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Synthesis of Vinylphosphines by Hydrophosphination of Alkynes in the Presence of Transition Metal Complexes*

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Abstract—Intermolecular hydrophosphination of terminal and internal alkynes with diphenylphosphine, catalyzed by palladium and nickel complexes, was accomplished for the first time. The reaction follows the *syn*-addition pattern. Conditions were found which ensure regioselective addition with predominant or exclusive formation of the corresponding α- or β-adduct.

The addition of compounds with a heteroelement–hydrogen bond (E−H) to alkynes is an important reaction leading to functionally substituted olefins. Of particular interest are processes catalyzed by transition metal complexes, which make it possible to effect regio- and stereoselective addition. Up to now, hydrosilylation [1–3], hydrostannylation [4–7], and hydroboration [8, 9] of alkynes, catalyzed by transition metal complexes, have been studied in sufficient detail. Tanaka and co-workers recently initiated studies on the addition of dialkyl hydrogen phosphites [10, 11] and phosphine oxides [12–14] to alkynes in the presence of palladium and rhodium complexes. The addition of phosphines to alkynes in the presence of metal complexes was reported by Marks and co-workers [15–17] who performed intramolecular cyclization of phosphinoalkynes under catalysis by organic lanthanide derivatives. In the present communication we describe a new synthetic route to vinylphosphines, which is based on palladium- or nickel-catalyzed direct addition of secondary phosphines to both terminal and internal alkynes.

Alkenylphosphines constitute an important class of phosphine ligands [18–20]. However, their application

is limited because of the lack of a simple and convenient procedure for their synthesis. Alkenylphosphines can be obtained by reactions of vinyl derivatives of nontransition metals (such as Li, Mg, and Sn) with halophosphines or of phosphide anion with alkenyl halides [21]. These compounds can also be obtained by addition of primary and secondary phosphines to alkynes. The first and the second methods include a laborious procedure for isolation of final products (removal of the metal salt); therefore, they are low efficient from the viewpoint of "green chemistry" requirements imposed on modern synthetic procedures [22–25]. Radical or thermal, as well as base-catalyzed, addition of primary and secondary phosphines to alkynes provides an optimal procedure sometimes ensuring 100% "atom efficiency." However, in the general case, it was studied insufficiently. Simple thermal addition of phosphines to alkynes requires severe conditions (prolonged heating at elevated temperature) and leads to mixtures of products which are usually formed in poor yields [26]. Several examples of radical addition of phosphines to alkynes were reported, but catalysis by bases (e.g., by potassium *tert*-butoxide) is used more frequently [27, 28]. In some cases, the addition was accelerated through the use of stoichiometric amounts of alkyne and phosphine complexes with metals (like Mo), which were prepared preliminarily [29, 30]; however, base catalysis was also necessary.

We were the first to effect palladium- or nickel-catalyzed addition of diphenylphosphine to alkynes As catalytic precursors we tried various palladium and

nickel compounds: Pd(PPh$_3$)$_4$, Pd$_2$(dba)$_3$, Pd(OAc)$_2$, NiBr$_2$, Ni(acac)$_2$, Ni[P(OEt)$_3$]$_4$, etc. All these complexes catalyze the addition of diphenylphosphine to phenylacetylene (**Ia**) in benzene or acetonitrile with formation of three products: diphenyl-(1-phenylethenyl)phosphine (**IIa**, α-adduct), (*E*)-diphenyl(2-phenylethenyl)phosphine (*E*-**IIIa**), and (*Z*)-diphenyl-(2-phenylethenyl)phosphine (*Z*-**IIIa**) (β-adducts) (Scheme 1).

Scheme 1.
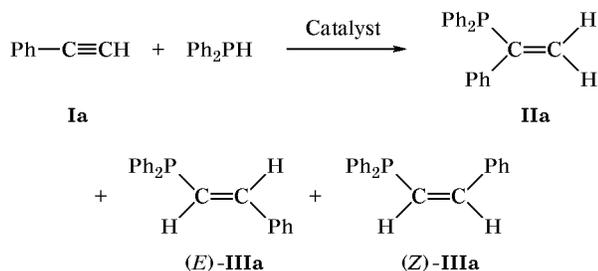
The optimal catalytic system and reaction conditions were selected on the basis of the data obtained by ^{31}P NMR monitoring of the reaction of diphenylphosphine with phenylacetylene, following the intensity of the Ph$_2$PH signal, δ$_P$ –41.6 ppm. The results are given in Table 1. The selectivity of the process, primarily the site of addition of the Ph$_2$P group, was found to strongly depend on the catalytic system. Reactions catalyzed by Pd(0) complexes, Pd(PPh$_3$)$_4$ and Pd$_2$(dba)$_3$, on heating at 130°C for 18 h resulted in formation of phosphine **IIIa** as the only product in acetonitrile (Table 1, run nos. 1, 2) or the major product in benzene (run nos. 3, 4). Both in acetonitrile and in benzene, the major isomer was *Z*-**IIIa**. By contrast, in the presence of palladium acetate as catalyst precursor, the corresponding α-adduct (phosphine **IIa**) was formed as the major product in both solvents (run nos. 5, 6). In this case, the reaction in acetonitrile was much faster than in benzene, and its regioselectivity was also higher (run no. 6).

Catalytic systems on the basis of nickel complexes or salts turned out to be more effective than palladium complexes. In the presence of tetrakis(triethyl phosphite)nickel(0), bis(acetylacetonato)nickel(II), or NiBr$_2$, the addition occurred at a sufficient rate in benzene at 80°C (run nos. 7–9). Here, the general relations were the same as in the catalysis by palladium complexes. Phosphine **IIIa** was the major product in the reaction catalyzed by the Ni(0) complex (run no. 7). The same product also predominates in the presence of Ni(acac)$_2$ (run no. 8), though its fraction is lower than in the presence of Ni[P(OEt)$_3$]$_4$.

Nickel(II) bromide was the best catalyst for the preparation of α-adduct **IIa**. Its fraction was 90%, and minor isomer *E*-**IIIa** was obtained with high stereoselectivity (run no. 9). When the hydrophosphination was performed in the presence of nickel complexes at 130°C, the reaction time was considerably shorter (1.5–2 h); the amount of the β-adduct did not change (run no. 10), whereas the fraction of the α-isomer slightly decreased (run no. 11).

The rate of hydrophosphination at 80°C strongly depends on the solvent. The reaction of diphenylphosphine with phenylacetylene in acetonitrile in the presence of 2 mol % of Ni(acac)$_2$ was very slow: the conversion was 80% in 200 h, i.e., its rate is comparable with that of the thermal reaction (no catalytic effect was observed). The same reaction in benzene takes 60 h (100% conversion), and the isomeric composition of the products almost does not change. It should be noted that nickel and palladium salts as catalytic precursors give rise to the α-adduct as the major product at both 80°C and 130°C (run nos. 5, 6, 9, 11) and that the minor β-adduct is formed exclusively as *E* isomer. The use of Ni(0) or Pd(0) complexes, as well as of Ni(acac)$_2$, leads to substantial change in the regioselectivity, so that β-adduct **IIIa** prevails among the products (run nos. 1–4, 8, 10), and it is formed as a mixture of *E* and *Z* isomers. In the catalysis by Pd complexes, the fraction of *Z*-**IIIa** is greater, whereas in the presence of Ni complex the major isomer has *E* configuration.

