Reactions of W(CCMe₃)(OCMe₃)₃ with terminal alkynes: metathesis and polymerization

André Mortreux [a,*], Francis Petit [1, a], Michèle Petit [a], Teresa Szymanska-Buzar [b]

[a] Ecole Nationale Supérieure de Chimie de Lille, Laboratoire de Chimie Organique Appliquée, UST Lille,
URA CNRS 402,BP 108, 59652 Villeneuve d'Ascq, France
[b] Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

Abstract

Catalytic metathesis of terminal alkynes $RC\equiv CH$ (R = alkyl, phenyl) is performed with the carbyne complex $WCCMe_3$ $(OCCMe_3)_3$ **1**. This reaction is rapidly masked by a polymerization reaction, which is the only process occurring at low temperature. The production of deprotiometallacyclic complexes $WC_3R_2(OCCMe_3)_2$ **2** by loss of *tert*-butyl alcohol from the metallacyclobutadiene intermediates is shown to be responsible for the deactivation in metathesis. Compounds of type **2** are extremely reactive in phenylacetylene polymerization.

Keywords: Alkynes; Carbyne complexes; Metathesis; Phenylacetylene; Polymerization; Tungsten

1. Introduction

The metathesis of internal acetylenes (Eq. 1) in a homogeneous phase was first reported to be catalyzed by $Mo(CO)_6$ in the presence of an excess of phenol in refluxing toluene [1]. Further investigations revealed other acetylene metathesis catalysts based on higher oxidation state molybdenum complexes [2,3]. However, the active species in these systems have never been detected.

Following the synthesis of well-defined tungstacarbyne complexes such as $W(CCMe_3)$ $(OCMe_3)_3$ by Schrock et al. [4,5] and their reactions with acetylenes, it is now well established

that alkylidyne complexes are catalytic active species (Eq. 2).

$$M\equiv CR + R^1C\equiv CR^2 \longrightarrow M \underset{R^2}{\overset{R}{\diamondsuit}} R^1 \longrightarrow M\equiv CR^2 + RC\equiv CR^1 \qquad (2)$$
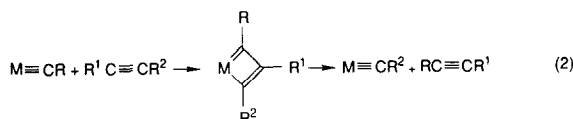
Although no metallacycles were observed, the expected new alkylidyne complexes could be detected in situ [4,5]. The first tungstenacyclobutadiene complex was prepared from $W(CCMe_3)(dme)Cl_3$ and one equivalent of 2-butyne or 3-hexyne [6]; later other complexes of the same type were observed in several cases [7–9].

Numerous studies on alkylidyne complexes have also revealed large differences as alkyne metathesis catalysts: depending upon the metal (W or Mo) and substituents at alkylidyne or

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* Corresponding author.
[1] Prof. Dr Francis Petit, deceased 30 December 1992.

alkoxide ligands, alkylidyne complexes metathesize acetylenes at varying rates, or do not react at all [10].

In contrast with internal acetylenes, the **catalytic** metathesis reaction of terminal acetylenes has not yet been observed, although $Mo(CCMe_3)(OCMe_3)_3$ reacts with $RC\equiv CH$ to give $(CH_3)_3CC\equiv CH$ and the new alkylidyne complex $Mo(CR)(OCMe_3)_3$ [11].

Schrock [10] gives several reasons why metathesis of terminal acetylenes cannot be observed. One possible reason is that degenerate metathesis is operative [11]. A second one is the formation of deprotiometallacycles from first formed disubstituted metallacyclobutadiene complexes. This reaction was very well documented by the same author [11–13]. We also think that a third possible reason could be the formation of stable methylidyne or ethyne complexes, which were observed by Chisholm et al. [14] in reaction of the tungsten alkoxides with alkynes.

However in the systems containing terminal alkynes and metal alkylidyne complexes other reactions were observed: most commonly, polymerization of the terminal alkynes occurs to give as yet unidentified polymers [15].

It is unclear at this time and we felt it valid to show what exactly occurs in terminal alkynes reactions with catalytically active tungsten alkylidyne complex. We wanted to see if it was possible to prevent the deactivation of initially formed metallacyclobutadiene and explain the transformation of an alkylidyne complex into a polymerization reaction catalyst.

This problem is not only important from the point of the metathesis mechanism but also the polymerization of terminal alkynes [16]. As one of the most active catalysts for the metathesis of dialkylacetylenes is $W(CCMe_3)(OCMe_3)_3$, we chose this compound for our studies. This paper will so deal with the catalytic and stoichiometric behaviour of terminal acetylenes with this complex [17].

2. Experimental

2.1. General details

All experiments were performed under dried and deoxygenated argon using standard Schlenk techniques. All solvents and reagents were dried, distilled, deoxygenated and stored under argon. Pentane, diethyl ether, tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl and all alkynes and solvents from CaH_2 at reduced pressure. tert-Butyl alcohol was distilled as a 30% benzene azeotrope and stored over molecular sieves.

