

Role of Paramagnetic Ni(I) and Ni(III) Complexes in Catalytic Reactions of Unsaturated Hydrocarbons

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Abstract—By analyzing experimental data collected by systematic investigation of Ni(I) complex formation conditions, it is demonstrated that, when a system simultaneously contains Ni(0) and Ni(II) complexes, whether cationic or electroneutral, stabilized by olefinic or organoelement ligands, the complexes undergo comproportionation to form Ni(I) complexes. Using individual Ni(II) complexes as examples, it is shown that the spontaneous decomposition of hydrido and organometallic Ni(II) complexes yields Ni(I) complexes. The Ni(I) and Ni(III) complexes are involved in the catalytic cycles of reactions of olefins and acetylenes.

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Progress in present-day industry is impossible without introducing hi-tech, economically efficient catalytic systems. The rapid advances in catalysis by metal complexes and extensive use of modern physical investigation techniques have led to a marked headway in the study of all key metal complexes, including those appearing during catalyst formation and those directly involved in the catalytic cycle. An important achievement in this area is the discovery and identification of Ni(I) in nickel complex catalysts by *in situ* EPR spectroscopy. It was convincingly demonstrated that Ni(I) complexes at a high concentration comparable with the initial concentration form in catalytic systems via the reduction of Ni(II) complexes under the action of organometallic compounds of nontransition metals [1–3] or via the oxidation of Ni(0) complexes involving Lewis or Brönsted acids [1–4]. After the EPR identification of Ni(I) compounds in Ziegler-type catalytic systems [5], there have been attempts to elucidate the role of the Ni(I) compounds in reactions of unsaturated hydrocarbons. Researchers did not observe symbiosis between the intensity of the EPR signal from Ni(I) and catalytic activity and concluded that the Ni(I) complexes are unstable intermediates undergoing rapid disproportionation via the reaction



and play only an auxiliary role in the formation of active Ni(II) complexes [6]. At the same time, it was reliably established that Ni(I) complexes are directly involved in the catalytic cycles of cross-coupling reactions [7–12] and in biochemical processes [13–16]. In recent years, it has increasingly frequently been claimed that Ni(I) complexes participate directly in various catalytic reactions of unsaturated hydrocarbons: olefin polymerization [17–19], cyclodimeriza-

tion of cyclic olefins [20, 21], and linear polymerization and cyclotrimerization of phenylacetylene [22]. In our opinion, this is primarily due to the fact that researchers have abandoned the long-standing stereotype that Ni(I) complexes are intermediates rapidly decomposing in the catalytic system and have realized that dinuclear diamagnetic Ni(I) complexes mask the true valence of nickel in the system.

Here, we analyze our and other researchers' data providing evidence that Ni(I) complexes are thermodynamically stable compared to Ni(II) and Ni(0) complexes and are directly involved in the catalytic cycles of reactions of unsaturated hydrocarbons.

EXPERIMENTAL

All experiments were carried out using standard Schlenk techniques with an argon–vacuum line and appropriate glassware. All chemicals were stored in argon in sealed tubes.

The reactants and solvents were purchased from Merck. Cycloocta-1,5-diene (COD), toluene, and hexane were additionally dried with a sodium–potassium alloy and were degassed.

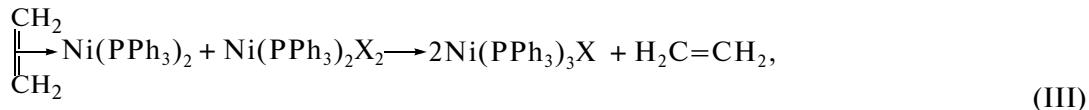
The synthesis of the nickel complexes considered in this article is described in detail in publications cited below. X-ray structure analysis of the complexes was carried out on crystals frozen into a drop of silicone oil.

