INITIATION OF POLYMERIZATION OF PHENYLACETYLENE WITH WOCl$_4$ AND WCl$_6$ "SINGLE-COMPONENT" METATHESIS CATALYSTS[†]

Jiří Vohlídal[1], Jan Sedláček[1], Marta Pacovská[1], Majda Žigon[2]

[1]*Department of Physical and Macromolecular Chemistry, Laboratory of Specialty Polymers[*], Faculty of Science, Charles University, Albertov 2030, CZ-128 40 Praha 2, Czech Republic, E-mail: vohlidal@prfdec.natur.cuni.cz*

[2]*Polymer Department, National Institute of Chemistry, Hajdrihova 19, SLO-61115 Ljubljana, Slovenia*

ABSTRACT

At low monomer-to-catalyst mole ratio (3:1) in benzene or toluene, phenylacetylene (PhA) reacts with WOCl$_4$ to arylderivatives belonging to five homologous series with increment equal to PhA unit, low amount of chloroderivatives and traces of PhA oligomers, mainl cyclotrimers. Aryls built in the derivatives originate from the solvent used. Hydrogen transfers between PhA units were found to participate in the overall reaction. An increase in the PhA/WOCl$_4$ mole ratio results in a lowered yield of arylderivatives, higher yield of cyclotrimers and formation of highe PhA oligomers (ratio 12:1) o poly(phenylacetylene) (ratio 100:1). Chloroderivatives are formed in comparable amounts at any PhA/WOCl$_4$ mole ratio so that they can be regarded as the key by-product of reduction of WOCl$_4$ to low-valent tungsten species. In reaction systems with the mole ratio up to 12:1, WOCl$_4$ is transformed into black solid assigned to WOCl$_2$. It dissolves in PhA inducing its polymerization in which only PhA cyclotrimers are the side products. Formation of aryl- and chloroderivatives as well as tungsten growing species is discussed in terms of reaction pathway presuming an important role of oxo ligand of tungsten species. Reaction of PhA wit WCl$_6$ results in a formation of various PhA chloroderivatives and a fine precipitate of reduced tungsten species, which polymerizes PhA after poorly reproducible induction period.

Key words: phenylacetylene, tungsten oxytetrachloride, tungsten hexachloride, Friedel-Crafts reaction, metathesis polymerization, substituted polyacetylenes

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INTRODUCTION

Tungsten hexachloride, WC_6, and tungsten oxytetrachloride, $WOCl_4$, are often used as single-component metathesis catalysts for polymerization of substituted acey-lenes [1-10]. WCl_6 is known as an efficient catalyst of these polymerizations performed under an inert gas atmosphere at concentrations of WCl_6 about 5 to 10 mmol/L [8-12]. In addition, phenylacetylene (PhA) has been found to act as an efficien cocatalyst o both olefin metathesis and metathesis polymerization induced by WCl_6 under the same reaction conditions [13-15]. These observations resulted in a formulation of the stoichi-ometric mechanism of formation of tungsten carbene species from WC_6 and PhA [3, 8]:

$$C \diagup \quad {}_4W=C=CClPh \ + \ HCl$$

$$WCl_6 \ + \ HC{\equiv}CPh \ \longrightarrow \ C\,_5W{-}CH{=}CClP \diagup$$

$$C \diagdown \quad {}_4W=CH{-}CCl_2Ph$$

Supplementary evidences supporting this mechanism were obtained from GC-MS analysis of the 1:1 stoichiometric mixture of PhA and WCl_6 in which various chloro-derivatives of PhA have been found [9]. However, if PhA polymerization is performed under conditions that better prevent the reaction system from a contamination like, e.g., by using vacuum technique, the activity of WC_6 becomes poorly reproducible mainly a lower catalyst concentrations (typically below 3 mmol/L). WCl_6 either does not polym-erize PhA at all or polymerizes it, however, after an unpredictably long induction period reaching from ca 30 min to one day. It is worth noting that binary and/or ternary catalys system involving an organotin or organoaluminiu cocatalyst to WC_6 exhibit reproduci-ble activity.

