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Crystal and Molecular Structure of a Tantalum–Benzylidyne Complex, $Ta(\eta^5-C_5Me_5)(CPh)(PMe_3)_2Cl$. Evidence for a Tantalum–Carbon Triple Bond

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The complex chloro(η^5-pentamethylcyclopentadienyl)bis(trimethylphosphine)benzylidynetantalum, $Ta(\eta^5-C_5Me_5)(CPh)(PMe_3)_2Cl$, has been studied via a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 10.5129$ (12) Å, $b = 13.8147$ (16) Å, $c = 18.1793$ (21) Å, $\beta = 102.945$ (9)°, $V = 2573.1$ (5) Å^3, and ρ(calcd) = 1.531 g cm^{-3} for $Z = 4$ and mol wt 592.91. Diffraction data for $4.5° < 2\theta < 45°$ (Mo Kα radiation) were collected via a coupled θ–2θ scan routine on a Syntex $P2_1$ automated diffractometer. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms other than the hydrogen atoms of the $\eta^5-C_5Me_5$ ligand were located directly, the structure being refined to $R_F = 4.1\%$ and $R_{wF} = 3.5\%$ for those 3140 reflections with $|F_o| > \sigma(|F_o|)$. The molecule has a central tantalum atom surrounded in a "four-legged piano stool" arrangement by the $\eta^5-C_5Me_5$ ring and four monodentate ligands. The pseudo-trans Cl–Ta–C(1) and P(1)–Ta–P(2) angles are equivalent, with values of 125.54 (22) and 125.41 (7)°, respectively. The tantalum–benzylidyne linkage is 1.849 (8) Å in length—some 0.181 (10) Å shorter than the tantalum–neopentylidene linkage of 2.030 (6) Å in $(\eta^5-C_5H_5)_2Ta(=CHCMe_3)Cl$ and 0.397 (14) Å shorter than the tantalum–methyl linkage of 2.246 (12) Å in $(\eta^5-C_5H_5)_2Ta(=CH_2)(CH_3)$. The Ta–C(1)–C(2) angle of 171.75 (56)° and the C(1)–C(2) distance of 1.467 (10) Å are consistent with sp hybridization of C(1) and with the presence of a tantalum–benzylidyne triple bond.

Introduction

The first examples of terminal carbyne (or "alkylidyne") complexes of the transition metals were the species *trans*-$X(OC)_4M{\equiv}CR$ (X = Cl, Br, I; M = Cr, Mo, W; R = Me, Ph), reported by Fischer and co-workers in 1973.[1] Structural studies on several of these group 6A complexes have appeared, and the results have been summarized in a recent article.[2]

Alkylidene and alkylidyne complexes of the group 5A elements niobium and tantalum have recently been synthesized by Schrock and co-workers.[3-11] X-ray structural analyses of the alkylidene species $(\eta^5-C_5H_5)_2Ta(=CH_2)(CH_3)$[8] and $(\eta^5-C_5H_5)_2Ta(=CHCMe_3)Cl$[12,13] have appeared previously. However, the only tantalum–alkylidyne derivative for which a crystal structure has been reported is the rather complex species $[(Me_3CCH_2)_3Ta{\equiv}CCMe_3]Li(dmp)$ (dmp = *N,N′*-dimethylpiperazine),[10] in which there is, apparently, some interaction between the Li^+ ion and the α-carbon atom of the neopentylidyne system.

We now report the results of a single-crystal X-ray structural analysis of the tantalum–benzylidyne complex $Ta(\eta^5-C_5Me_5)(CPh)(PMe_3)_2Cl$. A brief account of this study has appeared previously.[14]

Experimental Section

(A) Collection and Processing of Diffraction Data. A crystalline sample of $Ta(\eta^5-C_5Me_5)(CPh)(PMe_3)_2Cl$ was kindly supplied by Professor R. R. Schrock of the Massachusetts Institute of Technology. The complex forms orange-brown columnar crystals, which are extended along their *b* axes. The material may be handled in air for brief periods but decomposes to a white powder after some 24–36 h of exposure to the atmosphere.

Table I. Experimental Data for the X-ray Diffraction Study of $Ta(\eta^5-C_5Me_5)(CPh)(PMe_3)_2Cl$

(A) Crystal Parameters[a] at 24 °C

cryst system: monoclinic
space group: $P2_1/c$
$a = 10.5129$ (12) Å
$b = 13.8147$ (16) Å
$c = 18.1793$ (21) Å
$\beta = 102.945$ (9)°
$V = 2573.1$ (5) Å^3
$Z = 4$
mol wt 592.91
ρ(calcd) = 1.531 g cm^{-3}

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite, equatorial, $2\theta_{mono} = 12.2°$
reflections measd: $+h, +k, \pm l$
2θ range: 4.5–45°
scan type: coupled θ(cryst)–2θ(counter)
scan speed: 2.0°/min (in 2θ)
scan range: $[2\theta(\text{Mo K}\alpha_1) - 0.9]°$–$[2\theta(\text{Mo K}\alpha_2) + 0.9]°$
bkgd measurement: stationary crystal and counter at beginning and end of the scan, each measured for one-fourth of the scan time
standards: 3 every 97 reflections
reflections collected: 3625 total, yielding 3386 symmetry-independent data
absorption coeff: $\mu = 47.3$ cm^{-1}
absorption cor: empirical (see text)

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo $K\bar{\alpha}$ components of the 24 reflections of the forms $\{72\bar{4}\}$, $\{3,1,\overline{12}\}$, $\{19\bar{3}\}$, $\{284\}$, $\{2,2,10\}$, and $\{622\}$, all with $2\theta = 25$–30°.

