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Cyclotrimerization and Linear Oligomerization of Phenylacetylene on the Nickel(I) Monocyclopentadienyl Complex $CpNi(PPh_3)_2$

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Abstract—The reactions of the $CpNi(PPh_3)_2$ monocyclopentadienyl complex with phenylacetylene and diphenylacetylene in toluene have been studied by ESR. When an alkyne is in twofold molar excess over nickel, it substitutes rapidly for PPh_3 ligands to form the bisalkyne π complex $CpNi(\eta^2\text{-}C_2PhR)_2$, where R = H or Ph. In the case of phenylacetylene, two structural isomers of the Ni(I) π complex have been identified. Irreversible clustering occurs in the system as time passes. When phenylacetylene is in excess, it oligomerizes actively at ambient temperature. The composition of the oligomerization products depends substantially on the reaction temperature: at $T = 20°C$, the main product is 1,2,4-triphenylbenzene (97% of the conversion products); at $T = 40°C$, the main products are linear oligomers with an average molecular weight of 1050. The formation and stabilization of active complexes in the system take place when the substrate is in excess. Phenylacetylene trimerization and linear oligomerization schemes in which the Ni(I) monocyclopentadienyl complex stabilized by substrate molecules is the active species are suggested.

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INTRODUCTION

Nickelocene $NiCp_2$ in combination with organolithium compounds (LiR) is an efficient catalyst of alkyne oligomerization and polymerization [1–3]. The cyclopentadienyl group is exchanged for an alkyl group during catalyst formation to form the unstable 16-electron complex {CpNiR} [4, 5], which is converted into the highly reactive monocyclopentadienyl intermediate {CpNi} by the cross-coupling [6, 7] or homolytic decomposition of alkyl groups [8]. The {CpNi} intermediate exists in solution in dimeric and polymeric forms. A number of nickel clusters were isolated and characterized [9]. Based on systematic studies [1, 2], the {CpNiR} and {CpNiH} species stabilized by alkyne molecules were assumed to be reactive in polymerization and cyclotrimerization, respectively.

Previously, we demonstrated that catalyst formation in the presence of stabilizing ligands (L = PPh_3, $P(OEt)_3$, bipy/2, COD/2) affords Ni(I) mononuclear complexes with the general formula $CpNiL_2$ in the system [10].

In order to elucidate the role of the Ni(I) mononuclear complexes in the nickelocene-based catalysts of alkyne oligomerization, we studied the reactions of the $CpNi(PPh_3)_2$ complex with phenylacetylene (PhA) and diphenylacetylene (DPhA) and its catalytic activity in the cyclotrimerization and linear oligomerization of PhA.

EXPERIMENTAL

All procedures were carried out in purified argon using Schlenk techniques. Glass Schlenk filters were used in the filtration of precipitates. All prepared and synthesized reagents were stored in sealed tubes under argon.

Toluene, hexane, and tetrahydrofuran (Merck) were distilled from sodium metal under argon prior to use.

Commercial triphenylphosphine (PPh_3), triethyl phosphite ($P(OEt)_3$), and diphenylacetylene (Merck) were used as received.

Phenylacetylene was purified according to a standard procedure [11] and was distilled in vacuo prior to the experiment. Commercial diethylethoxyaluminum Et_2AlOEt was distilled in vacuo.

The $NiCp_2$ and $Ni(PPh_3)_4$ complexes were synthesized according to procedures described in [12, 13].

ESR spectra were recorded on a CMS-8400 spectrometer (operating frequency of 9.6 GHz) at the nitrogen boiling point. The diphenylpicrylhydrazyl free radical (DPPH) and Mn^{2+} in MgO were used to calibrate the scan ranges of the spectrometer. The ESR spectra were simulated according to our program [14] in which

