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STRUCTURE OF AN ASYMMETRIC DINUCLEAR ORGANOTANTALUM COMPLEX WITH THREE DIFFERENT BRIDGING LIGANDS: $[(\eta^5\text{-}C_5Me_4Et)TaCl_2](\mu\text{-}\eta^1\text{-}N,\eta^2\text{-}C,N\text{-}NCHMe)(\mu\text{-}Cl)(\mu\text{-}H)[(\eta^5\text{-}C_5Me_4Et)TaCl]$

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Summary

The complex $[(\eta^5\text{-}C_5Me_4Et)TaCl_2](\mu\text{-}\eta^1\text{-}N,\eta^2\text{-}C,N\text{-}NCHMe)(\mu\text{-}Cl)(\mu\text{-}H)[(\eta^5\text{-}C_5Me_4Et)TaCl]$, previously synthesized by the stoichiometric reaction of $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H_2)$ with acetonitrile, has been characterized by a complete three-dimensional X-ray diffraction study. The complex crystallizes in the non-centrosymmetric orthorhombic space group $Pbc2_1$ [C_{2v}^5; No. 29] with a 9.936(2), b 18.896(5), c 15.005(3) Å, V 2817.4(11) Å^3 and $Z = 4$. Diffraction data ($2\theta = 3.5°–50°$; Mo-K_α) were collected with a Syntex P2$_1$ automated four-circle diffractometer and the structure was refined to $R_F = 5.0$ and $R_{wF} = 4.1\%$ for all 4998 point-group independent reflections. The molecule contains a $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]$ and a $[(\eta^5\text{-}C_5Me_4Et)TaCl]$ fragment which are unsymmetrically triply-bridged by a chloride ligand (Ta(1)–Cl(4) 2.553(3), Ta(2)–Cl(4) 2.617(3) Å), a hydride ligand (Ta(1)–H(br) 2.18(9), Ta(2)–H(br) 1.70(9) Å), and a $\mu\text{-}\eta^1\text{-}N,\eta^2\text{-}C,N$-NCHMe ligand (Ta(1)–N 1.901(8), Ta(2)–N 2.059(8), Ta(2)–C(1) 2.195(10) Å); the Ta(1)–Ta(2) distance is 2.979(1) Å.

Introduction

Schrock and his coworkers have recently reported [1] the synthesis and characterization of a new class of binuclear hydridotantalum complexes, of which $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2H]_2$ (**1**) is an example. The structure I is proposed for this species, in keeping with the known structure II of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_3(Me)H_2$, but in contradistinction to the quadruply bridged species $[(PMe_3)_2TaCl_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2$ [2], see structure III.

Complex **1** has been shown to add carbon monoxide [3] producing the "side-on"

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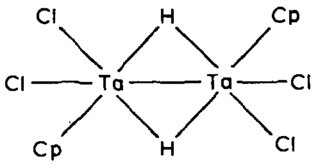
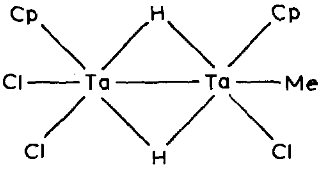


(I)



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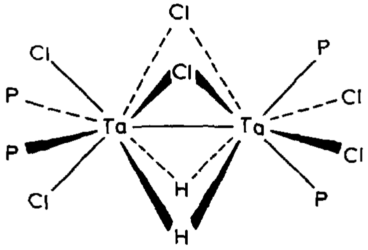

(III)

bridging formyl hydride complex $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2]_2(\mu\text{-}CHO)(\mu\text{-}H)$ (2) which further reacts with PMe_3 with cleavage of the carbon–oxygen bond and production of the hydrido-oxo-phosphoylide species $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2]_2(\mu\text{-}CHPMe_3)(\mu\text{-}O)(\mu\text{-}H)$ (3). X-ray structural studies of both **2** [4,5] and **3** [3,6] have been completed and have revealed that the gross metal atom coordination environment does not change appreciably upon cleavage of the carbon–oxygen bond in the μ-CHO ligand. In each of these structures the tantalum atoms have a "quasi-3,4,1" coordination geometry. However, the two tantalum atoms are nonequivalent, with the hydride ligands (not located directly) occupying bridging sites which span a radial position (*trans* to chloride) on one metal center and an axial position (*trans* to an $\eta^5\text{-}C_5Me_4Et$ ligand) on the other metal center.

Recently $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2H]_2$ (1) has been shown to react with one equivalent of acetonitrile (MeC≡N) to give a complex of stoichiometry $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4H(NCHMe)$ (4) [7]. We now report the results of a single-crystal X-ray structural analysis of this species, allowing recognition of the mode of bonding of the NCHMe fragment to the ditantalum unit and providing further insight into factors governing the structural geometry of these binuclear tantalum hydride adducts with electron-rich substrates. Furthermore, the present study has allowed direct location of the hydride ligand (albeit with the usual limited precision) confirming the position postulated from indirect evidence gleaned from previous structural studies on related complexes [3–6].

