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Coupled Hydrogenation of Alkenes and Arenes in the Presence of Catalytic Systems Based on Cobalt Bis(acetylacetonate) and Tributylphosphine

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Abstract—The effect of the composition of the catalytic systems based on $Co(acac)_2$ and tertiary phosphines on the activity and efficiency of cobalt catalysts in the coupled hydrogenation of alkenes and arenes is reported. The process occurs in the presence of cobalt catalysts formed under the action of both organoaluminum compounds and *tert*-butoxy derivatives of complex aluminum hydrides. NMR and IR spectroscopic methods show that the interaction of the components of the catalytic systems yields mono- and/or trihydrido cobalt phosphine complexes, whose composition depends on the nature of the reducing agent and gas atmosphere. The homogeneous character of the process is hypothesized. The most probable schemes are proposed for the reaction mechanism, according to which the kinetic coupling of alkene (alkadiene) and arene hydrogenations is due to the fact that the reaction proceeds through a σ-alkyl or σ-alkenyl cobalt complex with two phosphorus-containing ligands.

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The catalytic hydrogenation of mono- and polycyclic aromatic compounds is practically and theoretically significant for the development of catalysis theory. The hydrogenation of benzene to cyclohexane and that of phenol to cyclohexanone are among the most important large-scale industrial processes [1]. The partial hydrogenation of benzene to cyclohexene and the reduction of aromatic polymers, such as polystyrene, to poly(cyclohexaethylene) are equally significant, because the products of polymer hydrogenation acquire new thermal, oxidation, and optical properties [2]. The group VIII metals are usually used as catalysts in the hydrogenation of aromatic compounds. These metals can conventionally be arranged in the following order according to their activity in the hydrogenation of monocyclic arenes: Rh > Ru > Pt > Ni > Pd > Co [2]. The Raney catalyst and Rh/Al_2O_3 are the most popular.

The study of arene hydrogenation in the presence of homogeneous and nanosized catalysts based on transition metal complexes was started in the 1960s [3–5]. There has been a series of studies on the hydrogenation of benzene in the presence of cobalt π-allyl complexes, η^3-$C_3H_5CoL_3$, where L is phosphine or phosphite [6–8]. In spite of the comparatively low activity of this catalyst, which was ~2×10^{-3} (mol C_6H_6) × (g-atom Co)$^{-1}$ min^{-1} at 25°C and a hydrogen pressure of 1 atm, the results obtained were very significant for elucidating the mechanism of benzene hydrogenation. It was discovered [9, 10] that, in the presence of the $Co(acac)_2$–PBu_3–$AlEt_3$ system (where acac = acetylacetonate), the hydrogenation of alkenes, for example, styrene, is accompanied by benzene reduction to cyclohexene and cyclohexane. Benzene hydrogenation stopped after the conversion of the entire the alkene to the alkane. The simultaneous hydrogenation of styrene and benzene resumed after the introduction of a new portion of the alkene into the catalytic solution. That is why the process was accepted to be coupled.

The nature of the phosphorus-containing ligands plays the decisive role in the coupled hydrogenation of alkenes and arenes. The most active cobalt catalysts are based on trialkylphosphines. However, the replacement of only one alkyl radical by phenyl in the tertiary phosphine sharply decreases the rate of benzene hydrogenation. No benzene hydrogenation was observed on the cobalt catalysts formed in the presence of PPh_2Bu or PPh_3, whereas styrene was reduced to ethylbenzene at a high rate [10].

Researchers are still interested in arene hydrogenation [11–13]. Along with the necessity of enhancing the efficiency and thermal stability of arene hydrogenation catalysts, the problem of discriminating hypotheses about the nature of catalytically active species remains the key issue. The study of the conversion products of the metal-containing precursors by transmission electron microscopy demonstrated that most of the arene hydrogenation catalysts based on the rhodium ($RhCl_3 \cdot 3H_2O$, $[RhCl(diene)]_2$) or ruthenium ($RuCl_3 \cdot 3H_2O$) compounds in combination with various quaternary ammonium salts, which were initially claimed to be homogeneous, turned out to be metal nanoclusters 2–6 nm in diameter [2]. At the same time, the composition of products of the reaction between the components of Ziegler catalytic systems was experimentally found to depend substantially on the proportions of these components, on the reaction conditions, on the nature of the solvent, on the presence of moisture and other impurities in the reaction mixture, and on the introduction of various modifiers [14, 15]. Depending on the process conditions, either metal nanoclusters, or mono- or polynuclear complexes of transition metals in different oxidation states can be formed. Most researchers agree that the reactions of the acetylacetonate complexes of Group VIII metals (Fe, Co, Ni, Pd, Pt) with trialkylaluminum yield nanoparticles stabilized by $AlR_2(acac)$ and AlR_3 [16–19]. The redox process between MX_n and AlR_3 (or $AlR_2(OR)$) in the presence of a tertiary phosphine is one of the methods for the synthesis of the hydrido [20, 21], alkyl [22, 23], and nitrogen-containing phosphine complexes of transition metals in different oxidation states [24] and, at $PR_3 : M < 2$, nanoparticles [18]. The coupled hydrogenation of arenes and alkenes in the presence of the cobalt catalysts has been insufficiently studied to date, and the issue of its nature (homogeneous or nanosized) remains unclear.

The purpose of this work is to study the effect of the composition of the $Co(acac)_2$–PR_3–Red catalytic systems ($PR_3 = PBu_3$, PPh_3; Red = reducing agent) and the nature of the conversion products of Co(II) on the coupled hydrogenation of alkenes and arenes in order to discriminate hypotheses about the nature of catalysis in the systems and to establish the main causes the influence of tertiary phosphines on the properties of the cobalt catalysts.

EXPERIMENTAL

The solvents (benzene, toluene, and tetrahydrofuran (THF)), substrate (styrene, hex-1-ene, isoprene, and butadiene), and reactant (*tert*-butanol) were purified according to standard procedures used for organometallic compounds [25]. For deeper drying, benzene and toluene were additionally distilled from $LiAlH_4$ using a fractionation column, and they were stored under argon in sealed ampules over molecular sieve 4A. After the removal of peroxides, THF was successively distilled from sodium, $LiAlH_4$, and benzophenone ketyl and was also kept under argon in sealed ampules. The water concentration in benzene was measured by Fischer's method [26] to be 1.1×10^{-3} mol/L, and that in THF was 1.6×10^{-3} mol/L.

The synthesis of $Co(acac)_2$ was carried out via a standard procedure [27]. The resulting pale pink precipitate was dried in vacuo (45°C/10 Torr), recrystallized from toluene, and sublimed at 140–150°C and a pressure of 1–2 Torr. According to thermoanalytical data, the water content of the complex was 1.12%.

Triethylaluminum was distilled in vacuo (48–49°C/1 Torr). The ^1H NMR spectrum of $AlEt_3$ (C_6D_6 solvent) was characterized by the following parameters: $\delta(CH_3) = 1.22$ ppm (t, 3H, $^1J = 8.24$ Hz), $\delta(CH_2) = 0.45$ ppm (q, 2H, $^1J = 8.24$ Hz). Triethylaluminum was stored in a sealed ampule under argon. Solutions of $AlEt_3$ in hexane or octane were prepared in a Schlenk flask under argon. The concentration of $AlEt_3$ in the solution was determined volumetrically by decomposing an aliquot of the solution with water.

Diethylaluminum acetylacetonate was obtained by the dropwise addition of an acetylacetonate (1 mmol) solution in benzene to a stirred solution of triethylaluminum (1.1 mmol). ^1H NMR (C_6H_6): $\delta = 4.95$ (s, 1H, CH), 1.61 (s, 6H, CH_3), 0.53 (q, 4H, CH_2Al, $^1J = 8.24$ Hz), 1.54 (t, 6H, $^1J = 8.24$ Hz) ppm.

$C_6H_5CH_2MgCl$ was synthesized using a standard procedure by reacting an alkyl halide with magnesium in diethyl ether [28]. Its concentration was determined by titration of an aliquot with a 0.1 M H_2SO_4 solution.

$LiAlH(tert\text{-}BuO)_3$ was synthesized by the alcoholysis of $LiAlH_4$ with *tert*-butanol in THF at 30°C for 48 h [29] at a reactant molar ratio of $tert\text{-}BuOH : LiAlH_4 = 3$. The course of the reaction was monitored by ^{27}Al NMR. The ^{27}Al NMR spectrum (THF as the solvent) exhibited a singlet at $\delta = 78$ ppm.

