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The Comparison of Addition of Molecules Possessing P(V)–H Bond to Alkynes Catalyzed with Pd and Ni Complexes

V. P. Ananikov^a, L. L. Khemchyan^a, and I. P. Beletskaya^b

^aZelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia e-mail: val@ioc.ac.ru ^bLomonosov Moscow State University, Moscow, 119899 Russia e-mail: beletska@org.chem.msu.ru

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Abstract—Main factors have been analyzed necessary for creation of an efficient catalytic system for alkynes hydrophosphorylation based on nickel complexes, and a valid model system was suggested for the comparison with palladium complexes. It has been discovered for the first time that the insertion of an alkyne into the metal–hydrogen bond occurs with a considerably lower activation barrier than into the metal–phosphorus bond, whereas the variation in the reaction energy corresponds in both cases to an exothermic reaction. Under the optimized conditions the transformation catalyzed by nickel complexes does not require acid addition and may proceed even in the absence of a phosphine ligand.

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The hydroheterofunctionalization (the addition of molecules containing a bond hydrogen–heteroatom) of unsaturated organic compounds is among the leading methods of contemporary fine organic synthesis and underlies quite a number of industrial processes [1–3]. The creation of efficient catalytic systems proceeding from available complexes of transition metals is the common strategy in this field. Nowadays a dynamic development is observed, and in many cases a significant progress is achieved for catalytic reactions involving quite a number of heteroatoms and elements (B, Si, O, N, S, Se etc.) [1–7].

Notwithstanding the advances in this field, the situation in the investigations of addition to alkynes of molecules containing the phosphorus(V)–hydrogen bond is not clear. The products of the addition along Markownikoff rule were shown to be available in the presence of palladium and nickel catalyst as was reported by Tanaka [8–12], Han [13, 14], Montchamp [15–17], Toffano [18] and in our publications [19–21].

The accumulated array of the experimental data does

not form a general unambiguous pattern, and in some cases the results from various studies are contradictory. The following key problems can be revealed requiring keen attention and deep comprehension: (1)What is the efficience of catalysts based on palladium and nickel complexes in the addition of the P(V)–H bond to alkynes; (2)What is the reason of the significant difference in the activity of catalyst precursors containing bivalent and zero-valent metal compounds, M(II) and M(0); (3)Why the regioselectivity of addition reactions changes if all of them occur by the alkyne insertion into the metal–phosphorus bond; (4) Ambiguous results exist on the ligand and acid effect.

In this report we make the first attempt to understand the reason of some among these contradictions and to suggest the optimum strategy of the studies for their solution.

The investigation of catalytic activity of nickel and palladium complexes was carried out on a selected model hydrophosphorylation reaction of 1-heptyne (Scheme 1). It should be stated that similar model systems involving a terminal alkyne without substituents (1-hexyne, 1-hep-





tyne, or 1-octyne) is a common practice in the studies of the catalytic addition of molecules possessing P–H bonds and has been already used in many investigations [12, 17, 20].

The catalytic transformation was performed in THF medium at 100°C over 3 h. On completing the reaction the reaction mixture was analyzed by ¹H and ³¹P NMR. In contrast to most already published research papers in this study we determined not only the composition and structure of the reaction products but the residual amount of unreacted initial compounds and also the quantity of side products was estimated. In certain cases just the analysis of the general picture had the fundamental importance for the understanding of the nature of the observed processes.

The hydrophosphorylation of 1-heptyne catalyzed with palladium complex led to the formation of Markownikoff product **IIIa** in 63% yield (Table 1). Nickel complexes either did not show a considerable catalytic activity or the yield was negligible.

At the first sight, this result demonstrates the advantage of the palladium over nickel catalyst. However the more detailed consideration showed that in event of the nickel acetylacetonate both initial reagents **Ia** and **IIa** remained intact, and the NMR spectra lacked any signals of new compounds. The color and appearance of the reaction mixture did not change within 3 h of heating. Consequently, under these conditions the prfecursor of the catalyst was not activated, and the catalytically active metal complexes did not form.

