Dinuclear Carbene Complexes of Tungsten as Catalysts for Metathetical Polymerisation of Alkenes and Alkynes; *X*-Ray Crystal Structure of the Insertion Product of But-2-yne into a μ-Alkylidene Carbon–Tungsten Bond

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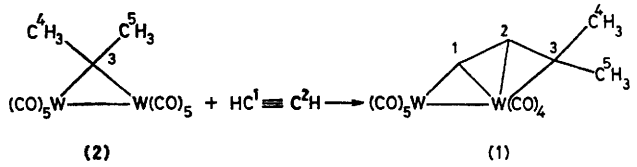
Summary Reaction of alkynes and alkenes with the bimetallic μ-alkylidene complex (**1**) gives polymers in a metathetical reaction; the product of the initial insertion of but-2-yne into one of the carbon–metal bonds of the bridging carbon atom could be isolated and its *X*-ray structure established.

RECENT reports[1–3] on the synthesis and chemistry of μ-alkylidene complexes of dimetallic compounds prompt us to describe our results in this field. We have already described the synthesis of a series of dinuclear μ-alkylidene complexes of tungsten.[4–6] The possible involvement of these complexes in the olefin metathesis reaction, as well as in the insertion–polymerisation reaction of alkynes, has also been suggested.[6,7] Evidence that this suggestion is essentially correct is now presented.

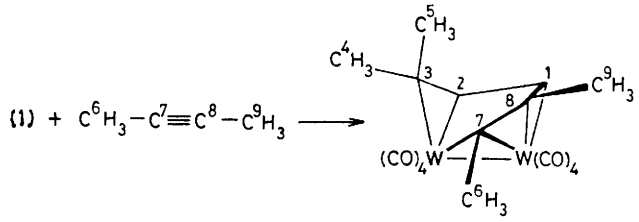
The formation of the complex (**1**)[6] could in principle be explained as resulting from the insertion of acetylene into one of the carbon–metal bonds of the bridging ligand of (**2**).[6,7] This hypothetical transformation (**2**)→(**1**), which has been observed with Fe and Ru complexes,[2] can be considered as the first step in the alkyne polymerisation reaction at a dimetal centre. We now report that the dinuclear complex (**1**) can react further with alkynes to give polymers, and also react with norbornene at 60 °C to give the ring-opened polyunsaturated polymer expected from a metathesis reaction.



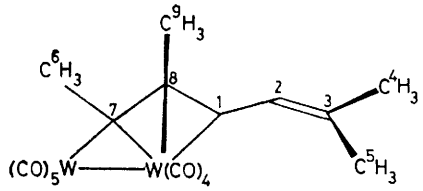
SCHEME 1

Thus, reaction of (**1**) with but-2-yne at room temperature gives a mixture of complex (**3**) (red crystals) in 30% yield and complex (**4**) (purple crystals) in 12% yield.†

† Complex (**3**): m.p. 108—110 °C, ν (CO)($CHCl_3$) 1910, 1930, 1970, 1990, 2008, and 2030 cm^{-1}; ^1H n.m.r. (C_6D_6) δ 4·22 (s, C^1H), 3·92 (s, C^2H), 3·30 (s, C^3H_3), 1·60 (s, C^9H_3), 1·47 (s, C^4H_3), and 1·30 (s, C^5H_3); *m/e* 714; complex (**4**) m.p. 75—76 °C, ν (CO)($CHCl_3$) 1935, 1965, 1990, 2025, and 2040 cm^{-1}; ^1H n.m.r. (C_6D_6) δ 5·70 (d, *J* 11 Hz, C^2H), 4·12 (d, *J* 11 Hz, C^1H), 3·50 (s, C^3H_3), 1·70 (s, C^9H_3 and C^4H_3), and 1·60 (s, C^5H_3); *m/e* 742.



(3)



(4)

SCHEME 2

Both (**3**) and (**4**) are fairly stable in the solid state under argon, but very unstable in solution. However, crystals of (**3**) suitable for *X*-ray analysis could be grown from a methanol solution,‡ and the Figure shows an ORTEP projection of its structure. Several features are noteworthy. Complex (**3**) results from the insertion of butyne into one of the bonds between the tungsten and the bridging carbene ligand; it contains a similar three-carbon unit ($C^7C^8C^1$) as the $C^1C^2C^3$ in (**1**) around the dimetal centre, resulting from the insertion reaction followed by a molecular rearrangement.