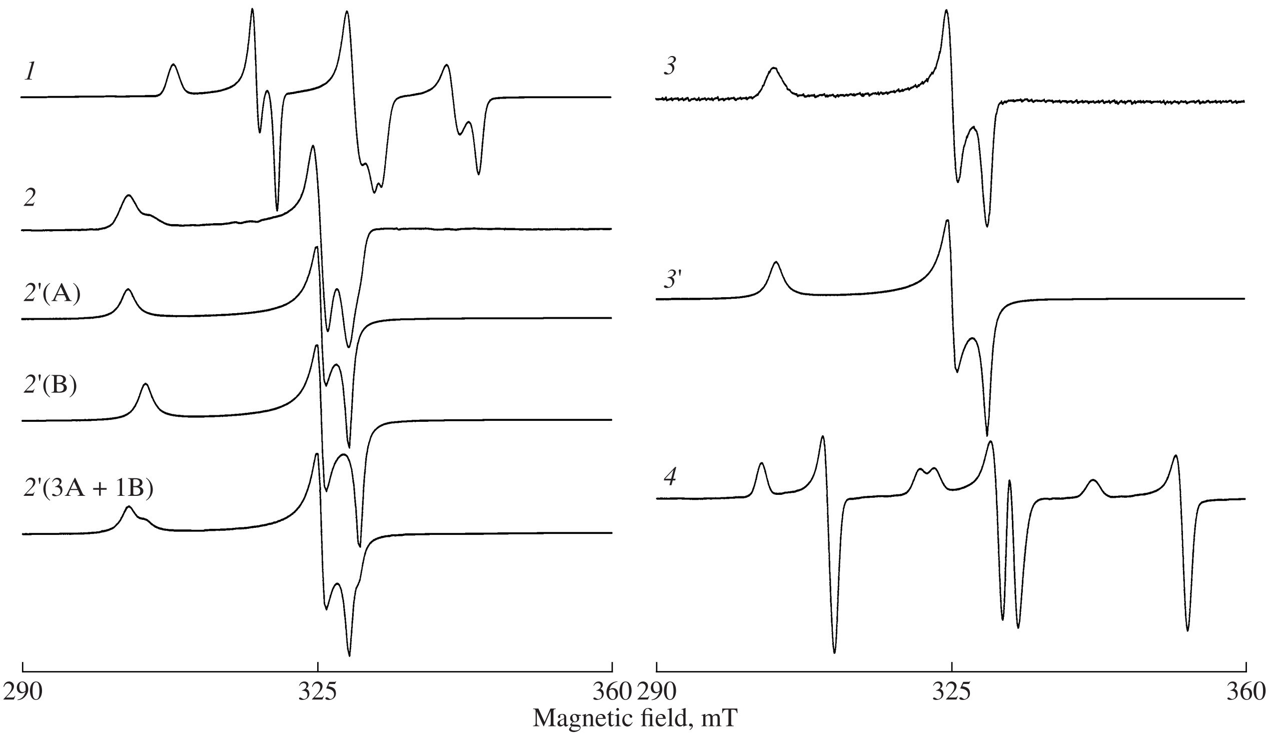


Fig. 1. (*1*–*4*) Experimental and (*2*', *3*') simulated ESR spectra of the Ni(I) complexes: (*1*) $CpNi(PPh_3)_2$, (*2*) $CpNi(\eta^2\text{-}C_2PhH)_2$, (*3*) $CpNi(\eta^2\text{-}C_2Ph_2)_2$, and (*4*) $CpNi(P(OEt)_3)_2$. The solvent is toluene, $C_{Ni} = 10^{-2}$ mol/l, and $T = 77$ K.

the hyperfine coupling (HFC) is truncated to second-order terms and the principal axes of the *g* tensor and HFC tensors coincide.

NMR spectra were recorded at 25°C on a VXR-500S spectrometer (Varian).

Mass spectra were obtained on an Agilent 5973N-6890 mass spectrometer with electron impact and chemical ionization coupled with a gas chromatograph (GC-MS). Mass spectra were identified using a database from the NIST Library of Mass Spectra and Subsets.

