

## New catalyst systems for polymerization of substituted acetylenes: $W(NO)_2(O_2CR)_2-MCl_4$ (M=Ti, Sn)

R. Matusiak, A. Keller\*

Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, PL-50-383 Wrocław, Poland

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### Summary

$W(NO)_2(O_2CR)_2$  - Lewis acid (LA) catalysts (LA =  $TiCl_4$ ,  $SnCl_4$ ; R =  $-CH(C_2H_5)(CH_2)_3CH_3$ ) induce substituted acetylenes (phenylacetylene, propargyl ether, 1,6-heptadiyne, diphenylacetylene) to polymerize or oligomerize. Their catalytic ability strongly depends on the Lewis acid and solvent. The polymerization reactions of phenylacetylene always accompany the cyclootrimerization reactions. In the system with  $TiCl_4$  in  $CH_2Cl_2$  the yield of polymer equals to 56% at 80% conversion of a monomer. However, in the system with  $SnCl_4$  in benzene, 42% cyclotrimers arise at 57% conversion of phenylacetylene. The mechanism of these reactions as well as the structure of the obtained polymers were determined.

### Introduction

Various polyacetylenes with aromatic and related pendant groups have been prepared and studied (1-11). Phenylacetylene is probably the most often employed to study among the substituted acetylenes (12-23). The mechanism of polymerization of phenylacetylene and microstructure of its polymers strongly depend on the catalyst, thermal history of the polymerization reaction and often on the solvent (15,16,23,24). This monomer undergoes polymerization by diverse mechanisms, also by the metathesis mechanism (14,19,24-28). Metathesis polymerization of substituted acetylenes attracts much interest as a method for the preparation of polymers offering useful applications.

Alkylidene (carbene) complexes, i.e. the catalysts of the reaction of olefin metathesis, belong to the most active catalysts of polymerization of acetylenes (29). Important effect on properties of this type of complexes have ligands coordination through oxygen atoms, for instance alcoholates (30, 31) or carboxylates (32).

Dinitrosyl alkylidene complexes of molybdenum and tungsten belong to the most active catalysts of olefin metathesis (29, 31-34). They are also very active catalysts of polymerization of acetylenes. The above was confirmed in the case of molybdenum complex (33, 35). Carbene complexes of this type, i.e.  $M(NO)_2(=CHR)L_2(AlCl_2)_2$  (M= Cr, Mo, W; L - alcoholate or carboxylate ligands) were obtained in reactions of dinitrosyl.

\* Corresponding author

complexes of  $\{M(NO)_2(OR)_2\}_n$  and  $M(NO)_2(O_2CR)_2$  type with  $AlCl_3$  (31, 32) Here, coordinated alkylidene ligands have nucleophilic character in spite of the low oxidation state of metals. Thus, they are different carbene complexes than Fischer (low oxidation states, electrophilic carbene ligands) or Schrock (high oxidation state, nucleophilic carbene ligands) complexes. In the syntheses of these complexes,  $AlCl_3$  plays two roles: it is an alkylating agent, but first of all it is a Lewis acid, emptying the coordination sites at metal in effect of breaking bridging bonds (in polymeric complexes) or chelate ones (31, 32). Thus, a similar effect could be caused by another Lewis acids, like those of  $MCl_4$  type. Terminal acetylenes present in such systems could generate formation of dinitrosyl carbene (vinylidene) catalysts. These complexes should contain metals at their low oxidation states, their stoichiometries,  $Mo(NO)_2(=CRR')L_2(LA)_2$ , are similar to other nitrosyl carbene complexes, but the carbene groups are electrophilic in character.

No literature data on polymerization of acetylenes by nitrosyl tungsten complexes are available.

The aim of this study was to test the catalytic activity of dinitrosyltungsten complexes - Lewis acid systems in polymerization reactions of phenylacetylene and other substituted acetylene (diphenylacetylene, propargyl ether and 1,6-heptadiyne), and to define the mechanism of these reactions, as well of the compound that is the real catalyst, and determination of the structure of the polymerization products.

