Low-Temperature Neutron Diffraction Studies of C–H–Metal Interactions in Two Tantalum–Neopentylidene Complexes: $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ [T = 110 K] and the First Alkylidene/Olefin Complex, $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$ [T = 20 K]

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Abstract: Neutron diffraction studies of the two title compounds, in which *precise* hydrogen atom location was essential, have established that the neopentylidene ligands are highly distorted. In $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$, the $Ta{=}C_\alpha{-}C_\beta$ angle is 161.2 (1)°, the $Ta{=}C_\alpha{-}H_\alpha$ angle is 84.8 (2)°, the $Ta{=}C_\alpha$ bond is short (1.898 (2) Å), the $C_\alpha{-}H_\alpha$ distance is long (1.131 (3) Å), and H_α is only 2.119 (4) Å from Ta. In $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$, the $Ta{=}C_\alpha{-}C_\beta$ angle is 170.0 (2)°, the $Ta{=}C_\alpha{-}H_\alpha$ angle is 78.1 (3)°, the $C_\alpha{-}H_\alpha$ bond is also long (1.135 (5) Å), the $Ta{=}C_\alpha$ bond length short (1.946 (3) Å), and H_α is only 2.042 (5) Å from Ta. We believe the neopentylidene ligand is distorted in each case primarily because the metal is attracting electron density from the $C_\alpha{-}H_\alpha$ bond. The tantalum—ethylene bonding in the second molecule is best described as that of a tantallacyclopropane ring on the basis of the long ethylene C—C bond (1.477 (4) Å) and the large angle (68.5°) between the normals to the two CH_2 planes. We believe the neopentylidene/ethylene complex does not decompose via a tantallacyclobutane complex because of the large separation between the neopentylidene and ethylene ligands.

Introduction

For some time we have known that ${}^1J_{CH_\alpha}$ and ν_{CH_α} in electron-deficient (<18 e) neopentylidene and benzylidene complexes of Nb and Ta are often surprisingly low compared to their values in 18-electron complexes.[2] X-ray structural studies of a bis(neopentylidene) complex[3] and, more recently, of a benzylidene complex[4] showed that these alkylidene ligands are distorted from the idealized sp^2-hybridized trigonal geometry of the carbene α-carbon atom; the $M{=}C_\alpha{-}C_\beta$ angles are abnormally large (150–170°). We therefore expected the $M{=}C_\alpha{-}H_\alpha$ angles to be small and suspected that some unusual feature of the $C{-}H_\alpha$ bond was the cause of low values for ${}^1J_{CH_\alpha}$ and ν_{CH_α}. This is in contrast to the Fischer-type carbene complexes $(CO)_5M{=}C_\alpha(R_1)R_2$ where the electrophilic α-carbon is usually stabilized with a normal sp^2 geometry by bonding to a heteroatom of one of the R groups.[40]

The first tantalum–alkylidene compound which gave crystals suitable for neutron diffraction studies was $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ (**1**).[5] The next was $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$ (**2**), a complex which is formed when *trans*-$Ta(\eta^5\text{-}C_5Me_5)(CCMe_3)(PMe_3)_2Cl$[6] is treated with $MgEt_2$(dioxane) (0.5 equiv).[7] In both complexes ${}^1J_{CH_\alpha}$ is low (101 and 74 Hz, respectively). The fact that an ethylene ligand is also present in the second molecule provided additional incentive since there are no neutron diffraction structural data of an early transition-metal ethylene complex available and since an alkylidene/olefin complex is a logical intermediate in olefin metathesis reactions.[2,8,9]

Table I. Crystal and Experimental Data for the Neutron Diffraction Studies of $[Ta(CHCMe_3)Cl_3]_2$ (1) and $Ta(C_5Me_5)(CHCMe_3)(C_2H_4)(PMe_3)$ (2)

	1[a]	2[b]
(a) Crystal Parameters		
space group	$P2_1/n$	$P2_1/n$
a, Å	10.920 (6)	16.557 (7)
b, Å	12.827 (7)	13.932 (5)
c, Å	10.553 (6)	9.393 (3)
β, deg	91.05 (2)	103.53 (3)
V, Å^3	1478 (1)	2107 (1)
Z, molecules/unit cell	2	4
(b) Data and Refinement Parameters		
neutron wavelength, Å	1.142 (1)	1.1629 (2)
independent data	2930	4799
abs coeff μ, cm^{-1}	2.37	2.90
isotropic extinction coeff 10^4g	0.56 (3)	0.071 (6)
$R(F_o)$	0.083	0.117
$R(F_o^2)$	0.078	0.106
$R_w(F_o^2)$	0.094	0.060

[a] All measurements at 110 K for 1. [b] All measurements at 20 K for **2**.

Results

Neutron Diffraction Study of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ (1).[10] This molecule is a member of a large class of monomeric and dimeric octahedral neopentylidene complexes which contain P, As, N, or O donor ligands.[11] This complex was chosen because crystals of suitable size for neutron diffraction studies were easily obtained (see Experimental Section). Crystal lattice and data refinement parameters are given in Table I. The final positional

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Table II. Final Positional[a] and Thermal[b] Parameters for $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
TA	-0.1640(1)	0.06374(9)	0.0440(1)	0.0090(5)	0.0112(5)	0.0104(5)	0.0006(4)	-0.0003(4)	-0.0003(4)
CL1	-0.05773(9)	0.21842(8)	0.08424(9)	0.0166(5)	0.0171(5)	0.0198(5)	-0.0051(4)	-0.0001(4)	-0.0024(4)
CL2	-0.01271(9)	-0.05099(8)	0.14623(9)	0.0125(4)	0.0210(5)	0.0144(4)	0.0039(4)	0.0010(3)	0.0037(3)
CL3	-0.25087(9)	-0.07227(7)	-0.08022(9)	0.0155(5)	0.0148(4)	0.0175(4)	-0.0004(4)	-0.0009(3)	-0.0030(3)
P	-0.3004(2)	0.1731(1)	-0.1108(2)	0.0130(8)	0.0139(8)	0.0147(7)	0.0016(6)	-0.0013(6)	0.0017(6)
C1	-0.2758(1)	0.0811(1)	0.1780(1)	0.0135(6)	0.0184(7)	0.0123(6)	0.0013(5)	0.0031(5)	-0.0013(5)
C2	-0.3345(1)	0.1219(1)	0.2955(1)	0.0166(7)	0.0217(7)	0.0141(6)	-0.0018(6)	0.0035(5)	-0.0049(5)
C3	-0.4622(2)	0.1649(2)	0.2619(2)	0.0164(8)	0.049(1)	0.0332(9)	0.0056(8)	0.0012(7)	-0.0197(9)
C4	-0.2568(2)	0.2098(1)	0.3516(2)	0.0265(9)	0.0327(9)	0.0234(8)	-0.0094(7)	0.0048(6)	-0.0125(7)
C5	-0.3459(2)	0.0343(1)	0.3920(2)	0.051(1)	0.033(1)	0.0196(8)	-0.0106(9)	0.0118(8)	0.0009(7)
C6	-0.2583(1)	0.1634(1)	-0.2754(1)	0.0224(8)	0.0327(9)	0.0161(7)	0.0057(7)	0.0003(6)	0.0056(6)
C7	-0.3084(2)	0.3121(1)	-0.0815(2)	0.0288(9)	0.0168(7)	0.0347(9)	0.0045(7)	-0.0029(7)	-0.0005(5)
C8	-0.4600(1)	0.1335(1)	-0.1110(2)	0.0112(6)	0.0289(9)	0.0272(8)	0.0013(6)	-0.0025(6)	0.0037(6)
H1	-0.3194(3)	0.0072(3)	0.1399(3)	0.035(2)	0.030(2)	0.038(2)	-0.008(1)	0.005(1)	-0.008(1)
H3A	-0.5223(4)	0.1061(5)	0.2213(5)	0.029(2)	0.089(3)	0.070(3)	-0.003(2)	-0.004(2)	-0.042(3)
H3B	-0.5045(4)	0.1963(4)	0.3456(5)	0.043(2)	0.078(3)	0.054(2)	0.008(2)	0.014(2)	-0.030(2)
H3C	-0.4579(5)	0.2274(4)	0.1946(5)	0.056(3)	0.073(3)	0.060(3)	0.031(2)	-0.006(2)	-0.004(3)
H4A	-0.2999(4)	0.2418(4)	0.4350(4)	0.059(2)	0.063(3)	0.037(2)	-0.014(2)	0.013(2)	-0.029(2)
H4B	-0.2466(5)	0.2733(3)	0.2844(4)	0.074(3)	0.037(2)	0.050(2)	-0.021(2)	0.012(2)	-0.007(2)
H4C	-0.1657(4)	0.1813(4)	0.3769(5)	0.034(2)	0.080(3)	0.064(3)	-0.009(2)	-0.010(2)	-0.022(2)
H5A	-0.3889(5)	0.0628(4)	0.4775(4)	0.087(4)	0.077(3)	0.027(2)	-0.017(3)	0.025(2)	-0.004(2)
H5B	-0.4019(6)	-0.0298(4)	0.3544(4)	0.101(4)	0.045(2)	0.050(2)	-0.035(3)	0.022(2)	-0.000(2)
H5C	-0.2560(6)	0.0037(5)	0.4180(5)	0.087(4)	0.075(3)	0.050(2)	0.017(3)	-0.001(2)	0.027(2)
H6A	-0.3222(4)	0.2070(4)	-0.3352(4)	0.044(2)	0.069(3)	0.032(2)	0.018(2)	-0.005(2)	0.018(2)
H6B	-0.2578(5)	0.0835(3)	-0.3026(4)	0.080(3)	0.046(2)	0.035(2)	0.010(2)	0.005(2)	-0.010(2)
H6C	-0.1672(4)	0.1948(4)	-0.2877(4)	0.035(2)	0.084(3)	0.044(2)	-0.007(2)	0.010(2)	0.011(2)
H7A	-0.3702(4)	0.3488(3)	-0.1507(5)	0.057(2)	0.032(2)	0.076(3)	0.015(2)	-0.020(2)	0.009(2)
H7B	-0.2181(4)	0.3471(3)	-0.0902(5)	0.051(3)	0.029(2)	0.086(3)	-0.008(2)	-0.003(2)	0.004(2)
H7C	-0.3402(5)	0.3263(3)	0.0131(4)	0.094(4)	0.036(2)	0.045(2)	0.009(2)	0.013(2)	-0.010(2)
H8A	-0.5115(3)	0.1750(3)	-0.1838(4)	0.030(2)	0.057(2)	0.052(2)	0.005(2)	-0.013(2)	0.015(2)
H8B	-0.4995(4)	0.1474(4)	-0.0195(4)	0.035(2)	0.087(3)	0.040(2)	-0.002(2)	0.011(2)	0.003(2)
H8C	-0.4655(4)	0.0509(3)	-0.1284(5)	0.034(2)	0.035(2)	0.094(3)	-0.007(2)	-0.009(2)	-0.006(2)

