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Crystal Structure and Molecular Geometry of a Dinuclear "Disrupted Formyl" Complex of Tantalum, $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$

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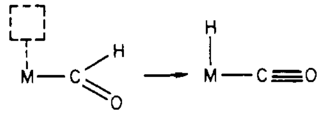
The reaction of the η^2-formyl complex $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\eta^2\text{-}CHO)$ (**1**) with PMe_3 leads to the formation of complex **2** of stoichiometry $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(CHO)(PMe_3)$, which is shown to be a "disrupted formyl" complex, better designated as $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$. The complex **2** crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (D_2^4; No. 19) with a = 17.937 (8) Å, b = 12.452 (4) Å, c = 14.022 (5) Å, and Z = 4. There is no crystallographically imposed symmetry. Diffraction data (Mo Kα, 2θ = 4.5–45°) were collected with a Syntex P2$_1$ automated four-cycle diffractometer, and the structure was solved and refined by conventional methods to R_F = 5.5% and R_{wF} = 4.2% for all 2338 reflections. The molecule consists of two $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]$ fragments separated by Ta(1)···Ta(2) = 2.992 (1) Å and bridged asymmetrically by a $>$CHPMe$_3$ phosphonium ylide fragment (for which Ta(1)–C(1) = 2.187 (17) Å, Ta(2)–C(1) = 2.354 (17) Å, and ∠Ta(1)–C(1)–Ta(2) = 82.3 (6)°) and by an oxide ion (Ta(1)–O = 1.895 (11) Å, Ta(2)–O = 1.958 (11) Å, and ∠Ta(1)–O–Ta(2) = 101.9 (5)°). The hydride ligand was not located directly during the structural analysis, but all data point toward its occupying an asymmetric bridging site between Ta(1) and Ta(2). Each tantalum atom has a coordination environment of the "3,4,1" variety in which the top three sites are occupied by the η^5-C$_5$Me$_4$Et ligand, terminal chloride ligands occupy two of the four equatorial sites, and the three remaining sites are associated with bridging ligands. The oxide ligand spans equatorial sites on both Ta(1) and Ta(2); the phosphonium ylide spans an equatorial site on Ta(1) and the unique axial site on Ta(2); the hydride ligand is believed to bridge an equatorial site on Ta(2) and the unique axial site on Ta(1).

Introduction

In contrast to the abundance of structural data available for σ-acyl complexes of the transition metals,[1,2] little is known of formyl complexes. Indeed, the first structural study of a metal–formyl complex $(\eta^5\text{-}C_5H_5)Re(PPh_3)(NO)(CHO)$ was not reported until 1979;[3] this complex is formally an 18-electron complex. There is good evidence that a formyl complex is unstable relative to the hydrido–carbonyl complex when a coordination site on the metal atom is vacant (i.e., for complexes with ≤16 outer valence electrons), as indicated by eq 1. In addition, it is well established that formyl complexes



(1)

can act as hydride donors to a variety of electrophiles.[4-12]

Schrock and co-workers have recently[13] attempted to stabilize formyl ligands by forming them on dinuclear metal complexes (see Scheme I).

Scheme I

$$Ta(\eta^5\text{-}C_5Me_4R)(\eta^2\text{-}CH_2{=}CHMe)Cl_2 \xrightarrow{+H_2}$$

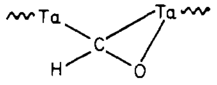
$$[(\eta^5\text{-}C_5Me_4R)TaCl_2]_2(H)_2 \xrightarrow{+CO}$$

$$\underset{\mathbf{1}}{[(\eta^5\text{-}C_5Me_4R)TaCl_2]_2(H)(CHO)} \xrightarrow{+PMe_3}$$

$$\underset{\mathbf{2}}{[(\eta^5\text{-}C_5Me_4R)TaCl_2]_2(H)(CHO)(PMe_3)}$$

R = Et or Me

The species **1** is believed,[13] on the basis of ^{1}H and ^{13}C NMR spectra, to contain an η^2-formyl group of type **3**. Attempts



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to crystallize this complex have been unsuccessful, but crystals of the PMe$_3$ derivative **2** have been obtained, and a single-crystal X-ray diffraction study of this species (with R = Et) has been carried out. A preliminary account of this work has already appeared;[13] a detailed description is given below.

The molecule is found to be $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-}CHPMe)(\mu\text{-}O)$ in which the C–O bond of the formyl derivative (**2**) has been cleaved, leaving a bridging oxide ion and a bridging phosphonium ylide (CHPMe$_3$) group. We refer to this complex as a "disrupted formyl".

Experimental Section

A. Collection and Processing of the Diffraction Data. A sample of $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$ was provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. The material forms yellow columnar crystals, extended along [001] and does not noticeably deteriorate upon brief exposures (<3 h) to the atmosphere.

The only available single crystal was rather irregular (with a slight reentrant angle) having approximate dimensions 0.18 × 0.20 × 0.35 mm. It was wedged into a thin-walled capillary which was purged with argon, flame sealed, inserted into a brass pin with beeswax, and mounted into a eucentric goniometer.