2.2. Preparations

$W(CCMe_3)(OCMe_3)_3$ was prepared by the high-yield reaction of $W_2(OCMe_3)_6$ and $(CH_3)_3CCN$ in a manner analogous to the preparation of $W(CR)(OCMe_3)_3$, where $R = CH_3$, Ph by Schrock et al. [18] as follows:

To the solution of $W_2(OCMe_3)_6$ (4 mmol, 3.2 g) in 70 ml hexane was added trimethylacetonitrile (4 mmol, 0.45 ml) and the reaction mixture stirred for 30 min during which time the solution turned from dark red to yellow and a white powdery precipitate of $[W(N)(OCMe_3)_3]n$ was formed. This was then allowed to settle and the light yellow solution of $W(CCMe_3)(OCMe_3)_3$ decanted by a canula.

This solution was always used in situ unless another solvent was required for further reactions and assumed to be 0.057 M. Removing hexane in vacuo produces a white crystalline precipitate on the side of the Schlenk tube, with a thin layer of light brown oil on the bottom.

The product can be recrystallized from ether by addition of acetonitrile and cooling to $-30°C$ but this procedure, recommended by Listemann and Schrock [19], considerably lowers the yield of $W(CCMe_3)(OCMe_3)_3$. The purity of $W(CCMe_3)(OCMe_3)_3$ was confirmed by ^1H, ^{13}C NMR measurements after hexane removal in vacuo from 1 ml of 0.057 M solution of the compound and dissolution of the residue in 0.3 ml

deuterated toluene. ^{1}H NMR (toluene-d_8) δ 1.43 (s,27,OCMe$_3$), 1.23 (s,9,CCMe$_3$) ^{13}C NMR (toluene-d_8) δ 272.25 (s,CCMe$_3$), 79.82 (s,OCMe$_3$), 50.71 (s,CCMe$_3$), 35.12 (s,CCMe$_3$), 33.49 (s,OCMe$_3$).

W$_2$(OCMe$_3$)$_6$ [20] was prepared by the reaction of W$_2$(NMe$_2$)$_6$ and *tert*-butyl alcohol. W$_2$(NMe$_2$)$_6$ [21] was prepared according to Chisholm et al. from WCl$_4$ (Aldrich) and LiNMe$_2$ (Aldrich) followed by recrystallization from hexane at $-20°$C.

2.3. Reaction procedure

Catalytic reactions of terminal alkynes were run in a 10 ml overall volume of solution containing from 1 to 2 ml of 0.057 M hexane solution of the catalyst W(CCMe$_3$) (OCMe$_3$)$_3$ and 10 to 150 equiv. of alkyne. In a typical reaction, the hexane solution of the catalyst was added to the stirred mixture of the alkyne and internal chromatographic standard (toluene or n-octane), diluted with an appropriate solvent and analyzed by GLC.

The solution was stirred for 1 min and, after this time, a first sample was removed with a syringe and injected into the column of a Girdel chromatograph fitted with a flame ionisation detector and recorded using a data analysis module. Separations were performed on a 3 m×0.32 mm 10% SE 30 column. For reactions for which products could not be resolved by GLC, the GC–MS (gas chromatography–mass spectrometry) was used in addition. Terminal alkynes RC≡CH, where R = C$_3$H$_7$, C$_4$H$_9$,C$_5$H$_{11}$,(CH$_3$)$_3$C, (CH$_3$)$_3$Si and C$_6$H$_5$ were used in these reactions.

Comparison of the catalytic activity of this system with terminal and internal alkynes was made taking 4-nonyne as the substrate for a standard reaction. For the analysis of the alkyne polymerization products, reactions were continued until all the starting alkyne was consumed and then the reaction mixture was evaporated to dryness under reduced pressure. The residue was recrystallized from CH$_2$Cl$_2$–methanol. The polymer was collected, dried in vacuo and analyzed by ^{1}H, ^{13}C

NMR and IR spectroscopy, and gel-permeation chromatography.

The poly(phenylacetylene) polymers were obtained as dark red–orange crystals or powder, soluble in halogenated and aromatic hydrocarbons. The polymers of 1-pentyne, 1-hexyne and 1-heptyne were reddish brown, rubbery solids, soluble in halogenated, aromatic and aliphatic hydrocarbons. 1-Trimethylsilylacetylene afforded a yellow polymer practically insoluble in most organic solvents except methylene chloride.

Analyses by GLC chromatography and mass spectrometry have shown that terminal alkynes are consumed only in metathesis and polymerization reactions. The amount of polymer analyzed gravimetrically corresponds exactly to the difference between the starting material and the metathesis products. On this basis, yields of polymerization for the time of the reaction were calculated as the difference between the conversion and metathesis reactions.

$$\text{conversion} = \frac{[\text{alkyne}]_i - [\text{alkyne}]_f}{[\text{alkyne}]_i} \times 100$$

yield of polymerization

= conversion − yield of metathesis

turnover number in metathesis

$$= \frac{2[\text{symmetrical alkyne}]}{[\text{W}]}$$

Molecular weights of the polyalkynes were measured by gel-permeation chromatography using toluene solutions, a refractive index monitor, and three Waters Associates columns (500 Å, 10^3 Å, 10^4 Å). The values recorded are the weights of polystyrene that would exhibit the chromatograms observed.

2.4. Spectroscopic studies: NMR studies of the reaction of W(CCMe$_3$)(OCMe$_3$)$_3$ with alkynes

The ^{1}H, ^{13}C and ^{13}C{^{1}H}NMR spectra of tungsten compounds and polyalkynes were recorded in dry and deoxygenated toluene-d_8 or methylene-

d$_2$ chloride on a Bruker AM (400 MHz) spectrometer.