[a] *x*, *y*, and *z* are fractional coordinates. [b] Anisotropic temperature factors of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + 2a^*b^*U_{12}hk + ...)]$.

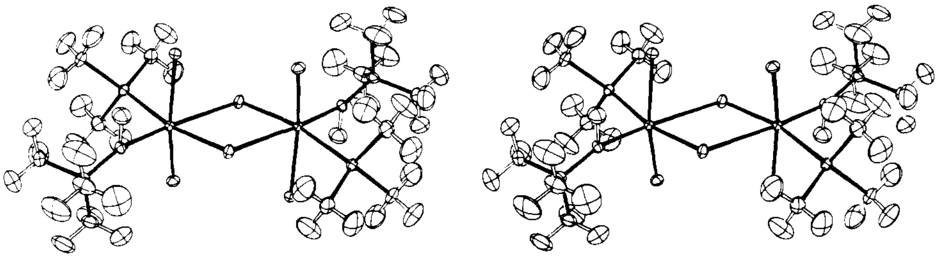

Figure 1. Stereoscopic view of the molecular structure of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ (**1**) at 110 K. The ellipsoids of thermal motion for all atoms are scaled to enclose 50% probability. Refer to Figure 2 for the atom-labeling scheme.

and thermal parameters are given in Table II, selected intramolecular distances and angles are presented in Table IV, and least-squares planes and distances are given in Table VI. A stereoscopic drawing of **1** is shown in Figure 1, whereas Figure 2 presents a perspective view about one of the metal centers.

$[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ (**1**) is a dimer containing bridging chloride ligands and a crystallographically imposed center of inversion. The first observation to be made regarding the bridging system is that it is asymmetric. The chloride ligand situated trans to the neopentylidene ligand is 2.815 (2) Å from tantalum while that which is trans to the phosphine ligand is 2.448 (2) Å from tantalum. Thus, it is safe to postulate that the former Ta–Cl bond is weaker than the latter, and this is probably why the dimer easily fragments into monomers at a rate which is on the order of the NMR time scale.[11] It should be noted that the Ta–Ta distance of 4.016 (2) Å precludes any significant direct metal–metal bonding.

The octahedral geometry about each Ta is highly distorted; P, Cl(1), Cl(2), and Cl(3) are bent away from the neopentylidene ligand with C(1)–Ta–L angles of 92.10 (8), 95.13 (7), 100.37 (7), and 104.01 (7)°, respectively (Figure 2). In fact, the spacial arrangement of the ligands about each metal can be considered "square pyramidal" with the neopentylidene ligand at the apex if one ignores the loosely bound bridging chloride trans to it. It is especially interesting that the C(1)–Ta–Cl(3) angle is the largest of the four, as if the greatest ligand–ligand repulsion is between Cl(3) and the neopentylidene. Consistent with this observation is the fact that the H(1)–Cl(3) distance (2.657 (4) Å) is the shortest contact between the alkylidene and other ligands. For comparison, the shortest contacts between the C(4) methyl hydrogen atoms and Cl(1) are 3.061 (5) and 3.360 (6) Å.

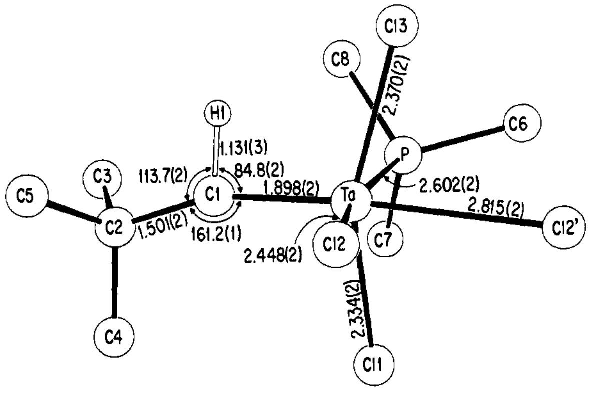

Figure 2. A perspective view of the coordination geometry around a single Ta atom in $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ (**1**). Except for H(1), all hydrogen atoms have been omitted for clarity. The thermal ellipsoids do not represent the experimental values (see Figure 1).

The most unusual aspect of the structure of **1** is the geometry of the neopentylidene ligand. It is essentially planar and oriented perpendicular to the Ta–Cl(2)–Cl(2)′–P–C(1) plane (Table VI), but Cl(1) and Cl(3) do not lie exactly in the Ta–C(1)–C(2)–H(1) plane. Several features deserve to be emphasized. First, the Ta–C(1) bond length of 1.898 (2) Å is much shorter[12] than the

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[12] Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578–6579.

Table III. Final Positional[a] and Thermal[b] Parameters for $Ta(C_5H_5)(CHCMe_3)(C_2H_4)(PMe_3)$