The above data led us to presume that predominant formation of the α-adduct is observed in the presence of those catalytic systems which could give rise to acid species. In fact, in the reaction with unpurified Ni[P(OEt)$_3$]$_4$, which may be contaminated with (EtO)$_2$P(O)Br and probably with (EtO)$_2$P(O)OH, the reaction mixture contained about 70% of the α-adduct (cf. run no. 7). In order to verify this assumption, hydrophosphination of phenylacethylene was carried

Scheme 2.
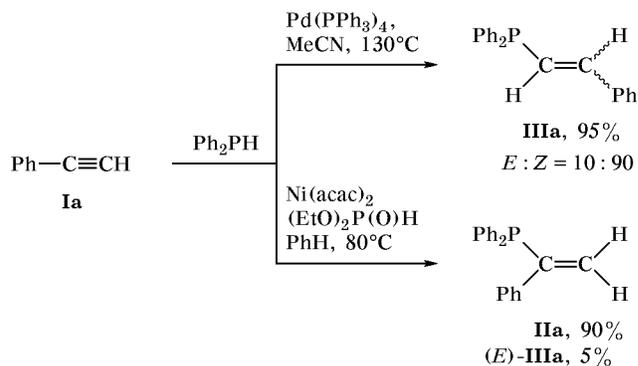
Table 1. Reaction of phenylacetylene (**Ia**) with diphenylphosphine in the presence of palladium and nickel complexes

Run no.	Catalyst	Solvent	Temperature, °C (time, h)	Yield,[a] %	Isomer ratio[a] **IIa**:**IIIa** (E/Z)
1	Pd(PPh₃)₄	Acetonitrile	130 (18)	95	0:100 (14/86)
2	Pd₂(dba)₃	Acetonitrile	130 (18)	98	0:100 (20/80)
3	Pd(PPh₃)₄	Benzene	130 (18)	95	7:93 (30/70)
4	Pd₂(dba)₃	Benzene	130 (18)	87[b]	25:75 (20/80)
5	Pd(OAc)₂	Benzene	130 (20)	90	64:36 (28/72)
6	Pd(OAc)₂	Acetonitrile	130 (7)	89	87:13 (53/47)
7	Ni[P(OEt)₃]₄	Benzene	80 (10)	93[b]	10:90 (50/50)
8	Ni(acac)₂	Benzene	80 (60)	82[b]	27:73 (67/33)
9	NiBr₂	Benzene	80 (10)	90[b]	86:14 (100/0)
10	Ni(acac)₂	Benzene	130 (2)	92[b]	27:73 (77/23)
11	NiBr₂	Benzene	130 (2)	85[b]	78:22 (100/0)
12	Ni(acac)₂ + (EtO)₂P(O)H	Benzene	80 (10)	90	95:5 (100/0)
13	Pd(PPh₃)₄ + MeCOOH	Acetonitrile	80 (12)	92[b]	92:8 (50/50)

[a] According to the ³¹P NMR data.
[b] After distillation.

out over Ni(acac)₂ at 80°C in benzene containing 2 mol % of diethyl hydrogen phosphite. As a result, we obtained almost pure α-isomer with an admixture of less than 5% of the β-adduct (run no. 12). Likewise, addition of a catalytic amount of acetic acid in the hydrophosphination catalyzed by Pd(PPh₃)₄ in acetonitrile (run no. 13) dramatically changed its regioselectivity. In this case, α-isomer **IIa** was also the major product, and the ratio **IIa**:**IIIa** (E:Z) was 92:8 (50:50) (cf. run no. 1; Scheme 2). Thus, by appropriate choice of the catalytic system we are able to control the selectivity of the addition and obtain phosphine **II** or **III** in high yield.

The structure of the products was confirmed by elemental analysis, and IR and ¹H, ¹³C, and ³¹P NMR spectroscopy. In the ¹H NMR spectra of α-adduct **IIa**, the vinyl protons give rise to an *ABX* spin system, δ 5.58 and 4.88 ppm, J_{PH} = 12.8, 5.6 Hz. Isomers E-**IIIa** and Z-**IIIa** of diphenyl(2-phenylethenyl)phosphine are much more difficult to identify, for signal from one of the vinyl protons falls into the region of aromatic protons. However, the proposed structures are confirmed by combination of our spectral data and those reported in [31–35] (¹H NMR for Z-**IIIa** and ¹³C NMR for Z-**IIIa** and E-**IIIa**).

The simplest explanation for the formation of the β-adduct may be the assumption that the reaction involves initial oxidative addition of diphenylphosphine to the Pd(0) or Ni(0) complex to give a hydride complex [36, 37], alkyne insertion into the M−H

bond, and subsequent reductive elimination with regeneration of the reactive species of the catalytic complex (cycle **A** in Scheme 3). Change of the regioselectivity in the reactions catalyzed by Pd(II) or Ni(II) complexes or in the presence of an acid occurs due to appearance of the second catalytic cycle **B** via oxidative addition of the acid species HX to the metal and insertion of phenylacetylene into the M−H bond according to the Markownikoff rule. The subsequent ligand exchange (X and PPh₂) regenerates HX and gives an intermediate species; reductive elimination from the latter yields the cross-coupling product.

Scheme 3.
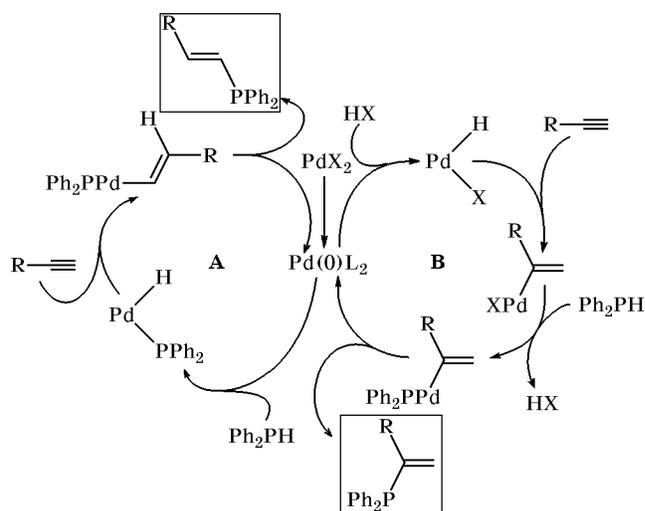
Regio- and stereoselective hydrophosphination was observed in the reaction of diphenylphosphine with *tert*-butylacetylene (**Ib**). The bulky substituent at the triple bond gives rise to *anti*-Markownikoff addition with formation of the β-adduct. Bis(acetylacetonato)-nickel(II) and nickel(II) bromide turned out to be the most efficient catalysts for hydrophosphination of *tert*-butylacetylene: the reaction was complete in 2–5 h at 130°C (Table 2; run nos. 1, 2) and in 12 h at 80°C, respectively (run no. 3; Scheme 4).