The IR spectra of polyalkynes were recorded on a Nicolet 510 FT-IR spectrometer as KBr pellets for powdery compounds or as films for rubber-like polymers.

After reaction of W(CCMe$_3$)(OCMe$_3$)$_3$ with different alkynes carried out as described above, the reaction mixture was evaporated to dryness at reduced pressure and the residue was extracted with toluene-d$_8$ and analyzed by ^{1}H and ^{13}C NMR spectroscopy. In samples obtained after reaction of 1-pentyne, 1-hexyne and 1-heptyne only polyalkynes were identified.

In the reaction mixture of tert-butylacetylene, phenylacetylene and 4-nonyne, new tungsten complexes were observed.

Low-temperature NMR studies of the reaction between W(CCMe₃)(OCMe₃)₃ and 1-pentyne

A solution of 0.1 mmol (0.042 g) of W(CCMe$_3$)(OCMe$_3$)$_3$ in 0.3 ml toluene-d$_8$ was frozen in a cold bath (143 K) in an NMR tube and 0.2 mmol (20 μl) of 1-pentyne was added through the serum cap via a microsyringe under argon. The sample was stored at 143 K prior to use and introduced into the precooled spectrometer probe (195 K) and monitored by ^{1}H and ^{13}C NMR spectroscopy from 203 to 293 K. The spectrum of the sample did not show any detectable change at these temperatures and only unreacted W(CCMe$_3$)(OCMe$_3$)$_3$ and poly(1-pentyne) were observed.

Reaction of W(CCMe₃)(OCMe₃)₃ with (CH₃)₃CC≡CH

After 5h reaction of W(CCMe$_3$)(OCMe$_3$)$_3$ (0.057 mmol, 0.024 g) with 50 equiv. (2.85 mmol) of tert-butylacetylene in 10 ml hexane in a closed system at room temperature, the reaction mixture was evaporated to dryness and the waxy reddish brown residue was extracted with toluene-d$_8$ and transferred through the canula into an NMR tube. The NMR results will be discussed in a later section.

Its mass spectrum (EI) gives m/e values corresponding only to decomposition products: $m/e = 56$: CH$_2$=C(CH$_3$)$_2$; 231: C$_5$(CMe$_3$)$_3$; 246: C$_6$H$_3$(CMe$_3$)$_3$.

Reaction of W(CCMe₃)(OCMe₃)₃ with PhC≡CH

A solution of W(CCMe$_3$)(OCMe$_3$)$_3$ (0.29 mmol, 0.12 g) and PhC≡CH (1.2 mmol, 1.22 g) in ether (20 ml) was stirred for 30 min at room temperature. The solution quickly turned red and a red precipitate was obtained. The solvent and excess PhC≡CH were removed in vacuo, and the red–orange residue was extracted with hexane. A red–orange solid, insoluble in hexane, was identified by ^{1}H NMR in methylene chloride-d$_2$ as poly(phenylacetylene) (^{1}H NMR δ = 5.96, 6.7, 7.9 ppm).

The hexane solution was evaporated to dryness in vacuo and the red solid was extracted with toluene-d$_8$ and transferred through a canula into the NMR tube. ^{1}H NMR (toluene-d$_8$) δ 11.75, 11.5, 1.66, 1.58 and 1.02 ppm. ^{13}C NMR (toluene-d$_8$) δ 238.5s, 232.4s, 201.7s, 200.7s, 164.9s, 159.2d, 82.9d, 31.46s, 31.13s.

Reaction of W(CCMe₃)(OCMe₃)₃ with C₄H₉C≡CC₃H₇

W(CCMe$_3$)(OCMe$_3$)$_3$ (0.057 mmol, 0.024 g) and 30 equiv. of 4-nonyne gave the 1:2:1 equilibrium mixture of 4-octyne/4-nonyne/5-decyne (by GLC), after less than 1 min reaction in hexane (10 ml) at room temperature. Evaporation of solvent and alkynes to dryness in vacuo and analysis of the entire residues by ^{1}H, ^{13}C NMR revealed the formation of a new tungsten alkylidyne compound W(CPr)(OCMe$_3$)$_3$ with a characteristic carbyne carbon signal at 262.5 ppm [18].

3. Results and discussion

3.1. Catalytic reactions of R–C≡CH with W(CCMe₃)(OCMe₃)₃

3.1.1. Preliminary experiments

When a solution of 0.057 mmol of **1** was introduced at room temperature into a 9 ml solution of 2.85 mmol of 1-heptyne in n-hexane, an initial

Table 1

Effect of the alkyne/W initial molar ratio on the conversion metathesis and polymerization reaction of 1-pentyne in hexane [a]

Initial 1-pentyne/ W ratio	Conversion		TN	
	%	TN	Metathesis	Polymerization
148	14.4	21.4	5.5	15.8
45	24.5	11.0	5.8	5.2
17	48.9	8.3	6.0	2.3

[a] $T = 21°C$; reaction time = 1 min.

burst of acetylene was evolved and detected by GC–MS spectrometry. Upon analysis of the liquid phase after 1 min, 0,14 mmol of 6-dodecyne were formed. These results are consistent with the following metathesis reaction

$$2C_5H_{11}C\equiv C-H \overset{[1]}{\rightleftharpoons}$$

$$C_5H_{11}C\equiv C-C_5H_{11} + HC\equiv CH$$
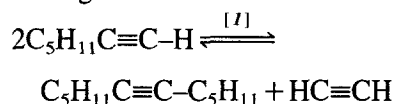
At that time, a 32% conversion of the starting material is calculated using an internal standard, indicating that a parallel polymerization reaction had already started. After 2 h at room temperature, there was no more change in the concentrations of the symmetrical alkyne ($C_5H_{11}-C\equiv C-C_5H_{11}$) and $Me_3CC\equiv CH$ formed at the early stage of the reaction. 1-Heptyne had however completely disappeared via the polymerisation process. Further investigations on this new catalytic reaction are described below.