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
TA	0.2750(1)	0.1286(1)	-0.0269(2)	0.0042(8)	0.0013(9)	0.015(1)	-0.0007(7)	0.0056(8)	0.0003(9)
P	0.3596(2)	0.2368(2)	0.1644(3)	0.005(1)	0.001(1)	0.017(2)	0.001(1)	-0.000(1)	-0.000(1)
C1	0.3663(1)	0.1249(1)	-0.1249(3)	0.0056(9)	0.003(1)	0.019(1)	0.0013(8)	0.0055(9)	0.004(1)
C2	0.4291(1)	0.1353(2)	-0.2186(3)	0.0053(9)	0.002(1)	0.017(1)	0.0004(8)	0.0058(9)	0.0015(9)
C3	0.4090(1)	0.0650(2)	-0.3501(3)	0.012(1)	0.002(1)	0.024(1)	-0.0000(8)	0.009(1)	-0.001(1)
C4	0.4258(1)	0.2393(2)	-0.2771(3)	0.010(1)	0.005(1)	0.023(1)	0.0018(9)	0.007(1)	0.004(1)
C5	0.5181(1)	0.1149(2)	-0.1293(3)	0.005(1)	0.012(1)	0.029(2)	0.0044(9)	0.009(1)	0.005(1)
C6	0.2648(1)	-0.0207(1)	0.0521(3)	0.006(1)	0.005(1)	0.017(1)	0.0007(8)	0.0055(9)	0.0026(9)
C7	0.2977(1)	0.0391(2)	0.1826(3)	0.010(1)	0.004(1)	0.022(1)	0.0022(8)	0.009(1)	0.004(1)
C8	0.4653(1)	0.1944(2)	0.2370(3)	0.006(1)	0.009(1)	0.028(2)	0.0000(9)	0.000(1)	-0.006(1)
C9	0.3814(1)	0.3605(2)	0.1140(3)	0.013(1)	0.004(1)	0.025(1)	-0.0027(9)	0.002(1)	-0.002(1)
C10	0.3269(1)	0.2583(2)	0.3343(3)	0.013(1)	0.008(1)	0.020(1)	0.002(1)	0.006(1)	-0.004(1)
C11	0.1562(1)	0.2378(1)	-0.0387(3)	0.0030(9)	0.001(1)	0.022(1)	-0.0007(8)	0.0042(9)	-0.0004(9)
C12	0.1852(1)	0.2507(1)	-0.1689(3)	0.0058(9)	0.004(1)	0.015(1)	0.0006(8)	0.0045(9)	0.0023(9)
C13	0.1703(1)	0.1636(1)	-0.2528(3)	0.0050(9)	0.005(1)	0.014(1)	0.0009(8)	0.0025(8)	-0.0005(9)
C14	0.1339(1)	0.0958(1)	-0.1712(3)	0.0049(9)	0.002(1)	0.019(1)	-0.0008(8)	0.0037(9)	-0.0009(9)
C15	0.1241(1)	0.1422(2)	-0.0405(2)	0.59(3)[c]					
C16	0.1460(1)	0.3154(2)	0.0659(3)	0.008(1)	0.005(1)	0.019(1)	0.0008(9)	0.004(1)	-0.003(1)
C17	0.2131(1)	0.3438(2)	-0.2243(3)	0.008(1)	0.004(1)	0.022(1)	0.0022(9)	0.007(1)	0.005(1)
C18	0.1808(1)	0.1496(2)	-0.4067(3)	0.009(1)	0.008(1)	0.016(1)	0.0003(9)	0.0029(9)	-0.001(1)
C19	0.0994(1)	-0.0004(2)	-0.2270(3)	0.007(1)	0.005(1)	0.024(1)	-0.0025(9)	0.005(1)	-0.004(1)
C20	0.0842(1)	0.0990(2)	0.0731(3)	0.010(1)	0.006(1)	0.024(2)	-0.0017(9)	0.010(1)	0.002(1)
H1	0.3774(3)	0.0570(3)	-0.0565(8)	0.032(3)	0.011(2)	0.065(4)	0.011(2)	0.030(3)	0.019(3)
H3A	0.4537(3)	0.0740(4)	-0.4201(7)	0.030(3)	0.030(3)	0.047(4)	-0.002(2)	0.027(3)	-0.010(3)
H3B	0.3461(3)	0.0767(4)	-0.4165(8)	0.017(2)	0.030(3)	0.060(4)	-0.005(2)	0.009(3)	-0.011(3)
H3C	0.4143(4)	-0.0094(3)	-0.3101(7)	0.047(3)	0.001(2)	0.056(4)	-0.002(2)	0.023(3)	-0.004(2)
H4A	0.4429(3)	0.2896(4)	-0.1873(8)	0.035(3)	0.016(3)	0.063(5)	-0.006(2)	0.019(3)	-0.008(3)
H4B	0.4704(3)	0.2481(4)	-0.3444(7)	0.025(3)	0.022(2)	0.048(3)	0.003(2)	0.022(3)	0.011(3)
H4C	0.3635(3)	0.2574(4)	-0.3350(7)	0.016(2)	0.026(3)	0.045(3)	0.006(2)	0.003(2)	0.012(3)
H5A	0.5232(3)	0.0406(4)	-0.0903(7)	0.028(3)	0.025(3)	0.049(4)	0.006(2)	0.009(3)	0.016(3)
H5B	0.5368(3)	0.1654(5)	-0.0409(8)	0.017(2)	0.048(4)	0.055(4)	-0.003(2)	0.002(3)	-0.014(3)
H5C	0.5622(3)	0.1201(4)	-0.1983(7)	0.015(2)	0.037(3)	0.051(4)	0.005(2)	0.019(2)	0.012(3)
H6A	0.2020(3)	-0.0499(3)	0.0362(7)	0.015(2)	0.018(2)	0.045(3)	-0.008(2)	0.011(2)	0.003(2)
H6B	0.3080(3)	-0.0728(3)	0.0229(6)	0.023(2)	0.015(2)	0.030(3)	0.011(2)	0.008(2)	-0.004(2)
H7A	0.2544(3)	0.0564(4)	0.2493(8)	0.026(3)	0.022(3)	0.056(4)	-0.004(2)	0.028(3)	-0.004(3)
H7B	0.3609(3)	0.0240(3)	0.2412(7)	0.017(2)	0.022(2)	0.046(4)	0.004(2)	-0.001(2)	0.003(3)
H8A	0.4990(3)	0.1907(5)	0.1524(8)	0.023(3)	0.064(4)	0.049(4)	0.012(3)	0.021(3)	-0.001(4)
H8B	0.4654(3)	0.1234(4)	0.2805(9)	0.024(3)	0.013(3)	0.092(6)	0.001(2)	0.000(3)	0.007(3)
H8C	0.4998(3)	0.2440(4)	0.3201(8)	0.022(2)	0.032(3)	0.060(4)	-0.007(2)	-0.007(3)	-0.025(3)
H9A	0.4086(4)	0.3596(4)	0.0216(8)	0.055(4)	0.019(3)	0.061(4)	-0.007(3)	0.036(3)	0.005(3)
H9B	0.3262(3)	0.4039(4)	0.0952(7)	0.024(3)	0.021(2)	0.054(4)	0.005(2)	0.010(3)	0.007(3)
H9C	0.4280(3)	0.3949(4)	0.2037(7)	0.030(3)	0.027(3)	0.043(3)	-0.015(2)	-0.007(3)	-0.010(3)
H10A	0.3210(4)	0.1894(4)	0.3847(8)	0.061(4)	0.018(3)	0.058(5)	-0.006(3)	0.033(4)	0.002(3)
H10B	0.2683(3)	0.2949(4)	0.3170(6)	0.029(3)	0.051(3)	0.029(3)	0.019(3)	0.016(2)	-0.002(3)
H10C	0.3741(4)	0.3021(4)	0.4093(8)	0.035(3)	0.036(3)	0.050(4)	-0.012(3)	0.008(3)	-0.019(3)
H16A	0.0860(3)	0.3539(4)	0.0247(7)	0.024(3)	0.026(3)	0.055(4)	0.016(2)	0.009(3)	-0.012(3)
H16B	0.1947(3)	0.3692(3)	0.0830(6)	0.022(2)	0.018(2)	0.042(3)	-0.012(2)	0.014(2)	-0.010(2)
H16C	0.1418(4)	0.2882(4)	0.1722(7)	0.055(4)	0.027(3)	0.027(3)	-0.001(3)	0.026(3)	-0.000(2)
H17A	0.1616(3)	0.3812(4)	-0.2946(8)	0.022(3)	0.023(3)	0.071(5)	0.006(2)	0.002(3)	0.022(3)
H17B	0.2628(3)	0.3338(4)	-0.2785(7)	0.027(3)	0.023(3)	0.056(4)	0.001(2)	0.027(3)	0.005(3)
H17C	0.2353(4)	0.3944(4)	-0.1390(8)	0.043(3)	0.022(3)	0.061(4)	-0.018(3)	0.015(3)	-0.005(3)
H18A	0.2295(3)	0.1967(4)	-0.4278(7)	0.030(3)	0.037(3)	0.050(4)	-0.014(2)	0.019(3)	0.000(3)
H18B	0.1978(4)	0.0760(3)	-0.4234(7)	0.049(3)	0.011(2)	0.036(3)	0.008(2)	0.018(3)	-0.002(2)
H18C	0.1219(3)	0.1659(5)	-0.4845(8)	0.019(3)	0.055(4)	0.051(4)	0.010(3)	0.001(3)	0.002(3)
H19A	0.1392(3)	-0.0354(4)	-0.2853(8)	0.030(3)	0.025(3)	0.069(5)	-0.003(2)	0.027(3)	-0.022(3)
H19B	0.0934(4)	-0.0488(4)	-0.1419(9)	0.066(4)	0.020(3)	0.063(5)	-0.022(3)	0.024(4)	0.002(3)
H19C	0.0372(3)	0.0055(4)	-0.2907(9)	0.017(3)	0.030(3)	0.086(6)	0.000(2)	-0.009(3)	-0.013(3)
H20A	0.0990(4)	0.0243(3)	0.0925(7)	0.054(3)	0.008(3)	0.049(4)	0.007(2)	0.028(3)	0.005(2)
H20B	0.0992(4)	0.1367(5)	0.1744(7)	0.050(3)	0.039(3)	0.035(4)	-0.015(3)	0.024(3)	-0.003(3)
H20C	0.0168(3)	0.1028(4)	0.0389(7)	0.015(2)	0.053(3)	0.048(4)	-0.006(2)	0.017(2)	0.007(3)

