

Journal of Organometallic Chemistry, 204 (1981) C17–C20
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

**X-RAY CRYSTALLOGRAPHIC STUDIES ON OCTAHEDRAL OXO
ALKYLIDENE COMPLEXES OF TUNGSTEN(VI):**

W(=O)(=CHCMe₃)(PMe₃)₂Cl₂ AND W(=O)(=CHCMe₃)(PEt₃)₂Cl₂

MELVYN ROWEN CHURCHILL*, ARNOLD L. RHEINGOLD**, WILEY J. YOUNGS

*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York
14214 (U.S.A.)*

RICHARD R. SCHROCK and JEFFREY H. WENGROVIUS

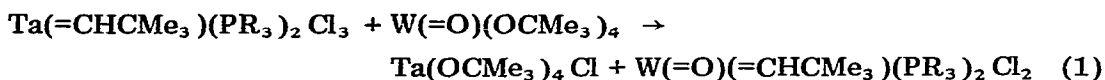
*Department of Chemistry, Massachusetts Institute of Technology, Cambridge,
Massachusetts 02139 (U.S.A.)*

(Received August 4th, 1980)

Summary

The reaction of Ta(=CHCMe₃)(PR₃)₂Cl₃ and W(=O)(OCMe₃)₄ yields mixed oxo-alkylidene complexes of tungsten(VI). Two have been subjected to single-crystal X-ray structural analysis. W(=O)(=CHCMe₃)(PEt₃)₂Cl₂ is disordered, but a full characterization of W(=O)(=CHCMe₃)(PMe₃)₂Cl₂ has been completed. The oxo and alkylidene ligands occupy mutually *cis* locations with W=O 1.701(15) Å, W=CHCMe₃ 2.006(15) Å and <O=W=C 101.6(8)°.

Although alkylidene derivatives of tantalum and niobium are now well characterized [1], there are few such complexes known for the other transition metals. Recently, alkylidene transfer from tantalum has been shown [2] to yield alkylidene complexes of tungsten, via eq. 1.



The resulting products of interest are formally oxo-alkylidene complexes of tungsten(VI) and are catalysts for the metathesis of both terminal and internal olefins [3].

We now report the results of single-crystal X-ray diffraction studies on the

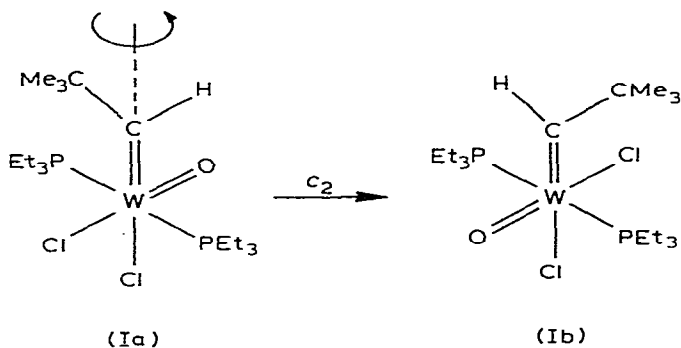
*Address correspondence to this author.

**On sabbatical leave from: Department of Chemistry, State University of New York College at Plattsburgh, Plattsburgh, New York 12901 (U.S.A.)

catalytically active complexes $W(=O)(=CHCMe_3)(PET_3)_2 Cl_2$ and $W(=O)(=CHCMe_3)(PMe_3)_2 Cl_2$.

The complex $W(=O)(=CHCMe_3)(PET_3)_2 Cl_2$ crystallizes in the centro-symmetric orthorhombic space group $Pbcn$ with a 14.397(4), b 13.755(4), c 12.388(3) Å, V 2453 Å³, M = 577.18, D_c = 1.56 g cm⁻³, Z = 4, and $\mu(Mo-K\alpha)$ 53.3 cm⁻¹.

Diffraction data were collected via the coupled θ (crystal)— 2θ (counter) technique [4] on a Syntex P2₁ diffractometer. Refinement of anisotropic thermal parameters for the tungsten atom and isotropic thermal parameters for the other non-hydrogen atoms led to R = 13.9% for 1139 independent reflections. While the overall coordination geometry was determined, there was a severe disorder problem. The molecule lies on a C_2 axis which results necessarily in disorder of chloride and oxo ligands (see Ia and Ib) and there is additional rotational disorder involving portions of the $CHCMe_3$ and PET_3 ligands. We therefore turned our attention to the species $W(=O)(=CHCMe_3)(PMe_3)_2 Cl_2$. This crystallizes in the non-centrosymmetric orthorhombic space group $P2_1 2_1 2_1$ with a 11.356(2), b 11.845(3), c 14.876(4) Å, V 2001 Å³, M = 493.02, D_c 1.64 g cm⁻³, Z = 4, and $\mu(Mo-K\alpha)$ 65.2 cm⁻¹.



Diffraction data were collected as before. All nonhydrogen atoms were located and refined (using anisotropic thermal parameters for the heavy atoms), leading to R 10.3% for 2629 independent reflections with $2\theta < 40^\circ$. This complex is ordered. The derived molecular geometry is shown in Fig. 1.

The tungsten(VI) atom has a rather distorted octahedral coordination environment. The tungsten—alkylidene bond length $W=C(1)$ is 2.006(15) Å, with the $W=C(1)-C(2)$ angle being increased from a normal sp^2 angle to a value of $141.1(16)^\circ$ (cf. $W=C$ 1.942(9) Å and $W=C-C$ $150.4(8)^\circ$ in $W(\equiv CMe_3)(=CHCMe_3)(CH_2CMe_3)[Me_2P(CH_2)_2PMe_2]$ [5,6]).