A crystal of maximum orthogonal dimensions 0.13 × 0.23 × 0.41 mm, approximating a trapezoidal prism, was mechanically wedged

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into a 0.2 mm diameter thin-walled capillary, which was purged with argon, flame-sealed, inserted into a brass pin with beeswax, and mounted into a eucentric goniometer. Preliminary precession and cone-axis photographs indicated that the crystal was of excellent quality and possessed C_{2h} $(2/m)$ Laue symmetry. The crystal was transferred to our Syntex $P2_1$ automated diffractometer. Crystal alignment, determination of orientation matrix and accurate cell dimensions, and data collection were all carried out as described previously.[15] Details specific to the present analysis appear in Table I. A survey of the complete data set revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$; the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) is uniquely indicated.

All crystallographic computations were carried out using our in-house Syntex XTL system, including the XTL interactive crystallographic program package[16] as modified by our research group at S.U.N.Y. at Buffalo.

Data were corrected for absorption ($\mu = 47.3$ cm^{-1}) by an empirical method, based on a series of ψ scans.[13] The reflections used to obtain the normalized absorption curves, their 2θ values, and their maximum:minimum intensity ratios were as follows: 051 [$2\theta = 14.93°$, max:min = 1.310:1], 060 [17.72°, 1.291:1], and 080 [23.70°, 1.265:1].

Redundant and equivalent data were averaged ($R(I) = 1.03\%$) 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 $|F_o| = 0$. Esd's, $\sigma_c(|F_o|)$, were based upon the larger of (i) the value propagated from $|F_o|^2$ and $\sigma\{|F_o|^2\}$ by finite differences or (ii) the internal esd obtained by averaging symmetry-equivalent reflections.

(B) Solution and Refinement of the Structure. The analytical form[17a] of the scattering factors for neutral tantalum, chlorine, phosphorus, carbon, and hydrogen was used throughout the analysis; both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion[17b] were applied to all nonhydrogen atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized during least-squares refinement. Here, the weights (w) are as defined in eq 1; p, the "ignorance factor", was set at a value

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

of 0.01. The discrepancy indices, R_F and R_{wF}, and the "goodness of fit" (GOF) are described by eq 2–4 (in eq 4, NO = number of

$$R_F = \left[\frac{\sum||F_o| - |F_c||}{\sum|F_o|}\right] \times 100\ (\%) \tag{2}$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%) \tag{3}$$

$$\mathrm{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\mathrm{NO} - \mathrm{NV}}\right]^{1/2} \tag{4}$$

observations and NV = number of variables refined).

Data were placed on an approximate absolute scale via a Wilson plot, which also provided the overall isotropic thermal parameter, $\bar{B}$ = 3.03 Å. Interpretation of a three-dimensional Patterson map led to the location of tantalum, chlorine, and phosphorus atoms. Full-matrix least-squares refinement of the scale factor and positional and isotropic thermal parameters for the TaP_2Cl moiety (17 parameters in all) led to $R_F = 15.4\%$ and $R_{wF} = 21.0\%$ after three cycles. Difference-Fourier syntheses and full-matrix least-squares refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms (244 parameters in all) converged with $R_F = 4.5\%$, $R_{wF} = 4.4\%$, and GOF = 2.02. A second difference-Fourier synthesis now revealed the presence of all hydrogen atoms other than those associated with the methyl groups of the highly librating η^5-C_5Me_5 ligand. Attempted refinement of the located hydrogen atoms was unsatisfactory, so these were included in the model in idealized positions with d(C–H) = 0.95 Å,[18] with either external-bisecting geometry (phenyl hydrogens) or perfectly staggered geometry (phosphine hydrogens), and with isotropic thermal parameters of 7.0 Å^2 (phenyl hydrogens) or 8.0 Å^2 (phosphine hydrogens). Hydrogen atoms of the η^5-C_5Me_5 ligand were not located and are indeterminate with respect to rotation about their C(ring)–CH_3 axes; these were not included in our model. (However, see discussion below.)

Table II. Final Positional and Isotropic Thermal Parameters (with Esd's) for $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$

