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Synthesis and Catalytic Properties of Di- and Trinuclear Palladium Complexes with PCP-Pincer Ligands

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Abstract—Linear and branched conjugated pincer ligands having Ph_2P groups were synthesized: 3,3′,5,5′-tetrakis(diphenylphosphinomethyl)diphenylacetylene, 3,3′,5,5′-tetrakis(diphenylphosphinomethyl)diphenyldiacetylene, 1,3,5-tris[3,5-bis(diphenylphosphinomethyl)phenylethynyl]benzene, and hexakis[3,5-bis(diphenylphosphinomethyl)phenylethynyl]benzene. Palladation of these ligands by heating with $Pd(BF_4)_2(MeCN)_4$ in boiling acetonitrile gave the corresponding di- and trinuclear ionic pincer palladium complexes. No individual complex was obtained from hexakis[3,5-bis(diphenylphosphinomethyl)phenylethynyl]benzene. The ionic complexes were converted into the corresponding chloride complexes by treatment with sodium chloride in a mixture of water with methylene chloride. The structure of the ionic palladium complex with 3,3′,5,5′-tetrakis(diphenylphosphinomethyl)diphenylacetylene was established by X-ray analysis. The obtained palladium complexes exhibited a considerable catalytic activity in the Heck reaction of iodobenzene with ethyl acrylate and in the Michael addition of ethyl cyanoacetate with methyl vinyl ketone. The catalytic activity per palladium atom decreases as the number of palladium atoms in the complex increases.

In the recent years much attention is given to the synthesis and study of properties of various polynuclear transition metal complexes. A number of such systems show interesting properties as catalysts, sensors, and molecular devices [1–5]. Dendrimer systems containing metallacycles with tridentate P,C,P′-coordinating (pincer) ligands are extensively studied [6]. We have developed procedures for the preparation of dinuclear linear pincer palladium complexes bridged through one or two acetylene fragments [7], as well as of related trinuclear complexes having a 1,3,5-triethynylbenzene moiety as a base unit [8]. When used as catalysts, such metal–dendrimer systems can be regenerated by separation from the reaction products via nanomembrane filtration [9–11].

In the present work we have synthesized conjugated pincer ligands **Ia**–**IVa** with both linear and branched structure, having Ph_2P groups as coordinating fragments (Scheme 1), and the corresponding polynuclear palladium complexes and examined their catalytic

activity in the Heck reaction and Michael addition at an activated double bond.

The starting material in the synthesis of ligands **Ia**–**IVa** was 3,5-bis(bromomethyl)iodobenzene [12] which was converted (via a sequence of Arbuzov and Sonogashira reactions) into phosphine oxide **Ib** as precursor of **Ia**; Likewise, phosphine oxide **VI** was obtained (Scheme 2). Phosphine oxide **Ib** was also prepared by the Sonogashira coupling of aryl iodide **V** with ethylnyl derivative **VI**. Dimerization of phosphine oxide **VI** gave diacetylene derivative **IIb**. Finally, tris- and hexakis-substituted benzenes **IIIb** and **IVb** were synthesized by reaction of phosphine oxide **VI** with 1,3,5-tribromobenzene and hexabromobenzene, respectively (Scheme 3).

The resulting polyphosphine oxides **Ib**–**IVb** were quantitatively reduced to the corresponding phosphines **Ia**–**IVa** by heating with trichlorosilane in *o*-dichlorobenzene at 110°C [13]. Ionic palladium comlexes **Ic**–**IIIc** with pincer ligands **Ia**–**IIIa** were
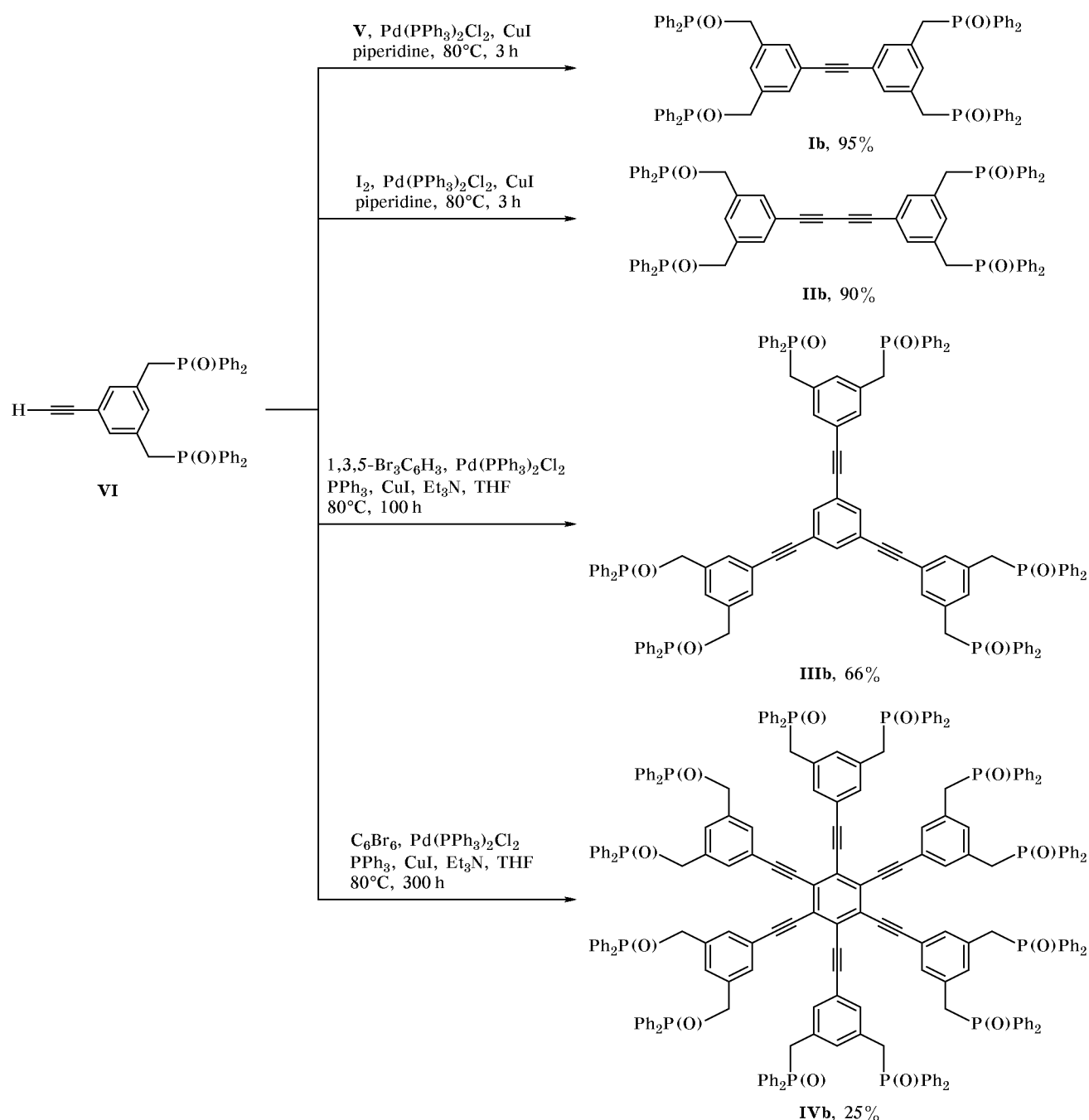
Scheme 1.

Ia

IIa

IIIa

IVa

Scheme 2.