[a] x, y, and z are fractional coordinates. [b] Anisotropic temperature factors of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \ldots + 2a^*b^*U_{12}hk + \ldots)]$. [c] Isotropic temperature factor B of the form $\exp(-B(\sin^2\theta)/\lambda^2)$.

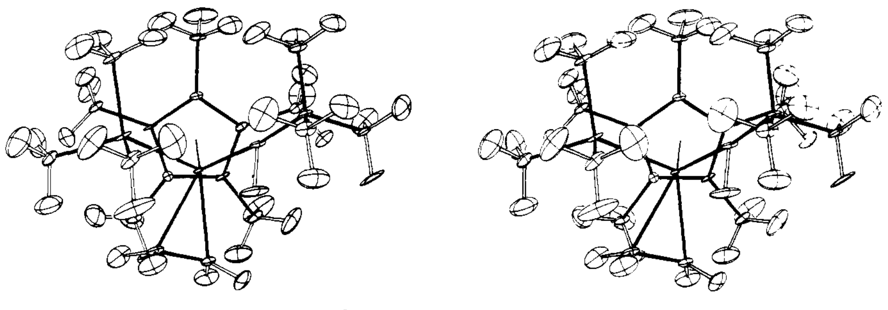

Figure 3. Stereoscopic view of the molecular structure of $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$ (**2**) at 20 K. The ellipsoids of thermal motion for all atoms are scaled to enclose 50% probability. Refer to Figure 4 for the atom-labeling scheme.

"normal" Ta–C double bond distance of 2.03 (1) Å in $Ta(\eta^5\text{-}C_5H_5)(CH_2)(CH_3)$.[12] Second, the Ta–C(1)–C(2) angle (161.2 (1)°) is much larger, and third, the Ta–C(1)–H(1) angle (84.8 (2)°) is much smaller than expected for an sp^2-hybridized carbene α-carbon atom. Fourth, the C(1)–H(1) distance (1.131 (3) Å) is significantly longer than the average C–H distance of 1.083 (2) Å in this structure. The combination of the last two features places H(1) only 2.119 (4) Å from Ta, as if the Ta⋯H_α interaction is incipient to C–H bond cleavage. Since the interligand contacts (vide supra) of the *tert*-butyl group are longer than those of the α-hydrogen atom, the distortion of the neopentylidene ligand cannot be explained by steric factors alone. In fact, it appears that steric factors play a minor role, i.e., that the Ta–C(1)–C(2) angle is "pulled open".

Neutron Diffraction Study of $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$ (2). Details of the structural determination are presented in the Experimental Section and Table I. Final positional and thermal parameters are given in Table III. Selected intramolecular distances and angles are given in Table V, and some important least-squares planes and dihedral angles are presented in Table VII. A stereoscopic drawing of **2** is shown in Figure 3, and a perspective drawing is presented in Figure 4.

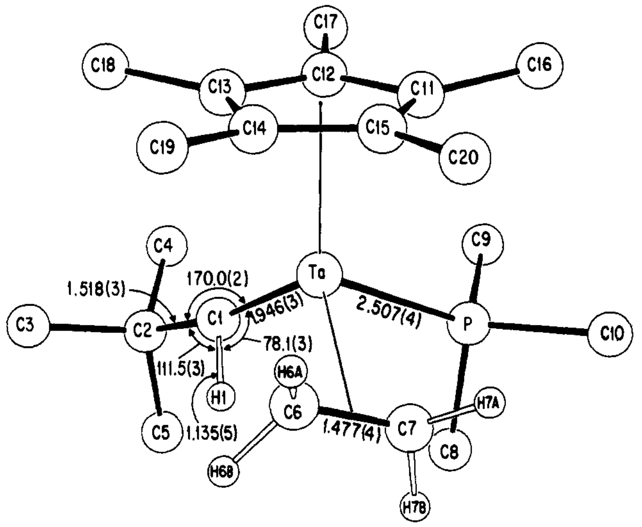

Figure 4. A perspective view of the molecular structure of Ta(η^5-C_5Me_5)($CHCMe_3$)(η^2-C_2H_4)(PMe_3) (**2**). Except for H(1) and the four ethylene hydrogen atoms, all hydrogen atoms have been omitted for clarity. The thermal ellipsoids do not represent the experimental values (see Figure 3).

The Ta coordination geometry in **2** may be described as highly distorted pseudotetrahedral if it is considered that the ethylene and cyclopentadienyl ligands each occupy a single coordination site. The three Cp–Ta–L angles vary only from about 116.7 to 122.1°, while the other three L–Ta–L′ angles are 89.4 (1), 94.4, and 110.7° (Table V). The last of these is the C(1)–Ta–C_2 angle (see footnotes in Table V for nomenclature), and it is roughly toward this opening that the neopentylidene α-hydrogen atom is turned (vide infra). The distances and angles within the η^5-C_5Me_5 and PMe_3 ligands appear normal. In the case of the permethylated cyclopentadienyl ligand, all of the methyl carbon atoms are bent away from the C(11)–C(15) ring plane and away from the Ta atom. Furthermore, each methyl group is oriented with one "axial" hydrogen atom exo to the Ta atom and two "equatorial" hydrogen atoms endo to the Ta atom. This type of conformation is commonly observed in structures of pentamethylcyclopentadienyl complexes.[13]

The neopentylidene ligand in **2** is more highly distorted than that in **1**. The Ta–C(1)–C(2) angle is 170.0 (2)°, the Ta–C(1)–H(1) angle is 78.1 (3)°, and the C(2)–C(1)–H(1) angle is 111.5 (3)°. The C(1)–H(1) bond length of 1.135 (5) Å is again significantly greater than the average of the other C–H distances in this molecule (1.085 (2) Å), and the Ta···H(1) distance is now only 2.042 (5) Å. The Ta–C(1) bond length (1.946(3) Å) is somewhat larger than that in **1** (1.898 (2) Å) but still shorter than what one would expect for a "true" Ta=C_α double bond.[2] The different distances in **1** and **2** can be attributed to the different oxidation states of Ta and the different coordination geometries in the two molecules.

Table IV. Selected Intramolecular Distances (Å) and Angles (Deg) for $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$

