# The influence of additives to the Speier catalyst on hydrosilylation of functionalized alkenes

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Hydrosilylation of several unsaturated compounds with triethoxysilane in the presence of the Speier catalyst with various additives influencing the reaction rate and selectivity was studied. The mechanism of hydrosilylation is discussed.

**Key words:** hydrosilylation, reduction, catalysis, catalysts, selectivity, regioselectivity, mechanism.

Previously,[1] we have shown that during competitive hydrosilylation of various olefins with triethoxysilane in the presence of the Speier catalyst (SC), which is a 0.1 $M$ solution of $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol, the reaction rates become close to one another, although the same compounds exhibit different reactivities when subjected to hydrosilylation individually, and in some cases, the reactivity series even changes. Hydrosilylation of allylamine with triethoxysilane catalyzed by $Pt(PPh_3)_4$, instead of the SC, occurs without an induction period and at a higher rate. The studies performed led to the conclusion that the presence of an olefin in the inner sphere of platinum is not a necessary condition for hydrosilylation and that, in some cases, olefin does not participate in the rate-determining step of the reaction.

We also found that some unsaturated ethers (*n*-butyl vinyl, allyl glycidyl, diallyl) added to the SC exert an activating influence during hydrosilylation of allylamine with triethoxysilane.[2] The second-order rate constant for this reaction in the presence of acetonitrile and allyl phenyl ether is lower, whereas that in the presence of diallyl ether is higher, than the rate constant observed without additives. Subsequent studies[3] showed that compounds added to the SC, in particular diallyl ether, have an effect on the rate and activation energy of the process.
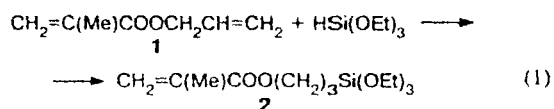
These results cannot be explained in terms of the generally accepted hydrosilylation mechanism,[4,5] according to which hydrosilane adds to an olefin coordinated to platinum. If the reaction proceeded by this mechanism, during hydrosilylation of allylamine in the presence of the Pt complex containing diallyl ether, the latter would be the first to react, while at the regeneration step, a complex with allylamine would arise. In this case, only elimination of the induction period would be observed. The increase in the reaction rate and the decrease in the activation energy indicate that diallyl

ether remains coordinated to platinum, and it is this complex that catalyzes the process.

Taking into account the fact that the diallyl ether incorporated in the Pt complex is much more reactive than allylamine, it can hardly be conceived that in the presence of two olefins in the inner sphere of platinum, the addition would be directed at the less reactive one. Apparently, the olefin that undergoes hydrosilylation occupies a special position, differing from that of the other olefin occurring in the inner sphere of the platinum complex.

Previously, it has been suggested[6] that the olefin undergoing hydrosilylation occupies the fifth coordination site above the plane of the square formed by other ligands, and this accounts for its special properties, not posessed by the other ligands. However, to the best of our knowledge, only derivatives of pentacoordinated platinum(II) with identical ligands, $[ML_5]^{n+}$ (L = $P(OR)_3$), having a trigonal-bipyramidal structure, have been described to date.[7] The increase in the activity of the SC by additives is much more promising from the practical viewpoint than the use of platinum complexes. Therefore, we continued the study of the effect of additives on hydrosilylation. The choice of appropriate additives is determined by the necessity of obtaining a relatively stable platinum complex in which the introduced ligand would be less prone to exchange. Catalysts prepared from the SC and tetramethyldivinyldisiloxane are known to be fairly stable and active.[8]

In the present work, we studied the effect of various organosilicon compounds with unsaturated substituents added to the SC on hydrosilylation of allyl methacrylate (1) with triethoxysilane.

$$CH_2=C(Me)COOCH_2CH=CH_2 + HSi(OEt)_3 \longrightarrow$$
$$\mathbf{1}$$
$$\longrightarrow CH_2=C(Me)COO(CH_2)_3Si(OEt)_3 \qquad (1)$$
$$\mathbf{2}$$

To prevent polymerization and substantial increase in the temperature, the reaction was carried out in dichloromethane, which was chosen owing to its boiling point.

