Crystal Structure and Molecular Geometry of Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$, a Mononuclear Tantalum–Benzyne Complex

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(η^2-Benzyne)(η^5-pentamethylcyclopentadienyl)dimethyltantalum, Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$, previously prepared by Schrock and co-workers by thermolysis of Ta(η^5-C$_5$Me$_5$)(η^1-C$_6$H$_5$)Me$_3$, has been subjected to a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (C_i^1; No. 2) with a = 8.8789 (12) Å, b = 9.2365 (14) Å, c = 11.3174 (18) Å, α = 71.769 (12)°, β = 76.101 (12)°, γ = 73.142 (11)°, V = 832.2 (2) Å^3, and Z = 2. Diffraction data were collected with a Syntex $P2_1$ diffractometer using Mo Kα radiation. The structure was solved via a combination of Fourier, Patterson, and least-squares refinement techniques. All atoms (including all hydrogen atoms) were located and refined, the final discrepancy indices being R_F = 2.5% and R_{wF} = 2.0% for all 3836 reflections with 4° < 2θ < 55°. The central tantalum atom is linked to an η^5-C$_5$Me$_5$ ligand (Ta–C = 2.408 (3)–2.500 (4) Å), two methyl groups (Ta–Me = 2.169 (6) and 2.181 (6) Å), and an "η^2-C$_6$H$_4$" ligand (Ta–C(1) = 2.059 (4) Å and Ta–C(2) = 2.091 (4) Å). The orientation of the η^2-C$_6$H$_4$ group (essentially perpendicular to the η^5-C$_5$Me$_5$ ligand and with its plane bisecting the Me–Ta–Me angle) and the detailed carbon–carbon bond lengths within the hexaatomic carbocyclic ring are discussed in relation to its formulation as a benzyne ligand.

Introduction

We have recently become interested in the detailed molecular geometry of tantalum complexes of small unsaturated organic fragments[1] and have reported the results of X-ray structural studies on a tantalum–alkylidene complex [Ta-(η^5-C$_5$H$_5$)$_2$(=CHCMe$_3$)Cl],[2,3] a tantalum–benzylidyne complex [Ta(η^5-C$_5$Me$_5$)(≡CPh)(PMe$_3$)$_2$Cl],[4,5] and a tantalum–bis(neopentylidene) complex [Ta(=CHCMe$_3$)$_2$-(mesityl)(PMe$_3$)$_2$].[6] We now report a single-crystal X-ray diffraction study of the tantalum–benzyne complex Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$.

There have previously been reports of a C$_6$H$_4$ ligand bridging two iridium atoms (see I)[7] and of a C$_6$F$_4$ ligand

I

II
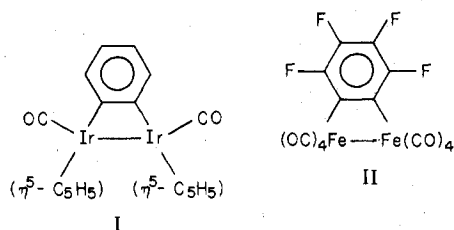
bridging two iron atoms (see II);[8] in each of these cases, however, the ligand behaves as an *o*-phenylene group. A similar situation pertains to the C$_6$H$_4$ units in the [Pt$_4$-(C$_6$H$_4$)$_2$Cl$_{14}$]$^{2-}$ anion (see III).[9]

III
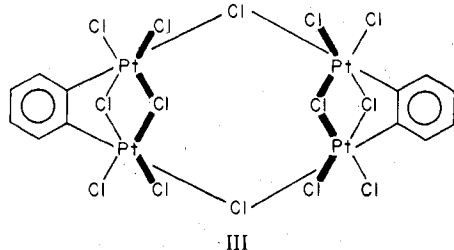
The reaction of Os$_3$(CO)$_{12}$ with PPh$_3$ (under forcing conditions) yields a variety of complexes, among which is that of stoichiometry Os$_3$(CO)$_7$(PPh$_2$)$_2$(C$_6$H$_4$) in which the C$_6$H$_4$ moiety now clearly behaves as a benzyne system, being linked to all three atoms of the triosmium cluster as is shown in IV.[10]

IV
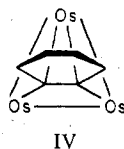
To the best of our knowledge, the present structural study provides the first example of a benzyne ligand stabilized by complexation to a single transition-metal atom. An account of the method of synthesis and preliminary details of the molecular geometry of Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$ have appeared earlier.[11]

Experimental Section

A. Collection and Processing of the X-ray Diffraction Data. A crystalline sample of Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$ was provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. The complex forms clear-brown columnar parallelepipeds, which are usually extended along their *c* axes. The material may be handled in air for short periods but decomposes to an amorphous white powder after some 10–20-h exposure to the atmosphere.

A well-formed crystal of approximate dimensions 0.10 × 0.12 × 0.43 mm was carefully wedged into a 0.1-mm diameter thin-walled glass capillary, which was then purged with argon, flame-sealed, fixed into an aluminum pin with beeswax, and mounted into a eucentric goniometer. Preliminary Weissenberg, precession, and cone-axis photographs (Mo Kα) indicated that the crystal was of excellent quality (data visible out to 2θ = 55°) and possessed only C_i ($\bar{1}$) Laue symmetry. The crystal was transferred to our Syntex $P2_1$ automated diffractometer. Crystal alignment, determination of unit cell parameters, and data collection were all carried out as described previously;[12] details are presented in Table I.

All calculations were performed using our Syntex XTL in-house structure-solving package as modified by our research group at S.U.N.Y. at Buffalo.[13] Data were corrected for absorption (μ = 69.5 cm^{-1}) by an empirical method based upon a two-parameter (2θ and ϕ) interpolation between a series of normalized ψ scans of close-to-axial (i.e., χ = 90 ± 10°) reflections.[14] The reflections used, their 2θ values, and their maximum:minimum intensity variation around ψ were as follows: 0$\bar{1}$2, 10.04°, 1.186:1; 0$\bar{2}$3, 16.80°, 1.211:1; 1$\bar{2}$5, 24.01°, 1.171:1; 1$\bar{3}$6, 30.77°, 1.163:1.