V, 98%

Ib, 92%

95%

VI, 97%
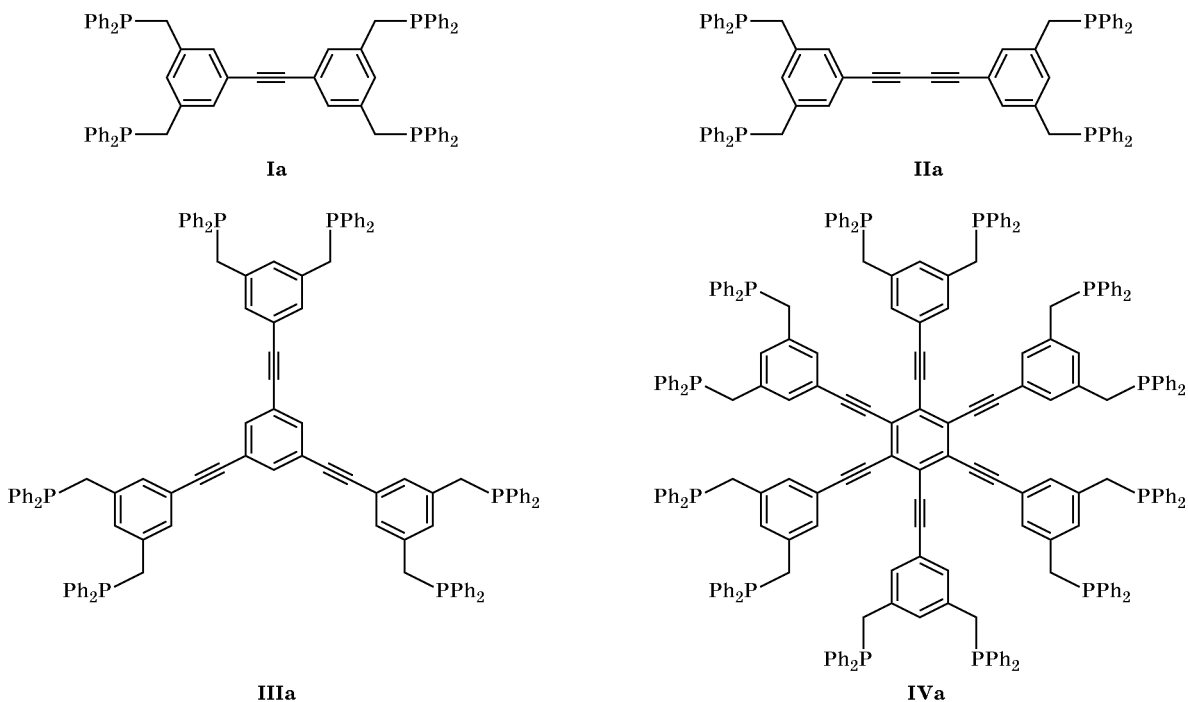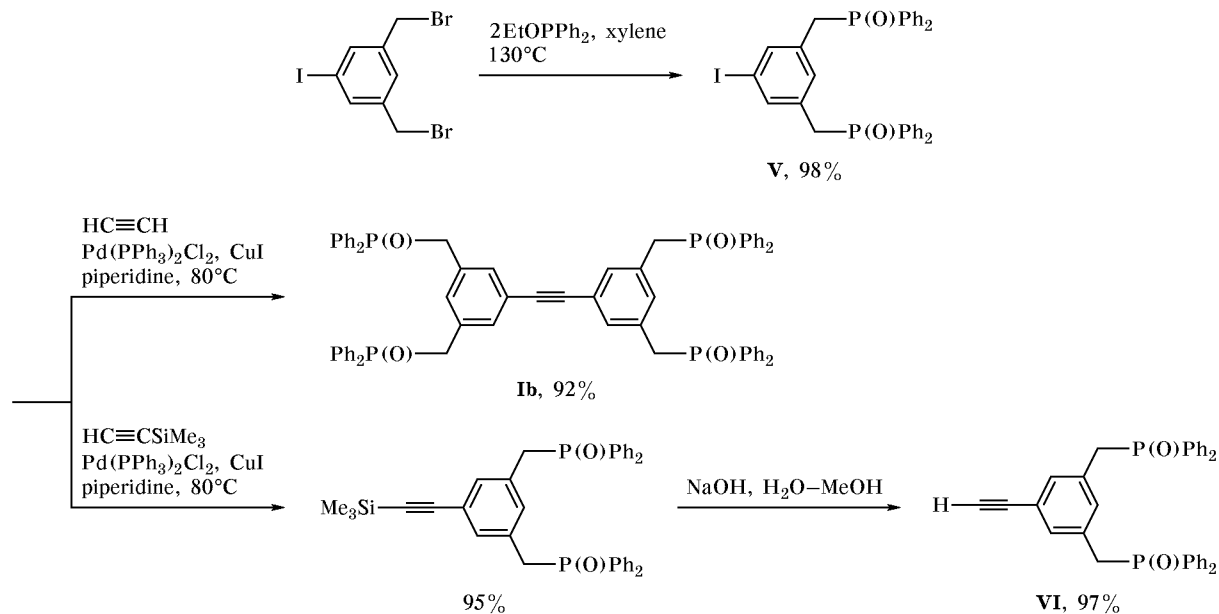
synthesized by direct electrophilic palladation of the ligands via treatment with [Pd(MeCN)₄](BF₄)₂ in boiling acetonitrile (reaction time 1 h). The reaction resulted in exhaustive palladation of ligands **Ia–IIIa** (Scheme 4). From ligand **IVa** we obtained a mixture of palladium complexes. The yields of complexes **Ic**, **IIc**, and **IIIc** were 51, 21, and 90%, respectively.

Presumably, the low yield of **IIc** is explained by the fact that conjugation with already present palladium atom hinders secondary palladation.

Ionic palladium complexes **Ic–IIIc** were quantitatively converted into the corresponding neutral chloride complexes **Id–IIId** by treatment with NaCl in CH₂Cl₂–H₂O (18°C, 3 h; Scheme 4).

Scheme 3.

V, Pd(PPh$_3$)$_2$Cl$_2$, CuI
piperidine, 80°C, 3 h

Ib, 95%

I$_2$, Pd(PPh$_3$)$_2$Cl$_2$, CuI
piperidine, 80°C, 3 h

IIb, 90%

1,3,5-Br$_3$C$_6$H$_3$, Pd(PPh$_3$)$_2$Cl$_2$
PPh$_3$, CuI, Et$_3$N, THF
80°C, 100 h

IIIb, 66%

C$_6$Br$_6$, Pd(PPh$_3$)$_2$Cl$_2$
PPh$_3$, CuI, Et$_3$N, THF
80°C, 300 h

IVb, 25%

All newly synthesized compounds were characterized by ^{1}H, ^{13}C, and ^{31}P NMR and UV spectra, MALDI-TOF-MS data, and elemental analyses.

X-Ray diffraction study of complex Ic. X-Ray structure analysis of complex **Ic** showed (Fig. 1, Table 1) that the palladium dication is located at the crystallographic inversion center and that two BF$_4^-$ anions reside in the outer coordination sphere. The

palladium atoms in the dication have a nearly square–planar configuration. Each Pd atom is linked to two P atoms [Pd–P 2.330(2) and 2.422(2) Å] arranged *trans* with respect to each other, one carbon atom [σ-bonded, Pd–C 2.019(6) Å], and nitrogen atom of the acetonitrile ligand [Pd–N 2.091(7) Å]. Specific geometric parameters of the tridendate pincer ligand are reflected in some deviations of the palladium
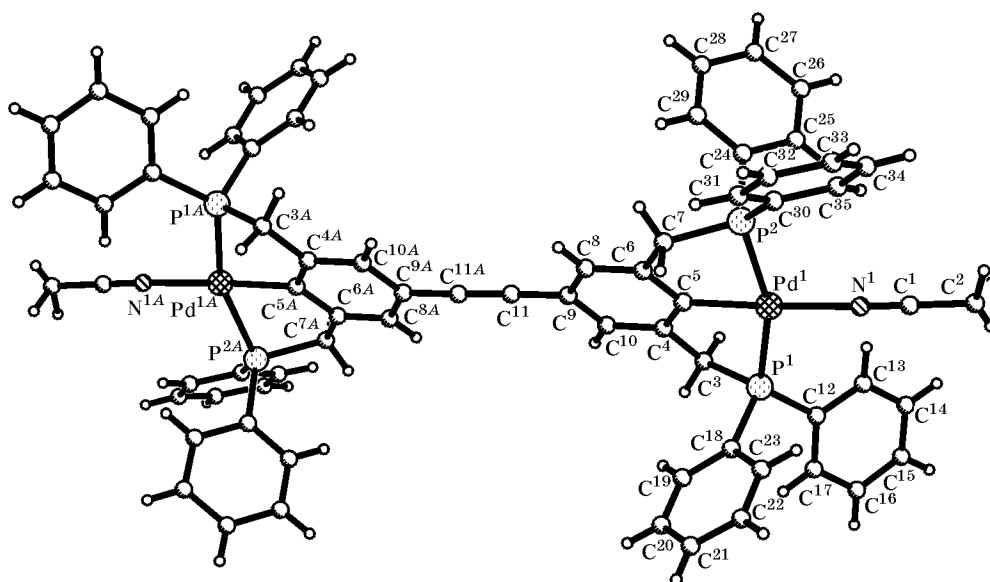
Scheme 4.