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(1) Churchill, M. R.; Chen, K. N. *Inorg. Chem.* **1976**, *15*, 788-792 and ref 1-3 given therein.
(2) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 91-164 (see, especially, pp 153-154 and Table 10 on p 154).
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(4) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544-2545.
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Table I. Experimental Data for the X-ray Diffraction Study of $[(\eta^5\text{-}C_5Me_5Et)TaCl_2]_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$

(A) Crystal Parameters at 25 °C

cryst system: orthorhombic
space group: $P2_12_12_1$
$a = 17.9369\ (79)$ Å
$b = 12.4523\ (42)$ Å
$c = 14.0223\ (53)$ Å
$V = 3131.9\ (21)$ Å^3
$Z = 4$
mol wt = 908.32
ρ(calcd) = 1.93 g cm^{-3}

(B) Measurement of Intensity Data

radiation: Mo Kα($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite, $2\theta_{\text{mono}} = 12.2°$, equatorial mode
reflctns measd: $+h$, $+k$, $+l$
scan type: coupled θ(crystal)–2θ(counter)
2θ range: $4.5° \rightarrow 45.0°$
scan speed: 2.0°/min in 2θ
scan width: $[2\theta(\text{Mo K}\alpha_1) - 0.9]° \rightarrow [2\theta(\text{Mo K}\alpha_2) + 0.9]°$
bkgd measmt: stationary-crystal, stationary-counter at beginning and end of each scan, each for one-fourth of the time taken for the scan
std reflctns: 127, 261, 822; these were measured after every 97 reflections
reflctns collected: 2360 total, yielding 2338 allowed symmetry independent data
abs coeff: $\mu = 77.7$ 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 16 reflections of the forms {755} and {355}.

Table II. Final Positional and Isotropic Thermal Parameters

atom	x	y	z	B_{iso}, Å^2
Ta(1)	−0.09901 (4)	−0.05681 (6)	−0.06428 (5)	
Ta(2)	0.04778 (4)	0.00098 (7)	0.02306 (5)	
Cl(1)	−0.09534 (27)	−0.0550 (4)	−0.23860 (29)	
Cl(2)	−0.14957 (27)	0.1231 (4)	−0.0868 (4)	
Cl(3)	0.14470 (28)	0.0153 (5)	−0.0947 (4)	
Cl(4)	0.1019 (4)	−0.1475 (4)	0.1100 (4)	
P	0.05578 (31)	−0.1976 (4)	−0.1673 (4)	
O	−0.0567 (6)	−0.0249 (8)	0.0562 (8)	2.09 (23)
C(1)	0.0065 (10)	−0.1444 (13)	−0.0704 (13)	1.96 (34)
C(2)	0.1427 (14)	−0.2620 (19)	−0.1262 (17)	5.1 (6)
C(3)	0.0764 (11)	−0.1112 (16)	−0.2700 (14)	3.4 (5)
C(4)	0.0047 (13)	−0.3101 (17)	−0.2215 (14)	3.6 (5)
C(11)	−0.1928 (11)	−0.2025 (15)	−0.1024 (14)	2.8 (4)
C(12)	−0.2328 (10)	−0.1055 (15)	−0.0759 (14)	2.8 (4)
C(13)	−0.2143 (10)	−0.0849 (14)	0.0210 (13)	2.4 (4)
C(14)	−0.1665 (11)	−0.1673 (16)	0.0544 (15)	3.3 (4)
C(15)	−0.1511 (11)	−0.2377 (15)	−0.0246 (13)	2.4 (4)
C(16)	−0.2035 (12)	−0.2587 (16)	−0.2000 (15)	3.4 (5)
C(17)	−0.2901 (12)	−0.0458 (17)	−0.1378 (15)	4.1 (5)
C(18)	−0.2477 (12)	0.0054 (21)	0.0831 (14)	4.1 (4)
C(19)	−0.1372 (12)	−0.1815 (17)	0.1566 (15)	3.8 (5)
C(20)	−0.1102 (12)	−0.3459 (16)	−0.0208 (15)	3.8 (5)
C(20A)	−0.1679 (12)	−0.4314 (19)	0.0146 (15)	4.3 (5)
C(31)	0.0034 (13)	0.1564 (17)	0.1188 (15)	3.6 (5)
C(32)	0.0503 (13)	0.0916 (16)	0.1802 (15)	3.8 (5)
C(33)	0.1260 (12)	0.0985 (16)	0.1459 (15)	3.6 (5)
C(34)	0.1245 (10)	0.1631 (14)	0.0649 (15)	2.6 (4)
C(35)	0.0489 (11)	0.1955 (14)	0.0435 (12)	2.3 (4)
C(36)	−0.0776 (13)	0.1849 (19)	0.1416 (16)	4.6 (5)
C(37)	0.0245 (11)	0.0320 (16)	0.2682 (15)	4.2 (5)
C(38)	0.1971 (14)	0.0533 (22)	0.1955 (17)	5.5 (6)
C(39)	0.1933 (14)	0.2060 (20)	0.0122 (18)	5.4 (6)
C(40)	0.0232 (11)	0.2751 (16)	−0.0268 (15)	3.4 (4)
C(40A)	0.0353 (13)	0.3953 (18)	0.0077 (16)	5.0 (6)

Since we were very concerned about the possibility of crystal decomposition, no preliminary Weissenberg or precession photographs were taken and the crystal was transferred directly to our Syntex P2$_1$ diffractometer. Crystal alignment, determination of orientation matrix and accurate cell dimensions, and data collection were all carried out as described previously.[14] Details specific to the present analysis appear in Table I.

A survey of the complete data set revealed the systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l = 2n + 1$; the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (D_2^4; No. 19) is uniquely indicated.