Experimental

A sample consisting of many suitable crystals of almost gem-like quality was supplied by Patricia Belmonte and Professor Richard R. Schrock of the Chemistry Department, Massachusetts Institute of Technology. Crystals were sealed into thin glass capillaries inside a KSE inert-atmosphere (Ar) dry-box which had been specially modified by addition of a protruding transparent port (allowing inspection

TABLE 1

EXPERIMENTAL DETAILS FOR THE X-RAY DIFFRACTION STUDY

Crystal parameters [a] *at 22°C*

a 9.936(2) Å
b 18.896(5) Å
c 15.005(3) Å
V 2817.4(11) Å^3
mol. wt. = 944.95

Cryst. system: orthorhombic
Space group: $Pbc2_1$ [b]
$Z = 4$
ρ(calc) 1.99 g cm^{-3}

Data collection

Radiation: graphite monochromatized Mo-K_α ($\bar{\lambda}$ 0.71073 Å)
Reflections measured: $+h$, $+k$, $\pm l$
Scan type: coupled θ(crystal)-2θ(counter)
2θ range: 3.5–50.0°
Scan speed: 2.55° min^{-1} in 2θ
Scan range: $[2\theta(\text{Mo-}K_{\alpha 1})\text{-}1.0]° - [2\theta(\text{Mo-}K_{\alpha 2}) + 1.0]°$
Reflections collected: 5103 total; 4998 unique
Abs. coeff: μ 85.7 cm^{-1}

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[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo-$K_{\bar{\alpha}}$ components of 25 reflections, all having $25° \leqslant 2\theta \leqslant 30°$. [b] Non-standard setting of the space group $Pca2_1$ [C_{2v}^5; No. 29] having the equipoints x,y,z; $-x,1/2+y,z$; $x,1/2-y,1/2+z$; $-x,-y,1/2+z$.

of crystals via an externally-mounted binocular polarizing microscope) mounted between the gloves.

The crystal selected for the diffraction study measured approximately 0.25 × 0.25 × 0.35 mm. It was mounted in a random orientation on our Syntex P2$_1$ automated four-circle diffractometer. The general procedures for aligning the crystal, determining lattice constants and collecting intensity data have appeared elsewhere [8]; details pertinent to the current analysis appear in Table 1.

The systematic absences ($0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$) are consistent with the centrosymmetric orthorhombic space group $Pbcm$ (D_{2h}^{11}; No. 57) or the noncentrosymmetric orthorhombic space group $Pbc2_1$ (a nonstandard setting of $Pca2_1$ (C_{2v}^5; No. 29) [9]).
The former, centrosymmetric, space group requires that the molecule be bisected by a crystallographic mirror plane; this is not the case. The latter, noncentrosymmetric, possibility was confirmed by the successful solution of the structure.

All data were corrected for Lorentz and polarization factors and for the effects of absorption.

Solution and refinement of the structure

Interpretation of an unsharpened Patterson map resulted in approximate coordinates for the two independent tantalum atoms. The origin was fixed by defining $z(\text{Ta}(1)) = 0$ (exactly). Subsequent difference-Fourier syntheses yielded the positions of all remaining non-hydrogen atoms. After several cycles of full-matrix least-squares refinement, minimizing $\Sigma w(|F_0| - |F_c|)^2$, the bridging hydride ligand was located from a difference-Fourier map. All other hydrogen atoms were placed in idealized calculated positions based upon C–H 0.95 Å [10] and the appropriate geometry. (While the positions of the hydrogen atoms of the methyl groups are, in principle,