The trimethylphosphine ligands and the oxo ligand are bent away from the neopentylidene moiety with $C(1)=W-P(1)$ $96.5(5)^\circ$, $C(1)=W-P(2)$ $92.8(6)^\circ$ and $C(1)=W=O$ $101.6(8)^\circ$; the angle $C(1)=W-Cl(1)$ is acute with a value of $85.5(6)^\circ$, while $C(1)=W-Cl(2)$ $168.2(6)^\circ$. The trimethylphosphine ligands are additionally bent away from the oxo ligand with $P(1)-W=O$ $97.0(6)^\circ$ and $P(2)-W=O$ $97.9(6)^\circ$, resulting in a *trans* angle, $P(1)-W-P(2)$, of only $160.5(2)^\circ$.

The tungsten—oxide linkage, $W=O$, is 1.701(15) Å in length, while the

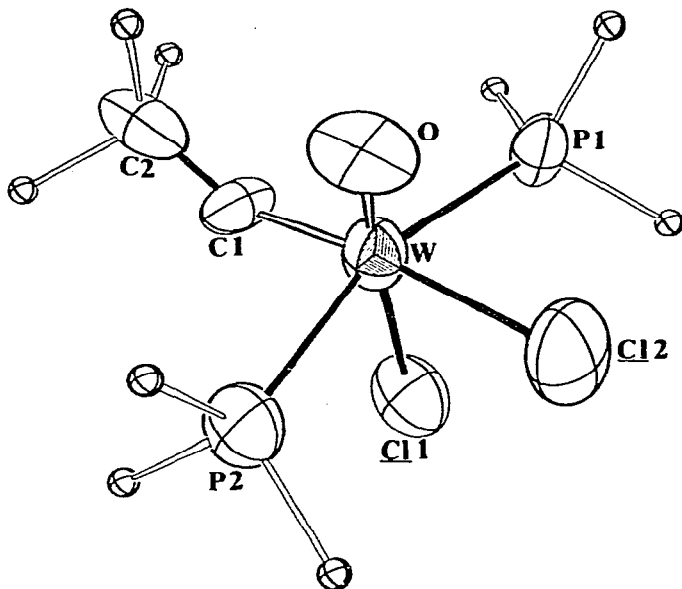
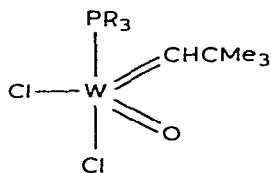


Fig. 1. The geometry of the $W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$ molecule. Hydrogen atoms are omitted and carbon atoms of the methyl groups are reduced for clarity.

tungsten—phosphine distances are $W-P(1)$ 2.536(7) Å and $W-P(2)$ 2.510(9) Å. The tungsten—chloride distances are slightly different, with that *trans* to the neopentylidene ligand being marginally longer than that *trans* to the oxo ligand. ($W-Cl(2)$ 2.508(8) Å vs. $W-Cl(1)$ 2.485(5) Å).

The complexes $W(=O)(=CHCMe_3)(PR_3)_2Cl_2$ undergo abstraction of phosphine with $Pd(NCPh)_2Cl_2$, yielding the five-coordinate oxo-alkylidene species $W(=O)(=CHCMe_3)(PR_3)Cl_2$, II, one example of which ($R = Et$) has previously been studied [3] and found to have bond lengths significantly shorter ($W=O$ 1.661(11) Å, $W=C$ 1.882(14) Å, $W-Cl$ 2.379(5)–2.389(5) Å) than in the octahedral species*.

The present tungsten(VI) oxo-alkylidene complexes are of particular interest because of their close chemical relationship to high oxidation state tungsten



(II)

*Additional tabular data on these two structures is available on NAPS document no. 03762, which contains 14 pages of Supplementary Material. Order from NAPS c/o microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, U.S. funds only \$ 5.00 for photocopies or \$ 3.00 for microfiche. Outside the U.S. and Canada add postage of \$ 3.00 for photocopy and \$ 1.00 for microfiche.

and molybdenum derivatives used industrially for carrying out olefin metathesis reactions [7-10].

This work was supported by the National Science Foundation (Grant CHE79-24560 to M.R.C. and CHE79-05307 to R.R.S.)

References

- 1 R.R. Schrock, *Acc. Chem. Res.*, **12** (1979) 93.
- 2 R.R. Schrock, S. Rocklage, J.H. Wengrovius, G.A. Rupprecht, and J.D. Fellman, *J. Molec. Catal.*, **8** (1980) 73.
- 3 J.H. Wengrovius, R.R. Schrock, M.R. Churchill, J.R. Missert and W.J. Youngs, *J. Amer. Chem. Soc.*, **102** (1980) 4515.
- 4 M.R. Churchill, R.A. Lashewycz, and F.J. Rotella, *Inorg. Chem.*, **16** (1977) 265.
- 5 M.R. Churchill and W.J. Youngs, *J. Chem. Soc. Chem. Commun.*, (1979) 321.
- 6 M.R. Churchill and W.J. Youngs, *Inorg. Chem.*, **18** (1979) 2454.
- 7 T.J. Katz, *Advan. Organometal. Chem.*, **16** (1977) 283.
- 8 R.J. Haines and G.J. Leigh, *Chem. Soc. Rev.*, **4** (1975) 155.
- 9 N. Calderon, E.A. Ofstead, and W.A. Judy, *Angew. Chem. Internat. Edn.*, **15** (1976) 401.
- 10 N. Calderon, J.P. Lawrence, and E.A. Ofstead, *Advan. Organometal. Chem.*, **17** (1979) 449.