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Stereo- and Regioselective Functionalization of Alkynes Catalyzed by Platinum(IV) and Palladium(II) Complexes in the System I⁻–I₃⁻–H₂O/MeOH

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Abstract—Activation of the $C\equiv C$ bond in acetylenic hydrocarbons, catalyzed by iodide complexes of platinum(IV), and the subsequent $C-C$ coupling reaction make it possible to synthesize 1,4-diiodo-substituted dienes with high stereo- and regioselectivity. The reaction involves intermediate formation of bis-σ-vinyl platinum(IV) complexes which can be isolated in the pure state. Under similar conditions palladium(II) complexes catalyze iodine addition to acetylene.

Activation of hydrocarbons is one of the fundamental and most important problems of modern organic chemistry. Processes of activation of acetylenic hydrocarbons include reactions involving cleavage of the $C\equiv C$ bond. As a result, derivatives having a double bond are formed; therefore, the most interesting are transformations occurring with high stereoselectivity. Recent progress in the field of stereoselective activation of triple bond is primarily determined by development of homogeneous metal-complex catalysis [1–4]. In such transformations properties of multiple bonds change appreciably as they enter coordination sphere of a metal; this make it possible to accomplish reactions which do not occur in the absence of metal complex [1–4].

A widely known activation process is based on nucleophile (Nu⁻) addition to triple bond coordinated to a metal. However, it requires attack of electrophile (HNu) to complete the reaction [5], which strongly restricts the scope of application of this procedure, for Nu⁻ should be formed from HNu in the absence of a base. The use of platinum compounds, especially of those including platinum in the highest oxidation state (Pt[IV]), as transition metal complexes capable of activating triple bond attracts interest from both methodical (to understand the mechanism of the process) and synthetic viewpoints (to accomplish new reactions).

The present article reports on the results of our studies aimed at developing a new catalytic system for stereo- and regioselective functionalization of triple bond with platinum(IV) complexes. Some results were reported previously as short communications [6–8].

CATALYTIC FUNCTIONALIZATION OF ACETYLENE

Description of the reaction and its possible mechanism. We have found that the system Pt(IV)–I⁻–I₃⁻ gives rise to stereoselective activation of acetylene, which promotes formation of a new $C-C$ bond to afford (*E,E*)-1,4-diiodo-1,3-butadiene. The catalytic process occurs under mild conditions, in methanolic or aqueous solution at room temperature. The reaction is carried out with a saturated solution of acetylene in methanol or by passing acetylene through aqueous solution. According to the ¹H NMR data obtained in deuterated methanol, the yield of the product is nearly quantitative with respect to acetylene, and the highest yield calculated on the initial amount of Pt(IV) is about 5000%; i.e., the required catalyst concentration is about 2 mol %. The reaction is characterized by high stereoselectivity: only the *E,E* isomer of 1,4-diiodo-1,3-butadiene was detected as final product (Scheme 1). A possible mechanism of the catalytic transformation includes two successive activations of

Scheme 1.

Mechanism of catalytic functionalization of acetylene
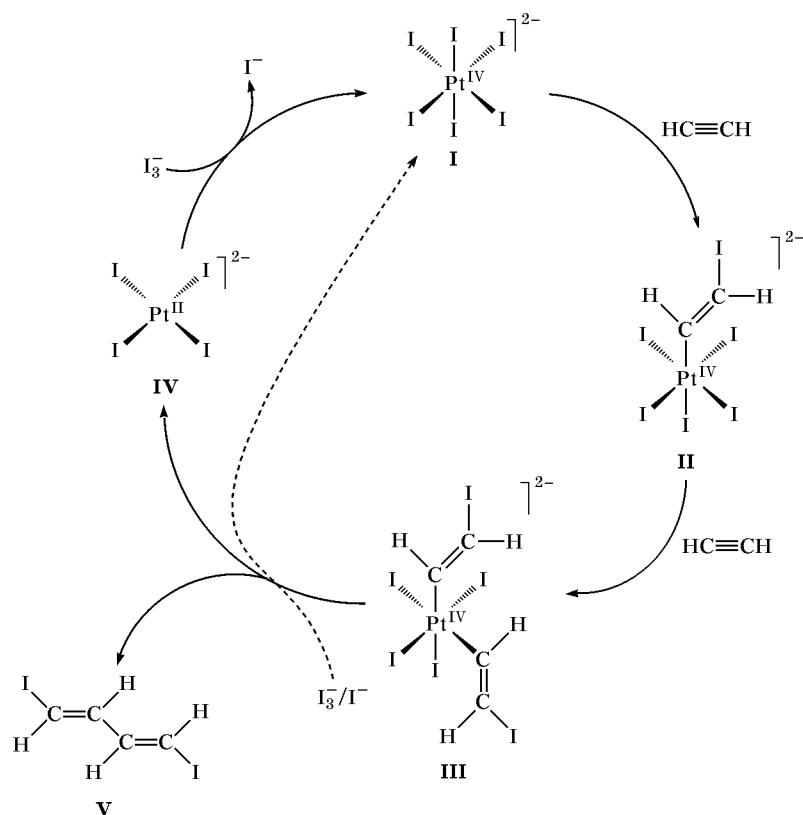
the triple bond of acetylene, which lead to formation of mono- and di-σ-vinyl platinum derivatives **I** and **II**, respectively. Final product **V** is formed by decomposition of divinyl complex **III** via inner-sphere reductive elimination. This stage may involve both oxidative assistance by iodine and intermediate formation of $[PtI_4]^{2-}$ (**IV**) and its subsequent oxidation (see below). The exclusive *trans* configuration of the products is determined by the triple bond activation via external nucleophilic attack by iodide ion.

The intermediate σ-vinyl complexes are so highly reactive that they can be neither isolated nor detected in the mixture. However, in the absence of I_2 and at the initial concentration ratio $[Pt(IV)]_0 > [C_2H_2]_0$ σ-vinyl complex is formed in an amount sufficient to detect it by ^1H NMR spectroscopy. We failed to achieve a concentration required for recording NMR spectra for the other nuclei because of the low solubility of the initial PtI_6^{2-} complex in methanol and the necessity of maintaining the initial concentration ratio. In a 2 M solution of NaI in methanol containing 0.02 mol/l of Pt(IV) and 0.01 mol/l of C_2H_2 (initial concentrations) at 297 K we succeeded in detecting σ-vinyl complex by ^1H NMR spectroscopy (Fig. 1).

It decomposes to form (*E,E*)-1,4-diiodo-1,3-butadiene (signals in the middle of the spectrum given in Fig. 1). This finding confirms the mechanism of catalytic reaction shown in Scheme 1.

Catalytic functionalization of acetylene in acid medium. Independent proofs for the proposed activation mechanism were obtained by trapping short-lived σ-vinyl intermediate by an acid. It is well known that iodide platinum(IV) complexes can be reduced in the presence of I^-; as a result, Pt(IV)/Pt(II) equilibrium establishes in solution. Unlike Pt(IV) complexes, analogous Pt(II) compounds are capable of undergoing protolytic decomposition at the Pt–C bond in the presence of an acid. In the system under study, the reduction process followed by protolysis leads to formation of vinyl iodide (**VII**) (Scheme 2). The formation of vinyl iodide from acetylene in the systems $PtI_6^{2-}–I^-–H_2O$ or $PtI_6^{2-}–I^-–CH_3OH$ in the presence of an acid over a wide concentration range was detected by chromatography.

NMR study confirmed the transformation of acetylene into vinyl iodide. When D^+ was used as electrophile (DCl, $DClO_4$), *trans*-HDC=CHI (**VII**) was obtained with almost 100% stereoselectivity (Scheme 2).
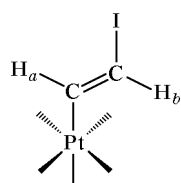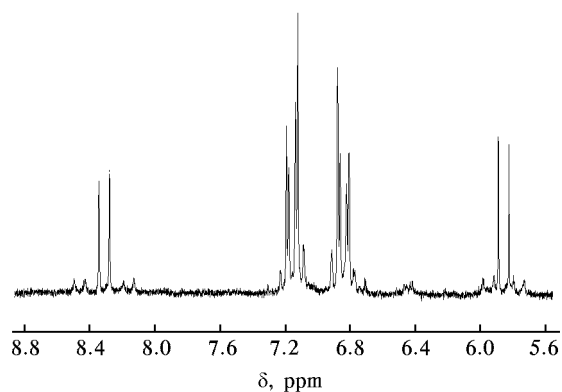
$\delta(H_a)$ 8.3 ppm;
$\delta(H_b)$ 5.9 ppm;
$J(H_a,H_b) = 13.5$ Hz;
$J(H_a,Pt) = 60.5$ Hz,
$J(H_b,Pt) = 37.4$ Hz.