Hydrosilylation of allyl methacrylate (1) by tri-ethoxysilane was carried out in the presence of the SC + $CH_2=CHSi(OEt)_3$ system in various solvents at 50 °C and $[Pt] = 2 \cdot 10^{-6}$ mol per mole of 1; molar ratio SC : additive = 1 : 10, reaction time 90 min:

| Solvent | Yield of 3-(triethoxysilyl)propyl methacrylate (%) |
|---|---|
| Pentane | 66 |
| Diethyl ether | 61 |
| Dichloromethane | 53 |
| Benzene | 46 |
| Toluene | 41 |
| Acetonitrile | 11 |
| THF | 6 |

The rate of hydrosilylation decreased in the following sequence: pentane > diethyl ether > dichloromethane > benzene > toluene ≫ acetonitrile > THF. Note that solvents have no effect on the hydrosilylation of allyl phenyl ether.[9]

The catalyst activity (Fig. 1) decreases in the series: SC > SC + 1 > SC + $CH_2=CHSi(OEt)_3$ > SC + $(EtO)_3SiCH=CCl_2$ > SC + $(EtO)_3SiC≡CSi(OEt)_3$ > SC + $[(EtO)_2(CH_2=CH)Si]_2O$ > SC + $((CH_2=CH)_3Si)_2O$; in the presence of the first three catalysts, the reaction proceeds without an induction period. The use of additives makes it possible to control the rate of hydrosilylation of allyl methacrylate.
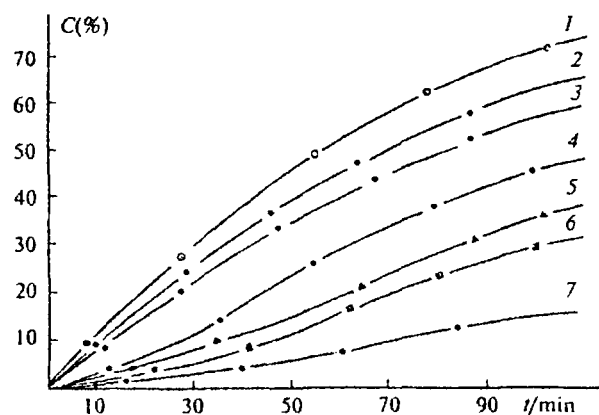


Fig. 1. Influence of unsaturated compounds added to the SC on the rate of hydrosilylation of 1 with triethoxysilane: without additives (1); 1 (2); $CH_2=CHSi(OEt)_3$ (3); $(EtO)_3SiCH=CCl_2$ (4); $(EtO)_3SiC≡CSi(OEt)_3$ (5); $[(EtO)_2(CH_2=CH)Si]_2O$ (6); $((CH_2=CH)_3Si)_2O$ (7). Dichloromethane is used as the solvent; temperature 50 °C; $[Pt]$ $2 \cdot 10^{-6}$ mol mol$^{-1}$ of 1; The volume ratio SC : additive = 1 : 10. C is the concentration of 3-(triethoxysilyl)propyl methacrylate in the reaction mixture without allowance for the solvent.
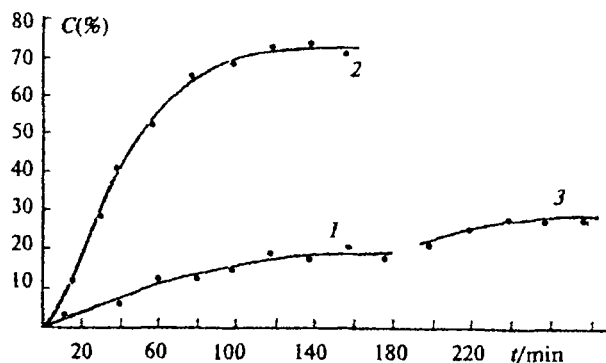