Tertiary phosphines (PPh_3, PBu_3) (Sigma-Aldrich) were used in experiments. Triphenylphosphine was additionally recrystallized from ethanol. Its ^{31}P NMR spectrum (in C_6H_6) contains a singlet at $\delta = -6$ ppm. Tributylphosphine was distilled in vacuo (100°C/8 Torr). Its ^{31}P NMR spectrum (in C_6H_6) exhibited a singlet at $\delta = -32$ ppm.

The substrates were hydrogenated in a glass temperature-controlled shaker at 30°C and an initial hydrogen pressure of 2 atm (0.20265 MPa) in the presence of a catalytic system formed in situ. A solution of PBu_3 in benzene ($PBu_3 : Co = 3$) and a solution of the reducing agent ($AlEt_3$, $AlEt_2(acac)$, $C_6H_5CH_2MgCl$, or $LiAlH(tert\text{-}BuO)_3$) were successively added to a solution of $Co(acac)_2$ (from 2×10^{-4} to 5×10^{-4} mol in 10 mL of benzene or THF). The Red : Co ratio was varied between 2 and 8 (Red = $AlEt_3$) or between 2 and 20 (Red = $LiAlH(tert\text{-}BuO)_3$). The reaction mixture was stirred for 2–3 min, and styrene (1 mL, 8.7 mmol) or another alkene (alkadiene) was then introduced. The total volume of the solution of was 12 mL. Thereafter, the reactor was sealed with a Teflon stopper with a rubber septum (for sampling), an excess hydrogen pressure (1 atm) was produced, and hydrogenation was carried out. The course of the reaction was monitored by measuring the pressure in the system with a manometer and analyzing the products by gas liquid chromatography on a Chrom-5 chromatograph (Czech Republic) with a flame-ionization detector using nitrogen as the carrier gas. The packed column, 3.6 m in length and 3 mm in diameter, contained the Carbowax 20M phase. The catalyzate composition was determined using the internal standard method.

Table 1. Coupled hydrogenation of benzene and alkenes in the presence of the cobalt catalysts

Catalytic system	Red : Co	Alkene[d]	Amount of alkene, mmol	Amount of C_6H_6 converted, mmol	Product ratio $\frac{C_6H_5C_2H_5}{C_6H_{10} + C_6H_{12}}$	C_6H_{10} formation selectivity, %
$Co(acac)_2$–Bu_3–$AlEt_3$	4	styrene	17.40	2.25	7.7	26.0
$Co(acac)_2$–Bu_3– $AlH(i\text{-}C_4H_9)_2$	4	styrene	17.40	2.70	6.5	22.1
$Co(acac)_2$–PBu_3– $Et_2Al(acac)$	4	styrene	17.40	6.78	2.6	27.0
$Co(acac)_2$–PBu_3–$P(OBu_3)_2$–$AlEt_3$[a]	4	styrene	8.70	8.40	1.1	66.5
$Co(acac)_2$–Bu_3–$C_6H_5CH_2MgCl$[b]	6	styrene	6.87	2.60	2.7	18.0
$Co(acac)_2$–Bu_3– $C_6H_5CH_2MgCl$[c]	6	styrene	8.70	3.80	2.3	13.2
$Co(acac)_2$–PBu_3–$AlEt_3$	4	hex-1-ene	5.40	0.70	7.7	5.3
$Co(acac)_2$–PBu_3–$AlEt_3$	4	butadiene	0.80	0.60	1.3	7.5
$Co(acac)_2$–PBu_3–$AlEt_3$	4	isoprene	5.10	0.65	7.8	12.3

Note: $C_{Co} = 1 \times 10^{-2}$ mol/L, $PR_3 : Co = 3$; solution volume, 20 mL; amount of C_6H_6, 5.03×10^{-2} mol; heptane solvent; $P_{H_2} = 2$ atm, 30°C.

[a] $PBu_3 : P(OBu_3) = 0.5$.

[b] $T = 20$°C.

[c] $T = 7$°C.

[d] Conversion of alkene and alkadiene is 100%.

The reaction of $Co(acac)_2$ with $AlEt_3$ or another reducing agent ($LiAlH(tert\text{-}BuO)_3$, $AlH(i\text{-}Bu)_2$) at different ratios of the starting components in the presence of a tertiary phosphine was studied in an anhydrous deoxygenated hydrogen atmosphere. For example, a solution (1 mL) of tributylphosphine (1.8 mmol) in benzene was poured dropwise to a stirred solution of $Co(acac)_2$ (0.1542 g, 0.6 mmol) in benzene (4 mL). The resulting solution was cooled to 0°C, and a solution (1 mL) of a reducing agent in benzene (Red = $AlEt_3$, $AlH(i\text{-}Bu)_3$) or in THF (Red = $LiAlH(tert\text{-}BuO)_3$) was added. The Red : Co molar ratio was varied between 2 and 4. The solution thus prepared, placed in an argon-purged and then sealed KBr cell with an optical path length of 0.112 mm, was analyzed on an FT-801 IR spectrometer (Simex, Novosibirsk, Russia). NMR studies were carried out in a similar way, using benzene-d_6 or THF-d_8 as the solvent. ^1H, ^{31}P, and ^{27}Al NMR spectra were recorded on a VXR-500S pulse spectrometer (Varian, United States). Chemical shifts of ^{27}Al signals were measured relative to an external standard (0.1 mol/L $Al(NO_3)_3$ solution). The ^{31}P chemical shifts are presented relative to 85% phosphoric acid, with their positive values corresponding to downfield shifts.

RESULTS AND DISCUSSION

It was earlier shown [30] that benzene is hydrogenated to cyclohexane in the presence of the $Co(acac)_2$–$AlEt_3$ catalytic system under mild conditions (30°C, $P_{H_2} = 2$ atm). The reaction occurs on cobalt nanoclusters 2–5 nm in diameter, which are formed under the hydrogenation conditions from the paramagnetic cobalt(0) complexes [19]. If $Co(acac)_2$ is reduced with triethylaluminum in the presence of tributylphosphine ($PBu_3 : Co = 3$), benzene hydrogenation occurs only over 4–5 min. This might seem to be reasonable attributable to the rapid deactivation of the catalyst. However, the hydrogenation of both styrene and benzene resumes after styrene is introduced into the $Co(acac)_2$–PBu_3–$AlEt_3$ catalytic system. The ratio of the hydrogenation products of unsaturated hydrocarbon and benzene, catalytic activity, and productivity depend on the nature of the reductant of the cobalt precursors. When an organoaluminum compound is used as the $Co(acac)_2$ reductant, the benzene conversion increases in the following order: $AlEt_3 < AlH(i\text{-}C_4H_9)_2 < AlEt_2(acac)$ (Table 1). In the presence of the $Co(acac)_2$–PBu_3–$AlEt_2(acac)$ system, the turnover frequency (TOF) in benzene hydrogenation calculated from the rate of benzene conversion within the initial 20 min (when the rate remains unchanged) is three times higher than in the case of the catalyst containing $AlEt_3$ as the reducing agent (Fig. 1). In addition, the replacement of $AlEt_3$ by $AlEt_2(acac)$ considerably extends the stable service life of the catalyst. In the presence of the $Co(acac)_2$–PBu_3–$AlEt_3$ catalytic system, the rate of benzene hydrogenation decreases sharply upon the introduction of additional portions of styrene (after the completion of the hydrogenation of the previous portion), whereas the decrease is insignificant when $AlEt_2(acac)$ is used.

Thus, use of $Et_2Al(acac)$ as the reducing agent affords a threefold increase in the benzene hydrogena-

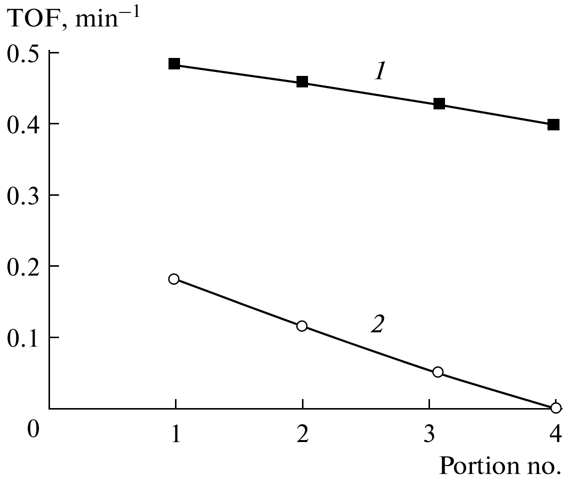


Fig. 1. Change in the turnover frequency of benzene hydrogenation coupled with styrene hydrogenation in the presence of the $Co(acac)_2$–$3PBu_3$–4Red catalytic systems, where Red is (*1*) $AlEt_2(acac)$ and (*2*) $AlEt_3$, with successive introduction of 1-mL portions of styrene. C_{Co} = 0.01 mol/L, Al : Co = 4, P_{H_2} = 1.5 atm, 30°C.