Fig. 1. ^1H NMR spectrum (300 MHz) of the system Pt(IV)–I⁻–C₂H₂.

The structure of **VII** was determined on the basis of its ^1H, ^2H, and ^{13}C NMR spectra (Fig. 2; for NMR parameters of substituted vinyl derivatives, see [9]). The coupling constant $J(H_a,H_b) = 15.7$ Hz indicates

trans arrangement of the H_a and H_b protons, and the coupling constant $J(H_b, D) = 1.2$ Hz falls into the range typical of *cis* orientation of the corresponding nuclei (taking into account the γ_H/γ_D correction factor equal to 6.5, the given coupling constant corresponds to an H–H coupling of 7.8 Hz).

The process occurs in the catalytic mode in the presence of excess acid and acetylene (Scheme 2); the catalytic series is closed by regeneration of the initial form of catalyst **I** via oxidation of complex **IV** with iodine. At the initial concentrations $[Pt(IV)]_0 = 0.016$ M, $[C_2H_2]_0 = 0.060$ M, $[DCl]_0 = 0.124$ M, and $[I_2]_0 = 0.126$ M almost complete conversion of acetylene is attained in several hours at room temperature. The yield is about 370% with respect to Pt(IV), taking into account the initial reactant concentrations. We made no attempts to optimize the conditions of the process. Nevertheless, our results are quite sufficient to prove the possibility for catalytic preparation of vinyl iodide with simultaneous introduction of deuterium label.

FUNCTIONALIZATION OF SUBSTITUTED ALKYNES

Catalytic reaction. (*E,E*)-2,5-Diiodo-2,4-hexadiene-1,6-diol (**X**) is formed in a catalytic reaction in

Scheme 2.

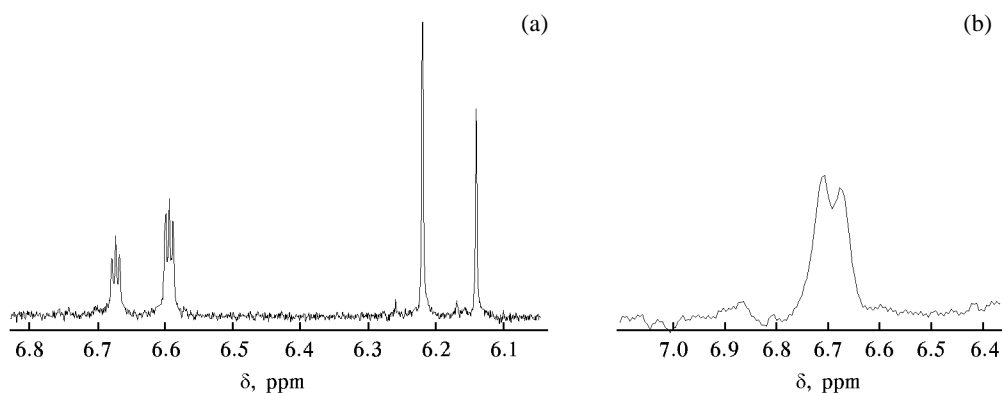Mechanism of catalytic functionalization of acetylene in acid medium
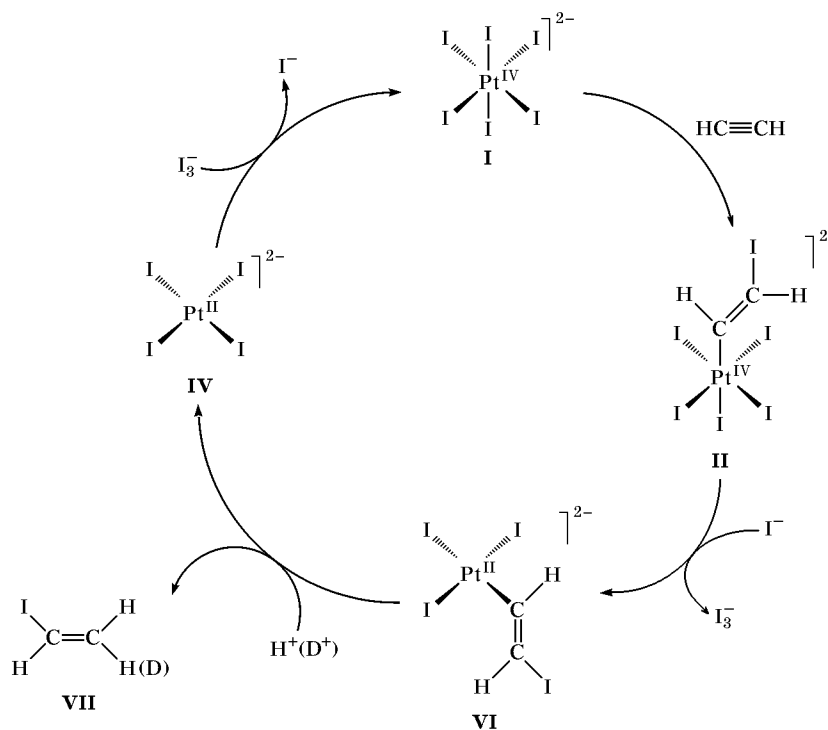
Fig. 2. (a) ^{1}H and (b) ^{2}H NMR spectra of *trans*-HDC=CHI (**VII**).

the presence of excess 2-propynyl alcohol and I_3^- in aqueous medium (Scheme 3). The catalytic transformation is accompanied by side iodine addition at the triple bond.

$$HC\equiv CCH_2OH \ + \ I_2 \ \longrightarrow \ ICH=CI-CH_2OH$$
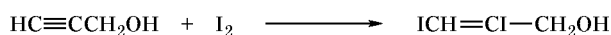
The product was identified by ^{1}H and ^{13}C NMR spectroscopy on the basis of published data [10].

To minimize the contribution of this side process the reaction was carried out at 15°C in the dark, and (after ~60 h) compound **X** was formed in about 600% yield with respect to the initial Pt(IV) salt. The final product is almost insoluble in water, and it can readily be isolated in the pure state. In keeping with our previous data, decomposition of complex **IX** by the reductive elimination mechanism can be facilitated due to oxidative assistance by molecular iodine. In

Scheme 3.

Catalytic functionalization of 2-propynyl alcohol

Scheme 4.

Synthesis of divinyl complexes **IX** and **XI** and reductive elimination

IX, X, R = H; **XI, XII**, R = Me.

this case, the final form of the metal complex is likely to be compound **I**, while intermediate complex **IV** should not be formed.

