New Olefinic and Acetylenic Complexes of Tungsten

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MANY chromium and molybdenum complexes of diolefins and triolefins have been prepared.[1] However, the greater inertness of hexacarbonyltungsten[2] has made the preparation of the tungsten analogues difficult or even impossible. We have now found that the readily accessible tris(acetonitrile)tricarbonyltungsten,[3] previously demonstrated[4] to be a suitable intermediate for

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[1] E. O. Fischer and H. Werner, "Metall-π-Komplexe mit di- und oligoolefinischen Liganden," Verlag Chemie, Weinheim/Bergstr., 1963.

[2] R. B. King, Ph.D. Dissertation, Harvard University, 1960; R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3590.

[3] D. P. Tate, J. M. Augl, and W. R. Knipple, *Inorg. Chem.*, 1962, **1**, 422.

[4] D. P. Tate and J. M. Augl, *J. Amer. Chem. Soc.*, 1963, **85**, 2174; D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasselli, *ibid.*, 1964, **86**, 3261.

the preparation of the tris(alkyne)carbonyltungsten complexes, $(RC{\equiv}CR')_3WCO$, is also an excellent intermediate for the preparation of olefin complexes of tungsten carbonyl.

Especially facile and efficient are the reactions between $(MeCN)_3W(CO)_3$ and cyclic olefins containing at least three double bonds (Table). Although the cycloheptatriene derivative, $C_7H_8W(CO)_3$, has been previously synthesized from cyclo-octa-1,5-dienetetracarbonyltungsten and cycloheptatriene,[5] the present synthesis from $(MeCN)_3W(CO)_3$ makes available for the first time $C_7H_8W(CO)_3$ in quantities sufficient for detailed chemical studies. The reaction between $(MeCN)_3W(CO)_3$ and cyclo-octatriene to give $C_8H_{10}W(CO)_3$ is entirely different from the reaction between hexacarbonyltungsten and cyclo-octatriene which gives $(C_8H_{10})_2W(CO)_2$.[6] The compound $C_8H_8W(CO)_3$ obtained from $(MeCN)_3W(CO)_3$ and cyclo-octatetraene appears to be the tungsten analogue of the recently reported $C_8H_8Mo(CO)_3$.[7]

Some of the reaction products from $(MeCN)_3W(CO)_3$ contain more than three carbonyl groups. For example, the chelating diolefins cyclo-octa-1,5-diene and bicyclo[2,2,1]heptadiene form the known (diolefin)$W(CO)_4$ derivatives.[8,9] However, cyclopentadiene reacts with $(MeCN)_3W(CO)_3$ to give the hydride $C_5H_5W(CO)_3H$.[10] Apparently the hydrogen lost by the cyclopentadiene to give the C_5H_5 ligand becomes attached to the tungsten atom.

In connection with another research programme a metal complex of hexafluorobut-2-yne with three equivalent $(CF_3)_2C_2$ ligands with non-equivalent ends was desired. Since compounds of the type (alkyne)$_3$WCO fall into this category, the reaction between $(MeCN)_3W(CO)_3$ and excess of hexafluorobut-2-yne in a sealed vessel at 100° was investigated. Instead of the expected product pure white air-stable $[(CF_3)_2C_2]_3W(NCMe)$, m.p. 116—117°, was isolated in 4% yield by sublimation at 80°/0·3 mm. The equivalence of the three hexafluorobut-2-yne ligands but the non-equivalence of the ends of these ligands is supported by the presence of two resonances of equal relative intensities at ϕ 57·6 and ϕ 60·5 in the ^{19}F n.m.r. spectrum.* This new complex $[(CF_3)_2C_2]_3W(NCMe)$

TABLE[a]

Olefin Complexes Obtained from $(MeCN)_3W(CO)_3$

Olefin	Product	Colour	m.p.	Yield, %[b]
Cycloheptatriene	$C_7H_8W(CO)_3$	red	115—121° (dec.) (lit.[5] m.p. 110°)	69
Cyclo-octatriene	$C_8H_{10}W(CO)_3$	orange	1081—13° (dec.)	66
Cyclo-octatetraene	$C_8H_8W(CO)_3$	red–brown	115—118° (dec.)	28
Cyclo-octa-1,5-diene	$C_8H_{12}W(CO)_4$	yellow	159—162° (dec.)	76
Bicycloheptadiene (Norbornadiene)	$C_7H_8W(CO)_4$	yellow	90—92°	74
Cyclopentadiene	$C_5H_5W(CO)_3H$	pale yellow	66–68° (lit.[10] m.p. 66—67°)	20

[a] All reactions listed in this table were carried out by heating the olefin (1 to 2 ml.) with $(MeCN)_3W(CO)_3$ (3 mmoles in boiling hexane (50 ml.) for at least 16 hr. All compounds listed in the above table analyzed satisfactorily for carbon, hydrogen, and oxygen.

[b] The yields are based on the number of available carbonyl groups in the $(MeCN)_3W(CO)_3$ used for the reaction.

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* The ϕ scale corresponds to p.p.m. shift upfield from internal CCl_3F. (See: G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.* 1959, **63**, 761.)

[5] T. A. Manuel and F. G. A. Stone, *Chem. and Ind.*, 1960, 231.

[6] E. O. Fischer and C. Palm, *Z. Naturforsch.*, 1959, **14**b, 347; E. O. Fischer, C. Palm, and H. P. Fritz, *Chem. Ber.*, 1959, **92**, 2645.

[7] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, 1965, **87**, 3267.

[8] E. O. Fischer and W. Fröhlich, *Chem. Ber.*, 1959, **92**, 2995; T. A. Manuel and F. G. A. Stone, *Chem. and Ind.*, 1959, 1349.

[9] M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 2037.

[10] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104; E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. anorg. Chem.*, 1955, **282**, 47.

appears to be analogous to the complexes (alkyne)$_3$WCO but with an acetonitrile ligand replacing the carbonyl ligand.

An extensive study of related reactions of (MeCN)$_3$W(CO)$_3$ is in progress and further results will be reported in future papers.

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