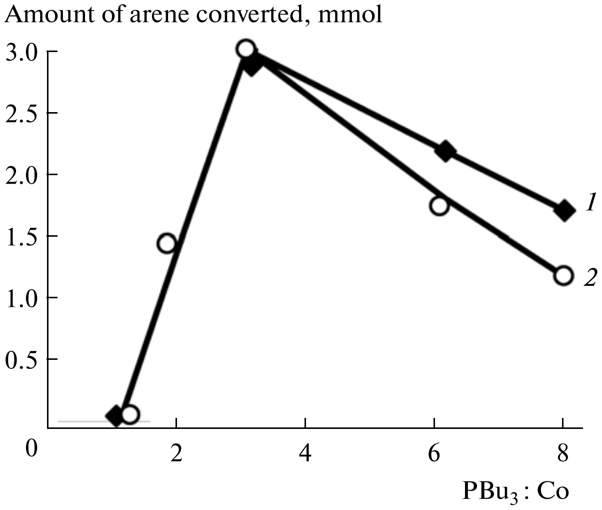


Fig. 2. Effect of the PBu_3 : Co molar ratio on the amount of (*1*) benzene and (*2*) toluene converted in the course of their coupled hydrogenation with styrene in the presence of the $Co(acac)_2$–PBu_3–$AlEt_3$ catalytic system; C_{Co} = 0.01 mol/L, Al : Co = 4, 30°C.

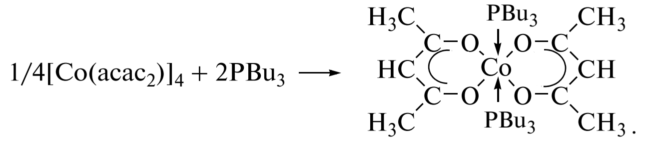
tion rate in the process coupled with styrene hydrogenation, an enhancement of the stability of the $Co(acac)_2$–PBu_3–$AlEt_2(acac)$ catalytic system compared to the $Co(acac)_2$–PBu_3–$AlEt_3$ system, and, as a consequence, an increase in the TOF of the reaction. However, $Et_2Al(acac)$ exerts almost no effect on the cyclohexene formation selectivity. As follows from Table 1, the $Co(acac)_2$–PBu_3–Red (Red = $AlEt_3$, $AlH(i\text{-}C_4H_9)_2$, and $AlEt_2(acac)$) catalytic systems are characterized by similar values of cyclohexene formation selectivity. If tributylphosphine is partially replaced by tributyl phosphate (in a ratio of 1 : 2), the selectivity increases to 66.5%, while the reaction rate decreases by a factor of 3. The increase in the selectivity of the process with the sharp decrease in its rate is not due to catalyst deactivation, because the conversion of benzene in this system is higher than in the $Co(acac)_2$–PBu_3–$AlEt_3$ system. Both the benzene conversion and cyclohexene formation selectivity decrease when styrene is replaced by hex-1-ene, isoprene, or butadiene (Table 1).

The PBu_3 : Co and Red : Co molar ratios exert a significant effect on the process considered. The coupled hydrogenation of styrene and benzene in the presence of the $Co(acac)_2$–PBu_3–Red catalytic systems was studied at PBu_3 : Co ≥ 2 (Fig. 2). At PBu_3 : Co < 2, only the hydrogenation of styrene to ethylbenzene occurs. This suggests that the complexes active in coupled hydrogenation most likely contain two tributylphosphine molecules in the coordination sphere of cobalt. Note that, as the PBu_3 : Co molar ratio is increased, the selectivity of the $Co(acac)_2$–PBu_3–$AlEt_3$ catalytic system in benzene conversion to cyclohexene increases from 25–26% for PBu_3 : Co = 3 to 35% for PBu_3 : Co = 6. The optimum Red : Co ratio that maximizes the rate of hydrogenation of both substrates depends on the nature of the reducing agent. In the case of triethylaluminum, this ratio is 4 (Figs. 3a, 3b). The benzene hydrogenation rate decreases sharply with a further increase in the Al : Co ratio, and only styrene is reduced at Al : Co = 8. An extremum in dependence of TOF on the reactant ratio (Red : Co) was earlier observed for Ziegler catalysts formed under the action of trialkylaluminum in the absence of tertiary phosphines [14, 15, 18]. The poisoning effect of excess $AlEt_3$ can be due to several factors. On the one hand, if metal nanoclusters form in the system considered, as in the MX_n–AlR_3 system, the inhibiting effect is most likely explained by the blocking of the active centers because of the formation of surface compounds. On the other hand, since the coupled hydrogenation of styrene and benzene occurs only in the presence of tributylphosphine at PBu_3 : Co ≥ 2 and the $Co(acac)_2$–PBu_3–$AlEt_3$ system contains both a Lewis acid and a Lewis base, the inhibiting effect of excess triethylaluminum can be caused by the displacement of tributylphosphine molecules from the coordination sphere of the catalytically active cobalt complexes via the interaction between PBu_3 and $AlEt_3$, which yields an adduct and thau changes the nature of catalytic activity carriers.

This hypothesis is consistent with the experimental results for the $Co(acac)_2$–PBu_3–$LiAlH(tert\text{-}BuO)_3$ system (Table 2). The fundamental distinction between the cobalt catalysts, whose formation involves $LiAlH(tert\text{-}BuO)_3$, and the organoaluminum compounds is that the reducing agent does not exert an inhibition effect up to Red : Co = 20. The total rate of coupled styrene and benzene hydrogenation in the presence of the $Co(acac)_2$–PBu_3–LiAlH(*tert*-BuO)$_3$ system increases sharply as the LiAlH(*tert*-BuO)$_3$: Co ratio increases from 1 to 5 and slowly increases as this ratio further increases to 20 (Fig. 4). The average rate of benzene hydrogenation is maximum at LiAlH(*tert*-BuO)$_3$: Co = 10.

The systems considered were studied by spectroscopic methods in order to discriminate the hypotheses about the nature of catalytic activity carriers.

Cobalt bis(acetylacetonate) exists in benzene solution as the tetranuclear association species $[Co(acac)_2]_4$, which interacts with tributylphosphine to form the $Co(acac)_2(PBu_3)_2$ complex [10]:



The introduction of triethylaluminum into a $Co(acac)_2$–$3PBu_3$ solution under argon changes the color of the solution from blue to dark brown. The brown color of the solutions for the reduction of transition metal compounds in the Ziegler systems is an indirect indication of the formation of metal nanoclusters [2]. However, the ^1H NMR spectrum of the $Co(acac)_2$–$3PBu_3$–$4AlEt_3$ reaction system contains a resonance signal in the strong field at $\delta = -20.9$ ppm (q, $^2J_{P-H} = 49$ Hz). The appearance of the resonance signal in this region is characteristic of transition metal hydrido complexes, and the splitting of the signal indicates that the coordination sphere of cobalt includes three tributylphosphine ligands. The ^1H NMR spectrum of the $Co(acac)_2$–$3PPh_3$–$4AlEt_3$ reaction system, with PBu_3 replaced by PPh_3, in argon also contains a resonance signal in the strong field at $\delta = -19.8$ ppm (q, $^2J_{P-H} = 51$ Hz), indicating the formation of a cobalt hydrido complex with three PPh_3 ligands. The presence of a doublet with a chemical shift of 47 ppm (d, $^2J_{P-H} = 50$ Hz) in the ^{31}P NMR spectrum of this reaction system indicates the formation of a cobalt monohydrido complex with three triphenylphosphine ligands. It should be mentioned that a similar chemical shift, $\delta = -19$ ppm (q, $^2J_{P-H} = 50$ Hz), was also observed in the ^1H NMR spectrum of the cobalt monohydrido complex $Co(H)(N_2)(PPh_3)_3$ with a trigonal bipyramid structure [31, 32]. At the same time, the cobalt carbonyl hydrido complexes $CoH(CO)(PR_3)_3$ (R = Ph, $PMePh_2$) with a similar structure, but with a strong electron-withdrawing ligand (CO), are characterized by a chemical shift of –13 ppm (q, $^2J_{P-H} = 50$ Hz) in the ^1H NMR spectrum [33].