3.1.2. Catalyst concentration

It was shown by Sancho and Schrock [5] that $W(CCMe_3)(OCMe_3)_3$ reacts with internal alkynes at a rate which is overall second order, first order in tungsten and first order in acetylene. We have now shown that in the case of terminal alkylacetylenes, the yield of metathesis is proportional to the initial mole ratio of alkyne to tungsten (Table 1). The turnover numbers (TN) calculated as the number of moles of 1-pentyne giving the metathesis reaction per mole of tungsten do not change over approximately 10^{-1} to 1 molar concentration of alkyne. We could not observe a similar dependence for the polymerization reaction. Yields of polymerization calculated as the

difference between conversion and metathesis are almost independent of the 1-pentyne/tungsten ratio and turnover numbers in polymerization depend upon the initial concentration of the catalyst (Table 1).

However overall conversions after two hours independently reach almost 90%.

3.1.3. Solvent and additives effects

Hexane, toluene, diethyl ether, THF and CH_2Cl_2 were used as the solvents in reactions of 1-heptyne in the presence of tungsten compound (Table 2). In CH_2Cl_2 and THF the metathesis reaction was not observed. THF can coordinate strongly through the oxygen to tungsten and effectively block coordination sites for the alkyne. CH_2Cl_2 with active C–Cl bond probably decomposes the alkylidyne ligand but polymerization occurs slowly through another active species.

The best solvent for alkyne metathesis is diethyl ether. The influence of ether can be explained by its soft coordination ability which is sufficient for removal of acetylene from the initially formed tungstenacyclobutadiene and for blocking coordination sites for alkynes which can coordinate and polymerize at the same metal centre. In this solvent the yield of polymerization in the first minute of the reaction is the smallest (Table 2).

The differences between toluene and hexane can be explained in terms of a greater solubility of the tungsten compound and of the polymer in aromatic rather than aliphatic hydrocarbons and thus aromatic hydrocarbons are better solvents for polymerization reactions [16].

Table 2

Influence of the solvent on the conversion, metathesis and polymerization reaction of 1-heptyne [a]

Solvent	Conversion		Metathesis		Polymerization	
	%	TN/W	%	TN/W	%	TN/W
toluene	40.8	20.4	7.5	3.7	33.3	16.7
hexane	32.0	16.0	9.6	4.8	22.4	11.2
diethyl ether	15.4	7.7	14.6	7.3	0.8	0.4
dichloromethane	7.2	3.6	-	-	7.2	3.6
tetrahydrofuran	1.4	0.7	-	-	-	-

[a] 1-Heptyne/W = 50; T = room temperature; reaction time = 1 min.

Table 3
Effect of additives on the reaction of terminal alkynes in the presence of 0.02 equiv. of $W(CCMe_3)(OCMe_3)_3$, at RT in hexane after 1 (and 100) min reaction time [a]

Alkyne	Addition compound (equiv./W)	Conversion % after 1 min (100 min)	Meta-thesis[b] (%)	Polymer-ization[b] (%)
1-heptyne	-	32.0 (97)	9.6	22.4
1-heptyne	pyridine (10)	16.0 (84)	6.5	9.5
1-pentyne	-	24.5 (83)	12.8	11.7
1-pentyne	acetonitrile (5)	24.5 (78)	11.6	12.9
1-pentyne	phenol (0.7)	33.6 (60)	8.5	25.1
1-pentyne	phenol (2)	11.2 (40)	1.5	9.7

[a] See text for conditions.
[b] After 1 min.

The influence of additional compounds on the reaction of alkynes was also studied by the introduction into the reaction mixture of 1 to 10 equiv. of compounds such as acetonitrile, pyridine or phenol (Table 3). All these compounds suppress both metathesis and polymerization reactions. The highest conversion during the first minute occurs in the presence of 0.7 equiv. of PhOH, but, after a prolonged reaction time, this was reduced below the conversion of 1-pentyne without PhOH. Two equiv. of PhOH per tungsten almost inhibit the metathesis reaction and polymerization occurs at a lower rate.

These results are in a good agreement with Freudenberger and Schrock [22] who observed protonation of the alkylidyne ligand by 2 equiv. of PhOH and formation of a stable dibutoxydiphenoxyalkylidene tungsten complex.

Acetonitrile, as a poor electron donor, does not greatly disturb coordination of the alkyne to tungsten and the formation of the catalytically active species. A tenfold pyridine excess sufficiently lowers polymerization but the influence on metathesis is rather small.

3.1.4. Temperature

The influence of temperature on the course of the reactions with 1-heptyne and phenylacetylene was investigated. Reactions of 1-heptyne in the presence of 0.02 equiv. of tungsten compound were carried out at temperatures from 0 to 70°C

in hexane and at 100°C in toluene (Table 4). At low temperature ($< -30°C$) metathesis does not occur, but the polymerization reaction can be run at lower temperature. This behaviour was also confirmed by low-temperature NMR studies. Even at temperatures as low as 203 K, all alkynes polymerize rapidly and intermediate tungsten-containing species are observed by NMR (see later). This suggests that the polymerization and metathesis of terminal alkynes can occur through different intermediate species. The active polymerization agent is probably present in trace amounts and must be extremely active.