TABLE 2

POSITIONAL PARAMETERS FOR THE Ta(μ-NCHMe)(μ-Cl)(μ-H)Ta COMPLEX

Atom	*x*	*y*	*z*	B_{iso}
Ta(1)	0.77033(5)	0.83168(2)	0.00000(0)	
Ta(2)	0.73286(5)	0.67576(2)	0.01580(3)	
Cl(1)	0.62726(36)	0.87677(16)	0.12223(19)	
Cl(2)	0.58082(33)	0.86564(16)	−0.08924(20)	
Cl(3)	0.89856(37)	0.60001(17)	0.08066(23)	
Cl(4)	0.85253(37)	0.75787(15)	0.13175(21)	
N	0.8104(10)	0.75048(40)	−0.06989(57)	
C(1)	0.8403(10)	0.68396(48)	−0.11156(63)	
C(2)	0.9825(13)	0.65966(64)	−0.12070(83)	
C(11)	0.8637(12)	0.93226(55)	−0.08766(63)	
C(12)	0.8457(10)	0.95784(43)	0.00037(83)	
C(13)	0.9324(13)	0.91915(61)	0.05527(73)	
C(14)	1.0021(10)	0.86764(45)	−0.00079(89)	
C(15)	0.9580(14)	0.87831(61)	−0.08768(92)	
C(16)	0.8019(17)	0.96752(71)	−0.16891(82)	
C(17)	0.7606(13)	1.01971(60)	0.0271(10)	
C(18)	0.9581(17)	0.93106(66)	0.15232(77)	
C(19)	1.1198(14)	0.82270(65)	0.0272(10)	
C(20)	1.0131(18)	0.84307(78)	−0.1689(10)	
C(21)	1.1292(18)	0.88109(88)	−0.20926(95)	
C(31)	0.6059(12)	0.58544(56)	−0.06621(69)	
C(32)	0.6088(11)	0.56237(51)	0.02332(81)	
C(33)	0.5419(13)	0.61452(68)	0.07609(81)	
C(34)	0.4918(12)	0.66775(47)	0.01607(68)	
C(35)	0.5365(10)	0.65112(57)	−0.07106(68)	
C(36)	0.6636(16)	0.54231(57)	−0.14252(80)	
C(37)	0.6615(15)	0.49252(64)	0.05456(94)	
C(38)	0.5169(15)	0.61143(90)	0.17439(84)	
C(39)	0.3952(13)	0.72383(75)	0.04163(90)	
C(40)	0.4966(13)	0.68831(55)	−0.15520(71)	
C(41)	0.3661(15)	0.65919(90)	−0.19322(88)	
H(br)	0.629(11)	0.7467(42)	0.0286(65)	1.2(25)
H(1)	0.8222	0.6652	−0.1690	6.0
H(2A)	0.9843	0.6149	−0.1495	6.0
H(2B)	1.0317	0.6930	−0.1550	6.0
H(2C)	1.0220	0.6555	−0.0632	6.0
H(16A)	0.8591	1.0045	−0.1888	6.0
H(16B)	0.7913	0.9335	−0.2150	6.0
H(16C)	0.7164	0.9865	−0.1535	6.0
H(17A)	0.8115	1.0620	0.0216	6.0
H(17B)	0.6839	1.0222	−0.0106	6.0
H(17C)	0.7323	1.0140	0.0871	6.0
H(18A)	1.0241	0.9670	0.1593	6.0
H(18B)	0.8770	0.9453	0.1806	6.0
H(18C)	0.9896	0.8884	0.1786	6.0
H(19A)	1.2007	0.8490	0.0207	6.0
H(19B)	1.1092	0.8091	0.0877	6.0
H(19C)	1.1238	0.7816	−0.0092	6.0
H(20A)	1.0415	0.7967	−0.1530	6.0
H(20B)	0.9433	0.8401	−0.2120	6.0
H(21A)	1.1594	0.8560	−0.2604	6.0
H(21B)	1.1020	0.9274	−0.2261	6.0

TABLE 2 (continued)

Atom	x	y	z	B_{iso}
H(21C)	1.2002	0.8840	−0.1670	6.0
H(36A)	0.5969	0.5106	−0.1642	6.0
H(36B)	0.6909	0.5731	−0.1891	6.0
H(36C)	0.7389	0.5160	−0.1219	6.0
H(37A)	0.5924	0.4579	0.0504	6.0
H(37B)	0.7354	0.4787	0.0183	6.0
H(37C)	0.6901	0.4964	0.1147	6.0
H(38A)	0.4371	0.5851	0.1856	6.0
H(38B)	0.5909	0.5891	0.2029	6.0
H(38C)	0.5066	0.6581	0.1969	6.0
H(39A)	0.3059	0.7064	0.0355	6.0
H(39B)	0.4105	0.7372	0.1018	6.0
H(39C)	0.4071	0.7637	0.0039	6.0
H(40A)	0.4851	0.7372	−0.1428	6.0
H(40B)	0.5660	0.6824	−0.1980	6.0
H(41A)	0.3440	0.6839	−0.2463	6.0
H(41B)	0.3768	0.6103	−0.2061	6.0
H(41C)	0.2958	0.6651	−0.1509	6.0

indeterminate, past experience has shown that these groups take up a conformation such that each will present one hydrogen atom pointing upward on the outer side (i.e., away from the metal atom) of the planar carbocyclic ring.)

Anisotropic thermal parameters were used for all non-hydrogen atoms and convergence ($(\Delta/\sigma)_{\max} < 0.1$) was reached with $R_F = 5.0$, $R_{wF} = 4.1\%$ and GOF = 1.20 for a model consisting of 283 variables refined against all 4998 point-group independent reflections with $3.5° < 2\theta < 50.0°$ (Mo-K_α radiation; no datum rejected). The overdetermination ratio is thus 17.7/1. (Discrepancy indices for those 4377 reflections with $|F_0| > 3.0\sigma$ were $R_F = 3.8$ and $R_{wF} = 3.9\%$.)

Refinement using inverted z-coordinates ($x', y', z' = x, y, -z$) led to significantly higher residuals ($R_F = 6.2$, $R_{wF} = 5.6\%$, GOF = 1.64); the original model therefore defined the correct enantiomorph.

All crystallographic computations were carried out using our in-house Syntex XTL system, including the XTL interactive program package as modified at SUNY/Buffalo. The analytical form of the scattering factors of the neutral atoms [11a] were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion [11b] were included for all non-hydrogen atoms.

Final positional and thermal parameters are collected in Tables 2 and 3.

Results and discussion

Intramolecular distances with their estimated standard deviations (e.s.d.'s) are collected in Table 4; selected interatomic angles are given in Table 5. Least-squares planes appear in Table 6. The labelling of non-hydrogen atoms is shown in Fig. 1, while Fig. 2 provides a stereoscopic view of the entire molecule.