In the case of bis(cycloctadiene)nickel some product formed in the system, but the reaction finished at the 10% conversion of reagent **IIa**. The analysis of the ¹H NMR spectrum showed the absence of the alkyne in the reaction mixture (conversion of **Ia** 100%), and a black insoluble precipitate formed in the course of the reaction. Evidently here the main contribution to the alkyne conversion originated not from the hydrophosphorylation but the oligomerization process that was well known for the nickel complexes [22, 23]. The hydrophosphorylation in the studied conditions stopped because the lack of the alkyne. As to the catalytic system based on Pd complexes, there was no alkyne oligomerization.

Therefore it is clear that this common model system cannot provide a valid comparison of the efficiency of catalytic systems based on palladium and nickel complexes in alkynes hydrophosphorylation.

Inasmuch as in the catalytic system $Ni(cod)_2/PPh_3$ the formation of a small amount of the desired product was found (Table 1), we carried out a more detailed investigation of this system for various alkynes (Scheme 2).

Scheme 2.



I, $R^1 = C_5H_{11}$, $R^2 = H$ (**a**); $R^1 = Ph$, $R^2 = H$ (**b**); $R^1 = R^2 = Et$ (**c**), $R^1 = R^2 = Ph$ (**d**); **II**, $R^3 = i - Pr$ (**a**), Ph (**b**), $C_{12}H_{25}$ (**c**); **III**, $R^1 = C_5H_{11}$, $R^2 = H$, $R^3 = i - Pr$ (**a**); $R^1 = R^2 = Ph$, $R^3 = i - Pr$ (**b**); $R^1 = R^2 = R^3 = Ph$ (**c**); $R^1 = R^2 = Ph$, $R^3 = C_{12}H_{25}$ (**d**).

The reaction with phenylacetylene **Ib** provided only traces of the Markownikoff product (Table 2). Same as in the case of 1-heptyne the most of H-phosphonate remained unreacted, and at the same time the complete conversion of the alkyne and oligomer formation was observed.

Table 1. Conditions and yields of hydrophosphorylation products of 1-heptyne on the complexes of palladium and nickel (100°C, 3 h, metal–ligand ratio 1 : 4, 6 mol% of catalyst, 0.5 ml of THF)

| Metal ^a complex and ligand | Yield of IIIa , % | Residue of IIa , % | Side products, % |
|---|--------------------------|---------------------------|------------------|
| Pd ₂ dba ₃ , PPh ₃ | 63 | 18 | 19 |
| $Ni(acac)_2$, PPh_3 | 0 | 100 | 0 |
| $Ni(cod)_2$, PPh_3 | 6 | 9 | 04 |

^a dba is dibenzylideneacetone, acac is acetylacetone, cod is cyclooctadiene.

The reaction with 3-hexyne **Ic** required more stringent conditions (140°C) and gave the addition product in 15% yield. The distinguishing feature of this process was the equal conversion of the alkyne and the H-phosphonate indicating the absence of the side reaction of the alkyne oligomerization.

Diphenylacetylene **Ie** reacted already at 120°C, and olefin **IIIc** formed in a very high yield, 95%. The complete conversion of H-phosphonate was observed in the system, and the amount of side products did not exceed 5%. The reaction proved to be of a general character, and the conversion of other H-phosphonates **IIb** and **IIc** also resulted in the 100% yield of addition products without any side reactions. The addition to 3-hexyne and diphenylacetylene occurs with a very high streoselectivity (E/Z > 99/1) as a *syn*-addition to the triple bond. The formation of the product corresponding to the *anti*-addition of the P–H bond to alkyne (*Z*-isomer) was not observed, and the side products found were of another character.

The experiments with the palladium catalyst and internal alkynes **Ic** and **Id** showed somewhat lower yields of the target products and considerably lower selectivity due to the formation of side products. In this model system the nickel complexes demonstrated considerable advantage over palladium. The results obtained show that the internal alkynes are significantly less prone to side oligomerization on the Ni catalyst than the terminal alkynes.