Ia $\xrightarrow[\text{51\%}]{\substack{\text{Pd(MeCN)}_4\text{(BF}_4)_2 \\ \text{MeCN, reflux, 1 h}}}$ **Ic**

$\xrightarrow[\text{98\%}]{\substack{\text{NaCl, H}_2\text{O/CH}_2\text{Cl}_2 \\ 18°\text{C, 3 h}}}$ **Id**

IIa $\xrightarrow[\text{21\%}]{\substack{\text{Pd(MeCN)}_4\text{(BF}_4)_2 \\ \text{MeCN, reflux, 1 h}}}$ **IIc**

$\xrightarrow[\text{98\%}]{\substack{\text{NaCl, H}_2\text{O/CH}_2\text{Cl}_2 \\ 18°\text{C, 3 h}}}$ **IId**

IIIa $\xrightarrow[\text{90\%}]{\substack{\text{Pd(MeCN)}_4\text{(BF}_4)_2 \\ \text{MeCN, reflux, 1 h}}}$ **IIIc**

$\xrightarrow[\text{98\%}]{\substack{\text{NaCl, H}_2\text{O/CH}_2\text{Cl}_2 \\ 18°\text{C, 3 h}}}$ **IIId**
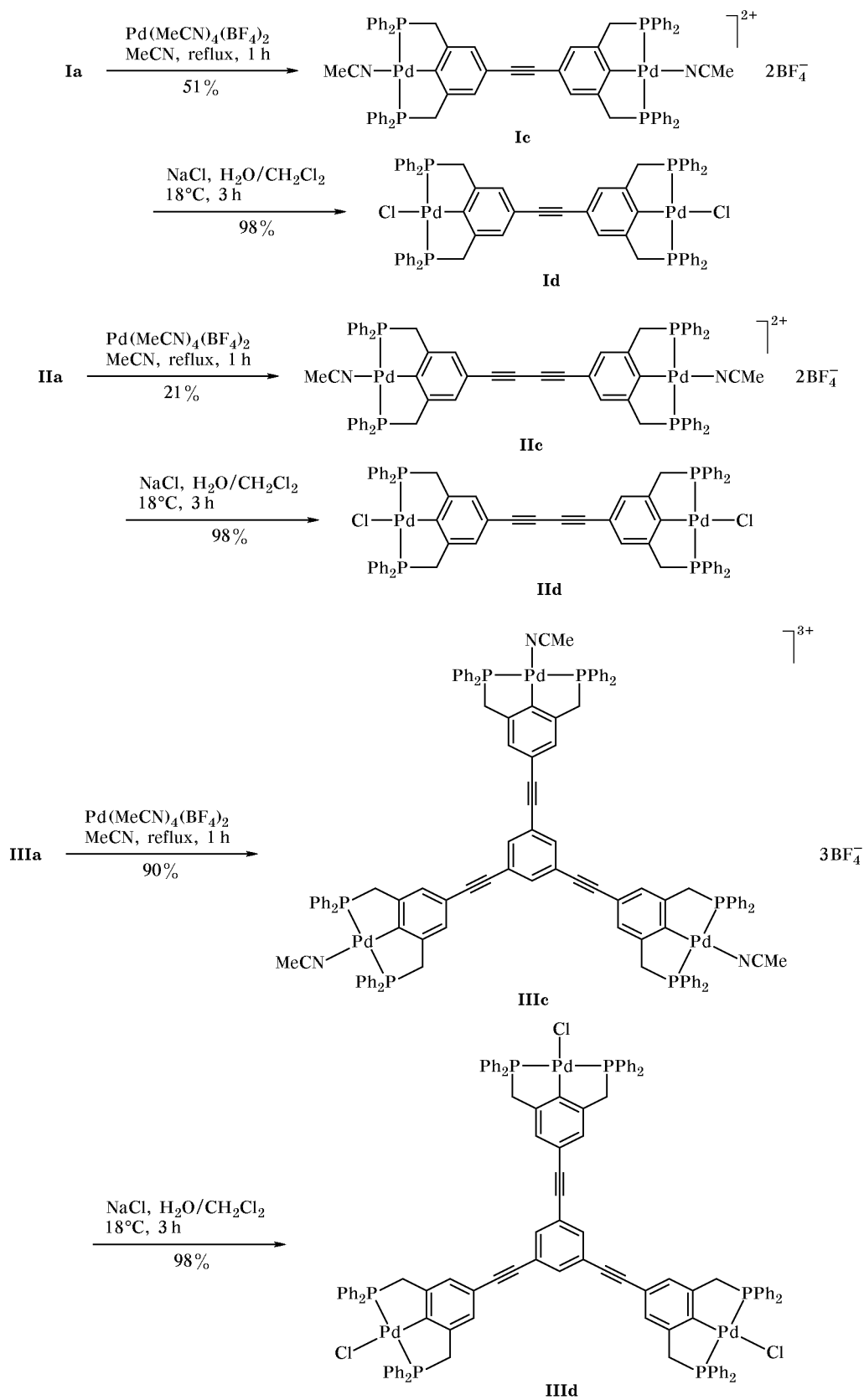
Fig. 1. Structure of dicationic complex **Ic** according to the X-ray diffraction data.

configuration from the classical square–planar structure. For example, the PPdP angle equal to $159.93\,(7)°$ considerably differs from $180°C$. In addition, the palladium atoms deviate from the ligand PCP plane to a distance of $0.111\,(2)$ Å, which, however, does not affect the geometry of the central carbon fragment [the CCC angle is $178.6\,(10)°$]. Here, some leveling of C–C distances in the almost linear central chain C^9–C^{11}–C^{11A}–C^{9A} is observed [C^9–C^{11} $1.394\,(8)$ Å, C^{11}–C^{11A} $1.306\,(12)$ Å]. Probably, this is the result of electron density redistribution in the above fragment, which gives rise to some contribution (at least, in crystal) of a delocalized $C{:}{:}{:}C{:}{:}{:}C{:}{:}{:}C$ structure.

Study of complexes Ic–IIIc and IId by UV spectroscopy. By studying the UV spectra of the palladium complexes synthesized in this work and comparing them with those of the corresponding phosphine oxides we were able to estimate mutual influence of the palladium-containing ring and the conjugated π-electron system of the carbon skeleton. The UV spectra of phosphine oxides in the region λ $260–420$ nm are almost similar to those of the corresponding hydrocarbons having no diphenylphosphinomethyl substituents. For example, the UV spectra of **Ib** and **IIb** are identical to the reported spectra of diphenylacetylene and 1,4-diphenylbutadiyne, and the spectra of **IIIb** and **IVb** are identical to those of 1,3,5-tris(phenylethynyl)benzene and hexakis(phenylethynyl)benzene. The observed similarity may be interpreted in terms of a weak effect of the *meta*-Ph$_2$P(O)CH$_2$ substituents on the conjugated π-electron system formed by the ethynyl group and

benzene rings, which is responsible for the long-wave absorption.

The spectral parameters of complexes **Ic**, **IIc**, **IId**, and **IIIc** and phosphine oxides **Ib**, **IIIb**, and **IVb** are collected in Table 2. These data show that the long-wave absorption bands of phosphine oxides **Ib**, **IIIb**, and **IVb** shift to the red region with increase of conjugation in their π-electron systems (Table 2, compounds **Ib**, **IIIb**, and **IVb**). All complexes absorb below 370 nm, and their long-wave absorption maxima are located at longer wavelengths than the maxima of the corresponding phosphine oxides. The largest difference ($\Delta\lambda$ ~40 nm) is observed for complex **Ic** (cf. the data for **Ib** and **Ic** in Table 2), and the smallest $\Delta\lambda$ value is characteristic of complex **IIIc** which has the most extended π-electron system. Differences in the position of the other (short-wave) absorption bands are much smaller, and no fine structure is observed.

The above long-wave shift is likely to result from charge transfer between the metal and pincer ligand. The charge transfer is not influenced by the counterion, so that complexes **IIc** and **IId** are characterized by almost similar positions of the long-wave absorption maxima (Table 2).

Catalytic activity of complexes Ic–IIIc. The catalytic properties of complexes **Ic–IIIc** were studied in the Heck and Michael reactions. The Heck reaction is known to be catalyzed by palladium(0) complexes, whereas Michael addition requires palladium(II) compounds which act as Lewis acids. All the examined

complexes turned out to efficiently catalyze both Heck and Michael reactions.

The Heck reaction is frequently used as a model process to estimate catalytic activities of metal complexes [14]. The complexes under study were tested in the reaction of iodobenzene with ethyl acrylate in the presence of Bu_3N. The reactions were carried out in dimethylacetamide (DMA) at 140°C. The progress of the reactions was monitored following the amount of released iodide ion by potentiometric titration. The other products were quantitated by GLC analysis using an internal standard. The reaction was found to occur in a selective fashion with quantitative formation of ethyl cinnamate (Scheme 5).

Scheme 5.

$$PhI + CH_2=CHCOOEt$$

$$\xrightarrow[-Bu_3N\cdot HI]{Bu_3N,\ DMA,\ catalyst}$$
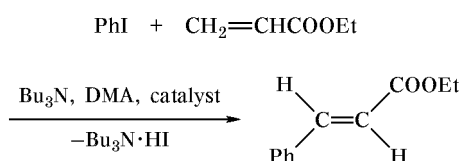
Table 3 contains the conversions of iodobenzene in 11 h after the reaction started, TON values (turnover number, i.e., the amount of product obtained with 1 mol of catalyst, which characterizes the efficiency of the latter), and TON/Pd values (specific activity of catalyst or catalytic activity per palladium atom). For comparison, given are the data obtained under similar conditions with mononuclear palladium complex **VII** derived from 2,6-bis(diphenylphosphinomethyl)benzene.