All crystallographic computations were carried out by using our in-house Syntex XTL system, including the XTL interactive crystallographic program package[15,16] as modified by our research group at SUNY at Buffalo.

Data were corrected for absorption by an empirical method, based upon a series of ψ scans. The reflections used to obtain the normalized absorption curves, their 2θ values, and the maximum/minimum intensity ratios were as follows: 004, $2\theta = 11.61°$, max/min = 1.48; 106, 17.60°, 1.41; 107, 20.52°, 1.48; 109, 26.41°, 1.43; 1,0,11, 32.39°, 1.44; 0,1,12, 35.50°, 1.47. Data 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 and $\sigma_c(|F_o|)$ were propagated from $|F_o|^2$ and $\sigma[|F_o|^2]$ by finite differences.

B. Solution and Refinement of the Structure. The analytical form[17a] of the scattering factors for *neutral* tantalum, chlorine, phosphorus, oxygen, and carbon were 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 2; p, the "ignorance factor", was set at a value

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

of 0.015. Data were placed on an approximate scale via a Wilson plot, which also provided the overall isotropic thermal parameter B_{iso} = 2.14 Å^2. Interpretation of a three-dimensional Patterson map led to the location of the two tantalum atoms. Full-matrix least-squares refinement of the scale factor and positional and isotropic thermal parameters for these two tantalum atoms led to $R_F = 19.5\%$ and $R_{wF} = 24.8\%$. A difference-Fourier synthesis now yielded the positions of the four chlorine atoms, the phosphorus atom, and the bridging oxygen atom, the bridging carbon atom, and the methyl carbon atoms bonded to the phosphorus. Several cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters for these 12 atoms led to $R_F = 10.8\%$ and $R_{wF} = 14.3\%$ for those data with $|F_o| > 3\sigma[|F_o|]$.

A second difference-Fourier synthesis, now phased by 12 atoms, indicated the positions of all 22 carbon atoms of the $\eta^5\text{-}C_5Me_4Et$ ligands.

Several cycles of full-matrix least-squares refinement, using anisotropic thermal parameters for the heavy atoms, resulted in convergence with $R_F = 4.3\%$, $R_{wF} = 4.1\%$, and GOF = 1.36 for those data with $|F_o| > 3\sigma[|F_o|]$.

A survey of intense low-angle data suggested that a minor correction for secondary extinction was necessary; the derived value for k (cf. eq 3) was 8.15×10^{-8}.

$$|F_o|_{\text{cor}} = |F_o|_{\text{uncor}}(1.0 + kI_o) \qquad (3)$$

Three more cycles of full-matrix least-squares refinement led to final convergence [$(\Delta/\sigma)_{\max} < 0.001$] with $R_F = 5.5\%$, $R_{wF} = 4.2\%$, and GOF = 1.34 for all 2338 reflections (none rejected). The discrepancy indices for those 2096 data with $|F_o| > 3\sigma[|F_o|]$ were $R_F = 4.2\%$ and $R_{wF} = 4.0\%$.

We now tested the chirality of the (noncentrosymmetric) crystal by inverting the coordinates ($x, y, z \rightarrow -x, -y, -z$) and refining to convergence once again. This led to higher residuals, indicating that our original choice of chirality was correct. These latter results were discarded.

Attempts to introduce anisotropic thermal parameters for the carbon atoms were not wholly successful and were abandoned.

The largest peak on a final difference-Fourier synthesis was of height 1.22 e Å^{-3} and was close to Ta(1). No indications of the hydride ligand or other hydrogen atoms were found. The function $\sum w(|F_o| - |F_c|)^2$ showed no significant dependence on $(\sin\theta)/\lambda$, sequence number, or

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(14) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

(15) The system has been described previously. See: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957–1962. (See, especially, p 1958.)

(16) "Syntex XTL Operations Manual", 2nd ed.; Syntex Analytical Instruments (now Nicolet XRD Division): Cupertino, CA, 1976.

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

Table III. Anisotropic Thermal Parameters (in Å^2) for the Heavier Atoms[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta(1)	1.534 (31)	2.046 (31)	2.066 (31)	0.033 (34)	0.164 (33)	0.072 (33)
Ta(2)	1.917 (33)	2.481 (33)	2.330 (31)	−0.09 (4)	−0.323 (32)	−0.13 (4)
Cl(1)	2.39 (20)	3.52 (21)	2.22 (18)	−0.11 (24)	−0.08 (19)	0.14 (19)
Cl(2)	2.42 (23)	2.88 (23)	4.33 (29)	0.73 (20)	0.34 (22)	0.32 (21)
Cl(3)	2.58 (23)	6.21 (35)	4.67 (28)	−1.49 (26)	1.10 (22)	−1.75 (27)
Cl(4)	5.70 (34)	3.76 (27)	5.17 (30)	0.68 (29)	−3.43 (31)	0.24 (23)
P	2.11 (24)	2.68 (24)	3.69 (27)	0.53 (22)	−0.07 (23)	−0.50 (21)

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

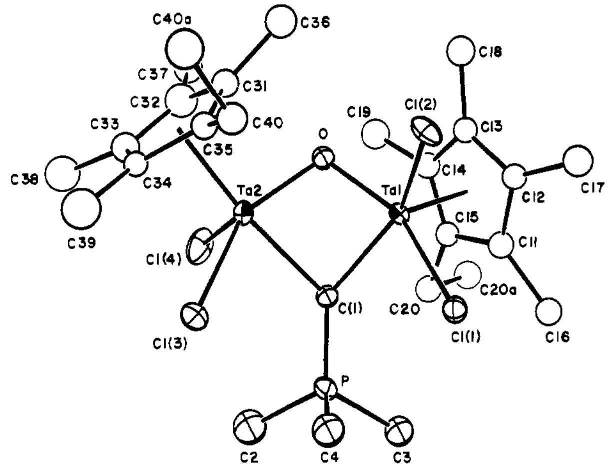

Figure 1. Labeling of atoms in the $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$ molecule (ORTEP diagram; 30% probability ellipsoids).

identity or parity of the Miller indices.

