Tris(methyl vinyl ketone)tungsten(0), a New Type of Zerovalent Metal Complex

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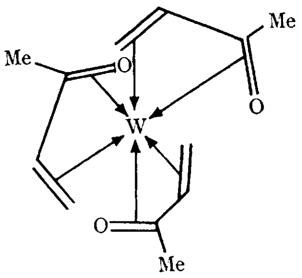
RECENTLY we reported some reactions between trisacetonitriletricarbonyltungsten $(MeCN)_3W(CO)_3$, and various cyclic polyolefins in boiling hexane to give olefin derivatives of tungsten carbonyl of the types $(triene)W(CO)_3$ and $(diene)W(CO)_4$.[1] We have now found that $(MeCN)_3W(CO)_3$ reacts with methyl vinyl ketone under similar conditions in boiling hexane with loss not only of the three acetonitrile ligands but also of all three carbonyl groups to give in up to 60% yield light yellow air-stable tris(methyl vinyl ketone)tungsten(0), $(MeCO{\cdot}CH{=}CH_2)_3W$, m.p. 136—139° (dec.)

This new complex is soluble in organic solvents including nonpolar ones such as hexane. It sublimes at 80°/0·1 mm. without decomposition. The positive-ion mass spectrum exhibits a strong peak at *m/e* 394 corresponding to the molecular ion $(MeCO{\cdot}CH{=}CH_2)_3W^+$ followed by a strong peak at *m/e* 324 corresponding to $(MeCO{\cdot}CH{=}CH_2)_2W^+$ with loss of one methyl vinyl ketone fragment.

Further fragmentation is more complex. The infrared spectrum exhibits no bands in the usual regions for ν_{CO} of either metal carbonyl or ketonic carbonyl groups. A strong band at 1495 cm.$^{-1}$ may arise from the ν_{CO} of a complexed ketonic carbonyl group. The drastic shift of this frequency to values below normal ketonic carbonyl frequencies suggests a delocalized π-bond of the carbon–oxygen double bond to the tungsten atom rather than a localized dative bond from the carbonyl oxygen atom to the tungsten atom. The proton n.m.r. spectrum in CS_2 solution exhibits resonances at τ 5·72 (double doublet, $J_1 = 6$, $J_2 = 7$ c./sec.), τ 7·87 (singlet) and 8·4 (complex multiplet) of relative intensities 1 : 3 : 2, respectively, due to the vinyl proton adjacent to the [ketonic] carbonyl group, the three methyl protons, and the two remaining "terminal" vinyl protons of each of the three equivalent $MeCO{\cdot}CH=CH_2$ ligands. The large difference between the chemical shifts of these vinyl protons and those of usual types of vinyl protons around τ 4 indicates that the carbon–carbon double bonds of the $MeCO{\cdot}CH=CH_2$ ligands are π-complexed to the tungsten atom in $(MeCO{\cdot}CH=CH_2)_3W$.[2]

These spectral data indicate that both the carbon–carbon and carbon–oxygen double bonds of the $MeCO{\cdot}CH=CH_2$ ligands are bonded to the tungsten atom in $(MeCO{\cdot}CH=CH_2)_3W$ suggesting structure (I) for this complex. In this structure three carbon–carbon and three carbon–oxygen double bonds are π-bonded to the tungsten atom[3] which is thus six-co-ordinate tungsten(0) as in $W(CO)_6$. The bonding of the methyl vinyl ketone ligand to the tungsten atom in $(MeCO{\cdot}CH=CH_2)_3W$ is probably similar to that of the cinnamaldehyde ligand to the iron atom in the complex $(PhCH=CH{\cdot}CHO)Fe(CO)_3$.[4] This cinnamaldehyde complex, like $(MeCO{\cdot}CH=CH_2)_3W$, is reported to exhibit no ν_{CO} bands in the normal ketonic carbonyl region.



(1)

The formation of $(MeCO{\cdot}CH=CH_2)_3W$ from $(MeCN)_3W(CO)_3$ and methyl vinyl ketone is especially surprising since the analogous reaction between $(MeCN)_3Mo(CO)_3$ and methyl vinyl ketone gives a complex orange material of composition $[(MeCO{\cdot}CH=CH_2)_2Mo(CO)_2]_n$.[5] The formation and stability of $(MeCO{\cdot}CH=CH_2)_3W$ indicates the ability for the bidentate $MeCO{\cdot}CH=CH_2$ ligand like the monodentate CO and PF_3 ligands to stabilize the tungsten(0) oxidation state.

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[1] R. B. King and A. Fronzaglia, *Chem. Comm.*, 1965, 547.

[2] The proton n.m.r. spectrum of uncomplexed methyl vinyl ketone in CS_2 solution exhibits resonances at τ 3·8 (complex assymmetric pattern with five discernible peaks), τ 4·23 (double doublet, $J_1 = 4{\cdot}3$, $J_2 = 8{\cdot}3$ c./sec.) and τ 7·84 (singlet) of relative intensities 2 : 1 : 3, respectively, due to the two $=CH_2$ protons, the one remaining proton adjacent to the carbonyl group, and the three methyl protons.

[3] Alternatively, the methyl vinyl ketone ligands can be considered as a delocalized system similar to butadiene donating four electrons to the tungsten atom.

[4] K. Stark, J. E. Lancaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch.*, 1964, **19b**, 284.

[5] D. P. Tate, A. A. Buss, J. M. Augl, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, 1965, **4**, 1323.