Catalytic reactions involving phenylacetylene were carried out as follows. Toluene, a weighed sample of the nickel complex, and the other reactants were successively loaded into a temperature-controlled reactor in an argon atmosphere. The concentration of the nickel complex was 1×10^{-4} mol/l. Freshly distilled phenylacetylene was added under vigorous stirring. ESR spectra were recorded after one procedure or another, depending on the purpose of the experiment. The amount of reacted phenylacetylene was determined by GLC on a GALS-311 gas chromatograph with a flame-ionization detector (50-m-long capillary column, Apiezon). After the reaction, the phenylacetylene conversion products were precipitated by adding excess ethanol, reprecipitated from toluene, and dried to constant weight in vacuo.

The molecular weight of the oligomers was determined by the isopiestic method in a toluene solution using azobenzene as the standard [15].

RESULTS AND DISCUSSION

The $CpNi(PPh_3)_2$ complex, which was synthesized by counter disproportionation between nickelocene and the phosphine complex $Ni(PPh_3)_4$ in toluene,

$$NiCp_2 + Ni(PPh_3)_4 \longrightarrow 2CpNi(PPh_3)_2, \qquad (I)$$

gives an intense ESR signal in which the hyperfine structure (HFS) from two nonequivalent ^{31}P nuclei is well resolved at $T = 77$ K [10] (Fig. 1, curve *1*). The nonequivalence of the coordinated phosphine ligands is due to the vibronic interaction in the Ni(I) complex, whose ground state is pseudodegenerate.

After the addition of phenylacetylene to the solution (PhA/Ni = 2), the initial ESR signal disappears immediately and two overlapped signals appear (Fig. 1, curves *2*(A), *2*(B)). Their ESR parameters are similar, and no HFC from ^{31}P is observed. The ratio between the intensities of the new ESR signals (3 : 1) is independent of the amount of phenylacetylene introduced into the solution.

If diphenylacetylene is introduced into the solution instead of phenylacetylene (DPhA/Ni = 2), the initial signal disappears as well, but only one signal, without HFS (Fig. 1, curve *3*), appears instead of the two sig-

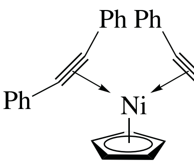
ESR data for the $CpNiL_2$ complexes

No.	Complex	g_x	g_y	g_z	A_x, mT	A_y, mT	A_z, mT	Reference
1	$CpNi(PPh_3)_2$	2.030	2.047	2.119	12.4(P_1) 11.6(P_2)	12.0(P_1) 11.4(P_2)	10.9(P_1) 9.35(P_2)	[10]
2	$CpNi(\eta^2\text{-}C_2PhH)_2$							
	Isomer A	2.040	2.061	2.221	–	–	–	
	Isomer B	2.033	2.061	2.206				
3	$CpNi(\eta^2\text{-}C_2Ph_2)_2$	2.035	2.061	2.206	–	–	–	
4	$CpNi(P(OEt)_3)_2$	2.032	2.032	2.093	20.1(P_1) 22.0(P_2)	20.1(P_1) 22.0(P_2)	18.9(P_1) 20.5(P_2)	[10]

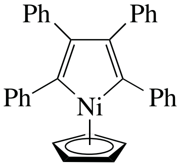
nals. The experimental ESR parameters of the Ni(I) complexes refined by simulation of the ESR spectra are listed in the table. The presence of two signals in the case of phenylacetylene indicates that the new paramagnetic complex, without phosphine ligands, can exist as two isomers.

Attempts to detect the Ni(I) complex with one phosphine ligand as an intermediate product of consecutive alkyne substitution for phosphine ligands by decreasing the amount of alkyne introduced were unsuccessful: only a mixture of signals from the initial complex and from the complex containing no phosphine ligands was detected.

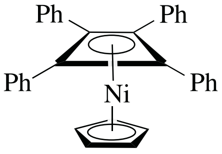
Let us consider the possible structures of the paramagnetic nickel alkyne complexes using DPhA as an example and known diamagnetic alkyne complexes of Co(I) and Co(III) as analogues [16–29]. These structures are the bisdiphenylacetylene π complex $CpNi(\eta^2\text{-}C_2Ph_2)_2$ (**I**), the metallocyclic σ complex $CpNi(1,4\text{-}\sigma\text{-}C_4Ph_4)$ (**II**), and the tetraphenylcyclobutadiene π complex $CpNi(\eta^4\text{-}C_4Ph_4)$ (**III**):