(a) Distances from the Tantalum Atom			
Ta–C(1)	1.898 (2)	Ta–Cl(2)′[a]	2.815 (2)
Ta–H(1)	2.119 (4)	Ta–Cl(3)	2.370 (2)
Ta–Cl(1)	2.334 (2)	Ta–P	2.602 (2)
Ta–Cl(2)	2.448 (2)	Ta–Ta	4.061 (3)
(b) Distances within the Neopentylidene Ligand			
C(1)–H(1)	1.131 (3)	C(3)–H(3C)	1.072 (7)
C(1)–C(2)	1.501 (2)	C(4)–H(4A)	1.087 (4)
C(2)–C(3)	1.535 (2)	C(4)–H(4B)	1.086 (5)
C(2)–C(4)	1.525 (2)	C(4)–H(4C)	1.089 (5)
C(2)–C(5)	1.524 (2)	C(5)–H(5A)	1.088 (4)
C(3)–H(3A)	1.083 (5)	C(5)–H(5B)	1.094 (5)
C(3)–H(3B)	1.081 (4)	C(5)–H(5C)	1.088 (7)
(c) Distances within the PMe_3 Ligand			
P–C(6)	1.808 (2)	C(7)–H(7A)	1.092 (4)
P–C(7)	1.811 (3)	C(7)–H(7B)	1.089 (5)
P–C(8)	1.816 (2)	C(7)–H(7C)	1.078 (4)
C(6)–H(6A)	1.087 (4)	C(8)–H(8A)	1.083 (4)
C(6)–H(6B)	1.065 (5)	C(8)–H(8B)	1.080 (4)
C(6)–H(6C)	1.084 (5)	C(8)–H(8C)	1.076 (4)
(d) Neopentylidene–Chlorine Contacts			
H(1)–Cl(3)	2.657 (4)	H(4C)–Cl(1)	3.360 (6)
H(4B)–Cl(1)	3.061 (5)		
(e) Angles around the Tantalum Atom			
Cl(1)–Ta–Cl(2)	95.83 (6)	Cl(2)–Ta–C(1)	100.37 (7)
Cl(1)–Ta–Cl(2)′	80.44 (5)	Cl(2)′–Ta–Cl(3)	80.52 (5)
Cl(1)–Ta–Cl(3)	156.81 (6)	Cl(2)′–Ta–P	88.58 (6)
Cl(1)–Ta–P	86.14 (7)	Cl(2)′–Ta–C(1)	175.47 (7)
Cl(1)–Ta–C(1)	95.13 (7)	Cl(3)–Ta–P	80.27 (7)
Cl(2)–Ta–Cl(2)′	79.24 (6)	Cl(3)–Ta–C(1)	104.01 (7)
Cl(2)–Ta–Cl(3)	80.52 (5)	P–Ta–C(1)	92.10 (8)
Cl(2)–Ta–P	167.13 (7)		
(f) Angles within the Neopentylidene Ligand			
Ta–C(1)–C(2)	161.2 (1)	C(3)–C(2)–C(4)	108.7 (1)
Ta–C(1)–H(1)	84.8 (2)	C(3)–C(2)–C(5)	109.5 (2)
C(2)–C(1)–H(1)	113.7 (2)	C(4)–C(2)–C(5)	109.8 (1)
C(1)–C(2)–C(3)	109.6 (1)	av C(2)–C–H[b,c]	110.9 (3)
C(1)–C(2)–C(4)	109.6 (1)	av H–C–H	108.0 (3)
C(1)–C(2)–C(5)	109.6 (1)		
(g) Angles within the PMe_3 Ligand			
Ta–P–C(6)	114.4 (1)	C(6)–P–C(8)	103.9 (1)
Ta–P–C(7)	116.9 (1)	C(7)–P–C(8)	103.1 (1)
Ta–P–C(8)	112.8 (1)	av P–C–H	110.0 (2)
C(6)–P–C(7)	104.2 (1)	av H–C–H	108.9 (4)

[a] The coordinates of Cl(2)′ are those of Cl(2) transformed by $-x$, $-y$, and $-z$. [b] This average does not include C(2)–C(1)–H(1). [c] The estimated standard deviations for average values are $[\Sigma_n(x_i - \bar{x})^2/n(n-1)]^{1/2}$.

The most important structural feature of the ethylene ligand in **2** is probably the unusually long C(6)–C(7) bond distance of 1.477 (4) Å. (For comparison, the C–C distance in free ethylene is 1.337 (2) Å,[14] and, on the basis of a neutron diffraction study,[15] it is 1.375 (4) Å in Zeise's salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$.) Of equal interest is the bending of the four hydrogen atoms away from the metal such that α = 68.5°, where α is the angle between the normals to the two CH_2 planes. The carbon atoms C(6) and C(7) are 0.341 (2) and 0.325 (2) Å, respectively, from the least-squares plane defined by the four ethylene hydrogen atoms (see Table VII). (In the neutron diffraction structure of Zeise's salt,[15] α is 32.5° and the two carbon atoms are 0.158 and 0.171 Å, respectively, from the plane of the four hydrogen atoms.) A third important point is that the Ta–C(7) distance (2.285 (3) Å) is noticeably longer than the Ta–C(6) distance (2.228 (3) Å). We postulate that this arises because C(7) is more "trans" to the alkylidene ligand than is C(6). This finding should be compared with a similar "trans" effect observed in **1**.

There is considerable structural[16,17] and spectroscopic[18] evidence, in addition to molecular orbital calculations,[19] which indicates that in $[(\eta^5\text{-}C_5H_5)ML_2Y]^{0,1+}$ complexes (Y = η^2-olefin or alkylidene), olefin and alkylidene ligands prefer a parallel and perpendicular orientation, respectively, with respect to the plane of the η^5-C_5H_5 ligand. (For an olefin, the parallel orientation means that the

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Table V. Selected Intramolecular Distances (Å) and Angles (Deg) for $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$

(a) Distances from the Tantalum Atom

Ta-C(1)	1.946 (3)	Ta-C(12)	2.441 (3)
Ta-H(1)	2.042 (5)	Ta-C(13)	2.454 (3)
Ta-C(6)	2.228 (3)	Ta-C(14)	2.453 (3)
Ta-C(7)	2.285 (3)	Ta-C(15)	2.478 (3)
Ta-C(11)	2.469 (3)	Ta-P	2.507 (4)

(b) Distances within the Neopentylidene Ligand

C(1)-H(1)	1.135 (5)	C(3)-H(3C)	1.099 (5)
C(1)-C(2)	1.518 (3)	C(4)-H(4A)	1.083 (7)
C(2)-C(3)	1.551 (4)	C(4)-H(4B)	1.084 (6)
C(2)-C(4)	1.545 (3)	C(4)-H(4C)	1.078 (5)
C(2)-C(5)	1.542 (3)	C(5)-H(5A)	1.094 (6)
C(3)-H(3A)	1.106 (6)	C(5)-H(5B)	1.077 (8)
C(3)-H(3B)	1.094 (6)	C(5)-H(5C)	1.086 (6)

(c) Distances within the Ethylene Ligand

C(6)-C(7)	1.477 (4)	C(7)-H(7A)	1.085 (6)
C(6)-H(6A)	1.095 (5)	C(7)-H(7B)	1.082 (5)
C(6)-H(6B)	1.098 (5)		

(d) Distances within the PMe_3 Ligand

P-C(8)	1.823 (4)	C(9)-H(9A)	1.068 (7)
P-C(9)	1.846 (4)	C(9)-H(9B)	1.075 (6)
P-C(10)	1.825 (4)	C(9)-H(9C)	1.109 (6)
C(8)-H(8A)	1.074 (7)	C(10)-H(10A)	1.084 (6)
C(8)-H(8B)	1.070 (7)	C(10)-H(10B)	1.075 (6)
C(8)-H(8C)	1.096 (6)	C(10)-H(10C)	1.105 (6)

(e) Distances within the C_5Me_5 Ligand

C(11)-C(12)	1.426 (3)	C(17)-H(17A)	1.082 (6)
C(11)-C(15)	1.432 (3)	C(17)-H(17B)	1.073 (6)
C(11)-C(16)	1.497 (3)	C(17)-H(17C)	1.066 (8)
C(12)-C(13)	1.436 (3)	C(18)-H(18A)	1.093 (6)
C(12)-C(17)	1.510 (3)	C(18)-H(18B)	1.084 (5)
C(13)-C(14)	1.436 (3)	C(18)-H(18C)	1.097 (6)
C(13)-C(18)	1.508 (3)	C(19)-H(19A)	1.068 (6)
C(14)-C(15)	1.430 (3)	C(19)-H(19B)	1.068 (8)
C(14)-C(19)	1.503 (3)	C(19)-H(19C)	1.066 (6)
C(15)-C(20)	1.506 (3)	C(20)-H(20A)	1.076 (5)
C(16)-H(16A)	1.115 (5)	C(20)-H(20B)	1.064 (8)
C(16)-H(16B)	1.085 (5)	C(20)-H(20C)	1.088 (6)
C(16)-H(16C)	1.086 (7)		

(f) H(neopentylidene)-H Interligand Contacts

H(1)-H(6B)	2.356 (7)	H(4C)-H(17B)	2.147 (7)
H(4A)-H(9A)	2.375 (9)	H(5B)-H(8A)	2.085 (9)

(g) Angles around the Tantalum Atom

C(1)-Ta-P	89.4 (1)	C(1)-Ta-C(6)	105.1 (1)
C(1)-Ta-Cp[a]	122.1	C(1)-Ta-C(7)	113.8 (1)
C(1)-Ta-C_2[b]	110.7	P-Ta-C(6)	113.3 (1)
P-Ta-Cp	116.7	P-Ta-C(7)	76.0 (1)
P-Ta-C_2	94.4	C(6)-Ta-C(7)	38.1 (9)
Cp-Ta-C_2	116.9		