atom	x	y	z	B, Å^2
Ta	0.28359 (3)	0.26367 (2)	0.09882 (2)	
Cl	0.36228 (23)	0.21456 (17)	0.23662 (11)	
P(1)	0.17838 (23)	0.39035 (16)	0.16974 (13)	
P(2)	0.24237 (22)	0.08070 (16)	0.09901 (14)	
C(1)	0.1131 (7)	0.2571 (5)	0.0437 (4)	
C(2)	−0.0146 (7)	0.2560 (5)	−0.0093 (4)	
C(3)	−0.0268 (7)	0.2381 (6)	−0.0868 (4)	
C(4)	−0.1445 (8)	0.2429 (6)	−0.1377 (5)	
C(5)	−0.2565 (8)	0.2654 (6)	−0.1147 (5)	
C(6)	−0.2489 (8)	0.2804 (6)	−0.0391 (6)	
C(7)	−0.1309 (7)	0.2758 (6)	0.0122 (5)	
C(11)	0.0681 (9)	0.3307 (7)	0.2206 (5)	
C(12)	0.0722 (9)	0.4795 (6)	0.1126 (6)	
C(13)	0.2737 (10)	0.4651 (7)	0.2446 (6)	
C(21)	0.1174 (10)	0.0546 (7)	0.1492 (6)	
C(22)	0.1787 (9)	0.0203 (6)	0.0100 (6)	
C(23)	0.3684 (11)	−0.0043 (7)	0.1442 (7)	
C(31)	0.4012 (8)	0.2533 (7)	−0.0009 (4)	
C(32)	0.4973 (8)	0.2404 (6)	0.0674 (5)	
C(33)	0.5111 (8)	0.3281 (8)	0.1100 (5)	
C(34)	0.4193 (9)	0.3955 (6)	0.0677 (6)	
C(35)	0.3537 (8)	0.3503 (7)	0.0007 (5)	
C(36)	0.3704 (12)	0.1860 (9)	−0.0685 (6)	
C(37)	0.5856 (11)	0.1496 (8)	0.0868 (7)	
C(38)	0.6111 (10)	0.3460 (11)	0.1831 (6)	
C(39)	0.4151 (13)	0.5023 (7)	0.0872 (8)	
C(40)	0.2599 (9)	0.4024 (9)	−0.0642 (7)	
H(3)	0.0491	0.2222	−0.1044	7.0
H(4)	−0.1484	0.2303	−0.1895	7.0
H(5)	−0.3375	0.2705	−0.1502	7.0
H(6)	−0.3260	0.2941	−0.0219	7.0
H(7)	−0.1287	0.2864	0.0640	7.0
H(11A)	0.0295	0.3779	0.2467	8.0
H(11B)	0.1160	0.2858	0.2557	8.0
H(11C)	0.0017	0.2974	0.1856	8.0
H(12A)	0.0390	0.5223	0.1446	8.0
H(12B)	0.1205	0.5152	0.0834	8.0
H(12C)	0.0017	0.4473	0.0798	8.0
H(13A)	0.2170	0.5071	0.2635	8.0
H(13B)	0.3191	0.4247	0.2841	8.0
H(13C)	0.3346	0.5023	0.2251	8.0
H(21A)	0.1027	−0.0132	0.1489	8.0
H(21B)	0.1443	0.0766	0.1997	8.0
H(21C)	0.0390	0.0865	0.1252	8.0
H(22A)	0.1684	−0.0467	0.0187	8.0
H(22B)	0.2377	0.0285	−0.0221	8.0
H(22C)	0.0964	0.0474	−0.0132	8.0
H(23A)	0.3347	−0.0683	0.1383	8.0
H(23B)	0.3950	0.0105	0.1964	8.0
H(23C)	0.4412	0.0005	0.1215	8.0

A survey of the data set now showed that a correction for secondary extinction was necessary. A correction of the form shown in eq 5 was

$$F_o(\mathrm{cor}) = (1.0 + gI_o)(F_o(\mathrm{uncor})) \tag{5}$$

made. The variable g was determined (by least-squares analysis of $|F_o|$ and $|F_c|$ values for intense reflections) to have a value of 1.8×10^{-7}. (We note here that the worst disagreement between $|F_o|$ and $|F_c|$ *before correction* was for the 020 reflection for which $|F_c|/|F_o| = 1.256$; this ratio is improved to 1.083 in our final model.)

Three more cycles of full-matrix least-squares refinement led to final convergence [$(\Delta/\sigma)_{\max} = 0.02$] with $R_F = 4.1\%$, $R_{wF} = 3.5\%$, and GOF = 1.61 for those 3140 reflections with $|F_o| > \sigma(|F_o|)$. The ratio NO:NV was 3140:244 or 12.87:1. The final residuals, including "unobserved" data (3386 total reflections), were $R_F = 4.8\%$, $R_{wF} = 3.5\%$, and GOF = 1.61.

The largest peak on a final difference-Fourier synthesis was of height 0.9 e Å^{-3} and was close to a methyl carbon of the η^5-C_5Me_5 system. The structure is thus complete. The function $\sum w(|F_o| - |F_c|)^2$ showed no significant dependence on $|F_o|$, $(\sin\theta)/\lambda$, sequence number, or identity or parity of the Miller indices; the weighting scheme is thus satisfactory.

Final positional and thermal parameters are collected in Tables II and III.

Table III. Final Anisotropic Thermal Parameters (Å^2) for Ta(η^5-C$_5$Me$_5$)(CPh)(PMe$_3$)$_2$Cl^a