Like with acetylene, the catalytic reaction with 2-propynyl alcohol is characterized by high stereoselectivity, and the corresponding *E,E* isomer is formed as the only product. Moreover, the process is regioselective: iodide ions add to the most substitu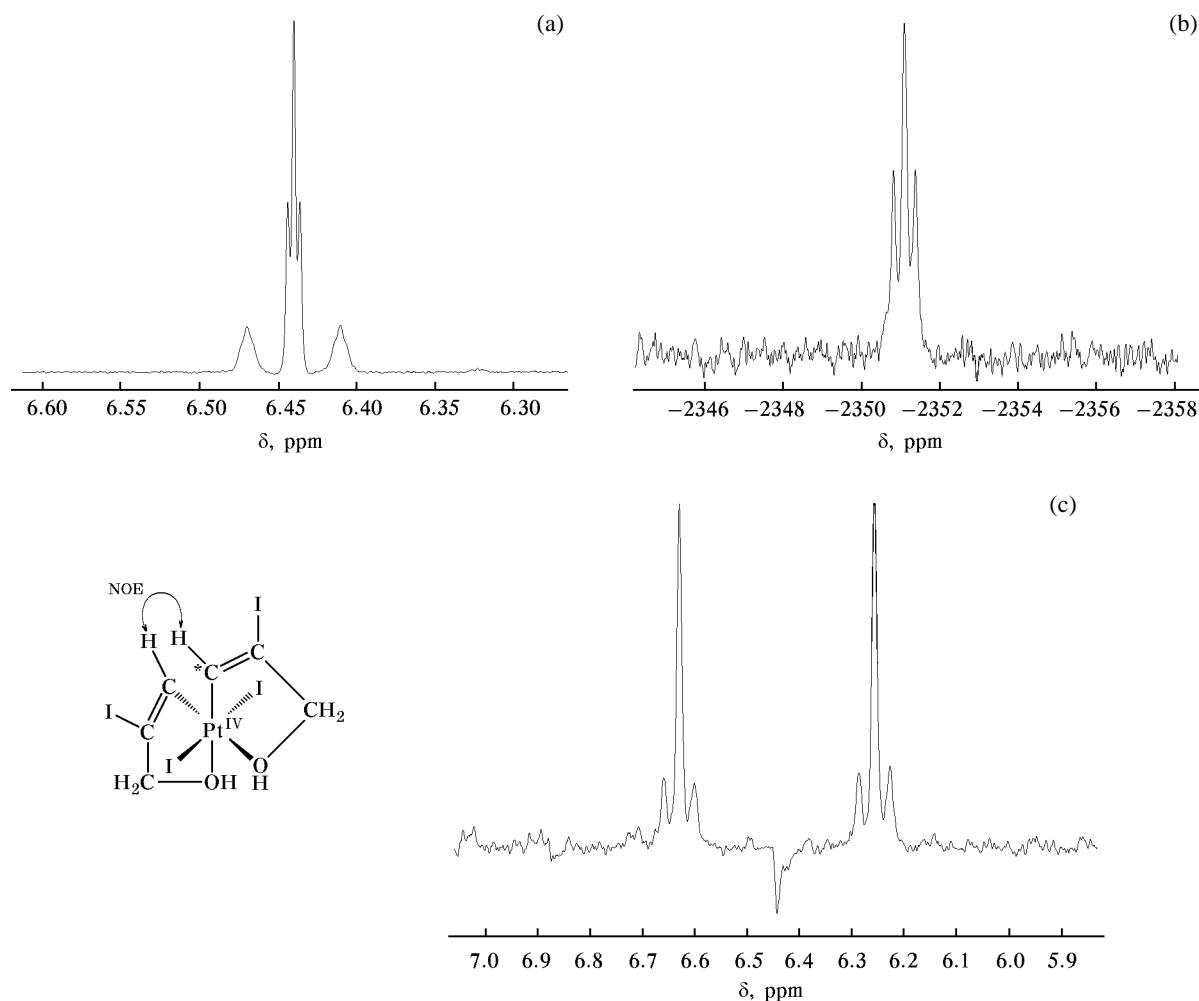ted carbon atom at the double bond. The most probable reason for the observed regioselectivity is stabilization of σ-vinyl platinum complexes **VIII** and **IX** through additional chelation (dative interaction).

Synthesis and structural study of stable σ-vinyl platinum(IV) complexes. As in the above processes, activation of the triple bond occurs in the reaction of 2-propynyl alcohol with PtI_6^{2-} taken at a ratio close to stoichiometric (Scheme 4). Coordination of the oxygen atoms to platinum gives rise to a neutral bicyclic complex which separates from the solution because of its poor solubility in water.

The presence of two vinyl ligands at one metal atom is confirmed by elemental analysis. The vinyl system in **IX** gives IR absorption band at 1630 cm^{-1} while no absorption band typical of C≡C stretching vibrations is present. The structure of **IX** was unambiguously proved by ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy. Figure 3 shows a fragment of the ^1H NMR spectrum, corresponding to the vinyl proton region. It appears as a triplet due to coupling with protons of the neighboring methylene group; also, satellites due to coupling with ^{195}Pt are observed. The coupling constant $^2J(Pt, H)$ is equal to 31.1 Hz, which is typical of such compounds, and ^{195}Pt satellites are appreciably broadened as compared with the central com-

ponent due to fast spin–lattice relaxation of ^{195}Pt nuclei [11, 12]. The presence of a vinyl group also follows from the ^{13}C chemical shifts, and the coupling constant $^1J(Pt, C) = 801.4$ Hz unambiguously indicates the presence of a metal–carbon σ-bond. Both vinyl ligands are equivalent in the ^1H and ^{13}C NMR spectra; therefore, it is difficult to determine their number on the basis of these spectra. However, appearance of a triplet signal from ^{195}Pt (Fig. 3, *c*) suggests that two equivalent groups are present. It should be noted that we succeeded in obtaining an appropriate ^{195}Pt NMR spectrum with narrow lines only for solutions in acetone. In methanol, the ^{195}Pt signal was considerably broadened.

The *cis* orientation of vinyl ligands, which is necessary for the reductive elimination to occur, was proved by the one-dimensional HMQC-NOESY technique (Fig. 3). Both vinyl ligands in **IX** are completely equivalent, which hampers determination of the geometric structure of the complex by usual NMR methods. However, selective excitation of ^{13}C satellites of one of the protons makes it possible to observe NOE with the other vinyl proton (H–C^{12} fragment). The occurrence of NOE (Fig. 3) indicates that the corresponding protons are spatially close, which is possible when they are arranged *cis* with respect to each other. The signal assignment in the ^1H, ^{13}C, and ^{195}Pt NMR spectra of complex **IX** was proved with the aid of the gsCOSY, gsNOESY, ^1H–^{13}C gsHMQC, and ^1H–^{195}Pt HMQC techniques.

We found that other substituted alkynes can also be involved in an analogous reaction. In particular, we synthesized and isolated bicyclic σ-vinyl complex **XI** (Scheme 4). The structure of **XI** was proved by X-ray

Fig. 3. NMR spectra of the complex [Pt(CH=CI−CH$_2$OH)$_2$I$_2$] (**IX**) in the vinyl proton region: (a) ^{1}H, (b) ^{195}Pt, and (c) HMQC-NOESY.

analysis [7]. Its structure in solution was established using a set of NMR techniques like those listed above for compound **X**. NMR study of the complex [Pt(CH=CI−CH$_2$OCH$_3$)$_2$I$_2$] (**XI**) revealed a fairly large coupling constant ^1J(Pt,C) (819.9 Hz) which might be expected for a metal–carbon σ-bond. In the ^{195}Pt NMR spectrum we observed a triplet at δ_{Pt} –2225.1 ppm, ^2J(Pt,H) = 41.0 Hz; the latter coincided with the coupling constant determined independently from the ^{1}H NMR spectrum. These data, together with the coupling constant J(Pt,H) = 4.8 Hz for the methyl protons, suggest that in solution the complex retains its symmetrical bicyclic structure. To complete identification of this compound, its IR and mass spectra were also recorded.

It should be emphasized that compound **XI** (by the moment of establishing its structure) was the first example of complexes in which the platinum(IV)

atom is linked to vinyl ligand through a σ-bond, i.e., of those having a Pt^{IV}−C=C structural fragment.

Reductive elimination from divinyl Pt(IV) complexes. As might be expected, heating of divinyl complexes **IX** and **XI** promotes reductive elimination to afford (*E,E*)-2,5-diiodo-2,4-hexadiene-1,6-diol (**X**) and (*E,E*)-2,5-diiodo-1,6-dimethoxy-2,4-hexadiene (**XII**), respectively. The steric structure of products **X** and **XII** was established on the basis of the ^{1}H and ^{13}C NMR spectra using two-dimensional LR-COSY, gsNOESY, gsHMQC, and gsHMBC techniques.

The *E* configuration of the double bond in the metal complex and in the resulting diene is retained during the reaction, and only one product is formed (Scheme 4). The process is most likely to follow the inner-sphere reductive elimination mechanism according to which C−C bond is formed through three-membered transition state and, after dissociation of
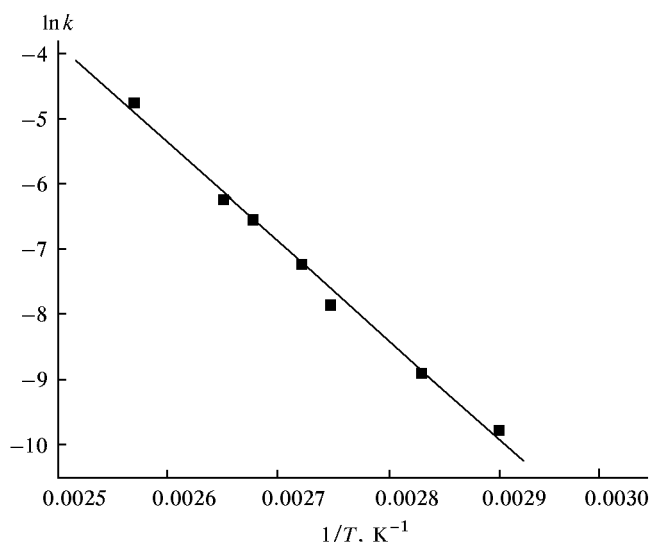
Fig. 4. Arrhenius plot for the reductive elimination: $y = (34 \pm 2) - (1.53 \pm 0.06) \times 10^4 x$; $r = 0.997$ (points nos. 5–11 in table).

the new organic molecule, the degree of oxidation of of the metal decreases.