3.1.5. Reaction of $W(CCMe_3)(OCMe_3)_3$ and $PhC≡CH$

Although the main features of the reaction of $PhC≡CH$ in the presence of $W(CCMe_3)(OCMe_3)_3$ are the same as those of other terminal alkynes, there are several differences. At first, yields of metathesis are very low and observable only at higher temperature (the highest, 4%, at 70°C). At room temperature, only a 'stoichiometric metathesis' reaction of $PhC≡CH$ and $W(CCMe_3)(OCMe_3)_3$ was observed with formation of quantitative amounts of tert-butylacetylene and polyphenylacetylene. The polymerization rate increases considerably with temperature (Fig. 1) and depends upon the solvent: polyphenylacetylene formed in ether is dark red, crystalline, and has a molecular weight twice as high as that obtained in hexane solution. These results suggest a stabilization effect of ether

Table 4
Influence of temperature on the conversion, metathesis and polymerization reaction of 1-heptyne [a]

Temperature °C	Conversion		Metathesis		Polymerization	
	%	TN/W	%	TN/W	%	TN/W
0	17.9	10.2	5.9	2.9	12.0	8.2
23	32.0	16.0	9.6	4.8	22.4	11.2
50	32.6	16.3	13.7	6.8	18.9	9.5
70	56.8	28.4	19.2	9.6	37.6	18.8
100	60.4	30.2	25.4	12.7	35.0	17.5

[a] Heptyne/W = 50; reaction time = 1 min; solvent = hexane, toluene only used at 100°C.

on the catalytically active species. Attempts to identify this species by NMR were made.

After the reaction of PhC≡CH with 0.2 equiv. of $W(CCMe_3)(OCMe_3)_3$, the formation of a mixture of different tungstenacycles was observed, whose ratio varied from one reaction to another. By comparison of NMR data obtained on similar tungsten compounds obtained by Freudenberger and Schrock [12], the following compounds were identified: $W(C_3Ph_2)(OCMe_3)_3$ (C_α 201.7, C_β 200.7 ppm), $W(C_3Ph_2H)(OCMe_3)_3$ (C_α 238.6, $C_\alpha{}'$ 232 and C_β 159.1 ppm and ^1H signal of proton ring at 11.75 ppm). Probably also $W[C_3(CMe_3)(H)(Ph)](OCMe_3)_3$ exists in this mixture because another proton with 1/3 intensity of the first one at 11.5 ppm was observed, but confirmation by ^{13}C NMR was not possible. It is interesting to note that we observed diethyl ether present in the coordination sphere of tungsten even after recrystallization of these compounds from hexane and drying in vacuo. Some starting alkylidyne compound was also present in this reaction mixture.

3.1.6. Reaction of $W(CCMe_3)OCMe_3)_3$ with $Me_3CC≡CH$

The reaction of tert-butylacetylene with $W(CCMe_3)(OCMe_3)_3$ is not catalytic. Even after prolonged reaction time (5–24 h) no more than three molecules of $Me_3CC≡CH$ were converted per tungsten atom and less than one molecule of di-tert-butylacetylene was formed. This result suggests the formation of a stable tungsten complex from the starting alkylidyne and tert-butylacetylene. The ^1H and ^{13}C NMR spectra of the residue obtained after evaporation of both solvent and unreacted alkyne from this reaction mixture have been analyzed. These spectra show the presence of two tungsten compounds; one has a deprotiotungstenacyclobutadiene structure [WC_3 ($Bu^t)_2$ ($OBu^t)_2$] 2 and the other is the ethynebridged ditungsten compound m-$C_2H_2[W(OBu^t)_3]_2$ 3. No attempt was made to separate these complexes, but as their relative ratio was solvent and temperature dependent, one could easily establish their NMR characteristics:
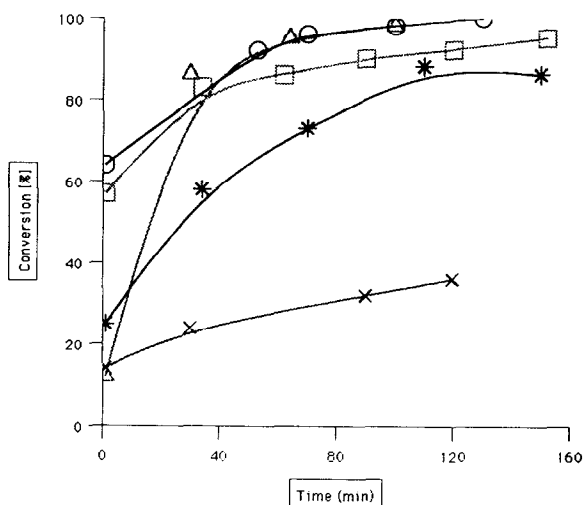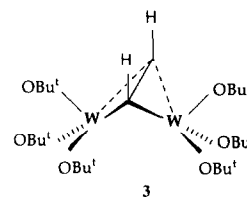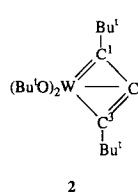

Fig. 1. Conversion vs. time for the polymerization of PhC≡CH at different temperatures, in the presence of 0.02 equiv of $W(CCMe_3)(OCMe_3)_3$. ×: −21°C; *: −70°C; O: −70°C in hexane; □: −100°C in toluene; △: −21°C in ether.