VII
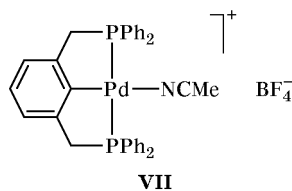
It is seen that the efficiency of the complexes at a concentration of 0.1 mol % changes in the series **VII** > **Ic** > **IIc** > **IIIc** and that the TON value does not exceed 1000. Usually, the TON value in the Heck reaction increases as the catalyst concentration decreases [14, 15]. This is the case of complex **Ic** (Table 3, run nos. 2 and 3). However, complexes **IIc** and **IIIc** show the reverse relation: the conversion sharply decreases, and TON considerably falls down.

The above differences in the behavior of complexes **VII**, **Ic**, **IIc**, and **IIIc** (Table 3; run nos. 1, 2, 4, and 6) become even stronger in going to TON/Pd values

Table 1. Bond lengths d and bond angles ω in dinuclear palladium complex **Ic**

Bond	d, Å	Bond	d, Å
Pd^1-P^1	2.330 (2)	Pd^1-P^2	2.422 (2)
Pd^1-N^1	2.091 (7)	Pd^1-C^5	2.019 (6)
P^1-C^3	1.828 (7)	P^1-C^{12}	1.823 (8)
P^1-C^{18}	1.809 (8)	P^2-C^7	1.803 (7)
P^2-C^{24}	1.796 (8)	P^2-C^{30}	1.822 (7)
N^1-C^1	1.121 (9)	C^1-C^2	1.458 (12)
C^3-C^4	1.505 (10)	C^6-C^7	1.529 (9)
C^9-C^{11}	1.394 (8)	$C^{11}-C^{11A}$	1.306 (12)

Angle	ω, deg	Angle	ω, deg
$P^1Pd^1P^2$	159.93 (7)	$P^1Pd^1N^1$	102.0 (2)
$P^2Pd^1N^1$	97.7 (2)	$P^1Pd^1C^5$	79.8 (2)
$P^2Pd^1C^5$	80.6 (2)	$N^1Pd^1C^5$	177.6 (3)
$Pd^1P^1C^3$	99.5 (3)	$Pd^1P^1C^{12}$	124.9 (3)
$Pd^1P^1C^{18}$	110.5 (3)	$Pd^1P^2C^7$	97.7 (2)
$Pd^1P^2C^{24}$	113.5 (3)	$Pd^1P^2C^{30}$	124.8 (3)
$Pd^1N^1C^1$	177.4 (9)	$N^1C^1C^2$	179.5 (13)
$P^1C^3C^4$	104.6 (5)	$Pd^1C^5C^4$	120.2 (6)
$Pd^1C^5C^6$	121.1 (5)	$P^2C^7C^6$	106.6 (5)
$C^8C^9C^{11}$	120.3 (7)	$C^{10}C^9C^{11}$	120.3 (7)
$C^9C^{11}C^{11A}$	178.6 (10)		

Table 2. UV spectra of complexes **Ic**, **IIc**, **IId**, and **IIIc** and phosphine oxides **Ib**, **IIIb**, **IVb** in MeCN

Compound no.	λ_{max}, nm (ε_{max}, l mol^{-1} cm^{-1})
Ic	240 (10.1), 324 (8.7), 344 (6.9)
Ib	238 (10.5), 272 (5.9), 290 (8.3), 298 (6.1), 308 (7.1)
IIc	242 (12.5), 294 (9.6), 314 (9.2), 340 (9.2), 366 (8.2)
IId	240 (12.4), 316 (8.9), 340 (8.1), 368 (7.1)
IIIc	240 (18.6), 314 (21.6), 330 (19.2)
IIIb	238 (18.1), 272 (13.0), 292 (22.5), 300 (19.5), 310 (23.5)
IVb	238 (88.2), 258 (60.1), 356 (114.0), 380 (65.0)

(Table 3; run nos. 1, 2, 4, 6 and 3, 5, 7). It follows that the catalytic activity of mononuclear complex **VII** is greater by a factor of 4 than the activity of complex **IIIc** having the most branched structure. Presumably, this is the result of a considerable contribution of

Table 3. Reaction of ethyl acrylate with iodobenzene in the presence of complexes **Ic–IIIc** and **VII**[a]

Run no.	Com- plex	Pd, mol %	Conversion of PhI,[b] %	TON[c]	TON/Pd[d]
1	**VII**	0.1	90	900	900
2	**Ic**	0.1	90	900	450
3	**Ic**	0.05	92	1840	920
4	**IIc**	0.1	79	790	400
5	**IIc**	0.05	28	560	280
6	**IIIc**	0.1	64	640	210
7	**IIIc**	0.034	15	440	147

[a] The reactions were carried out in DMA (1 ml) at 140°C (reaction time 11 h); amounts of the reactants: iodobenzene, 0.049 mmol; ethyl acrylate, 0.061 mmol; tributylamine, 0.05 mmol.

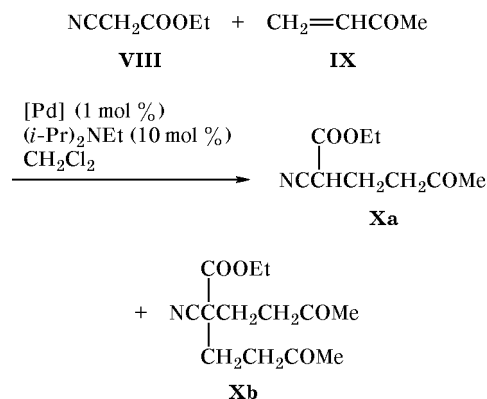[b] Determined by titration of the librated iodide ion and confirmed by the GLC data.

[c] The number of moles of the product obtained with 1 mol of catalyst.

[d] TON/Pd = TON/n, where n is the number of palladium atoms in the complex.

steric factor due to large size of the dendrimer-like molecule.

The catalytic activities of ionic complexes **Ic** and **VII** in the Michael addition were compared using the reaction of of ethyl cyanoacetate (**VIII**) with methyl vinyl ketone (**IX**) as model. This reaction is often used [16–18] (together with the aldol condensation of benzaldehyde with ethyl isocyanoacetate [19–22]) while studying the activity of platinum metal complexes as Lewis acids. The reactions were carried out in methylene chloride at room temperature in the presence of 10 mol % of ethyl(diisopropyl)amine and 1 mol % of the complex. According to the GC–MS

Fig. 2. Conversion of ethyl cyanoacetate **VIII** and yields of products **Xa** and **Xb** (%) in the reaction with methyl vinyl ketone in the presence of complex **VII**.

data, addition products **Xa** and **Xb** are formed with participation of one or two molecules of ketone **IX**, repsectively (Scheme 6).

Scheme 6.

$$NCCH_2COOEt \ + \ CH_2{=}CHCOMe$$

$$\text{VIII} \qquad\qquad \text{IX}$$

[Pd] (1 mol %)
(*i*-Pr)$_2$NEt (10 mol %)
CH$_2$Cl$_2$
$\longrightarrow$

$$\overset{\displaystyle COOEt}{\underset{}{NCCHCH_2CH_2COMe}}$$

Xa

$$+ \ \ \overset{\displaystyle COOEt}{\underset{\displaystyle CH_2CH_2COMe}{NCCCH_2CH_2COMe}}$$

Xb

The data given in Table 4 include the conversion of ester **VIII** and overall yield of products **Xa** and **Xb**, depending on the reaction time, in the catalytic and noncatalytic processes. The plots of the conversion of **VIII** and the yields of **Xa** and **Xb** versus time in the reaction catalyzed by complex **VII** are shown in Fig. 2. It is seen that the yield of monoadduct **Xa** initially increases and then decreases due to the secondary process leading to bis-adduct **Xb**. The yield of **Xb** changes correspondingly. As follows from the data in Table 4, complexes **Ic** and **VII** accelerate the Michael reaction approximately twofold with almost equal efficiencies. Acceleration of the process also affects the ratio of products **Xa** and **Xb**. By the end of the reaction (after 24 h), when the conversion of initial ester **VIII** is complete, the ratio **Xb**:**Xa** is equal to ~20, while in the noncatalytic reaction it is equal to ~3. An analogous effect on the product ratio was observed in the reaction catalyzed by trifluoromethanesulfonate platinum complexes with an NCN pincer ligand [17].