(h) Angles within the Neopentylidene Ligand

Ta-C(1)-C(2)	170.0 (2)	C(3)-C(2)-C(4)	109.0 (2)
Ta-C(1)-H(1)	78.1 (3)	C(3)-C(2)-C(5)	108.4 (2)
C(2)-C(1)-H(1)	111.5 (3)	C(4)-C(2)-C(5)	108.4 (2)
C(1)-C(2)-C(3)	110.7 (2)	av C(2)-C-H[c,d]	110.5 (2)
C(1)-C(2)-C(4)	108.9 (2)	av H-C-H	108.4 (8)[e]
C(1)-C(2)-C(5)	111.3 (2)		

(i) Angles within the Ethylene Ligand

Ta-C(6)-C(7)	73.0 (1)	Ta-C(7)-C(6)	68.8 (1)
Ta-C(6)-H(6A)	116.4 (3)	Ta-C(7)-H(7A)	112.2 (4)
Ta-C(6)-H(6B)	115.4 (3)	Ta-C(7)-H(7B)	119.3 (3)
C(7)-C(6)-H(6A)	118.5 (4)	C(6)-C(7)-H(7A)	116.1 (4)
C(7)-C(6)-H(6B)	116.4 (3)	C(6)-C(7)-H(7B)	116.0 (3)
H(6A)-C(6)-H(6B)	112.0 (4)	H(7A)-C(7)-H(7B)	116.1 (5)

(j) Angles within the PMe_3 Ligand

Ta-P-C(8)	113.6 (2)	C(8)-P-C(10)	100.4 (2)
Ta-P-C(9)	119.2 (2)	C(9)-P-C(10)	100.7 (2)
Ta-P-C(10)	119.7 (2)	av P-C-H	110.6 (4)
C(8)-P-C(9)	99.8 (2)	av H-C-H	108.3 (7)

(k) Angles within the C_5Me_5 Ligand

C(12)-C(11)-C(15)	107.8 (2)	C(13)-C(14)-C(15)	107.9 (2)
C(12)-C(11)-C(16)	125.7 (2)	C(13)-C(14)-C(19)	125.1 (2)
C(15)-C(11)-C(16)	125.5 (2)	C(15)-C(14)-C(19)	126.3 (2)
C(11)-C(12)-C(13)	108.4 (2)	C(11)-C(15)-C(14)	108.3 (2)
C(11)-C(12)-C(17)	126.6 (2)	C(11)-C(15)-C(20)	125.9 (2)
C(13)-C(12)-C(17)	124.3 (2)	C(14)-C(15)-C(20)	125.8 (2)
C(12)-C(13)-C(14)	107.6 (2)	av C-C-H	111.8 (3)
C(12)-C(13)-C(18)	126.3 (2)	av H-C-H	107.0 (7)
C(14)-C(13)-C(18)	125.6 (2)		

[a] Cp is the centroid of the cyclopentadienyl ring as defined by atoms C(11) through C(15). [b] C_2 is the centroid of the ethylene ligand as defined by C(6) and C(7). [c] This average does not include C(2)-C(1)-H(1). [d] The estimated standard deviations for average values are $[\Sigma_n(x_i-\bar{x})^2/n(n-1)]^{1/2}$. [e] This average may not be meaningful, since the angles ranged from 104.6 (5) to 112.4 (5)°.

Table VI. Least-Squares Planes[a] and Distances (Å) of Atoms from the Planes for $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$

(a) Ta-C(1)-C(2)-H(1) Plane

$$-0.5844X + 0.5663Y - 0.5812Z - 1.2530 = 0$$

Ta	−0.008 (1)	Cl(2)'	−0.0837 (9)
C(1)	0.024 (1)	Cl(3)	0.3059 (9)
C(2)	−0.011 (1)	C(3)	1.318 (2)
H(1)	−0.005 (3)	C(4)	−0.206 (2)
Cl(1)	0.195 (1)	C(5)	−1.156 (2)

(b) Ta-Cl(2)-Cl(2)'-P-C(1) Plane

$$-0.4591X - 0.8196Y - 0.3428Z + 0.0049 = 0$$

Ta	0.002 (1)	C(1)	−0.093 (1)
Cl(2)	0.089 (1)	Cl(1)	−2.299 (1)
Cl(2)'	−0.079 (1)	Cl(3)	2.3053 (9)
P	0.082 (2)		

	Dihedral Angle, Deg
plane a-plane b	89.8

[a] In the equations of the planes, *X*, *Y* and *Z* are coordinates (Å) referred to unit orthogonal axes parallel to a, b, and (a × b).

olefinic C–C vector lies parallel to the C_5H_5 plane. For an alkylidene, a dihedral angle of 90° between the $M{=}C(R_1)R_2$ plane and the C_5H_5 plane is defined as the perpendicular orientation.) In **2**, both the neopentylidene and ethylene ligands are twisted from these ideal orientations. The dihedral angle between the neopentylidene plane (*a*, Table VII) and the cyclopentadienyl plane (*b*, Table VII) is 58.9°, which is a 37.7° rotation around the C(1)–Ta bond away from the perpendicular orientation such that the C(1)–H(1) vector is pointing toward the ethylene ligand. Concurrently, the ethylene C(6)–C(7) vector is turned 20.6° about the Ta–C_2 "bond" (see Table V, footnote *b*) away from a parallel orientation relative to the cyclopentadienyl plane. Alternatively, the ethylene ligand may simply be twisting away from H(1), which may also explain why the C(1)–Ta–C_2 angle of 110.7° is the largest of the three angles between C(1), C_2, and P (cf. the C(1)–Ta–Cl(3) angle in **1**). Again it is the angle between C(1) and the ligand toward which H(1) points which is the largest of the three interligand angles (cf. **1**).

Except for the twisting of the neopentylidene ligand, the *tert*-butyl group points toward the η^5-C_5Me_5 ligand. Due to the large Ta–C(1)–C(2) angle the interaction of the *tert*-butyl group with the η^5-C_5Me_5 ring is minimal. Again it seems likely that the neopentylidene Ta–C_α–C_β angle is not being "pushed" but is being "pulled open".

Discussion

The distortions of alkylidene ligands we have observed in **1** and **2** also occur in crowded 18-electron complexes such as $Ta(\eta^5\text{-}C_5H_5)_2(CHPh)(CH_2Ph)$[20] and $Ta(\eta^5\text{-}C_5H_5)_2(CHCMe_3)Cl$,[21] although to a lesser extent. The Ta═C_α—R bond angle is larger for R = CMe_3 than for R = Ph, and J_{CH_α} is smaller for R = CMe_3

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Table VII. Least-Squares Planes[a] and Distances (Å) of Atoms from the Planes for $Ta(C_5Me_5)(CHCMe_3)(C_2H_4)(PMe_3)$

(a) Ta-C(1)-C(2)-H(1) Plane			
$-0.4167X - 0.5304Y - 0.7383Z + 2.6992 = 0$			
Ta	0.009 (2)	C(4)	−0.392 (3)
C(1)	−0.024 (2)	C(5)	−0.971 (3)
C(2)	0.012 (2)	C(6)	0.722 (2)
H(1)	0.003 (6)	C(7)	−0.707 (3)
C(3)	1.437 (3)		
(b) C(11) through C(15) Plane			
$-0.8189X + 0.3259Y - 0.4723Z + 0.9413 = 0$			
C(11)	0.001 (2)	C(16)	0.228 (2)
C(12)	−0.007 (2)	C(17)	0.177 (2)
C(13)	0.010 (2)	C(18)	0.192 (2)
C(14)	−0.010 (2)	C(19)	0.162 (2)
C(15)	0.006 (2)	C(20)	0.066 (3)
Ta	−2.136 (2)		
(c) Ta-P-C(1) Plane			
$0.2583X - 0.7984Y + 0.5439Z + 0.3727 = 0$			
Ta	0.0	C(6)	1.965 (11)
P	0.0	C(7)	2.015 (12)
C(1)	0.0		
(d) Ta-C(6)-C(7) Plane			
$0.9787X - 0.1888Y - 0.0802Z - 4.1957 = 0$			
Ta	0.0	H(6A)	−0.896 (16)
C(6)	0.0	H(6B)	0.921 (16)
C(7)	0.0	H(7A)	−0.941 (19)
P	0.534 (9)	H(7B)	0.893 (16)
(e) H(6A)-H(6B)-H(7A)-H(7B) Plane			
$0.1384X + 0.7908Y - 0.5962Z + 0.2620 = 0$			
H(6A)	−0.033 (5)	Ta	2.463 (2)
H(6B)	0.034 (5)	C(6)	0.341 (2)
H(7A)	0.033 (6)	C(7)	0.325 (2)
H(7B)	−0.034 (5)		
(f) Dihedral Angles, Deg			
a-b	58.9	b-d	−34.4
a-c	−85.1	b-e	64.8
a-d	−75.6	c-d	68.9
a-e	−87.9	c-e	−23.1
b-c	−43.2	d-e	88.1

[a] In the equations of the planes, X, Y, and Z are coordinates (Å) referred to unit orthogonal axes parallel to a, b, and (a × b).