I

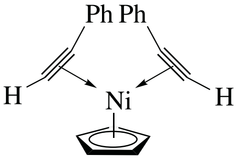


II

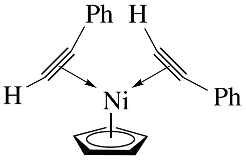


III

According to quantum chemical calculations, the thermodynamic stability of the analogous Co complexes increases in the order **I** < **II** < **III** [30]. However, structure **III** seems improbable for the paramagnetic Ni complex because the ESR parameters of the DPhA complex do not coincide with the data reported for the intermediate complex detected in the chemical reduction of the cationic complex $[CpNi(\eta^4\text{-}C_4Ph_4)]PF_6$ with sodium amalgam in THF ($g_1 = 2.143$, $g_2 = 2.035$, $g_3 = 1.993$) [31]. Structure **II** also seems improbable because mononuclear metallocyclic Co(III) complexes are stabilized only as $CpCo(PPh_3)(1,4\text{-}\sigma\text{-}C_4R_4)$ phosphine complexes [17, 20–23, 25, 27]. The known metallocyclic Ni(III) complexes involving no stabilizing ligands exist only in dinuclear or polynuclear form [9, 32, 33]. Therefore, the bisdiphenylacetylene π complex $CpNi(\eta^2\text{-}C_2Ph_2)_2$ (**I**) seems to be the most likely structure. In the case of phenylacetylene, the presence of two isomers is likely due to the existence of the π complex $CpNi(\eta^2\text{-}C_2PhH)_2$ as *cis* (**IA**) and *trans* (**IB**) isomers:



IA



IB

Further investigation is necessary to assign the ESR signals to particular isomers of the π complex. The signal with the largest *g* tensor components is conventionally assigned to the isomer A.

The formation of the bisphenylacetylene π complex can be represented as follows:

$$CpNi(PPh_3)_2 + PhC{\equiv}CH \longrightarrow CpNi(PPh_3)(\eta^2\text{-}C_2PhH) + PPh_3, \quad (II)$$

$$2CpNi(PPh_3)(\eta^2\text{-}C_2PhH) \longrightarrow CpNi(\eta^2\text{-}C_2PhH)_2 + CpNi(PPh_3)_2. \quad (III)$$

According to experimental data, the unstable mixed-ligand complex $CpNi(PPh_3)(\eta^2\text{-}C_2PhH)$, which results from the substitution of PhA for coordinated PPh_3, disproportionates rapidly into a bisphenylacetylene π complex and the initial Ni(I) bistriphenylphosphine complex.

The ESR signals from the Ni(I) phenylacetylene complex decrease in time (Fig. 2) and disappear completely in 30 min. In the case of diphenylacetylene, the ESR signal intensity changes so slowly that the signal is still detected after 24 h.

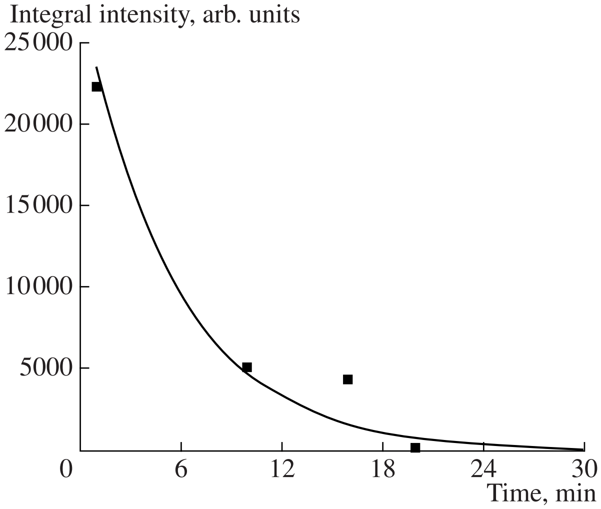
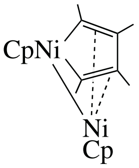
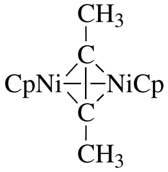
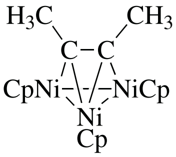


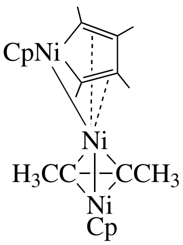
Fig. 2. Time variation of the intensity of the ESR signals from the $CpNi(\eta^2\text{-}C_2PhH)_2$ complex (PhA/Ni = 2, $T = 20°C$).