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta	3.164 (15)	3.307 (15)	2.494 (14)	−0.019 (14)	0.651 (10)	0.178 (13)
Cl	6.75 (13)	6.28 (12)	2.96 (3)	−0.16 (10)	0.40 (9)	0.79 (9)
P(1)	4.39 (12)	4.66 (11)	3.47 (11)	−0.19 (9)	1.19 (9)	−0.65 (9)
P(2)	4.56 (12)	3.63 (10)	4.84 (12)	−0.16 (8)	0.68 (10)	0.43 (9)
C(1)	5.2 (4)	2.2 (3)	3.5 (3)	0.44 (30)	2.27 (30)	0.67 (28)
C(2)	3.2 (3)	2.8 (3)	3.9 (4)	0.07 (28)	0.51 (28)	0.75 (30)
C(3)	3.6 (4)	4.8 (4)	4.1 (4)	0.1 (3)	0.44 (30)	−0.8 (4)
C(4)	4.4 (4)	6.2 (5)	4.7 (4)	0.4 (4)	−0.2 (4)	−0.7 (4)
C(5)	3.8 (4)	4.4 (4)	6.0 (5)	−0.4 (4)	−0.7 (4)	0.3 (4)
C(6)	3.2 (4)	4.8 (4)	6.7 (5)	0.3 (3)	1.3 (4)	0.8 (4)
C(7)	3.4 (4)	4.9 (4)	5.1 (4)	−0.2 (3)	1.3 (3)	0.6 (4)
C(11)	5.8 (5)	7.4 (6)	5.7 (5)	−0.4 (4)	3.0 (4)	−1.0 (4)
C(12)	4.7 (5)	4.7 (5)	8.1 (7)	0.6 (4)	2.0 (5)	−0.3 (4)
C(13)	7.1 (6)	6.3 (5)	6.3 (6)	−0.6 (4)	2.4 (5)	−2.4 (5)
C(21)	7.3 (7)	5.4 (5)	7.4 (7)	−2.2 (4)	2.4 (5)	0.2 (4)
C(22)	5.6 (5)	5.1 (5)	7.3 (6)	−0.7 (4)	1.3 (5)	−0.9 (4)
C(23)	7.4 (7)	4.5 (5)	11.2 (9)	0.1 (4)	−0.3 (6)	2.3 (5)
C(31)	5.7 (5)	6.2 (5)	3.4 (4)	−1.0 (4)	2.4 (3)	0.6 (4)
C(32)	4.0 (4)	6.0 (5)	4.9 (4)	0.4 (4)	2.5 (3)	1.4 (4)
C(33)	4.0 (5)	8.3 (6)	3.4 (4)	−1.2 (4)	1.5 (4)	−0.2 (4)
C(34)	4.2 (5)	5.1 (5)	6.9 (6)	−0.9 (4)	3.2 (4)	0.4 (4)
C(35)	3.0 (4)	6.7 (5)	4.1 (5)	−0.6 (4)	0.7 (3)	2.5 (4)
C(36)	12.1 (9)	10.1 (8)	5.6 (6)	−4.7 (7)	5.1 (6)	−3.9 (6)
C(37)	7.4 (7)	9.4 (7)	13.2 (10)	5.2 (6)	6.5 (7)	6.4 (7)
C(38)	5.9 (6)	19.1 (12)	4.9 (6)	−5.2 (7)	−0.1 (5)	−0.8 (7)
C(39)	14.1 (10)	3.4 (5)	17.2 (12)	−2.2 (5)	11.2 (10)	−1.4 (6)
C(40)	3.8 (5)	14.0 (9)	9.7 (8)	−0.0 (5)	−0.4 (5)	8.8 (7)

^{a} The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-{}^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

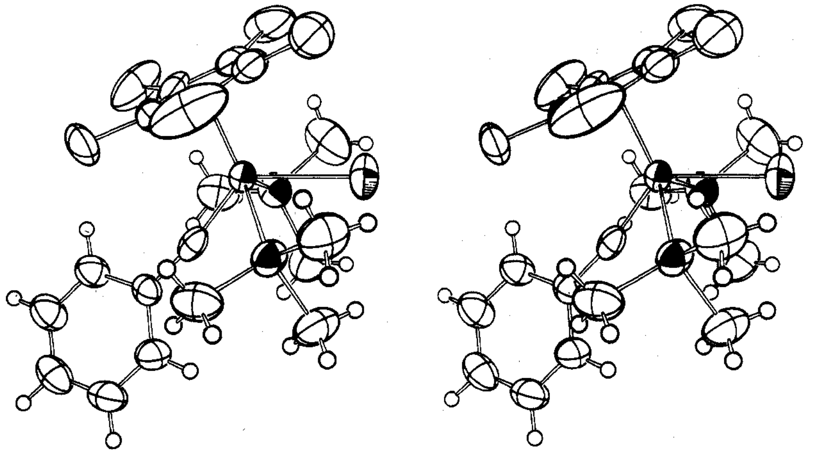


Figure 1. Stereoscopic view of the Ta(η^5-C$_5$Me$_5$)(CPh)(PMe$_3$)$_2$Cl molecule (ORTEP-II diagram; 50% ellipsoids for all nonhydrogen atoms).

Results and Discussion

Intramolecular distances and their esd's are listed in Table IV, while interatomic angles (with esd's) are given in Table V. Least-squares planes, and deviations of atoms therefrom, are collected in Table VI. The overall molecular geometry is shown as a stereoscopic view in Figure 1. The molecule consists of a central tantalum atom linked to an η^5-pentamethylcyclopentadienyl ring, an η^1-benzylidyne ligand, a chloride ligand, and two trimethylphosphine ligands. The immediate coordination geometry about the tantalum atom resembles a four-legged piano stool, as shown in Figure 2. The centroid of the pentaatomic carbocyclic ring (designated "Cp") is almost symmetrically disposed relative to the monodentate ligands, individual angles being ∠(Cp–Ta–C(1)) = 121.21°, ∠(Cp–Ta–Cl) = 113.25°, ∠(Cp–Ta–P(1)) = 116.33°, and ∠(Cp–Ta–P(2)) = 117.63°. Among the monodentate ligands the two "pseudo-trans" angles (see Figure 3) are equivalent with ∠(C(1)–Ta–Cl) = 125.54 (22)° and ∠(P(1)–Ta–P(2)) = 125.41 (7)°. The "pseudo-cis" angles are similarly symmetrical, with ∠(C(1)–Ta–P(1)) = 80.29 (22)°, ∠(C(1)–Ta–P(2)) = 78.96 (22)°, ∠(Cl–Ta–P(1)) = 76.66 (7)°, and ∠(Cl–Ta–P(2)) = 75.76 (7)°.

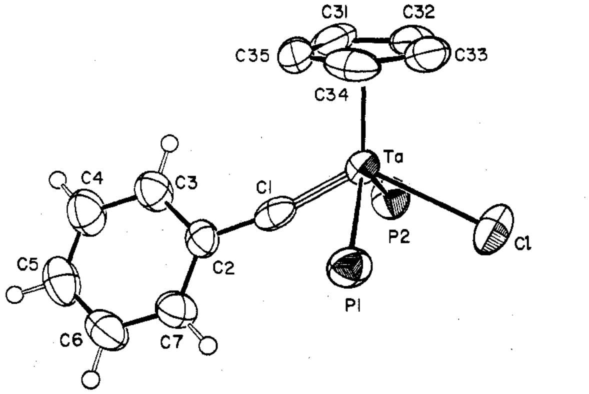


Figure 2. Coordination geometry about tantalum in the Ta(η^5-C$_5$Me$_5$)(CPh)(PMe$_3$)$_2$Cl molecule. Methyl groups are eliminated for clarity.