Comparison of the specific catalytic activity of complexes **Ic** and **VII** (per palladium atom) shows that the latter is twice as active as dinuclear complex **Ic**. The lower catalytic activity of **Ic** may be explained by steric factor or conjugation between the two palladium atoms. Thus, in the Michael addition, as well as in the Heck reaction, the specific activity of pincer palladium complexes decreases as the number of metal atoms in the catalyst molecule rises. An analogous pattern was observed in the same reaction for another three-nuclear NCN′-pincer system based on 1,3,5-triphenylbenzene [18]. However, in some reactions catalyzed by dendrimeric cyclopalladated
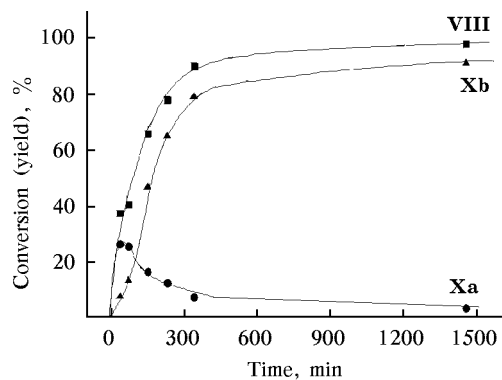
Table 4. Reaction of ethyl cyanoacetate (**VIII**) with methyl vinyl ketone (**IX**), catalyzed by complexes **Ic** and **VII**[a]

Reaction time, min	Noncatalytic reaction			Catalyzed by complex **VII**			Catalyzed by complex **Ic**		
	conversion of **VIII**, %	yield of **Xa + Xb**,[b] %	ratio **Xb : Xa**	conversion of **VIII**, %	yield of **Xa + Xb**,[b] %	ratio **Xb : Xa**	conversion of **VIII**, %	yield of **Xa + Xb**,[b] %	ratio **Xb : Xa**
35	9	8	0.14	42	39	0.56	38	35	0.3
70	–	–	–	54	51	1.7	41	40	0.54
95	31	30	0.25	–	–	–	–	–	–
150	41	40	0.3	63	60	1.7	66	64	2.8
230	55	54	0.69	90	86	6.1	78	78	5.0
340	–	–	–	92	87	8.7	90	87	9.9
1460	75	73	3.1	98	93	18	98	95	22

[a] The reactions were carried out in methylene chloride (1 ml) at 18°C in the presence of 10 mol % of $(i\text{-Pr})_2$NEt and 1 mol % of complex **Ic** or **VII**; amounts of the reactants: ethyl cyanoacetate, 0.6 mmol; methyl vinyl ketone, 1.43 mmol.
[b] Determined by GLC using dodecane as internal standard.

carbosilane-based CN-systems, the catalytic activity was reported to increase with rise in the number of catalytic centers [23].

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian VXR-400 and Bruker AC-200 spectrometers using TMS (^{1}H and ^{13}C) and 85% phosphoric acid (^{31}P) as external reference. The MALDI-TOF mass spectra were obtained on a Voyager-DE Bio-Spectrometry Workstation (PerSeptive Biosystems Inc., Flamingham, MA), equipped with a nitrogen laser (λ 337 nm). The UV spectra were measured on an M-40 spectrophotometer (Carl Zeiss, Jena).

GLC analysis was performed on a Hewlett–Packard 5890 Series II Plus chromatograph equipped with a flame-ionization detector. The Heck reaction products were analyzed using an HP-1701 capillary column (15 m × 0.32 mm × 0.25 μm); oven temperature programming from 35 to 280°C at 7 deg/min. The Michael reaction products were analyzed using an HP-1 capillary column (25 m × 0.32 mm × 0.25 μm); oven temperature programming from 80 to 280°C at 10 deg/min. Iodide ion determination was performed with a Radiometer Titrator TTT1c complex, Titrigraph SBR2c, equipped with an ABU1 0.25-ml autoburette and Selectrode F1212S electrode; the titrant was a 0.03 M $AgNO_3$/0.1 M HNO_3 solution; titration accuracy 2%. The product yields determined by GLC and by titration coincided within 7%.

X-Ray diffraction study of a single crystal of complex **Ic** was performed on a Syntex P21 automatic diffractometer (graphite monochromator, 293 K). The structure was solved by the direct method and was refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. The positions of hydrogen atoms were refined according to the "rider" model. The calculations were performed using SHELX97 software package [24, 25]. The principal bond lengths and bond angles are given in Table 1, and the crystallographic data, in Table 5.

Heck reaction procedure. A specified amount of palladium complex was dissolved in 1 ml of dimethylacetamide. The solution was utilized within 24 h; it was purged with argon prior to use. An ampule was charged with a mixture of 10.0 mg (0.049 mmol) of iodobenzene, 6.11 mg (0.061 mmol) of ethyl acrylate, 9.27 mg (0.05 mmol) of tributylamine, a solution of 1,4-di-*tert*-butylbenzene (internal standard) in dimethylacetamide, about 10 μl of the catalyst solution, and 1 ml of dimethylacetamide. The solution was degassed under high vacuum (two freezing–evacuation cycles), and the ampule was sealed off and heated for 11 h at 140°C on an oil bath. A 20–50-μl sample of the reaction mixture was withdrawn for titration (it was preliminarily mixed with 1.5 ml of 0.1 M HNO_3). For GLC analysis, a sample of the mixture was diluted with 5% hydrochloric acid and extracted with diethyl ether (3 × 2 ml), and the organic phase was dried over $MgSO_4$.

Michael reaction procedure. The reaction was carried out at 25°C under argon pressure. Ethyl cyanoacetate, 0.204 g (1.80 mmol), methyl vinyl ketone, 0.301 g (4.29 mmol), ethyl(diisopropyl)amine, 31 μl (10 mol %), and dodecane, 29.3 mg (standard), were dissolved in 3 ml of methylene chloride, and 1 ml of this solution was added to 6 mmol (1 mol %)

Table 5. Crystallographic parameters of complex **Ic**

Parameter	Ic
Formula	$C_{70}H_{64}B_2F_8N_2P_4Pd_2$
Molecular weight	1443.53
Space group	P-1
a, Å	9.834 (3)
b, Å	12.925 (3)
c, Å	14.659 (3)
α, deg	65.449 (15)
β, deg	75.912 (19)
γ, deg	77.431 (18)
V, Å^3	1629.5 (6)
Z	1
ρ_{calc}, g/cm^3	1.471
μ, mm^{-1}	0.716
Radiation	Mo-K$_\alpha$ (λ = 0.71073 Å)
θ–2θ scan range, deg	1.55–26.05
Number of independent reflections	6352
Number of reflections with $I \geq 2\sigma(I)$	5954
R_1	0.0602
wR_2	0.1353

of solid catalyst. Samples of the colorless transparent solution were withdrawn for GLC analysis. For calibration, compounds **Xa** and **Xb** were isolated by HPLC (colorless oily liquids). Mass spectrum, m/z (I_{rel}, %): **Xa**: 183 (100), 168 (35), 140 (97), 127 (7), 113 (15); **Xb**: 183 (100), 182 (39), 180 (43), 164 (27), 138 (26), 137 (49), 124 (35), 122 (24), 110 (42), 109 (26).

The ligands and palladium complexes were synthesized from commercial reagents using commercial solvents which were purified by standard procedures; their parameters coincided with published data.

3,5-Bis(diphenylphosphinoylmethyl)iodobenzene (V). A mixture of 14 g (35.9 mmol) of 3,5-bis(bromomethyl)iodobenzene and 16.6 g (72 mmol) of ethyl diphenylphosphinite in 20 ml of *m*-xylene was heated to 130°C and was stirred for 1 h at that temperature. It was then cooled to room temperature and concentrated under reduced pressure. Benzene, 70 ml, was added to the residue, and the mixture was heated, filtered while hot, and left to stand for crystallization. The precipitate, crystalline 3,5-bis(diphenylphosphinoylmethyl)iodobenzene–benzene solvate (1:1), was filtered off and washed with benzene on a filter. Yield 25 g (98%), mp 91°C. Found, %: C 64.14; H 4.75; P 8.80. $C_{32}H_{27}O_2P_2I \cdot C_6H_6$. Calculated, %: C 64.21;

H 4.73; P 8.71. Pure bis(diphenylphosphinoylmethyl)iodobenzene was isolated as an amorphous substance by decomposition of the solvate at 91°C under reduced pressure. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.43 d [4H, CH$_2$P(O), J = 13.8 Hz], 6.95 t (1H, H$_{arom}$, J = 1.8 Hz), 7.15 d (2H, H$_{arom}$, J = 1.8 Hz), 7.3–7.7 m [20H, P(O)Ph$_2$]. ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ$_C$, ppm: 37.8 d (J = 65.9 Hz), 94.1, 128.8 d (J = 12 Hz), 131.3 d (J = 9.7 Hz), 131.7 t (J = 5.0 Hz), 132.2, 133.1, 133.6 d (J = 10.6 Hz), 137.5 t (J = 3.7 Hz). ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ$_P$ 30.2 ppm. Found, %: C 60.63; H 4.45; P 9.66. $C_{32}H_{27}O_2P_2I$. Calculated, %: C 60.77; H 4.30; P 9.79.