In contradistinction to WCl_6, $WOCl_4$ used as a single-component catalyst always polymerizes PhA and other substituted acetylenes reproducibly under the same reaction conditions, see, e.g., refs [5-7]. Irreproducibility of reactions induced by WC_6 was also observed in experiments performed with an increased care under inert gas and it was concluded that the activity of WC_6 is induced by traces of WOC_4 that is curren im-purity present in WCl_6 [10]. Also Makovetsk et all. [9] observed: *(i)* total loss of the activity of WC_6/PhA catalyst in the metathesis polymerization of cyclopentene upon

careful purification of the reaction mixture; and *(ii)* good activity of WOC $_4$/PhA catalys in this polymerization under the same experimental conditions. Therefore, a question is arising as to a difference in catalytic activity of these two chemically similar tungsten compounds, which we try to elucidate in the present paper by using PhA as the substrate.

EXPERIMENTAL

Materials. WCl$_6$ free of WOC $_4$ was obtained by the sublimation of crude WCl $_6$ (Pierce Inorganic) under argon (pressure about 0.15 MPa at sublimation temperature) i a sealed all-glass apparatus [4]. WOC $_4$ (Aldrich) was purified in the same way. Purifi a-tion of phenylacetylene (PhA) is described elsewhere [4]. Purity of PhA was ascertained to be better than 99.7% according to GC-MS method. Only styrene in amounts below 0.3% and negligible traces o bromostyrene and acetophenone were impurities detected. Benzene and toluene were pre-purified by the standard procedure [16] and then purified by a long-time refluxing with P$_2$O$_5$ [4]. Finally, degassed benzene or toluene was mixed in vacuum with a saturated WC $_6$ solution (4 mL per 500 mL of the respective solvent) and, after two days of stirring and additional degassing, the solvent was distilled int break-seal evacuated ampoules. Purity of the solvents was controlled: (i) by the GC-MS method and found to be better than 99.999%; and (ii) by means of the long-time stability (for at least one week) of the UV spectrum of a solution (5×10^4 mol/L) prepared from the tested solvent and standard stock solution of WCl$_6$.

Methods. GC-MS analyses were carried out using a Varian 3400 gas chroma o-graph equipped with DB-5 column J&W (length 30 m, diameter 0.32 mm, and film thickness 0.25 mm) and an Incos 50 (Finnigan-MAT Corp.) mass spectrometer. Heliu as a carrier gas (overpressure 5 psi) and splitless injection at 250 $^{\circ}$C (280 $^{\circ}$C) were ap-plied. In a typical analysis, temperature was set at 40 $^{\circ}$C for 2 min (5 min), then increased to 250 $^{\circ}$C (300 $^{\circ}$C) with the rate of 15 $^{\circ}$C/min and finally kept at 250 $^{\circ}$C (300 $^{\circ}$C) to the end of analysis (values in brackets refer to analyses of samples prepared in toluene). Mass spectrometer was operated in EI mode scanning from 35 to 500 (650) amu in 0.32 (0.43) s, the ion source temperature of 150 $^{\circ}$C, emission current of 800 mA and ionizing

electron energy of 70 eV were used. Size exclusion chromatography (SEC) analyses were performed with a Tsp HPLC chromatograph equipped with RI and UV detectors and a series of two columns: PL Mixed-B and Mixed-C (Polymer Laboratories, Bristol). Tetrahydrofurane, THF, was used as the eluent and SEC records were evaluated by the calibration curve method based on polystyrene standards.

Procedures. Reactions were performed at room temperature in all-glass apparatuses by using the standard break-seal vacuum technique (initial vacuum was better than 1 mPa). In a typical experiment, solution of PhA in benzene or toluene (10 mL, 14.4 mmol/L) was added to a respective solution of WCl_6 or $WOCl_4$ (5 mL, 9.6 mmol/L) and the mixture was allowed to react for a given time. Reaction was quenched by methanol (45 mL) added under vacuum, decomposed catalyst and eventually formed polymer was allowed to sediment and the supernatant was isolated and analyzed by GC-MS method. If a polymer [poly(phenylacetylene), PPhA] was formed, the sediment was dried, PPhA extracted by THF and its yield was determined by the gravimetry and molecular weigh by the SEC method.

RESULTS AND DISCUSSION

Reaction o PhA with WCl_6

At the monomer-to-catalyst mole ratio of 3:1 in benzene PhA is fast transformed (conversion of 80 % is achieved within ten minutes) mainly to chloroderivatives of PhA and PhA dimers of various degrees of unsaturation. Other products of PhA transformation are formed in traces only (see Fig. 1 and Table 1, sample **A**). If the reaction time is prolonged to one month, fine precipitate of reduced tungsten species occurs. Upon mixing with PhA, this solid induces PhA polymerization after an induction period lasting from 10 min to a few hours.