Table IV. Intramolecular Distances (Å), with Esd's, for $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$

(A) Distances from the Tantalum Atom			
Ta-C(1)	1.849 (8)	Ta-C(31)	2.417 (8)
Ta-P(1)	2.567 (2)	Ta-C(32)	2.460 (8)
Ta-P(2)	2.565 (2)	Ta-C(33)	2.518 (9)
Ta-Cl	2.548 (2)	Ta-C(34)	2.455 (9)
Ta-Cp[a]	2.128	Ta-C(35)	2.397 (9)
(B) Distances within Benzylidyne Ligand			
C(1)-C(2)	1.467 (10)	C(5)-C(6)	1.375 (14)
C(2)-C(3)	1.408 (10)	C(6)-C(7)	1.375 (12)
C(3)-C(4)	1.370 (12)	C(7)-C(2)	1.392 (11)
C(4)-C(5)	1.371 (12)		
(C) Phosphorus-Carbon Distances			
P(1)-C(11)	1.832 (10)	P(2)-C(21)	1.795 (11)
P(1)-C(12)	1.822 (10)	P(2)-C(22)	1.810 (10)
P(1)-C(13)	1.819 (10)	P(2)-C(23)	1.823 (11)
(D) Distances within C_5Me_5 Ligand			
C(31)-C(32)	1.426 (12)	C(31)-C(36)	1.517 (14)
C(32)-C(33)	1.429 (13)	C(32)-C(37)	1.554 (14)
C(33)-C(34)	1.434 (13)	C(33)-C(38)	1.518 (14)
C(34)-C(35)	1.404 (13)	C(34)-C(39)	1.521 (13)
C(35)-C(31)	1.433 (13)	C(35)-C(40)	1.537 (15)

[a] Cp is the centroid of the pentaatomic ring defined by atoms C(31)→C(35).

Table V. Interatomic Angles (deg), with Esd's, for $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$

(A) Angles around the Tantalum Atom			
C(1)-Ta-Cl	125.54 (22)	Cp-Ta-C(1)	121.21
P(1)-Ta-P(2)	125.41 (07)	Cp-Ta-Cl	113.25
C(1)-Ta-P(1)	80.29 (22)	Cp-Ta-P(1)	116.33
C(1)-Ta-P(2)	78.96 (22)	Cp-Ta-P(2)	117.63
Cl-Ta-P(1)	76.66 (07)		
Cl-Ta-P(2)	75.76 (07)		
(B) Angles within the Benzylidyne Ligand			
Ta-C(1)-C(2)	171.75 (56)	C(3)-C(4)-C(5)	120.80 (81)
C(1)-C(2)-C(3)	121.65 (64)	C(4)-C(5)-C(6)	118.57 (82)
C(1)-C(2)-C(7)	123.05 (66)	C(5)-C(6)-C(7)	120.75 (81)
C(3)-C(2)-C(7)	115.26 (67)	C(6)-C(7)-C(2)	122.33 (75)
C(2)-C(3)-C(4)	122.24 (73)		
(C) Angles within the PMe_3 Ligands			
Ta-P(1)-C(11)	109.83 (32)	C(11)-P(1)-C(12)	102.46 (44)
Ta-P(1)-C(12)	116.88 (32)	C(12)-P(1)-C(13)	101.96 (45)
Ta-P(1)-C(13)	122.38 (33)	C(13)-P(1)-C(11)	100.51 (45)
Ta-P(2)-C(21)	109.98 (34)	C(21)-P(2)-C(22)	101.25 (46)
Ta-P(2)-C(22)	118.80 (32)	C(22)-P(2)-C(23)	101.08 (48)
Ta-P(2)-C(23)	121.97 (37)	C(23)-P(2)-C(21)	100.51 (50)
(D) Interior Angles of the C_5Me_5 Ligand			
C(35)-C(31)-C(32)	106.3 (7)	C(33)-C(34)-C(35)	108.5 (8)
C(31)-C(32)-C(33)	109.4 (8)	C(34)-C(35)-C(31)	109.2 (8)
C(32)-C(33)-C(34)	106.6 (8)		
(E) Exterior C-C-C Angles of the C_5Me_5 Ligand			
C(36)-C(31)-C(35)	125.3 (8)	C(38)-C(33)-C(34)	127.9 (9)
C(36)-C(31)-C(32)	127.6 (8)	C(39)-C(34)-C(33)	123.8 (9)
C(37)-C(32)-C(31)	124.8 (8)	C(39)-C(34)-C(35)	126.8 (9)
C(37)-C(32)-C(33)	125.4 (8)	C(40)-C(35)-C(34)	124.4 (9)
C(38)-C(33)-C(32)	125.4 (9)	C(40)-C(35)-C(31)	126.0 (8)

Table VI. Least-Squares Planes and Atomic Deviations (Å) Therefrom, for $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$[a,b]