RESULTS AND DISCUSSION

Ni(I) Complexes Are Thermodynamically Stable Compounds

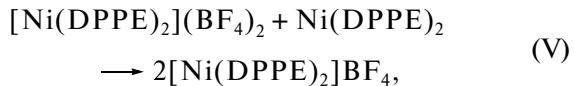
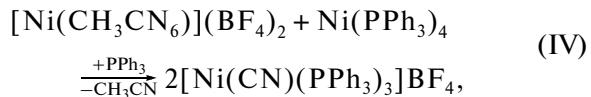
Comproportionation reaction between Ni(II) and Ni(0) complexes. For the first time, a spontaneous

change in the oxidation state of nickel in a solution containing both Ni(II) and Ni(0) was reported in 1964 [23]. A number of nickel(I) complexes were obtained



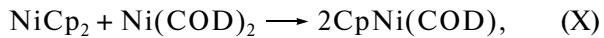
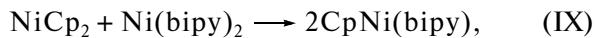
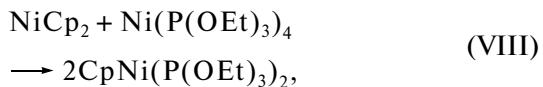
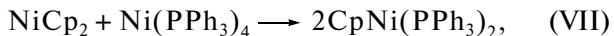
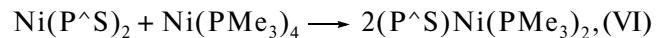
where X = Cl, Br, or I. The yield of nickel(I) complexes resulting from reactions (II) and (III) was close to 100%.

We discovered that a comproportionation reaction can also take place between a cationic Ni(II) complex and a Ni(0) phosphine complex in a toluene + acetonitrile (1 : 1) mixture at room temperature:



where DPPE = bis(diphenylphosphino)ethane.

The quantitative yield of the Ni(I) complexes is also attained by carrying out a comproportionation reaction between electroneutral Ni(II) and Ni(0) complexes, including organometallic ones, in toluene solution [25, 26]:



where $\text{P}^{\wedge}\text{S}$ = 2-(diphenylphosphanyl)thiophenolate, Cp = η^5 -cyclopentadienyl, bipy = 2,2'-bipyridyl, and COD = cycloocta-1,5-diene.

The Ni(I) complexes synthesized via comproportionation have been isolated in the individual state and reliably identified by modern methods (EPR, X-ray structure determination). The Ni(I) complexes in solution remain unchanged at room temperature in an inert atmosphere for at least 1 month. Note that the comproportionation reaction practically comes to completion even when the initial Ni(II) compound is poorly soluble [24, 25]. It was demonstrated by the example of the CpNi(COD) complex synthesized via reaction (X) that Ni(I) can be stabilized in solution by unsaturated hydrocarbons in the absence of a conventional P- or N-containing donor ligand.

Thus, contrary to common views, the equilibrium

by reacting equimolar amounts of nickel(II) and nickel(0) triphenylphosphine complexes in diethyl ether:



in solution is almost completely shifted to the right-hand side.

The following natural question arises here: Why is there no idea about the chemistry of Ni(I) solutions, while the chemistry of Ni(II) solutions is developed well? We think that the rarity of Ni(I) compounds is due to their low kinetic stability, i.e., their capacity for readily entering into chemical reactions.

Since the Ni(I) complexes are thermodynamically more stable than the Ni(II) and Ni(0) complexes, they can be both identified by *in situ* EPR spectroscopy and isolated directly from real catalytic systems. For example, among the cationic Ni(I) complexes, whose formation in the catalytic system $\text{Ni}(\text{PPh}_3)_4/\text{BF}_4 \cdot \text{OEt}_2$ was demonstrated for the first time by Tkach et al. [27], the individual tricoordinated complex $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$ [28] was isolated from the reaction system and was comprehensively characterized, including by X-ray structure determination (Fig. 1).

Formation of Ni(I) complexes via the spontaneous decomposition of hydrido and organometallic Ni(II) complexes. In 1969, the pentacoordinated nickel(II) hydrido complex $[\text{HNi}(\text{P}(\text{OEt})_3)_4]^+$ was synthesized by protonation of a nickel(0) phosphite complex in acid media [29]. Later, reactions of conjugated dienes [30, 31] and olefins [32] involving this nickel(II) complex were studied by NMR spectroscopy. These studies, which were carried out on a model system, provided a basis for the universally accepted hydride mechanism of the conversion of unsaturated hydrocarbons catalyzed by nickel complexes [30, 32]. However, an analysis of numerous studies of the mechanisms of reactions catalyzed by real active catalytic systems suggests that, the higher the activity of the catalytic system, the smaller the chance of detecting a Ni(II) hydrido complex in this system not only during the functioning of the metal complex catalyst, but also during its formation [33, 34]. In our opinion, this is due to the low stability of the coordinatively unsaturated Ni(II) hydrido complexes in solution. The decomposition of the Ni(II) hydrido complexes typically yields Ni(I) complexes [25, 35]. For example, the individual complex hydrido(2-diphenylphosphine)thionaphthalato[P,S]bis(trimethylphosphine)nickel (I), which is stable in the solid state in an argon atmosphere for a long time, decomposes spontaneously to yield a nickel(I)