## Experimental

All experiments were carried out under argon atmosphere using either Schlenk techniques or vacuum - line systems. Reagents were purified by standard methods. Solvents were distilled under argon using appropriate drying agents.  $Mo(NO)_2(O_2CEH)_2$  was prepared according to the published method (36) The IR spectra were recorded on a Nicolet Impact 400 spectrophotometer.  $^1H$  and  $^{13}C$  NMR spectra were measured at room temperature on a Bruker 300 spectrometer. Tetramethylsilane (TMS) was used as an internal or external standard.

### *Synthesis of $[W(NO)_2(MeNO_2)_4](BF_4)_2$*

To the suspension of  $W(CO)_6$  (2.0 g, 5.6 mmol) in  $MeNO_2$  (10 mL) the stoichiometric amount of  $NOBF_4$  was added. The reaction mixture was stirred for 3 h at  $60^\circ C$ . The olive-green complex was precipitated with hexane, filtered off, washed with hexane and dried *in vacuo*.

IR (nujol mulls):  $\nu(NO)$  1789 vs, 1673 vs;  $\nu_{as}(NO_2)$  1557 m;  $\nu(BF_4)$  1091 s  $cm^{-1}$ .  $^1H$  NMR ( $CD_3CN$ ,  $20^\circ C$ ):  $\delta$  4.42 (s, 12H,  $CH_3$ ) ppm.

Anal.: Calc. for  $C_4H_{12}N_6B_2F_8O_{16}W$ : C 7.25, H 1.83, N 12.69%. Found: C 7.48, H 1.87, N 12.30%.

### *Synthesis of $W(NO)_2(O_2CEH)_2$ ( $EH = -CH(C_2H_5)(CH_2)_3CH_3$ )*

To  $W(NO)_2(MeNO_2)_4](BF_4)_2$  (2.0 g, 3.02 mmol) dissolved in  $MeNO_2$  (20 mL) and  $MeCN$  (5 mL), solid  $Li(O_2CEH)$  (0.52 g, 6.04 mmol) was added under vigorous stirring. The reaction mixture was stirred for 15 min at room temperature. The green-brown solution was filtered off and removed under vacuum. The complex was extracted from the remnant with a small amount of  $CH_2Cl_2$  and precipitated with hexane.

IR (nujol mulls):  $\nu(NO)$  1752 vs, 1644 vs;  $\nu_{as}(CO)$  1532 s  $cm^{-1}$ .  $^1H$  NMR ( $CD_2Cl_2$ ,  $20^\circ C$ ):

$\delta$  2.30 (m, 2H;  $\text{CO}_2\text{CH}(\text{C}_2\text{H}_5)\text{-}$ ), 1.45 (s, 4H;  $\text{CO}_2\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{-}$ ), 1.25 (s, br, 12H;  $\text{-CH}(\text{CH}_2\text{CH}_3)\text{-}(\text{CH}_2)_3\text{-}$ ), 0.85 (s, br, 12H;  $\text{-(CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$ ) ppm.

Anal.: Calc. for  $\text{C}_{16}\text{H}_{30}\text{N}_2\text{O}_6\text{W}$ : C 36.22, H 5.70, N 5.28 %. Found: C 36.35, H 5.74, N 4.98%.

#### *Synthesis of $\text{W}(\text{NO})_2(\text{OEt})_2\text{EtOH}_n$*

To  $[\text{W}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$  (2.0 g, 3.02 mmol) dissolved in EtOH (10 mL) at about  $0^\circ\text{C}$ , the solution of NaOEt (0.21 g, 6.04 mmol) in EtOH was added at the same temperature; at the same temperature the reaction mixture was stirred for 15 min. The solution was filtered off and removed under vacuum. The complex was extracted from the remnant with a small amount of  $\text{CH}_2\text{Cl}_2$  and precipitated with hexane.

IR (nujol mulls):  $\nu(\text{NO})$  1745 vs, 1627 vs;  $\nu(\text{OR})$  1091 m, 1022 s, 960 w,  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ):  $\delta$  4.45, 4.24 (s, br, 4H;  $\text{OCH}_2\text{CH}_3$ ), 3.69 (q, 2H;  $\text{CH}_3\text{CH}_2\text{OH}$ ), 1.35 (s, 6H;  $\text{OCH}_2\text{CH}_3$ ), 1.20 (t, 3H;  $\text{CH}_3\text{CH}_2\text{OH}$ ) ppm.