(A) Plane of Phenyl Group			
$0.1788X + 0.9744Y - 0.1363Z - 3.4360 = 0$			
C(2)*	0.011 (6)	Ta	0.3358 (3)
C(3)*	−0.008 (8)	Cl	−0.610 (2)
C(4)*	−0.006 (9)	P(1)	1.620 (2)
C(5)*	0.015 (8)	P(2)	−2.205 (2)
C(6)*	−0.007 (8)	C(1)	0.099 (6)
C(7)*	−0.008 (8)		
(B) Cyclopentadienyl Plane			
$0.8273X + 0.3192Y - 0.4622Z - 4.6126 = 0$			
C(31)*	0.004 (9)	C(36)	0.221 (12)
C(32)*	−0.007 (8)	C(37)	0.136 (12)
C(33)*	0.008 (9)	C(38)	0.112 (12)
C(34)*	−0.005 (10)	C(39)	0.205 (14)
C(35)*	0.000 (9)	C(40)	0.165 (11)
Ta	−2.1257 (3)	P(1)	−3.302 (2)
Cl	−3.251 (2)	P(2)	−3.293 (2)
C(1)	−3.001 (7)		
(C) Dihedral Angle			
$A/B = 58.53°$ (121.47°)			

[a] Equations are in orthonormal coordinates. [b] Atoms marked with an asterisk (only) are used in calculating the least-squares planes.

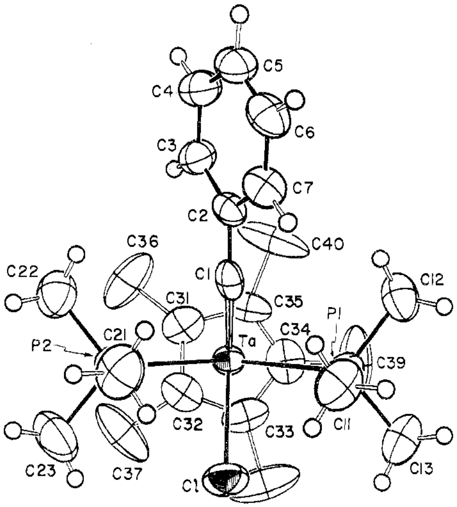


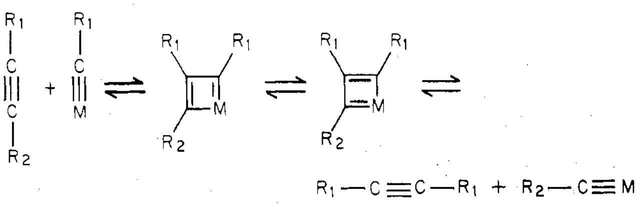
Figure 3. The $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$ molecule projected onto the plane defined by the pentaatomic carbocyclic ring.

The tantalum–chlorine bond length of 2.548 (2) Å suggests that the covalent radius of tantalum in this class of compound is about 1.56 Å (based upon $r(Cl) = 0.99$ Å).[19] This suggests that a tantalum–alkyl distance should be approximately 2.33 Å ($r(Ta) = 1.56$ Å and $r(C(sp^3)) = 0.77$ Å)[20] in this class of compound. The tantalum–methyl distance observed in $(\eta^5\text{-}C_5H_5)_2Ta({=}CH_2)(CH_3)$ is rather shorter than this, with Ta–Me = 2.246 (12) Å,[8] while the tantalum–benzyl linkage in $(\eta^5\text{-}C_5H_5)_2Ta({=}CHC_6H_5)(CH_2C_6H_5)$[3] is 2.30 (1) Å in length.

The known tantalum–alkylidene distances are 2.030 (6) Å for the tantalum–neopentylidene bond in $(\eta^5\text{-}C_5H_5)_2Ta({=}CHCMe_3)Cl$,[12,13] 2.026 (10) Å for the tantalum–methylene linkage in $(\eta^5\text{-}C_5H_5)_2Ta({=}CH_2)(CH_3)$,[8] and 2.07 (1) Å for the tantalum–benzylidene linkage in $(\eta^5\text{-}C_5H_5)_2Ta({=}CHC_6H_5)(CH_2C_6H_5)$.[3]

The tantalum–benzylidyne linkage, Ta–C(1), in the present $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$ molecule is reduced to 1.849 (8) Å—some 0.181 (10) Å shorter than the tantalum–neopentylidene double bond in $(\eta^5\text{-}C_5H_5)_2Ta({=}CHCMe_3)Cl$ and 0.397 (14) Å shorter than the tantalum–methyl single bond in $(\eta^5\text{-}C_5H_5)_2Ta({=}CH_2)(CH_3)$. The Ta–C(1)–C(2) angle in the present molecule is 171.75 (56)°, the system being bent very slightly with C(2) being displaced from collinearity with the Ta–C(1) vector such that it lies closer to the $\eta^5\text{-}C_5Me_5$ system than it would if it remained collinear with the Ta–C(1) vector. The reason for the bend in the Ta–C(1)–C(2) system is not at all clear. There are no abnormally short *intra-* or *inter*molecular contacts involving this group. For comparison, the tantalum–neopentylidyne (i.e., $Ta{\equiv}C$) bond length in $[(Me_3CCH_2)_3Ta{\equiv}CCMe_3]Li(dmp)$[10] is 1.76 (2) Å, the three tantalum–neopentyl (Ta–C(sp³)) bond lengths are 2.18 (2), 2.26 (2), and 2.26 (2) Å, and the $Ta{\equiv}C{-}C$ angle is 165 (1)°; the bend in this last angle is attributed in this molecule to an

Scheme I



intramolecular C(α)···Li$^+$ interaction (d(C···Li) = 2.19 (3) Å).

The phenyl group of the benzylidyne ligand has a root-mean-square deviation from planarity of 0.011 Å. There is a very slight distortion away from true planarity and toward a "boat" conformation. Thus the mutually para atoms C(2) and C(5) lie +0.011 (6) and +0.015 (8) Å from the least-squares plane, whereas all other atoms are displaced in the opposite direction, individual atomic deviations being −0.008 (8) Å for C(3), −0.006 (9) Å for C(4), −0.007 (8) Å for C(6), and −0.008 (8) Å for C(7). It should be stressed, however, that these deviations from planarity are each, individually, on the borderline of statistical significance. Atoms C(1) and Ta lie +0.099 (6) and +0.3358 (3) Å, respectively, from the plane of the phenyl ring.