Presence o chloroderivatives in the fraction distilled quickly (in vacuum, at roo temperature) from the non-terminated reaction mixture proves that the chloroderivatives are formed *in situ* and not at quenching the reaction with methanol (Table 1, sampl **B**).

Table 1.

Relative height of total ion current peaks (% with respect to the highest one) of main compounds found in the PhA/WCl$_6$ mixtures reacted in benzene; numerical subscrip denotes number of observed isomers if it is higher than one; M$^+$ is relative molecular weight of molecular ion. Conditions of preparation of analyzed samples:

A [WC$_6$] = 3.2 mmol/L, [PhA] = 9.6 mmol/L, reaction time 10 min;

B the same as in **A**, distillate;

C distillation residue fro **B** dissolved in benzene and decomposed by methanol.

M$^+$	Compound	A	B	C[1]
	Residua from monomer and products from solvent			
102	residual PhA	20	28	16
104	residual styrene	3	1	3
112	chlorobenzene	1	24[2]	2
154	biphenyl	1	2	2
	Derivatives o PhA			
138	chlorostyrenes HCl(PhA)	100$_3$	100$_3$	-
140	H$_3$Cl(PhA)	-	19	-
174	H$_2$Cl$_2$(PhA)	2	80	2
182	H$_3$Ph(PhA)	2	1	2
	Dimers of PhA and their derivatives			
204	(PhA)$_2$	2$_2$	-	2$_2$
206	H$_2$(PhA)$_2$	2	-	2
238	ClPh(C$_2$)(PhA)	50$_3$	-	100$_3$
240	HCl(PhA)$_2$	4$_2$	-	15$_3$
242	H$_3$Cl(PhA)$_2$	8$_2$	-	7$_2$
274	Cl$_2$(PhA)$_2$	2$_2$	-	3$_3$

[1] Further derivatives detected: M$^+$ 280, Ph$_2$C$_2$(PhA), 1; M$^+$ 306, cyclotrimers (PhA)$_3$, 1$_2$; M$^+$ 308, H$_2$(PhA)$_3$, <1$_2$; M$^+$ 340, Cl$_2$(C$_2$Ph)(PhA), <1$_2$; M$^+$ 342, ClH(PhA)$_3$, 3$_3$; M$^+$ 376, Cl$_2$(PhA)$_3$, 1$_2$; [2] presumably formed at final stage of distillation if the concentration of WCl$_x$ species is high.

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Figure 1. Total ion current (TIC) chromatogram of the PhA/WCl $_6$ mixture (9.6 mM / 3.2 mM) reacted for 10 min in benzene at room temperature and decomposed b methanol (Table 1, mixture **A**). Numerical labels denote relative mass of respective o-lecular ions; PhCl stands for chlorobenzene and Sty for styrene.

Distillation residue **C** mainly contains higher chloroderivatives and traces o PhA cyclo-trimers and phenylated dimers. Surprisingly, it also contains significant amount o unre-acted PhA that should have been removed by distillation. Binding of PhA in complexes with low-valent tungsten-halide species WCl$_x$ (x < 6) [9, 18] formed in the reduction of WCl$_6$ by PhA [9, 19] and subsequent releasing of PhA upon addition of methanol can be suggested as an explanation of this observation. Presence of virtually unchanged PhA molecules in low-valent tungsten species points to an obstacle of PhA transformation into growing centers in this reaction system. This obstacle might be a cause of the observed, unpredictably long induction period of PhA polymerization with WCl$_6$, however, present data do not provide information on a rational lying behind it.

Reaction o PhA with WOCl₄

At the substrate-to-catalyst mole ratio of 3:1, the reaction o   PhA with WOCl$_4$ in benzene is slow. Only 2 % of feed PhA is transformed into chlorostyrene (M$^+$ 138, 1,5 %) and chlorodimer of PhA (M$^+$ 238, 0,5 %) after 10 min. If the reaction time is pr o-longed to one month, virtually absolute conversion is achieved and the reaction mixture splits to a yellowish solution and dark solid that is unstable in air. The solution contains (according to TIC chromatogram) traces o PhA cyclotrimers (M$^+$ 306), ca 15 to 20 % of chloroderivatives of bot   PhA and PhA oligomers and, mainly, more than 80 % of phenyl derivatives of bot   PhA and PhA oligomers (Fig. 2 and Table 2, sampl **D**). If the same reaction is performed in toluene, it is much faster than in benzene and correspon d-ing tolyl- instead of the phenylderivatives are formed (Fig. 3 and Table 2, sampl **E**). This proves that aryls built in formed aryl derivatives come from the used aromatic sol-vent and, moreover, that the arylation can be a Friedel-Crafts type reaction [20].