Complex (**3**) reacts further with but-2-yne to give unsaturated polymers and it reacts in solution to give complex

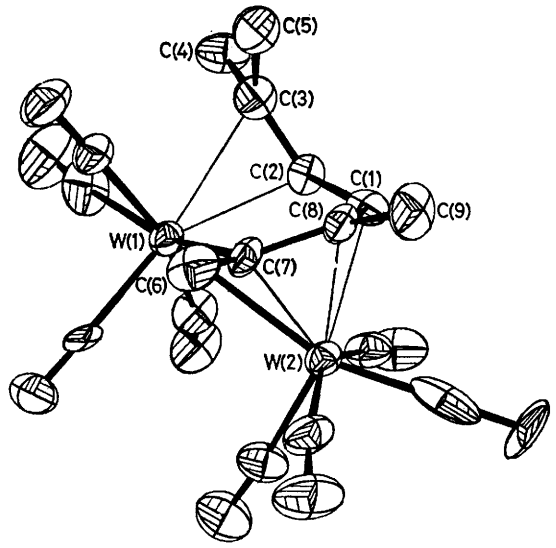
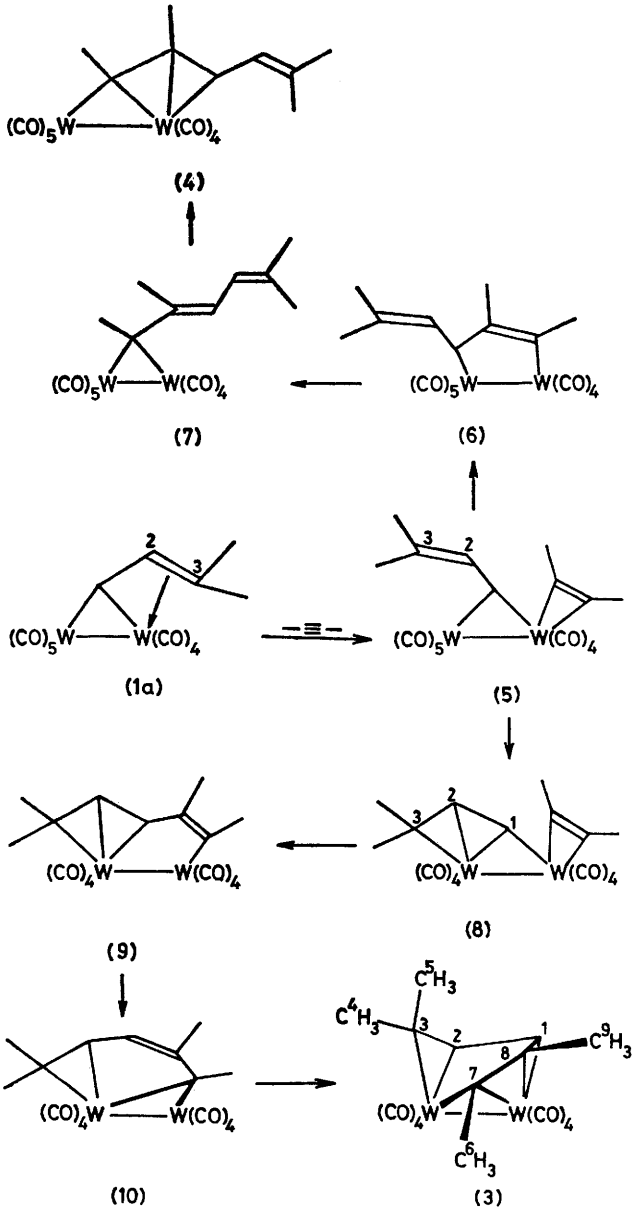