Carbon–carbon distances within the phenyl ring range from 1.370 (12) to 1.408 (10) Å, the average value being 1.382 [15] Å.[21] Angles within the phenyl ring show substantial deviations from D_{6h} symmetry and indicate the lower C_{2v} (or even C_s—vide supra) symmetry. The internal angle at C(2), ∠C(3)–C(2)–C(7), is reduced to 115.26 (67)°, and the angle at the para carbon is ∠C(4)–C(5)–C(6) = 118.57 (82)°; angles at the ortho carbon atoms [∠C(2)–C(3)–C(4) = 122.24 (73)° and ∠C(6)–C(7)–C(2) = 122.33 (75)°] and at the meta carbon atoms [∠C(3)–C(4)–C(5) = 120.80 (81)° and ∠C(5)–C(6)–C(7) = 120.75 (81)°] are internally consistent and are, presumably, increased from the ideal trigonal value of 120.00° principally to compensate for the compression at C(2).

Deviations from the ideal value (120°) of the internal angle (α) of the unique externally bound carbon atom of a phenyl group have been discussed in detail by Domenicano, Vaciago, and Coulson.[22] In the absence of major conjugative interactions, a small (i.e., < 120°) value for α is indicative of a relatively electropositive substitutent. However, chemical studies show that an external nucleophile will attack a metal–alkylidyne complex *at the metal*.[23] The carbyne carbon is believed to be subject to electrophilic attack as is the carbene carbon in metal–alkylidene complexes. The observed deviations of the phenyl ring from idealized D_{6h} geometry must therefore be interpreted as evidence for significant conjugative interactions within the Ta≡C–C_6H_5 system.

The C(1)–C(2) distance of 1.467 (10) Å appears to be slightly longer than expected for a normal C(sp)–C(sp^2) single bond. (The predicted value is 1.432 Å, on the basis of covalent radii of 0.7415 Å for sp^2-hybridized carbon and 0.6905 Å for sp-hybridized carbon.)[24]

The relative orientations of the η^5-pentamethylcyclopentadienyl ligand and the set of four monodentate ligands is shown clearly in Figure 3. Individual tantalum–carbon bonding distances are (cyclically, around the ring) Ta–C(31) = 2.417 (8) Å, Ta–C(32) = 2.460 (8) Å, Ta–C(33) = 2.518 (9) Å, Ta–C(34) = 2.455 (9) Å, and Ta–C(35) = 2.397 (9) Å. The shortest two distances involve the atoms lying below (in Figure 3) the carbyne atom C(1); it seems probable that the inequivalence of the Ta–C(cyclopentadienyl) distances results from a "tipping" of the η^5-C_5Me_5 system to minimize C(cyclopentadienyl)···(monodentate ligand) repulsive interactions.

The pentaatomic carbocyclic ring defined by atoms C(31) through C(35) has a root-mean-square deviation from planarity of 0.006 Å—i.e., is strictly planar within the limits of experimental error. The tantalum atom lies −2.1257 (3) Å from this plane. The five methyl groups are each displaced from the cyclopentadienyl ring, being *bent away from the tantalum atom*; individual deviations are +0.221 (12) Å for C(36), +0.136 (12) Å for C(37), +0.112 (12) Å for C(38), +0.205 (14) Å for C(39), and +0.165 (11) Å for C(40). Individual carbon–carbon distances within the cyclopentadienyl ring range from C(34)–C(35) = 1.404 (13) Å to C(33)–C(34) = 1.434 (13) Å; the mean value is 1.425 [12] Å.[21] As can clearly be seen in Figure 3 and from Table III, the η^5-C_5Me_5 ligand is undergoing substantial librational motion about its metal–(ring centroid) axis. This eliminates the possibility of locating the methyl hydrogen atoms by direct crystallographic methods. Nevertheless, previous experience with structural studies of the η^5-C_5Me_5-containing complexes [(η^5-C_5Me_5)RhCl]$_2$(μ-H)(μ-Cl)[25] and (η^5-C_5Me_5)Ta(C_6H_4)(CH_3)$_2$[26] suggests that each methyl group will take up a rotational conformation such that one hydrogen atom points essentially perpendicularly above the open face of the cyclopentadienyl plane.

The two tantalum–phosphine bond lengths are Ta–P(1) = 2.567 (2) Å and Ta–P(2) = 2.565 (2) Å. The phosphorus atoms have the usual distorted tetrahedral coordination geometry, with Ta–P–C angles ranging from 109.83 (32) through 122.38 (33)°, averaging 116.6 [56]°, and with C–P–C angles varying only from 100.51 (50) through 102.46 (44)°, averaging 101.30 [78]°.

Finally, we point out that the present structural study may yield information relevant to the metathesis of acetylenes, a process which has been suggested[27,28] to involve a metal carbyne intermediate (see Scheme I). However, we should emphasize that more structural and chemical information will be required before the details of the metathesis reaction are revealed unequivocally.