Scheme 4.
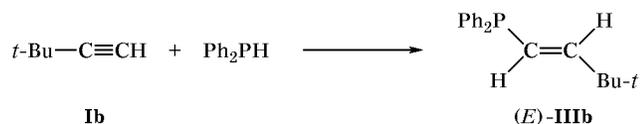
On the other hand, both triethyl phosphite Ni(0) complex and dichlorobis(triphenylphosphine)palladium(II) exhibit considerably lower catalytic activity (Table 2, run nos. 4–6). However, in comparison to the thermal addition which does not occur at all in 200 h at 130°C, the catalytic effect of these complexes can be regarded as satisfactory. The only addition product (both that detected in the reaction mixture and isolated therefrom) was (*E*)-diphenyl(2-*tert*-butyl-ethenyl)phosphine (*E*-**IIIb**). The yield of the isolated phosphine was 95%, and its structure was proved by elemental analysis and ^1H, ^{13}C, and ^{31}P spectroscopy. The configuration of the double bond in *E*-**IIIb** was assigned on the basis of the $^3J_{HH}$ coupling constant equal to 17.0 Hz, which corresponds to *trans* arrangement of the vicinal protons, i.e., the reaction of diphenylphosphine to *tert*-butylacetylene over transition metal complexes follows the *syn*-addition pattern. This is consistent with the known data on addition of M−H compounds to alkynes under catalysis by metal complexes [38].

Table 2. Reaction of *tert*-butylacetylene with diphenylphosphine in benzene

Run no.	Catalyst	Temperature, °C	Time, h	Conversion of **Ib**, %
1	Ni(acac)$_2$	130	2	100
2	NiBr$_2$	130	5	100
3	NiBr$_2$	80	12	100
4	PdCl$_2$(PPh$_3$)$_2$	80	50	0
5	PdCl$_2$(PPh$_3$)$_2$	130	65	65
6	Ni[P(OEt)$_3$]$_4$	80	60	20
7	Thermal reaction	130	200	–

The *E* isomer of phosphine **IIIb** turned out to be the most stable, and no *E–Z* isomerization occurred in the reactions over metal complexes, in contrast to the reactions with phenylacetylene.

The addition of diphenylphosphine to 1-pentyne in acetonitrile at 130°C in the presence of bis(acetylacetonato)nickel(II) leads to formation of mixtures of the α- and β-adducts, the former prevailing (α:β = 70:30). Under analogous conditions in benzene, 70% of the β-adduct (a mixture of *E*-**IIIc** and *Z*-**IIIc**) and 30% of α-adduct **IIc** were obtained. After distillation, the overall yield was 70% (Scheme 5).

Scheme 5.
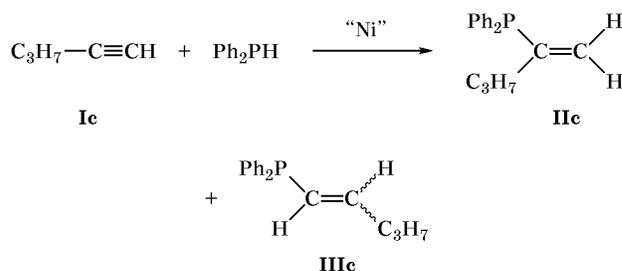
The reaction of diphenylphosphine with 1-heptyne (**Id**) at 130°C in acetonitrile or benzene in the presence of Ni(acac)$_2$ was complete in 1.5–5 h to afford 85% of a mixture of three phosphines: α-adduct **IId** and β-adducts *E*-**IIId** and *Z*-**IIId** at an α:β ratio of 55:45 (Scheme 6).

Scheme 6.
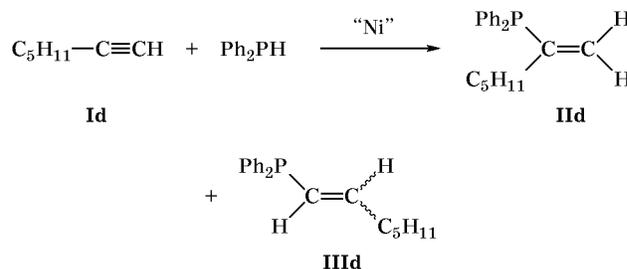
Methyl 2-propynyl ether (**Ie**) reacted with diphenylphosphine over nickel complex [Ni(acac)$_2$] at 130°C in acetonitrile, yielding mainly α-adduct **IIe** (yield 87%, reaction time 3 h; Scheme 7).

Scheme 7.
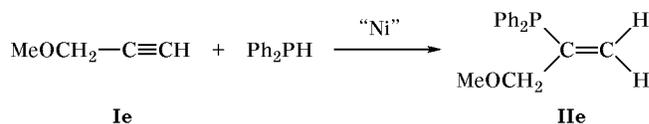
3-Dimethylaminopropyne (**If**) is less reactive than methyl 2-propynyl ether (**Ie**), and its reaction with diphenylphosphine in acetonitrile over Ni(acac)$_2$ requires heating for 60 h at 130°C. Distillation of the reaction mixture gave 84% of a mixture of addition products containing approximately equal amounts of α-adduct **IIf** and *E*- and *Z*-isomeric β-adducts **IIIf** (Scheme 8).

Scheme 8.
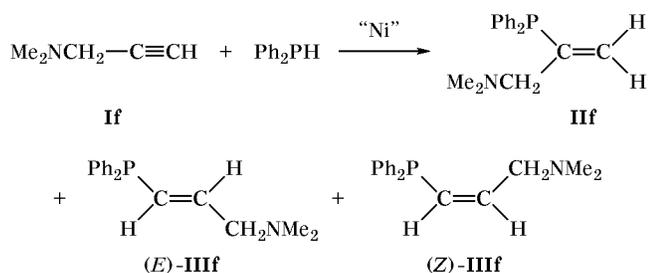
Internal alkynes are also capable of reacting with diphenylphosphine under catalysis by transition metal complexes. Using tolan as an example, we showed that the reaction catalyzed by bis(acetylacetonato)-nickel(II) occurs under fairly mild conditions (12 h at 80°C) and yields (*E*)-1,2-diphenylethenylphosphine (**IIIg**) in quantitative yield (Scheme 9).

Scheme 9.
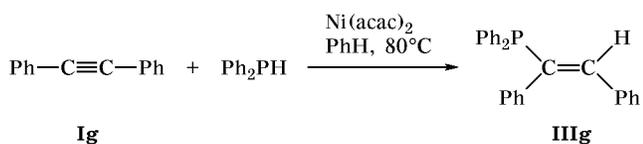
Thus, we were the first to accomplish transition metal-catalyzed addition of diphenylphosphine at the triple bond and find optimal conditions for selective preparation of a number of tertiary alkenylphosphines.

EXPERIMENTAL

All operation with readily hydrolyzable and oxidizable compounds and transition metal complexes were carried out under dry argon; the glassware was kept in a drying box or heated by a burner prior to use. To remove traces of moisture, argon was passed through a column filled with phosphoric anhydride. The solvents were dried and purified by standard methods: petroleum ether, hexane, pentane, benzene, and diethyl ether were refluxed and distilled over metallic sodium, and acetonitrile was distilled over calcium hydride. Tetrakis(triphenylphosphine)palla-

dium(0) [39], tetrakis(triethyl phosphite)nickel(0) [40], diphenylphosphine [41], and *tert*-butylacetylene [42] were synthesized by known methods. Phenylacetylene, 1-pentyne, 1-heptyne, and methoxymethylacetylene were commercial products.