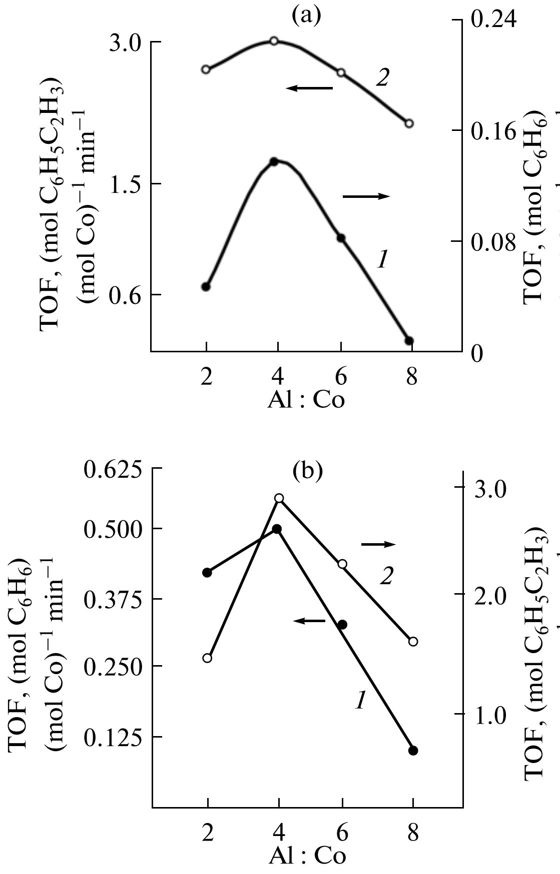


Fig. 3. Effect of the Red : Co molar ratio on the turnover frequency of the coupled hydrogenation of (*1*) benzene and (*2*) styrene in the presence of the $Co(acac)_2$–PBu_3–Red catalytic system, where Red is (a) $AlEt_3$ and (b) $AlEt_2(acac)$; $C_{Co} = 0.01$ mol/L, [styrene] = 0.45 mol/L, PBu_3 : Co = 3, $P_{H_2} = 1.5$ atm, 30°C.

The spectrum changes if a hydride derivative (AlH(*i*-Bu)$_2$, LiAlH(*tert*-BuO)$_3$) is used as the reducing agent for the cobalt(II) phosphine complexes: the resonance signals from the cobalt hydrido complexes appear predominantly between –13 and –14 ppm. In particular, the spectrum of the $Co(acac)_2$–$3PBu_3$–AlH(*i*-Bu)$_2$ system exhibits a quartet at $\delta = -13.4$ ppm, which is transformed into a singlet upon broadband phosphorus decoupling, indicating that the proton interacts with the three equivalent phosphorus nuclei. The resonance signals in the strong field in the spectra of the $Co(acac)_2$–$3PR_3$–4LiAlH(*tert*-BuO)$_3$ reaction systems (R = Bu, Ph) appear at $\delta = -13.6$ ppm (q, $^2J_{P-H} = 37$ Hz) for tributylphosphine and at $\delta = -12.8$ ppm (q, $^2J_{P-H} = 45$ Hz) for triphenylphosphine. It should be mentioned that, in this case, the cobalt hydrido complexes formed under the action of the aluminum hydride derivatives have similar spectral characteristics regardless of the nature of the phosphine ligand. The considerable difference between the chemical shifts in the spectra of the cobalt hydrido complexes obtained under the action of triethylaluminum and a hydride derivative (LiAlH(*tert*-BuO)$_3$ or AlH(*i*-Bu)$_2$) is possibly due to the different symmetries of the resulting cobalt complexes. Cobalt phosphine monohydrido complexes ($Co(H)(N_2)(PR_3)_3$ [22, 31], $Co(H)(CH_2{=}CH_2)(dppe)_2$ [34], and $Co(H)(PR_3)_4$

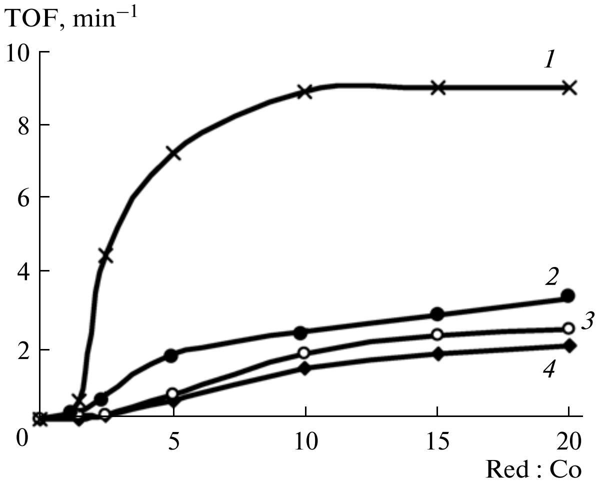


Fig. 4. Initial rates of styrene and benzene hydrogenation in the presence of the $Co(acac)_2$–PBu_3–LiAl(*tert*-BuO)$_3$ catalytic system vs. LiAl(*tert*-BuO)$_3$: Co molar ratio upon the successive introduction of the (*1*) first, (*2*) second, (*3*) third, and (*4*) fourth 1-mL portions of styrene; $C_{Co} = 1.67 \times 10^{-2}$ mol/L, $P_{H_2} = 2$ atm, 30°C.

[23]) and a trihydrido complex ($H_3Co(PR_3)_3$ [21]) are known. Most of the hydrido complexes, whose structure was proved by X-ray diffraction, were not characterized previously by NMR because of their low solubility and the insufficient sensitivity of the spectrometers [34, 35]. The signals from the hydrides of the $H_3Co(PPh_3)_3$ complex synthesized using a standard procedure [21] were detected in the ^1H NMR spectrum of a benzene solution at $\delta = -11.8$ ppm, and in the ^{31}P NMR spectrum they occur at 68 ppm. The hydride ions of the iron trihydrido complex PhBP(*i*-Pr)$_3$Fe(H)$_3$ show themselves in the same spectral region ($\delta = -12.4$ ppm, q, $^3J_{P-H} = 7.3$ Hz) [36].

Note that the ^{31}P NMR spectrum of the $H_3Co(PPh_3)_3$ complex under argon contains the resonance signal at 68 ppm and also broad low-intensity signals corresponding to the phosphorus nuclei in the cobalt monohydrido complex with PPh_3 ligands (δ = 47 ppm) and in free triphenylphosphine ($\delta = -6$ ppm). Similar ^{31}P NMR characteristics were also observed for the $Co(acac)_2$–$4PPh_3$–Red reaction solution (Red = LiAlH(*tert*-BuO)$_3$ or AlH(*i*-Bu)$_2$). The interaction of the components was also studied under a hydrogen atmosphere in order to bring the analysis conditions closer to the real conditions of the catalytic reaction. The reduction of $Co(acac)_2$ by triethylaluminum or diethylethoxyaluminum under hydrogen in the presence of a tertiary phosphine (PPh_3, PBu_3) also results in the formation of cobalt hydrido complexes. Along with the resonance signal in the range from –20 to –21 ppm, the ^1H NMR spectrum contains an unresolved broad signal between –12.1 and –12.2 ppm. The broadening of the ^1H and ^{31}P NMR signals can be due to several factors, namely, the presence of paramagnetic species, inter- or intramolecular exchange, and the formation of a microheterogeneous system. Since all of the signal undergo broadening, the main causes are likely the inter- or intramolecular exchange and the presence of paramagnetic cobalt complexes in the solution.