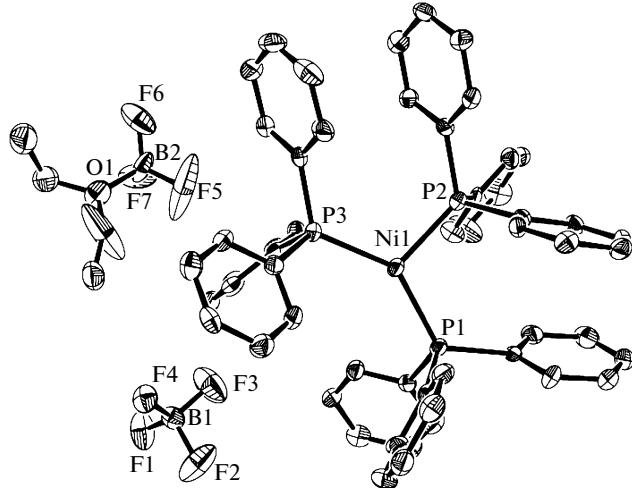
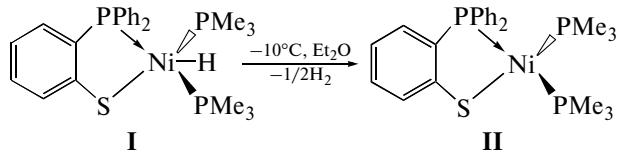


Fig. 1. Molecular structure of the cationic complex $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$ (CCDC 682428) [28]. Bond lengths, Å: P1–Ni1 2.2149(16), P2–Ni1 2.2089(17), P3–Ni1 2.1826(16). Bond angles, deg: P3–Ni1–P2 110.9(6), P3–Ni1–P1 141.98(7), P2–Ni1–P1 107.00(6).

complex (**II**) on being dissolved in diethyl ether even at -10°C [25].



Complex **II** was isolated as an individual compound [25] and was comprehensively studied, including by EPR spectroscopy and X-ray crystallography (Fig. 2). Complex **II** is stable in solution in an argon atmosphere at room temperature for more than half a year.

The same complex **II** results from the decomposition of the light-sensitive Ni(II) methyl complex **III** [25]:

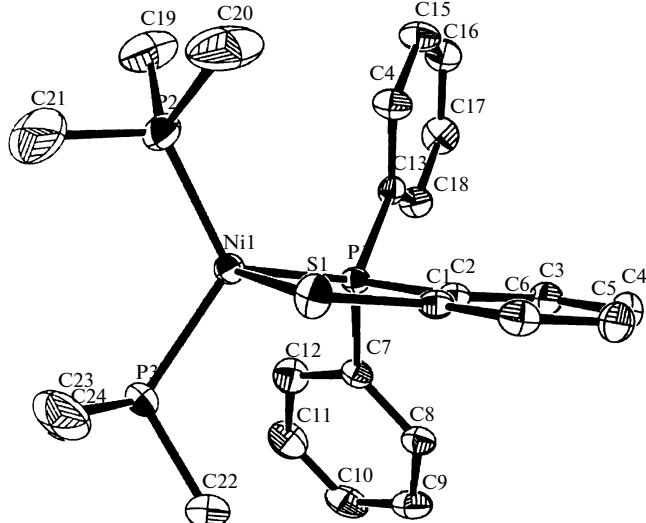
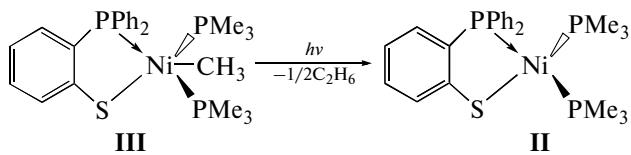
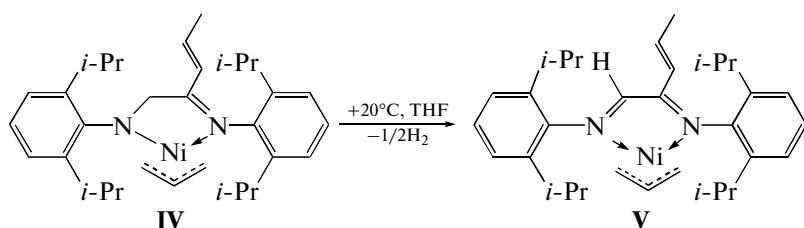