Fig. 2. Hydrosilylation of allylbenzene with triethoxysilane in the presence of: SC + $CH_2=CHCH_2Ph$ (1) ( To eliminate the effect of the SC itself, the catalyst containing allylbenzene was first prepared); SC + $CH_2=CHSi(OEt)_3$ (2); SC + $CH_2=CHCH_2Ph$ after the addition of a new portion of $CH_2=CHCH_2Ph$ (3), 70 °C, $[Pt]$ $5 \cdot 10^{-6}$ mol mol$^{-1}$ of $CH=CHCH_2Ph$. The volume ratio SC : additive = 1 : 10. C is the concentration of triethoxy(3-phenylpropyl)silane.

The SC + $CH_2=CHSi(OEt)_3$ system was tested in the hydrosilylation of other unsaturated compounds. Hydrosilylation of allylbenzene (Eq. (2)) occurs at a substantially higher rate and gives the adduct in a higher yield than in the presence of the SC (Fig. 2). The low yield of the addition product in the presence of SC is caused apparently by competing isomerization (Eq. (3)). According to published data,[10] isomerization proceeds fairly readily. The propenylbenzene thus formed is inactive in hydrosilylation. The fact that the reaction is revived upon addition of a new portion of allylbenzene confirms the hypothesis that hydrosilylation is retarded due to isomerization of the olefin rather than the catalyst poisoning.
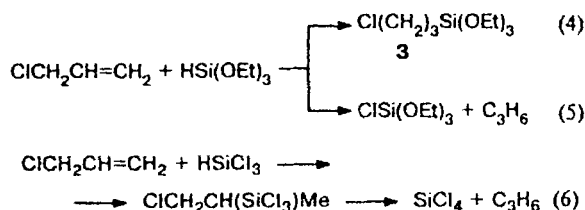
$$RCH_2CH=CH_2 + HSi(OEt)_3 \longrightarrow R(CH_2)_3Si(OEt)_3 \quad (2)$$

$$RCH_2CH=CH_2 \rightleftharpoons RCH=CHMe \quad (3)$$
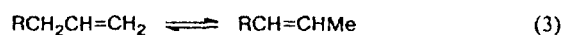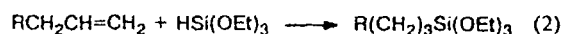
$$R = Ph, OPh$$

The addition of triethoxysilane to allyl phenyl ether in the presence of this catalyst occurs with a higher yield that that catalyzed by the SC (82.5% compared to 70%) and is not accompanied by the allyl-propenyl isomerization of allyl phenyl ether (see Eq. (3)) observed in our previous study.[9] According to the current views on the mechanism of isomerization, it involves coordination of the olefin to a platinum atom.[11] The fact that hydrosilylation is not accompanied by isomerization indicates that the platinum complex with vinyltriethoxysilane is fairly stable and no platinum complexes with allyl phenyl ether or allylbenzene are formed. This also can serve as additional evidence supporting the assumption that in this process, olefin is not coordinated to platinum. Thus, the role of the platinum compound

in the catalysis of hydrosilylation consists apparently in activation of the silane.

When allyl chloride is hydrosilylated with triethoxysilane in the presence of the SC, the yield of (3-chloropropyl)triethoxysilane (3) is as low as 9.6%, and the A/R ratio is 0.19, while in the presence of the SC with vinyltriethoxysilane additive, the yield of 3 is 22.7%, and A/R is 0.42; here A/R is the molar ratio of the addition products (reaction (4)) to reduction products (reaction (5)). Similar results were obtained in the presence of the SC with an additive of allyl glycidyl ether; however, in the presence of the SC and potassium 7,8-dicarba-*nido*-undecaborate (DCUB), no reduction products were detected (Table 1).