Redundant data were averaged [$R(I)$ = 1.21% for 249 averaged pairs] 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.

B. Solution and Refinement of the Structure. The analytical form of the scattering factors[15a] for neutral tantalum, carbon, and hydrogen were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion[15b] were introduced for all nonhydrogen atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized during least-squares refinement; an "ignorance factor" (p) of 0.01 was used throughout the analysis. All crystallographic formulas are available as and are defined in the supplementary material.

Data were converted to an (approximate) absolute scale by use of a Wilson plot, which also provided the overall isotropic thermal parameter ($\bar{B}$ = 2.92 Å^2). Interpretation of a three-dimensional Patterson map led to the location of the tantalum atom. Refinement of the scale factor along with the positional and isotropic thermal
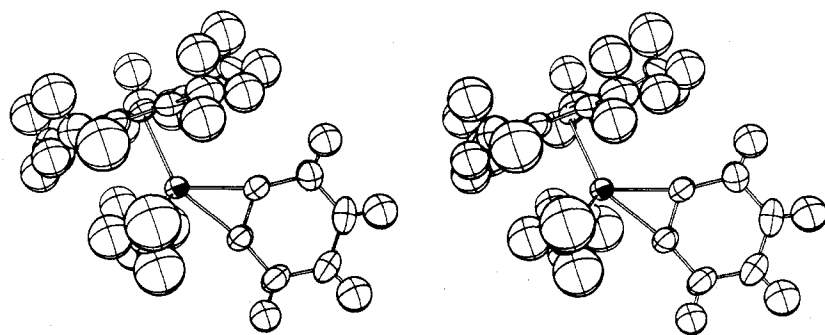
Figure 1. Stereoscopic view of the $Ta(\eta^5-C_5Me_5)(\eta^2-C_6H_4)Me_2$ molecule. The 50% probability contours are shown for the atomic vibrations of all atoms, *including* hydrogen atoms (ORTEP-II diagram).

Table I. Experimental Data for the X-ray Diffraction Study of $Ta(\eta^5-C_5Me_5)(\eta^2-C_6H_4)Me_2$

(A) Crystal Parameters at 26 °C

crystal system: triclinic $\alpha = 71.769\ (12)°$
space group: $P\bar{1}$ $\beta = 76.101\ (12)°$
mol wt 422.35 $\gamma = 73.142\ (11)°$
$a = 8.8789\ (12)$ Å[a] $V = 832.2\ (2)$ Å^3
$b = 9.2365\ (14)$ Å $Z = 2$
$c = 11.3174\ (18)$ Å $\rho(calcd) = 1.685$ g cm^{-3}

(B) Collection of Intensity Data

radiation: Mo $K\alpha$ ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite, $2\theta_{mono} = 12.2°$, equatorial mode
reflections measd: $+h, \pm k, \pm l$
scan type: coupled θ(crystal)–2θ(counter)
2θ range: 4.0–55.0°
scan speed: 2.0°/min in 2θ
scan width: $[2\theta(\text{Mo } K\alpha_1) - 0.9]° - [2\theta(\text{Mo } K\alpha_2) + 0.9]°$
bgd measurement: stationary-crystal, stationary-counter at beginning and end of each scan, each for one-fourth of the time taken for the scan
standard reflections: 600, 060, 006; these were measured after each 97 reflections
reflections collected: 4085 total, yielding 3836 symmetry-independent data (3692 observed reflections, with $I > 0$)
absorption coeff: $\mu = 69.5$ cm^{-1}

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo $K\bar{\alpha}$ components of 24 reflections of the forms $\{2\bar{1}6\}$, $\{2\bar{1}5\}$, $\{1\bar{1}6\}$, $\{116\}$, $\{151\}$, $\{\bar{1}61\}$, $\{15\bar{1}\}$, $\{15\bar{2}\}$, $\{6\bar{2}2\}$, $\{5\bar{1}1\}$, $\{5\bar{1}2\}$, and $\{6\bar{1}\bar{1}\}$, all with 2θ between 20 and 30°.

parameters of the tantalum atom (five parameters only) converged with $R_F = 14.6\%$, $R_{wF} = 19.6\%$, and GOF = 12.44. A difference-Fourier synthesis now yielded the positions of all 18 carbon atoms. Continued refinement of positional and isotropic thermal parameters for all nonhydrogen atoms (77 parameters) led to $R_F = 7.1\%$, $R_{wF} = 8.1\%$, and GOF = 4.73. The introduction of anisotropic thermal parameters for all nonhydrogen atoms (172 parameters) resulted in convergence with $R_F = 3.1\%$, $R_{wF} = 3.2\%$, and GOF = 2.09. A second difference-Fourier synthesis now quickly and unambiguously revealed the locations of all 25 hydrogen atoms in the molecule. Further refinement, including positional and isotropic thermal parameters for all hydrogen atoms (272 parameters in all), led to convergence with $R_F = 2.6\%$, $R_{wF} = 2.2\%$, and GOF = 1.41. A careful survey of the data provided unequivocal evidence that a correction for secondary extinction was mandatory. This was done by using the approximation shown in eq 1. The value of g was determined, graphically, to be 8.5 × 10^{-6}.

$$F_o^{cor} = (1.0 + gI_o)F_o^{uncor} \qquad (1)$$

Five more cycles of full-matrix least-squares refinement led to final convergence $[(\Delta/\sigma)_{max} = 0.02]$ with $R_F = 2.5\%$, $R_{wF} = 2.0\%$, and GOF = 1.30 for all 3836 reflections (*none rejected*) and $R_F = 2.1\%$ and $R_{wF} = 2.0\%$ for those 3559 reflections with $|F_o|/\{\sigma(F_o)\} > 3.0$. The data-to-parameter ratio was 14.1:1. The largest peak on a third and final difference-Fourier synthesis was of height 0.5 e Å^{-3} and was close to the position of atom C(11). The structure is thus complete. The usual tests of the residual $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, $(\sin \theta)/\lambda$,