The progress of reactions was monitored, and the products were identified, by IR and ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra were recorded on Tesla BS-467 and Varian VXR-400 spectrometers at 60 and 400 MHz, respectively, using TMS, HMDS, or residual solvent signals as reference. The ^{13}C NMR spectra were obtained on a Varian VXR-400 instrument operating at 100.6 MHz; the chemical shifts were measured relative to the solvent signals: CD$_2$Cl$_2$, CD$_3$CN, C$_6$D$_6$, and CDCl$_3$. The ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer at 32.2 MHz using 85% H$_3$PO$_4$ as external reference.

The reactions were carried out in 8-mm (i.d.) ampules filled with argon, which were charged with 0.57 g (0.56 ml, 3 mmol) of diphenylphosphine, 0.3 g (0.36 ml, 3 mmol) of phenylacetylene, 2 ml of appropriate solvent, and catalyst. The ampule was sealed and heated to a required temperature.

Reaction of diphenylphosphine with phenylacetylene in the presence of Pd(PPh$_3$)$_4$. A 40-mg (1.2 mol %) amount of tetrakis(triphenylphosphine)-palladium(0) was used. *a. In acetonitrile at 130°C.* The reaction mixture was heated at 130°C. After 2 h (10% conversion), the ^{31}P NMR spectrum of the mixture contained a signal from initial diphenylphosphine and a signal at δ$_P$ –24.72 ppm from phosphine *Z*-**IIIa**. After 8 h, the only product was diphenyl(2-phenylethenyl)phosphine (**IIIa**) as a mixture of *E* and *Z* isomers at a ratio of 14:86.

b. In benzene at 130°C. After 2 h (85% conversion), the ^{31}P NMR spectrum of the mixture contained signals belonging to phosphines **IIa**, *E*-**IIIa**, and *Z*-**IIIa** at a ratio of 1:3:7. After 8 h (95% conversion), the product ratio was the same. The mixture was heated for 18 h to obtain 0.86 g (100%) of a mixture of phosphines **IIa**, *E*-**IIIa**, and *Z*-**IIIa** at a ratio of 7:93 (**IIa**:**IIIa**) (*E*:*Z* = 30:70) [43, 44].

Phosphine (IIa). ^{31}P NMR spectrum: δ$_P$ –5.3 ppm. ^{1}H NMR spectrum, δ, ppm: 4.88 d.d (1H, *cis*-H, J_{HH} = 1.0, $^3J_{PH}$ = 5.6 Hz), 5.58 d.d (1H, *trans*-H, J_{HH} = 1.0, $^3J_{PH}$ = 12.8 Hz), 7.3 m (15H, H$_{arom}$). ^{13}C NMR spectrum, δ$_C$, ppm: 125.07 d (CH$_2$, $^2J_{PC}$ = 3.9 Hz), 142.44 d (CP, $^1J_{PC}$ = 21.4 Hz), 136.13 d (C^i, $^1J_{PC}$ = 13.0 Hz).

Phosphine *E*-IIIa. ^{31}P NMR spectrum: δ$_P$ –11.54 ppm. ^{1}H NMR spectrum, δ, ppm: 6.88 d.d (1H, *cis*-H, J_{HH} = 10.8, $^3J_{PH}$ < 1 Hz), 7.32 d.d (1H,

PCH, J_{HH} = 10.8, $^2J_{PH}$ < 1 Hz), 7.3 m (15H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 126.65 d (CPh, $^2J_{PC}$ = 11.4 Hz), 143.71 d (CP, $^1J_{PC}$ = 30.5 Hz), 136.85 d (C^i, $^1J_{PC}$ = 13.1 Hz).

Phosphine Z-IIIa. ^{31}P NMR spectrum: δ_P –24.72 ppm. ^{1}H NMR spectrum, δ, ppm: 6.40 d.d (1H, *trans*-H, J_{HH} = 12.5, $^3J_{PH}$ < 1 Hz), ~7.3 d.d (1H, PCH, J_{HH} = 12.5, $^2J_{PH}$ < 1 Hz), 7.3 m (15H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 129.34 d (CPh, $^2J_{PC}$ = 12.2 Hz), 144.89 d (CP, $^1J_{PC}$ = 20.9 Hz), 138,12 d (C^i, $^1J_{PC}$ = 9.4 Hz).

Reaction of diphenylphosphine with phenylacetylene in the presence of Pd$_2$(dba)$_3 \cdot$CHCl$_3$. A 20-mg (0.5 mol %) amount of dibenzylideneacetone palladium complex was used. *a. In acetonitrile at 130 ℃.* The reaction mixture was heated for 18 h at 130°C. Appropriate treatment of the mixture (without distillation) gave 0.86 g (100%) of phosphine **IIIa** as the only product (*E*:*Z* = 20:80).

b. In benzene at 130 ℃. After 2 h (70% conversion), the ^{31}P NMR spectrum of the mixture contained signals from initial diphenylphosphine and products **II**, *E*-**IIIa**, and *Z*-**IIIa** (ratio 1.5:1:3). After 8 h (95% conversion), the product ratio was 2.2:1:4. The mixture was heated for 18 h. By appropriate treatment (without distillation) we isolated 0.86 g (100%) of a mixture of phosphines **IIa** and **IIIa** at a ratio of 25:75 (the *E*/*Z* isomer ratio of **IIIa** was 20:80).

Reaction of diphenylphosphine with phenylacetylene in the presence of Pd(OAc)$_2$. A 13-mg (2 mol %) of palladium(II) acetate was used. *a. In benzene at 130 ℃.* After 20 h, the ^{31}P NMR spectrum of the reaction mixture contained signals from phosphines **IIa**, *E*-**IIIa**, and *Z*-**IIIa**. The ratio **IIa**:**IIIa** was 64:36 (*E*/*Z* ratio 28:72). The solvent was distilled off, and the residue was kept for 3 h under reduced pressure (1–2 mm, oil pump) to obtain 0.78 g (90%) of a mixture of phosphines **IIa**, *E*-**IIIa**, and *Z*-**IIIa** at the same ratio.

b. In acetonitrile at 130 ℃. The reaction mixture was heated for 7 h at 130°C and was then filtered through a thin layer of silica gel on a glass filter to remove the catalyst. The filtrate was evaporated under reduced pressure to obtain 0.77 g (89%) of a mixture of diphenyl(1-phenylethenyl)phosphine (**IIa**), (*E*)-diphenyl(2-phenylethenyl)phosphine (*E*-**IIIa**), and (*Z*)-diphenyl(2-phenylethenyl)phosphine (*Z*-**IIIa**); **IIa**/**IIIa** ratio 87:13 (*E*/*Z* 53:47).

Reaction of diphenylphosphine with phenylacetylene in the presence of Ni[P(OEt)$_3$]$_4$. A 25-mg (1 mol %) amount of tetrakis(triethyl phosphite)-nickel(0) was used. The reaction mixture (a suspension in benzene) was heated at 80°C in a sealed ampule. After 8 h (80% conversion), the ^{31}P NMR spectrum of the mixture contained signals at δ_P –5.3 (**IIa**), –11.54 (*E*-**IIIa**), and –24.72 ppm (*Z*-**IIIa**) at a ratio of 0.1:1:1. The mixture was heated for 10 h at 80°C, and by the end of the reaction the isomer ratio **IIa**:**IIIa** (*E*/*Z*) was 10:90 (50:50). The mixture was filtered through a thin layer of silica gel on a glass filter to remove the catalyst. The filtrate was evaporated under reduced pressure, and the residue was distilled in a vacuum to obtain 0.8 g (93%) of a mixture of phosphines **IIa**, *E*-**IIIa**, and *Z*-**IIIa** at the same ratio. bp 140–145°C (7×10^{-2} mm).

