

## Alkyne Polymerizations Initiated by $\mu$ -Alkylidene Complexes of Tungsten. X-Ray Crystal Structure of a Chain-carrier Intermediate

By JACQUES LEVISALLES, FRANCOISE ROSE-MUNCH, and HENRI RUDLER\*

(Laboratoire de Chimie Organique, Equipe de Recherche Associée au CNRS No. 127, Tour 45,  
4 Place Jussieu, 75230 Paris, Cedex 05, France)

JEAN-CLAUDE DARAN, YVES DROMZEE, and YVES JEANNIN

(Laboratoire de Chimie des Métaux de Transition, Equipe de Recherche Associée au CNRS No. 608,  
4 Place Jussieu, 75230 Paris, Cedex 05, France)

and DOMINIQUE ADES and MICHAEL FONTANILLE

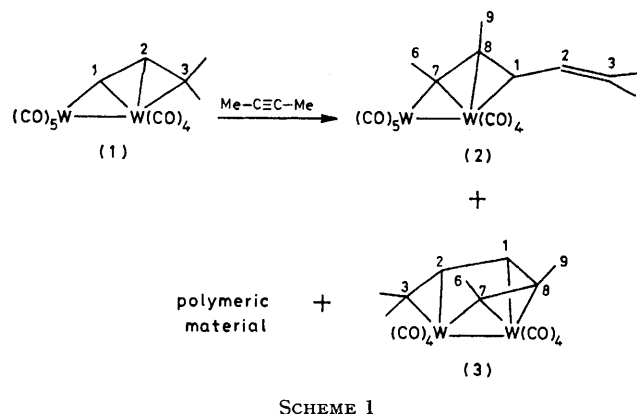
(Laboratoire de Recherche sur les Macromolécules, Equipe de Recherche Associée au CNRS No. 607,  
Avenue Jean Baptiste Clément, 93430 Villetaneuse, France)

**Summary** The  $\mu$ -alkylidene complex (**1**)  $W_2(CO)_9(C_8H_8)$  reacts with but-2-yne to give a new chain-carrier complex (**2**) by insertion of the monomer into the  $\mu$ -alkylidene bridge and complex (**1**) catalytically reacts with terminal alkynes to give polyalkynes in good yields.

THE present interest in alkyne polymerization and in the physical properties<sup>1,2</sup> of polyalkynes has prompted us to

report our results in this field. In a recent communication<sup>3</sup> we described the behaviour of alkynes towards complex (**1**), a  $\mu$ -alkylidene complex of tungsten.

Complex (**1**) reacts with stoichiometric amounts of but-2-yne to give two complexes (**2**) and (**3**) and some polymeric material (Scheme 1). The structure of complex (**3**) has already been given.<sup>3</sup> However, because of its low yield and instability, complex (**2**) could only be characterized by mass



and  $^1\text{H}$  n.m.r. spectra. After much effort, the structure of (2) has been ascertained by an X-ray crystal structure determination. An ORTEP projection is shown in the Figure.

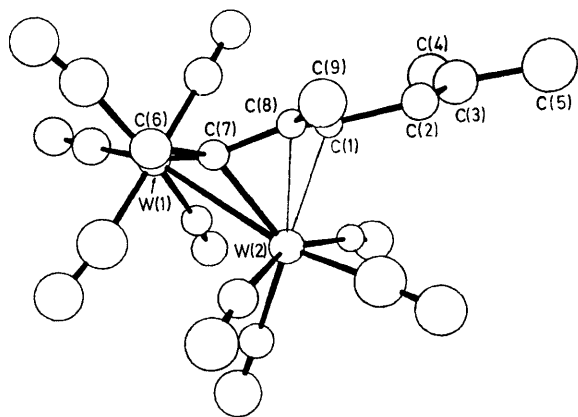
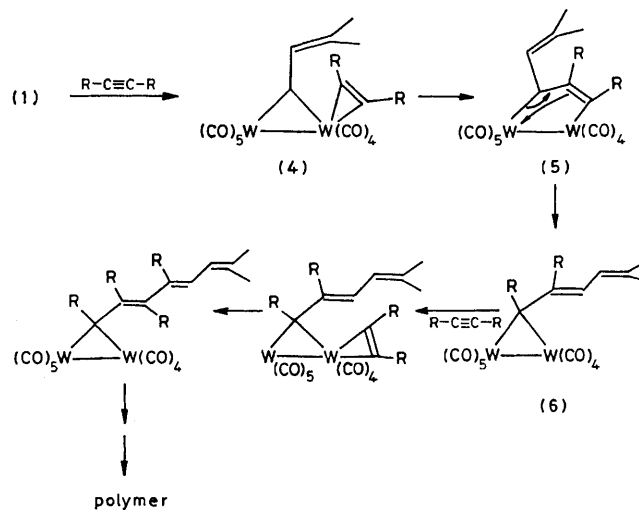


FIGURE. ORTEP view of structure (2). Important bond lengths (Å): W(1)–W(2) 3.139(2), W(1)–C(7) 2.22(3), W(2)–C(7) 2.18(4), W(2)–C(8) 2.40(3), W(2)–C(1) 2.39(4), C(8)–C(7) 1.44(5), C(8)–C(1) 1.45(5), and C(2)–C(3) 1.35(6). Important bond angles ( $^\circ$ ): W(1)–C(7)–C(8) 133(2), C(7)–C(8)–C(1) 108(3), C(8)–C(1)–C(2) 114(3), W(2)–C(7)–W(1) 91(1), W(2)–C(7)–C(8) 80(2), W(2)–C(8)–C(7) 64(2), and W(2)–C(8)–C(1) 72(2).