Fig. 2. Molecular structure of $\text{Ni}(\text{P}^{\text{S}})(\text{PMe}_3)_2$ (CCDC 705063) [25]. Bond lengths, Å: Ni–S1 2.241(1), Ni–P1 2.147(9), Ni–P2 2.184(1), Ni–P3 2.199(1). Bond angles, deg: P1–Ni–P2 123.91(3), P1–Ni–P3 116.02(4), P2–Ni–P3 118.57(4), P1–Ni–S1 91.08(3), P2–Ni–S1 97.01(4), P3–Ni–S1 94.04(4).



Individual Ni(II) π -allyl complexes are also very stable [36], but they may decompose in solution in the course of time to yield Ni(I) complexes as well. For example, the individual Ni(II) π -allyl imine–amido complex **IV** in the solid state remains unchanged for a long time [36]. A solution of complex **IV** sealed in a vacuumized tube is stable for a few hours, according to NMR data. Thereafter, line broadening is observed in the NMR spectrum. After 10–12 h, the EPR spectrum shows a strong signal from the Ni(I) π -allyl diimine complex **V**:



Complex **V** is stable in solution in a sealed tube at room temperature for over 2 years.

Evidently, the above spontaneous decomposition reactions of the individual Ni(II) hydrido and organo-

metallic complexes also occur in catalytic systems during the formation of a metal complex catalyst.

Ni(I) Complexes Are Real Active Species in Catalytic Reactions of Olefins and Acetylenes

The above data suggest that generation of Ni(I) complexes is very likely to take place in the formation of various catalytic systems. Although the nonparamagnetic species of Ni(I) complexes are difficult to detect and identify, some data reported in the literature indicate that Ni(I) complexes are directly involved in the catalytic cycles of reactions of unsaturated hydrocarbons.

In the formation of the catalytic system $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3 \cdot \text{OEt}_2$, which is among the most active systems for α -alkene oligomerization, the entire Ni(0) oxidizes to Ni(I), which is then stabilized in the solution in the form of mononuclear cationic complexes by triphenylphosphine ligands [37]. After the introduction of a substrate (ethylene, propylene, or styrene) into the system, the EPR signal from Ni(I) disappears immediately and does not reappear until complete oligomerization. However, upon the introduction of the catalyst poison triethyl phosphite into the system (P : Ni = 2 : 1), the reaction terminates immediately and an intense EPR signal from the coordinatively saturated complex $[(\text{PPh}_3)_2\text{Ni}(\text{P}(\text{OEt})_3)_2]\text{BF}_4$ appears, indicating that the active form of the Ni(I) complex is dinuclear. The intensity of this EPR signal is proportional to the activity of the system at the instant the catalyst poison was introduced (Fig. 3) [38].

The individual cationic Ni(I) complex $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$ isolated from the catalytic system $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3 \cdot \text{OEt}_2$ shows, without being additionally activated, approximately the same activity in styrene oligomerization as the $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3 \cdot \text{OEt}_2$ system itself [39, 40].

In order to elucidate the mechanism of the activation of the multiple bond in the dinuclear Ni(I) complex, we investigated the formation of the $[\text{Ni}(\text{PPh}_3)_3]\text{BF}_4$ –styrene complex by NMR and UV spectroscopy [39, 40]. It was inferred from spectroscopic data that, in this Ni(I) styrene complex, positive charge is transferred from the nickel atom to the styrene ligand, resulting in the formation of a carbocationic Ni(I) complex, most likely $(\text{PPh}_3)_2\text{NiCH}_2\text{C}^+\text{HPh}$, which is dimerized in solution [39, 40]. The same multiple bond activation mechanism was suggested for explaining experimental data concerning alkene polymerization catalyzed by cationic Zr(IV) complexes [41, 42], regiospecific and stereospecific styrene dimerization catalyzed by cationic Fe(III) complexes [43], ethylene and α -olefin codimerization catalyzed by cationic Pt(II) complexes [44], vinyl ester polymerization catalyzed by cationic Pd(II) complexes [45], and olefin hydrovinylation and

