$$

dev: C(12), −1.245 (7); C(16), −1.192 (7)

(C) Cl(1)-Ta-Cl(2) Plane (Exact)

$$0.1658X - 0.7981Y - 0.5793Z + 2.9509 = 0$$

(D) Cyclopentadienyl Plane (C(1) → C(5))

$$0.6658Z - 0.7234Y - 0.1827Z + 2.9879 = 0$$

dev: C(1),[b] 0.002 (6); C(2),[b] 0.003 (6); C(3),[b] −0.006 (6); C(4),[b] 0.007 (6); C(5),[b] −0.005 (6); Ta, +2.0939 (2); C(6), −0.136 (8); C(7), −0.113 (9); C(8), −0.157 (8); C(9), −0.050 (9); C(10), −0.145 (9); C(11), 2.852 (6); C(17), 2.824 (7); H(6A), −0.90 (7); H(6B), 0.16 (10); H(6C), 0.34 (8); H(7A), −0.92 (8); H(7B), 0.34 (8); H(7C), 0.16 (8); H(8A), −0.93 (8); H(8B), 0.27 (10); H(8C), 0.01 (10); H(9A), −0.86 (8); H(9B), 0.28 (12); H(9C), 0.20 (11); H(10A), −0.98 (8); H(10B), 0.24 (12); H(10C), 0.01 (10)

Interplanar Angles (Deg) for Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2

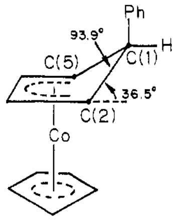
A/B	122.64	B/C	117.83
A/D	97.95	B/D	155.31
C/D	142.52		

[a] Orthonormal coordinates. [b] These atoms used in defining the plane.

(ii) The tantalum–carbon σ bonds are much longer than any other bonds around the metallacyclopentane ring. Values are 2.217 (8) Å for the $-C_4H_8-$ complex and 2.196 [6] Å for the $-C_7H_{12}-$ complex.

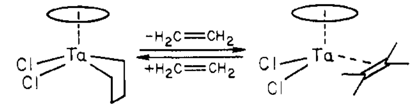
(iii) The molecules contain very acute C(α)–Ta–C(α′) angles (72.45 (28)° in the $-C_4H_8-$ complex and 71.47 (25)° in the $-C_7H_{12}-$ complex). These may, however, result simply as a geometric requirement of item ii.

It is interesting to note that a number of metal complexes of cyclopenta*diene* ligands have an "opened-envelope" conformation, along with abnormally small (substantially less than 109.28°) internal angles at C(1). Thus, Co(η^5-C_5H_5)(η^4-C_5H_5Ph) (III) has an internal angle of 93.9 (15)° at C(1) and has a bend of 36.5° across the C(2)···C(5) vector.[17,18]



II

A final thought is that the orientation of the metallacyclopentane ligand may, in some way, facilitate the observed[6] reversible loss of olefin from this class of Complexes (see eq 4). Possibly, some direct Ta···C(β) interaction is more easily attainable in this geometry.



III IV (4)

We have determined that the resultant olefin complex (IV in eq 4) has a solid-state geometry in which the olefinic C–C vector lies parallel to the Cl···Cl vector.[19] The acetylene complex Ta(η^5-C_5Me_5)(η^2-PhC≡CPh)Cl_2 has a similar arrangement;[20] but the benzyne complex Ta(η^5-C_5Me_5)(η^2-C_6H_4)Me_2 has the benzyne ligand lying perpendicular to the C(Me)···C(Me) vector.[12,21]

Acknowledgment. We thank Professor R. R. Schrock for providing the samples. This work was supported by the National Science Foundation (Grant CHE77-04981, to M.R.C.).

Registry No. Ta(η^5-C_5Me_5)(C_4H_8)Cl_2, 71936-69-1; Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2, 71936-59-9.

Supplementary Material Available: A table of data-processing formulas and listings of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of California, Irvine, California 92717

Crystal and Molecular Structure of the Hydrogen-Bonded Dimer of ((Phenylazo)acetaldoximato-*N*,*N'*)((phenylazo)acetaldoxime-*N*,*N'*)copper(I)

MICHAEL H. DICKMAN and ROBERT J. DOEDENS*

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The product of the reaction of (phenylazo)acetaldoxime, $C_6H_5N{=}C(CH_3){=}NOH$ (LH), with copper(II) acetate has been shown by a crystal structure analysis to be a copper(I) complex, Cu(L)(LH), which is associated into dimers through short O–H–O hydrogen-bonding interactions. Crystals of this material are monoclinic, space group $C2/c$, with $a = 9.727$ (3) Å, $b = 21.824$ (7) Å, $c = 16.948$ (5) Å, and $\beta = 106.66$ (2)°. Least-squares refinement, based on 2723 nonzero data, converged to a conventional R factor of 0.063. Evidence for formulation as a copper(I) complex includes the distorted tetrahedral geometry about the metal ion and a pair of short O···O intermolecular contacts of 2.425 (5) Å, indicative of strong hydrogen bonding between monomers. The resulting dimer has crystallographic twofold symmetry and virtual D_2-222 symmetry. The ligands are nearly planar, with a mean Cu–N distance of 1.992 (6) Å. The observed structure and the copper(I) formulation are consistent with other physical and chemical properties of this compound.

Introduction

A series of compounds derived from arylazo oximes, LH = ArN═NC(R)═NOH, and copper(II) acetate have been reported by Chakravorty et al.[1] These compounds were formulated as copper(II) bis chelates of the deprotonated oximes. Surprisingly, all were found to be diamagnetic. A

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