In the absence of the side oligomerization reaction the efficiency of catalytic systems based on nickel and palladium proved to be quite comparable, same as the selectivity.

The high efficiency of a simple catalytic system Ni/ PPh₃ we discovered for the first time. It was previously reported that this system was not suitable for synthetic purposes due to low yields and poor selectivity [13]. Evidently this conclusion originated from the application of a noninformative model system with 1-octyne prone to the side reactions involving the alkyne [13].

Since we showed in this study that in the absence of the side polymerization of alkyne the nickel complexes catalyze the stereoselective hydrophosphorylation of the triple bond we regarded as desirable the use of $Ni(acac)_2$ as the precursor of catalyst. The nickel acetylacetonate is stable in air and considerably cheaper than the bis(cycloctadiene)nickel that is obviously an advantage for developing synthetic procedures.

We found that $Ni(acac)_2$ could be reduced *in situ* directly in the reaction mixture by adding a catalytic quantity of diisobutylaluminum hydride (DIBAL). No

| Catalytic system | Alkyne I | H-phosphonate II | Temperature, °C | Time, h | Yield of III , % | Residue of II , % | Side products, % |
|---|--|---|--------------------|---------|----------------------------|-----------------------------|------------------|
| Ni(cod) ₂ , PPh ₃ | Ph-=== | O | 100 | 19 | 1 | 90 | 9 |
| Ni(cod) ₂ , PPh ₃ | Ib Et———————————————————————————————————— | (<i>i</i> -PrO)2 ^µ −H IIa IIa | 140 | 19 | 15 | 85 | 0 |
| | Ic | | | | | | |
| Ni(cod) ₂ , PPh ₃ | PhPh | IIa | 120 | 4 | 95 | 0 | 5 |
| | Id | | | | | | |
| Ni(cod) ₂ , PPh ₃ | Id | O | 120 | 4 | 100 | 0 | 0 |
| | | (PhO) ₂ P̈́—H IIb | | | | | |
| Ni(cod) ₂ , PPh ₃ | Id | O | 120 | 4 | 100 | 0 | 0 |
| | | (C ₁₂ H ₂₅ O) ₂ P–H Ис | | | | | |
| Pd ₂ dba ₃ , PPh ₃ | Ic | IIa | 140 | 19 | 12 | 53 | 35 |
| Pd ₂ dba ₃ , PPh ₃ | Id | IIa | 120 | 19 | 70 | 0 | 30 |

Table 2. Conditions and yields of hydrophosphorylation products of alkynes on the complexes of palladium and nickel, THF,9 mol% of catalyst

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addition occurred without the reducer (1 ml of THF, 4 h, 120°C, 9 mol% of catalyst). In the presence of DIBAL olefin **IIIb** formed in a high yield (96%) and selectivity (the yield of side products 4%). This result is comparable with that for bis(cycloctadiene)nickel (Table 2).

This discovery opens additional prospects for the design of catalyst of alkynes hydrophosphorylation based on available Ni(II) salts.

Note that the use of bivalent nickel salts as catalyst precursor was described for the addition of $(RO)P(O)H_2$ without reduction [16]. In certain cases the role of reucer may play one of the reagents or the phosphine ligand. It was also shown that the stage of activation of the catalyst precursor was very sensitive to water traces [24].

The data obtained unambiguously show that the lack of reaction not always means the unsuitability of the given metal compound as a catalyst and that the stage of the activation of the catalyst precursor for hydrophosphorylation requires a special attention.

It was previously reported on the strong effect of the catalytic amounts of Ph₂P(O)OH on alkynes hydrophosphorylation in the presence of Pd complexes [9, 12, 13]. Our recent study showed that the region- and stereoselective addition of H-phosphonates to alkynes was also possible with the catalytic system Pd-PPh₃-CF₃COOH [21]. The addition of acid was necessary to increase the yield of the Markownikoff product and to improve the chemo- and regioselectivity of the addition. To our surprise, even small additives of CF₃COOH into the nickel-based catalytic system completely suppressed the catalytic activity. At the attempt to carry out the reaction of H-phosphonate IIa with diphenylacetylene (Id) in the presence of 10 mol% of CF₃COOH no formation of olefin IIIb was observed and also no notable conversion of initial reagents.

