# Structure of Tris(methyl vinyl ketone)tungsten

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*Summary* The structure of tris(methyl vinyl ketone)tungsten has been solved by single-crystal *X*-ray diffraction methods; its gross geometry is trigonal prismatic.

ONE of the most unusual products derived from the complex $(MeCN)_3W(CO)_3$ has been tris(methyl vinyl ketone)tungsten, first prepared by King in 1966.[1] We were attracted to this compound because it is the only known complex in which a transition metal is co-ordinated solely by $\alpha\beta$-unsaturated ketones, and because of the unconventional butadiene-type of co-ordination which had been proposed for it. We report the results of a single-crystal *X*-ray diffraction study of its structure.

The crystals used in this work were selected from a batch prepared by published methods and recrystallized from ethyl acetate. Crystal data: space group *Pc* (monoclinic); $a = 6{\cdot}26$ Å, $b = 11{\cdot}86$ Å, $c = 8{\cdot}77$ Å, $\beta = 106{\cdot}4°$, $V = 625$ Å$^3$, $D_m = 2{\cdot}03$, $D_c = 2{\cdot}07$ for $Z = 2$. Two quadrants of data were collected on an automated Nonius CAD-3 diffractometer, corrected for absorption effects, and merged to give 558 independent non-zero reflections. The structure was solved by heavy-atom methods and refined to a final *R* factor of 3·1%.†

The geometry of the complex is shown in the Figure. Average bond distances are given in the Table. One feature that is immediately noticeable is the remarkable trigonal prismatic co-ordination about the tungsten atom. Also evident is the predicted "sideways" co-ordination of the enone ligands, similar to that found in butadiene complexes but with some distortion (*vide infra*).

It can be seen that the atoms within bonding distance of the tungsten atom can be divided into two sets: a set of six "inner" atoms [O(1), O(2), O(3), C(1), C(2), C(3)] which define a trigonal prism of base 2·90 Å and height 2·59 Å;

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† All the major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's group at the California Institute of Technology.

TABLE. *Average distances in tris(methyl vinyl ketone)tungsten*

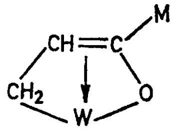
(a) Average bonding distances (in Å)

| | | | |
|---|---|---|---|
| W–O(1), W–O(2), W–O(3) | 2·11(2) | C(1)–C(4), C(2)–C(5), C(3)–C(6) | 1·45(4) |
| W–C(1), W–C(2), W–C(3) | 2·12(2) | C(4)–C(7), C(5)–C(8), C(6)–C(9) | 1·32(4) |
| W–C(4), W–C(5), W–C(6) | 2·29(2) | C(7)–C(10), C(8)–C(11), C(9)–C(12) | 1·48(4) |
| W–C(7), W–C(8), W–C(9) | 2·42(2) | C(7)–O(1), C(8)–O(2), C(9)–O(3) | 1·37(4) |

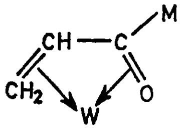
(b) Average non-bonding distances (in Å)

| | | | |
|---|---|---|---|
| W ... C(10), W ... C(11), W ... C(12) | 3·60(2) | O(1) ... O(2), O(2) ... O(3), O(3) ... O(1) | 2·88(4) |
| O(1) ... C(12), O(2) ... C(11), O(3) ... C(10) | 3·07(4) | C(1) ... C(2), C(2) ... C(3), C(3) ... C(1) | 2·92(4) |
| O(1) ... C(9), O(2) ... C(7), O(3) ... C(8) | 2·80(4) | O(1) ... C(1), O(2) ... C(2), O(3) ... C(3) | 2·59(4) |
| C(1) ... C(6), C(1) ... C(4), C(3) ... C(5) | 2·84(4) | | |

and a set of six "outer" atoms [C(4), C(5), C(6), C(7), C(8), C(9)]. This effect is caused primarily by steric interactions between non-bonding atoms [interactions such as O(1) ··· C(9), C(1) ··· C(6)]. The enone ligands themselves are virtually planar (to within ± 0·08 Å), and make an average angle of 70° with the rectangular faces of the trigonal prism. The differences in the bonding distances to the W atom, coupled with the long:short:long trend of bond lengths along the C–C–C–O backbone, seem to suggest that the interaction between the enone ligands and the tungsten atom is closer to $\sigma/\pi$-type (I) than $\pi$-type (II):



(I)



(II)

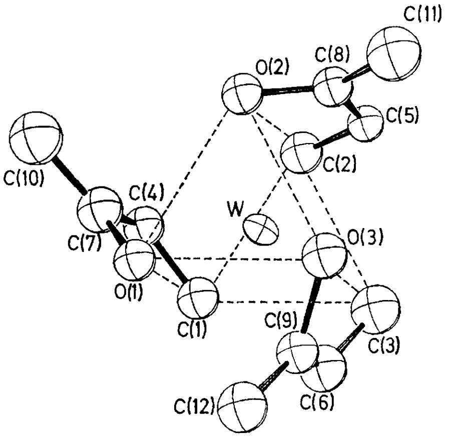


FIGURE. *The geometry of tris(methyl vinyl ketone)tungsten. The bonds to the tungsten atom have been omitted for clarity. The dashed lines are drawn to indicate the trigonal prismatic nature of the immediate co-ordination around the* W *atom. Weaker interactions exist between* W *and atoms* C(4) *to* C(9) (*which are significantly farther away*).

The question then arises of why the gross geometry of the complex should be trigonal prismatic rather than octahedral. Trigonal prismatic co-ordination is an extremely rare geometrical arrangement, largely confined (in molecular complexes, at least) to a few tris(1,2-dithiolene) complexes[2–4] and to $\{Co[Co(OCH_2CH_2NH_2)_3]_2\}^{2+}$.[5] One way of rationalising this is to point out that the bonding about the tungsten atom can be visualized as tricapped trigonal prismatic [imagine the three rectangular faces of the trigonal prism being "capped" by bonding interactions between the W atom and the C=C $\pi$ electrons, as in (I)]. Only by adopting a trigonal prismatic pattern of $\sigma$ bonds can the W atom participate in such a bonding scheme.

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[1] R. B. King and A. Fronzaglia, *Chem. Comm.*, 1966, **274**; *Inorg. Chem.*, 1966, **5**, 1837.
[2] R. Eisenberg and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 3776; *Inorg. Chem.*, 1966, **5**, 411.
[3] A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Amer. Chem. Soc.*, 1965, **87**, 5798.
[4] R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, 1966, **88**, 2874; *Inorg. Chem.*, 1967, **6**, 1844.
[5] J. A. Bertrand, J. A. Kelley, and E. G. Vassian, *J. Amer. Chem. Soc.*, 1969, **91**, 2304.