Table II. Final Positional and Isotropic Thermal Parameters for $Ta(\eta^5-C_5Me_5)(\eta^2-C_6H_4)Me_2$

atom	x	y	z	B, Å^2
Ta	0.33112 (1)	0.25809 (1)	0.23307 (1)	
C(1)	0.5757 (4)	0.1884 (4)	0.2175 (3)	
C(2)	0.5289 (4)	0.1106 (4)	0.1534 (3)	
C(3)	0.6419 (5)	−0.0003 (4)	0.0958 (4)	
C(4)	0.7979 (5)	−0.0271 (5)	0.1063 (4)	
C(5)	0.8462 (5)	0.0549 (5)	0.1706 (4)	
C(6)	0.7371 (4)	0.1635 (5)	0.2269 (4)	
C(11)	0.2642 (9)	0.3751 (8)	0.0483 (5)	
C(12)	0.2258 (7)	0.0551 (6)	0.3121 (7)	
C(21)	0.0988 (4)	0.4569 (4)	0.3064 (3)	
C(22)	0.2308 (4)	0.5261 (3)	0.2574 (3)	
C(23)	0.3490 (4)	0.4464 (4)	0.3332 (3)	
C(24)	0.2927 (4)	0.3241 (4)	0.4296 (3)	
C(25)	0.1361 (4)	0.3331 (4)	0.4145 (3)	
C(31)	−0.0596 (6)	0.5099 (7)	0.2621 (6)	
C(32)	0.2363 (8)	0.6737 (5)	0.1519 (5)	
C(33)	0.5012 (5)	0.4961 (6)	0.3230 (5)	
C(34)	0.3788 (7)	0.2109 (6)	0.5331 (4)	
C(35)	0.0216 (7)	0.2425 (7)	0.5078 (5)	
H(3)	0.611 (4)	−0.065 (4)	0.052 (3)	5.1 (9)
H(4)	0.883 (5)	−0.105 (5)	0.068 (4)	6.4 (10)
H(5)	0.955 (5)	0.029 (5)	0.171 (4)	6.2 (10)
H(6)	0.778 (5)	0.206 (5)	0.280 (4)	5.7 (9)
H(11A)	0.220 (7)	0.300 (7)	0.028 (6)	9.1 (16)
H(11B)	0.169 (6)	0.459 (6)	0.041 (5)	8.7 (14)
H(11C)	0.326 (9)	0.383 (9)	−0.011 (7)	13.3 (28)
H(12A)	0.124 (7)	0.069 (6)	0.335 (2)	9.1 (16)
H(12B)	0.239 (9)	0.007 (9)	0.399 (8)	14.3 (29)
H(12C)	0.269 (8)	−0.016 (8)	0.271 (6)	12.1 (21)
H(31A)	−0.120 (6)	0.605 (7)	0.283 (5)	9.7 (15)
H(31B)	−0.046 (7)	0.580 (7)	0.165 (7)	11.2 (19)
H(31C)	−0.085 (6)	0.448 (7)	0.239 (5)	8.7 (17)
H(32A)	0.207 (6)	0.762 (6)	0.185 (5)	8.8 (14)
H(32B)	0.176 (6)	0.680 (6)	0.089 (5)	9.0 (15)
H(32C)	0.344 (8)	0.663 (7)	0.109 (6)	11.1 (20)
H(33A)	0.547 (5)	0.523 (5)	0.229 (5)	7.2 (12)
H(33B)	0.579 (6)	0.406 (6)	0.377 (5)	8.0 (13)
H(33C)	0.475 (6)	0.601 (7)	0.350 (6)	10.9 (17)
H(34A)	0.368 (6)	0.110 (7)	0.550 (5)	8.8 (15)
H(34B)	0.354 (5)	0.253 (5)	0.603 (5)	7.8 (13)
H(34C)	0.496 (6)	0.205 (5)	0.501 (4)	7.2 (12)
H(35A)	0.093 (8)	0.132 (8)	0.547 (6)	12.2 (21)
H(35B)	−0.050 (6)	0.236 (5)	0.462 (4)	6.9 (13)
H(35C)	−0.047 (6)	0.308 (5)	0.567 (5)	9.2 (15)

sequence number, and identity or parity class of the Miller indices indicated that the weighting scheme is satisfactory.

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

Results and Discussion

Intramolecular distances and their estimated standard deviations (esd's) are listed in Table IV; interatomic angles (with esd's) are given in Table V. A stereoscopic view of the entire molecule is shown in Figure 1. The scheme used for labeling atoms is illustrated in Figure 2. The molecule consists of a central tantalum atom linked to an η^5-pentamethyl-