Obviously this notable difference between Pd and Ni catalysts is worth special consideration. The elucidation of the causes of this dramatic suppression of the catalytic activity of the nickel complexes will be the object of further research.

The currently assumed mechanism of the alkynes hydrophosphorylation catalyzed by palladium and nickel complexes involves a stage of the oxidative addition with the formation of complex IV and the subsequent alkyne insertion into the metal–phosphorus bond to give complex V (Scheme 3). At the reductive elimination of the C–H bond from complex V the formation of olefin III occurs and the regeneration of the compound of the zero-valent metal.

For the nickel and palladium complexes the alternative reaction pathway involving the alkyne insertion into the metal-hydrogen bind was not considered. In this case intermediate complex **VI** would form which undergoes the reductive elimination of the C–P bond with the formation of olefin **III** and the regeneration of the compound of the zero-valent metal (Scheme 3).

The alkyne insertion into the metal-hydrogen bond was formerly presumed only for the rhodium complexes, and this reaction resulted in the other product, *anti*-Markownikoff isomer in the case of terminal alkynes [18, 25, 26]. And the explanation of the Markownikoff regioselectivity in the reactions catalyzed by palladium and nickel complexes was based just on the suggestion of the insertion into the metal-phosphorus bond.

Note that depending on the position of substituents R^1 and R^2 in complexes V and VI both pathways can lead to the formation of identical reaction products or of regioisomers. Strictly speaking, the structure of the reaction product is not an unambiguous proof of a certain reaction mechanism in the case of internal alkynes.



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The comparative analysis of both routes we performed by the quantum-chemical calculation using density functional theory B3LYP in the basis Lanl2dz for the metal and 6-31G(d) for the other atoms. The calculation was carried out for a model reaction of acetylene insertion in a complex [Ni(H)(P(O)(OMe)_2)(PH_3)] (see the figure). The insertion of acetylene in the nickel–phosphorus bond from the π -complex **VII** occurs through the transition state **VIII**-TS, and the value of the calculated activation barrier was 14.5 kcal mol⁻¹. The insertion of acetylene is an exothermic reaction, and the energy gain at the formation of complex **IX** is 26.0 kcal mol⁻¹.

In the course of attempts to localize the transition state X-TS for the stage of acetylene insertion into the metal-hydrogen bond complex XI spontaneously formed. In come cases its formation occurred already at the stage of the optimization of the geometry of π -complex VII. These results evidence the small activation barrier in this stage (see the figure). The insertion of acetylene into the Cc π 3and metal-hydrogen bond is also an exothermic reaction that leads to the formation of three-coordinate complex XI with an energy gain of 26.7 kcal mol⁻¹.

Unlike compound XI the insertion of acetylene into the metal–phosphorus bond affords a four-coordinate complex IX due to the interaction with the metal of the oxygen atom of one of the methoxy groups. The additional coordination of the oxygen to the metal strbilizes complex IX and results in comparable values of the reaction energies 26.0 and 26.7 kcal mol⁻¹. Three-coordinate complex XI is somewhat higher in energy as expected taking into account the difference in the activation barriers for the transition states VIII-TS, X-TS. Complexes IX and XI are the model analogs of above considered compounds V and VI (Scheme 3). The calculations performed unexpectedly indicate that the alkyne insertion into the metal–hydrogen bond may occur even easier than the insertion into the metal–phosphorus bond.