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 shown in Table IV; interatomic angles and their esd's are given in Table V. Important least-squares planes (and deviations of atoms therefrom) are collected in Table VI. The scheme used for numbering nonhydrogen atoms is shown in Figure 1, and a stereoview of the molecule can be seen in Figure 2.

The diffraction study shows clearly that the molecule contains two tantalum atoms [Ta(1)···Ta(2) = 2.992 (1) Å, each of which is linked to an η^5-C_5Me_4Et ligand [Ta(1)···Cp(1) = 2.165 Å and Ta(2)···Cp(2) = 2.172 Å][18] and two chloride ligands [Ta(1)–Cl(1) = 2.445 (4) Å and Ta(1)–Cl(2) = 2.437 (5) Å; Ta(2)–Cl(3) = 2.405 (5) Å and Ta(2)–Cl(4) = 2.417 (6) Å]. The two tantalum atoms are bridged *asymmetrically* by an oxide ion and by a carbon atom (C(1)) of a $CHPMe_3$ ligand. Thus, the attack of PMe_3 on **1** results in total cleavage of the formyl moiety's carbon–oxygen bond with concomitant utilization of the CH fragment in formation of a phosphonium ylide.

The presence of a hydride ligand has been demonstrated[13] by ^{1}H NMR (resonance at δ 10.0), but its location was not determined directly from the X-ray structural analysis. We can, however, make a reasonable assessment of its position by considering the coordination geometry about the two tantalum atoms.

Table IV. Intramolecular Distances with Esd's for $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$

atoms	dist, Å	atoms	dist, Å
(A) Distances from the Tantalum Atoms			
Ta(1)···Ta(2)	2.992 (1)		
Ta(1)–Cl(1)	2.445 (4)	Ta(2)–Cl(3)	2.405 (5)
Ta(1)–Cl(2)	2.437 (5)	Ta(2)–Cl(4)	2.417 (6)
Ta(1)–C(1)	2.187 (17)	Ta(2)–C(1)	2.354 (17)
Ta(1)–O	1.895 (11)	Ta(2)–O	1.958 (11)
Ta(1)–C(11)	2.531 (20)	Ta(2)–C(31)	2.486 (22)
Ta(1)–C(12)	2.481 (19)	Ta(2)–C(32)	2.477 (20)
Ta(1)–C(13)	2.414 (18)	Ta(2)–C(33)	2.532 (21)
Ta(1)–C(14)	2.476 (20)	Ta(2)–C(34)	2.513 (18)
Ta(1)–C(15)	2.502 (18)	Ta(2)–C(35)	2.439 (17)
Ta(1)···Cp(1)	2.165	Ta(2)···Cp(2)	2.172
(B) Distances within the $CHPMe_3$ Ligand			
P–C(1)	1.751 (19)		
P–C(2)	1.846 (26)		
P–C(3)	1.835 (21)		
P–C(4)	1.838 (22)		
(C) Internal C–C Distances for the η^5-C_5Me_4Et Ligands			
C(11)–C(12)	1.452 (27)	C(31)–C(32)	1.448 (31)
C(12)–C(13)	1.422 (27)	C(32)–C(33)	1.442 (31)
C(13)–C(14)	1.416 (27)	C(33)–C(34)	1.392 (29)
C(14)–C(15)	1.439 (27)	C(34)–C(35)	1.446 (26)
C(15)–C(11)	1.394 (27)	C(35)–C(31)	1.420 (28)
(D) External C(sp^2)–C(sp^3) Distances for the η^5-C_5Me_4Et Ligands			
C(11)–C(16)	1.549 (28)	C(31)–C(36)	1.531 (33)
C(12)–C(17)	1.536 (29)	C(32)–C(37)	1.512 (29)
C(13)–C(18)	1.545 (30)	C(33)–C(38)	1.557 (33)
C(14)–C(19)	1.536 (30)	C(34)–C(39)	1.534 (31)
C(15)–C(20)	1.535 (28)	C(35)–C(40)	1.472 (26)
(E) External C(sp^3)–C(sp^3) Distances for the η^5-C_5Me_4Et Ligands			
C(20)–C(20A)	1.565 (31)	C(40)–C(40A)	1.588 (30)

The coordination environment about Ta(1) appears (at first sight) to be quite regular and apparently of the "four-legged piano stool" or "3,4" type (however, vide infra). It is characterized by essentially equivalent Cp(1)–Ta(1)–L angles, viz, Cp(1)–Ta(1)–Cl(1) = 106.0°, Cp(1)–T(1)–Cl(2) = 106.9°, Cp(1)–Ta(1)–C(1) = 112.2°, and Cp(1)–Ta(1)–O = 102.0° (see Figure 3). In addition, the *cis*-L–Ta(1)–L′ angles show only moderate variations [Cl(1)–Ta(1)–Cl(2) = 82.7 (2)°, Cl(2)–Ta(1)–O = 94.1 (3)°, O–Ta(1)–C(1) = 78.0 (6)°, and C(1)–Ta(1)–Cl(1) = 86.7 (5)°] and the *trans*-L–Ta(1)–L′ angles are reasonably similar [Cl(1)–Ta(1)–O = 151.5 (3)° and Cl(2)–Ta(1)–C(1) = 140.9 (5)°].