The use of *n*-butyl vinyl ether as an additive to the SC for hydrosilylation of allyl chloride with methyl dichlorosilane made it possible to increase the yield of dichloro(chloropropyl)methylsilane from 46.3 to 66.9%,[12] while the isomerized product was not detected. In order to rule out the possibility that it had decomposed at an elevated temperature, we carried out hydrosilylation of allyl chloride with trichlorosilane at room temperature; however, in this case, too, the β-isomer was not detected by $^1$H NMR spectroscopy. Hence, reaction (6) apparently did not occur.

$$CICH_2CH=CH_2 + HSi(OEt)_3 \longrightarrow \begin{cases} Cl(CH_2)_3Si(OEt)_3 \quad (4) \\ \mathbf{3} \\ ClSi(OEt)_3 + C_3H_6 \quad (5) \end{cases}$$

$$CICH_2CH=CH_2 + HSiCl_3 \longrightarrow$$
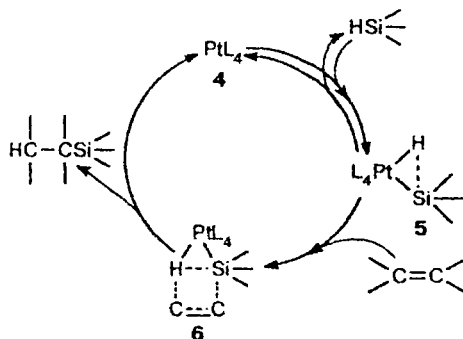$$\longrightarrow CICH_2CH(SiCl_3)Me \longrightarrow SiCl_4 + C_3H_6 \quad (6)$$

The effects of other additives on the hydrosilylation of allylamine is outlined in Table 2. It can be seen that additives influence not only the reaction rate and the yield of the adduct but also the regioselectivity of the process. The ratio of the 3- and 2-isomers of (triethoxysilyl)propylamine increases when the thermodynamic equilibrium is attained with bulkier ligands. Table 2 contains an example (the bottom line) that does

not fit in the general tendency, because in this case, the reaction mixture did not reach a constant boiling temperature, which normally points to completion of the reaction.

Apparently, hydrosilylation follows the scheme proposed in our previous study[13] but with some modifications. According to the current views on homogeneous catalysis, catalytic activity is exhibited by coordinatively unsaturated complexes,[5] for example, planar-square Pt$^{II}$ complexes,[14] which directly participate in the catalytic cycle of hydrosilylation. As time passes, Pt$^{IV}$ in the SC is reduced to Pt$^{II}$,[15] and the required complexes are thus formed (Eq. (7)). Silanes can also reduce Pt$^{IV}$.

$$2\ H_2PtCl_6 + 2\ Pr^iOH \longrightarrow H[(C_3H_6)PtCl_3] +$$
$$+ H_2PtCl_4 + MeCOMe + H_2O + 3\ HCl \quad (7)$$
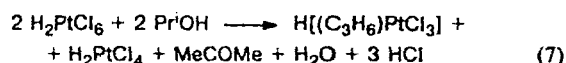
Hydrosilylation can be represented by the following scheme:



L is halogen, olefin, silane, solvent, *etc.*,

$HSi{\displaystyle \stackrel{\angle}{\angle}}$ is silane.

In conformity with the above scheme, catalyst **4** reacts initially with the silane to give complex **5**, which contains a Pt—H—Si three-center bond. Platinum complexes with three-center Pt—H—Si bonds (7, 8) have been isolated in a pure state and characterized by X-ray diffraction analysis.[16,17] Complexes of type **7** are more active catalysts for hydrosilylation than the SC.[18]

Table 1. Influence of compounds added to the SC on hydrosilylation of allyl chloride with triethoxysilane

| [Pt] · 10$^4$ | Additive | SC : additive (mol mol$^{-1}$) | $T$ /°C | $t$ of the synthesis /h | Yield of the adduct (%) | A/R$^a$ |
|---|---|---|---|---|---|---|
| 4 mol L$^{-1}$ | DCUB | 1 : 2 | 70—120 | 3.0 | 17.8 | $b$ |
| | (CH$_2$=CHCH$_2$)$_2$O | 1 : 50 | 70—120 | 1.5 | 19.6 | 0.38 |
| 0.4 mol mol$^{-1}$ of olefin | CH$_2$=CHSi(OEt)$_3$ | 1 : 150 | 50—80 | 4.0 | 22.7 | 0.42 |
| 1 mol mol$^{-1}$ of olefin | AGE$^c$ | 1 : 150 | 55—100 | 4.0 | 22.5 | 0.40 |

$^a$ A/R is the molar ratio of the addition products to reduction products.
$^b$ Reduction product was not found.
$^c$ Allyl glycidyl ether.