The results obtained prompted us to study the possibility of the hydrophosphorylation of the triple bond in alkynes with a catalyst without phosphine ligand. The reaction proved to be impossible for terminal alkynes **Ia** and **Ib** due to the above mentioned side oligomerization reaction (Table 3). A little of the hydrophosphorylation product was found in the reaction of internal alkynes **Ic** and **Id** with H-phosphonate **IIa**. A considerable amount of product (20%) formed in the reaction of diphenylacetylene with H-phosphonate **IIb**, and in the reaction of H-phosphonate **IIc** was obtained a good yield (57%).

It should be stated that the hydrophosphorylation of alkynes in the absence of a phosphine ligand we are first to discover. Notwithstanding the low yields and selectivity compared with the analogous process in the presence of the ligand (Table 2) this reaction type is promising for creation of nontoxic and cheap catalytic systems in keeping with modern trends of the "green" chemistry.

It is not excluded that the proper compounds of the trivalent phosphorus forming as a result of tautomerization of H-phosphonate $(RO)_2P^V(O)H \leftrightarrow P^{III}(RO)_2(OH)$ might coordinate to the metal and act as a ligand. This assumption is to a certain extent in agreement with the great difference in the reactivity of the H-phosphonates (Table 3) that is not observed in the reaction with the triphenylphosphine as the ligand.



Calculated potential energy surface for acetylene insertion into the Ni-P and Ni-H bonds.

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| Alkyne | H-phosphonate II | Temperature, °C | Yield of III, % | Residue of II, % | Side products, % |
|---|---|-----------------|-----------------|------------------|------------------|
| C ₅ H ₁₁ == Ia | О (<i>i</i> -PrO) ₂ Р–Н Па | 100 | 0 | 100 | 0 |
| Ph—==== Ib | IIa | 100 | 0 | 100 | 0 |
| Et———————————————————————————————————— | IIa | 140 | 12 | 85 | 3 |
| Ph———Ph Id | IIa | 120 | 9 | 80 | 11 |
| Id | О (PhO) ₂ Р—Н Пb | 120 | 20 | 80 | 0 |
| Id | $(C_{12}H_{25}O)_{2}P-H$ IIc | 120 | 57 | 21 | 22 |

Table 3. Conditions and yields of hydrophosphorylation products of alkynes on $Ni(cod)_2$ in the absence of phosphine ligand (1 ml of THF, 19 h, 9 mol% of catalyst)

Thus we have shown that the use of an "invalid" model reaction leads to false results in estimation of relative catalytic activity of various metal complexes. The necessary conditions of the valid comparison is the absence of the side reactions involving the chosen reagents and the necessary activation of the catalyst precursor. We suggest to use for the comparison of various catalysts based on the transition metal complexes the diphenylacetylene in the model reaction of hydrophosphorylation of alkynes. We suggest as the precursor of the bivalent nickel catalyst Ni(acac)₂/DIBAL.

An extremely important result of this research is the evidence of the alkyne insertion in the metal-hydrogen bond instead of the traditional concept on the insertion into the metal-phosphorus bond. The results obtained call for the reconsideration of the mechanisms of the catalytic cycles of hydrophosphorylation not only of alkynes but also of the other unsaturated compounds.

The found possibility of the "ligandless" hydrophosphorylation of alkynes and the exclusion of acid additives in the reaction catalyzed by nickel complexes are interesting finds for creation of resource-economical processes of the selective formation of the carbon–phosphorus bond.

EXPERIMENTAL

NMR spectra were registered on a spectrometer Bruker Avance (500 MHz) using as internal references TMS (¹H), solvent signals (¹³C), and aqueous H_3PO_4 as external reference (³¹P). The reaction products were purified by flash-chromatography on a dry column [27]. Ni(acac)₂ before use was dried in a vacuum (0.01– 0.02 mm Hg, 60°C, 30 min).

All reactions were carried out at stirring with a magnetic stirrer at temperature-controlled heating on an oil bath. The reactions were carried out in hermetically closed test tubes with a screw-top and Teflon gasket. The manipulations with $Ni(cod)_2$ were performed in the argon box, the rest of catalysts were charged in air and before the heating the test tubes were flushed with argon. In all experiments the THF used was purified and distilled under argon.