Decomposition of divinyl complex **IX** (Scheme 4) follows first-order kinetics; the corresponding rate constants are given in table. It is seen that the reaction rate weakly depends on the solvent (CD_3COOD and BuOD-d_{10}; points nos. 1 and 3). In all cases, considerable heating is necessary for the reaction to proceed at an appreciable rate. The activation parameters determined from the temperature dependence of the rate constants for reductive elimination (Fig. 4) are

Rate constants for reductive elimination from the complex $[Pt(CH=CI-CH_2OH)_2I_2]$ (**IX**)

No.	T, K	Solvent	$k \times 10^4$, s^{-1}	[I_2], M
1	363.5	CD_3COOD	2.9 ± 0.1[a]	0
2	363.5	CD_3COOD	5.9 ± 0.5[a]	0.46
3	363.5	BuOD-d_{10}	3.2 ± 0.1[a]	0
4	363.5	BuOD-d_{10}	38.9 ± 1.8[a]	0.46
5	345.0	BuOH	0.57 ± 0.01[b]	0
6	353.5	BuOH	1.36 ± 0.01[b]	0
7	364.0	BuOH	3.9 ± 0.1[b]	0
8	367.5	BuOH	7.2 ± 0.1[b]	0
9	373.5	BuOH	14.4 ± 0.2[b]	0
10	377.2	BuOH	19.7 ± 0.7[b]	0
11	389.0	BuOH	87 ± 6[b]	0

[a] Determined from the ^{1}H NMR data.
[b] Determined by spectrophotometry.

as follows: $E_a = 127 \pm 5$ kJ/mol and $A = 5.83 \times 10^{14}$ s^{-1} (preexponential factor). In the determination of activation parameters we used the results of spectrophotometric measurements (points nos. 5–11; see table), which allowed us to cover a wider temperature range. The rate constants determined from the NMR and spectrophotometric data at the same temperature were very similar (cf. nos. 3 and 7). It should be noted that the energy of activation is fairly high.

It is interesting that the rate of reductive elimination increases in the presence of an oxidant (nos. 1–4 in table). Addition of I_2 considerably accelerates the reaction, and a very strong solvent effect is observed. The reaction rate in acetic acid increases by a factor of 2, whereas in butanol it increases by more than an order of magnitude. These findings could readily be interpreted if the reaction occurred with Pt(II) complex. In this case decomposition of the complex would be preceded by its oxidation to Pt(IV) compounds which are more reactive in reductive elimination processes. However, in our case the initial compound is Pt(IV) derivative whose oxidation with I_2 is quite improbable. Moreover, addition of iodine does not cause appreciable variation of the spectral parameters of the complexes; therefore, no essential structural reorganization is possible. A plausible explanation includes formation of an intermediate complex between I_2 and iodide ligands in the coordination sphere to give a ligand like I_3^-. It is well known that iodide systems are prone to form various polynuclear compounds, and the formation constant of I_3^- from I_2 and I^- is >700 l/mol [13]. An analogous pattern was observed in the decomposition of the divinyl iridium complex $Cp^*Ir(CH=CH_2)_2(Me_2SO)$ to give 1,3-butadiene only in the presence of an oxidant [14]. Thus we were the first to directly observe oxidative assistance to reductive elimination from Pt(IV) complexes.

Mechanism of reductive elimination from cyclic σ-vinyl Pt(IV) complexes. According to the results of X-ray diffraction and NMR studies, the obtained σ-vinyl complexes have a bicyclic chelate structure due to coordination of oxygen to the metal. Such chelates are less reactive than σ-derivatives obtained from acetylene. Furthermore, compound **X** is formed in a catalytic process at 15°C, whereas decomposition of the corresponding individual chelate **IX** occurs at an appreciable rate only above 70°C (see above). The difference in their reactivity may be explained on the assumption that reductive elimination requires preliminary decomposition of the chelate structure, which is achieved under catalytic conditions (no such process is necessary for acetylene complexes). In fact,

**Scheme 5.**

Reductive elimination
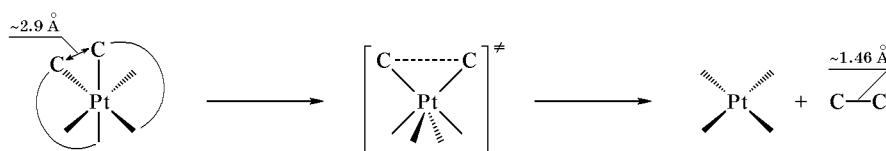
three-membered transition state (Scheme 5) was proposed in [1, 4] for the reductive elimination process. The length of the central C−C bond in butadienes is usually ~1.46 Å [15]. Taking into account a fairly high activation energy of the reductive elimination process, the Hammond postulate suggests that the transition state should be structurally similar to the products. In other words, we can expect a relatively short distance between the carbon atoms in the transition state. According to the X-ray diffraction data, the distance between the vinyl carbon atoms in the initial complex is about 2.9 Å. Obviously, the formation of transition state should be preceded by considerable structural reorganization (Scheme 5). It seems improbable that this process could occur with retention of the cyclic structure of both chelated ligands, for dative bonds are usually characterized by a relatively low energy.

In order to elucidate these problems we performed a separate study of the mechanism of reductive elimination from cyclic σ-vinyl complexes. As noted above, decomposition of complexes in a catalytic system occurs under considerably milder conditions than does direct reductive elimination. An essential difference between these processes is the presence of iodide ions in the former case. Presumably, iodide ion is capable of entering coordination sphere of the metal with displacement of one of the oxygen atoms. The appearance of a less rigid acyclic ligand should notably facilitate formation of transition state, thus favoring decomposition of the complex (Scheme 6).

This assumption was verified by special experiment, namely by decomposition of complex **IX** in the presence of NaI. The results showed that complete decomposition of **IX** in a 2 M solution of NaI at 55°C takes about 2 h, while in the absence of iodide ions the half-conversion period $\tau_{1/2}$ is 7 h at 72°C. Therefore, iodide ions do accelerate the reductive elimination. Moreover, by adding NaI to a methanolic solution of **IX** we succeeded in detecting by NMR spectroscopy formation of complex **XIII**. These data led us to conclude that there exists an equilibrium between complexes **IX** and **XIII**. Figure 5 shows the vinyl proton region of the two-dimensional ^{1}H–^{195}Pt HMQC spectrum, where we clearly see the presence of two individual compounds. The vinyl protons in **XIII** are nonequivalent, and they give rise to two cross-peaks with ^{195}Pt. The downfield signal is characterized by much greater Pt–H coupling constant, and no allylic coupling is observed. Therefore, the signal at δ 7.9 ppm was assigned to the acyclic ligand. A considerable downfield shift and increase in the coupling constant with the metal were also observed for analogous vinyl proton in the complex obtained from acetylene (Fig. 1), in which the vinyl ligands do not form chelate structure. As expected, the ^{195}Pt signal shifts upfield by more than 500 ppm upon coordination of an additional iodide ligand. Variation of the NaI concentration showed that the equilibrium between complexes **IX** and **XIII** shifts toward opening of one chelate ring as the concentration of iodide in solution increases. The equilibrium constant

Scheme 6.

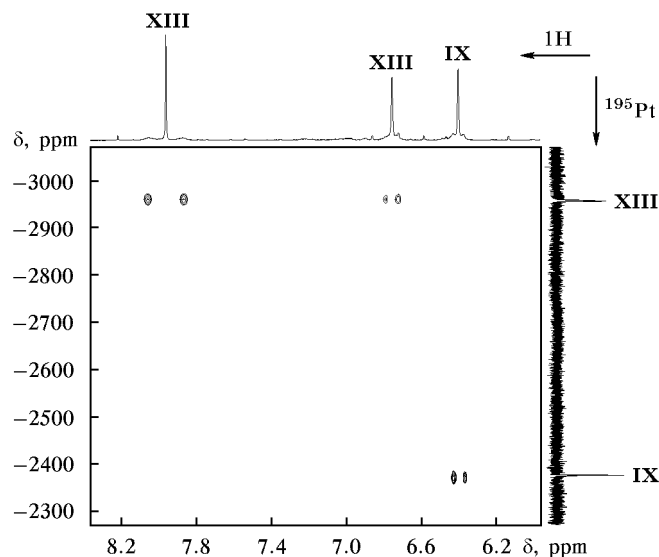Mechanism of catalytic reductive elimination (in the presence of iodide ions)
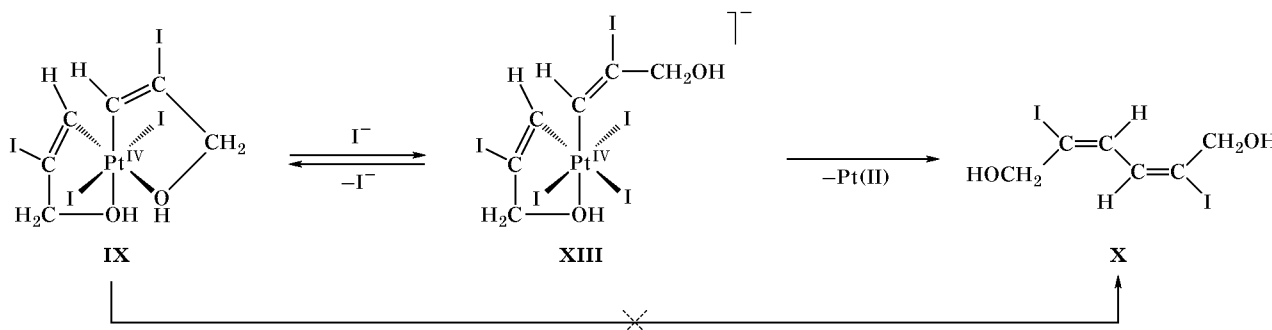
Fig. 5. Two-dimensional $^1H–^{195}Pt$ HMQC spectrum of a mixture of complexes **IX** and **XIII**.