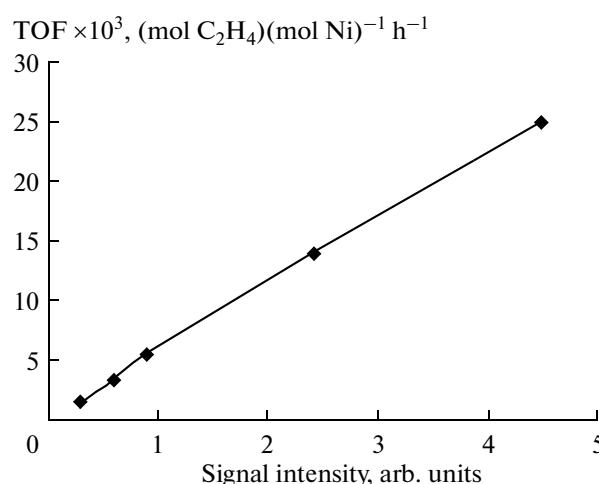


Fig. 3. Activity of the $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3 \cdot \text{OEt}_2/\text{HBF}_3\text{OEt}$ system (TOF) as a function of the Ni(I) concentration.

hydroarylation catalyzed by dicationic Pd(II) and Pt(II) complexes [45, 46].

The formation of the catalytic system $\text{Ni}(\text{COD})_2/\text{BF}_3 \cdot \text{OEt}_2$, which is among the most efficient systems for the cycloisomerization and [2 + 2] cyclodimerization of COD [21] and for the addition polymerization of norbornene (NB) [19], also involves the quantitative oxidation of Ni(0) to Ni(I), which is stabilized in solution by substrate molecules in the absence of conventional organometallic ligands.

Two types of paramagnetic nickel complex are generated during the formation of this system, namely, a cationic Ni(I) complex coordinated with COD molecules and a carbocationic Ni(I) complex covalently bonded with COD [21]. Figure 4 (curves 1, 2) presents the EPR spectra of these Ni(I) complexes and the corresponding most likely structures.

As distinct from alkene oligomerization in the $\text{Ni}(\text{PPh}_3)_4$ -based system, which begins with the conversion of mononuclear Ni(I) complexes into dinuclear diamagnetic structures, the catalytic conversion of COD or NB in the $\text{Ni}(\text{COD})_2$ -based system involves mononuclear paramagnetic nickel complexes. We demonstrated by *in situ* EPR spectroscopy that the [2 + 2] cyclodimerization of COD and the addition polymerization of NB are accompanied by the oxidative addition of the substrate (COD or NB) to a cationic Ni(I) complex with the formation of metallacyclic low-spin Ni(III) complexes (spectra 3 and 4 and the corresponding structures in Fig. 4) [19]. Taking into account these EPR data and the cyclic structure of the COD conversion products, we suggested metallacyclic mechanisms involving Ni(I) and Ni(III) complexes for the [2 + 2] cyclodimerization of COD and the addition polymerization of NB [19].

The individual mononuclear nickel(I) complex $\text{CpNi}(\text{PPh}_3)_2$, which was synthesized via a comproportionation reaction between $\text{Ni}(\text{PPh}_3)_4$ and NiCp_2 , is

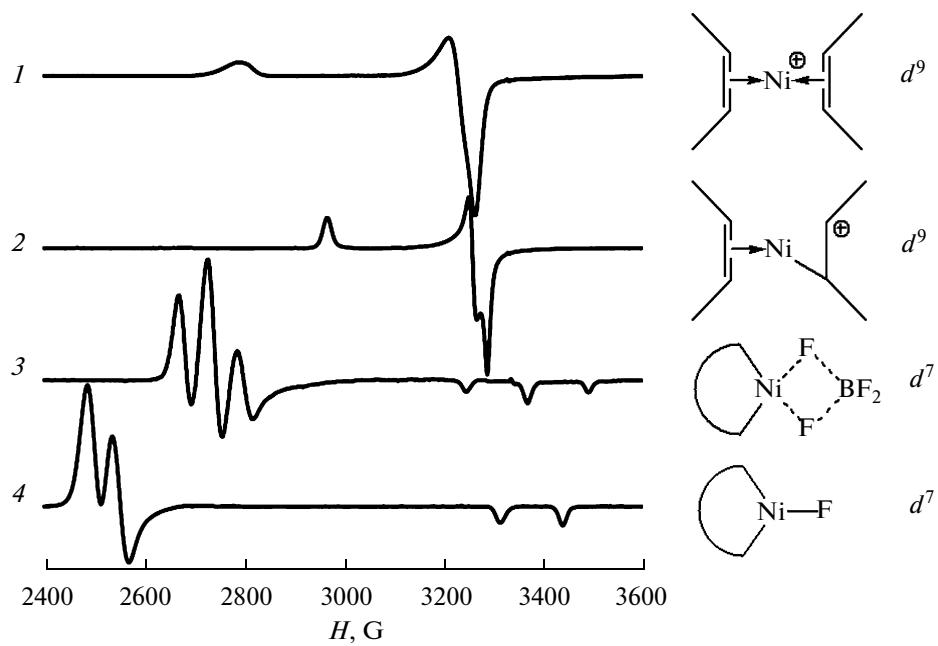


Fig. 4. EPR spectra and the corresponding most likely structures of Ni(I) and Ni(III) complexes [19, 21].

