Reactivity of Unsaturated μ-Alkylidene Complexes of Tungsten: X-Ray Crystal Structure of the Zwitterionic Complex Obtained with Trimethylphosphine

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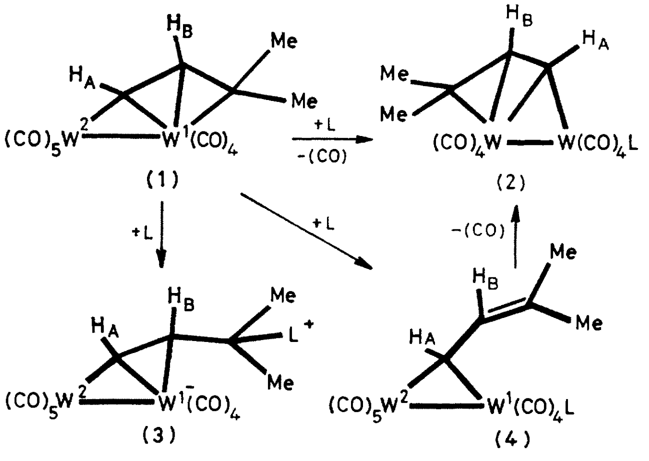
Summary Reaction of phosphines with the bimetallic unsaturated μ-alkylidene tungsten complex (**1**) proceeds *via* either substitution of one of the CO groups or nucleophilic attack at the γ-carbon on the unsaturated chain, as shown by the *X*-ray crystal structure of one of the resulting zwitterionic complexes.

REACTIONS of phosphorus-containing nucleophiles with monometallic alkylidene complexes of tungsten are known to give two types of product, arising either from CO displacement[1,2] or from addition[3] to the C=W double bond (Scheme 1).

$$\overset{+}{L}\text{–}R_2C\text{–}\overset{-}{W}(CO)_5 \leftarrow R_2C{=}W(CO)_5 + L \rightarrow R_2C{=}WL(CO)_4 + CO$$

SCHEME 1. L = Ligand.

During a study of bimetallic unsaturated μ-alkylidene tungsten complexes,[4] complex (**1**) was treated with a variety of phosphorus-containing nucleophiles and the results are summarised in Scheme 2.



a; L = PPh_3
b; L = $P(OMe)_3$
c; L = $P(OEt)_3$
d; L = PMe_3
e; L = PMe_2Ph

SCHEME 2.

Reaction of triphenylphosphine with (**1**) gave the compound (**2a**), apparently arising *via* the simple displacement of carbon monoxide from W(2). Reaction of trimethyl phosphine with (**1**) gave (**3d**), a zwitterionic compound whose spectra show an appropriate signal at 31 p.p.m. (^{31}P n.m.r.) and a band at 1840 cm^{-1} (i.r.). As interpretation of the ^1H n.m.r. spectrum was difficult (see Table 1), an *X*-ray diffraction study of (**3d**) was undertaken, the result of which is shown in the Figure.

Crystal data: $W(CO)_4[W(CO)_5C_5H_8P(CH_3)_3]$, $M = 764$, orthorhombic, space group *Pbca*, $a = 49{\cdot}89(1)$, $b = 15{\cdot}22(1)$ Å, $Z = 8$, $D_c = 2{\cdot}30$, $D_m = 2{\cdot}31$ g cm^{-3}, μ(Mo-K_α) = 112 cm^{-1} (three-circle diffractometry, 2279 independent reflections). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares. The unit cell contains eight of the molecules shown in the Figure. The conventional R value is 0·058 using anisotropic temperature factors for all atoms.†