Anal.: Calc. for  $\text{C}_6\text{H}_{16}\text{N}_2\text{O}_5\text{W}$ : C 18.94, H 4.23, N 7.37 %. Found: C 19.16, H 4.56, N 7.67%.

#### *Synthesis of $\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2(\text{MCl}_4)_2$ ( $M = \text{Ti, Sn}$ ; $\text{EH} = \text{-CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3$ )*

The  $\text{CH}_2\text{Cl}_2$  solution of  $\text{MCl}_4$  was added to a solution of  $\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2$  in  $\text{CH}_2\text{Cl}_2$  in molar ratio 1:2. The yellow-brown precipitate was filtered off, washed with  $\text{CH}_2\text{Cl}_2$  and hexane and dried *in vacuo*.

#### *$\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2(\text{TiCl}_4)_2$*

IR (nujol mulls):  $\nu(\text{NO})$  1771 s, 1659 vs,  $\nu(\text{CO}_2)$  1553 s  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ,  $20^\circ\text{C}$ ): 2.32 (m, 2H;  $\text{CO}_2\text{CH}(\text{C}_2\text{H}_5)\text{-}$ ), 1.56 (s, 4H;  $\text{CO}_2\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{-}$ ), 1.27 (s, br, 12H;  $\text{-CH}(\text{CH}_2\text{CH}_3)\text{-}(\text{CH}_2)_3\text{-}$ ), 0.87 (s, br, 12H;  $\text{-(CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$ ) ppm.

Anal.: Calc for  $\text{C}_{16}\text{H}_{30}\text{N}_2\text{Cl}_8\text{Ti}_2\text{W}$ : C 21.20, H 3.34, N 3.09 %. Found: C 21.67, H 3.01, N 2.98%.

#### *$\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2(\text{SnCl}_4)_2$*

IR (nujol mull):  $\nu(\text{NO})$  1764 s, 1656 vs,  $\nu(\text{CO}_2)$  1556 s  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (in  $\text{CD}_3\text{CN}$  at  $20^\circ\text{C}$ ): 2.35 (m, 2H;  $\text{CO}_2\text{CH}(\text{C}_2\text{H}_5)\text{-}$ ), 1.57 (s, 4H;  $\text{CO}_2\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{-}$ ), 1.26 (s, br, 12H;  $\text{-CH}(\text{CH}_2\text{CH}_3)\text{-}(\text{CH}_2)_3\text{-}$ ), 0.87 (s, br, 12H;  $\text{-(CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$ ) ppm.

Anal.: Calc for  $\text{C}_{16}\text{H}_{30}\text{N}_2\text{Cl}_8\text{Sn}_2\text{W}$ : C 18.29, H 2.88, N 2.67 %. Found: C 18.56, H 3.01, N 2.80%.

#### *Polymerization reaction*

A standard polymerization procedure was as follows: to the solution of a complex in the appropriate solvent and the monomer with internal standard the appropriate solution of  $\text{MCl}_4$  was added. The mixture was kept in the dark for a some time, and then the polymerization reaction was quenched with methanol. Methanol-insoluble products were dried *in vacuo*, and polymer yields were determined gravimetrically. The samples for further analyses were stored under argon at  $-20^\circ\text{C}$ . Monomer conversions were determined by GC - MS (HP - 5890 II + 5971 A). The weight- and number-average molecular weights of polymers ( $\overline{M}_w$  and  $\overline{M}_n$  respectively) were determined by gel-permeation chromatography (GPC; HPLC - HP 1090 II with DAD-UV/VIS and IR detector HP 7047 A) using toluene as eluent and polystyrene calibration.