In contrast to this, the observable angles about Ta(2) show a substantial and obvious "hole" in the coordination surface, consistent with the presence of a hydride ligand in an equatorial site (see Figure 4). Thus, while the Cp(2)–Ta(2)–L (equatorial) angles are equivalent [Cp(2)–Ta(2)–Cl(3) = 101.1°, Cp(2)–Ta(2)–Cl(4) = 104.7°, and Cp(2)–Ta(2)–O = 100.3°], there is a clear "hole" in the distribution of the equatorial ligands [i.e., Cl(3)–Ta(2)–Cl(4) = 96.5 (2)° and Cl(4)–Ta(2)–O = 98.0 (3)°, but Cl(3)–Ta(2)–O = 150.2 (3)°]. We therefore believe that a hydride ligand occupies an equatorial site on Ta(2) (between Cl(3) and O). The coordination geometry about Ta(2) is completed by the *axial* ligand (bonded through atom C(1)) and is of an unusual "3,4,1" variety.

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[18] Cp(1) is the centroid of the cyclopentadienyl ligand defined by atoms C(11)–C(15); Cp(2) is the centroid of the cyclopentadienyl ligand defined by atoms C(31)–C(35).

Table V. Interatomic Angles (in Deg) for $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$

atoms	angle	atoms	angle
	(A) Angles around the Tantalum Atoms		
Cl(1)-Ta(1)-Cl(2)	82.7 (2)	Cl(3)-Ta(2)-Cl(4)	96.5 (2)
Cl(1)-Ta(1)-C(1)	86.7 (5)	Cl(3)-Ta(2)-C(1)	84.4 (4)
Cl(1)-Ta(1)-O	151.5 (3)	Cl(3)-Ta(2)-O	150.2 (3)
Cl(2)-Ta(1)-C(1)	140.9 (5)	Cl(4)-Ta(2)-C(1)	79.6 (5)
Cl(2)-Ta(1)-O	94.1 (3)	Cl(4)-Ta(2)-O	98.0 (3)
C(1)-Ta(1)-O	78.0 (6)	C(1)-Ta(2)-O	72.8 (5)
	(B) Angles and Estimated Angles from Cp(1) and Cp(2)		
Cp(1)-Ta(1)-Cl(1)	106.0	Cp(2)-Ta(2)-Cl(3)	101.1
Cp(1)-Ta(1)-Cl(2)	106.9	Cp(2)-Ta(2)-Cl(4)	104.7
Cp(1)-Ta(1)-C(1)	112.2	Cp(2)-Ta(2)-H(est)	109
Cp(1)-Ta(1)-O	102.0	Cp(2)-Ta(2)-O	100.3
Cp(1)-Ta(1)-H(est)	177	Cp(2)-Ta(2)-C(1)	172.5
	(C) Angles within the $CHPMe_3$ Ligand		
Ta(1)-C(1)-Ta(2)	82.3 (6)	C(1)-P-C(4)	111.0 (9)
Ta(1)-C(1)-P	131.0 (10)	C(2)-P-C(3)	109.2 (10)
Ta(2)-C(1)-P	124.4 (9)	C(2)-P-C(4)	102.7 (11)
C(1)-P-C(2)	110.4 (10)	C(3)-P-C(4)	102.9 (10)
C(1)-P-C(3)	119.3 (9)		
	(D) Angle at the Oxygen Atom and Hydride Ligand		
Ta(1)-O-Ta(2)	101.9 (5)	Ta(1)-H(est)-Ta(2)	92
	(E) Interior Angles of the C_5Me_4Et Ligands		
C(15)-C(11)-C(12)	109.1 (17)	C(35)-C(31)-C(32)	107.4 (18)
C(11)-C(12)-C(13)	106.2 (16)	C(31)-C(32)-C(33)	108.4 (18)
C(12)-C(13)-C(14)	109.1 (16)	C(32)-C(33)-C(34)	106.7 (18)
C(13)-C(14)-C(15)	107.6 (17)	C(33)-C(34)-C(35)	110.4 (17)
C(14)-C(15)-C(11)	107.9 (17)	C(34)-C(35)-C(31)	106.8 (16)
	(F) Exterior Angles of the C_5Me_4Et Ligands		
C(16)-C(11)-C(15)	128.0 (17)	C(36)-C(31)-C(35)	128.4 (19)
C(16)-C(11)-C(12)	122.7 (17)	C(36)-C(31)-C(32)	123.8 (19)
C(17)-C(12)-C(11)	126.1 (17)	C(37)-C(32)-C(31)	125.5 (19)
C(17)-C(12)-C(13)	127.5 (17)	C(37)-C(32)-C(33)	126.1 (19)
C(18)-C(13)-C(12)	125.5 (17)	C(38)-C(33)-C(32)	126.9 (19)
C(18)-C(13)-C(14)	125.1 (17)	C(38)-C(33)-C(34)	126.1 (19)
C(19)-C(14)-C(13)	126.8 (18)	C(39)-C(34)-C(33)	125.4 (18)
C(19)-C(14)-C(15)	125.6 (18)	C(39)-C(34)-C(35)	123.9 (17)
C(20)-C(15)-C(14)	126.9 (17)	C(40)-C(35)-C(34)	128.3 (17)
C(20)-C(15)-C(11)	124.1 (17)	C(40)-C(35)-C(31)	123.3 (17)
C(15)-C(20)-C(20A)	107.0 (16)	C(35)-C(40)-C(40A)	112.8 (17)