The completed diffraction study shows the complex to be an unsymmetrical

TABLE 3

ANISOTROPIC THERMAL PARAMETERS (B_{ij}'s, in Å^2) FOR NON-HYDROGEN ATOMS IN THE Ta(μ-NCHMe)(μ-Cl)(μ-H)Ta COMPLEX [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta(1)	2.874(24)	2.202(15)	2.762(27)	0.236(14)	0.174(39)	−0.042(15)
Ta(2)	2.441(22)	2.316(16)	3.299(32)	0.227(13)	−0.130(38)	0.092(15)
Cl(1)	5.93(19)	4.27(15)	3.73(12)	0.16(14)	1.58(12)	−0.62(10)
Cl(2)	4.13(16)	3.78(14)	4.71(13)	0.51(13)	−0.67(11)	0.59(11)
Cl(3)	4.43(17)	4.22(15)	6.56(18)	1.03(13)	−1.22(13)	0.58(13)
Cl(4)	6.66(20)	3.62(13)	3.85(12)	−0.46(13)	−1.81(12)	0.43(10)
N	3.09(41)	3.45(47)	3.95(41)	0.78(33)	0.42(35)	0.03(28)
C(1)	2.60(47)	2.63(43)	3.72(43)	−0.52(36)	0.38(34)	−1.21(33)
C(2)	3.86(64)	3.68(57)	7.10(68)	0.98(49)	1.62(52)	−1.03(49)
C(11)	4.22(60)	3.31(50)	2.94(43)	−0.32(45)	−0.13(38)	0.05(35)
C(12)	2.86(48)	2.31(35)	4.19(46)	−0.12(32)	−0.68(46)	0.53(42)
C(13)	4.22(67)	3.75(53)	3.18(51)	−1.42(47)	−0.08(45)	−0.08(38)
C(14)	2.25(42)	2.39(37)	5.76(58)	0.19(32)	−0.22(49)	0.37(48)
C(15)	3.78(69)	4.12(60)	5.17(68)	−1.50(51)	1.65(53)	−0.74(48)
C(16)	7.9(10)	5.83(71)	4.94(59)	−0.18(70)	−1.06(59)	2.41(52)
C(17)	5.97(75)	2.99(46)	8.90(89)	0.26(50)	1.66(65)	0.23(54)
C(18)	10.0(12)	4.77(68)	3.91(56)	−3.28(72)	−0.93(58)	−0.07(45)
C(19)	4.09(67)	5.04(63)	10.4(10)	1.19(52)	−1.33(71)	0.73(65)
C(20)	8.7(11)	5.62(73)	6.17(71)	−1.85(75)	3.85(72)	−1.68(58)
C(21)	7.3(10)	8.5(10)	6.96(74)	−3.44(86)	3.39(70)	−2.19(66)
C(31)	3.56(61)	3.13(49)	3.27(48)	−0.34(46)	0.31(42)	−0.42(36)
C(32)	2.78(48)	2.87(40)	4.61(60)	−0.67(35)	0.02(46)	0.67(43)
C(33)	2.62(60)	4.92(65)	4.13(56)	−1.35(53)	−0.36(43)	0.19(45)
C(34)	4.82(59)	2.68(41)	3.27(47)	0.30(35)	0.13(41)	0.03(44)
C(35)	2.14(47)	3.48(53)	4.19(46)	−0.70(42)	−1.21(35)	0.68(38)
C(36)	6.82(88)	2.42(48)	6.57(69)	−0.02(53)	1.33(58)	−0.71(44)
C(37)	6.41(86)	3.55(58)	8.06(79)	−0.96(59)	−0.80(67)	2.86(52)
C(38)	4.32(73)	10.3(11)	4.20(60)	−1.47(75)	0.57(50)	0.35(63)
C(39)	3.33(61)	6.12(68)	7.46(75)	0.57(56)	1.29(54)	−0.07(58)
C(40)	4.78(65)	3.09(52)	4.52(52)	−0.18(46)	−1.39(45)	0.57(39)
C(41)	4.45(75)	10.2(11)	5.96(72)	−2.24(77)	−1.28(56)	2.19(67)

[a] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form: $\exp(-0.25(h^2a^{*2}B_{11} + \ldots 2hka^*b^*B_{12} + \ldots))$.

dinuclear species in which the Ta(1)–Ta(2) distance is 2.979(1) Å (cf. Ta–Ta 2.992(1) Å in $[\mathrm{Ta}(\eta^5\text{-}C_5Me_4Et)Cl_2]_2(\mu\text{-CHPMe}_3)(\mu\text{-O})(\mu\text{-H})$ (**3**) and Ta–Ta 3.186(1) Å in $[\mathrm{Ta}(\eta^5\text{-}C_5Me_4Et)Cl_2]_2(\mu\text{-CHO})(\mu\text{-H})$ (**2**)).

The two tantalum atoms in the present complex are nonequivalent. Ta(1) is linked symmetrically to an η^5-C_5Me_4Et ligand (with individual tantalum–carbon distances ranging from Ta(1)–C(14) 2.401(10) Å through Ta(1)–C(12) 2.499(8) Å and with Ta(1) ··· Cp(1) 2.142 Å) and to two terminal chloride ligands (Ta(1)–Cl(1) 2.472(3) and Ta(1)–Cl(2) 2.398(3) Å). Ta(2) is linked to an η^5-C_5Me_4Et ligand (with Ta–C distances from Ta(2)–C(35) 2.392(10) Å through Ta(2)–C(32) 2.474(10) Å and Ta(2) ··· Cp(2) 2.101 Å) and to a single terminal chloride ligand (Ta(2)–Cl(3) 2.389(3) Å).