was calculated by the equation $K = [\mathbf{XIII}]/[\mathbf{IX}] \times [I^-]$ under the constraint $[I^-] \gg [\mathbf{IX}]_0$ at 273 K; it is equal to 1.8 ± 0.1 l/mol. It should be noted that in the examined concentration range we detected no complexes having two acyclic ligands.

Thus we have shown that the reductive elimination process requires preliminary opening of at least one cyclic ligand. This fact confirms the general character of the reductive elimination mechanism for both acyclic and cyclic complexes.

Reactivity of alkynes having electron-acceptor substituents. Activation of the triple bond in methyl 2-propynoate $HC{\equiv}CCOOMe$ with the PtI_6^{2-} complex

in a 2 M solution of NaI in methanol gives rise to formation of compound **XV** (Scheme 7). A possible mechanism of this reaction includes initial nucleophilic attack by iodide ion on the terminal carbon atom (C^1), leading to formation of the $Pt–C^2$ σ-bond (intermediate **XIV**). The regioselectivity of alkyne activation corresponds to the expected one, taking into account the effect of electron-acceptor substituent. However, in the next stage the regioselectivity changes for steric reasons: nucleophilic attack occurs at the most substituted atom at the triple bond (C^6), whereas bond with the metal is formed through the terminal carbon atom (C^5).

Scheme 7.

Activation of the triple bond in methyl 2-propynoate and C−C-coupling reaction from the corresponding bis-σ-vinyl derivative
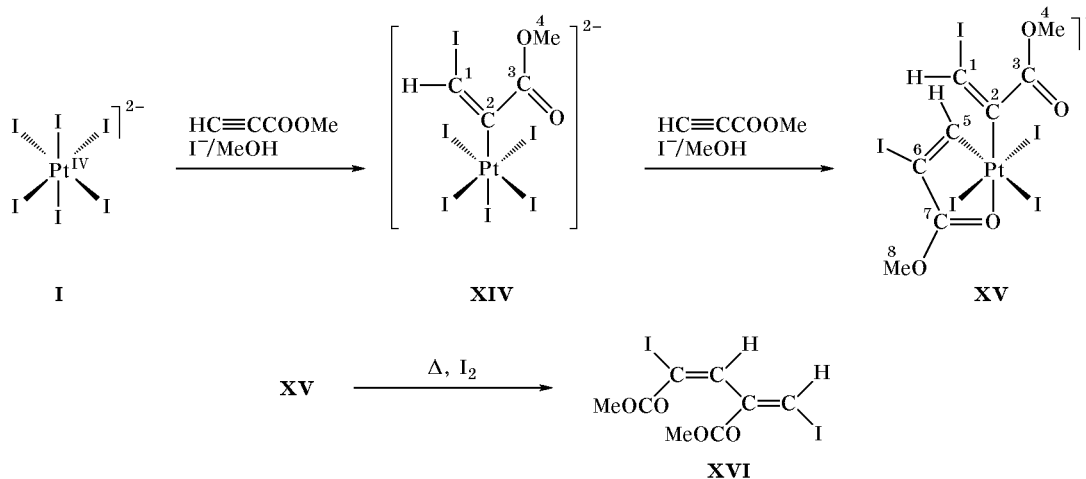
Scheme 8.

Synthesis and structure determination of unsymmetrical derivative **XVII**.

2D LR-COSY   2D NOESY
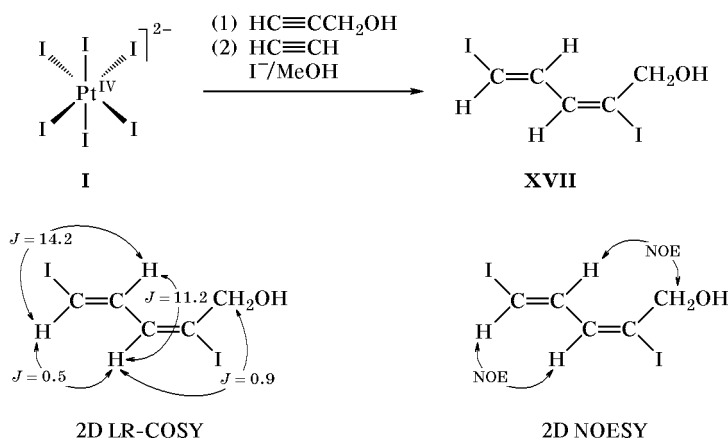
The structure of product **XV** was determined by ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopy. The coupling constants $^1J(Pt, C^5) = 674.4$ Hz and $^1J(Pt, C^2) = 923.5$ Hz unambiguously confirm the above regioselectivity of activation. Detailed assignment of the ^{1}H and ^{13}C signals in the NMR spectra was done using two-dimensional HMQC and HMBC techniques.

The final bis-σ-vinyl product was isolated by carrying out the reaction in aqueous medium in the absence of iodide ions. According to the ^{1}H NMR data for solutions in CD_3OD, the iodide ligand in the platinum coordination sphere is replaced by solvent molecule to afford two compounds

$$[Pt(CH=CI-COOMe)(CIH=C-COOMe)(Sol)_{3-n}I_n]^{2-n}$$
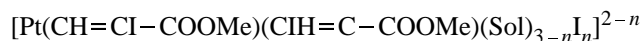
at a ratio of 1:4 for $n = 3$ and 2, respectively. The existence of equilibrium between the two forms of metal complexes was proved using 2D NOESY exchange spectroscopy and 2D ^{1}H–^{195}Pt HMQC heteronuclear correlation technique.

Heating of the mixture of complexes in methanol in the presence of I_2 leads to formation of C–C-coupling product **XVI** (Scheme 7). This reaction is analogous to those described above (Schemes 3, 4), but the methoxycarbonyl groups in the resulting diene occupy positions *1* and *3*.

Thus in the first stage activation of the triple bond in methyl 2-propynoate in the system under study formally follows the Markownikoff rule for acetylenic hydrocarbons with electron-acceptor substituents, and in the next stage it changes to the reverse. Finally, we obtain 1,3-disubstituted diene, in contrast to reactions of alkynes having electron-donor substituent which give rise to 1,4-derivatives.

Synthesis of mixed diene derivatives. Proceeding from the reaction mechanism leading to formation of symmetrical conjugated dienes, we believed it possible to develop a new approach to unsymmetrical derivatives. In fact, when a mixture of alkynes was taken as substrate, the final product was unsymmetrical conjugated compound. By adding to the system Pt(IV)–I$^-$ at room temperature first 2-propynyl alcohol [at a molar ratio of 1:1 with respect to initial platinum(IV)] and then acetylene, we observed formation of 75% of (*E,E*)-2,5-diiodo-2,4-pentadien-1-ol (**XVII**) (Scheme 8). In addition, 25% of (*E,E*)-1,4-diiodo-1,3-butadiene (**V**) was formed [in both cases the yields are given with respect to the initial amount of Pt(IV)]. Obviously, the first reaction stage gives monocyclic σ-vinyl derivative **VIII**, and the second iodoplatination stage involves acetylene molecule, leading to the mixed-ligand metal complex

$$[Pt(CH=CI-CH_2OH)(HC=CHI)I_3]^-.$$
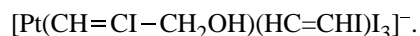
Its decomposition via reductive elimination yields final product **XVII**. The formation of (*E,E*)-1,4-diiodo-1,3-butadiene (**V**) suggests a concurrent reaction with participation of two acetylene molecules. It is important that we detected no symmetrical product of coupling of two 2-propynyl alcohol molecules, (*E,E*)-2,5-diiodo-2,4-hexadiene-1,6-diol (**X**). The order of addition of alkynes is significant. When acetylene was added first to the reaction mixture, the major product was (*E,E*)-1,4-diiodo-1,3-butadiene (**V**). These results are explained by different reactivities of the alkynes: acetylene is considerably more reactive than substituted alkynes. The same factor is responsible for our failure to synthesize mixed product under catalytic conditions.