3,5-Bis(diphenylphosphinoylmethyl)trimethylsilylethynylbenzene. 3,5-Bis(diphenylphosphinoylmethyl)iodobenzene–benzene solvate, 11.2 g (15.8 mmol), trimethylsilylacetylene, 1.8 g (19 mmol), dichlorobis(triphenylphosphine)palladium, 0.1 g (0.14 mmol), and copper(I) iodide, 30 mg (0.16 mmol), were dissolved in succession in 65 ml of piperidine, and the mixture was stirred for 3 h at 80°C. The solvent (piperidine) was removed under reduced pressure, the residue was dissolved in 200 ml of methylene chloride, and the solution was washed with water (5 × 200 ml), dried over MgSO$_4$, and evaporated. The solid residue was recrystallized from benzene. Yield 9 g (95%), colorless solid, mp 205°C. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 0.12 s (9H, Me$_3$Si), 3.48 d [4H, CH$_2$P(O), J = 13.2 Hz], 6.94 t (1H, H$_{arom}$, J = 1.4 Hz), 7.04 d (2H, H$_{arom}$, J = 1.4 Hz), 7.3–7.7 m [20H, P(O)Ph$_2$]. ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ$_C$, ppm: 0.14, 37.8 d (J = 66 Hz), 94.5, 104.7, 123.5, 128.8 d (J = 12 Hz), 131.1 d (J = 9.6 Hz), 131.8 d (J = 10.1 Hz), 132.0, 132.2–132.6 m, 133.3. ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ$_P$ 30.2 ppm. Found, %: C 73.64; H 6.13; P 10.34. $C_{37}H_{36}O_2P_2Si$. Calculated, %: C 73.73; H 6.02; P 10.28.

3,5-Bis(diphenylphosphinoylmethyl)ethynylbenzene (VI). To a solution of 9.0 g (15 mmol) of 3,5-bis(diphenylphosphinoylmethyl)trimethylsilylethynylbenzene in 100 ml of methanol we added 3.5 ml of a 5 M aqueous solution of NaOH. The mixture was stirred for 2 h at room temperature, and 100 ml of water and 100 ml of methylene chloride were added. The organic phase was separated, washed with water (2 × 100 ml), dried over MgSO$_4$, and evaporated under reduced pressure, and the residue was recrystallized from benzene to isolate 8.9 g (97%) of 1:1 3,5-bis(diphenylphosphinoylmethyl)ethynylbenzene–benzene solvate as colorless crystals with mp 110°C. Found, %: C 78.85; H 5.75; P 10.16.

$C_{40}H_{34}O_2P_2$. Calculated, %: C 78.93; H 5.63; P 10.18. 3,5-Bis(diphenylphosphinoylmethyl)ethynylbenzene was isolated as a colorless amorphous substance by decomposition of the solvate at 110°C under reduced pressure. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 2.89 s (1H, HC≡), 3.48 d [4H, CH$_2$P(O), J = 13.6 Hz], 7.0 s (3H, H$_{arom}$), 7.3–7.7 m [20H, P(O)Ph$_2$]. ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ$_C$, ppm: 37.9 d (J = 66 Hz), 77.6, 83.2, 122.4, 128.8 d (J = 12.6 Hz), 131.2 d (J = 10 Hz), 131.9 d (J = 10 Hz), 132.1, 132.4 t (J = 3.7 Hz), 132.8 t (J = 5.0 Hz), 133.2. ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ$_P$ 30.2 ppm. Found, %: C 76.88; H 5.51; P 11.57. $C_{34}H_{28}P_2O_2$. Calculated, %: C 76.97; H 5.32; P 11.68.

3,3′,5,5′-Tetrakis(diphenylphosphinoylmethyl)-diphenylacetylene (Ib). *a.* 3,5-Bis(diphenylphosphinoylmethyl)iodobenzene–benzene solvate, 1.35 g (1.9 mmol), 3,5-bis(diphenylphosphinoylmethyl)-ethynylbenzene–benzene solvate, 1.15 g (1.9 mmol), dichlorobis(triphenylphosphine)palladium, 13 mg (0.018 mmol), and CuI, 3 mg (0.016 mmol), were dissolved in succession in 12 ml of piperidine. The mixture was stirred for 4 h at 80°C, the solvent was removed under reduced pressure, and the residue was washed with benzene and dissolved in 40 ml of methylene chloride. The solution was washed with water (3 × 40 ml), dried over MgSO$_4$, and evaporated under reduced pressure. The crude product was dispersed in 30 ml of benzene, and the mixture was heated for 30 min under reflux and cooled to room temperature. The precipitate was filtered off and dried at 100°C under reduced pressure. Yield 1.86 g (95%).

b. 3,5-Bis(diphenylphosphinoylmethyl)iodobenzene–benzene solvate, 11.23 g (15.6 mmol), dichlorobis(triphenylphosphine)palladium, 0.1 g (0.142 mmol), and copper iodide, 30 mg (0.18 mmol), were dissolved in succession in 60 ml of piperidine. The mixture was heated to 80°C, and acetylene was bubbled through the mixture over a period of 3 h under stirring. The solvent was removed under reduced pressure, the solid residue was washed with benzene and dissolved in 150 ml of methylene chloride, and the solution was washed with water (3 × 150 ml), dried over MgSO$_4$, and evaporated under reduced pressure. The crude product was dispersed in 150 ml of benzene, and the mixture was heated for 30 min under reflux and cooled to room temperature. The precipitate was filtered off and dried at 100°C under reduced pressure. Yield 7.5 g (92%), mp 285°C. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.47 d [8H, CH$_2$P(O), J = 13.6 Hz], 7.0 s (6H, H$_{arom}$), 7.3–7.7 m

[40H, P(O)Ph$_2$]. ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ$_C$, ppm: 38.0 d (J = 65 Hz), 89.4, 123.6, 128.8 d (J = 12 Hz), 131.2 d (J = 9.2 Hz), 131.6–132.4 m, 133.3. ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ$_P$ 30.3 ppm. Found, %: C 76.43; H 5.30; P 11.82. $C_{66}H_{54}O_4P_4$. Calculated, %: C 76.59; H 5.26; P 11.97.

1,4-Bis[3,5-bis(diphenylphosphinoylmethyl)phenyl]butadiyne (IIb). 3,5-Bis(diphenylphosphinoylmethyl)ethynylbenzene–benzene solvate, 1.15 g (1.9 mmol), iodine, 0.3 g (1.2 mmol), dichlorobis(triphenylphosphine)palladium, 0.013 g (0.018 mmol), and copper(I) iodide, 3 mg (0.016 mmol), were dissolved in succession in 12 ml of piperidine. The mixture was stirred for 4 h at 80°C, the solvent was removed under reduced pressure, the residue was washed with benzene and dissolved in 20 ml of methylene chloride, and the solution was washed with water (3 × 20 ml), dried over MgSO$_4$, and evaporated. The crude product was dispersed in 15 ml of benzene, and the mixture was heated for 30 min under reflux and cooled. The precipitate was filtered off and dried at 100°C under reduced pressure. Yield 0.9 g (90%), mp 287°C. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.46 d [8H, CH$_2$P(O), J = 13.6 Hz], 6.97 d (4H, H$_{arom}$, J = 1.8 Hz), 7.0 t (2H, H$_{arom}$, J = 1.8 Hz), 7.3–7.7 m [40H, P(O)Ph$_2$]. ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ$_C$, ppm: 37.9 d (J = 66.3 Hz), 74.3, 81.1, 122.0, 128.8 d (J = 12.4 Hz), 131.2 d (J = 9.7 Hz), 132.0, 132.2, 132.6 t (J = 3.7 Hz), 133.1, 133.3 t (J = 5.0 Hz). ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ$_P$ 30.3 ppm. Found, %: C 77.22; H 5.02; P 11.43. $C_{68}H_{54}O_4P_4$. Calculated, %: C 77.12; H 5.14; P 11.70.

1,3,5-Tris[3,5-bis[(diphenylphosphinoylmethyl)-phenylethynyl]benzene (IIIb). 1,3,5-Tribromobenzene, 1 g (3.17 mmol), 3,5-bis(diphenylphosphinoylmethyl)ethynylbenzene–benzene solvate, 8 g (13.16 mmol), dichlorobis(triphenylphosphine)palladium, 0.19 g (0.27 mmol), triphenylphosphine, 35 mg (0.14 mmol), triethylamine, 3.64 g (5 ml, 36 mmol), and copper(I) iodide, 20 mg (0.11 mmol), were dissolved in succession in 50 ml of THF. The mixture was heated for 100 h under reflux with stirring, the solvent was removed under reduced pressure, the residue was washed with benzene and dissolved in 100 ml of methylene chloride, and the solution was washed with water (4 × 100 ml), dried over MgSO$_4$, and evaporated. The residue was recrystallized from benzene and dried at 100°C under reduced pressure. Yield 3.5 g (66%), mp 158–159°C. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.55 d [12H, CH$_2$P(O), J = 13.6 Hz], 7.10 s (9H, H$_{arom}$), 7.36–7.76 m [63H,

P(O)Ph$_2$, H$_{arom}$]. ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ_C, ppm: 38.0 d (J = 65.8 Hz), 88.2, 90.3, 123.1, 124.1, 128.8 d (J = 12.0 Hz), 131.3, 132.0, 132.1, 132.6, 133.3, 134.1. ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ 30.2 ppm. MALDI-TOF-MS data (3,5-dihydroxybenzoic acid matrix): m/z 1770.10 [M + Ag]$^+$). C$_{108}$H$_{84}$AgO$_6$P$_6$. Calculated: M 1771.65.