Table III. Anisotropic Thermal Parameters[a] (in A²) for the Nonhydrogen Atoms in $Ta(\eta^5-C_5Me_5)(\eta^2-C_6H_4)Me_2$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta	2.883 (5)	2.850 (6)	3.301 (6)	−0.306 (4)	−0.688 (4)	−1.278 (4)
C(1)	3.49 (14)	3.34 (13)	3.53 (14)	−0.54 (11)	−0.20 (11)	−1.31 (11)
C(2)	3.66 (4)	3.41 (14)	4.03 (15)	−0.16 (11)	−0.81 (12)	−1.38 (12)
C(3)	4.56 (18)	3.97 (16)	4.82 (18)	0.31 (13)	−0.74 (14)	−1.94 (14)
C(4)	4.04 (17)	4.43 (18)	4.67 (18)	0.62 (14)	−0.35 (14)	−1.40 (15)
C(5)	2.93 (15)	5.92 (21)	5.02 (19)	−0.24 (15)	−0.27 (14)	−0.79 (16)
C(6)	3.62 (16)	5.84 (21)	5.24 (19)	−1.23 (14)	−0.56 (14)	−2.03 (16)
C(11)	8.22 (32)	7.21 (30)	4.53 (22)	3.09 (26)	−3.05 (23)	−3.09 (21)
C(12)	4.87 (23)	4.92 (22)	10.34 (41)	−2.31 (18)	0.67 (24)	−3.64 (26)
C(21)	3.39 (14)	3.25 (14)	4.32 (16)	−0.09 (11)	−0.41 (12)	−1.79 (12)
C(22)	4.20 (15)	2.39 (12)	3.49 (14)	−0.44 (11)	−0.15 (11)	−0.98 (10)
C(23)	3.48 (13)	3.51 (14)	3.71 (14)	−1.08 (11)	−0.11 (11)	−1.89 (11)
C(24)	4.42 (15)	3.29 (13)	3.00 (13)	−0.70 (12)	−0.60 (11)	−1.21 (11)
C(25)	4.29 (16)	3.54 (14)	4.14 (16)	−1.42 (12)	0.47 (12)	−1.55 (12)
C(31)	3.92 (19)	6.10 (26)	9.02 (36)	0.59 (18)	−1.99 (20)	−3.68 (26)
C(32)	7.79 (30)	3.68 (18)	5.00 (22)	−1.26 (19)	−0.72 (21)	−0.50 (16)
C(33)	5.07 (21)	6.40 (25)	6.18 (24)	−2.69 (19)	−0.46 (18)	−2.94 (20)
C(34)	7.15 (29)	5.48 (24)	4.13 (19)	−0.58 (20)	−2.08 (19)	−1.17 (17)
C(35)	6.40 (27)	6.85 (29)	5.64 (24)	−3.70 (23)	1.86 (21)	−2.23 (22)

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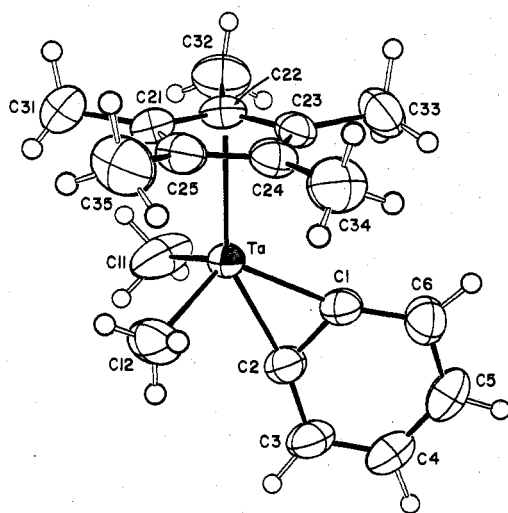

Figure 2. Labeling of atoms within the $Ta(\eta^5-C_5Me_5)(\eta^2-C_6H_4)Me_2$ molecule. Hydrogen atoms are shown with artificially reduced thermal parameters for the sake of clarity (ORTEP-II diagram; 50% ellipsoids for nonhydrogen atoms).

cyclopentadienyl ligand, an $\eta^2-C_6H_4$ (or "benzyne") ligand, and two methyl groups.

These four ligands take up a pseudotetrahedral geometry about the tantalum atom. Angles between Cp (the centroid of the cyclopentadienyl ring), Bz (the midpoint of the C(1)–C(2) linkage), and the two methyl groups are as follows: Cp–Ta–Bz = 133.52°, Cp–Ta–C(11) = 106.72°, Cp–Ta–C(12) = 107.56°, Bz–Ta–C(11) = 100.45°, Bz–Ta–C(12) = 98.83°, C(11)–Ta–C(12) = 107.72 (26)°.

The tantalum–methyl bond lengths observed in $Ta(\eta^5-C_5Me_5)(\eta^2-C_6H_4)Me_2$, Ta–C(11) = 2.169 (6) Å and Ta–C(12) = 2.181 (6) Å [average 2.175 ± 0.008 Å],[16] are substantially shorter than the Ta–C(sp³) bond distances found in $Ta(\eta^5-C_5H_5)_2(=CH_2)Me$[17] (Ta–Me = 2.246 (12) Å) and $Ta(\eta^5-C_5H_5)_2(=CHPh)(CH_2Ph)$[18] (Ta–CH₂Ph = 2.30 (1) Å) but are comparable to the shortest of the Ta–CH₂CMe₃ linkages found in $Ta(CH_2CMe_3)_3(\equiv CCMe_3)Li(dmp)$[19] (dmp = *N*,-*N*′-dimethylpiperazine; Ta–CH₂CMe₃ = 2.18 (2), 2.26 (2), and 2.26 (2) Å; Ta–CH₂CMe₃(av) = 2.23 ± 0.05 Å[16]).

The carbon atoms of the cyclopentadienyl system vary in their distance from the tantalum atom—Ta–C(21) = 2.500 (4) Å, Ta–C(22) = 2.455 (3) Å, Ta–C(23) = 2.411 (3) Å, Ta–C(24) = 2.408 (3) Å, and Ta–C(25) = 2.486 (4) Å. The

Table IV. Intramolecular Distances with Esd's for $Ta(\eta^5-C_5Me_5)(\eta^2-C_6H_4)Me_2$ (A)

(A) Distances from the Tantalum Atom

Ta–C(1)	2.059 (4)	Ta–C(21)	2.500 (4)
Ta–C(2)	2.091 (4)	Ta–C(22)	2.455 (3)
Ta–C(11)	2.169 (6)	Ta–C(23)	2.411 (3)
Ta–C(12)	2.181 (6)	Ta–C(24)	2.408 (3)
Ta–Cp[a]	2.137 (−)	Ta–C(25)	2.486 (4)
Ta–Bz[b]	1.960 (−)		