7

8
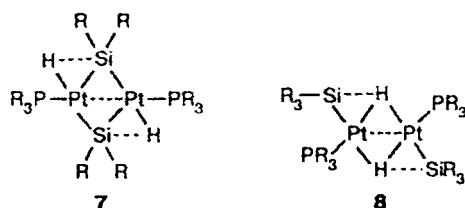
We cannot rule out the possibility of oxidative addition of hydrosilane to platinum(II) to give hydride complexes; however, this route seems less likely. It is known that some iridium compounds enter into oxidative addition of silanes; however, the resulting hydride complexes do not catalyze hydrosilylation,[19] and in the presence of the platinum hydride complex $HClPt(PPh_3)_2$, hydrosilylation starts after an induction period.[20]

The suggestion that the Si—H bond in the intermediates involved in the catalytic cycle is not completely cleaved was theoretically substantiated in a previous study.[21] Activation of the Si—H bond during hydrosilylation through $\eta^2$-coordination has been assumed by another researcher.[22]

According to the scheme proposed here, intermediate complex 5 reacts with noncoordinated olefin to give activated complex 6, which gives rise to the hydrosilylation product and the catalyst, and the latter starts a new cycle. The reaction of noncoordinated olefin is a principal feature of our mechanism distinguishing it from the mechanism proposed by Chalk and Harrod, which implies reaction between the olefin and silane both coordinated to platinum. Outer-sphere attacks are known in metal-complex catalysis.[23] This reaction might occur by a four-center mechanism.

The abnormally low magnitudes of the preexponential factor in the kinetic equations for hydrosilylation of allylamine and allyl glycidyl ether[9] ($10^3$—$10^5$ L mol$^{-1}$ s$^{-1}$) compared to the normal values typical of bimolecular reactions ($10^{11}$ L mol$^{-1}$ s$^{-1}$) imply a complicated activated complex and steric hindrance involved in the interaction of the reactants. Apparently, the selectivity of this

process is also due to steric restrictions for the noncoordinated olefin created by the ligands.

The proposed mechanism of hydrosilylation explains adequately both our data and published data: hydrosilylation in the presence of catalysts that are relatively stable to ligand exchange with olefins, for example $Pt(Ph_3)_4$,[24] the influence of the structure of olefin on the hydrosilylation in the presence of the SC under conditions of individual reactions,[14] and the nondependence of the reaction rate on the type of olefin under conditions of competing reactions.[25] The proposed scheme can be used to select appropriate catalysts using a broad range of compounds active toward hydrosilylation as additives to the SC.

Based on the studies performed, we can outline the main principles for selection of additives to the SC: an additive should readily form a complex with platinum, and the complex should be sufficiently stable under hydrosilylated conditions, in order to ensure that the ligand exchange is hampered.

## Experimental

Reaction mixtures were analyzed using an LKhM-72 (or LKhM-80) chromatograph with a katharometer as the detector equipped with a 4×2000 mm column with Chromaton N-AW+15% PMS 20000 (or E-301) as the stationary phase; rate of the carrier gas (helium) 60 mL min$^{-1}$; temperature of the evaporator 550 °C, that of the column 50—250 °C, temperature programming rate 20 deg min$^{-1}$.

Kinetic studies were carried out for reaction mixtures maintained at a constant temperature with an accuracy of ±0.1 °C.

The catalyst was prepared immediately prior to the synthesis in the same reactor. The SC with (or without) additives was heated for 30 min at 50 °C.