The two tantalum atoms are bridged by a chloride ligand (Cl(4)), a bridging

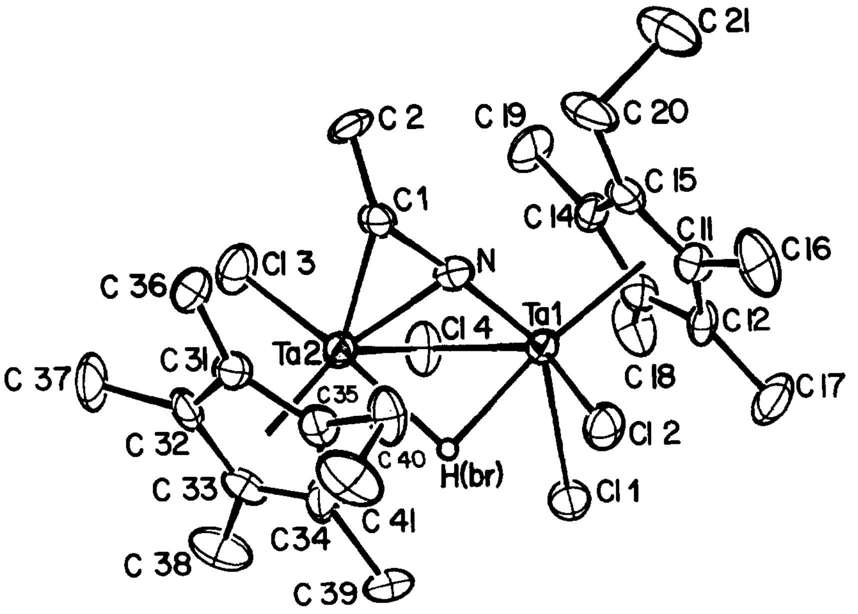

Fig. 1. Labeling of all non-hydrogen atoms within the [(η-C_5Me_4Et)$TaCl_2$](μ-η^1-*N*,η^2-*C*,*N*-NCHMe)(μ-Cl)(μ-H)[(η^5-C_5Me_4Et)TaCl] molecule. (ORTEP-II diagram, 30% ellipsoids.)

hydride ligand (H(br)) and by a unique μ-η^1-*N*,η^2-*C*,*N*-NCHMe ligand (derived by hydrogenation of acetonitrile, N≡C–Me). Each of the bridges is asymmetric; the Ta(1)–Cl(4) bond length of 2.553(3) Å is slightly shorter than the Ta(2)–Cl(4) bond length of 2.617(3) Å, while the Ta(1)–H(br) bond distance of 2.18(9) Å is somewhat longer than the Ta(2)–H(br) bond distance of 1.70(9) Å. The Ta(1)–N distance of 1.901(8) Å is indicative of some multiple-bond character in this linkage (cf. Ta=N = 1.765(5) Å in *mer*-Ta(=NPh)(THF)(PEt_3)Cl_3 [12]). In contrast to this, the values Ta(2)–N 2.059(8) and Ta(2)–C(1) 2.195(10) Å are closer to single-bond distances.

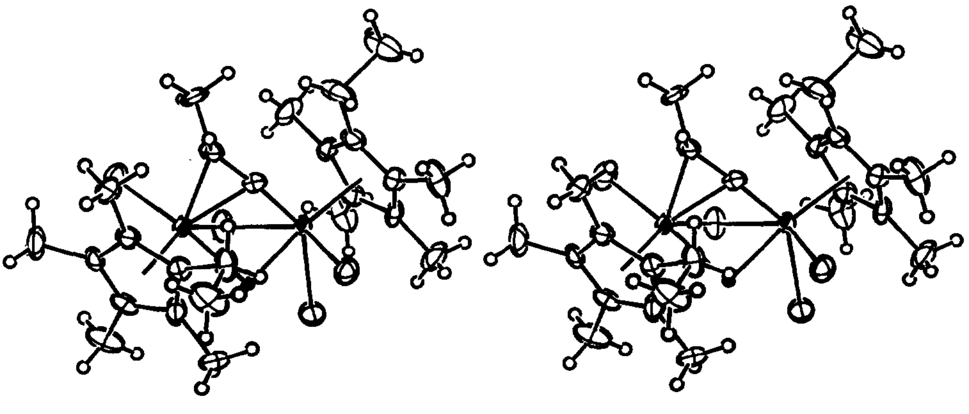

Fig. 2. Stereoscopic view of the molecule, with all hydrogen atoms artificially reduced for clarity.

Bond lengths within the bridging NCHMe ligand are N–C(1) 1.435(12) and C(1)–C(2) 1.491(16) Å, with N–C(1)–C(2) 120.4(9)°.