Reaction of diphenylphosphine with phenylacetylene in the presence of Ni(acac)$_2$. A 20-mg (1.3 mol %) of bis(acetylacetonato)nickel(II) was used. *a. In benzene at 80 ℃.* After 10 h (40% conversion), the ^{31}P NMR spectrum of the reaction mixture contained signals from phosphines **IIa**, *E*-**IIIa**, and *Z*-**IIIa** at a ratio of 1:17.3:3. The mixture was heated for 50 h and filtered through a thin layer of silica gel on a glass filter to remove the catalyst. The filtrate was evaporated to obtain 0.86 g (100%) of a mixture of phosphines **IIa** and **IIIa** at a ratio of 27:73 ((*E*/*Z* ratio in **IIIa** 67:33). Distillation gave 0.7 g (82%) of a product mixture with the same isomer ratio. bp 140–145°C (7×10^{-2} mm).

b. In benzene at 130 ℃. The mixture was heated for 2 h at 130°C and was then treated as described above to obtain 0.86 g (100%) of a mixture of phosphines **IIa** and **IIIa** at a ratio of 27:73 (*E*/*Z* ratio in **IIIa** 77:23). Vacuum distillation gave 92% of the same mixture.

c. In acetonitrile at 130 ℃. An ampule was purged with argon, charged with 0.56 g (0.56 ml, 0.003 mol) of diphenylphosphine and 20 mg (1.3 mol %) of bis-(acetylacetonato)nickel(II) in 2 ml of anhydrous acetonitrile, and sealed. The mixture was heated for 3 h at 140°C, the ampule was opened, 0.3 g (0.36 ml, 0.003 mol) of phenylacetylene was added to the yellow solution, and the ampule was sealed and heated for 1.5 h at 130°C. When the reaction was complete, the mixture was treated as described above to obtain 0.86 g (100%) of a mixture of phosphines **IIa**, *E*-**IIIa**, and *Z*-**IIIa** at a ratio of 2.14:5.43:1. Further heating of the isomer mixture for 25 h at 140°C resulted in change of the **IIa**:**IIIa** ratio to 25:75 (*E*/*Z* 84:26).

Reaction of diphenylphosphine with phenylacetylene in the presence of NiBr$_2$. A 10-mg (1 mol %) amount of nickel(II) bromide was used. *a. In benzene at 80 ℃.* The mixture was heated for

10 h at 80°C in a sealed ampule. After appropriate treatment (without distillation), 0.86 g (100%) of a mixture of phosphines **IIa** and *E*-**IIIa** at a ratio of 86:14 was obtained. Vacuum distillation gave 90% of the same product mixture.

b. In benzene at 130°C. The mixture was heated for 2 h at 130°C in a sealed ampule. After appropriate treatment (without distillation), 0.85 g (100%) of a mixture of spectrally pure phosphines **IIa** and *E*-**IIIa** at a ratio of 78:22 was obtained. Vacuum distillation gave 0.73 g (85%) of the same product mixture.

Reaction of diphenylphosphine with phenyl-acetylene in the presence of Ni(acac)$_2$ and diethyl hydrogen phosphite. A solution of 0.57 g (0.56 ml, 0.003 mol) of diphenylphosphine, 0.3 g (0.36 ml, 0.003 mol) of phenylacetylene, 20 mg (1.3 mol %) of bis(acetylacetonato)nickel(II), and 20 mg (2.5 mol %) of diethyl hydrogen phosphite in 2 ml of dry benzene was heated for 10 h at 80°C in a sealed ampule. After appropriate treatment (without distillation), 0.86 g (100%) of a mixture of phosphines **IIa** and *E*-**IIIa** at a ratio of 95:5 was obtained. Vacuum distillation gave 90% of the same product mixture.

Reaction of diphenylphosphine with phenyl-acetylene in the presence of Pd(PPh$_3$)$_4$ and acetic acid. A solution of 0.57 g (0.56 ml, 0.003 mol) of diphenylphosphine, 0.3 g (0.36 ml, 0.003 mol) of phenylacetylene, 40 mg (1.2 mol %) of tetrakis(tri-phenylphosphine)palladium(0), and 10 mg (2.5 mol %) of acetic acid in 2 ml of dry benzene was heated for 12 h at 80°C in a sealed ampule. After appropriate treatment (without distillation), 0.86 g (100%) of a mixture of phosphines **IIa** and *E*-**IIIa** at a ratio of 92:8 was obtained. Vacuum distillation gave 92% of the same product mixture.

Reaction of diphenylphosphine with *tert*-butyl-acetylene in the presence of Ni(acac)$_2$. An ampule was purged with argon and charged with 0.57 g (0.56 ml, 3 mmol) of diphenylphosphine, 0.42 g (0.63 ml, 5 mmol) of *tert*-butylacetylene (**Ib**), and 20 mg (1.3 mol %) of bis(acetylacetonato)nickel(II) in 2 ml of dry benzene. The ampule was sealed and heated for 2 h at 130°C. After appropriate treatment (without distillation), we obtained 0.81 g (100%) of (*E*)-(2-*tert*-butylethenyl)diphenylphosphine (*E*-**IIIb**). Vacuum distillation gave 0.73 g (90%) of phosphine *E*-**IIIb**. bp 92–95°C (2 mm). ^{31}P NMR spectrum: δ_P –14.56 ppm. ^{1}H NMR spectrum, δ, ppm: 0.99 s (9H, CH$_3$), 6.18 d.d (1H, PCH, $^3J_{HH}$ = 17.00, $^2J_{PH}$ = 3.3 Hz), 6.31 d.d (1H, HC=, $^3J_{HH}$ = 17, $^3J_{PH}$ = 17.1 Hz), 7.30 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 29.51 d (CH$_3$, $^4J_{PC}$ = 7.7 Hz), 33.53 d

(**C**CH$_3$, $^3J_{PC}$ = 12.0 Hz), 120.08 d (CR, $^2J_{PC}$ = 9.1 Hz), 157.96 d (CP, $^1J_{PC}$ = 32.5 Hz), 138.06 d (C^i, $^1J_{PC}$ = 9.7 Hz). Found, %: C 80.99; H 7.64; P 11.40. C$_{18}$H$_{21}$P. Calculated, %: C 80.30; H 7.81; P 11.52.

Reaction of diphenylphosphine with *tert*-butyl-acetylene in the presence of NiBr$_2$. A suspension of 0.57 g (0.56 ml, 3 mmol) of diphenylphosphine, 0.42 g (0.63 ml, 5 mmol) of *tert*-butylacetylene (**Ib**), and 10 mg (1.5 mol %) of nickel(II) bromide in 2 ml of dry benzene was heated for 5 h at 130°C. Vacuum distillation gave 0.77 g (95%) of (*E*)-(2-*tert*-butyl-ethenyl)diphenylphosphine (*E*-**IIIb**).