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Figure 2. TIC chromatogram of the PhA/WOCl$_4$ mixture (9.6 mM / 3.2 mM) re-acted for 1 month in benzene and decomposed by methanol (Table 2, mixture **D**).

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Figure 3. TIC chromatogram of the PhA/WOCl$_4$ mixture (9.6 mM / 3.2 mM) re-acted for 1 day in toluene and decomposed by methanol (Table 2, mixture **E**).

Both aryl- and chloroderivatives formed can be arranged into five homologous se-ries of three degrees o unsaturation: *(i)* Y(C$_2$)(PhA)$_{x-1}$, *(ii)* HY(PhA)$_x$ and Y$_2$(PhA)$_x$, *(iii)* H$_3$Y(PhA)$_x$ and H$_2$Y$_2$(PhA)$_x$, where Y is Cl or aryl and x = 1, 2, 3, etc. This points to a participation of the hydrogen transfers involving PhA units in the overall reaction. First members of homologous series of di- and triphenylderivatives have been identified as 1,1- or 1,1,1-isomers by using corresponding compounds as the chromatographic and mass spectra standards.

The unstable solid isolated from one-month-old PhA/WOCl $_4$ (3:1) mixture in-duces polymerization of PhA. Upon mixing with benzene solution of PhA (resulting concentrations: [PhA] = 4.5 mol/L, [W] = 1·10^{-2} mol/L) the solid dissolves and a yield of 95 % of PPhA of <M>$_w$ = 150 000 is achieved within one hour. Only PhA cyclo-trimers (M$^+$ = 306) but neither chloro- nor phenyl-derivatives have been found in super-natant from this polymer isolation. By both the appearance and reactivity the solid does

Table 2

Relative height of total ion current peaks (% with respect to the highest one) of main compounds found in the PhA/WOCl$_4$ mixtures reacted in benzene and toluene; numerica subscript denotes number of observed isomers if it is higher than one; M$^+$ is relative molecular weight of molecular ion. Conditions of preparation of analyzed samples:

D benzene, [WOC$_4$] = 3.2 mmol/L, [PhA] = 9.6 mmol/L, reaction time 1 month[1];

E toluene, [WOCl$_4$] = 3.2 mmol/L, [PhA] = 9.6 mmol/L, reaction time 1 day;

F benzene, [WOC$_4$] = 5.6 mmol/L, [PhA] = 68 mmol/L, reaction time 1 month[2];

G supernatant from PhA polymerization in benzene, [WOC$_4$] = 5.6 mmol/L, [PhA] = 560 mmol/L, reaction time 6 h; yield of polymer 98 %, $<M>_w$ = 85 000.

M$^+$ [3]	Compound	D	E	F	G
	Residua from monomer				
102	residual PhA	2	2	2	41
104	residual styrene	<1	1	1	15
	Derivatives o PhA				
138	chlorostyrenes HCl(PhA)	<1	-	5	65$_3$
172	Cl$_2$(PhA)	<1	-	<1	<1
174	H$_2$Cl$_2$(PhA)	2	<1	<1	-
180[4] (194)	HAr(PhA)	<1	100$_3$	30	20
182[4] (196)	H$_3$Ar(PhA)	4	4$_3$	3	1
258[4] (286)	H$_2$Ar$_2$(PhA)	13	19$_3$	<1	-
	Dimers of PhA and their derivatives				
238	ClPh(C$_2$)(PhA)	17$_2$	2$_2$	7$_2$	21$_2$
240	HCl(PhA)$_2$	1$_2$	-	8$_2$	2$_2$
242	H$_3$Cl(PhA)$_2$	<1$_2$	-	<1$_2$	3$_2$
274	Cl$_2$(PhA)$_2$	2$_2$	<1	5$_2$	<1$_2$
280 (294)	ArPh(C$_2$)(PhA)	1	-	1	2
282 (296)	HAr(PhA)$_2$	100$_3$	97$_5$	100$_3$	13$_3$
284 (298)	H$_3$Ar(PhA)$_2$	8$_2$	-	5$_4$	1$_2$