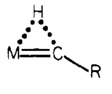
than for R = Ph[20] (see Table VIII). Therefore, we assumed the primary reason for the distortion in these complexes was steric in origin, which would not lead us to expect the M—C_α—R angle to be significantly larger in less crowded molecules. Yet this is precisely the case in the two molecules discussed in this study.

One of the major differences between the two molecules in this study and the 18-electron molecules mentioned above is that **1** has 14 and **2** has 16 electrons per metal. Therefore, it is reasonable to suspect that the alkylidene ligands distort in order to donate more than two electrons to the electron-deficient metal, somewhat like oxo[22] or imido[23] ligands do (no doubt more readily) in certain circumstances. This is an interesting way of interpreting the results until one observes that the neopentylidene ligand is most distorted in the more reduced (formally) 16-electron complex, **2**. The alkylidene ligand seems to change its character from undistorted ("hard") to distorted ("soft") according to the nature of the metal to which it is bonded.

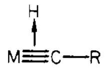
In the distorted neopentylidene ligands in **1** and **2**, the C_α–H_α bond is understandably long and weak if the electron density in the C_α–H_α is being drawn into the M–C_α bond. This accounts for the low CH_α stretching frequencies (2605 and 2520 cm^{-1}, respectively) and the low values of $^1J_{CH_\alpha}$ (101 and 74 Hz, respectively). In the more extreme of the two cases (**2**), the Ta···H(1) distance of 2.042 (5) Å is indicative of a weak Ta—H_α bond. (In $Ta(\eta^5\text{-}C_5H_5)_2H_3$,[24] the average Ta–H distance is 1.774 (3) Å). Under certain circumstances, the α-hydrogen atom could possibly transfer to the metal to produce an 18-electron alkylidyne hydride complex, which is formally a 2-electron oxidation of the metal. This is consistent with our observation that **2**, which is more reduced and should therefore have a greater tendency toward oxidation relative to **1**, is also the molecule with the most highly distorted neopentylidene ligand. Conceivably, the α-hydrogen atoms also ultimately could migrate to another ligand. We know, for example, that such alkylidene ligands can lose their α-hydrogen atom to an alkyl ligand to yield an alkylidyne complex and 1 equiv of alkane.[6] For hydrogen transfer to a ligand which remains bound to the metal (e.g., an olefin), the driving force (electron count and entropy) is not as great as in the former case. Perhaps this is why a neopentylidyne ethyl complex does not form from **2**.

Table VIII lists some data for all the tantalum–neopentylidene or –benzylidene complexes whose structures are known (in addition to the benzylidyne complex $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$[25]) according to the magnitude of the Ta–C_α–C_β angle. Note that $^1J_{CH_\alpha}$ generally decreases with the increasing Ta–C_α–C_β angle; the environment into which H_α is placed must change smoothly as the Ta–C_α–R angle varies. Note also that in some cases the Ta═C_α bond length varies inversely with the Ta–C_α–C_β angle and directly with $^1J_{CH_\alpha}$, although the variation is not uniform over all of the compounds. Therefore, perhaps we should place more emphasis on the Ta–C_α–C_β bond angle and/or $^1J_{CH_\alpha}$ if we are to identify distorted alkylidene ligands.

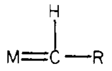
We believe the best description of such a distorted alkylidene ligand is the 3-center, 6-electron C–H–M interaction depicted by A. Descriptions B and C are variations in which the α-carbon atom is sp rather than sp^2 hybridized.



A



B



C

The latter is a classical valence bond description in which the CH_α bond is formed with a pure carbon $2p_z$ orbital which can also π bond to the metal; one sp-hybridized orbital forms the σ part of the M═C_α bond and the second a bond between C_α and R, while the carbon $2p_y$ orbital π bonds with the metal. In comparing the structures of **1** and **2**, the increase from **1** to **2** of 8.8 (2)° in the Ta—C(1)—C(2) angle leads to a 6.7 (4)° decrease in the Ta—C(1)—H(1) angle and only a 2.4 (3)° decrease in the C(2)—C(1)—H(1) angle. These results indicate a resistance on the part of the α-carbon atom to convert from sp^2 to sp hybridization with a C_β—C_α—H_α angle approaching 90°.

Of several selected ethylene complexes shown in Table IX, that in **2** has the largest value for α and the largest C–C bond length, both of which can be used as an index of the degree to which we may describe the system as a metallacyclopropane complex. The situation which bears the closest resemblance is found in $Nb(\eta^5\text{-}C_5H_5)_2(C_2H_4)(C_2H_5)$,[29] a complex in which the metal is in a higher formal oxidation state than Ta is in **2**. However, it may be argued that Ta prefers to be in a higher oxidation state than Nb, which is consistent with the structural results, since the formation of a tantallacyclopropane from a tantalum–ethylene species can be considered a 2-electron oxidation of the metal. We should note that long C—C bond lengths are also known for ethylene coordinated to later transition metals in low oxidation

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Table VIII. Structural Features of Tantalum-Alkylidene and -Alkylidyne Complexes

compd	Ta-C_α-C_β, deg	$^1J_{CH_\alpha}$, Hz	Ta-C_α, A	method	ref
Ta(η^5-C_5Me_5)(CPh)(PMe_3)$_2$Cl	171.8 (6)		1.849 (8)	*a*	25
Ta(η^5-C_5Me_5)($CHCMe_3$)(η^2-C_2H_4)(PMe_3)	170.0 (2)	74	1.946 (3)	*b*	this work
Ta($CHCMe_3$)$_2$(mesityl)(PMe_3)$_2$	168.9 (6)	91	1.932 (7)	*a*	3
Ta(η^5-C_5Me_5)(CHPh)(CH_2Ph)$_2$	166.0 (10)	82	1.883 (14)	*a*	4
[Ta($CHCMe_3$)(PMe_3)Cl_3]$_2$	161.2 (1)	101	1.898 (2)	*b*	this work
Ta($CHCMe_3$)$_2$(mesityl)(PMe_3)$_2$	154.0 (6)	104	1.955 (7)	*a*	3
Ta(η^5-C_5H_5)$_2$($CHCMe_3$)Cl	150.4 (2)	121	2.030 (6)	*a*	21
Ta(η^5-C_5H_5)$_2$(CHPh)(CH_2Ph)	135.2 (7)	127	2.07 (1)	*a*	20

[a] X-ray diffraction. [b] Neutron diffraction.

Table IX. Structural Features of Metal-Ethylene Complexes[26]

compd	C-C, Å	α,[a] deg	method	ref
C_2H_4	1.337 (2)	0.0	*b*	14
Rh(η^5-C_5H_5)(η^2-C_2H_4)-(η^2-C_2F_4)	1.358 (9)	42.4	*c*	27
KPt(η^2-C_2H_4)Cl_3·H_2O	1.375 (4)	32.5	*d*	15
Ru(η^2-C_2H_4)(CO)-(PMe_2Ph)$_2$$Cl_2$	1.376 (10)	24 (11)	*c*	28
Nb(η^5-C_5H_5)$_2$(η^2-C_2H_4)-(C_2H_5)	1.406 (13)	52.5	*c*	29
Rh(η^5-C_5Me_5)(η^2-C_2H_4)-(PPh_3)	1.408 (16)		*c*	30
Ni[P(O-*o*-Tol)$_3$]$_2$(η^2-C_2H_4)	1.46 (2)		*c*	31
Fe(CO)$_4$(η^2-C_2H_4)	1.46 (6)		*b*	32
Ta(η^5-C_5Me_5)($CHCMe_3$)-(η^2-C_2H_4)(PMe_3)	1.474 (3)	68.5	*d*	this work

[a] The angle between the normals to the two H-C-H planes. [b] Electron diffraction. [c] X-ray diffraction. [d] Neutron diffraction.

states. For example, the C—C bond lengths of 1.46 (2) Å in Ni[P(O-*o*-Tol)$_3$]$_2$(H_2C=CH_2)[31] and of 1.46 (6) Å in Fe(CO)$_4$(H_2C=CH_2)[32] have been reported (see Table IX).