Details of the core geometry can be seen from Fig. 3. Angles at the bridging atoms are Ta(1)–Cl(4)–Ta(2) 70.35(8), Ta(1)–N–Ta(2) 97.5(4) and Ta(1)–H(br)–Ta(2) 99(4)°. There is no requirement for a direct tantalum–tantalum bond other than that involved in the two-electron, three-center Ta(μ-H)Ta system.

Atom Ta(1) has a rather precise "quasi-3,4,1" coordination geometry, with the η^5-C_5Me_4Et ligand formally taking up three adjacent coordination sites (whence the designation "quasi-3"). The Cp(1)–Ta(1)–L(equatorial) angles are close to equivalent, with Cp(1)–Ta(1)–Cl(1) 106.4, Cp(1)–Ta(1)–Cl(2) 105.3, Cp(1)–Ta(1)–Cl(4) 106.9 and Cp(1)–Ta–N 109.1°; the Cp(1)–Ta(1)–L(axial) angle is Cp(1)–Ta(1)–H(br) = 176°. The *cis*-diequatorial angles (cyclically) are Cl(1)–Ta(1)–Cl(2) 82.5(1), Cl(2)–Ta(1)–N 94.2(3), N–Ta(1)–Cl(4) 85.4(3) and Cl(4)–Ta(1)–Cl(1) 78.3(1)°. The *trans*-diequatorial angles are Cl(1)–Ta(1)–N 143.9(3) and Cl(2)–Ta(1)–Cl(4) 146.1(1)°.

The coordination geometry about Ta(2) is necessarily more complicated, because atoms C(1) and N (which are linked together, with a N–Ta(2)–C(1) angle of only 39.3(4)°) formally occupy two distinct equatorial sites in a rather distorted "quasi-3,4,1" arrangement. Within the framework of this description, the Cp(2)–Ta(2)–L(equatorial) angles are as follows: Cp(2)–Ta(2)–Cl(3) 108.1, Cp(2)–Ta(2)–C(1) 108.5, Cp(2)–Ta(2)–N 126.1 and Cp(2)–Ta(2)–H(br) 86°; the axial angle is then Cp(2)–Ta(2)–Cl(4) 142.3°. The *cis*-diequatorial angles about Ta(2) vary substan-

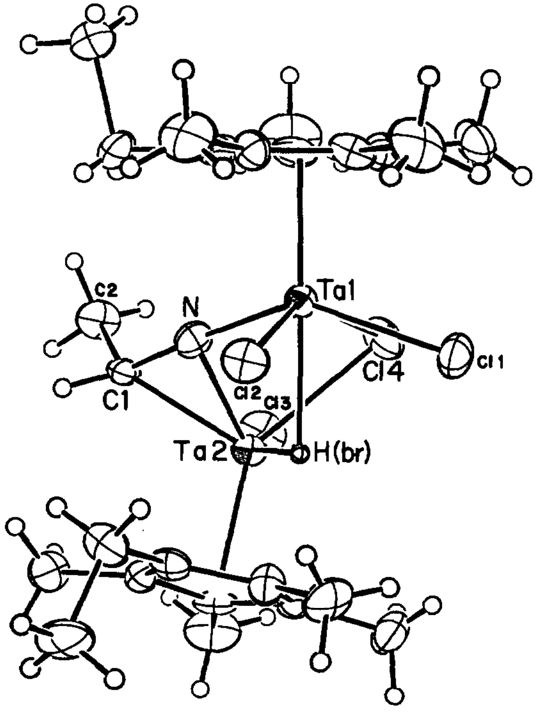

Fig. 3. A view of the molecule approximately parallel to the (η^5-C_5Me_4Et) rings, showing the geometry of the Ta(μ-NCHMe)(μ-Cl)(μ-H)Ta core.

TABLE 4

INTRAMOLECULAR DISTANCES WITH e.s.d.'s IN PARENTHESES

Atom	Distance (Å)	Atom	Distance (Å)
Distances from the tantalum atoms (A)			
Ta(1)–Ta(2)	2.979(1)	Ta(2)–Cl(3)	2.389(3)
Ta(1)–Cl(1)	2.472(3)	Ta(2)–Cl(4)	2.617(3)
Ta(1)–Cl(2)	2.398(3)	Ta(2)–N	2.059(8)
Ta(1)–Cl(4)	2.553(3)	Ta(2)–C(1)	2.195(10)
Ta(1)–N	1.901(8)	Ta(2)–H(br)	1.70(9)
Ta(1)–H(br)	2.18(9)	Ta(2)–C(31)	2.453(11)
Ta(1)–C(11)	2.491(10)	Ta(2)–C(32)	2.474(10)
Ta(1)–C(12)	2.499(8)	Ta(2)–C(33)	2.400(13)
Ta(1)–C(13)	2.452(12)	Ta(2)–C(34)	2.400(12)
Ta(1)–C(14)	2.401(10)	Ta(2)–C(35)	2.392(10)
Ta(1)–C(15)	2.447(13)	Ta(2)–Cp(2) [b]	2.101(-)
Ta(1)–Cp(1) [a]	2.142(-)		
Distances within the bridging NCHMe ligand (B)			
N–C(1)	1.435(12)	C(1)–C(2)	1.491(16)
Internal C–C distances within the η^5-C_5Me_4Et ligands (C)			
C(11)–C(12)	1.418(15)	C(31)–C(32)	1.413(16)
C(12)–C(13)	1.398(16)	C(32)–C(33)	1.429(17)
C(13)–C(14)	1.461(16)	C(33)–C(34)	1.439(16)
C(14)–C(15)	1.390(19)	C(34)–C(35)	1.416(15)
C(15)–C(11)	1.385(17)	C(35)–C(31)	1.422(15)
External $C(sp^2)$–$C(sp^3)$ distances for the η^5-C_5Me_4Et ligands (D)			
C(11)–C(16)	1.519(17)	C(31)–C(36)	1.518(16)
C(12)–C(17)	1.497(15)	C(32)–C(37)	1.495(16)
C(13)–C(18)	1.495(16)	C(33)–C(38)	1.497(18)
C(14)–C(19)	1.505(17)	C(34)–C(39)	1.480(17)
C(15)–C(20)	1.492(20)	C(35)–C(40)	1.498(15)
External $C(sp^3)$–$C(sp^3)$ distances for the η^5-C_5Me_4Et ligands (E)			
C(20)–C(21)	1.488(24)	C(40)–C(41)	1.520(20)