Mixed dienes are also formed with high stereo- and regioselectivity. The structure of (*E*,*E*)-2,5-diiodo-2,4-pentadien-1-ol was established using two-dimensional ^{1}H NMR spectroscopy (Scheme 8). Activation of both alkynes is achieved via *trans*-addition ensuring *E* configuration of the double bond ($J = 14.2$ Hz, NOE). Activation of 2-propynyl alcohol is regioselective, for I$^-$ adds only to the most substituted carbon atom.

TRIPLE BOND ACTIVATION WITH PALLADIUM COMPLEXES

Taking into account that complexes of palladium, which is an isoelectron analog of platinum, are considerably cheaper and readily accessible, it seemed reasonable to examine the possibility of using them for catalytic transformations of alkynes under similar conditions. We have found that the system obtained by dissolution of PdCl$_2$, NaI, and I$_2$ in methanol promotes at 55°C catalytic stereoselective transformation of acetylene to *trans*-1,2-diiodoethylene in quantitative yield (Scheme 9).

Scheme 9.

Activation of the triple bond in acetylene by palladium complexes

HC≡CH $\xrightarrow{\text{PdCl}_2-\text{I}^--\text{I}_3^--\text{MeOH, 55°C}}$

XVIII
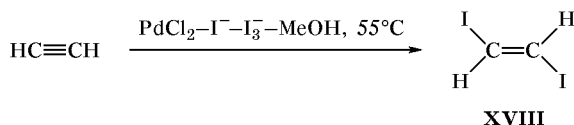
^{1}H NMR monitoring of the system revealed that decrease in intensity of the acetylene signals (δ 2.26 ppm) is accompanied by appearance and increase in intensity of a signal at δ 7.25 ppm, which belongs to *trans*-1,2-diiodoethylene; ^{13}C NMR data: δ 85.4 ppm, $^1J(\text{C},\text{H}) = 197.8$, $^2J(\text{C},\text{H}) = 2.0$ Hz. The coupling constant $^3J(\text{H},\text{H}) = 14.2$ Hz is typical of *trans* configuration.

Under analogous conditions but in the absence of palladium the iodination of acetylene occurs at a considerably lower rate: the conversions are 85% and 9% for the catalytic and noncatalytic reactions at 55°C (1.5 h). It should be noted that noncatalytic iodination of substituted acetylenes (such as propyne, 2-propynyl alcohol, phenylacetylene, and diphenylacetylene) is fairly fast, so that no catalytic effect of palladium is observed.

Thus the palladium-containing catalytic system does not give diene products under analogous conditions. The most probable reason is that divinyl derivatives of palladium cannot be formed because of the

high reactivity of monovinyl intermediate which decomposes via either C−I elimination or iodolysis of the Pd−C(sp^2) bond.

In the present work we revealed and studied for the first time catalytic activation of acetylenic compounds in the presence of platinum(IV) complexes. The mechanisms of catalytic stereo- and regioselective synthesis of conjugated dienes and stereoselective addition of iodine to triple bond were examined in detail. A number of diiodo-substituted 1,3-dienes were synthesized for the first time; among these, (*E*,*E*)-1,4-diiodo-1,3-butadiene is the most important representative. Triple bond activation in methyl 2-propynoate should be specially noted. In this case the regioselectivity of activation changes during the process, giving rise to mixed-ligand metal complex and unsymmetrical diene product.

Organometallic compounds of a new class, σ-vinyl platinum(IV) complexes, were obtained, and their structure was proved by X-ray analysis. All the products were extensively studied by mono- and two-dimensional NMR spectroscopy, including ^{1}H, ^{13}C, and ^{195}Pt nuclei. The catalytic activities of platinum and palladium complexes in iodide system with respect to acetylene were compared.

In the I$^-$–I$_3^-$–H$_2$O/MeOH system, triple bond activation begins with dissociation of one iodide ligand to afford a vacant coordination site in the complex (Scheme 10). π-Coordination of acetylene to complex **XIX** leads to intermediate **XX**. The triple bond is activated through external nucleophilic attack by iodide ion to give σ-vinyl derivative **II**. Thus alkyne functionalization to β-iodovinyl ligand is achieved by successive electrophilic addition of the metal complex to the triple bond and attack by external nucleophile. Obviously, the formation of π-complex enhances the reactivity of the triple bond. As a result, products having *E* configuration are formed exclusively, ensuring high stereoselectivity of the process as a whole.

The catalytic synthesis of substituted dienes is based on the possibility for regeneration of Pt(IV) via oxidation with iodine of Pt(II) formed as a result of reductive elimination. The presence of molecular iodine in the reaction mixture does not promote rupture of the Pt(IV)−C(sp^2) bond in the monovinyl complex and does not hamper the reaction with the second alkyne molecule. The unique property of the examined system is a fine equilibration between the redox potentials of PtI$_6^{2-}$/PtI$_4^{2-}$ and I$^-$/I$_3^-$. No such equilibration exists in the case of palladium complexes; therefore, the corresponding monovinyl derivative rapidly decomposes, and C−C coupling is impossible.

Scheme 10.

Activation of triple bond via attack by external nucleophile
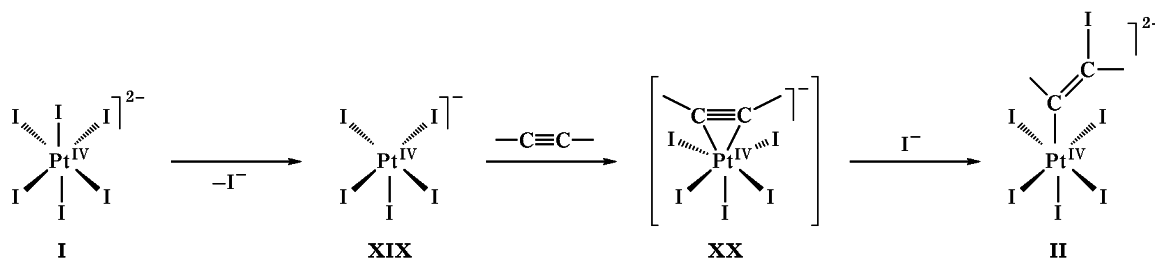
Activation of the triple bond in substituted alkynes having a heteroatom capable of coordinating to metal through unshared electron pair is regioselective due to stabilization of organometallic derivatives by chelation. Detailed study of the process of C−C bond formation in the coordination sphere showed the necessity of opening of at least one chelate ring. On the one hand, chelation makes the activation process regioselective and, on the other, it considerably reduces the reactivity of organometallic intermediates. As a result, the scope of application of the catalytic system becomes somewhat narrower.

EXPERIMENTAL

Solvents were purified by standard procedures; deuterated solvents (>99.8% of deuterium) were used without additional purification. Platinum salts K_2PtCl_6 and K_2PtCl_4 were synthesized as described in [16]. NMR experiments were carried out with anhydrous NaI which was calcined just before use; in the other cases, the crystal hydrate $NaI \cdot 2H_2O$ was used. 2-Propynyl alcohol and methyl 2-propynoate were purified by distillation. Acetylene was obtained by the procedure described in [17]. The purity of all the alkynes was checked by ^{1}H and ^{13}C NMR spectroscopy.

NMR studies. The NMR spectra were recorded on a Bruker DRX-500 spectrometer at 500, 125, and 107 MHz for ^{1}H, ^{13}C, and [195]Pt, respectively. In some cases, unidimensional proton spectra were obtained on Bruker AC-200 (200 MHz) and Bruker AM-300 (300 MHz) instruments. Solvent signals served as reference for ^{1}H and ^{13}C NMR spectra, and $Na_2PtCl_6 \cdot D_2O$ was used as external reference for [195]Pt NMR spectra. The two-dimensional spectra were recorded on a Bruker DRX-500 instrument coupled with a Silicon Graphics workstation; XWINNMR software package was used [version 2.0, © 1998 Bruker Analytik GmbH]. The following pulse sequences were applied in two-dimensional experiments: gsCOSY

[18], gsNOESY [19], LR-COSY [20], gsHMQC [21, 22], gsHMBC [21,22], and HMQC-NOESY [23]; the acquisition and data processing parameters were taken from [23]. Unless otherwise stated, all measurements were performed at room temperature. The chemical shifts (δ) are given in ppm, and coupling constants (J), in Hz.