## Results and Discussion

### *Interaction of dinitrosyltungsten precatalysts with Lewis acids*

The new dinitrosyltungsten complexes  $\{W(NO)_2(OEt)_2EtOH\}_n$  and  $W(NO)_2(O_2CEH)_2$ , air and moisture sensitive complexes, were synthesized in a similar way as their molybdenum (37, 38) and chromium (33) analogues. Their IR spectra exhibit two  $\nu(NO)$  bands typical of *cis*- $\{M(NO)_2\}^6$  cores (39-41) and the  $^1H$  NMR spectra - all the signals of protons of the coordinated ligands (see Experimental Section). These complexes form the 1:2 adducts with Lewis acids ( $TiCl_4$ ,  $SnCl_4$ ). The attack of two Lewis acid molecules towards the oxygen atoms of the alkoxy and carboxylic ligands results in the appearance of free coordination sites on the central atom. Next the sites are successively occupied by chlorines of Lewis acids to form the W-Cl-M (M= Ti, Sn) bridges. The results of the theoretical calculation of the electronic structure of carboxylatodinitrosylmolybdenum complexes (38) showed that oxygens of carboxylate ligands in *trans* positions to NO are most pliant to attack of the Lewis acid molecules.

The  $W(NO)_2(O_2CEH)_2(MCl_4)_2$  (M = Ti, Sn) adducts were synthesized and characterized by means of the IR and  $^1H$  NMR spectroscopies (see Experimental Section).

### *Polymerization of substituted acetylenes by $W(NO)_2(O_2CEH)_2$ - Lewis acid catalyst*

#### *Effect of catalyst systems*

Neither the dinitrosyl tungsten complexes nor their adducts with Lewis acid exhibit catalytic activity in the polymerization reaction of phenyl- and other acetylenes, but conversion was observed after addition of a Lewis acid (LA =  $TiCl_4$ ,  $SnCl_4$ ) to solution of  $W(NO)_2(O_2CEH)_2$  with an excess of terminal acetylenes.

No polymerization occurred in the systems based on dialkoxydinitrosyl complexes, for example  $\{W(NO)_2(OEt)_2EtOH\}_n$  - PA -  $MCl_4$  (M = Ti, Sn). The steric effect, easier formation of a stable adduct caused lack of catalytic activity in this system.

**Table 1. Effect of catalyst systems on polymerization of phenylacetylene (PA)<sup>a</sup>**

Complex	Lewis acid (LA)	Conv. (%)	Yield (%)		$\overline{M}_w^c$
			Linear oligomer <sup>b</sup>	Cyclotrimers	
$Mo(NO)_2(O_2CEH)_2$	$TiCl_4$	4	1	3	1000
	$SnCl_4$	32	9	22.5	750
$W(NO)_2(O_2CEH)_2$	$TiCl_4$	80	56	24	1900
	$SnCl_4$	20	5	15	800

<sup>a</sup>Reaction conditions: solvent  $CH_2Cl_2$ ; concentration of complex  $[M] = 0.25$  mmol;  $[LA]/[M] = 2$ ;  $[PA]/[M] = 50$ ; 24 h; room temperature. <sup>b</sup>Methanol insoluble part. <sup>c</sup>Weight-average molecular weight of methanol insoluble products.

Table 1 shows the effect of catalytic systems (metal complex and Lewis acid) on polymerization of phenylacetylene (PA) examined in  $M(NO)_2(O_2CEH)_2$  (M=Mo, W) based systems. The monomer conversion (80%) and polymer yield (56%) are the highest for the tungsten complex and  $TiCl_4$  as Lewis acid. The weight-average molecular weights ( $\overline{M}_w$ ) of product insoluble in methanol obtained in this system is also the highest; however, its value is not very large ( $1.9 \times 10^3$ ). Low molecular weight of polyphenylacetylene can be caused by kinetic effects as well as by possible degradation induced by the polymerization catalyst. Considerably lower monomer conversion (20%) with the relatively high yield of cyclotrimers (15%) was obtained for the metal system with  $SnCl_4$ . Such a relatively high

yield of cyclotrimers was also observed in the system of molybdenum with  $\text{SnCl}_4$  (conversion 32%; yield of cyclotrimers 22.5%). However, the dependence of monomer conversion and yield of insoluble methanol products on the Lewis acid in the molybdenum systems is different than that observed in the tungsten system. In the case of molybdenum complex this difference can be caused by the stronger tendency to form stable adducts.