The structures of the products of hydrosilylation with triethoxysilane of allyl methacrylate, allylbenzene, allyl phenyl ether, allylamine, and allyl chloride were established previously.[9,25-28] The compounds obtained were identified by GLC using comparison with authentic samples.

Hydrosilylation of allylamine and allyl chloride. An equimolar mixture of hydrosilane, an unsaturated compound, and the

Table 2. Influence of compounds added to the SC on hydrosilylation of allylamine with triethoxysilane ([Pt] is $1.1 \cdot 10^{-4}$ mol mol$^{-1}$ of allylamine)

| Additive | Pt : additive (mol mol$^{-1}$) | $t$ of the synthesis /h | Yield of (3-amino-propyl)triethoxy-silane (%) | Isomer ratio $\gamma : \beta$ |
|---|---|---|---|---|
| Allyl glycidyl ether | 1 : 100 | 13 | 74.8 | 5.0 : 1 |
| Diallyl ether | 1 : 100 | 12 | 65.8 | 4.0 : 1 |
| Acetylacetone | 1 : 13$^a$ | 26 | 31.0 | 5.0 : 1 |
| Benzonitrile | 2 : 1$^a$ | 13 | 48.3 | 4.5 : 1 |
| Triphenylphosphine | 2 : 1$^a$ | 15 | 41.0 | 4.5 : 1 |
| Triallylamine | 1 : 2$^a$ | 13 | 66.0 | 4.5 : 1 |
| DCUB | 1 : 10 | 6 | 69.0 | 6.0 : 1 |
| None | | 24 | 61.3 | 4.0 : 1 |
| | | 12$^b$ | 11.7 | 2.5 : 1 |

$^a$ Volume ratio.

$^b$ The sample was withdrawn before a constant temperature was attained.

catalyst was refluxed in a flask equipped with a reflux condenser and a thermometer. The end point of the reaction was taken as the attainment of a constant temperature in the mixture. The completeness of the reaction was checked by GLC.

**Hydrosilylation of allyl phenyl ether.** An equimolar mixture of allyl phenyl ether and triethoxysilane was added to a catalyst at 80 °C. The reaction mixture was heated for 2 h at 100—110 °C.

**Hydrosilylation of allyl methacrylate.** A mixture of allyl methacrylate and triethoxysilane (0.1 mol each) in 20 mL of a solvent and a catalyst were stirred for 2 h at 50 °C.