Table 2, continued

M^+	Compound	D	E	F	G
316 (330)	$ArCl(PhA)_2$	-	12_3	-	-
318 (332)	$H_2ArCl\ PhA)_2$	1	-	24_3	2
358 (386)	$Ar_2(PhA)_2$	4	9_6	3	-
360 (388)	$H_2Ar_2(PhA)_2$	76_2	46_7	52_2	3
	Trimers of PhA and their derivatives				
306	cyclotrimers $(PhA)_3$	5_2	1_2	18_2	100_2
306	other trimers $(PhA)_3$	1_2	-	3_2	2_2
382 (396)	$ArPh(C_2)(PhA)_2$	1	-	-	<1
384 (398)	$HAr(PhA)_3$	4_5	-	3_5	-
386 (400)	$H_3Ar(PhA)_3$	2_3	-	8_3	-
460 (488)	$Ar_2(PhA)_3$	2_2	-	1_2	-
462 (490)	$H_2Ar_2(PhA)_3$	3_2	-	1_2	-

[1] After 10 min, only 2 % of feed PhA is reacted to chlorostyrene (M^+ 138, 1,5 %) and chlorodimer (M^+ 238, 0,5 %); [2] 40 % of PhA was converted to oligomers with $<M>_w = 1\ 500$; [3] values of M^+ for tolyl derivatives are in parenthesis; [4] by using standards as well as according to mass spectra identified as 1,1 or 1,1,1 isomers.

not differ from that one obtained by the reduction of WOCl$_4$ with tetraphenyltin, which was ascribed to WOCl$_2$ [17].

At the PhA/WOC$_4$ mole ratio of 12:1, in benzene (Table 2, sample **F**), about 40 % of PhA is transformed into oligomers ($<M>_w = 1\ 500$) and 60 % o PhA into chloro- and arylderivatives. Relative content of chloroderivatives with respect to the arylderivatives is approximately twice as that one found for the 3:1 system. Also content of cyclotrimers is higher at the 12:1 ratio, ca triple as that one found for the 3:1 mixture.

At the mole ratio equal to 100 (Table 2, sample **G**), about 98 % of PhA is transformed into polymer ($<M>_w = 85\ 500$) within 6 h, PhA cyclotrimers become majority byproducts and chloroderivatives become more abundant than arylderivatives.

It can be concluded tha chloroderivatives are formed in comparable amounts a

any PhA/WOCl$_4$ mole ratio. Dimeric chloroderivatives prevail at low while the mono-meric ones at higher values of the PhA/WOCl$_4$ mole ratio. The chloroderivatives can be regarded as the main byproduct of the reduction of WOCl$_4$ to low-valent tungsten species that are active in PhA polymerization and cyclotrimerization. As to arylderivatives, their yield decreases as the PhA/WOC$_4$ ratio increases. It can be explained in two ways. *(i)* Arylated PhA units bound to tungsten species are transformed into growing centers and so built in formed oligomer or polymer. *(ii)* Formation of arylderivatives is su p-pressed at high PhA concentration. As concerns t PhA cyclotrimers, they are onl formed on the low-valent tungsten species as side products o PhA polymerization and/or oligomerization but not on the high-valent tungsten species predominating in the initiation stage.

Mechanistic considerations on reaction o PhA with WOCl$_4$

    A mechanism describing reaction o PhA with WOCl$_4$ must explain arylation and chlorination of PhA unit as well as transfers of hydrogen between them. These transfers can be mediated b oxo ligand of tungsten species as it has been proposed already [17]. In WOCl$_4$ molecule, one of the two lone electron pairs of oxygen is aligned with the W to O bond axis pointing at the empty σ orbital of W giving rise to a partial triple bond. The latter pair remains as normal non-bonding lone pair on oxygen [20, 21]. A molecule of PhA π-coordinated to WOC$_4$ species increases electron density at the metal center thereby partly displacing electrons back upon oxygen. As a result, rearrangement o acetylenic hydrogen onto oxo ligand can occur leading to species **I** (Scheme 1). It can be supposed that addition of PhA molecule to other high-valent oxo tungsten species pro-ceeds in this way, too (see ref. [17]).