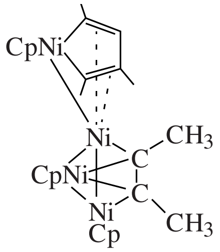
The noticeable decrease in the intensity of the ESR signals in the case of phenylacetylene likely arises both from the clustering of the Ni(I) complexes, which is characteristic of Ni(I) monocyclopentadienyl complexes, and from the change in the oxidation state of the transition metal due to the oxidative addition of phenylacetylene and metallocycle formation. For instance, a number of di-, tri-, and tetranuclear nickel clusters were described in the literature. They were isolated from a reaction mixture prepared from nickelocene $NiCp_2$, methyllithium $LiCH_3$, and dimethylacetylene $H_3CC{\equiv}CCH_3$ in tetrahydrofuran and were characterized by X-ray diffraction [9, 32, 33]:











It is noteworthy that the processes that occur in the system considered are irreversible, as is indicated by the fact that no ESR signals are detected after triethyl phosphite, a reactive ligand, is introduced into the system ($P(OEt)_3$/Ni = 3) at the end of the experiment. If $P(OEt)_3$ is introduced into a system in which the ESR signals from the phenylacetylene complex are still detected, the signals immediately transform into a stable signal from the $CpNi(P(OEt)_3)_2$ complex (Fig. 1, curve *4*), whose ESR spectrum was described in detail [10].

If excess phenylacetylene is added to the $CpNi(PPh_3)_2$ complex (PhA/Ni = 200) in toluene, the active oligomerization of the alkyne begins after a short induction period. The PhA consumption curves at three reaction temperatures (20, 30, and 40°C) are shown in Fig. 3. The maximum PhA conversion is 77% (at $T = 30°C$).

Note that, taken separately, the starting Ni(II) and Ni(0) complexes used in the synthesis of $CpNi(PPh_3)_2$ via reaction (I) exhibit no activity in phenylacetylene oligomerization under the conditions examined.

The composition of the PhA oligomerization products depends substantially on the reaction temperature. For example, at $T = 20°C$, the major reaction product is 1,2,4-triphenylbenzene (97% of the conversion products), whereas the major reaction products at $T = 40°C$ are linear oligomers with an average molecular weight of 1050 (9–10 PhA molecules). The product of phenylacetylene cyclotrimerization was identified by mass spectrometry and NMR: ^1H NMR ($CDCl_3$): δ 7.84, 7.77, 7.49, 7.38 ppm; ^{13}C NMR ($CDCl_3$): δ 141.5, 141.1, 140.9, 140.5, 140.3, 139.5 (quaternary carbon atoms), 129–126 ppm (CH atoms). These NMR data are identical to the data reported for 1,2,4-triphenylbenzene [34].