Reaction of diphenylphosphine with 1-pentyne in the presence of Ni(acac)$_2$. A suspension of 0.57 g (0.56 ml, 3 mmol) of diphenylphosphine, 0.34 g (0.49 ml, 5 mmol) of 1-pentyne (**Ic**), and 20 mg (1.3 mol %) of bis(acetylacetonato)nickel(II) in 2 ml of dry benzene was heated for 1.5 h at 130°C. Distillation gave 0.67 g (88%) of a mixture of diphenyl-(1-propylethenyl)phosphine (**IIc**), (*E*)-diphenyl(2-pro-pylethenyl)phosphine (*E*-**IIIc**), and (*Z*)-diphenyl-(2-propylethenyl)phosphine (*Z*-**IIIc**) at a ratio of 32:68 (**IIc**:**IIIc**), *E/Z* 85:15. bp 110–115°C (2 mm). Found, %: C 79.83; H 7.52; P 12.22. C$_{17}$H$_{19}$P. Calculated, %: C 80.31; H 7.48; P 12.20.

Phosphine IIc. ^{31}P NMR spectrum: δ_P –4.41 ppm. ^{1}H NMR spectrum, δ, ppm: 0.83 t (3H, RCH$_3$), 1.39 m (2H, RC**H**$_2$CH$_3$), 2.11 t (2H, =CC**H**$_2$R), 4.93 d.d. (1H, *cis*-H, $^2J_{HH}$ = 1.1, $^3J_{PH}$ = 9.1 Hz), 5.55 d.d (1H, *trans*-H, $^2J_{HH}$ = 1.1, $^3J_{PH}$ = 19.3 Hz), 7.32 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 13.46 s (RCH$_3$), 21.58 s (RCH$_2$CH$_3$), 36.92 d (=CCH$_2$R, $^3J_{PC}$ = 12.2 Hz), 122.41 d (=CH$_2$, $^2J_{PC}$ = 10.7 Hz), 148.45 d (CP, $^1J_{PC}$ = 13.8 Hz).

Phosphine *E*-IIIc. ^{31}P NMR spectrum: δ_P –14.80 ppm. ^{1}H NMR spectrum, δ, ppm: 0.81 t (3H, RCH$_3$), 1.34 m (2H, RC**H**$_2$CH$_3$), 2.07 d.t (2H, =CC**H**$_2$R), 6.18 q.t (1H, =CH, $^3J_{HH}$ = 13.5, $^3J_{PH}$ = 15.1 Hz), 6.23 d.d (1H, PCH, $^3J_{HH}$ = 13.5, $^2J_{PH}$ = 5.5 Hz, 7.13 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 13.57 s (RCH$_3$), 21.58 s (RCH$_2$CH$_3$), 36.71 d (=CCH$_2$R, $^3J_{PC}$ = 11.4 Hz), 134.44 d (=CR, $^2J_{PC}$ = 10.7 Hz), 148.21 d (CP, $^1J_{PC}$ = 33.6 Hz), 139.21 d (C^i, $^1J_{PC}$ = 9.2 Hz).

Phosphine *Z*-IIIc. ^{31}P NMR spectrum: δ_P –32.49 ppm. ^{1}H NMR spectrum, δ, ppm: 0.81 t (3H, RCH$_3$), 1.34 m (2H, RC**H**$_2$CH$_3$), 2.37 d.t (2H, =CC**H**$_2$R), 6.32 q.t (1H, =CH, $^3J_{HH}$ = 11.3, $^3J_{HH}$ = 7.1, $^3J_{PH}$ = 23.6 Hz), 6.13 d.q (1H, PCH, $^3J_{HH}$ = 11.3, $^3J_{HH}$ = 1.1, $^2J_{PH}$ = 2.2 Hz), 7.13 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 13.52 s (RCH$_3$), 22.18 s (RCH$_2$CH$_3$), 32.73 d (=CCH$_2$R, $^3J_{PC}$ = 19.8 Hz),

133.58 d (=CR, $^2J_{PC}$ = 10.9 Hz), 147.31 d (=CP, $^1J_{PC}$ = 24.5 Hz, 139.25 d (C^i, $^1J_{PC}$ = 9.2 Hz).

Reaction of diphenylphosphine with 1-heptyne in the presence of Ni(acac)$_2$. A mixture of 0.57 g (0.56 ml, 3 mmol) of diphenylphosphine, 0.48 g (0.65 ml, 5 mmol) of 1-heptyne (**Id**), and 20 mg (1.3 mol %) of bis(acetylacetonato)nickel(II) in 2 ml of anhydrous acetonitrile was heated for 1.5 h at 130°C in a sealed ampule. After appropriate treatment (without distillation), 0.84 g (100%) of a mixture of (1-pentylethenyl)diphenylphosphine (**IId**), (*E*)-(1-heptenyl)diphenylphosphine (*E*-**IIId**), and (*Z*)-(1-heptenyl)diphenylphosphine (*Z*-**IIId**) was obtained; **IId** : **IIId** ratio 55 : 45. Vacuum distillation gave 0.71 g (85%) of the same product mixture. bp 135–140°C (2 mm). Found, %: C 80.00; H 8.14; P 11.09. C$_{19}$H$_{23}$P. Calculated, %: C 80.85; H 8.15; P 10.99.

Phosphine IId. ^{31}P NMR spectrum: δ_P –3.57 ppm. ^{1}H NMR spectrum, δ, ppm: 5.04 d.d (1H, *cis*-H, $^2J_{HH}$ = 1.4, $^3J_{PH}$ = 9.7 Hz), 5.53 d.d (1H, *trans*-H, $^2J_{HH}$ = 1.4, $^3J_{PH}$ = 20.6 Hz), 7.40 m (10H, H$_{arom}$).

Phosphine *E*-IIId. ^{31}P NMR spectrum: δ_P –14.56 ppm. ^{1}H NMR spectrum, δ, ppm: 0.79 t (3H, RCH$_3$), 1.35 m (6H, RC**H**$_2$CH$_3$), 2.13 d.t (2H, =CC**H**$_2$R), 6.18 q.t (1H, =CH, $^3J_{HH}$ = 8.5, $^3J_{PH}$ = 18.4 Hz), 6.24 d.d (1H, PCH, $^3J_{HH}$ = 8.8, $^2J_{PH}$ = 5.8 Hz), 7.43 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 13.75 s (R**C**H$_3$), 22.18 s (R**C**H$_2$CH$_3$), 28.01 (R**C**H$_2$**C**H$_2$CH$_3$) 34.76 d (=C**C**H$_2$R, $^3J_{PC}$ = 13.44 Hz), 138.93 d (=CR, $^2J_{PC}$ = 9.2 Hz), 148.75 d (CP, $^1J_{PC}$ = 33.5 Hz).

Phosphine Z-IIId. ^{31}P NMR spectrum: δ_P –32.51 ppm. ^{1}H NMR spectrum, δ, ppm: 0.79 t (3H, RCH$_3$), 1.21 m (6H, RC**H**$_2$CH$_3$), 2.45 d.t (2H, =CC**H**$_2$R, $^3J_{HH}$ = 11.2, $^3J_{HH}$ = 7.5, $^3J_{PH}$ = 23.6 Hz), 6.13 d.q (1H, PCH, $^3J_{HH}$ = 11.2, $^3J_{HH}$ = 1.4, $^2J_{PH}$ = 2.2 Hz), 7.37 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 13.75 s (R**C**H$_3$), 22.18 s (R**C**H$_2$CH$_3$), 28.57 s (R**C**H$_2$**C**H$_2$CH$_3$), 31.06 s (=C**C**H$_2$**C**H$_2$R), 30.82 d (=C**C**H$_2$R, $^3J_{PC}$ = 21.4 Hz), 139.28 d (=CR, $^2J_{PC}$ = 9.1 Hz), 147.61 d (CP, $^1J_{PC}$ = 24.4 Hz), 134.44 d (C^i, $^1J_{PC}$ = 9.2 Hz).