Hexakis[3,5-bis(diphenylphosphinoylmethyl)-phenylethynyl]benzene (IVb). Hexabromobenzene, 1 g (1.81 mmol), 3,5-bis(diphenylphosphinoylmethyl)-ethynylbenzene–benzene solvate, 8 g (13.16 mmol), dichlorobis(triphenylphosphine)palladium, 190 mg (0.27 mmol), triphenylphosphine, 35 mg (0.14 mmol), triethylamine, 3.64 g (5 ml, 36 mmol), and copper(I) iodide, 20 mg (0.11 mmol), were dissolved in succession in 50 ml of THF. The mixture was heated for 300 h under reflux with stirring, the solvent was removed under reduced pressure, the residue was washed with benzene and dissolved in 100 ml of methylene chloride, and the solution was washed with water (4 × 100 ml), dried over MgSO$_4$, and evaporated. The residue was dissolved in 5 ml of methanol, the solution was filtered, the filtrate was evaporated, and the residue was recrystallized in succession from benzene and 2-propanol and dried at 100°C under reduced pressure. Yield 1.5 g (25%), yellow substance, mp 169°C (a sample for elemental analysis was preliminarily melted under reduced pressure). ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.40 d [24H, CH$_2$P(O), J = 13.6 Hz], 6.91 s (6H, H$_{arom}$), 7.08 s (12H, H$_{arom}$), 7.18–7.68 m [120H, P(O)Ph$_2$]. ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ, ppm: 37.6 d (J = 65.9 Hz), 87.4, 99.1, 123.3, 127.5, 128.7 d (J = 12 Hz), 131.3 d (J = 9.7 Hz), 131.5, 132.0, 132.2 d (J = 10.6 Hz), 133.1, 133.4. ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ_P 30.1 ppm. MALDI-TOF-MS data (3,5-dihydroxybenzoic acid matrix): m/z 3355.94 [M + Ag]$^+$. C$_{210}$H$_{162}$O$_{12}$P$_{12}$. Calculated: M 3249.27. Found, %: C 77.50; H 5.06; P 11.38. C$_{210}$H$_{162}$O$_{12}$P$_{12}$. Calculated, %: C 77.63; H 5.03; P 11.44.

3,3′,5,5′-Tetrakis(diphenylphosphinomethyl)diphenylacetylene (Ia). 3,3′,5,5′-Tetrakis(diphenylphosphinoylmethyl)diphenylacetylene, 1.14 g (1.1 mmol), was dispersed in 25 ml of *o*-dichlorobenzene under argon, and 1.8 g (13 mmol) of trichlorosilane was added through a syringe. The mixture was heated to 100°C under stirring until it became homogeneous and cooled, excess trichlorosilane was removed under reduced pressure, and a degassed solution of 2.5 g (62.2 mmol) of sodium hydroxide in 15 ml of water was added. The mixture was stirred for 15 min, and

the organic phase was separated, dried over MgSO$_4$, and evaporated. The residue was washed with hexane and dried under reduced pressure. Yield 1.05 g (98%), mp 187°C. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.34 s (8H, CH$_2$P), 6.86 t (2H, H$_{arom}$, J = 1.2 Hz), 7.05 d (4H, H$_{arom}$, J = 1.2 Hz), 7.3–7.5 m (40H, PPh$_2$). ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ_C, ppm: 36.1 d (J = 16.1 Hz), 89.5, 123.4, 128.7 d (J = 6.4 Hz), 129.0, 130.4 d (J = 6.9 Hz), 130.8 t (J = 7 Hz), 133.2 d (J = 18.4 Hz), 137.9 d (J = 8.2 Hz), 138.4 d (J = 15.2 Hz). ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ_P –9.0 ppm. Found, %: C 81.45; H 5.55; P 12.56. C$_{66}$H$_{54}$P$_4$. Calculated, %: C 81.64; H 5.61; P 12.76.

1,4-Bis[3,5-bis(diphenylphosphinomethyl)phenyl]-1,3-butadiyne (IIa). 1,4-Bis[3,5-bis(diphenylphosphinoylmethyl)phenyl]butadiyne, 5 g (4.7 mmol), was dispersed in 100 ml of *o*-dichlorobenzene under argon, and 9 g (65 mmol) of trichlorosilane was added through a syringe. The mixture was heated to 100°C, stirred at that temperature until the initial phosphine oxide dissolved completely, and cooled, excess trichlorosilane was removed under reduced pressure, and a degassed solution of 12 g (300 mmol) of sodium hydroxide in 70 ml of water was added. The mixture was stirred for 15 min, and the organic phase was separated, dried over MgSO$_4$, and evaporated. The residue was washed with hexane and dried under reduced prssure. Yield 4.6 g (98%), mp 195°C. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.32 s (8H, CH$_2$P), 6.93 t (2H, H$_{arom}$, J = 1.5 Hz), 7.03 d (4H, H$_{arom}$, J = 1.5 Hz), 7.3–7.5 m (40H, PPh$_2$). ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ_C, ppm: 36.0 d (J = 16.6 Hz), 74.0, 81.9, 121.8, 128.7 d (J = 6.5 Hz), 129.1, 131.3 d (J = 6.9 Hz), 131.9 t (J = 7 Hz), 133.1 d (J = 18.9 Hz), 138.1 d (J = 15.2 Hz), 138.1 d (J = 8.2 Hz). ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ_P –8.7 ppm. Found, %: C 81.96; H 5.32; P 12.40. C$_{68}$H$_{54}$P$_4$. Calculated, %: C 82.08; H 5.47; P 12.45.

1,3,5-Tris[3,5-bis(diphenylphosphinomethyl)-phenylethynyl]benzene (IIIa). 1,3,5-Tris[3,5-bis(diphenylphosphinoylmethyl)phenylethynyl]benzene, 1.7 g (1 mmol), was dispersed in 30 ml of benzene under argon, and 4 g (30 mmol) of trichlorosilane was added through a syringe. The mixture was heated for 16 h under reflux, excess trichlorosilane was removed under reduced pressure, and a degassed solution of 3 g (75 mmol) of sodium hydroxide in 15 ml of water was added. The mixture was stirred for 15 min, and the organic phase was separated, dried over MgSO$_4$, and evaporated under reduced pressure. Yield 1.5 g

(98%), mp 74–75°C. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.32 s (12H, CH$_2$P), 6.85 s (3H, H$_{arom}$), 7.04 s (6H, H$_{arom}$), 7.3–7.5 m (60H, PPh$_2$), 7.52 d (3H, H$_{arom}$, J = 0.8 Hz). ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ$_C$, ppm: 36.0 d (J = 16.1 Hz), 87.8, 90.9, 122.8, 124.3, 128.7 d (J = 6.9 Hz), 129.1, 130.5 d (J = 4.6 Hz), 131.2 t (J = 6.9 Hz), 133.1 d (J = 18.4 Hz), 134.1, 137.9 d (J = 6.4 Hz), 138.1 d (J = 13.4 Hz). ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ$_P$ –9.0 ppm. Found, %: C 82.58; H 5.54; P 11.71. C$_{108}$H$_{84}$P$_6$. Calculated, %: C 82.74; H 5.40; P 11.85.

Hexakis[3,5-bis(diphenylphosphinomethyl)phenylethynyl]benzene (IVa). Hexakis[3,5-bis(diphenylphosphinoylmethyl)phenylethynyl]benzene, 1.2 g (0.37 mmol), was dispersed in 25 ml of *o*-dichlorobenzene under argon, and 1.8 g (13.4 mmol) of trichlorosilane was added through a syringe. The mixture was stirred for 5 h at 110°C and cooled, excess trichlorosilane was removed under reduced pressure, and a degassed solution of 2.5 g (62.5 mmol) of sodium hydroxide in 15 ml of water was added. The mixture was stirred for 15 min, and the organic phase was separated, dried over MgSO$_4$, and evaporated under reduced pressure. The residue was washed with hexane and dried under reduced pressure. Yield 1.1 g (98%), yellow amorphous powder. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.14 s (24H, CH$_2$P), 6.67 s (6H, H$_{arom}$), 7.04 s (12H, H$_{arom}$), 7.1–7.4 m (120H, PPh$_2$). ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ$_C$, ppm: 36.1 d (J = 16.5 Hz), 87.2, 99.7, 123.2, 127.6, 128.6 d (J = 6.4 Hz), 129.0, 130.7 d (J = 5.1 Hz), 131.4 t (J = 7.1 Hz), 133.0 d (J = 18.4 Hz), 134.1, 137.8 d (J = 7.8 Hz), 138.2 d (J = 15.6 Hz). ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ$_P$ –9.1 ppm. Found, %: C 82.36; H 5.34; P 12.10. C$_{210}$H$_{162}$P$_{12}$. Calculated, %: C 82.50; H 5.34; P 12.16.