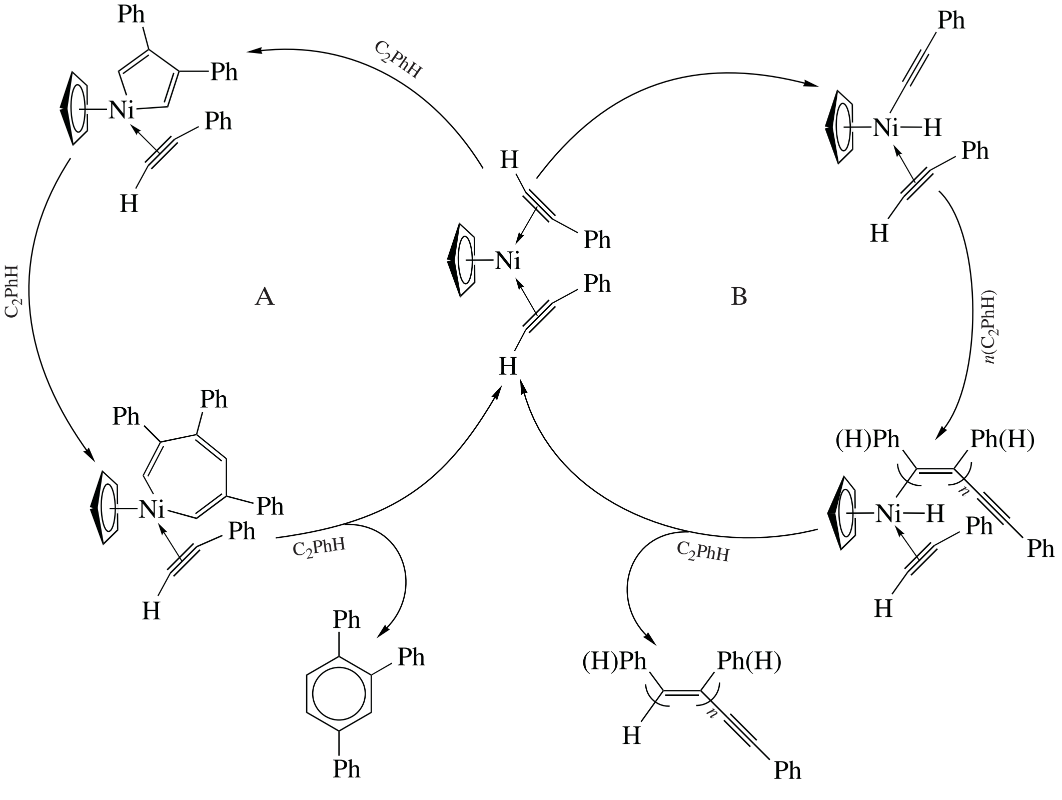
The linear oligomerization products isolated from the reaction medium give a weak symmetric ESR signal characteristic of organic semiconductors with a developed polyconjugated system [35]. The NMR spectra of the linear products confirm the presence of conjugated double bonds in the oligomer chain (^{13}C NMR ($CDCl_3$): δ 151–148.5, 138–132, 109–110 ppm).

The intensity of the ESR signals from the $CpNi(\eta^2\text{-}C_2PhH)_2$ complex decreases rapidly during the induction period preceding the active stage of phenylacetylene oligomerization, so the oligomerization process occurs in the absence of any ESR signals. However, if the catalytic poison triethyl phosphite is introduced into the system ($P(OEt)_3/Ni = 3$) during oligomerization, the reaction ceases immediately and an intense signal from $CpNi(P(OEt)_3)_2$ appears. If triethyl phosphite is introduced at the end of the oligomerization reaction, no ESR signals appear. Therefore, during oligomerization, the nickel present in the system is either in the Ni(I) state (e.g., as dinuclear structures) or in the high-spin state Ni(III) (e.g., as tetrahedral structures characterized by short spin–lattice relaxation times, which readily turn into mononuclear Ni(I) complexes upon the substitution of triethyl phosphite for coordinated phenylacetylene). Since the known schemes of alkyne trimerization on various transition metal complexes include metallocyclopentadiene formation steps [36–39], it seems most likely that most of the nickel is in the Ni(III) state during phenylacetylene oligomerization.

Note that a mixture of $CpNi(PPh_3)_2$ with a twofold excess of PhA held for 0.5 h in toluene exhibits no oligomerization activity after excess phenylacetylene is added. Therefore, the formation and, what is most important, stabilization of the active complexes in the system take place when phenylacetylene is in excess, as was noted in earlier publications [1, 2]. The lower limit of the substrate excess necessary to maintain the nickel complexes in their active state is 50–60 molar parts, as was estimated from the amount of unreacted phenylacetylene (Fig. 3).