For compound 2, ^{13}C resonances of the four-membered ring are found at 215.5, and 170.8 ppm, both coupled to ^{183}W ($J=1/2$, 14.3% natural abundance) with value of $J_{CW}=139.5$ and 25.8 Hz respectively. These two resonances, whose intensities are in a 2:1 ratio, can be assigned to two equivalent $C_\alpha=C(1)$ and $C(3)$, and $C_\beta=C(2)$. The resonance of the tert-butoxy ligand is at 78.7 ppm. and the two equivalent tert-butyl groups of the ring are localized at 41.97 ppm. Carbon signals at 34.1, 33.1 and 32.7 ppm are assigned to the methyl carbons of the butoxy and tert-butyl groups. Resonances of protons were observed at 1.85, 1.53 and 1.06 ppm. These ^1H

Table 5
Comparison of NMR data of [W-C$_3$(CMe$_3$)$_2$(OCMe$_3$)$_2$] and μ-C$_2$H$_2$[W(OCMe$_3$)$_3$]$_2$ and tungstenacycles obtained by Freudenberger and Schrock [12] in the reaction of tungsten alkylidyne complexes and Me$_3$CC$\equiv$CH [a]

Compound	H (J_{HW})	C$_\alpha$ (J_{CW})	C$_\beta$ (J_{CH}, J_{CW}) and other carbons of the ring
W[C$_3$H(CMe$_3$)$_2$][OCH(CF$_3$)$_2$]$_3$	10.01 (15.3)	252.7 (122)	128.3 (J_{CH}=202) (J_{cw}≈0)
W[C$_3$(CMe$_3$)$_2$][OCH(CF$_3$)$_2$]$_2$(py)$_2$	-	219.2	206.7
W[C$_3$H(CMe$_3$)$_2$][O-2,6-C$_6$H$_3$)-i-Pr$_2$)$_3$]	9.34 (12.8)	248.6	114.6 (J_{CH}=197)
W[C$_3$H(CMe$_3$)$_2$][O-2,6-C$_6$H$_3$)-i-Pr$_2$)$_2$]Cl	8.99 (11.6)	259.1	113.5 (J_{CH}=200)
W[C$_3$(CMe$_3$)$_2$][O-2,6-C$_6$H$_3$)-i-Pr$_2$)$_2$]py	-	223.2	208.1, 181.4
W[C$_3$(CMe$_3$)$_2$][O-2,6-C$_6$H$_3$)-i-Pr$_2$)$_2$]	-	227.0	168.5
W[C$_5$H(CMe$_3$)$_2$][O-2,6-C$_6$H$_3$)-i-Pr$_2$)$_2$]	7.65 (15.3)	277.9	194.4, 185.8 (J_{CH}=15.5), 159.8, 155.1 (J_{CH}=148)
W[C$_3$(CMe$_3$)$_2$(OCMe$_3$)$_2$(OCMe$_3$)$_2$]		215.5 (139.5)	170.8 J_{CW}=25.8
μ-C$_2$H$_2$[W(OCMe$_3$)$_3$]$_2$	7.56	μC$_2$H$_2$ 120,5 (58.7) $^1J_{CH}$=152,6, $^2J_{CH}$=6.6	

[a]Position of signals δ (ppm), J_{CH} and J_{CW} (Hz).

and ^{13}C NMR spectra of **2** are similar to those of other metallacycles obtained by Schrock et al. following reactions of *tert*-butylacetylene with tungsten or molybdenum alkylidyne complexes (Table 5) [11,13]. For all metallacycles of that type so far characterized, the range for the C$_\alpha$ signals is larger (218–278 ppm) than that for the C$_\beta$ signals (113–155 ppm). The coupling constant between C$_\alpha$ and the metal is close to what would be expected for a tungsten–carbon double bond (J_{CW} ≈ 120 Hz). That between C$_\beta$ and the tungsten is much smaller (J_{CW} = 25 Hz).

Another significant feature of the NMR spectra of these metallacycles is that the resonance of Cα in deprotiometallacycles formed by loss of 1 equiv. of alcohol are about 30 ppm lower, and that of C$_\beta$ 50 ppm higher, than those observed in analogous MC$_3$MR$_2$ cycles. The positions of C$_\alpha$ (215.5 ppm) and C$_\beta$ (170.8 ppm) are in full agreement with structure **2**.