Thus, the NMR study of the $Co(acac)_2$–PR_3–Red catalytic systems showed that they involve the formation of cobalt hydrido complexes, whose nature depends considerably on whether the reducing agent contains the hydride ion. The interaction of the components of the catalytic systems was studied by IR spectroscopy to gain additional information. Since the gas atmosphere in the process (Ar, H_2, N_2) affects the composition of the resulting cobalt complexes, the IR spectra were recorded under different conditions. Absorption bands at 1585, 1533, 1380, and 1296 cm^{-1}, which are characteristic of vibrations of the acac ligand in $AlEt_2(acac)$, were detected in the spectrum of the $Co(acac)_2$–$3PPh_3$–$4AlEt_3$ reaction system under argon 5 min after the mixing of the components [18, 19]. The absence of the characteristic absorption bands of these ligands in the spectrum of $Co(acac)_2$ (1592, 1520, and 1259 cm^{-1}) indicates their almost quantitative transfer from cobalt to aluminum. In addition to the absorption bands listed above, the IR spectrum also includes bands at 1484, 1434, 774, and 744 cm^{-1}

Table 2. Coupled hydrogenation of benzene and styrene in the presence of the $Co(acac)_2$–PBu_3–LiAlH(*tert*-BuO)$_3$ catalytic system

Red : Co	Amount of substrate converted, mmol		Product ratio $\frac{C_6H_5C_2H_5}{C_6H_{10} + C_6H_{12}}$	Cyclohexene formation selectivity, %
	styrene	C_6H_6		
2.5	17.4	1.3	13.9	18.5
5	26.1	2.2	11.7	8.8
10	34.8	3.3	10.5	7.5
15	68.0	3.2	21.6	5.3
20	52.2	2.5	21.0	5.7

Note: $C_{Co} = 2 \times 10^{-2}$ mol/L; PBu_3 : Co = 3; solution volume, 25 mL; amount of C_6H_6, 5.03×10^{-2} mol, heptane solvent; $P_{H_2} = 2$ atm; 30°C.

corresponding to vibrations of the phenyl moiety in PPh_3 and also weak bands similar in intensity at 2130 and 2090 cm^{-1} (Fig. 5).

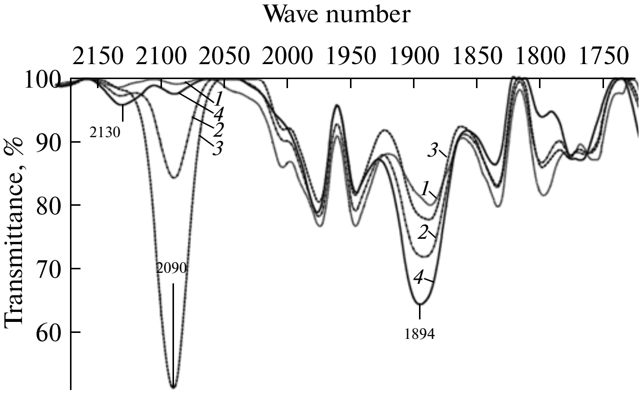


Fig. 5. IR spectra of the of the $Co(acac)_2–3PPh_3–4AlEt_3$ reaction system in benzene recorded (*1*) 30 and (*2*) 15 min after the beginning of the reaction under an argon atmosphere, (*3*) 30 min after argon was replaced by nitrogen, and (*4*) after another purging of the solution with argon; $C_{Co} = 0.10$ mol/L, 25°C.

The presence of an absorption band at 2090 cm^{-1} in the spectrum of the $Co(acac)_2–3PPh_3–4AlEt_3$ reaction system formed in argon was unexpected, because the N≡N stretching vibrations in the nitrogen-containing triphenylphosphine cobalt complexes show themselves in this region [21, 23, 24, 31, 33]. A similar spectrum was observed for the process under helium. When helium is replaced by nitrogen, the absorption band intensity at 2090 cm^{-1} in the IR spectrum of the $Co(acac)_2–3PPh_3–4AlEt_3$ reaction system formed under helium (or argon)increases sharply (by a factor of ~30) and the intensity of the band at 2130 cm^{-1} in this spectrum decreases considerably. The reverse replacement of nitrogen by helium or argon induces opposite changes: the intensity of the band at 2090 cm^{-1} decreases by a factor of ~10 and that of the band at 2130 cm^{-1} increases by a factor of ~6. The intensity ratio of the bands at 2090 and 2130 cm^{-1} takes the initial value. The band at 1894 cm^{-1} also appears in the spectrum (Fig. 5). Absorption bands at 2090 and 2130 cm^{-1} with an intensity ratio close to 2 were detected at the initial moment in the IR spectrum in experiments on the interaction of the components of the $Co(acac)_2–3PPh_3–4AlEt_3$ catalytic system directly under argon. Within 1 h, the intensity of the band at 2090 cm^{-1} increased by a factor of ~10 and that of the band at 2130 cm^{-1} decreased by a factor of ~6 times. Within the next 2 h, the intensity of the former band increased by a factor of 5 and that of the latter decreased to zero. The replacement of nitrogen by helium or argon was again accompanied by a decrease in the intensity of the band at 2090 cm^{-1} and an increase in the intensity of the band at 2130 cm^{-1} and the appearance of an absorption band at 1890 cm^{-1}.

The observed correlation between the spectroscopic data and the composition of the gas atmosphere, with the relevant literature taken into account, data, suggests the IR band assignment presented in Table 3. The absorption band at 2090 cm^{-1} is usually attributed to the stretching vibrations of the N≡N bond of coordinated nitrogen in the cobalt complexes with triphenylphosphine ligands $Co(H)(N_2)(PPh_3)_3$ [23, 35]. However, there is another opinion [31]. Although the band of the M–H bond was not detected in the spectra of some hydrido complexes of transition metals, the IR spectrum of a suspension of single crystals of the $Co(H)(N_2)(PPh_3)_3$ complex in Nujol exhibited two intense bands at 2100 and 2085 cm^{-1}, which were assigned to the stretching vibrations of the N≡N and Co–H bonds [31]. The high-frequency 100–200 cm^{-1} shift of the Co–H band can be due to the *trans*-arrangement of hydrogen with respect to nitrogen [31]. The bands at 2100 and 2083 cm^{-1} were assigned [23] to the crystal effect, since only one band at 2088 cm^{-1} was detected in the spectrum of a solution of the $Co(H)(N_2)(PPh_3)_3$ complex. Based from the structure of the $Co(H)(N_2)(PPh_3)_3$ complex determined by X-ray diffraction [31], one can suggest that the vibrations of the N≡N and Co–H bonds occur along one axis and are coupled to each other through the cobalt atom. The frequencies of these vibrations are close. This suggests that a joint vibration of the N≡N and Co–H bonds appears, and the intensity of the corresponding band is mainly determined by the change in the dipole moment of the N≡N bond, since the integral intensity of the same band in the spectrum of the $Fe(N_2)(H_2)(PPh_3)_3$ complex is 4.9×10^4 L mol^{-1} cm^{-2} [24].

Based on the aforesaid, we assigned the absorption band at 2090 cm^{-1} to the joint vibration of the N≡N and Co–H bonds, although its intensity and shape are mainly determined by the N≡N bond vibration. In our opinion, the splitting of this band into absorption bands at 2100 and 2083 cm^{-1} [23, 31] is due to the separation of the joint vibration into two joint vibrations under the action of the crystal field. These two joint vibrations may differ in the ratio of contributions introduced into them by a change in the N≡N and Co–H bond lengths. In addition, these changes may be cophasal or noncophasal. Note that, for the $Co(H)(N_2)(PPh_3)_3$ complex synthesized according to a standard procedure under nitrogen [31], a weakly pronounced shoulder at 2130 cm^{-1} is detected along with the fairly intense band at 2090 cm^{-1} corresponding to the vibrations described above. Since the stretching bands of the Co–H bond in the spectra of the $Co(H)(PR_3)_4$ cobalt monohydrido complexes (in the solid phase) shift to higher frequencies with a decreasing basicity of the phosphine ligand ($\nu_{Co–H}$ in the spectra of $Co(H)(Me_2PPh)_4$ and $Co(H)(MePPh_2)_4$ are 1880 and 1958 cm^{-1}, respectively) [37], we assigned the band at 2130 cm^{-1} to the stretching vibrations of the Co–H bond in the monohydrido complex $Co(H)(PPh_3)_3(Solv)$, where Solv is solvent. The numerical value of the frequency of the absorption

Table 3. Assignment of absorption bands in the IR spectra of the $Co(acac)_2$–$3PR_3$–$4AlEt_3$ systems