Finally, we are left to ask why **2** is stable toward formation (and/or rearrangement) of a tantallacyclobutane complex. We feel that it is probably the formation of the tantallacycle which is unfavorable, largely because C(1) is distant from C(6). A higher coordination number could result in the placement of C(1) in closer proximity to C(6), but either there is too little space available for another ligand (C_2H_4, PMe_3, etc) or else it adds reversibly between the neopentylidene and ethylene which forces them further apart. We favor the former explanation since the neopentylidene and ethylene ligands appear to be trying to rotate into a mutually perpendicular orientation (with the C(6)–C(7) vector normal to the Ta–C(1)–H(1) plane); i.e., since H(1) appears to be important sterically, the coordination sphere is always too crowded for a fifth ligand.

Experimental Section

Crystal Structure Determination of [Ta(CHCMe$_3$)(PMe$_3$)Cl$_3$]$_2$ (1). A crystal weighing 30 mg, with approximate dimensions of 3.0 × 3.4 × 5.6 mm, was sealed in a lead-glass capillary under a nitrogen atmosphere for protection. The crystal was mounted in a general orientation on the automated four-circle diffractometer at the Argonne CP-5 reactor.[33] The sample was maintained at 110 K during alignment and data collection by using a cold N_2 gas flow apparatus of the Strouse design.[34] Since neither the space group nor the unit cell dimensions were known, a hemisphere of reciprocal space was systematically surveyed by using an autosearch routine. Nine reflections with 7.80° $\leq 2\theta \leq$ 11.80° (λ = 1.142 (1) Å) were located, centered, and indexed by using Jacobson's program BLIND,[35] which indicated the unit cell to be primitive monoclinic. Examination of the systematically unobserved data ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) in the 7° < 2θ < 20° shell established the space group uniquely as $P2_1/n$. The unit cell dimensions presented in Table I were obtained from a least-squares refinement of the angular settings of 25 automatically centered reflections (48° < 2θ < 53°).

Two octants of intensity data were measured out to $(\sin\theta)/\lambda = 0.62$ Å^{-1} by using coupled θ–2θ step scans with 0.1° (2θ) step intervals. A total of 2930 independent F_o^2 values were obtained after applying Lorentz and absorption corrections (μ_{calcd} = 2.37 cm^{-1}) to the integrated intensity data. Two standard reflections were measured periodically and showed no significant intensity changes during data collection. The structural solution was derived by using the program MULTAN,[36] from which the positional coordinates of all independent nonhydrogen atoms were obtained. The 19 hydrogen atoms were subsequently located on a Fourier map calculated by using phase angles derived from the refined nonhydrogen atom coordinates. In the final stages of least-squares refinement, the data were corrected for secondary extinction[37] and anisotropic thermal motion corrections were made for all atoms. The final discrepancy indices are given in Table I and the positional and thermal parameters from the final least-squares cycle are presented in Table II. A scaled difference Fourier map based on the final least-squares determined parameters was featureless.

Crystal Structure Determination of Ta(η^5-C$_5$Me$_5$)(CHCMe$_3$)(η^2-C$_2$H$_4$)(PMe$_3$) (2). A ca. 35-mg crystal was sealed in a lead-glass capillary under nitrogen. Preliminary unit cell dimensions and the space group were obtained at the CP-5 neutron source, using techniques as described for **1**. The crystal was then transported to the high flux beam reactor at Brookhaven National Laboratory, where it was mounted in a Displex closed-cycle helium refrigerator and cooled to 20 K for alignment and data collection.[38] The unit cell parameters were obtained from a least-squares fit of the angular settings of 32 automatically centered reflections (40° $\leq 2\theta \leq$ 50°, λ = 1.1629 (2) Å).

Two octants of intensity data were measured out of $(\sin\theta)/\lambda = 0.64$ Å^{-1} by using coupled θ–2θ step scans with 0.04° or 0.06° (2θ) step intervals. The intensities of three standard reflections, which were measured periodically during data collection, exhibited a maximum variation of 10%. The data were corrected for Lorentz effects and absorption (μ_{calcd} = 2.90 cm^{-1}) to yield 4799 F_o^2 values. The majority of the nonhydrogen atom positions were obtained by direct methods by using MULTAN[36] with a partial data set ($2\theta \leq$ 60°). The initial model was refined by using the differential Fourier synthesis procedure[39] to an $R(F_o^2)$ value of 0.59 with all nonhydrogen atoms. The location of the hydrogen atoms and least-squares refinement of the structural parameters proceeded in a conventional manner. In the final full-matrix least-squares refinement cycle, all atoms except C(15) were treated anisotropically and the data were corrected for secondary extinction.[37] Attempts to refine the thermal parameters of C(15) by using an anisotropic model always converged with a negative root-mean-square displacement. The final parameters are presented in Table III.

The problem associated with the C(15) thermal parameters and the generally poorer internal consistency of the structural parameters of **2** relative to **1** is probably related to the large peak widths associated with crystal **2** data and, therefore, to the difficulty in obtaining highly accurate intensity data. We suspect that cycling between room temperature and 20 K may have radically altered the crystal's mosaicity. In addition, during the initial alignment procedure, when it was necessary to warm the crystal to room temperature in order to remount it, we noticed it had a powdery surface. The powdery appearance had increased considerably

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by the time all data had been collected. However, since the integrated intensities of the standard reflections did not decrease monotonically during data collection, apparently only the surface of the crystal had been affected.

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Supplementary Material Available: Listings of structure factor amplitudes for compounds **1** and **2** (24 pages). Ordering information is given on any current masthead page.

Crystal and Molecular Structure of the Isobacteriochlorin: (2,3,7,8-Tetrahydro-5,10,15,20-tetraphenylporphinato)(pyridine)zinc(II) Benzene Solvate

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Abstract: The structure of the isobacteriochlorin, (2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphinato)(pyridine)zinc(II) benzene solvate, has been determined by three-dimensional X-ray diffraction. The compound crystallizes with one molecule each of benzene and reduced porphyrin per asymmetric unit in the triclinic space group $P\bar{1}$ with a = 11.452 (5) Å, b = 13.332 (4) Å, c = 14.718 (6) Å, α = 99.05 (2)°, β = 94.37 (4)°, and γ = 104.88 (4)°. It is isomorphous with the corresponding chlorin, (2,3-dihydrotetraphenylporphinato)(pyridine)zinc(II) benzene solvate. The structure has been refined by least squares in three matrix blocks to $R_F = 0.073$, on the basis of 6217 reflections with $F_o > 0$. The results unambiguously confirm the structure, previously deduced by spectroscopic techniques, for the general class of isobacteriochlorins (and for siroheme, the prosthetic group of nitrite and sulfite reductases) as porphyrins in which two adjacent pyrrole rings are reduced. In addition, the data indicate that successive saturation of the pyrrole rings in porphyrins, chlorins, and isobacteriochlorins exerts no major effect on the stereochemistry of the macrocycles and suggest that the geometric details of high spin iron siroheme will not deviate substantially from those of iron(III) porphyrins.

Introduction

The many-faceted roles which porphyrin derivatives fulfill biochemically are controlled by their metals, axial ligands, protein environment, and the nature of the porphyrin itself. Respiration, electron transport, peroxide decomposition, and hydroxylations are mediated by macromolecules which contain iron porphyrins (I), Figure 1, as prosthetic groups.[2–8] Photosynthetic reactions, on the other hand, are photocatalyzed by free base and magnesium compounds evolved from dihydroporphyrins (II), pheophytins, and chlorophylls, in algae and green plants, and from tetrahydroporphyrins (III), bacteriopheophytins and -chlorophylls, in purple bacteria.[9–11] Biologically active isomers of III in which two adjacent pyrrole rings are reduced have been proposed, and a number of compounds assigned structure IV have been reported.[12–24]

Isobacteriochlorins (IV) have recently elicited considerable

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