

Evidence for an Almost 'T-Shaped' Co-ordination Geometry for Carbon in the Bis(alkylidene) Complex $\text{Ta}(\text{=CH}\cdot\text{CMe}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{PMe}_3)_2$: X-Ray Crystal Structure

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Summary An X-ray structural analysis of the five-coordinate species $\text{Ta}(\text{=CH}\cdot\text{CMe}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{PMe}_3)_2$ shows a trigonal bipyramidal arrangement of ligands about the tantalum atom, with the phosphine ligands in axial sites; the Ta-C $_{\alpha}$ -C $_{\beta}$ angles in the two neopentylidene ligands are extraordinarily obtuse, with values of 154.0(6) and 168.9(6)°.

STRUCTURAL studies of the monoalkylidene complexes $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{=CHPh})(\text{CH}_2\text{Ph})^1$ (**1**) and $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{=CH}\cdot\text{CMe}_3)\text{Cl}^2$ (**2**) have indicated that the Ta-C $_{\alpha}$ -C $_{\beta}$ angle in the alkylidene groups is quite flexible, the relevant angles being 135.2(7)° for (**1**) and 150.4(5)° for (**2**).

Recently Schrock and his co-workers have reported³ the synthesis of a wide range of bis-alkylidene complexes having the general formula $\text{M}(\text{=CHR})_2(\text{X})(\text{PMe}_3)_2$ (M = Ta or Nb; R = CMe₃ or Ph; X = alkyl, aryl, or halide); these complexes have some anomalous physical properties (including $\nu(\text{C-H}_{\alpha})$ stretches with frequencies as low as 2500 cm⁻¹ and $^1J(\text{C-H}_{\alpha})$ values <100 Hz) which suggest that the stereochemistry at C $_{\alpha}$ may be unusual and that $\angle\text{Ta-C}_{\alpha}\text{-C}_{\beta}$ may be approaching 180°. We have now completed a single crystal X-ray diffraction study of the species $\text{Ta}(\text{=CH}\cdot\text{CMe}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{PMe}_3)_2$.

Crystal data: C₂₅H₄₀P₂Ta, *M* = 592.56, monoclinic, space group C2/c (C_{2h}⁶; No. 15), *a* = 17.966(3), *b* = 18.217(4), *c* = 18.531(3) Å, β = 97.99(2)°, *U* = 6006(2) Å³, *D_c* = 1.311 g cm⁻³, *Z* = 8, $\mu(\text{Mo-K}\alpha)$ = 39.7 cm⁻¹. Diffraction data were collected by a coupled $\theta(\text{crystal})$ - $2\theta(\text{counter})$ technique, using a Syntex P2₁ four-circle automated diffractometer and Mo-K $_{\alpha}$ radiation. All non-hydrogen atoms were located and refined (using anisotropic thermal parameters) leading to *R* = 5.3% for 3943 reflections in the range 4.5° < 2 θ < 45° (no datum being rejected). The resulting structure is shown in the Figure. Note that the terminal methyl groups of one neopentylidene ligand are subject to disorder. It was because of this, we believe, that

we were unable to locate all of the hydrogen atoms in the structure.†

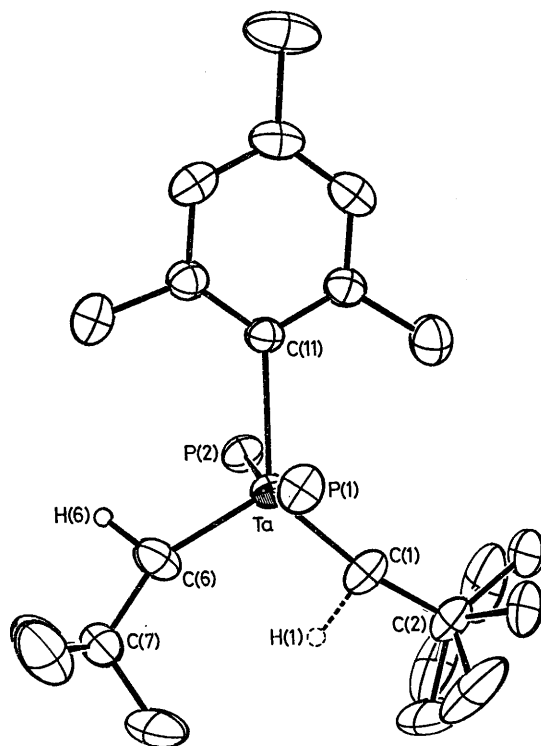


FIGURE. The geometry of the $\text{Ta}(\text{=CH}\cdot\text{CMe}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{PMe}_3)_2$ molecule, showing the equatorial co-ordination plane. The methyl groups attached to P(1) and P(2) have been omitted for clarity. Methyl groups attached to C(2) are disordered. Atom H(6) is in the position indicated by a difference-Fourier synthesis and H(1) is in its predicted position (it was not located directly) (ORTEP-II diagram; 50% ellipsoids).

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The tantalum(v) atom is in a trigonal bipyramidal environment. The two PMe_3 ligands are in axial sites, with $\text{Ta-P}(1) = 2.565(2)$ and $\text{Ta-P}(2) = 2.569(2)$ Å, and $\angle \text{P}(1)\text{-Ta-P}(2) = 166.34(7)^\circ$. The three organic ligands occupy equatorial co-ordination sites, with $\angle \text{C}(1)\text{-Ta-C}(6) = 109.0(3)$, $\angle \text{C}(1)\text{-Ta-C}(11) = 132.4(3)$, and $\angle \text{C}(6)\text{-Ta-C}(11) = 118.6(3)^\circ$. The mesityl ligand makes an angle of only 1.2° with the equatorial plane and has $\text{Ta-C}(11) = 2.303(6)$ Å.

The β carbon atoms of the neopentylidene ligands lie in the equatorial co-ordination plane. The $\text{Ta-C}(6)\text{-C}(7)$ angle is $154.0(6)^\circ$ and is associated with a $\text{Ta-C}(6)$ distance of $1.955(7)$ and a $\text{C}(6)\text{-C}(7)$ distance of $1.511(11)$ Å. The $\text{Ta-C}(1)\text{-C}(2)$ angle is increased to the extraordinarily high value of $168.9(6)^\circ$, suggesting an almost 'T-shaped' co-ordination geometry for the carbon atom C(1). The $\text{Ta-C}(1)$ distance is $1.932(7)$ and the $\text{C}(1)\text{-C}(2)$ distance is $1.527(11)$ Å.

It is interesting that the more obtuse $\text{Ta-C}_\alpha\text{-C}_\beta$ angle is associated with the shorter Ta-C_α bond length. It should also be noted that we have considered and rejected the possibility that atoms C(1) and/or C(2) are disordered; the shapes of the thermal vibration ellipsoids of these atoms are indistinguishable from those of atoms C(6) and C(7).

Finally we note that the flexibility of $\text{M=C}_\alpha\text{-C}_\beta$ systems may well be of importance in olefin metathesis; also, the unusual hybridization at C_α may provide a partial explanation for the ease of α -hydride migration in tantalum alkylidene complexes.

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¹ R. R. Schrock, L. W. Messerle, C. D. Wood, and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 1978, **100**, 3793.

² M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1978, **17**, 1957.

³ J. D. Fellmann, G. A. Rupprecht, C. D. Wood, and R. R. Schrock, *J. Amer. Chem. Soc.*, 1978, **100**, press.