$$
\begin{array}{ccccc}
\mathrm{O} & & \mathrm{O} \cdots \mathrm{H} & & \mathrm{OH} \\
\| & \xrightarrow{+\ \mathrm{CH \equiv CPh}} & \| \ \vdots & \longrightarrow & | \\
\mathrm{C}_4\mathrm{W} & & \mathrm{C}_4\mathrm{W}\!\!-\!\!\mathrm{C}\!\equiv\!\mathrm{CPh} & & \mathrm{Cl}_4\mathrm{W}\!-\!\mathrm{C}\!\equiv\!\mathrm{CPh}
\end{array}
$$

<div align="right">

I
</div>
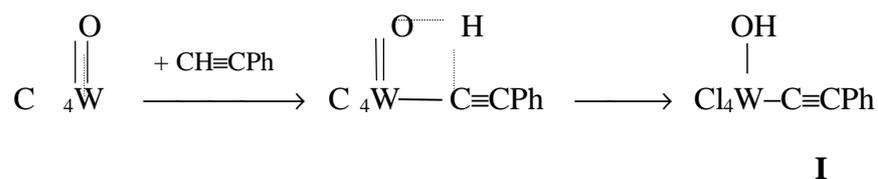
Scheme 1. Addition of PhA molecule to WOC$_4$ species.

Chlorination of PhA units. Transformation of PhA ligands into precursors of chloroderivatives can be explained in terms of merely two types o β-rearrangement: *(i)* that of a chlorine from tungsten atom onto C^2 carbon and *(ii)* that of hydrogen from OH group onto C^1 carbon of the linked PhA unit ($L_nW-C^1\equiv C^2Ph$). Formation of a chlorinated molecule can be then accomplished either by reductive elimination of two ligands from one tungsten species or by reverse H-rearrangement onto C^1 carbon of a changed PhA unit as it is shown for the most abundant chloroderivatives in Scheme 2.

Scheme 2. Formation of chloroderivatives

Dichlorostyrene (M^+ 172) can be obtained by reductive elimination from species **II**. Hydrogenated chloroderivatives can be derived by analogous reaction sequence starting from WOCl$_3$H species (**IV**).

Arylation of PhA units. Addition of aromatic solvent to a substrate undergoing metathesis (usually referred to as the solven alkylation) has already been reported for various catalysts and substrates including substituted acetylenes [3, 9, 14, 23-29]). This addition is in general regarded as the Friedel-Crafts type side reaction that does not lead to metal carbene species. For the arylation to proceed as a Friedel-Crafts reaction some positively charged species or sites must be available. High- valent tungsten species with σ-alkynyl (or σ-alkenyl) ligands like, for example, **II** and **III** come into consideration in this respect. In such species, a partial transfer o π-electrons towards the tungsten centra atom can efficiently polarize the organic ligand. As a result, a positive charge should occur on the C^2 atom on which the arylation can take place (Scheme 3):

$$O \quad\quad\quad\quad O^- \quad\quad\quad\quad O^- \quad\quad H-Ar \quad\quad OH$$

$$Ar \overset{\parallel}{}$$

$$[W]-C^1{\equiv}C^2Ph \longleftrightarrow [W]{=}C^1{=}C^2Ph \xrightarrow{+H\text{-}Ar} [W]{=}C^1{=}C^2 \longleftrightarrow [W]{=}C^1{=}C^2$$