Catalytic system	Gas atmosphere	ν, cm^{-1}		Assumed complex
		N≡N + Co–H	Co–H	
$Co(acac)_2$–PPh_3–$4AlEt_3$	Ar, He or N_2	2090		$Co(H)(N_2)(PPh_3)_3$
			2130	$Co(H)(PPh_3)_3(Solv)$
			1894	$[Co(H)(PPh_3]_n$
$Co(acac)_2$–$3PBu_3$–$4AlEt_3$	Ar, He or N_2	2045		$Co(H)(N_2)(PBu_3)_3$
			2065	$Co(H)(PBu_3)_3(Solv)$
			1884	$[Co(H)(PBu_3)_3]_n$
$Co(acac)_2$–$3PPh_3$–$4AlEt_3$	H_2	2090		$Co(H)(N_2)(PPh_3)_3$
			2130	$Co(H)(PPh_3)_3(Solv)$
			1894	$[Co(H)(PPh_3]_n$
			1754	$H_3Co(PPh_3)_3$
$Co(acac)_2$–$3PBu_3$–$4AlEt_3$	H_2	2045		$Co(H)(N_2)(PBu_3)_3$
			1717	$H_3Co(PBu_3)_3$
			1884	$[Co(H)(PBu_3)_3]_n$

band at 1894 cm^{-1} and an increase in its intensity upon the replacement of nitrogen by helium or argon allow one to assign this band to the stretching vibrations of the Co–H bridging bond in the association species resulting from the dissociation of the $Co(H)(N_2)(PPh_3)_3$ complex in the solution

$$Co(H)(N_2)(PPh_3)_3$$
$$\xleftrightarrow[-N_2]{} Co(H)(PPh_3)_3 \longleftrightarrow 1/n[Co(H)(PPh_3)_3]_n.$$

Therefore, the reduction of $Co(acac)_2$ by triethylaluminum in the presence of triphenylphosphine in an inert gas (helium, argon) or nitrogen atmosphere affords the cobalt monohydrido complexes $Co(H)(N_2)(PPh_3)_3$ and $Co(H)(PPh_3)_3(Solv)$ and the association species $[Co(H)(PPh_3)_3]_n$. The ratio of their concentrations is determined by the process conditions. It follows from the experimental data that, under the conditions of the dominant formation of the $Co(H)(PPh_3)_3(Solv)$ complex, the band at 2130 cm^{-1} is many times weaker than the band at 2090 cm^{-1} in under the conditions of the dominant formation of the $Co(H)(N_2)(PPh_3)_3$ complex. This confirms the determining role of the contribution from the N≡N bond vibrations to the intensity of the band at 2090 cm^{-1}. The formation of the cobalt monohydrido complex $Co(H)(N_2)(PPh_3)_3$ in argon or helium is probably due to the presence of traces of nitrogen in these gases and on the walls of the reactor. The reduction of $Co(acac)_2$ by triethylaluminum in helium (or argon) in the presence of PBu_3 results in the appearance of a weak absorption band at 2045 cm^{-1} (Fig. 6) in the IR spectrum of the solution of $Co(acac)_2$–$3PBu_3$–$4AlEt_3$ in the 1800–2100 cm^{-1} range. This band is characteristic of the cobalt monohydrido complex $Co(H)(N_2)(PBu_3)_3$ [23]. During the purging of the reaction solution with argon, the intensity of the absorption band at 2045 cm^{-1} decreased, which was accompanied by the appearance of a band at 2065 cm^{-1} in the high-frequency region and a band at 1884 cm^{-1}. The replacement of argon by nitrogen or performing the process under a nitrogen atmosphere increased the intensity of the absorption band at 2045 cm^{-1} by a factor of 30. The opposite situation is observed for the back replacement of nitrogen by argon (Fig. 6). Based on the above considerations, we ascribed the absorption band at 2045 cm^{-1} to the joint vibration of the N≡N and Co–H bonds in the $Co(H)(N_2)(PBu_3)_3$ complex, and the band at 2065 cm^{-1} was assigned to the Co–H stretching vibrations in the $Co(H)(PBu_3)_3(Solv)$ monohydrido complex. The slight change in the absorption band intensity at 1884 cm^{-1}, depending on the reaction conditions, indicates weak association between the cobalt monohydrido tributylphosphine complexes, as distinct from the triphenylphosphine hydrido complexes (Fig. 6).

A band at 1754 cm^{-1} is present in the IR spectrum of the $Co(acac)_2$–$3PPh_3$–$4AlEt_3$ reaction system in hydrogen along with the absorption bands at 2090, 2130, and 1894 cm^{-1} corresponding to stretching vibrations of the cobalt monohydrido complexes $Co(H)(N_2)(PPh_3)_3$ and $Co(H)(PPh_3)_3(Solv)$ and their association species $[Co(H)(PPh_3)_3]_n$. The intensities of the bands at 2090, 2130, and 1894 cm^{-1} decrease and that of the band at 1754 cm^{-1} increases during the process. In the system with tributylphosphine, the replacement of argon or helium by hydrogen exerts only an insignificant effect on the spectral characteristics of the $Co(acac)_2$–$3PBu_3$–$4AlEt_3$ system: an absorption band of the Co–H stretching vibrations appears at 2045 cm^{-1} and the intensity of the band at 1717 cm^{-1} increases slightly. It is known that the trihydrido complex $H_3Co(PPh_3)_3$ can result from the substitution of hydrogen for nitrogen in the $Co(H)(N_2)(PPh_3)_3$ monohydrido complex [23, 35]:

$$Co(H)(N_2)(PPh_3)_3 + H_2 \leftrightarrow H_3Co(PPh_3)_3 + N_2.$$

The stretching vibrations of the Co–H bond in the $H_3Co(PPh_3)_3$ complex synthesized via the procedure reported by Sacco and Rossi [21] show themselves in the IR spectrum in Nujol at 1745 (s) and 1934 (m) cm^{-1}, which is in agreement with the literature [35]. In a benzene solution of the $H_3Co(PPh_3)_3$ complex, the Co–H vibration is detected at 1754 cm^{-1}. The second band of the Co–H stretching vibrations is overlapped with the band at 1945 cm^{-1} from overtones of benzene.

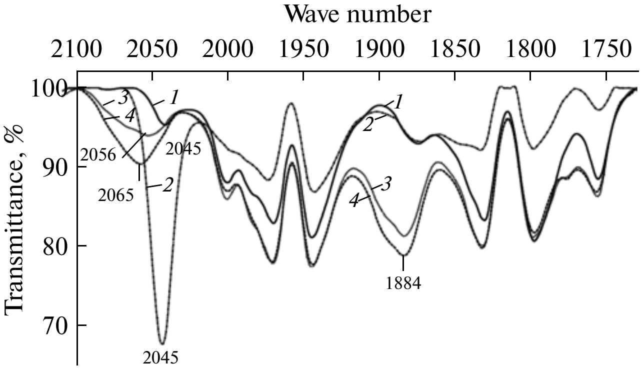


Fig. 6. IR spectra of the of the $Co(acac)_2$–$3PBu_3$–$4AlEt_3$ reaction system in benzene recorded (*1*) 20 min after the beginning of the reaction under an argon atmosphere, (*2*) after argon was replaced by nitrogen, and (*3*) 30 and (*4*) 120 min after the beginning of the second purging of the solution with argon; $C_{Co} = 0.10$ mol/L, 25°C.