#### *The effect of solvent*

Activities of the tested systems strongly depend on the applied solvent. The effect of solvent on conversion of phenylacetylene, selectivity, yield of polymer and its molecular weight was examined with  $\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2 - \text{MCl}_4$  ( $\text{M} = \text{Ti}, \text{Sn}$ ) in benzene, chlorobenzene, toluene and  $\text{CH}_2\text{Cl}_2$  and the results are shown in Table 2. Activity of the system with  $\text{SnCl}_4$  in polymerization of other substituted acetylenes (1,6-hexadiyne, propargyl ether) was also the subject of our investigations (Table 2).

**Table 2. Effect of the solvent on polymerization of phenylacetylene (PA) examined with  $\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2$  - Lewis acid (LA) systems<sup>a</sup>**

LA	Solvent	Monomer	Conv. (%)	Yield (%)		$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
				polymer <sup>b</sup>	cyclotrimers		
$\text{TiCl}_4$	$\text{C}_6\text{H}_6$	PA	31	11	20	10950	6.96
$\text{SnCl}_4$	$\text{C}_6\text{H}_6$	PA	57	15	42	720	1.45
$\text{TiCl}_4$	$\text{C}_6\text{H}_5\text{Cl}$	PA	20	10	10	28200	1.69
$\text{SnCl}_4$	$\text{C}_6\text{H}_5\text{Cl}$	PA	47	32	15	1060	1.50
$\text{TiCl}_4$	$\text{C}_6\text{H}_5\text{CH}_3$	PA	0				
$\text{SnCl}_4$	$\text{C}_6\text{H}_5\text{CH}_3$	PA	30	20	10	760	1.65
$\text{TiCl}_4$	$\text{CH}_2\text{Cl}_2$	PA	80	56	24	1900	4.99
$\text{SnCl}_4$	$\text{CH}_2\text{Cl}_2$	PA	20	5	15	800	1.56
$\text{SnCl}_4$	$\text{C}_6\text{H}_5\text{Cl}$	PE <sup>c</sup>	21	20 <sup>d</sup>			
$\text{SnCl}_4$	$\text{C}_6\text{H}_5\text{Cl}$	1,6-HD <sup>e</sup>	20	10 <sup>d</sup>			

<sup>a</sup>Reaction conditions: concentration of complex  $[\text{W}] = 0.25$  mmol;  $[\text{LA}]/[\text{W}] = 2$ ;  $[\text{monomer}]/[\text{W}] = 50$ ; 24 h; room temperature. <sup>b</sup>Methanol insoluble part. <sup>c</sup>Propargyl ether.

<sup>d</sup>Insoluble in organic solvents. <sup>e</sup>1,6-Heptadiyne.

The polymerization reaction of phenylacetylene was never selective in the systems tested. It was always accompanied by cyclotrimerization reaction. The most effective catalyst polymerization is the system with  $\text{TiCl}_4$  in  $\text{CH}_2\text{Cl}_2$ . Despite of the relatively high polarity of this solvent (14,24), the monomer conversion is 80%; the yield of the polymer is 56%, and that of cyclotrimers is 24%. However, the molecular weight of that polymer is not very high. Nevertheless,  $\overline{M}_w$  and  $\overline{M}_n$  of the polymers for  $\text{TiCl}_4$  system in  $\text{CH}_2\text{Cl}_2$  and other solvents always exceed those obtained with  $\text{SnCl}_4$ . The highest weight-average molecular weight ( $\overline{M}_w = 2.8 \times 10^4$ ) was that of polymer formed in PhCl. In the system with  $\text{TiCl}_4$ , conversion of phenylacetylene depends on the solvent as follows:  $\text{CH}_2\text{Cl}_2$  (80%) >  $\text{C}_6\text{H}_6$  (31%) >  $\text{C}_6\text{H}_5\text{Cl}$  (20%) >>  $\text{C}_6\text{H}_5\text{CH}_3$  (0%). The decrease of polymers yield and increase of their molecular weights ( $\overline{M}_w$ ) are in the same row of solvents as above. Inactivity of  $\text{TiCl}_4$  system in toluene is undoubtedly caused by the interaction of  $\text{TiCl}_4$  with a solvent. This interaction annihilates its acid properties.