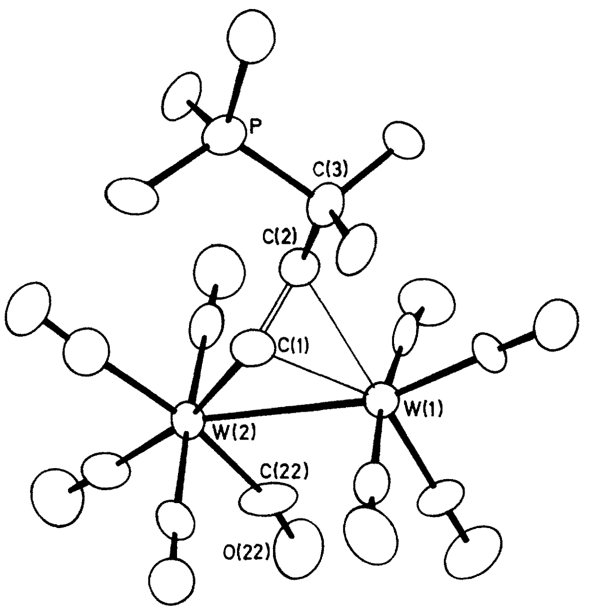


FIGURE. ORTEP view of the molecule of (**3d**). Some important bond lengths are: W(1)–W(2) 3·140(1), W(2)–C(1) 2·22(2), W(1)–C(1) 2·26(2), W(1)–C(2) 2·49(2), and W(1)–C(22) 2·99(3) Å. Some important bond angles are: W(1)–W(2)–C(1) 46·1(6), W(2)–W(1)–C(1) 45·0(6), W(2)–C(22)–O(22) 168(3), W(2)–C(1)–C(2) 130(2), and C(1)–C(2)–C(3) 127(2)°.

Several features are noteworthy: (a) The metal–metal single bond length is the same as in (**1**) [W(1)–W(2) = 3·14 Å]. (b) The C(1)–C(2) bond is now a co-ordinated double bond [C(1)–C(2) = 1·41 Å]. (c) As already indicated by the i.r. spectrum, there is a semi-bridging CO group,[5] C(22)–O(22), with a W(1)–C(22) contact distance of 2·99 Å, a W(1)–W(2)–C(22) angle of 66° and a W(2)–C(22)–O(22) angle of 167°.

TABLE. ^1H N.m.r. parameters

	δ		J/Hz	
Complex	H_A[a]	H_B[b]	H_A–H_B	H_A–P
(**2a**)[c]	8·60	4·65	12	9
(**2b**)[c]	8·82	4·75	12	9
(**2c**)[c]	9·1	4·71	12	9
(**3c**)[d]	8·60	4·66[e]	14	3[f]
(**3e**)[d]	8·44	4·48[e]	14	4[f]
(**3d**)[d]	8·25	4·50	14	4[f]
(**4b**)[c]	10·0	6·6	14	6
(**4c**)[c]	10·35	6·9	11·3	6

[a] Quartet in each case. [b] Doublet unless noted otherwise. [c] In C_6D_6. [d] In $(CD_3)_2CO$. [e] Quartet. [f] $J(H_B\text{–}P)$ 3 Hz.

A similar reaction was observed with phenyl(dimethyl)phosphine, giving (**3e**). These zwitterionic complexes are very stable to air at room temperature, probably because of the multicentre bonding, as has already been observed by Churchill *et al.*[6] in other complexes.

Reaction of trimethyl phosphite gave compound (**4b**) arising from the displacement of the co-ordinated double bond in (**1**) by the nucleophile. Compound (**4b**) was unstable and lost carbon monoxide to afford (**2b**) (see the

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† 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.

Table). Finally reaction of triethyl phosphite gave two products, (**3c**) and (**4c**), which were not interconvertible under the reaction conditions. As with (**4b**), compound (**4c**) subsequently lost carbon monoxide to afford (**2c**).

Although the appropriate intermediate (**4a**) could not be isolated, it is tempting to assume that compound (**2a**) is not formed from (**1**) by the mere displacement of carbon monoxide from W(2), but arises from the displacement of the double bond co-ordinated to W(1), followed by the displacement of carbon monoxide by the free double bond on W(2).

Thus bimetallic μ-alkylidene complexes like (**1**) react in a way which is reminiscent of the monometallic complexes; nucleophilic reactions can take place either at a carbon atom (for the stronger nucleophiles) or at a metal atom (for the weaker nucleophiles). However, with compound (**1**), there is the additional difficulty due to the existence of two metal atoms, but apparently only the one which bears the co-ordinated double bond is attacked.

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