(B) Distances within the η^2–Benzyne Ligand

C(1)–C(2)	1.364 (5)		
C(2)–C(3)	1.410 (5)		
C(3)–C(4)	1.362 (6)	C(3)–H(3)	1.02 (4)
C(4)–C(5)	1.403 (6)	C(4)–H(4)	1.00 (4)
C(5)–C(6)	1.375 (6)	C(5)–H(5)	0.93 (5)
C(6)–C(1)	1.408 (6)	C(6)–H(6)	1.00 (4)

(C) Carbon–Hydrogen Distances within the Methyl Ligands

C(11)–H(11A)	1.00 (6)	C(12)–H(12A)	0.86 (7)
C(11)–H(11B)	0.97 (6)	C(12)–H(12B)	0.96 (8)
C(11)–H(11C)	0.75 (8)	C(12)–H(12C)	0.87 (7)

(D) Distances within the Pentamethylcyclopentadienyl System

C(21)–C(22)	1.411 (5)	C(21)–C(31)	1.502 (7)
C(22)–C(23)	1.403 (5)	C(22)–C(32)	1.509 (6)
C(23)–C(24)	1.418 (5)	C(23)–C(33)	1.517 (6)
C(24)–C(25)	1.417 (5)	C(24)–C(34)	1.499 (6)
C(25)–C(21)	1.419 (5)	C(25)–C(35)	1.507 (7)
C(31)–H(31A)	0.95 (6)	C(34)–H(34A)	0.92 (6)
C(31)–H(31B)	1.09 (7)	C(34)–H(34B)	0.94 (5)
C(31)–H(31C)	0.80 (6)	C(34)–H(34C)	1.01 (6)
C(32)–H(32A)	0.95 (6)	C(35)–H(35A)	1.06 (7)
C(32)–H(32B)	0.97 (6)	C(35)–H(35B)	0.94 (5)
C(32)–H(32C)	0.95 (7)	C(35)–H(35C)	1.01 (6)
C(33)–H(33A)	1.02 (5)		
C(33)–H(33B)	1.05 (5)		
C(33)–H(33C)	1.05 (6)		

[a] Cp is the centroid of the carbocyclic ring defined by C(21) through C(25). [b] Bz is the midpoint of the C(1)–C(2) bond.

five atoms of the carbocyclic ring are, nevertheless, close to coplanar (the root-mean-square deviation from planarity is only 0.009 Å—see Table VI). The tantalum atom lies +2.1346 (1) Å from the plane of the cyclopentadienyl system. The methyl groups of the $\eta^5-C_5Me_5$ ligand are each displaced from the plane of the carbocyclic ring in a direction *away from* the tantalum atom; individual deviations vary significantly: −0.083 (7) Å for C(31), −0.146 (5) Å for C(32), −0.187 (6) Å for C(33), −0.014 (5) Å for C(34), and −0.220 (6) Å for C(35). The greatest displacements involve C(35) (which is in an eclipsed conformation relative to the methyl group centered

Table V. Selected Interatomic Angles with Esd's for Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$ (deg)

(A) Angles around the Tantalum Atom

C(1)-Ta-C(2)	38.36 (13)	Cp-Ta-C(1)	114.21 (-)
C(1)-Ta-C(11)	110.05 (21)	Cp-Ta-C(2)	152.49 (-)
C(1)-Ta-C(12)	110.32 (20)	Cp-Ta-C(11)	106.72 (-)
C(2)-Ta-C(11)	90.15 (21)	Cp-Ta-C(12)	107.56 (-)
C(2)-Ta-C(12)	86.89 (20)	Bz-Ta-C(11)	100.45 (-)
C(11)-Ta-C(12)	107.72 (26)	Bz-Ta-C(12)	98.83 (-)
Cp^a-Ta-Bz^b	133.52 (-)		

(B) Angles within the "η^2-Benzyne" Ligand

Ta-C(1)-C(2)	72.11 (21)	Ta-C(2)-C(1)	69.53 (20)
Ta-C(1)-C(6)	166.09 (29)	Ta-C(2)-C(3)	169.76 (29)
C(6)-C(1)-C(2)	121.75 (33)	C(3)-C(4)-C(5)	121.26 (39)
C(1)-C(2)-C(3)	120.45 (33)	C(4)-C(5)-C(6)	121.05 (40)
C(2)-C(3)-C(4)	118.20 (37)	C(5)-C(6)-C(1)	117.27 (38)
H(3)-C(3)-C(2)	123.1 (22)	H(5)-C(5)-C(4)	114.6 (28)
H(3)-C(3)-C(4)	118.6 (22)	H(5)-C(5)-C(6)	124.3 (28)
H(4)-C(4)-C(3)	121.3 (26)	H(6)-C(6)-C(1)	125.8 (24)
H(4)-C(4)-C(5)	117.4 (26)	H(6)-C(6)-C(5)	116.4 (24)

(C) Angles within the Methyl Ligands

Ta-C(11)-H(11A)	105.3 (26)	Ta-C(12)-H(12A)	119.4 (41)
Ta-C(11)-H(11B)	119.0 (33)	Ta-C(12)-H(12B)	111.2 (51)
Ta-C(11)-H(11C)	121.4 (64)	Ta-C(12)-H(12C)	111.8 (49)

(D) Internal C-C-C Angles within the Pentamethylcyclopentadienyl System

C(25)-C(21)-C(22)	107.62 (30)	C(23)-C(24)-C(25)	107.48 (30)
C(21)-C(22)-C(23)	108.51 (30)	C(24)-C(25)-C(21)	108.08 (31)
C(22)-C(23)-C(24)	108.28 (29)		