*Crystal Data:*  $\text{C}_{18}\text{H}_{14}\text{O}_9\text{W}_2$ ,  $M = 714$ , monoclinic, space group  $P2_1/c$ ,  $a = 9.505(3)$ ,  $b = 12.350(14)$ ,  $c = 37.00(27)$  Å,  $\beta = 96.02(6)^\circ$ ,  $Z = 8$ ,  $D_c = 2.20$ ,  $D_m = 2.18$  g cm $^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 113.1$  cm $^{-1}$ . Data were collected on a three-circle automatic diffractometer at room temperature. The structure was solved by standard Patterson–Fourier techniques, and refined by least-squares using anisotropic temperature-factors for tungsten atoms and isotropic for the remainder. The conventional agreement index,  $R$ , is now 0.078.† The asymmetric unit contains two molecules of compound (2) with the structure shown in the Figure.

† The crystal size was  $0.35 \times 0.24 \times 0.23$  mm. An analytical absorption correction was made; the minimum and maximum absorption coefficients were 0.068 and 0.170, respectively. Structure factors were weighted by  $1/\sigma \times Lp$  where  $\sigma$  is the standard deviation of  $F$  and  $Lp$  the Lorentz and polarization correction. In the final cycle of least squares no shift was larger than one-tenth of its corresponding estimated standard deviation. 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. 23181 (23 pp.) from the British Library, Lending Division (for details see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1979, Index issue).

Several features are of interest in this structure. (i) Complex (2) like complex (3), results from the insertion of but-2-yne into one of the tungsten–carbon bonds of the bridging alkylidene ligand. (ii) Complex (2) contains the same three-carbon-atom framework ( $\pi$ -allyl system) as the starting material. (iii) The terminal double bond C(2)–C(3) is not co-ordinated to the metal centres.



Therefore, complex (2) can be considered as a new initiator bearing 4 extra carbon atoms in the carbon chain which, from a theoretical viewpoint could promote the butyne polymerization reaction. But further insertions of the monomer into compound (2) are slow. Therefore, we treated complex (1), in catalytic amounts, with terminal alkynes at various temperatures. The results are given in the Table. At room temperature, a fast reaction was observed. Although the insertion products of type (2) and (3) were detectable by thin layer chromatography (t.l.c.) they were unstable and could not be isolated. At higher temperatures, a fast polymerization reaction occurred which gave polyalkynes of high molecular weight which were soluble in hydrocarbon solvents.

Oxygen inhibited the initiation of the polymerization reaction, but once started, neither  $\text{O}_2$  nor water prevented the reaction (Table). The best results are obtained under high-vacuum conditions with carefully purified alkynes (Table). This behaviour is reminiscent of that which has been observed in the case of the polymerization of cycloolefins with diphenylcarbenepentacarbonyltungsten.<sup>4</sup>

Reaction of complex (1) with but-2-yne to give the complexes (2) and (3) and with terminal alkynes to give polyalkynes, allows us to outline the following possible mechanism for the polymerization of alkynes (Scheme 2).

TABLE. Polymerization conditions and molecular weights of the polyalkynes.<sup>a</sup>

Expt.	Monomer	Additives <sup>b</sup>	Conditions <sup>c</sup>	T/°C	t/h	Yield (%)	$\bar{M}_n^d$	$\bar{M}_w/\bar{M}_n$
1	P		Argon	62	60	65	800 1000 <sup>e</sup>	
2	P		H.v.	62	60	73	3300 4400 <sup>e</sup>	
3	P		Air	62	60	0		
4	H		H.v.	62 then 25	20 then 24	33	16500	2.3
5	H		H.v.	10	135	6.8		
6	H	O <sub>2</sub>	H.v.	62	96	48	8000	2.8
7	H	H <sub>2</sub> O	H.v.	62	96	52.5	6000	3.3

<sup>a</sup> Monomer/Initiator = 330; P = pentyne; H = heptyne. <sup>b</sup> Added after initiation: (O<sub>2</sub>)/(W) = 3, (H<sub>2</sub>O)/(W) = 0.1, (W) = moles of inhibitor. <sup>c</sup> H.v. = high vacuum. <sup>d</sup> Value estimated from g.p.c.-polystyrene standards.  $\bar{M}_w$  = weight-average molecular weight,  $\bar{M}_n$  = number-average molecular weight. <sup>e</sup> By tonometry.

(i) Deco-ordination of the double bond in complex (1) by the alkyne could give the intermediate (4), a reaction which has been observed in the case of phosphines.<sup>5</sup> (ii) Insertion with carbon-carbon bond formation, followed by rearrangement could give complex (6). (iii) Complex (6), being coordinatively unsaturated, might react further with the monomer. Therefore successive insertions of monomers could lead to a polymer which grows on two metal centres.

Although numerous systems convert alkynes into polyalkynes, this report describes for the first time the reaction of a stable promoter with alkynes and, moreover, describes the insertion products of one molecule of monomer into the promoter.

(Received, 13th July 1981; Com. 821.)

<sup>1</sup> T. J. Katz and S. J. Lee, *J. Am. Chem. Soc.*, 1980, **102**, 422.

<sup>2</sup> J. C. W. Chien, *J. Polym. Sci., Polym. Lett. Ed.*, 1981, **19**, 249.

<sup>3</sup> J. Levisalles, F. Rose-Munch, H. Rudler, J. C. Daran, Y. Dromzee, and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, 1981, 152.

<sup>4</sup> M. Fontanille, personal communication.

<sup>5</sup> J. Levisalles, F. Rose-Munch, H. Rudler, J. C. Daran, Y. Dromzee, and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, 1980, 685.