The methanol insoluble products formed in the system with  $\text{SnCl}_4$  are linear oligomers (weight-average molecular weights 700 - 800) and cyclotrimers. The solvent used decides which of the reaction products will be predominant. Oligomers prevail (over 60%

conversion of monomer) in chlorobenzene and toluene, while in benzene and dichloromethane the are main products (~75% conversion of monomer) are cyclotrimers. Here the increase of conversion degree of phenylacetylene depending on the solvent was observed in the order:  $C_6H_6$  (57%) >  $C_6H_5Cl$  (47%) >  $C_6H_5CH_3$  (30%) >  $CH_2Cl_2$  (20%).

Propargyl ether and 1,6-heptadiyne also polymerized in the system with  $SnCl_4$ . However, the yield of obtained polymers insoluble in any organic solvent was 20% (21% conversion of propargyl ether) and 10% (20% conversion of 1,6-heptadiyne). In the case of 1,6-heptadiyne, except the polymer, a mixture of light oligomers was also formed.

The systems under investigation are not very active. Among the catalysts of phenylacetylene polymerization based on different types of complexes of molybdenum and tungsten they can be placed in the group of the catalysts of relatively low activity (24).

Diphenylacetylene (DPA) does not undergo the polymerization reaction in these binary systems but after addition of  $MCl_4$  (M is for instance  $SnCl_4$ ) to solution of the precursor complex with phenylacetylene ([W]: [PA] = 1:1 or 1:2) and next an excess of diphenylacetylene its conversion was observed (Table 3). Such ternary systems (complex-PA-LA) also catalyze ROMP of norbornene (Table 3).

**Table 3. Polymerization of diphenylacetylene (DPA) and ROMP<sup>a</sup> of norbornene (NB) by  $W(NO)_2(O_2CEH)_2$  - PA - LA system<sup>b</sup>**

LA	Solvent	[W]/[PA]/LA	Monomer	Yield of polymer [%]	% <i>cis</i> <sup>c</sup>
$SnCl_4$	$C_6H_5Cl$	1/-/2	DPA	0	
$SnCl_4$	$C_6H_5Cl$	1/1/2	DPA	15 <sup>d</sup>	
$SnCl_4$	$C_6H_5CH_3$	1/-/2	NB	0	
$TiCl_4$	$CH_2Cl_2$	1/-/2	NB	0	
$SnCl_4$	$C_6H_5CH_3$	1/1/2	NB	12	73.1
$TiCl_4$	$CH_2Cl_2$	1/2/2	NB	25	79.6

<sup>a</sup>Characterized by IR (42) and  $^{13}C$  NMR (42, 43) spectra. <sup>b</sup>Reaction conditions: concentration of complex [W] = 0.25 mmol; [LA]/[W] = 2; [monomer]/[W] = 50; 24 h; room temperature. <sup>c</sup>Calculated from  $^{13}C$  NMR spectra(42). <sup>d</sup>Insoluble in organic solvents.

#### *Reaction mechanism and structure of polymers*

Masuda (24) proposed a mechanism of polymerization (by metal carbene) and cyclotrimerization (by metallacyclopentadiene) of acetylenes for systems with metal chloride - based catalyst. When the catalysts are metal carbenes, cyclic trimers are formed only through the *cis-cisoidal* - induced backbiting and/or intramolecular reactions (23), and the polymerization reaction exhibits a mechanism similar to that of polymerization of cycloolefins (14, 19, 24-28). As it follows from Tables 1 and 2, in the systems under investigation phenylacetylene undergoes cyclotrimerization, oligomerization or polymerization; which reaction prevails depends on the complex, the Lewis acid and the solvent.