(E) External C-C-C Angles of the Pentamethylcyclopentadienyl System

C(25)-C(21)-C(31)	124.63 (37)	C(24)-C(23)-C(33)	126.00 (34)
C(22)-C(21)-C(31)	127.55 (37)	C(23)-C(24)-C(34)	126.57 (35)
C(21)-C(22)-C(32)	125.77 (35)	C(25)-C(24)-C(34)	125.88 (35)
C(23)-C(22)-C(32)	125.30 (35)	C(24)-C(25)-C(35)	125.38 (37)
C(22)-C(23)-C(33)	125.31 (34)	C(21)-C(25)-C(35)	125.99 (37)

(F) C-C-H Angles in the Pentamethylcyclopentadienyl System

C(21)-C(31)-H(31A)	110.9 (37)	C(23)-C(33)-H(33C)	110.5 (34)
C(21)-C(31)-H(31B)	109.3 (36)	C(24)-C(34)-H(34A)	113.7 (36)
C(21)-C(31)-H(31C)	116.4 (43)	C(24)-C(34)-H(34B)	109.6 (32)
C(22)-C(32)-H(32A)	110.5 (34)	C(24)-C(34)-H(34C)	106.4 (29)
C(22)-C(32)-H(32B)	110.5 (35)	C(25)-C(35)-H(35A)	105.3 (39)
C(22)-C(32)-H(32C)	106.9 (41)	C(25)-C(35)-H(35B)	106.8 (31)
C(23)-C(33)-H(33A)	106.1 (28)	C(25)-C(35)-H(35C)	109.1 (33)
C(23)-C(33)-H(33B)	109.8 (29)		

^{a} Cp is the centroid of the carbocyclic ring defined by atoms C(21) through C(25). ^{b} Bz is the centroid of the C(1)-C(2) linkage within the η^2-C$_6$H$_4$ ligand.

on C(12)) and C(33) (which lies asymmetrically below the benzyne ligand); the smallest displacement involves C(34) which has no close intramolecular contacts. These interactions are clearly shown in Figure 3.

It is interesting to note that the longest Ta–C bond distance is for Ta–C(21), i.e., the linkage trans to the η^2-C$_6$H$_4$ ligand. While there may be some electronic significance to this observation, one cannot discount the possibility that it is brought about principally by the repulsion between C(12) and C(35) (vide supra).

Carbon–carbon bond lengths within the η^5-C$_5$Me$_5$ ligand are normal, with C(ring)–C(ring) distances ranging from 1.403 (5) to 1.419 (5) Å [average 1.414 ± 0.007 Å] and C(ring)–Me distances ranging from 1.499 (6) to 1.517 (6) Å [average 1.507 ± 0.007 Å]. Carbon–hydrogen distances range from 0.80 (6) to 1.09 (7) Å, averaging 0.98 ± 0.07 Å, in good agreement with the value of 0.95 Å expected[20] for an "X-ray determined" C–H bond length. The rotational conformation taken up by the methyl groups is such that one hydrogen atom of each methyl group lies above the plane of the cyclopentadienyl ligand, pointing away from the tantalum atom. This can be seen from Figures 1 and 2; numerical data are available in Table VI (section B).

We turn now to a consideration of the η^2-C$_6$H$_4$ system and of the Ta–(η^2-C$_6$H$_4$) bonding. The most likely valence-bond structures for the Ta–(η^2-C$_6$H$_4$) bonding are shown as Va,b and VI. Structures Va,b are the two principal canonical forms
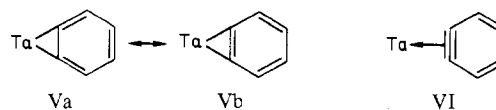
corresponding to the o-phenylene structure, while structure VI is the extreme form of the acetylenic benzyne structure. (It is worth noting that a better description of the metal-bound acetylenic ligand is given by a linear combination of VI and Vb, the contribution of form Vb usually being dictated by the amount of metal–acetylene back-donation; however, vide infra.) In any of these forms, the tantalum atom in Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$ has only 14 outer valence electrons—i.e., the metal atom is highly electron deficient. A survey of bond distances within the Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$ molecule suggests some favoring of canonical structure Vb; this does not, however, help in deciding between the o-phenylene or benzyne formalisms. Thus, carbon–carbon bond distances within the η^2-C$_6$H$_4$ ligand show a pattern of D_{3h} symmetry—the possible D_{6h} symmetry is broken by a slight, but unmistakable, alternation in bond length around the system: C(1)–C(2) = 1.364 (5) Å, C(3)–C(4) = 1.362 (6) Å, C(5)–C(6) = 1.375 (6) Å [average 1.367 ± 0.007 Å], vs.

Table VI. Least-Squares Planes and Atomic Deviations Therefrom for Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$ (Å)

(A) Benzyne Plane: $0.1412X + 0.5172Y - 0.8442Z - 0.1208 = 0$

C(1)^a	−0.007 (3)	C(11)	1.725 (6)
C(2)^a	0.004 (3)	C(12)	−1.775 (7)
C(3)^a	0.003 (4)	H(3)	−0.05 (4)
C(4)^a	−0.008 (4)	H(4)	−0.02 (4)
C(5)^a	0.003 (4)	H(5)	0.01 (4)
C(6)^a	0.006 (4)	H(6)	−0.11 (4)
Ta	−0.0783 (1)		

(B) Cyclopentadienyl Plane:
$0.0616X - 0.8097Y - 0.5836Z + 5.7039 = 0$

C(21)^a	0.005 (3)	C(31)	−0.083 (7)
C(22)^a	0.002 (3)	C(32)	−0.146 (5)
C(23)^a	−0.008 (3)	C(33)	−0.187 (6)
C(24)^a	0.011 (3)	C(34)	−0.014 (5)
C(25)^a	−0.011 (3)	C(35)	−0.220 (6)
Ta	2.1346 (1)	C(11)	2.822 (7)
C(1)	2.886 (3)	C(12)	2.837 (7)
C(2)	3.939 (3)	H(33B)	0.35 (5)
H(31A)	−0.95 (6)	H(33C)	−1.15 (6)
H(31B)	0.25 (7)	H(34A)	0.54 (6)
H(31C)	0.53 (6)	H(34B)	−0.91 (5)
H(32A)	−1.05 (6)	H(34C)	0.36 (5)
H(32B)	0.30 (6)	H(35A)	0.26 (7)
H(32C)	0.35 (7)	H(35B)	0.16 (5)
H(33A)	0.43 (5)	H(35C)	−1.20 (6)