[a] Cp(1) is the centroid of the carbocyclic ring on Ta(1), defined by C(11) → C(15). [b] Cp(2) is the centroid of the carbocyclic ring on Ta(2), defined by atoms C(31) → C(35).

tially, with Cl(3)–Ta(2)–C(1) 93.5(3), Cl(1)–Ta(2)–N 39.3(4), N–Ta(2)–H(br) 76.0(32) and H(br)–Ta(2)–Cl(3) 147.5(32)°.

In our previous study of $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2]_2(\mu\text{-}CHPMe_3)(\mu\text{-}O)(\mu\text{-}H)$ [6], in which the metal atoms have a similar quasi-3,4,1 coordination environment, we observed that the unique axial bond about each metal atom appeared to be longer (i.e., weaker) than the four equatorial bonds. A similar pattern is observed in the present structure. Thus the (distorted) axial Ta(2)–Cl(4) bond length of 2.617(3) Å is longer than the equatorial Ta(1)–Cl(4) distance of 2.553(3) Å; similarly the axial Ta(1)–H(br) bond length of 2.18(9) Å is longer than the equatorial Ta(2)–H(br) distance of 1.70(9) Å. The asymmetry of the Ta(1)–Cl(4)–Ta(2) and Ta(2)–H(br)–Ta(1) bridges is thereby explained.

TABLE 5

SELECTED INTERATOMIC ANGLES (deg) WITH e.s.d.'s IN PARENTHESES

Angles around the tantalum atoms (A)			
Cl(1)–Ta(1)–Cl(2)	82.5(1)	Cl(3)–Ta(2)–Cl(4)	76.8(1)
Cl(1)–Ta(1)–Cl(4)	78.3(1)	Cl(3)–Ta(2)–N	114.0(3)
Cl(1)–Ta(1)–N	143.9(3)	Cl(3)–Ta(2)–C(1)	93.5(3)
Cl(1)–Ta(1)–H(br)	74.7(25)	Cl(3)–Ta(2)–H(br)	147.5(32)
Cl(2)–Ta(1)–Cl(4)	146.1(1)	Cl(4)–Ta(2)–N	80.7(3)
Cl(2)–Ta(1)–N	94.2(3)	Cl(4)–Ta(2)–C(1)	108.4(3)
Cl(2)–Ta(1)–H(br)	78.5(25)	Cl(4)–Ta(2)–H(br)	74.6(32)
Cl(4)–Ta(1)–N	85.4(3)	N–Ta(2)–C(1)	39.3(4)
Cl(4)–Ta(1)–H(br)	69.6(25)	N–Ta(2)–H(br)	76.0(32)
N–Ta(1)–H(br)	69.5(25)	C(1)–Ta(2)–H(br)	109.8(32)
Angles from Cp(1) and Cp(2) (B)			
Cp(1)–Ta(1)–Cl(1)	106.4	Cp(2)–Ta(2)–Cl(3)	108.1
Cp(1)–Ta(1)–Cl(2)	105.3	Cp(2)–Ta(2)–Cl(4)	142.3
Cp(1)–Ta(1)–Cl(4)	106.9	Cp(2)–Ta(2)–N	126.1
Cp(1)–Ta(1)–N	109.1	Cp(2)–Ta(2)–C(1)	108.5
Cp(1)–Ta(1)–H(br)	176	Cp(2)–Ta(2)–H(br)	86
Angles involving the bridging ligands (C)			
Ta(1)–Cl(4)–Ta(2)	70.35(8)	Ta(2)–C(1)–N	65.3(5)
Ta(1)–N–Ta(2)	97.5(4)	Ta(2)–C(1)–C(2)	121.3(7)
Ta(1)–H(br)–Ta(2)	99(4)	N–C(1)–C(2)	120.4(9)
Ta(1)–N–C(1)	172.3(7)	Ta(2)–N–C(1)	75.5(5)
Internal angles of η^5-C_5Me_4Et ligands (D)			
C(15)–C(11)–C(12)	109.7(10)	C(35)–C(31)–C(32)	109.1(10)
C(11)–C(12)–C(13)	107.0(9)	C(31)–C(32)–C(33)	107.8(10)
C(12)–C(13)–C(14)	107.5(10)	C(32)–C(33)–C(34)	107.2(10)
C(13)–C(14)–C(15)	107.1(10)	C(33)–C(34)–C(35)	108.3(9)
C(14)–C(15)–C(11)	108.7(11)	C(34)–C(35)–C(31)	107.4(9)