(*E,E*)-1,4-Diiodo-1,3-butadiene (V). Anhydrous NaI, 0.6 g (4 mmol), was dissolved in 5 ml of methanol, the solution was saturated with acetylene, 0.36 g (1.4 mmol) of I_2 and 27 mg (0.048 mmol) of $Na_2PtCl_6 \cdot 6H_2O$ were added, and the mixture was left to stand at room temperature. After 6 h, the product was precipitated with water. The precipitate was separated and washed with water, a saturated solution of NaI, and water again until the washings contained no I^- ions. The precipitate was extracted with methanol, the extract was evaporated at room temperature, and the residue was dried under reduced pressure. We isolated 60 mg (0.19 mmol) of a colorless crystalline substance. The overall yield of the final product was 410% with respect to platinum(IV).

The ^{1}H NMR spectrum shows an *AA'BB'* pattern. The spectrum was analyzed using the known procedure [24]; the spectral parameters were consistent with published data for structurally related compounds (cf., e.g., the spectrum of (*E,E*)-1,4-dichloro-1,3-butadiene [25]). IR spectrum (KBr), ν, cm^{-1}: 3020 v.w (=C−H), 1620 m (C=C), 1530 s, 1380 m, 1280 s, 1140 s, 1010 m and 960 v.s (δ=C−H). ^{1}H NMR spectrum (CD$_3$OD): $\delta(H_a) = \delta(H_{a'}) = 7.13$, $\delta(H_b) = \delta(H_{b'}) = 6.82$, $J(a,b) = 14.39$, $J(a,b') = -0.60$, $J(a,a') = 0.50$, $J(b,b') = 10.19$. [13]C−{^{1}H} NMR spectrum (CD$_3$OD), δ_C, ppm: 145.5 s (CH), 83.1 s (CI). Mass spectrum: 306 [M^+], 179 [CHI=CH−CH=CH]$^+$, 127 [I]$^+$. Found, %: C 16.2; H 1.5. $C_4H_4I_2$. Calculated, %: C 15.69; H 1.31.

NMR monitoring of the formation of vinyl iodide (VII) under catalytic conditions. A solution of Na_2PtCl_6 (0.02 M) and NaI (2 M) in CD$_3$OD, 0.4 ml, was mixed with 0.1 ml of a solution of C_2H_2

(0.3 M) and NaI (1 M) in CD_3COCD_3. The concentration of acetylene in the initial solution was determined preliminarily by ^{1}H NMR spectroscopy on addition of a known amount of *tert*-butyl alcohol to the ampule. To the resulting mixture we added 16 mg (0.06 mmol) of I_2 and, after stirring, 5 μl of 12.4 M DCl in D_2O. The initial concentrations were: $[NaI]_0$ 1.8 M, $[Pt(IV)]_0$ 0.016 M, $[C_2H_2]_0$ 0.060 M, $[DCl]_0$ 0.124 M, $[I_2]_0$ 0.126 M. The solution was transferred into an NMR ampule. *trans*-Deuterovinyl iodide was detected as the only product which was formed in nearly quantitative yield. ^{1}H NMR spectrum (CD_3OD; for denotations of atoms, see Fig. 2), δ, ppm: 6.26 d [H_a, $J(H_a, H_b) = 15.7$], 6.72 d.t [H_b, $J(H_a, H_b) = 15.7$, $J(H_b, D) = 1.2$]. ^{2}H NMR spectrum (CD_3OD), δ, ppm: 6.70 d [D, $J(H_b, D) = 1.2$]. ^{13}C–{^{1}H} NMR spectrum (CD_3OD), $δ_C$, ppm: δ 131.1 t [CHD, $J(C, D) = 24.2$], 86.6 s (CHI).

2,5-Diiodo-2,4-hexadiene-1,6-diol (X). A 4.85-g (26-mmol) portion of $NaI \cdot 2H_2O$ was dissolved in 5 ml of H_2O, and 0.2 g (0.8 mmol) of I_2 and 10.5 mg (0.02 mmol) of $Na_2PtCl_6 \cdot 6H_2O$ were added to the solution. The solution was stirred for 1.5 h at room temperature, and 6×10 μl of 2-propynyl alcohol was added at equal time intervals over a period of 60 h at 15°C (the reaction was carried out in the dark). The yellow precipitate was separated by centrifugation and was washed with water (5×10 ml) over a period of 2 h. The final product was extracted with 10 ml of methanol and was dried under reduced pressure. Yield 42.4 mg, [614% with respect to Pt(IV) or 14.4% with respect to 2-propynyl alcohol]. ^{1}H NMR spectrum (CD_3COCD_3), δ, ppm: 7.17 s (CH), 4.31 d [CH_2, [3]$J(H, H) = 6.0$], 4.81 t [OH, [3]$J(H, H) = 6.0$]. ^{13}C–{^{1}H} NMR spectrum (CD_3COCD_3), $δ_C$, ppm: 136.7 s (CH), 110.6 s (CI), 65.8 s (CH_2). Mass spectrum: 366 [M^+], 254, 239 [$M-I$], 238, 221, 193, 183 [$M-C_3H_4OI$], 165, 152, 141, 127, 128, 119, 112 [$M-2I$], 111, 105, 94. Found, % : C 19.68; H 2.36; I 67.98. $C_6H_8O_2I_2$. Calculated, %: C 19.67; H 2.19; I 69.40.

The reaction is accompanied by iodine addition at the triple bond of 2-propynyl alcohol with formation of 2,3-diiodo-2-propen-1-ol as by-product. Its ^{1}H NMR spectrum coincides with that given in [14]. ^{1}H NMR spectrum (CD_3OD), δ, ppm: 7.19 t [CHI, [4]$J(H, H) = 0.9$], 4.21 d [CH_2, [4]$J(H, H) = 0.9$]. ^{13}C–{^{1}H} NMR spectrum (CD_3OD), $δ_C$, ppm: 80.1 s (CHI), 106.0 s (CI), 70.9 s (CH_2).

[Pt(CH=CI–CH₂OH)₂I₂](CH₃OH) (IX). A 0.2-g (0.412-mmol) portion of K_2PtCl_6 was added to 10 ml of a 5 M aqueous solution of KI, and the mixture

was left to stand for 1 h at room temperature. The precipitate of K_2PtI_6 was separated and dissolved in 10 ml of H_2O. To minimize possible reduction of iodide platinum(IV) complexes, 0.15 ml of a solution containing 1 mol/l of I_2 (0.15 mmol) and 5 mol/l of NaI was added. 2-Propynyl alcohol, 1.39 mmol, was added in portions at 5°C over a period of 2 h. After 6 h, the precipitate was separated and washed with two portions of water, two portions of a 1 M aqueous solution of KI, and water again until the washings contained no I^-. Extraction with methanol and drying under reduced pressure gave 95 mg of a dark brown substance [28% with respect to the initial Pt(IV)]. IK spectrum (KBr), ν, cm^{-1}: 3030, 2920, 2860, 1630, 1430, 1000, 940. ^{1}H NMR spectrum (CD_3OD), δ, ppm: 6.44 t with [195]Pt satellites, [CH, $J(H, H) = 2.0$, $J(Pt, H) = 31.1$], 4.50 d.t with [195]Pt satellites [CH_2, $J(H, H) = 2.0$, $J(Pt, H) = 2.5$]. ^{13}C–{^{1}H} NMR spectrum (CD_3COCD_3), δ, ppm: 100.9 s with [195]Pt satellites [CH, $J(C, Pt) = 801.4$], 82.3 s with [195]Pt satellites [CI, $J(C, Pt) = 24.4$], 72.6 s with [195]Pt satellites [CH_2, $J(C, Pt) = 30.2$]. [195]Pt NMR spectrum (CD_3COCD_3), $δ_{Pt}$, ppm: –2351.1 t [$J(Pt, H) = 31.1$]. Found, %: C 9.8; H 1.4; Pt 23.0. $C_7H_{12}O_3I_4Pt$. Calculated, %: C 9.92; H 1.42; Pt 23.02.