catalytically very active in the cyclotrimerization and linear polymerization of phenylacetylene in toluene in the absence of any activator [22]. The selective forma-

tion of 1,2,4-triphenylbenzene and a linear polymer can be explained in terms of the metallacyclic (A) and alkylidene (B) mechanisms (Fig. 5). These mecha-

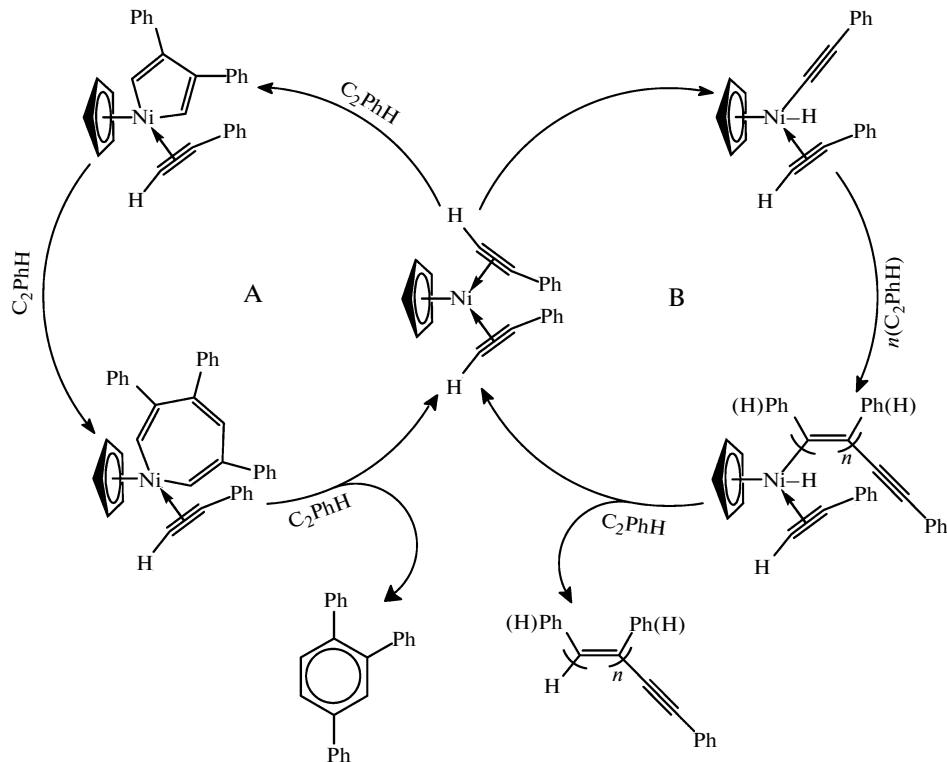


Fig. 5. Scheme of the selective formation of 1,2,4-triphenylbenzene (A) and a linear polymer (B) from phenylacetylene in the $\text{CpNi}(\text{PPh}_3)_2$ -based system [22].

nisms include the formation of Ni(III) complexes via the oxidative addition of phenylacetylene molecules to an electroneutral Ni(I) complex [22].

Thus, the above analysis of the results of systematic experimental studies suggests the following conclusions:

(1) When a system simultaneously contains Ni(0) and Ni(II) complexes, whether cationic or electroneutral, stabilized by olefinic or organoelement ligands, the complexes undergo comproportionation to form Ni(I) complexes.

(2) Both the protolytic and spontaneous decomposition of Ni(II) hydrido complexes yields Ni(I) complexes.

(3) The spontaneous decomposition of Ni(II) allyl imine–amido complexes yields Ni(I) complexes.

(4) The Ni(I) complexes readily get involved in the oxidative addition of alkenes and alkynes, turning into Ni(III) complexes. This indicate that they can be directly involved in the catalytic cycles of reactions of olefins and acetylenes.

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