In addition to compound **2**, the NMR spectra revealed the presence of another compound, **3**. The position of the carbon resonance at 120.1 ppm (J_{CW} = 58.7 Hz, $^1J_{CH}$ = 152.6 and $^2J_{CH}$ = 6.55 Hz) is characteristic for tungsten complexes with bridging alkyne ligands. Complexes of this type were obtained by Chisholm et al. [26] during the reactions of ethyne with ditungsten hexaalkoxides, and have been characterized by NMR analysis and by X-ray crystallography [14]. For
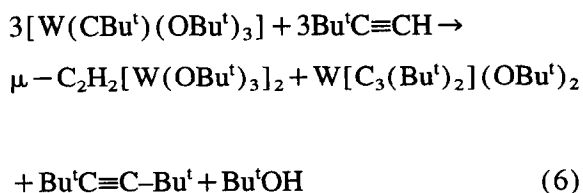
W$_2$(OCCMe$_3$)$_6$ (py) (μ-C$_2$H$_2$) the carbon resonance of the bridging alkyne was observed at 120.1 ppm (J_{CW} = 44.1 Hz and $^1J_{CH}$ = 184 Hz)

Similarly to Chisholm et al. [26], we have also observed by NMR an equilibrium between W$_2$(μ-C$_2$H$_2$) and W$\equiv$CH moieties. Indeed, in ^{1}H NMR spectra, a proton signal appears with a very small intensity at 7.85 ppm. The intensity ratio of this signal and that of the dimeric ethyne protons is 1:14. Moreover, in the carbyne region there appears, with trace intensity, a resonance at 269.9 ppm which may be assigned to the carbon methylidyne ligand.

Signals at 151.1 (=CBu^t), 123.93 (=CH) 35.99 (CMe$_3$) and 31.98 ppm (CMe$_3$) are assigned to small amounts of poly(*tert*-butylacetylene).

3.2. Reaction mechanism between 1 and tert-butylacetylene

By NMR spectroscopy and GLC chromatography, the reaction of **1** with Bu^{t}C$\equiv$CH in hexane appears to be almost quantitative according to Eq. 6:

$$3[W(CBu^t)(OBu^t)_3] + 3Bu^tC\equiv CH \rightarrow$$

$$\mu - C_2H_2[W(OBu^t)_3]_2 + W[C_3(Bu^t)_2](OBu^t)_2$$

$$+ Bu^tC\equiv C–Bu^t + Bu^tOH \qquad (6)$$

We are now able to propose how the above tungsten compounds might be formed (Scheme 1). *tert*-Butylacetylene adds to W(CCMe₃)(OCMe₃)₃ giving two possible tungstenacyclobutadiene complexes (symmetrical and unsymmetrical). The unsymmetric tungstenacyclobutadiene decomposes to release di-*tert*-butylacetylene and form a methylidyne complex. This reacts with another molecule of *tert*-butylacetylene to give ethyne and regenerate the alkylidyne ligand (metathesis process). From the symmetric tungstenacyclobutadiene, *tert*-butyl alcohol is lost to give a deprotiotungstenacyclobutadiene. The tungstenamethylidyne complex formed in the metathesis process can easily dimerize, particularly at lower temperature, to produce the ethyne-bridged ditungsten compound **3**.

The formation of alkyne adducts with dimeric tungsten compounds has been very well documented [14,29]. An equilibrium between monomer and dimer was observed in many tungsten compounds [25–28]. For alkylidyne compounds

Scheme 1.

[(Me₃CO)₃W≡CX], X = Me [26], NH₂ [27], Chisholm et al. observed a loose association to generate a dimeric structure. In the case of [W₂(OCMe₃)₆(py)(μ-C₂H₂)], there is evidence for an equilibrium in toluene solution between the ethyne adduct and the methylidyne complex.

3.3. Polymerization reaction of terminal alkynes in the presence of 1

In our investigations on the reactions of terminal alkynes in the presence of W(CCMe₃)(OCMe₃)₃ we observed competition between the metathesis and polymerization reactions only in the first minute of the reaction (Table 6). The metathesis catalytic species are deactivated after a few turnovers but polymerization occurs with high rate and high yield except with BuᵗC≡CH. The resulting polymers are tractable, dissolving easily in halogenated and aromatic hydrocarbons, except for the polymer of (CH₃)₃SiC≡CH which is only partially soluble in CH₂Cl₂. The molecular weights are high, from 10³ to 10⁴ (Table 6). The structures of the polymers are also clearly defined.

Polyphenylacetylenes formed in ether are dark red and crystalline, with molecular weight of 159×10³, that is, considerably higher than any reported, and comparable only to polyphenylacetylenes obtained in reactions initiated by the carbyne tungsten complex (C₆H₅C≡W(CO)₄Br) [30]. Polyphenylacetylene formed in hexane is an orange powder with molecular weight about one half of that above. The structures of both polyphenylacetylenes were determined according to the Simionescu et al. [31] using IR and ¹H NMR spectroscopies and were identified as *cis*-transoidal.

The polymer has a typical NMR spectrum with three proton resonances at 5.87, 6.70 and 7.05 ppm and IR bands at 740, 895 and 1380 cm⁻¹. The *cis* content in *cis*-transoidal poly(phenylacetylene) was determined from NMR spectra as 97.5%.