$$Ph \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Ph$$

VII
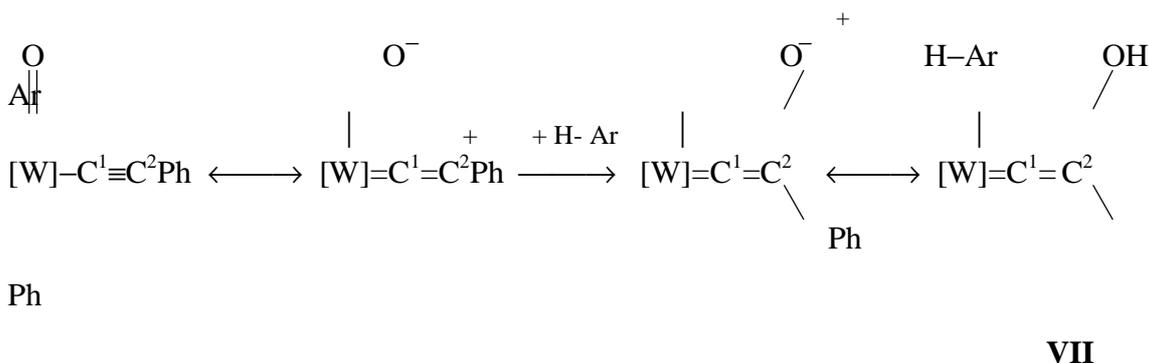
Scheme 3. Arylation of PhA unit

After H-shift to C^1, **VII** yields a species **VIII**: O=[W]–CH=C^2PhAr is formed that can either: *(i)* add a new PhA molecule and release CH$_2$=CPhAr (M^+ 180 or 194) or PhC≡C– CH=C^2PhAr (M^+ 280 or 294), or *(ii)* undergo further arylation at ^{2} carbon leading to precursor of CH$_3$–CPhAr$_2$ (M^+ 258 or 286) and PhC≡C–CH$_2$–CPhAr$_2$ (M^+ 360 or 388) derivatives. Formation of other detected derivatives can be explained in terms of an alogues reaction sequences.

Formation of tungsten carbene growing species. In metathesis propagation, a for-

mation of metallacyclobutene intermediate should be accompanied with a displacemen
of electrons from oxygen to tungsten atom [21, 22]. If the intermediate is formed from a
hydroxo tungsten carbene species (like **VII**), the hydrogen of OH ligand will be destabi-
lized and easily rearranged to one of two carbons linked to tungsten atom. As a result,
tungsten carbene species will be transformed into alkyl tungsten species that are not ca-
pable of metathesis propagation (Scheme 4). Therefore, hydroxo tungsten carbene spe-
cies can most probably act as oligomerization but not polymerization centers.
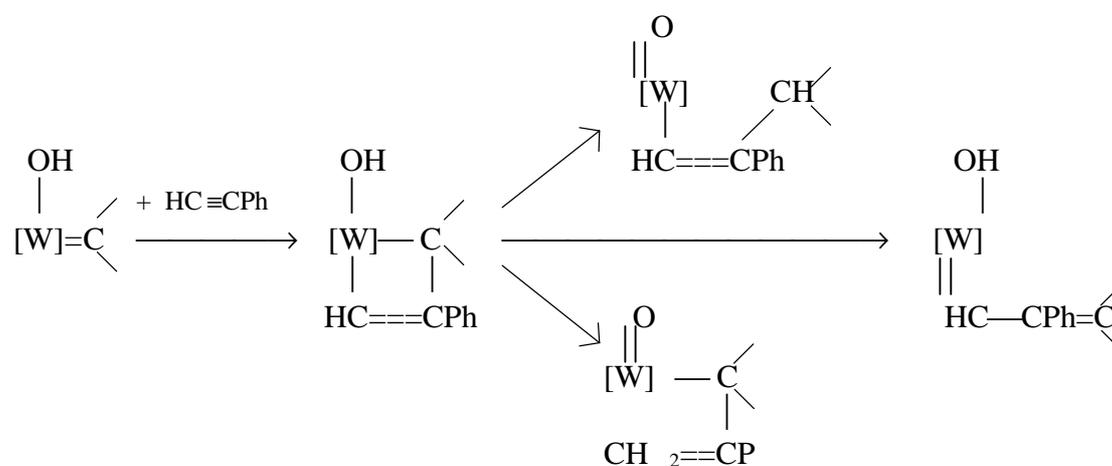
Scheme 4. Insertion of PhA molecule on hydroxo-tungsten carbene species

Performed experiments have clearly shown that the solid assigned as WOC$_2$ gives
rise to long living polymerization centers. Possible mechanism of these species formation
is suggested in Scheme 5.

$$\longrightarrow \quad C_2W{=}HC{-}CPh{=}C{=}CHPh \quad \longrightarrow \quad polymerization$$
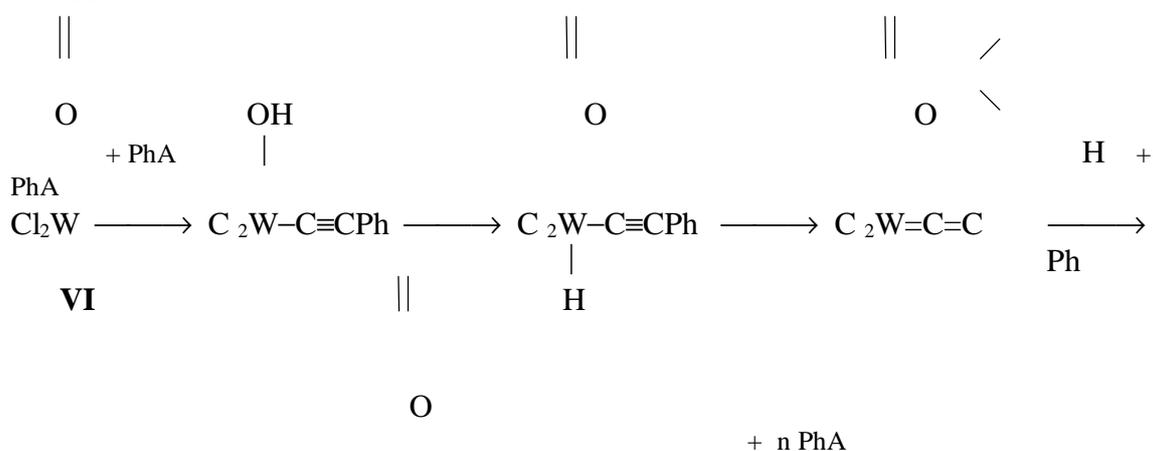
Scheme 5. Formation of growing oxo-tungsten carbene species