For the  $W(NO)_2(O_2CR)_2$  -  $MCl_4$  systems we propose the following mechanism of oligomerization, polymerization and cyclotrimerization of phenylacetylene and other terminal acetylenes (i.e. propargyl ether and 1,6-heptadiyne). The reaction of catalyst precursor complexes with Lewis acids causes that free coordination sites are reached in *trans* positions towards NO ligands (34, 38). In the presence of phenylacetylene or another terminal acetylene in the reaction system, it coordinates to the metal forming vinylidene complex (44, 45) and further polymerization proceeds by metal carbene mechanism. The trimerization mechanism of phenylacetylene is backbiting of propagating carbenes in a *cis-*

cisoidal grown chain to form triphenylbenzene derivatives. When the free coordination sites are blocked by, for instance, chlorines of the Lewis acids, inactive adducts are formed and reaction is terminated. The route of reaction in the case of phenylacetylene (polymerization or/and cyclotrimerization) depends mainly on the Lewis acid and on the solvent.

The above mechanism can be proven by  $^1\text{H}$  NMR spectrum of the  $\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2 - \text{SnCl}_4 - \text{PA}$  ( $[\text{W}]/[\text{Sn}]/[\text{PA}]=1/2/1$ ) system, as well as tests of activity of ternary systems  $\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2 - \text{PA} - \text{LA}$  ( $[\text{W}]/[\text{PA}]/[\text{LA}]=1/1$  or  $2/2$ ) in polymerization reactions of diphenylacetylene and ROMP of norbornene (Table 3).

$^1\text{H}$  NMR investigations of the  $\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2 - \text{SnCl}_4 - \text{PA}$  ( $[\text{W}]/[\text{Sn}]/[\text{PA}]=1/2/1$ ) system in  $\text{CD}_2\text{Cl}_2$  did not allow to identify the vinylidene complexes, because of their fast reaction with phenylacetylene (even at the concentration ratio of reagents  $[\text{W}]/[\text{PA}]=1/1$ ). Therefore, this spectrum exhibit the proton resonances of polyphenylacetylene, ( $\delta = 7.10 - 7.30$  ppm) and signals at 12.20, 12.80 ppm, typical of  $\text{H}_\alpha$  protons of vinyl alkylidene complexes of tungsten (46). Catalytic activity of the  $\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2 - \text{SnCl}_4 - \text{PA}$  ( $[\text{W}]/[\text{Sn}]/[\text{PA}]=1/2/1$ ) system in the polymerization reaction of diphenylacetylene, in particular of ROMP of norbornene (Table 3) proves that carbene complexes are formed in this system.

Values of the chemical shift of polyphenylacetylene proton resonances (7.10 - 7.30 ppm) in spectra of these systems indicate the *trans*-cisoidal structure (15, 16) of the polymers formed. These spectra show also weak signals at 5.82, 6.70 and 6.80 ppm due to proton resonances of a small amount of polymer with *cis*-transoidal structure (15, 16) and weak signals at  $\delta = 7.60 - 7.80$  ppm, due to the protons of triphenylbenzene (16, 23). The structure of all the obtained polyphenylacetylenes was determined by the  $^1\text{H}$  NMR and IR spectroscopies (14-16, 19, 23). We identified these polyphenylacetylenes as *trans*-cisoidal ones. The  $^1\text{H}$  NMR spectra of all the obtained polyphenylacetylenes show also weak signals of proton resonances of polymer with the *cis*-transoidal structure, and in addition weak and broad singlets at  $\delta = 3.5 - 4.0$  ppm. These broad singlets correspond to the methynic proton signal arising from the 1,3- and or 1,4-cyclohexadiene structures (16, 23).

When the polymerization mechanism can be described by the propagation through metal carbenes and cyclometallabutene intermediates, the polymer structure is determined by two mechanisms: (i) isomerization prior to the double bond formation - resulting in *cis*-transoidal isomer or *trans*-cisoidal isomer depending on the mode of cyclometallabutene opening (17, 18, 20, 23, 47), (ii) thermal isomerization after double bond formation - resulting in the *cis* to *trans* isomerization and cyclohexadiene sequences. The obtained results suggest that this mechanism decides on the microstructure of polyphenylacetylene formed in  $\text{W}(\text{NO})_2(\text{O}_2\text{CEH})_2 - \text{Lewis acid}$  systems. The cyclohexadiene structure can undergo further rearrangement leading to chain scission and aromatization products (17, 18, 20, 23, 47).

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