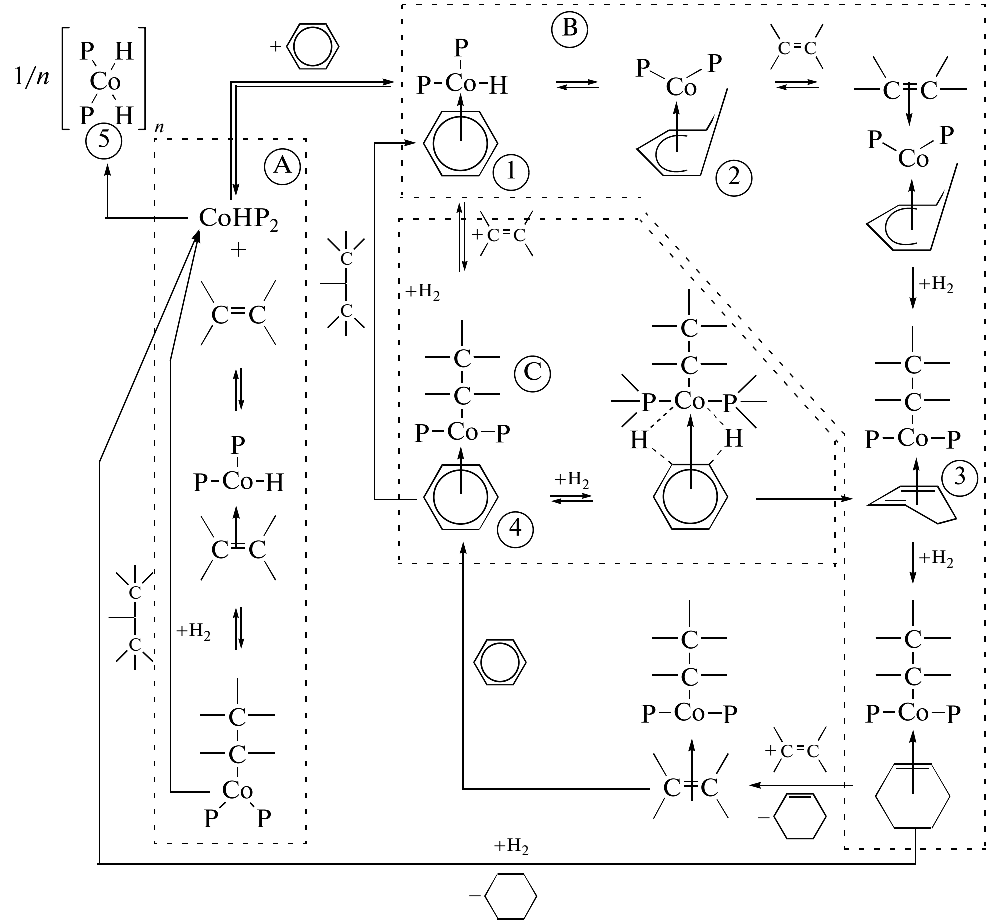
Thus, the study of the $Co(acac)_2$–$3PR_3$–4Red catalytic systems by IR and NMR spectroscopy showed that the reactions of the components both in the presence of tributylphosphine and in the presence of triphenylphosphine yield the cobalt monohydrido and/or trihydrido complexes, whose composition depends on the choice of tertiary phosphine, but is mainly determined by the nature of the reducing agent and the gas atmosphere in the reaction medium. The formation of the cobalt hydrido phosphine complexes in the $Co(acac)_2$–$3PR_3$–4Red systems radically distinguishes them from the classical Ziegler systems, in which metal nanoclusters form due to reduction. Of course, the cobalt nanoclusters forming in the $Co(acac)_2$–$AlEt_3$ system are active in the hydrogenation of various substrates (both benzene and styrene) under mild conditions [14, 19]. It is seemingly reasonable to assume that these nanoclusters, even if they form in insignificant amounts along with the cobalt hydrido complex in the $Co(acac)_2$–$3PR_3$–4Red system, are responsible for the catalytic styrene and benzene hydrogenation reactions, which should compete in this case. If this were so, benzene hydrogenation would occur in the absence of the alkene as well, but this contradicts the experimental data. This fact and the finding that benzene hydrogenation in the $Co(acac)_2$–$3PBu_3$–$6C_6H_5CH_2MgCl$ system also occurs in the absence of styrene and the nature of tertiary phosphine substantially affects the process suggests that the catalytic cycle includes the σ-alkyl cobalt complex formation stage rather than occurring on active surface sites of the cobalt nanoclusters formed in the classical Ziegler systems. In the framework of the proposed hypothesis, the more rapid deactivation of the $Co(acac)_2$–PBu_3–$AlEt_3$ system during benzene hydrogenation in the absence of the alkene compared to the deactivation of the cobalt nanoclusters formed in the $Co(acac)_2$–$AlEt_3$ system can be attributed to the change in the character of catalysis. Since the redox process involving $Co(acac)_2$ and triethylaluminum in the presence of PBu_3 proceeds through alkyl complexes of Co(I) with the tributylphosphine ligands [22], they are probably responsible for the hydrogenation of arenes in the $Co(acac)_2$–PBu_3–$AlEt_3$ system in the absence of styrene.

In spite of the spectral and catalytic studies carried out, the cause of the determining effect of the phosphine nature on the coupled hydrogenation of alkenes with arenes in the $Co(acac)_2$–$3PBu_3$–4Red catalytic system remains unclear. The available experimental data array does not allow one to unambiguously elucidate the causes of the influence of the tertiary phosphine nature on the activity of the $Co(acac)_2$–$3PR_3$–4Red system in coupled alkene and arene hydrogenation. In our opinion, at least three factors play the most important role. Firstly, trialkylphosphines are stronger bases than triarylphosphines and, therefore, they should induce a significant *trans* effect. Therefore, one of the causes of the effect of the tertiary phosphine nature can be the electronic factor, namely, the enhancement of the Co–H bond strength upon the replacement of tributylphosphine (stronger base) by triphenylphosphine. This conception is consistent with the IR spectroscopic data. Secondly, the steric factor cannot be neglected, since the conic angle in PBu_3 (129°) is smaller than that in PPh_3 (145°) [38]. In addition, triphenylphosphine has a more rigid structure. Thirdly, the cobalt hydrido complexes with triphenylphosphine ligands are more prone to association.

The NMR and IR spectroscopic identification of the cobalt hydrido complexes with phosphine ligands along with the results of catalytic experiments suggests the homogeneous character of the process and allows one to propose (taking into account published and earlier obtained data) the most probable reaction mechanism. In a hydrogen atmosphere, the reaction system contains an equilibrium mixture of the mono- and trihydrido (coordinatively saturated) cobalt complexes:

$$\begin{tikzcd}
\mathrm{Co(acac)_2 + 3PBu_3 + Red} \arrow[r] & \mathrm{Co(H)(PBu_3)_3} \arrow[r, shift left, "H_2"] \arrow[d, shift left] & \mathrm{Co(H)_3(PBu_3)_3} \arrow[l, shift left] \\
& \mathrm{Co(H)(PBu_3)_2 + PBu_3.} \arrow[u, shift left] &
\end{tikzcd}$$

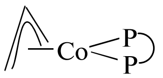
The reaction of the cobalt monohydrido complex with the alkene or alkadiene yields the cobalt σ-alkyl or σ-alkenyl complex, respectively, with two phosphorus-containing ligands. In our opinion, it is this complex that is the active species in benzene hydrogenation. The specified stages ensure the kinetic coupling of the hydrogenation reactions of alkenes (alkadienes) and arenes. As was established by the kinetic studies, the reactions are first-order with respect to hydrogen and cobalt, and their order with respect to benzene is close to zero [30]. The kinetic isotope effect observed [39] for benzene hydrogenation in the presence of the π-$C_3H_5Co[P(OC_3H_7)_3]_3$ complex ($k_H/k_D = 1.4$–1.5), with the first order with respect to hydrogen taken into account, suggests that hydrogen is involved in the rate-determining step. However, since, the isotope effect is weak and the hydrogenation rate decreases with an increasing number of cyclic structures in the arene, it can be assumed that the concerted addition of hydrogen to the complex containing arene as a ligand occurs in the rate-determining step. Based on the aforesaid, we propose the following mechanism for the coupled hydrogenation of alkenes with arenes.



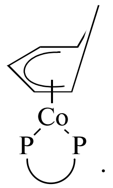
Here P is tributylphosphine and several stages (oxidative hydrogen addition) are omitted for simplicity.

Route A includes two-step hydrogen transfer to the unsaturated bond and corresponds to the commonly accepted scheme of the mechanism of alkene hydrogenation in the presence of metal complex catalysts.

Route B predicts the transformation of cobalt hydrido complex 1 with two phosphine ligands into complex 2 with the cyclohexadienyl ligand in the coordination sphere of cobalt. The possibility of this stage taking place was convincingly proved [40] by the finding that the reaction of the π-allyl cobalt complex



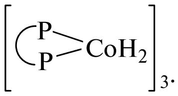
($\overset{\frown}{P\;\;P}$ = $Cy_2PC_2H_4PCy_2$, Cy = cyclohexyl) with hydrogen under mild conditions at 20°C results in the hydrogenation of the allyl ligand to propane and the resulting hydrido complex $[Co(H)P_2]$ interacts with benzene, turning into the cyclohexadienyl diphosphine complex



This complex reacts with hydrogen very slowly to form cyclohexene. Unfortunately, no quantitative characteristics of this process were presented [40]. In the scheme proposed by us, route B includes alkene coordination with cobalt complex 2 and the subsequent addition of hydrogen to the coordinated alkene and to the cyclohexadienyl ligand, which yields complex 3 containing cyclohexadiene in the coordination sphere of cobalt.