Complex Ic. A solution of 1.83 g (4.12 mmol) of Pd(CH$_3$CN)$_4$(BF$_4$)$_2$ in 150 ml of acetonitrile was added to 2.0 g (2.06 mmol) of 3,3′,5,5′-tetrakis(diphenylphosphinomethyl)diphenylacetylene (**Ia**). The mixture was heated for 2 h under reflux and cooled, and the solvent was removed under reduced pressure. The residue was recrystallized from acetonitrile. Yield 1.5 g (51%), colorless crystals. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 4.21 t [8H, CH$_2$P, J = 4.8 Hz], 7.34 s (4H, H$_{arom}$), 7.6–8.0 m (40H, PPh$_2$). ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ$_C$, ppm: 40.5 t (J = 15.2 Hz), 89.4, 122.1, 126.9 t (J = 11.7 Hz), 129.70 t (J = 5.3 Hz), 130.2 t (J = 22.3 Hz), 132.2, 133.2 t (J = 6.9 Hz), 148.70 t (J = 10.4 Hz), 156.9. ^{31}P NMR spectrum (80.96 MHz, CD$_3$CN):

δ$_P$ 48.03 ppm. Found, %: C 58.31; H 4.01; N 1.81. C$_{70}$H$_{58}$B$_2$F$_8$N$_2$P$_4$Pd$_2$. Calculated, %: C 58.48; H 4.07; N 1.95.

Complex IIc. A solution of 1.15 g (2.59 mmol) of Pd(CH$_3$CN)$_4$(BF$_4$)$_2$ in 100 ml of acetonitrile was added to 1.3 g (1.31 mmol) of 1,4-bis[3,5-bis(diphenylphosphinomethyl)phenyl]-1,3-butadiyne (**IIa**). The mixture was heated for 1 h under reflux and cooled, and the solvent was removed under reduced pressure. The residue was recrystallized from acetonitrile. Yield 0.4 g (21%), colorless crystals. ^{1}H NMR spectrum (400 MHz, CDCl$_3$), δ, ppm: 4.21 t (8H, CH$_2$P, J = 4.8 Hz), 7.38 s (4H, H$_{arom}$), 7.6–7.9 m (40H, PPh$_2$). ^{31}P NMR spectrum (161.9 MHz, CD$_3$CN): δ$_P$ 46.8 ppm. Found, %: C 59.32; H 4.08; N 1.83. C$_{72}$H$_{58}$B$_2$F$_8$N$_2$P$_4$Pd$_2$. Calculated, %: C 59.17; H 4.00; N 1.92.

Complex IIIc. A 0.39-g (2.2-mmol) portion of PdCl$_2$ was dissolved in 50 ml of boiling acetonitrile, and a solution of 0.86 g (4.4 mmol) of AgBF$_4$ in 20 ml of acetonitrile was added. The mixture was stirred for 5 min, cooled to room temperature, filtered, degassed, and added under nitrogen to 1.15 g (0.73 mmol) of 1,3,5-tris[3,5-bis(diphenylphosphinomethyl)phenylethynyl]benzene. The resulting mixture was heated for 1 h under reflux, cooled, and evaporated under reduced pressure. The residue was dissolved in 50 ml of CH$_2$Cl$_2$, the solution was filtered, and the filtrate was evaporated under reduced pressure. The residue was recrystallized from acetonitrile–methanol. Yield 1.5 g (90%), colorless crystals. ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 4.20 t (12H, CH$_2$P, J = 4.7 Hz), 7.38 s (6H, H$_{arom}$), 7.6–8.0 m (63H, PPh$_2$, H$_{arom}$). ^{13}C NMR spectrum (50.3 MHz, CDCl$_3$), δ$_C$, ppm: 38.7 t (J = 15.2 Hz), 86.2, 88.7, 119.7, 122.5, 125.2 t (J = 12 Hz), 127.9 t (J = 5.1 Hz), 128.3 t (J = 22.6 Hz), 130.4, 131.3 t (J = 6.9 Hz), 132.2, 146.9 t (J = 9.9 Hz), 155.7. ^{31}P NMR spectrum (80.96 MHz, CDCl$_3$): δ$_P$ 46.1 ppm. MALDI-TOF-MS data (9-nitroanthracene matrix): m/z 1921.73 [M – 3CH$_3$CN – 2BF$_3$ – BF$_4$]$^+$. C$_{108}$H$_{81}$F$_2$P$_6$Pd$_3$. Calculated: M 1921.95. Found, %: C 60.21; H 4.01. C$_{114}$H$_{90}$B$_3$F$_{12}$N$_3$P$_6$Pd$_3$. Calculated, %: C 60.39; H 4.00.

Complex Id. A suspension of 0.35 g (0.24 mmol) of complex **Ic** in 40 ml of methylene chloride was mixed with 40 ml of a saturated aqueous solution of sodium chloride, and the mixture was stirred for 12 h. The organic phase was separated and dried over MgSO$_4$, and the solvent was distilled off under reduced pressure. Yield 0.3 g (98%). ^{1}H NMR spectrum (200 MHz, CDCl$_3$), δ, ppm: 3.92 t (8H, CH$_2$P,

J = 4.6 Hz), 7.26 s (4H, H_{arom}), 7.3–8.0 m (40H, PPh_2). ^{13}C NMR spectrum (50.3 MHz, $CDCl_3$), δ_C, ppm: 42.7 t (J = 14.5 Hz), 89.8, 120.8, 126.1 t (J = 11.2 Hz), 129.1 t (J = 5.3 Hz), 130.9, 131.9 t (J = 21.7 Hz), 133.2 t (J = 6.7 Hz), 148.3 t (J = 10.8 Hz), 161.6. ^{31}P NMR spectrum (80.96 MHz, $CDCl_3$): δ_P 34.3 ppm. Found, %: C 63.10; H 4.05. $C_{66}H_{52}Cl_2P_4Pd_2$. Calculated, %: C 63.28; H 4.18.

Complex IId. A suspension of 0.2 g (0.14 mmol) of complex **IIc** in 20 ml of methylene chloride was mixed with 20 ml of a saturated aqueous solution of sodium chloride, and the mixture was stirred for 12 h. The organic phase was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Yield 0.17 g (97%). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 3.96 t (8H, CH_2P, J = 4.2 Hz), 7.29 s (4H, H_{arom}), 7.3–8.0 m (40H, PPh_2). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm: 42.40 t (J = 14.5 Hz), 73.95, 81.89, 118.94, 126.64 t (J = 11.4 Hz), 128.8 t (J = 5.4 Hz), 130.71, 131.50 t (J = 21.4 Hz), 132.91 t (J = 6.8 Hz), 148.17 t (J = 11.2 Hz), 163.05. ^{31}P NMR spectrum (161.6 MHz, $CDCl_3$): δ_P 32.8 ppm. Found, %: C 63.78; H 4.01. $C_{66}H_{52}Cl_2P_4Pd_2$. Calculated, %: C 63.97; H 4.10.

Complex IIId. A suspension of 0.2 g (0.09 mmol) of complex **IIIc** in 20 ml of methylene chloride was mixed with 20 ml of a saturated aqueuos solution of sodium chloride, and the mixture was stirred for 12 h. The organic phase was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Yield 0.172 g (98%). ^1H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 3.92 t (12H, CH_2P, J = 4.4 Hz), 7.28 s (6H, H_{arom}), 7.30–7.46 m (36H, PPh_2), 7.54 s (3H, H_{arom}), 7.76–7.96 m (24H, PPh_2). ^{13}C NMR spectrum (50.3 MHz, $CDCl_3$): δ_C, ppm: 42.7 t (J = 14.7 Hz), 88.1, 91.2, 120.2, 124.4, 126.3 t (J = 11.5 Hz), 129.1 t (J = 5.1 Hz), 131.0, 131.9 t (J = 21.9 Hz), 133.2 t (J = 6.7 Hz), 148.4 t (J = 10.8 Hz), 162.3. ^{31}P NMR spectrum (80.96 MHz, $CDCl_3$): δ_P 34.2 ppm. MALDI-TOF-MS data (9-nitroanthracene matrix): m/z 1954.79 $[M - Cl]^+$. $C_{108}H_{81}Cl_2P_6Pd_3$. Calculated: m/z 1954.86. Found, %: C 65.01; H 4.12. $C_{108}H_{81}Cl_3P_6Pd_3$. Calculated, %: C 65.18; H 4.10.

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