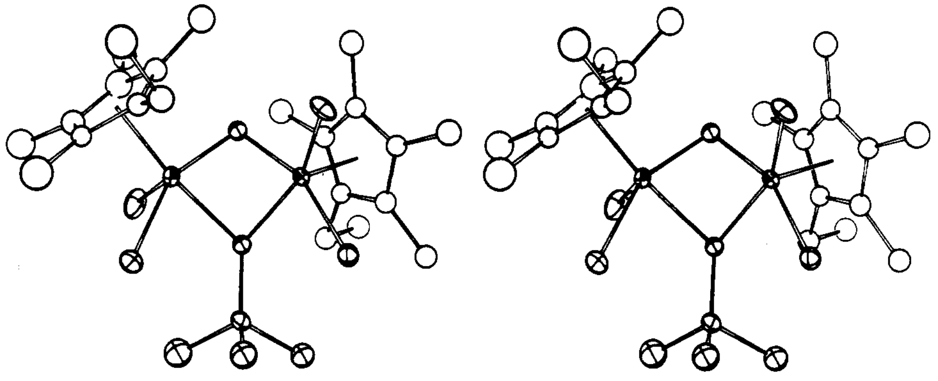


Figure 2. Stereoscopic view of the $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$ molecule.

On the basis of the preceding arguments we had previously suggested[13] that Ta(2) is linked to a terminal hydride ligand. Further consideration suggests rather that the hydride ligand occupies an *asymmetric* bridging site associated with the Ta(1)···Ta(2) system. It is clear that the hydride ligand is associated with an equatorial site on Ta(2). If one calculates the probable position of this hydrogen atom on the basis of coplanarity with the Cp(2)–Ta(2)–Cl(4) plane, a Cl(4)–Ta(2)–H angle of 150.0° (i.e., the same as the Cl(3)–Ta(2)–O angle), and a Ta(2)–H distance of 2.00 Å, the resulting coordinates (for the point which we will term "H(2)") are (–0.007 67, 0.057 66, –0.089 98). The position of "H(2)" is, however, only 2.20 Å from Ta(1) and is in such a site as to provide a Cp(1)–Ta(1)–H(2) angle of 174°: This suggests that the coordination geometry about Ta(1) is of the same "3,4,1" type as Ta(2) but with the hydride ligand taking up now an *axial* site on Ta(1) (in contrast to an *equatorial* site on Ta(2)).

If we calculate the probable position of a hydride ligand (termed H(1)) on an *axial* site on Ta(1) [i.e., Cp(1)–Ta(1)–H(1) = 180° and Ta(1)–H(1) = 2.00 Å] we obtain the coordinates (–0.013 56, 0.038 17, –0.100 08); i.e., the idealized location of H(1) is only 0.30 Å from that determined for H(2). We therefore assumed, for the purpose of subsequent calculation, that the hydride ligand was truly of the μ_2 variety (spanning an equatorial site on Ta(2) and an axial site on

Table VI

Least-Squares Planes[a] and Atomic Deviations (in Å) Therefrom for $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$

atom	dev, Å	atom	dev, Å
(A) Cyclopentadienyl Plane 1			
$0.7807X + 0.5572Y - 0.2831Z + 3.6879 = 0$			
C(11)*	−0.011 (20)	C(16)	−0.163 (21)
C(12)*	−0.003 (19)	C(17)	−0.145 (22)
C(13)*	0.015 (18)	C(18)	−0.073 (23)
C(14)*	−0.021 (20)	C(19)	−0.114 (21)
C(15)*	0.020 (19)	C(20)	−0.173 (21)
Ta(1)	2.1625 (7)	C(20A)	−1.715 (22)
Cl(1)	2.918 (5)	Cl(2)	2.792 (5)
(B) Cyclopentadienyl Plane 2			
$-0.1573X - 0.8165Y - 0.5555Z + 2.4955 = 0$			
C(31)*	−0.030 (21)	C(36)	−0.268 (23)
C(32)*	0.018 (20)	C(37)	0.012 (21)
C(33)*	0.002 (21)	C(38)	−0.126 (26)
C(34)*	−0.020 (19)	C(39)	−0.239 (25)
C(35)*	0.031 (17)	C(40)	−0.159 (20)
Ta(2)	2.1711 (8)	C(40A)	−1.684 (23)
Cl(3)	2.669 (6)	Cl(4)	2.851 (6)
(C) Ta(1)–O–Ta(2) Plane			
$-0.2011X + 0.9699Y - 0.1376Z + 0.2049 = 0$			
Ta(1)*	0.000	O*	0.000
Ta(2)*	0.000		
(D) Ta(1)–C(1)–Ta(2) Plane			
$0.2498X + 0.4987Y - 0.8300Z + 0.0482 = 0$			
Ta(1)*	0.000	C(1)*	0.000
Ta(2)*	0.000		
(E) Ta(1)–H(est)–Ta(2) Plane			
$0.4451X - 0.7181Y - 0.5350Z - 0.1997 = 0$			
Ta(1)*	0.000	H(est)*	0.000
Ta(2)*	0.000		
(F) O–Ta(2)–C(1) Plane			
$-0.2873X + 0.6359Y - 0.7163Z + 0.4701 = 0$			
Ta(2)*	0.000	C(1)*	0.000
O*	0.000		
(G) O–Ta(1)–C(1) Plane			
$0.4465X + 0.8055Y - 0.3897Z + 1.0115 = 0$			
Ta(1)*	0.000	C(1)*	0.000
O*	0.000		
(H) Cl(3)–Ta(2)–Cl(4) Plane			
$-0.4909X - 0.6444Y - 0.5863Z + 0.6182 = 0$			
Ta(2)*	0.000	Cl(4)*	0.000
Cl(3)*	0.000		
(I) Cl(1)–Ta(1)–Cl(2) Plane			
$-0.9252X - 0.3785Y - 0.0284Z - 1.9365 = 0$			
Ta(1)*	0.000	Cl(2)*	0.000
Cl(1)*	0.000		
Dihedral Angles of Note (in Deg)			
A/I	157.7 (22.3)	C/E	135.4 (44.6)
B/H	158.3 (21.7)	D/E	101.4 (78.6)
C/D	123.2 (56.8)	F/G	131.5 (48.5)