Quantum-chemical calculations. The geometry optimization and energy calculation were carried out using a hybrid potential B3LYP [28–30] in the basis Lanl2dz [31–34] for metal atoms and the basis 6-31G(d) [35, 36] for the other atoms. The type of the found stationary points was controlled by the calculation of the eigenvalues of the matrices of the second derivatives of the energy (the absence of imaginary frequencies for intermediates and one imaginary frequency for transition states). The character of the transition states was confirmed by the calculation of the internal reaction coordinate. The thermodynamic functions were calculated in the framework of the model harmonic oscillator–rigid rotator. All calculations were carried out applying the software GAUSSIAN 03 [37]. The molecular structures and oscillations were visualized by the use of the graphic packages MOLDEN [38] and GABEDIT [39].

Alkynes hydrophosphorylation catalyzed by Pd and Ni . A mixture of the catalyst $[Pd_2dba_3 \ 0.03 \ mmol$ $(31.1 \ mg)$, Ni(acac)₂ 0.06 mmol (15.4 mg), or Ni(cod)₂ 0.06 mmol (16.5 mg)], 63 mg (0.24 mmol) of triphenylphosphine, and 0.5 ml of THF was stirred at room temperature for 3–4 min till the appearance of the yellowbrown color in the case of Pd₂dba₃ and Ni(cod)₂ and of the green color in the case of Ni(acac)₂. To the solution obtained was added 1 mmol of H-phosphonate II and 1 mmol of alkyne Ia–Ic. The solid alkyne Id was charged into the test tube the first (before the catalyst).

Synthesis and isolation of olefins IIIb–IIId. A mixture of 214 mg (1.2 mmol) of diphenylacetylene, 24.8 mg (0.09 mmol) of Ni(cod)₂, 94.4 mg (0.36 mmol) of triphenylphosphine, and 1 ml of THF was stirred at room temperature for 3–4 min till the formation of homogeneous yellow-brown solution, then 1 mmol of H-phosphonate **IIa** was added, and the mixture was heated for 4 h at 120°C. On completion of the reaction all compounds were isolated in pure state by the flash-chromatography, eluent a mixture of petroleum ether and ethyl acetate. The obtained compounds were identified by comparison with the published spectral data [21], the purity of compounds were proved by the ¹H and ³¹P NMR spectra.

Hydrophosphorylation catalyzed by the system $Ni(acac)_2/DIBAL$. A mixture of 23.1mg (0.09 mmol) of Ni(acac)_2 and 1 ml of THF was stirred for 5 min, the obtained homogeneous green solution was cooled to 5°C, afterwards at stirring in the flow of argon was added 0.18 ml of 1 M solution of DIBAL in THF. The solution from green turned to black. The stirring was continued for 3 min, then 214 mg (1.2 mmol) of diphenylacetylene, 94.0 mg (0.36 mmol) of triphenylphosphine, 0.167 ml (1 mmol) of H-phosphonate **IIa** was added , and the mixture was heated for 4 h at 120°C.

The catalytic reaction in the presence of acid was performed as above described hydrophosphorylation of alkynes catalyzed by Pd and Ni. Into the test tube was charged the catalyst, the ligand, and the solvent, the mixture was stirred at room temperature for 3–4 min. To the obtained solution 1 mmol of H-phosphonate II, 1 mmol of alkyne I, and 7.7 μ l (0.1 mmol) of trifluoroacetic acid was added. The color of the reaction mixture in the course of heating did not change (the time and temperature of the reaction analogous to the experiment without acid).

The catalytic reaction in the absence of phosphine ligand. A mixture of 214.0 mg (1.2 mmol) of diphenyl-acetylene and 24.8 mg (0.09 mmol) of Ni(cod)₂ in 1 ml of THF was stirred at room temperature for 3-4 min till the formation of the homogeneous light-brown solution. To the obtained solution was added 1 mmol of H-phosphonate II, then liquid alkynes Ia–Ic. Data on the time and temperature of the reaction are given in Table 3.

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