As was expected, the overall molecular geometry of the present complex closely resembles that of $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2]_2(\mu\text{-}CHPMe_3)(\mu\text{-}O)(\mu\text{-}H)$ (**3**) and of $[Ta(\eta^5\text{-}C_5Me_4Et)Cl_2]_2(\mu\text{-}CHO)(\mu\text{-}H)$ (**2**). The principal difference is that in both **3** and **2** the reduced CO ligand is still capable of acting as a double bridge between the tantalum atoms (we have independent Ta–C–Ta and Ta–O–Ta bridges in **3** and a μ-η^2-*C,O*-η^2-*C,O*-HCO bridge in the Ta(HCO)Ta system of **2**). In the present complex, C(1) is saturated (by linkages to N, C(2), H(1) and Ta(2)) and cannot be involved in further bonding to Ta(1). To compensate for this, atom Cl(4) moves from a terminal position on Ta(2) to a bridging position between Ta(2) and Ta(1) to complete a closed triply-bridged structure analogous to that observed for the "disrupted formyl" species **3** and the bridging formyl complex **2**.

All other bond lengths and bond angles in the structure are normal (see Tables 4 and 5). The η^5-C_5Me_4Et ligands take up the usual configuration (cf. [5,6]) with the terminal carbon atom of each ethyl group pointing vertically above the pentaatomic carbocyclic plane (see Fig. 3) and with all substituents on the cyclopentadienyl

TABLE 6

ATOMIC DEVIATIONS (Å) FROM LEAST-SQUARES PLANES

Atom	dev	Atom	dev
Cyclopentadienyl plane 1 (A)			
C(11)[a]	0.001(11)	C(16)	0.183(15)
C(12)[a]	−0.006(9)	C(17)	0.096(13)
C(13)[a]	0.009(12)	C(18)	0.125(15)
C(14)[a]	−0.008(9)	C(19)	0.215(13)
C(15)[a]	0.005(13)	C(20)	0.144(16)
Ta(1)	−2.1428(4)	C(21)	1.556(17)
Cl(1)	−2.889(3)	N	−2.717(9)
Cl(2)	−2.885(3)	C(1)	−3.245(10)
Cl(4)	−2.777(3)	C(2)	−2.500(13)
H(br)	−4.31(10)	Ta(2)	−4.4163(4)
Cyclopentadienyl plane 2 (B)			
C(31)[a]	0.004(12)	C(36)	0.080(15)
C(32)[a]	0.011(11)	C(37)	0.160(15)
C(33)[a]	−0.022(13)	C(38)	0.016(15)
C(34)[a]	0.024(11)	C(39)	0.262(13)
C(35)[a]	−0.018(10)	C(40)	0.145(13)
Ta(2)	−2.0981(5)	C(41)	1.607(16)
Cl(3)	−2.924(4)	Cl(2)	−2.383(3)
C(1)	−2.825(10)	Cl(1)	−3.322(3)
N	−3.286(10)	C(2)	−3.783(13)
H(br)	−1.91(10)	Ta(1)	−3.8572(5)
Cl(4)	−4.131(4)		
Ta(NC)Ta plane (C)			
Ta(1)[a]	−0.0136(4)	C(2)	−1.224(13)
Ta(2)[a]	0.0016(5)	H(br)	0.91(11)
N[a]	0.031(10)	Cl(4)	−1.763(4)
C(1)[a]	−0.019(10)		
Ta(μ-Cl)Ta plane (D)			
Ta(1)[a]	0.000	H(br)	−1.19(11)
Ta(2)[a]	0.000	C(1)	1.798(10)
Cl(4)[a]	0.000	N	1.062(10)
Ta(μ-H)Ta plane (E)			
Ta(1)[a]	0.000	Cl(4)	−2.047(3)
Ta(2)[a]	0.000	N	0.993(9)
H(br)[a]	0.000	C(1)	1.587(10)
Angles between normals to planes (°)			
A/B	159.42	B/C	38.55
A/C	121.53	B/D	127.45
A/D	52.52	B/E	68.65
A/E	93.49		
C/D	123.75	D/E	75.71
C/E	48.04		

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[a] These atoms (only) used in calculating least-squares plane.

ligands being displaced from the plane in a direction away from the appropriate tantalum atom (see Table 6) *.

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* Additional data. See NAPS document no. 04062 for 28 pages of Supplementary Material (list of observed and calculated structure factor amplitudes). Order from NAPS c/o Microfiche Publications, P.O.Box 3513, Grand Central Station, New York N.Y. 10163. Remit in advance in U.S. funds only $\$10^{15}$ for photocopies or \$4.00 for microfiche. Outside the U.S. and Canada add postage of \$4.50 for the first 20 pages and \$1.00 for each page thereafter. \$1.50 for microfiche postage.