FIGURE. ORTEP view of the structure of (**3**). Important bond lengths: W(1)–W(2) 3·049(1), W(1)–C(7) 2·25(2), W(2)–C(7) 2·25(2), W(2)–C(8) 2·30(2), W(2)–C(1) 2·34(3), W(1)–C(2) 2·43(3), W(1)–C(3) 2·60(3), C(8)–C(7) 1·45(3), C(1)–C(8), 1·44(4), C(1)–C(2) 1·52(4), C(2)–C(3) 1·37(4) Å; important bond angles: W(1)–C(7)–W(2) 85·2(8), W(1)–C(7)–C(8) 116(2), W(1)–C(7)–C(6) 120(2), C(6)–C(7)–C(8) 121(2), C(7)–C(8)–C(1) 114(2), C(7)–C(8)–C(9) 123(2), C(1)–C(8)–C(9) 123(2), C(8)–C(1)–C(2) 120(2), C(1)–C(2)–C(3) 125(2), C(2)–C(3)–C(4) 117(3), C(2)–C(3)–C(5) 125(3), C(4)–C(3)–C(5) 114(3)°.



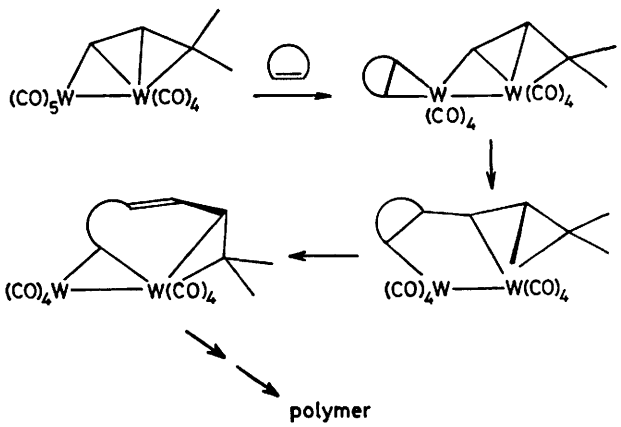
SCHEME 3

‡ *Crystal data*: $C_{13}H_{14}O_8W_2$, M = 714, monoclinic, space group $C2/c$, a = 33·64(1), b = 8·743(4), c = 13·681(2) Å, β = 98·18(3)°, Z = 8, D_c = 2·38, D_m = 2·38 g cm^{-3}, μ(Mo-K_α) = 122·8 cm^{-1} (three-circle diffractometry, 1805 independent reflections). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares. The conventional R value is 0·051 using anisotropic temperature factors for all non-hydrogen atoms. 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. The structure factor table is available as Supplementary Publication No. SUP 23037 (13 pp.) from the British Library, Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton* or *Perkin Trans.*, Index Issues.

(**4**), together with decomposition products. The ^{1}H n.m.r. and mass spectra of (**4**) show that the terminal double bond is no longer co-ordinated but there is one additional CO group.

These observations, along with the fact that (**1**) can be represented, according to its *X*-ray structure,[6] as (**1a**), a μ-alkylidene complex bearing a weakly bound double bond C^2=C^3, show that insertion of butyne may take place by the route in Scheme 3, possibly through the displacement of the double bond C^2=C^3 in (**1a**) by butyne giving (**5**), and reco-ordination of the free double bond to the other metal centre with displacement of one CO group to give (**8**). This reaction is reminiscent of the reactions of phosphines and phosphites with (**1**).[8] Insertion of the co-ordinated butyne unit in (**8**) into the C^1–W bond followed by rearrangement could give (**3**).

As (**4**) is formed from (**1**) much faster than from (**3**), there must be a direct route from (**1**) to (**4**) as shown in Scheme 3; direct insertion of butyne into (**5**) could give complex (**6**) which upon rearrangement could give (**7**) then (**4**). Scheme 3 therefore provides a reasonable picture of the manner by which the polymerization of alkynes could take place around two metal centres. Similar reaction sequences may be used to explain the ring-opening polymerization of cyclic olefins (Scheme 4).§



SCHEME 4

These results show for the first time that alkyne and cyclic olefin polymerization reactions can be performed on the same bimetal centre.

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§ Full details of the polymerization reactions induced by (**1**) will be published elsewhere.

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