[a] Atoms used in calculating the plane are marked with an asterisk. Planes are in Cartesian (Å) coordinates.

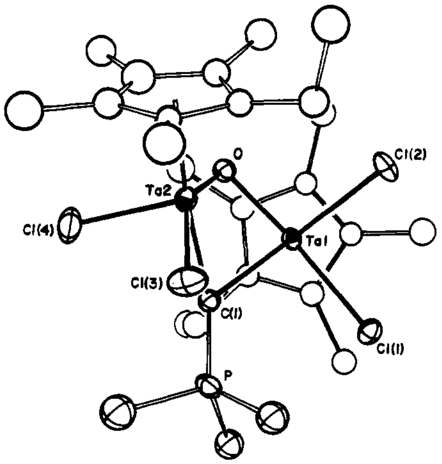


Figure 3. Determined molecular structure, projected onto the C(11) → C(15) plane, showing the distribution of equatorial ligands about Ta(1). The deduced position of the hydride ligands is not shown; however, see Figures 4 and 5.

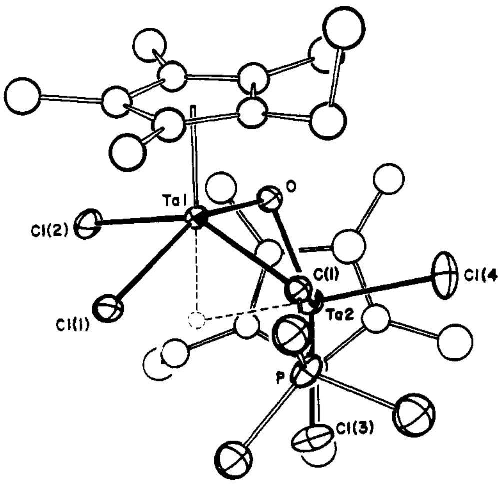


Figure 4. Molecule projected onto the C(31) → C(35) plane, showing the distribution of ligands about Ta(2). The hydride ligand is shown as a broken circle in its deduced position (see text).

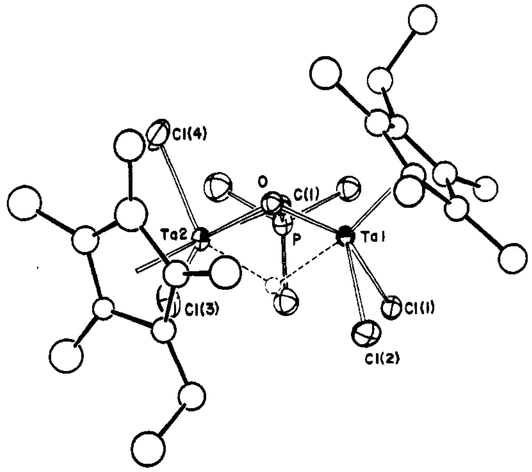


Figure 5. View of the Ta(μ-O)(μ-C)Ta bridge, showing the probable location of the μ-H ligand. The estimated Ta(1)–H(est)–Ta(2) angle is 92°.

Ta(1)) and that its coordinates (labeled as H(est)) were the average of those for H(1) and H(2)—i.e., (−0.01062, 0.04792, −0.09503)—which yields Ta(1)–H(est) = 2.10 Å and Ta(2)–H(est) = 2.05 Å.

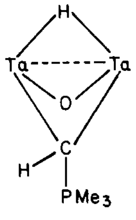
The observed asymmetry of Ta(1)–O–Ta(2) and Ta(1)–C(1)–Ta(2) bridges [and the probable (contrary) asymmetry of the Ta(1)–H–Ta(2) system] can be explained by assuming that the axial bond in each "3,4,1" stereochemistry is longer (weaker) than the four equatorial bonds.