CONCLUSIONS

Formation of active species in the WOC_4/PhA system can be compared with a course of this process in the system WOC_4/Ph_4Sn/PhA [17]. In the latter system, $WOCl_4$ is first allowed to react with Ph_4Sn (mole ratio 1:2). The ligand exchange yields species Ph_2WOCl_2 that slowly undergo reductive elimination leading to a formation of biphenyl Ph-Ph and solid $WOCl_2$. In both benzene and toluene, freshly ripened catalyst reacts with PhA (1:10) to a hemipolymer (40 - 60 %) and the rest mainly to PhA cyclotrimers and, even in toluene, mostly to various phenylderivatives of PhA. Only low amount of tolyl-derivatives M^+ 194 was detected. It is thus evident that phenyls inserted into byproducts by a transfer from Ph_2WOCl_2 species and Friedel-Craft arylation of PhA units is onl marginal in this system. This can be explained by fast decay of high-valent tungsten species owing to the easy rearrangement of phenyl ligand from the tungsten to C^2 atom of a σ-bound PhA unit.

It can bee suggested, with regards to the above, that the phenyl derivatives formed in $WOCl_4$/Ph_4Sn/PhA system are, actually, the counterpart o chloroderivatives but not counterpart of arylderivatives formed in the $WOCl_4$/PhA system. It means that reduction of the high-valent L_2WOCl_2 species (L is Cl or Ph) is the key step in their transformati into polymerization centers and that PhA acts as the reducing agent in both discussed systems. PhA molecules accept chlorine atoms in the system without Ph_4Sn while pheny groups in the system with Ph_4Sn. As a result, it can be suggested that true, long-living growing centers should be derived from low-valent tungsten species WOC_2.

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POVZETEK

Pri nizkem molskem razmerju monomera in katalizatorja (3:1) nastanejo pri reakciji fenilacetilena (PhA) z $WOCl_4$ v benzenu ali toluenu aril derivati peti homolognih serij (ki se razlikujejo po številu PhA enot), manjša količina kloroderivatov in sledovi PhA oligomerov, pretežno ciklotrimerov. Arili v aril derivati izvirajo iz uporabljenih topil. Pri celokupni reakciji sodelujejo tudi prenosi vodika med PhA enotami. S povečevanjem molskega razmerja PhA/$WOCl_4$ se zniža

delež aril derivatov, poveča delež ciklotrimerov in nastajajo višji PhA oligomeri (pri razmerju 12:1) ali polifenilacetelen (pri razmerju 100:1). Kloroderivati nastanejo v primerljivih količinah pri kateremkoli molskem razmerju PhA/WOCl$_4$, tako da jih lahko smatramo za ključne stranske produkte redukcije WOCl$_4$ v nižjevalentne volframove spojine. Pri reakcijskih sistemi z molskim razmerjem do 12:1 se WOCl$_4$ spremeni v črno trdno snov, ki je bila pripisana WOCl$_2$. Ta se raztopi v PhA in sproži polimerizacijo, pri kateri so PhA ciklotrimeri stranski produkti. Nastanek aril i kloroderivatov kot tudi volframovih reaktivnih zvrsti lahko razložimo z mehanizmom, v katerem ima pomembo vlogo okso ligand volframovih zvrsti. Pri reakciji PhA z WCl$_6$ nastanejo različni kloroderivati PhA in oborina reduciranih volframovih zvrsti, ki polimerizira PhA po nekem indukcijskem času, katerega ponovljivost pa je slaba.