Aliphatic acetylenes give brownish red, rubbery polymers with very good solubility even in
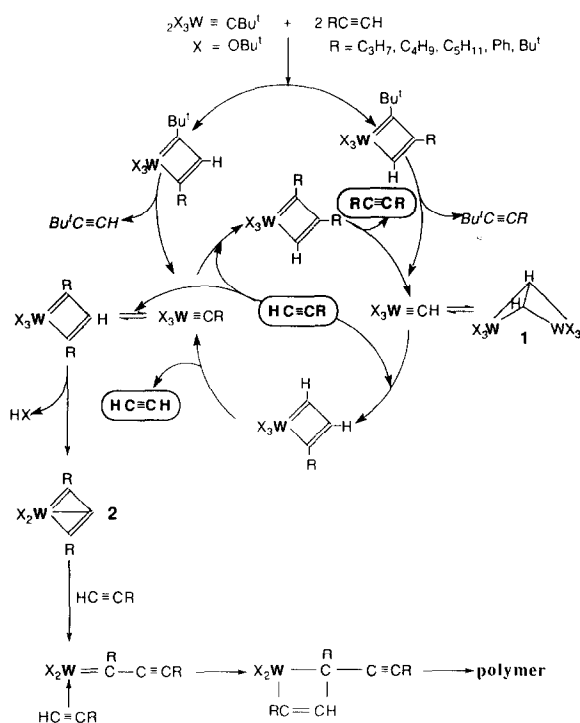
Table 6
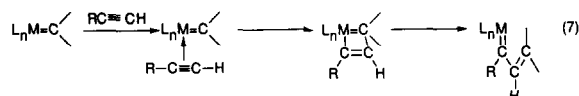Comparison of alkyne reactivity in the presence of $W(CCMe_3)(OCMe_3)_3$ after 1 min reaction at room temperature

Alkyne	Conversion (%)	Time to 100% conversion/h	Metathesis (%)	Polymerization (%)	Alkyne/W	Solvent	Molecular weight (MW) polyalkane	
							highest MW (10^{-3})	average MW (10^{-3})
$C_3H_7C{\equiv}CH$	24.5	2	12.8	11.7	45	hexane	158	18
$C_4H_9C{\equiv}CH$	57.3	2	6.9	50.4	50	pentane	16	1
$C_5H_{11}C{\equiv}CH$	32.0	1.5	9.6	22.4	50	hexane	200	25
$C_5H_{11}C{\equiv}CH$	15.4	>3	14.6	0.8	50	ether	-	-
$C_4H_9C{\equiv}CC_3H_7$	50	equilibrium < 1 min	50.0	0	30	hexane	-	-
$(CH_3)_3CC{\equiv}CH$	2.3	max conv. 3%	1.3	0	50	hexane	-	-
$(CH_3)_3SiC{\equiv}CH$	15.2	6	0	15.2	50	hexane	-	-
$C_6H_5C{\equiv}CH$	14.2	2	0	14.2	58	hexane	79	11
$C_6H_5C{\equiv}CH$	60.0	1.5	0	60	50	ether	159	20

aliphatic hydrocarbons and with high molecular weights. Again such high molecular weight polymers were obtained only in the presence of carbene or carbyne compounds [30,32].

tert-Butylacetylene does not polymerize in good yield in the presence of 1 for the reason given earlier, that is formation of stable compounds 2 and 3, but small amounts of poly (*tert*-butylacetylene) which were formed also have a *cis* structure, determined by ^{13}C NMR [16]. 1 also polymerizes the silicon-containing acetylene $(CH_3)_3SiC{\equiv}CH$, but the polymer is only partly soluble in CH_2Cl_2. It was characterized only by IR spectroscopy.

It has been proposed that the mechanism of alkyne polymerization by molybdenum and tungsten-based catalysts occurs via metal alkylidene intermediates (Eq. 7) [33].

$$L_nM{=}C\overset{/}{\underset{\backslash}{}} \xrightarrow{RC{\equiv}CH} L_nM{=}C\overset{/}{\underset{\backslash}{}} \longrightarrow L_nM{=}C\overset{/}{\underset{\backslash}{}} \longrightarrow L_nM \quad (7)$$

It has been suggested that these metal alkylidene intermediates are formed during the photo-assisted polymerization of terminal alkynes by $W(CO)_6$ via a rearrangement of an acetylene complex to a vinyl alkylidene complex [23,24]. However, no example of such a rearrangement has so far been reported in the literature using high oxidation state complexes.

As we have observed in the reactions of 1 and terminal alkynes, metathesis and polymerisation are initially parallel reactions.

The tungstenacyclobutadiene intermediate, the catalytically active species for the metathesis reaction, can be deactivated by deprotonation, with the formation of complex 2. Alternatively, deactivation can occur via dimerization of the tungstenamethylidyne complex and formation of compound 3. Complex 2 obtained in a separate reaction initiates the very rapid polymerization of phenylacetylene. Therefore, the probable pathway for initiation of the polymerization reaction is the isomerization of the deprotiotungstenacyclobutadiene complex into intermediate carbene species in the presence of an excess of terminal alkyne [15] (Scheme 1).

A further argument in support of our hypothesis that polymerization and metathesis occur through different intermediate species is the detection of the starting alkylidyne, metallacyclobutadienes and deprotiometallacyclobutadienes in the residue obtained after the rapid polymerization of phenylacetylene.

Internal alkynes which could not form intermediate vinylidene ligands do not polymerize in the presence of alkylidyne complexes, but their polymerization was observed by Katz et al. [32] in the presence of alkylidene compounds.

4. Conclusion

This paper has demonstrated the ability of tungstacarbyne complexes to promote the metathesis reaction of terminal acetylenes. Although the catalyst's stability still remains very low, due to deprotonation of the metallacyclobutadiene species, it is highly probable that by changing either the nature of the alkoxy ligand and the metal itself (molybdenum complexes are also suitable for the metathesis reaction of alkynes), one might be able to stabilize active complexes for metathesis. Another interesting feature described in this paper is the ability of the deprotiometallacyclobutadiene complexes to polymerize, with high efficiency, terminal acetylenes into high molecular weight polymers with a high *cis* content, which therefore provides a new interesting catalyst for polymer chemistry.

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