(C) $0.1144X + 0.5438Y - 0.8314Z - 0.0383 = 0$

Ta^a	0.000	C(2)^a	0.000
C(1)^a	0.000		

(D) $0.5878X - 0.6953Y - 0.4136Z + 0.5675 = 0$

Ta^a	0.000	C(12)^a	0.000
C(11)^a	0.000		

Dihedral Angles (deg)

plane A/plane B	85.27	plane B/plane C	87.03
plane A/plane C	2.28	plane B/plane D	32.80
plane A/plane D	85.84	plane C/plane D	88.11

^{a} Atoms used in calculating plane.
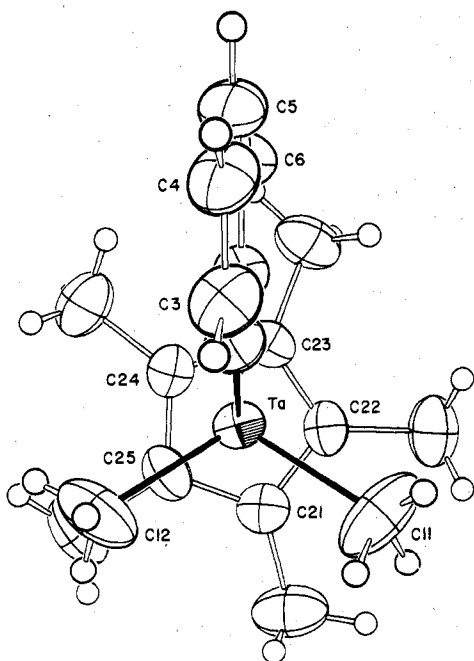
Figure 3. The Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$ molecule, projected onto the plane of the cyclopentadienyl ligand (ORTEP-II diagram; 50% vibration ellipsoids for nonhydrogen atoms; hydrogen atoms shown with artificially reduced thermal parameters).

C(2)–C(3) = 1.410 (5) Å, C(4)–C(5) = 1.403 (6) Å, C(6)–C(1) = 1.408 (6) Å [average 1.407 ± 0.004 Å]. Note

that the C(1)–C(2) bond length is indistinguishable from the C(3)–C(4) and C(5)–C(6) distances.

The Ta–C(1) and Ta–C(2) distances (2.059 (4) and 2.091 (4) Å, respectively; average 2.075 ± 0.023Å) are significantly (i.e., approximately 0.10 Å) shorter than the tantalum–methyl bonds in the molecule. However, this is precisely the difference between iron–(σ-vinyl) and iron–(σ-alkyl) distances found in Fe(η^5-C$_5$H$_5$)(CO)$_2$R complexes.[21,22]

A comparison of niobium–ethyl and niobium–ethylene linkages in the more closely related species Nb(η^5-C$_5$H$_5$)$_2$-(C$_2$H$_5$)(C$_2$H$_4$)[23] shows a Nb–C$_2$H$_5$ bond length of 2.316 (8) Å as compared to Nb–C(ethylene) distances of 2.277 (9) and 2.320 (9) Å [average 2.299 ± 0.021 Å].

Other physical methods lead to the same point of equivocation: ^{1}H and ^{13}C NMR studies[11] of Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$ indicate that the η^2-C$_6$H$_4$ ligand is rotating rapidly about the Ta–Bz bond in solution, with $\Delta G^* \leq 9$ kcal mol^{-1}. Such rotation is well established for acetylene ligands on transition metals[24] and also occurs for ethylene in Ta(η^5-C$_5$Me$_5$)(C$_2$H$_4$)Cl$_2$.[25] However, tantalacyclopentane complexes[26] and simple alkyl complexes such as Ta(η^5-C$_5$Me$_5$)Me$_3$Cl[25] also pseudorotate with fairly low barriers (ΔG^* = 10–15 kcal mol^{-1}); one therefore cannot entirely discount the possibility of an *o*-phenylene ring becoming involved in pseudorotation.

Our preference for the η^2-C$_6$H$_4$ ligand's being regarded as a benzyne ligand (rather than as an *o*-phenylene complex) comes from a consideration of the relative juxtaposition of ligands in the solid-state structure. Here, the η^2-C$_6$H$_4$ ligand makes an angle of 2.28° with the Ta–C(1)–C(2) plane and lies at an angle of 85.27° with respect to the η^5-cyclopentadienyl system and at an angle of 85.84° to the C(11)–Ta–C(12) plane. If the η^2-C$_6$H$_4$ ligand is regarded as a benzyne ligand, then the coordination about tantalum may be regarded as of the "three-legged piano stool" variety—i.e., the expected geometry for any simple M(η^5-C$_5$H$_5$)L$_3$ complex. If, on the other hand, the η^2-C$_6$H$_4$ ligand is regarded as an *o*-phenylene ligand and is bonded to the tantalum atom via two independent σ bonds, one is left with the unanswered question: Why does this system not adopt the "four-legged piano stool" geometry common to all known M(η^5-C$_5$H$_5$)L$_4$ complexes (i.e., with the C(1)–C(2) linkage *parallel* to the η^5-C$_5$Me$_5$ ring and the C(11)···C(12) vector)?

In the benzyne approximation, one may assume that the perpendicular geometry allows maximum overlap of the benzyne's π orbitals with both empty σ-acceptor (primarily) and π-acceptor (secondarily) orbitals on the electron-deficient metal atom. This would certainly act so as to stabilize the complex. Within this framework, however, the equality of the C(1)–C(2) bond length with those of C(3)–C(4) and C(5)–C(6) occurs fortuitously.