Since the complete substitution of phenylacetylene for PPh_3 in the $CpNi(PPh_3)_2$ complex occurs already at a twofold molar excess of PhA over nickel, the role of PPh_3 in PhA oligomerization on $CpNi(PPh_3)_2$ is negligible under the conditions examined. It follows from this conclusion that the behavior of the individual $CpNi(PPh_3)_2$ complex in excess phenylacetylene is equivalent to the behavior of the Ni(I) monocyclopentadienyl complexes in the catalytic system $NiCp_2/LiR$ in phenylacetylene oligomerization.

Based on systematic studies of the oligomerization of a wide variety of alkynes on the catalytic system $NiCp_2/LiR$, it was assumed that the Ni(II) complexes {CpNiR} and {CpNiH} stabilized by alkyne molecules are active in the polymerization and cyclotrimerization, respectively, of the monomers [1, 2]. In our system, which is based on the Ni(I) monocyclopentadienyl complex $CpNi(PPh_3)_2$, the formation of the {CpNiR} and {CpNiH} species is not so evident as in the $NiCp_2/LiR$ catalytic system. Therefore, although we do not rule out the participation of these Ni(II) complexes in phenylacetylene oligomerization, we suggest an alternative mechanism involving the Ni(I) and Ni(III) monocyclopentadienyl complexes (scheme), which is in best agreement with experimental data:



Scheme.

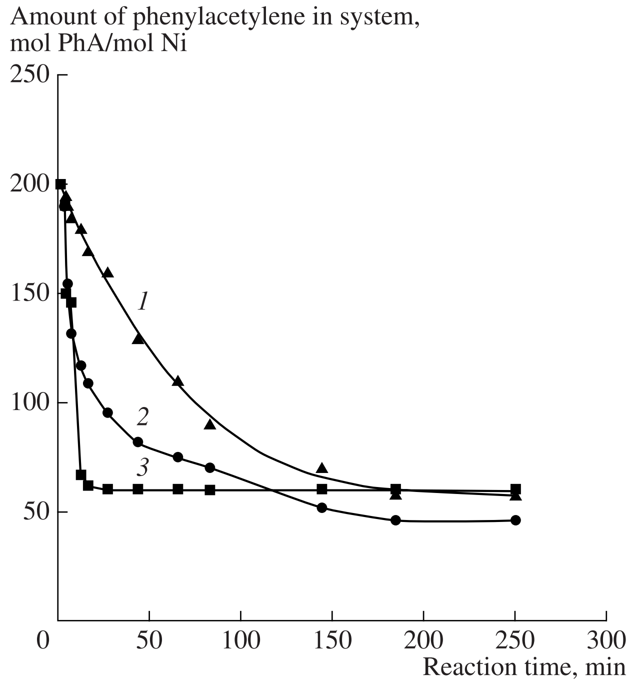


Fig. 3. Phenylacetylene consumption kinetics in the PhA/CpNi$(PPh_3)_2$ system. $C_{Ni} = 10^{-4}$ mol/l; T = (*1*) 20, (*2*) 30, and (*3*) 40°C.

According to this scheme, the Ni(I) complex, stabilized by substrate molecules, is the active species in the catalytic cycles of phenylacetylene trimerization (A) and linear oligomerization (B). The catalytic cycle of PhA trimerization includes the consecutive transformations of the Ni(I) π complex into the metallocyclopendiene and metallocycloheptatriene complexes. The closure of the carbon ring results in the formation of asymmetric 1,2,4-triphenylbenzene and in the reduction of the initial Ni(I) π complex.

In the catalytic cycle of linear oligomerization, the oxidative addition of a PhA molecule to Ni(I) affords a Ni(III) hydride complex. After the insertion of PhA molecules into the Ni–C bond followed by reductive elimination, linear oligomers are formed and the initial Ni(I) π complex is regenerated.

According to the scheme, the organometallic Ni(III) complexes in both catalytic cycles are pseudotetrahedral and are in the high-spin state corresponding to this geometry (S = 3/2). This is the likely reason for the absence of ESR signals during oligomerization. The short induction period preceding phenylacetylene formation is likely due to the substitution of PhA for coordinated PPh_3 and the conversion of Ni(I) into Ni(III) via the oxidative addition of PhA.

Catalyst deactivation is likely caused by the clustering of the complexes, whose rate increases as the amount of the substrate in the system decreases.

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