Route C includes alkene coordination to complex 1 and the formation of the σ-alkyl complex 4. Its subsequent interaction with hydrogen also yields complex 3. As a result of the action of hydrogen on complex 3, cyclohexadiene is reduced to cyclohexene. At the next stage, cyclohexene is hydrogenated to cyclohexane or displaced by alkene from the coordination sphere of cobalt. The competition between these two processes determines the selectivity of arene hydrogenation to cycloolefins and, as a consequence, the effect of the composition of the catalytic system and process conditions on the yield of cycloolefins.

It was shown [40] that, in the catalytic process, the cobalt complex of type 1 turns into the catalytically inactive cluster.



The similar clusterization of complex 1 into complex 5 can be among the causes of the deactivation of the catalyst during the coupled hydrogenation of alkenes with arenes.

According to the proposed mechanism of the coupled hydrogenation of the alkene and arene, the cyclohexene formation selectivity should be determined by the ratio of the rates of cyclohexene hydrogenation to cyclohexane and cyclohexene substitution by other ligands (styrene or another alkene, or a phosphorus-containing compound) in the coordination sphere of cobalt. This ratio depends, in turn, on the nature of the phosphorus-containing compound and alkene, P to Co ratio, and temperature. More detailed elaboration of the mechanism of coupled hydrogenation requires identification of intermediate complexes by physical methods and a study of their reactivity.

Thus, arenes, on the one hand, and alkenes, alkadienes, or arylalkenes, on the other hand, can participate in coupled hydrogenation. The process occurs under mild conditions and is catalyzed by the cobalt-containing systems formed only in the presence of trialkylphosphines under the action of various reducing agents, namely, organoaluminum and organomagnesium compounds and *tert*-butoxy derivatives of lithium tetrahydroaluminate. The IR and NMR identification of the cobalt hydrido complexes with phosphine ligands, whose composition depends, to a considerable extent, on the reducing agent and gas atmosphere in the reaction, along with the results of catalytic experiments, suggested that this process is homogeneous. The most probable schemes of the reaction mechanism were proposed.

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REFERENCES

1. *New Pathways for Organic Synthesis: Practical Application of Transition Metals*, Colquhoun, H.M., Holton, J., Thompson, D.J., and Twigg, M.V., Eds., New York: Plenum, 1984.
2. Widegren, J.A. and Finke, R.G., *J. Mol. Catal. A: Chem.*, 2003, vol. 191, p. 187.
3. Lipovich, V.G., Shmidt, F.K., and Kalechits, I.V., *Kinet. Katal.*, 1967, vol. 8, no. 4, p. 812.
4. Lipovich, V.G., Shmidt, F.K., and Kalechits, I.V., *Kinet. Katal.*, 1967, vol. 8, no. 6, p. 1099.
5. James, B.R., *Homogeneous Hydrogenation*, New York: Wiley, 1973.
6. Stuhl, L.S., Rakowski, D.M., Hirsekorn, F.J., Bleeke, J.R., Stetens, A.E., and Muetterties, E.L., *J. Am. Chem. Soc.*, 1978, vol. 100, no. 8, p. 2405.
7. Muetterties, E.L. and Bleeke, J.R., *Acc. Chem. Res.*, 1979, vol. 12, no. 9, p. 324.
8. Bleeke, J.R. and Muetterties, E.L., *J. Am. Chem. Soc.,* 1981, vol. 103, no. 3, p. 556.
9. Schmidt, F.K., Levkovsckii, Yu.S., Saraev, V.V., Ryutina, N.M., Kosinskii, O.L., and Bakunina, T.I., *React. Kinet. Catal. Lett.*, 1977, vol. 7, no. 4, p. 445.

10. Shmidt, F.K., Levkovskii, Yu.S., and Ryutina, N.M., *Kinet. Katal.*, 1982, vol. 23, no. 2, p. 360.
11. Besson, C., Finney, E.E., and Finke, R.G., *J. Am. Chem. Soc.*, 2005, vol. 127, no. 22, p. 8179.
12. Vangelis, C., Bouriazos, A., Sotiriou, S., Samorski, M., Gutsche, B., and Papadogianakis, G., *J. Catal.*, 2010, vol. 274, p. 21.
13. Aruna, V., Sridevi, N., Robinsona, P.P., Manjua, S., and Yusuff, K.K.M., *J. Mol. Catal. A: Chem.*, 2009, vol. 304, p. 191.
14. Schmidt, F.K., Ratovskii, G.V., Dmitrieva, T.V., Ivleva, I.N., and Borodko, Yu.G., *J. Organomet. Chem.*, 1983, vol. 256, p. 309.
15. Shmidt, F.K., *Kataliz kompleksami metallov pervogo perekhodnogo ryada reaktsii gidrirovaniya i dimerizatsii* (Hydrogenation and Dimerization Catalyzed by Complexes of First-Row Transition Metals), Irkutsk: Irkutsk. Gos. Univ., 1986.
16. Alley, W.M., Hamdemir, I.K., Johnson, K.A., and Finke, R.G., *J. Mol. Catal. A: Chem.*, 2010, vol. 315, nos. 1–2, p. 1.
17. Bonnemann, H. and Richards, R.M., *Eur. J. Inorg. Chem.*, 2001, vol. 2001, no. 10, p. 2455.
18. Belykh, L.B., Goremyka, T.V., Skripov, N.I., Umanets, V.A., and Shmidt, F.K., *Kinet. Catal.*, 2006, vol. 47, no. 3, p. 367.
19. Shmidt, F.K., Nindakova, L.O., Shainyan, B.A., Saraev, V.V., Chipanina, N.N., and Umanetz, V.A., *J. Mol. Catal. A: Chem.*, 2005, vol. 235, nos. 1–2, p. 161.
20. Nakazawa, H. and Itazaki, M., *Top. Organomet. Chem.*, 2011, vol. 33, p. 27.
21. Sacco, A. and Rossi, M., *Inorg. Synth.*, 1970, vol. 12, p. 18.
22. Ikariya, T. and Yamamoto, A., *J. Organomet. Chem.*, 1976, vol. 116, p. 239.
23. Yamamoto, A., Kitazume, S., Pu, S., and Ikeda, S., *J. Am. Chem. Soc.*, 1971, vol. 93, no. 2, p. 371.
24. Borod'ko, Yu.G. and Shilov, A.E., *Russ. Chem. Rev.*, 1969, vol. 38, no. 5, p. 355.
25. Gordon, A.J. and Ford, R.A., *A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
26. Mitchell, J. and Smith, D.M., *Aquametry*, New York: Wiley, 1977.
27. Ellern, J.B. and Ragsdale, R., *Inorg. Synth.*, 1968, vol. 11, p. 82.
28. *Preparatyka organiczna: Praca zbiorowa*, Polaczkowa, W., Ed., Warsaw, 1954.
29. Schuldt, B., Heller, B., Storz, F., and Madeja, K., *J. Mol. Catal.*, 1993, vol. 81, no. 2, p. 195.
30. Titova, Yu.Yu., Belykh, L.B., and Shmidt, F.K., Vestn. *IrGTU*, 2010, vol. 42, no. 2, p. 198.
31. Enemarbke, J.H., Davis, B.R., McGinnety, J.A., and Ibers, J.A., *Chem. Commun.*, 1968, p. 96.
32. Misono, A., Uchida, Y., and Araki, M., *Chem. Commun.*, 1968, p. 1044.
33. Otsuka, S. and Rossi, M., *J. Chem. Soc. A,* 1969, p. 497.
34. Sacco, A. and Ugo, R., *J. Chem. Soc.*, 1964, p. 3274.
35. Sacco, A. and Rossi, M., *Inorg. Chim. Acta*, 1968, vol. 2, no. 2, p. 127.
36. Daida, E.J. and Peters, J.C., *Inorg. Chem.*, 2004, vol. 43, no. 23, p. 7474.
37. Sacco, A. and Rossi, M., *Chem. Commun.*, 1969, p. 471.
38. Tolman, C., *Chem. Rev.*, 1977, vol. 77, no. 3, p. 313.
39. Zadov, V.E., *Extended Abstract of Cand. Sci. (Chem.) Dissertation*, Krasnoyarsk: Siberian Technological Inst., 1983.
40. Jonas, K., *Pure Appl. Chem.*, 1984, vol. 56, no. 1, p. 63.

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