Reaction of diphenylphosphine with methyl 2-propynyl ether. An ampule was purged with argon and charged with 0.57 g (0.56 ml, 3 mmol) of diphenylphosphine, 0.28 g (0.28 ml, 4 mmol) of methyl 2-propynyl ether (**Ie**), and 20 mg (1.3 mol %) of bis-(acetylacetonato)nickel(II) in 2 ml of anhydrous acetonitrile. The ampule was sealed and heated for 10 h at 130°C. After appropriate treatment (without distillation), 0.77 g (100%) of a mixture of phosphines **IIe**,

E-**IIIe**, and *Z*-**IIIe** was obtained; **IIe** : **IIIe** ratio 88 : 12 (*E/Z* 83 : 17). Distillation gave 0.57 g (87%) of a mixture of phosphines **IIe** and **IIIe** at the same ratio. bp 135–140°C (2 mm).

(1-Methoxymethylethenyl)diphenylphosphine (IIe). ^{31}P NMR spectrum: δ_P –8.76 ppm. ^{1}H NMR spectrum, δ, ppm: 3.25 s (3H, OCH$_3$), 3.88 d (2H, OCH$_2$, $^3J_{PH}$ = 1 Hz), 5.21 d.d (1H, *cis*-H, $^2J_{HH}$ = 1.5, $^3J_{PH}$ = 10.2 Hz), 5.91 d.d (1H, *trans*-H, $^2J_{HH}$ = 1.5, $^3J_{PH}$ = 22.2 Hz), 7.35 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 55.46 s (O**C**H$_3$), 74.71 d (O**C**H$_2$, $^2J_{PC}$ = 22.9 Hz), 124.83 d (=CH$_2$, $^2J_{PC}$ < 1 Hz), 145.24 d (=CP, $^1J_{PC}$ = 16.8 Hz), 135.64 d (C^i, $^1J_{PC}$ = 10.7 Hz).

(*E*)-(3-Methoxy-1-propenyl)diphenylphosphine (*E*-IIIe). ^{31}P NMR spectrum: δ_P –15.5 ppm. ^{1}H NMR spectrum, δ, ppm: 3.3 s (3H, OCH$_3$), 3.95 d.d (2H, OCH$_2$, $^3J_{HH}$ = 5.0, $^4J_{HH}$ = 1.5 Hz), 6.11 q.t (1H, =CH, $^3J_{HH}$ = 16.8, $^3J_{HH}$ = 5.0, $^3J_{PH}$ = 13.5 Hz), 6.48 q.t (1H, PCH, $^3J_{HH}$ = 16.8, $^4J_{HH}$ = 1.6, $^2J_{PH}$ = 9.3 Hz), 7.41 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 55.5 d (O**C**H$_3$, J_{PC} = 6.1 Hz), 73.55 d (O**C**H$_2$, J_{PC} = 12.2 Hz), 132.40 d (=**C**HCH$_2$, $^2J_{PC}$ = 19.9 Hz), 142.0 d (=CP, $^1J_{PC}$ = 27.5 Hz), 126.25 d (C^i, $^1J_{PC}$ = 13.8 Hz).

Reaction of diphenylphosphine with 3-dimethylaminopropyne. An ampule was purged with argon and charged with 0.57 g (0.56 ml, 3 mmol) of diphenylphosphine, 0.33 g (0.43 ml, 4 mmol) of 3-dimethylaminopropyne (**If**), and 20 mg (1.3 mol %) of bis(acetylacetonato)nickel(II) in 2 ml of anhydrous acetonitrile. The ampule was sealed and heated for 1.5 h at 130°C. The conversion was 10%, and the ^{31}P NMR spectrum of the mixture contained signals at δ_P –6.34, –14.83, and –31.37 ppm, belonging to (1-dimethylaminomethylethenyl)diphenylphosphine (**IIf**), (*E*)-(3-dimethylamino-1-propenyl)diphenylphosphine (*E*-**IIIf**), and (*Z*)-(3-dimethylamino-1-propenyl)diphenylphosphine (*Z*-**IIIf**), respectively, at a ratio of 1.5 : 2 : 1. The mixture was then heated for 10 h (35% conversion), and the product ratio changed to 1.3 : 1.3 : 1; it no longer changed on subsequent heating for 30 h. After 60 h at 130°C, the reaction was complete, and the ratio **IIf** : **IIIe** was 43 : 57 (*E/Z* 50 : 50). After appropriate treatment (without distillation), 0.81 g (100%) of a mixture of phosphines **IIf**, *E*-**IIIf**, and *Z*-**IIIf** was obtained. Distillation gave 0.68 g (83%) of the same mixture. bp 145–150°C (2 mm). Found, %: P 12.4. C$_{17}$H$_{20}$NP. Calculated, %: P 11.85.

Phosphine IIf. ^{31}P NMR spectrum: δ –6.34 ppm. ^{1}H NMR spectrum, δ, ppm: 2.18 s (6H, NCH$_3$),

3.26 d (2H, NCH$_2$, $^3J_{PH}$ = 6.4 Hz), 5.01 d.d (1H, cis-H, $^2J_{HH}$ < 1, $^3J_{PH}$ = 7.7 Hz), 5.77 d.d (1H, trans-H, $^2J_{HH}$ < 1, $^3J_{PH}$ = 17.7 Hz), 7.35 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 44.96 s (NCH$_3$), 64.40 d (NCH$_2$, J_{PC} = 21.4 Hz), 130.32 d (=**C**CH$_2$N), $^2J_{PC}$ = 12.2 Hz), 143.95 d (=CP, $^1J_{PC}$ = 27.5 Hz), 137.15 d (C^i, $^1J_{PC}$ = 10.7 Hz).

Phosphine E-IIIf. ^{31}P NMR spectrum: δ_P –14.83 ppm. ^{1}H NMR spectrum, δ, ppm: 2.17 s (6H, NCH$_3$), 2.99 d (2H, NCH$_2$, $^3J_{PH}$ = 6.0 Hz), 6.16 m (1H, =CH), 6.43 m (1H, PCH), 7.21 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 44.98 s (NCH$_3$), 63.12 d (NCH$_2$, J_{PC} = 12.3 Hz), 129.85 d (=**C**HCH$_2$N, $^2J_{PC}$ = 10.0 Hz), 146.32 d (=CHP, $^1J_{PC}$ = 16.8 Hz), 137.95 d (C^i, $^1J_{PC}$ = 10.7 Hz).

Phosphine Z-IIIf. ^{31}P NMR spectrum: δ_P –31.73 ppm. ^{1}H NMR spectrum, δ, ppm: 2.16 s (6H, NCH$_3$), 2.93 d (2H, NCH$_2$, $^3J_{PH}$ = 6.6 Hz), 6.16 m (1H, =**C**HCH$_2$N), 6.43 m (1H, =CHP), 7.21 m (10H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 45.0 s (NCH$_3$), 58.50 d (NCH$_2$, J_{PC} = 21.4 Hz), 130.32 d (=**C**HCH$_2$N, $^2J_{PC}$ = 12.2 Hz), 143.95 d (=CHP, $^1J_{PC}$ = 21.3 Hz), 138.6 d (C^i, $^1J_{PC}$ = 9.1 Hz).