There have been previous structural studies on complexes in which a coordinated acetylene is incorporated in a six-membered carbocyclic ring. Among these are (i) a cyclohexyne complex of platinum(0) [Pt(cyclohexyne)(PPh$_3$)$_2$], in which 16-electron complex the acetylene linkage is 1.289 (17) Å[27] in length, and (ii) a perfluorocyclohex-1-yn-3-ene complex of cobalt(0) [Co$_2$(CO)$_6$(C$_6$F$_6$)], in which the acetylenic linkage is 1.29 Å in length.[28]

Finally, it should be noted that a recent structural study of Ta(η^5-C$_5$H$_5$)(η^2-C$_2$H$_4$)Cl$_2$ has shown that the C=C bond of the ethylene ligand in this complex lies *parallel* with the η^5-C$_5$H$_5$ ligand and the Cl···Cl vector.[29]

Supplementary Material Available: A listing of crystallographic data processing formulas and observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Migration of Triphenylboron from Iron to an η⁵-Cyclopentadienyl Ligand

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Triphenylborane and $(C_2H_5)_4N^+(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ form a 1:1 adduct $Ph_3BFe(CO)_2Cp^-NEt_4^+$, **1**. Analyses of spectroscopic data (IR, ¹H NMR, and ¹¹B NMR) from **1** and the analogous $(n\text{-}C_4H_9)_4N^+$ salt, including comparisons with $Ph_3BOCH_3^-NEt_4^+$ and $Ph_3AlFe(CO)_2Cp^-NEt_4^+$, strongly indicate the presence of an iron-to-boron bond and suggest that the negative charge is localized on the boron atom. In dilute tetrahydrofuran solutions, **1** spontaneously converted to $Ph_3BC_5H_4Fe_2$-$(CO)_4Cp^-NEt_4^+\cdot^1/_2THF$, **2**, and $Ph_3BH^-NEt_4^+$, **3**. From X-ray diffraction analysis, the crystal structure of **2** was refined to $R = 0.097$ in $C2/c$ with $a = 40.357$ (6) Å, $b = 9.943$ (2) Å, $c = 20.453$ (2) Å, and $\beta = 111.72$ (1)° with $Z = 8$. Partial disorder in the cation required two-state parameterization. The anion consists of a central di-μ-carbonyl-diiron unit (Fe–Fe = 2.540 (2) Å) with a terminal carbonyl and an η⁵-cyclopentadienyl ligand on each metal atom; the configuration of the rings is cis. The nearly tetrahedral Ph₃B group is η¹ bonded to one of the rings at the position farthermost from the other ring. The bonding geometry around the iron atoms is essentially that found in *cis*-[CpFe(CO)₂]₂. In acetone, the conductivity of **2** is similar to that of $Ph_4B^-NEt_4^+$. The IR spectra of **2** in dimethyl sulfoxide and in methylene chloride show different intensities of corresponding ν(CO), indicative of a cis–trans isomer distribution. Compound **3** is identical with $Ph_3BH^-NEt_4^+$ prepared from Ph₃B and KH followed by metathesis with $Et_4N^+Br^-$. The single B–H bond in **3** was identified from the stretching frequency of 2198 ± 1 cm⁻¹, observed by Raman and infrared spectroscopy and from ¹H and ¹¹B NMR spectroscopy. A prominent absorption at 2136 cm⁻¹ seen only in the infrared was assigned as a combination band. A mechanism is proposed for the conversion of **1** to **2** and **3** via an intramolecular nucleophilic attack on the Cp ring by Ph₃B⁻, followed by hydride elimination.

Introduction

Aromatic substitution of a π-bonded ligand by a group already bonded to the same metal has been limited to a few cases mainly involving organic groups. McCleverty and Wilkinson reported the migration of the σ-bonded ethyl group of EtMoCp(CO)₃ (Cp = η⁵-C₅H₅) to the cyclopentadienyl ring with formation of [(η⁵-C₅H₄Et)Mo(CO)₃]₂.[1] Subsequently Nesmeyanov and co-workers described analogous behavior for PhMoCp(CO)₃.[2] Phenyl migration has been promoted by nucleophiles; Schrock, Guggenberger, and English showed that the phenyl group of PhM(C₈H₈)₂ (M = Nb or Ta) migrated to one cyclooctatetraene ligand upon treatment with chelating phosphines or arsines.[3] Similarly, the reaction of PhVCp₂ with carbon monoxide gave [CpV(η⁵-C₅H₄Ph)(CO)₂]₂.[4] Examples wherein a migrating phenyl, trimethylsilyl, or trimethylgermyl group substitutes an incoming olefin have been described by Stone and co-workers.[5]

The present work originated with a study of the reaction of (η⁵-cyclopentadienyl)dicarbonylferrate(–I), FeCp(CO)₂⁻, with triphenylborane. In tetrahydrofuran (THF) solution the resulting adduct, Ph₃BFeCp(CO)₂⁻ as the tetraethylammonium salt, **1**, spontaneously converted to tetraethylammonium [di-μ-carbonyl-((η⁵-cyclopentadienyl)carbonyliron)(carbonyliron))-η⁵-cyclopentadienyl]triphenylborate(*Fe–Fe*) hemikis(tetrahydrofuranate), **2**, and tetraethylammonium hydridotriphenylborate, **3**. The evidence described herein shows that this transformation formally involves a novel metal-to-ring migration and aromatic substitution by the triphenylboron group.

Experimental Section

Unless stated otherwise all operations were carried out under a purified argon atmosphere. The apparatus and techniques employed for handling air-sensitive compounds have been described in detail.[6] Infrared (IR) spectra were obtained on a Perkin-Elmer Model 337