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Registry No. Ta(η^5-C_5Me_5)(CPh)(PMe_3)$_2$Cl, 68307-57-3.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Palladium(II) and Platinum(II) Complexes with Nucleobases and Nucleosides. Crystal Structure of *trans*-Bis(adeninato)bis(tri-*n*-butylphosphine)palladium(II)

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The synthesis and degradation of the dinuclear and tetranuclear complexes $[L(n\text{-}Bu_3P)MCl]_2$ and $[Cl_2(n\text{-}Bu_3P)M(L)M(P\text{-}n\text{-}Bu_3)Cl]_2$ [M = Pd(II), Pt(II)] with the anion of adenine (L) have been studied. A series of complexes *trans*-$(n\text{-}Bu_3P)_2PdL_2$ and $[L(n\text{-}Bu_3P)PdCl]_n$ with L = adeninate, cytosinate, guaninate, guanosinate, inosinate, theophyllinate, thyminate, uracilate, and uridinate, as well as adenosine-bridged complexes $Cl_2(n\text{-}Bu_3P)M$–adenosine–$M(P\text{-}n\text{-}Bu_3)Cl_2$ [M = Pd,Pt], have been synthesized. The spectroscopic data of the new complexes are reported. Crystals of *trans*-$(n\text{-}Bu_3P)_2Pd(\text{adeninate})_2{\cdot}4CH_3OH$ are triclinic (space group $P\bar{1}$) with the cell parameters a = 10.993 (2) Å, b = 11.945 (2) Å, c = 10.140 (2) Å, α = 105.36 (1)°, β = 91.80 (1)°, and γ = 93.16 (1)°. The structure was refined to R_1 = 0.045 and R_2 = 0.051. The X-ray structure determination shows that adeninate is coordinated via N(9) and that the purine rings are virtually orthogonal to the coordination plane P_2PdN_2. The colorless crystals are stabilized by hydrogen bonds between the oxygen atoms of the methanol molecules and N(3) and N(7) of adenine. Intermolecular hydrogen bonding is observed between the amino group $N(6)H_2$ and N″(1). Thus, with the exception of the metalated N(9) atom all of the adeninate N atoms are involved in hydrogen bonding.

As a result of the antitumor activity of some transition-metal complexes,[2] considerable interest has been shown in the design of model complexes which could mimic the interaction of metal ions with DNA.[2-4] A number of studies have established that the nucleobases are the preferred sites of attack by *cis*-diammine platinum(II) compounds.[2] As a continuation of our previous studies on the preparation and isolation of a number of metal complexes with nucleobases and nucleosides,[5] we report new palladium and platinum complexes and reactions thereof. An X-ray structure determination of a palladium(II) complex with anionic adenine has been carried out.

Preparative Results

We have particularly studied the reactions of chloro-bridged $[Pd(PBu_3)Cl_2]_2$ with adenine. One of our aims in this chemistry was to prepare palladium and platinum compounds which contain complementary nucleobases in cis or trans positions, $[L_2M(\text{nucleobase})(\text{nucleobase}')]$. Such compounds could be considered as a simple model for a cross-linking system where the metal bridges two DNA strands. Cross-linking of DNA strands is one of the likely mechanisms for the antineoplastic properties of Pt(II) complexes.[2]

For this purpose the tetranuclear and binuclear palladium adeninate complexes Ia and IIa[5] have been reacted with phosphines in order to produce monomeric compounds of the type $(R_3P)_2PdClL$ (L = adeninate) which could be further treated with another anionic nucleobase L′ to give the desired complexes $(R_3P)_2PdLL'$.

The synthesis and degradation of monomeric, dimeric, and tetranuclear adeninate palladium complexes are summarized in Scheme I, where L is the anion of adenine.

By reaction of the chloro-bridged complex $[n\text{-}Bu_3PPdCl_2]_2$ with an excess of potassium adeninate all chloro ligands could be replaced by adeninate giving V.[5] V was also obtained from IIa with adeninate. An analogous complex both with terminal and bridging anionic heterocycles has previously been described with triazolate.[6]

The reaction of IIa with phosphine yields the monomeric bis(adeninate) complex IVa and *trans*-$Cl_2Pd(PBu_3)_2$. Obviously the expected complex $Cl(L)Pd(PBu_3)_2$ (III) is not stable and disproportionates to IVa and $Cl_2Pd(PBu_3)_2$.

Similarly, the tetranuclear platinum compound $[Pt_2(PBu_3)_2LCl_3]_2$ (Ib) prepared by the same method as described for Ia[5] reacts with phosphines to give dimeric $L(Bu_3P)PtCl_2Pt(PBu_3)L$ (IIb) and *cis*-$Cl_2Pt(PBu_3)_2$. The trans and cis structures of $Cl_2Pd(PBu_3)_2$ and $Cl_2Pt(PBu_3)_2$, respectively, are established by their infrared spectra. The trans complex shows only one (350 cm^{-1}) ν(M–Cl) stretching band, while the cis compound shows two ν(M–Cl) stretching bands (280, 305 cm^{-1}).

Disproportionation has also been observed when IIa was reacted with tributylphosphine in the presence of the second nucleobase thyminate (L′) to give IVa and IVf.

Further monomeric and chloro-bridged complexes of the type $L_2Pd(PBu_3)_2$ and $[L(Cl)PdPBu_3]_n$ have been obtained by nucleophilic substitution of chloride by an anionic nucleobase L^-:

$$\textit{trans}\text{-}Cl_2Pd(PBu_3)_2 \xrightarrow[-2Cl^-]{2L^-} \underset{\text{IV}}{\textit{trans}\text{-}L_2Pd(PBu_3)_2}$$

$$[Cl_2Pd(PBu_3)]_2 \xrightarrow[Cl^-]{L^-} \underset{\text{II}}{[L(Bu_3P)PdCl]_n}$$

complex		L	complex		L
IIa	IVa	adeninate	IIf	IVf	thyminate
	IVb	theophillinate		IVg	uracilate
IIc	IVc	guanosinate		IVh	uridinate
IId	IVd	inosinate		IVi	guaninate
IIe	IVe	cytosinate			

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