Reaction of diphenylphosphine with diphenylacetylene. An ampule was purged with argon and charged with 0.28 g (0.28 ml, 1.5 mmol) of diphenylphosphine, 0.27 g (1.5 mol) of diphenylacetylene (**Ig**), and 10 mg (1 mol %) of bis(acetylacetonato)nickel(II) in 2 ml of dry benzene. The ampule was sealed and heated for 10 h at 80°C. As a result, 0.56 g (100%) of (E)-diphenyl(1,2-diphenylethenyl)phosphine (**IIIg**) was isolated. ^{31}P NMR spectrum: δ_P –10.02 ppm. mp 114–115°C [45].

REFERENCES

1. *Comprehensive Handbook on Hydrosilylation,* Marciniec, B., Ed., Oxford: Pergamon, 1992.

2. *The Chemistry of Organic Compounds,* Rappoport, Z. and Apeaig, U., Ed., Chichester: Wiley, 1998, vol. 2.

3. Schouman, H., Keitsch, M.R., Winterfeld, J., Muhle, S., and Molander, G.A., *J. Organomet. Chem.,* 1998, vol. 559, p. 181.

4. Pereyre, M., Quintard, J.-P., and Rahm, A., *Tin in Organic Synthesis,* London: Butterworth, 1987.

5. Harrison, P.G., *Chemistry of Tin,* Glasgow: Blachie, 1998.

6. Davies, A.G., *Organotin Chemistry,* Weinheim: VCH, 1997.

7. Lautens, M., Smith, N.D., and Ostrovsky, D., *J. Org. Chem.,* 1997, vol. 62, p. 8970.

8. Burgess, K. and Ohlmeyer, M.J., *Chem. Rev.,* 1991, vol. 91, p. 1179.

9. Beletskaya, I.P. and Pelter, A., *Tetrahedron,* 1997, vol. 53, p. 4957.

10. Han, L.-B. and Tanaka, M., *J. Am. Chem. Soc.,* 1996, vol. 118, p. 1571.

11. Zhao, Ch.-Q., Han, L.-B., Goto, M., and Tanaka, M., *Angew. Chem., Int. Ed.,* 2001, vol. 40, p. 1929.

12. Han, L.-B., Choi, N., and Tanaka, M., *Organometallics,* 1996, vol. 15, p. 3259.

13. Han, L.-B., Hua, R., and Tanaka, M., *Angew. Chem., Int. Ed.,* 1998, vol. 37, p. 94.

14. Han, L.-B., Zhao, Ch.-Q., and Tanaka, M., *J. Org. Chem.,* 2001, vol. 66, p. 5929.

15. Douglass, M.R. and Marks, T.J., *J. Am. Chem. Soc.,* 2000, vol. 122, p. 1824.

16. Douglass, M.R., Stern, Ch.L., and Marks, T.J., *J. Am. Chem. Soc.,* 2001, vol. 123, p. 10221.

17. Douglass, M.R., Ogasanara, M., Hang, S., Metz, M.R., and Marks, T.J., *Organometallics,* 2002, vol. 21, p. 283.

18. Weber, L., Kaminski, O., Boese, R., and Blaser, D., *Organometallics,* 1995, vol 14, p. 820.

19. Soulivong, D., Wieser, C., Marcellin, M., Matt, D., Harriman, A., and Toupet, L., *J. Chem. Soc., Dalton Trans.,* 1997, p. 2257.

20. Fruzuk, M.D., Gal, X., and Rettig, S.G., *Can. J. Chem.,* 1985, vol. 73, p. 1175.

21. Gilheany, D.C. and Mitchell, S.M., *The Chemistry of Organophosphorus Compounds,* Hartley, F.R., Ed., New York: Wiley, 1990, vol. 1, chap. 7, pp. 151–190.

22. Trost, B.M., *Science,* 1991, vol. 254, p. 1471.

23. Sheldon, R.A., *CHEMTECH,* 1994, vol. 24, p. 38.

24. Trost, B.M., *Angew. Chem., Int. Ed.,* 1995, vol. 34, p. 259.

25. Sheldon, R.A., *Chem. Ind.,* 1997, p. 12.

26. *Organic Phosphorus Compounds,* Kosolapoff, G.M. and Mayer, L., Eds., New York: Wiley, 1972, 2nd ed., vol. 1.

27. Wolfsberger, W., *Chem.-Ztg.,* 1988, vol. 112, p. 53.

28. Bookham, J.L., Smithies, D.M., Wright, A., Tronton-Pett, M., and McFarlane, W., *J. Chem. Soc.,* 1998, p. 811.

29. Moitra, K., Katalano, V.G., and Nelsom, J.H., *Bull. Soc. Chim. Fr.,* 1997, vol. 134, p. 471.

30. Moitra, K., Katalano, V.G., and Nelsom, J.H., *J. Organomet. Chem.,* 1997, vol. 529, p. 409.

31. Duncan, M. and Gallagher, M.J., *Org. Magn. Reson.,* 1981, vol. 15, p. 37.

32. Mitchell, T.N., Heesche-Wagner, K., and Belt, H.G., *Magn. Reson. Chem.,* 1991, vol. 29, p. 78.

33. Taileffer, M. and Cristau, H.J., *Tetrahedron Lett.,* 1998, vol. 39, p. 7857.

34. Mitchell, T.N. and Heesche, K., *J. Organomet. Chem.,* 1991, vol. 409, p. 163.

35. Reetz, M.T. and Schinzer, D., *Angew. Chem.,* 1997, vol. 89, p. 46.

36. Pringle, P.G. and Snith, M.B., *J. Chem. Soc., Chem. Commun.,* 1990, p. 1701.

37. Wicht, D.K., Kourkine, I.V., Lew, B.M., Nthenge, J.M., and Glueck, D.S., *J. Am. Chem. Soc.,* 1997, vol. 119, p. 5039.

38. *Comprehensive Organometallic Chemistry,* Abel, E.W., Gordon, F., Stone, A., and Wilkinson, G.W., Eds., New York: Pergamon, 1995, vol. 9, p. 12.

39. Coulson, D.R., *Inorg. Chem.,* 1972, vol. 13, p. 121.

40. Berdnik, I.V., Krasil'nikova, E.A., and Sentemov, V.V., *Zh. Obshch. Khim.,* 1989, vol. 59, p. 2508.

41. Gee, N., Shaw, R.A., and Smith, B.C., *Inorg. Synth.,* 1967, vol. 9, p. 19.

42. Barlet, W. and Rosen, G., *J. Am. Chem. Soc.,* 1942, vol. 64, p. 543.

43. Aquiar, A.M. and Daigle, D., *J. Org. Chem.,* 1965, vol. 30, p. 2826.

44. Aquiar, A.M. and Archibald, T.G., *Tetrahedron Lett.,* 1966, no. 45, p. 5471.

45. Bookham, J.L., McFarlane, W., Tornton-Pett, M., and Jones, S., *J. Chem. Soc., Dalton Trans.,* 1990, p. 3621.