

X-Ray Crystal Structure of $W(\equiv CMe_3)(=CHCMe_3)(CH_2CMe_3)(Me_2PCH_2CH_2PMe_2)$, an Ordered Five-co-ordinate Tungsten(vi) Complex with Metal-Alkyl, Metal-Alkylidene, and Metal-Alkylidyne Linkages

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Summary An X-ray structural analysis of the complex $W(\equiv CMe_3)(=CHCMe_3)(CH_2CMe_3)(Me_2PCH_2CH_2PMe_2)$ shows a distorted five-co-ordinate geometry about the tungsten atom.

SCHROCK and his co-workers have demonstrated the synthesis of alkylidene, alkylidyne,¹ and benzyne² complexes of the Group 5 elements, tantalum and niobium, *via* α -hydrogen abstraction. X-Ray diffraction studies show that: (i) $M-C(\alpha)-C(\beta)$ angles in alkyl complexes are frequently greater than 120° , (ii) $M=C(\alpha)-C(\beta)$ angles in alkylidene complexes vary widely [up to $168.9(6)^\circ$ in $Ta(=CHCMe_3)_2(2,4,6-Me_3C_6H_3)(PMe_3)_2$],³ and (iii) $M=C(\alpha)-C(\beta)$ angles in alkylidyne complexes are easily deformed from linearity {e.g., an angle of $171.8(6)^\circ$ is found in $Ta(=C-Ph)(\eta^5-C_5Me_5)(PMe_3)_2Cl$ ⁴ and a value of $165(1)^\circ$ is found in the $[Ta(=C-CMe_3)(CH_2CMe_3)_3]^-$ anion⁵}. The overall result of the ease of deformation and/or flexibility of these angles is that many mixed alkyl-alkylidene and alkylidene-alkylidyne complexes are disordered in the solid state.⁶

Clark and Schrock⁷ have recently synthesized some mixed alkyl-alkylidene-alkylidyne complexes of tungsten, which have been shown by $^{13}C\{^1H\}$ n.m.r. spectroscopy to be rigid in solution (*i.e.*, no interconversion of ligand sites on the

n.m.r. time scale). We have now undertaken an X-ray diffraction study of the species $W(\equiv CMe_3)(=CHCMe_3)(CH_2CMe_3)(Me_2PCH_2CH_2PMe_2)$ with the expectation of being able to compare the geometry of closely-related alkyl, alkylidene, and alkylidyne ligands at a common metal centre.

Crystal data: $C_{21}H_{46}P_2W$, $M = 544.39$, monoclinic, space group $P2_1/n$, $a = 9.784(3)$, $b = 29.200(8)$, $c = 9.859(2)$ Å, $\beta = 109.54(2)^\circ$, $U = 2654(1)$ Å³, $D_c = 1.36$ g cm⁻³, $Z = 4$, $\mu(Mo-K_\alpha) = 47.3$ cm⁻¹.

Diffraction data were collected by the 'wandering ω -scan technique'⁸ using a Syntex $P2_1$ automated diffractometer and $Mo-K_\alpha$ radiation. All non-hydrogen atoms were located and refined (using anisotropic thermal parameters) leading to $R = 4.3\%$ for 2475 independent reflections with $4.5^\circ < 2\theta < 40^\circ$ (no datum being rejected). The resulting, ordered structure is shown in the Figure.†

The tungsten atom has a rather distorted co-ordination sphere which is slightly closer to a square-pyramidal geometry than to the predicted⁷ trigonal-bipyramidal arrangement [$\angle C(1)-W-C(6) = 108.0(6)$, $\angle C(1)-W-C(11) = 108.8(5)$, $\angle C(1)-W-P(1) = 98.4(4)$, $\angle C(1)-W-P(2) = 91.1(4)$, $\angle P(1)-W-P(2) = 75.3(1)$, $\angle P(2)-W-C(6) = 92.0(4)$, $\angle C(6)-W-C(11) = 104.1(5)$, $\angle C(11)-W-P(1) = 77.9(4)$, $\angle C(6)-W-P(1) = 150.9(4)$, and $\angle C(11)-W-P(2) = 148.6-$

† 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.

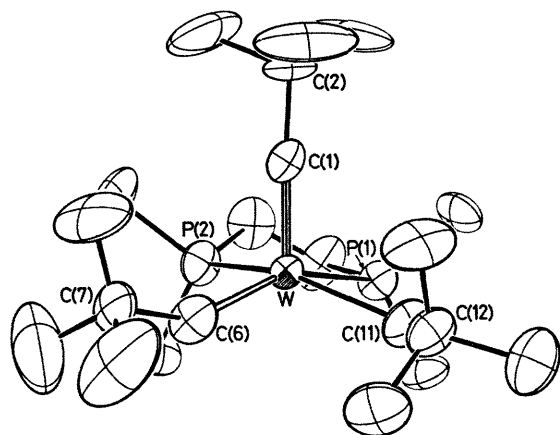


FIGURE. Geometry of the $W(=CCMe_3)(=CHCMe_3)(CH_2CMe_3)(Me_3PCH_2CH_2PMe_3)$ molecule. Hydrogen atoms are not shown (ORTEP-II diagram; 50% probability ellipsoids).

(4)^o]. Within this approximation, the neopentylidyne ligand occupies the apical co-ordination site [$W=C(1) = 1.808(12)$, $C(1)-C(2) = 1.513(18)$ Å, $\angle W=C(1)-C(2) = 175.2(10)^\circ$]. The neopentylidene ligand is 'pseudo-trans' to

P(1), with $W=C(6) = 1.982(13)$, $C(6)-C(7) = 1.467(20)$ Å, and $\angle W=C(6)-C(7) = 149.7(11)^\circ$. The neopentyl ligand is 'pseudo-trans' to P(2), with $W-C(11) = 2.258(14)$, $C(11)-C(12) = 1.524(21)$ Å, and $\angle W-C(11)-C(12) = 125.1(10)^\circ$.

The tungsten-phosphorus distances are non-equivalent, with $W-P(1) = 2.581(4)$ and $W-P(2) = 2.456(4)$ Å.

Benzylidyne (and related) complexes [e.g., *trans*- $W(=C-Ph)(CO)_4I^9$ and $W(=C-C_6H_4Me)(\eta^5-C_5H_5)(CO)_2^{10}$] and a diphenylcarbene complex of tungsten [$W(=CPh_2)(CO)_6^{11}$] have been examined previously by X-ray crystallography. However, the present complex contains the first structurally characterized tungsten-alkylidyne and tungsten-alkylidene linkages and also affords the first internal comparison of metal-carbon bond lengths and $M-C(\alpha)-C(\beta)$ angles in a set of aliphatic ligands related by successive α -hydrogen abstraction.

The present complex is of additional interest in that tungsten-alkylidenes are implicated as intermediates in olefin metathesis reactions.¹²

We are indebted to Professor R. R. Schrock for providing the crystalline sample and to the National Science Foundation for support.

(Received, 5th January 1979; Com. 015.)

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