**Hydrosilylation of allylbenzene** was carried out in a similar way but without a solvent at 70 °C.

# References

1. Z. V. Belyakova, L. K. Knyazeva, and E. A. Chernyshev, *Zh. Obshch. Khim.*, 1983, 53, 1591 [*J. Gen. Chem. USSR*, 1983, 53 (Engl. Transl.)].
2. Z. V. Belyakova, L. K. Knyazeva, and E. A. Chernyshev, *Zh. Obshch. Khim.*, 1978, 48, 1373 [*J. Gen. Chem. USSR*, 1978, 48 (Engl. Transl.)].
3. E. A. Chernyshev, Z. V. Belyakova, V. G. Bykovchenko, L. K. Knyazeva, A. V. Kisin, and V. M. Nosova, in *Khimiya kremniiorganicheskikh soedinenii* [*Chemistry of Organosilicon Compounds*], GNIIKhTEOS/NIITEKhIM, Moscow, 1988, 13 (in Russian).
4. A. J. Chalk and J. F. J. Harrod, *J. Am. Chem. Soc.*, 1965, 87, 16.
5. J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, J.Wiley, New York, 1978.
6. V. M. Kopylov, T. G. Kovyazina, T. M. Buslaeva, N. M. Sinitsina, V. V. Kireev, and A. V. Gorshkov, *Zh. Obshch. Khim.*, 1987, 57, 1117 [*J. Gen. Chem. USSR*, 1987, 57 (Engl. Transl.)].
7. Yu. N. Kukushkin, *Khimiya koordinatsionnykh soedinenii* [*Chemistry of Coordination Compounds*], Vysshaya Shkola, Moscow, 1985, 81 (in Russian).
8. US. Pat. No. 4421903, 1983.
9. Z. V. Belyakova, M. G. Pomerantseva, V. G. Bykovchenko, and E. A. Chernyshev, *Zh. Obshch. Khim.*, 1976, 46, 1034 [*J. Gen. Chem. USSR*, 1976, 46 (Engl. Transl.)].
10. L. Roos and M. Orchin, *J. Am. Chem. Soc.*, 1965, 87, 5502.
11. Yu. M. Zhorov, G. M. Panchenkov, and G. S. Volokhova, *Izomerizatsiya olefinov* [*Isomerization of Olefins*], Khimiya, Moscow, 1977, 113 (in Russian).
12. USSR Pat. 426683, *Byul. Izobret.*, 1974, 17 (in Russian).
13. E. A. Chernyshev, Z. V. Belyakova, L. K. Knyazeva, L. A. Yagodina, and E. V. Nikitinskii, *VIIIth Fechem Conference on Organometallic Chemistry*, Abstracts, Veszprem-Balatonfured (Hungary), 1989, 48.
14. E. Lukevics, Z. V. Belyakova, M. G. Pomerantseva, and M. G. Voronkov, *J. Organometal. Chem. Library*, 1977, 5, 1.
15. V. I. Perevalova, N. B. Shitova, L. Ya. Al't, and V. K. Duplyakin, *Zh. Obshch. Khim.*, 1988, 58, 1694 [*J. Gen. Chem. USSR*, 1988, 58 (Engl. Transl.)].
16. M. Cirano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 1978, 801.
17. M. Auburn, M. Cirano, J. A. K. Howard, M. Murray, N. F. Pugh, J. L. Spenser, F. G. H. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 659.
18. M. Green, J. L. Spenser, F. G. A. Stone, and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 1977, 1519.
19. C. A. Tsipis, *J. Organometal. Chem.*, 1980, 187, 427.
20. T. P. Khvatova, Ph. D. (Chem.) Thesis, LTI, Leningrad, 1977, 154 pp. (in Russian).
21. H. Rabaa, J.-Y. Saillard, and U. Schubert, *J. Organometal. Chem.*, 1987, 330, 397.
22. N. K. Skvortsov, Sc. D. (Chem.) Thesis, St.Petersburg Polytechnical Institute, St.Peterburg, 1995, 40 pp. (in Russian).
23. A. A. Bagatur'yants, *Kvantovaya khimiya metallokompleksnogo kataliza "Kinetika i kataliz". Itogi nauki i tekhniki* [*Quantum Chemistry of Metal Complex Catalysis. "Kinetics and Catalysis". Results in Science and Engineering*], VINITI, Akad. Nauk SSSR, Moscow, 1985, 14, 3 (in Russian).
24. W. Fink, *Helv. Chim. Acta*, 1971, 54, 1304.
25. V. N. Tarasenko, Ph. D. (Chem.) Thesis, Moscow Chemico-Technological Institute, Moscow, 1974, 184 pp. (in Russian).
26. Z. V. Belyakova, V. N. Bochkarev, S. A. Golubtsov, Z. V. Belikova, M. S. Yamova, A. A. Ainshtein, G. G. Baranova, L. A. Efremova, and K. K. Popkov, *Zh. Obshch. Khim.*, 1972, 42, 858 [*J. Gen. Chem. USSR*, 1972, 42 (Engl. Transl.)].
27. Z. V. Belyakova, M. G. Pomerantseva, and Z. V. Belikova *Zh. Obshch. Khim.*, 1974, 44, 2439 [*J. Gen. Chem. USSR*, 1974, 44 (Engl. Transl.)].
28. E. A. Chernyshev, Z. V. Belyakova, V. M. Shevchenko, L. A. Yagodina, A. V. Kisin, A. A. Bernadskii, V. D. Sheludyakov, and V. N. Bochkarev, *Zh. Obshch. Khim.*, 1984, 54, 2031 [*J. Gen. Chem. USSR*, 1978, 54 (Engl. Transl.)].