The *axial* Ta(2)–C(1) distance of 2.354 (17) Å is 0.167 Å longer than the *equatorial* Ta(1)–C(1) distance of 2.187 (17) Å. We suspect that the *axial* Ta(1)–H distance is appreciably longer than the *equatorial* Ta(2)–H distance. The asymmetry of this system thus will compensate (at least in part) for the asymmetry in the Ta(1)–C(1)–Ta(2) bridge. From this viewpoint, the asymmetry in the diequatorial Ta(1)–O–Ta(2) bridge [Ta(2)–O = 1.958 (11) Å and Ta(1)–O = 1.895 (11) Å] occurs simply to act as the final balance between the asymmetric (four-electron) system Ta(1)–C(1)–Ta(2) and the asymmetric (two-electron) system Ta(1)–H–Ta(2).

It is also worthy of note that the Ta(1)···Ta(2) distance of 2.992 (1) Å is ~0.12 Å greater than the Ta–Ta single bond length of ~2.872 Å predicted from the average Ta–Cl distance of 2.426 Å found in the present complex and the accepted covalent radius for chlorine of 0.99 Å.[19] This difference of ~0.12 Å is precisely that which we found between M–(H)–M and M–M distance in a variety of μ_2-hydrido-bridged species.[20]

It would appear that the present complex has sufficiently unusual characteristics as to merit a *neutron*-diffraction study.

The analysis strongly suggests that the complex should be written as $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$ with a central *core* as in **4**. Angles at the bridging atoms are as follows: Ta(1)–C(1)–Ta(2) = 82.3 (6)° and Ta(1)–O–Ta(2) = 101.9 (5)°. The geometry of this bridge is illustrated in Figure 5.



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Other points of interest are as follows: (1) The C(1)···O distance in the "disrupted formyl" system is 2.580 (20) Å.

(2) The >CH–PMe$_3$ system is best regarded as a phosphonium ylide, the C(1)–P distance of 1.751 (19) Å being substantially shorter than the three equivalent P–Me distances [P–C(2) = 1.846 (26) Å, P–C(3) = 1.835 (21) Å, and P–C(4) = 1.838 (22) Å]. A similar pattern was found within the $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$ molecule.[21]

(3) The cyclopentadienyl systems are planar within the limits of experimental error (cf. Table VI). In each case the substituents are displaced from the pentaatomic carbocyclic system with the terminal CH$_3$ group of the CH$_2$CH$_3$ group pointing directly *away* from the appropriate tantalum atom.

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Supplementary Material Available: Listings of observed and calculated structure factors and data-processing formulas (15 pages). Ordering information is given on any current masthead page.

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Synthesis of Alkyne Complexes of the Type Ta(η^5-C$_5$Me$_5$)(alkyne)Cl$_2$ and Crystal Structure of Ta(η^5-C$_5$Me$_5$)(PhC≡CPh)Cl$_2$

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$Ta(\eta^5\text{-}C_5Me_5)(olefin)Cl_2$ complexes (olefin = styrene or cyclooctene) react with alkynes (PhC≡CPh, PhC≡CH, 2-butyne, 3-hexyne, HC≡CH) to give analogous $Ta(\eta^5\text{-}C_5Me_5)(alkyne)Cl_2$ complexes which do not react with additional alkyne, CO, HCl, or ethylene with one exception; $Ta(\eta^5\text{-}C_5Me_5)(HC{\equiv}CH)Cl_2$ reacts with ethylene at 80 °C to give $(\eta^5\text{-}C_5Me_5)Cl_2\overline{TaCH{=}CHCH_2CH_2}$ irreversibly. The diphenylacetylene ligand in $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_2$ is bonded parallel to the η^5-C$_5$Me$_5$ ring with a long "acetylenic" linkage (1.337 (8) Å) and short Ta–C(alkyne) bonds (2.067 (6) Å and 2.075 (6) Å), consistent with it being a 4-electron donor. The lack of reactivity of these alkyne complexes is postulated to be due to this strong metal–alkyne bond.

Introduction

We recently prepared several benzyne complexes of the type $M(\eta^5\text{-}C_5Me_5)(C_6H_4)X_2$ (M = Nb, X = Me; M = Ta, X = Cl or Me).(1) An X-ray structure of one of them(2) (M = Ta, X = Me) showed that the benzyne ligand was oriented perpendicular to the η^5-C$_5$Me$_5$ ring. This would be unusual if the benzyne ligand were behaving strictly as an alkyne because simple alkyne (and olefin) ligands bond more or less parallel to the ring in monocyclopentadienyl complexes of many metals. Therefore we became interested in making analogous complexes of "normal" alkynes in order to compare them structurally and chemically with the benzyne complexes. At first this did not seem as though it would be a simple task. We thought that the obvious route, displacement of an olefin from $Ta(\eta^5\text{-}C_5Me_5)(olefin)Cl_2$,(3) would not work since the resulting acetylene complex should react with a second equivalent of acetylene to give a tantalacyclopentadiene complex. However, this approach was successful since the alkyne complexes, like the benzyne complexes, are surprisingly unreactive. We report here the preparation and characterization of several alkyne complexes of this type, including one of acetylene itself, along with an X-ray structural study of the diphenylacetylene complex.

Results

Preparation and Reactions of Ta(η^5-C$_5$Me$_5$)(alkyne)Cl$_2$ Complexes. When 1 equiv of diphenylacetylene was added to a toluene solution of $Ta(\eta^5\text{-}C_5Me_5)(styrene)Cl_2$, the color slowly changed from purple to red-orange over several hours. Removal of the solvent in vacuo gave an orange, crystalline

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