[Pt(CH=CI–CH₂OCH₃)₂(I)₂] (XI). A 0.2-g (0.36-mmol) portion of $Na_2PtCl_6 \cdot 6H_2O$ was dissolved in 10 ml of a 5 M aqueous solution of KI, and the mixture was stirred for 1 h. The precipitate of K_2PtI_6 was separated by centrifugation and dissolved in 10 ml of water, and 0.2 ml of a solution of I_2 (0.9 M) and NaI (4.5 M) was added. To the resulting mixture 80 μl of 3-methoxypropyne was added in 20-μl portions over a period of 48 h (every 10–12 h) at 5°C. The orange precipitate was separated by centrifugation, washed with water (3×10 ml) and cold acetone (2×1 ml), and dried under reduced pressure. Yield 85 mg [28% on the initial amount of Pt(IV)]. IR spectrum (KBr), ν, cm^{-1}: 3012 w, 2938 m, 2907 m, 2838 m, 1431 m, 1363 w, 1240 w, 1190 w, 1153 m, 1085 w, 1036 s, 980 w, 937 m, 814 w, 752 m, 709 w, 665 m, 635 w, 523 w, 431 w. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.29 t. with [195]Pt satellites [CH, [4]$J(H, H) = 2.0$, $J(Pt, H) = 41.0$], 4.49 d with [195]Pt satellites [CH_2, [4]$J(H, H) = 2.0$, $J(Pt, H) = 4.8$], 3.90 s with [195]Pt satellites [CH_3, $J(Pt, H) = 4.8$]. ^{13}C–{^{1}H} NMR spectrum (CD_3COCD_3), $δ_C$, ppm: δ 97.9 s with [195]Pt satellites [CH, $J(Pt, C) = 819.9$], 81.8 s with [195]Pt satellites [CH_2, $J(Pt, C) = 38.3$], 76.9 s with [195]Pt satellites [CI, $J(Pt, C) = 12.9$], 61.8 s (CH_3). [195]Pt NMR spectrum ($CDCl_3$), $δ_{Pt}$, ppm: –2225.1 t [$J(Pt, H) = 41.0$]. Mass spectrum: 843 [M^+], 714

$[M^+ - 2H - I]$. Found, %: C 11.5; H 1.5; Pt 23.3. $C_8H_{12}O_2I_4Pt$. Calculated, %: C 11.39; H 1.42; Pt 23.13.

Reductive elimination from the complex $[Pt(CH=CI-CH_2OH)_2I_2]$ (IX). The kinetics of reductive elimination were studied by spectrophotometry and NMR spectroscopy. In the latter case, the progress of the reaction was monitored following the disappearance of the signal at δ 4.50 ppm. The reaction was carried out directly in an NMR ampule: 15 mg (1.77×10^{-5} mol) of complex **IX** was dissolved in 0.6 ml of 1-butanol or acetic acid, and (if necessary) 70 mg (2.76×10^{-4} mol) of I_2 was added. The ampule was maintained in an external thermostat at a specified temperature, and the spectra were recorded at definite time intervals. The product, (*E*,*E*)-2,5-diiodo-2,4-hexadiene-1,6-diol, was identified using the available NMR data.

Spectrophotometric measurements were performed following the optical density at λ 375 nm using a Specord UV-Vis spectrophotometer. The results were treated by the equation

$$\ln(D_\tau - D_\infty) = -k\tau + const,$$

where D_τ is the optical density at a moment τ, and D_∞ is the optical density after 4–5 half-conversion periods. Complex **IX**, 10 mg, was dissolved in 0.6 ml of 1-butanol, and a 50-μl portion of the solution was added to a spectrophotometric cell containing 2.5 ml of a solution maintained at a required temperature.

Reductive elimination from the complex $[Pt(CH=CI-CH_2OCH_3)_2I_2]$ (XI). Complex **XI**, 2 mg, was dissolved in 0.5 ml of CD_3COOD placed in an NMR ampule, and the ampule was kept at 95°C for about 6 h in an external thermostat. The progress of the reaction was monitored by ^1H NMR spectroscopy. The structure of the product, (*E*,*E*)-2,5-diiodo-1,6-dimethoxy-2,4-hexadiene (**XII**), was derived from the ^1H and ^{13}C NMR data obtained with the use of two-dimensional LR-COSY, gsNOESY, gsHMQC, and gsHMBC techniques. No by-products were formed during the process. ^1H NMR spectrum (CD_3COOD), δ, ppm: 7.29 s (CH), 4.26 s (CH_2), 3.33 s (CH_3). ^{13}C–$\{^1H\}$ NMR spectrum (CD_3COOD), $δ_C$, ppm: 139.2 s (CH), 105.3 s (CI), 74.9 s (CH_2), 57.6 s (CH_3).

Determination of the equilibrium constant for coordination of iodide ion (Scheme 6). The equilibrium constant was determined by NMR spectroscopy by carrying out the reaction directly in an NMR ampule. The initial concentration of complex **IX** in

CD_3OD was 0.05 M. The concentration of NaI was varied from 0.5 to 3.1 M; measurements were performed for NaI concentrations of 0.50, 1.00, 1.55, 2.10, 2.61, and 3.10 M. The ratio **IX**:**XIII** was determined from the ^1H signal intensities in the vinyl proton region. All measurements were performed at 0°C. The equilibrium constant $K = 1.8 \pm 0.1$ l/mol was calculated from the equation $K = [\textbf{XIII}]/([\textbf{IX}]\,[I^-])$, taking into account that $[I^-]_0 \gg [\textbf{IX}]_0$.

NMR monitoring of activation of the triple bond in acetylene by palladium complexes. Palladium(II) chloride was added to a solution containing 3 mol/l of NaI, 0.4 mol/l of I_2, and 0.2 mol/l of C_2H_2 in CD_3OD to a concentration of 0.01 M. The mixture was maintained at 55°C, and ^1H NMR spectra were recorded every 20–30 min. Quantitative conversion of acetylene into *trans*-1,2-diiodoethylene required ~3 h.

The reactions with substituted acetylenes (propyne, 2-propynyl alcohol, phenylacetylene, and diphenylacetylene) were carried out with similar initial reactant concentrations. In all cases, blank experiments were performed (without addition of palladium chloride) under the same conditions to estimate the efficiency of the catalyst.

NMR spectra of *trans*-1,4-diiodoethylene, δ, ppm: ^1H (CD_3OD): 7.25 [^3J(H,H) = 14.2; measured for ^{13}C satellites]. ^{13}C (CD_3OD): 85.4 [^1J(C,H) = 197.8, ^{21}J(C,H) = 2.0].

NMR monitoring of triple bond activation in $HC\equiv C-COOMe$ (Scheme 7). A saturated solution of PtI_6^{2-} was prepared from 20 mg (0.036 mmol) of $Na_2PtCl_6 \cdot 6H_2O$ and 0.5 ml of a 2 M solution of NaI in CD_3OD. To simplify NMR measurements, the undissolved material was separated by centrifugation, and the solution was placed in an NMR ampule. A stoichiometric amount of methyl 2-propynoate was added, and the progress of the reaction was monitored over a period of 6–8 h at room temperature.

Isolation of the product of triple bond activation in methyl 2-propynoate. A 45-mg (0.080-mmol) portion of $Na_2PtCl_6 \cdot 6H_2O$ was dissolved in 2 ml of a 5 M aqueous solution of NaI, 30 μl of methyl 2-propynoate was added, and the mixture was kept for 12 h at room temperature. The dark brown precipitate was washed with water (3×10 ml) and extracted with 10 ml of methanol. Evaporation of the extract gave 60 mg of the final product [85% on the initial amount of platinum(IV)]. IR spectrum (KBr), ν, cm^{-1}: 3060 v.s, 2950 v.s, 1844 m, 1698 s, 1616 m, 1556 s, 1510 m, 1440 s, 1356 s, 1266 s, 1196 s, 1170 s, 1006 m, 988 m, 934 m, 756 m. NMR spectra of

complex **XV** in a 2 M solution of NaI in CD_3OD, δ, ppm: [1]H: 9.15 s with [195]Pt satellites [1-H, $J(Pt,H)$ = 31.3], 6.58 s with [195]Pt satellites [5-H, $J(Pt,H)$ = 52.4], 4.13 s (4-H), 3.72 s (8-H); [13]C–{[1]H}: 183.0 s with [195]Pt satellites [C^7, $J(Pt,C)$ = 45.7], 171 s with [195]Pt satellites [C^3, $J(Pt,C)$ = 23.1], 167.6 s with [195]Pt satellites [C^5, $J(Pt,C)$ = 674.4], 96 s with [195]Pt satellites [C^2, $J(Pt,C)$ = 923.5], 85.5 s with [195]Pt satellites [C^1, $J(Pt,C)$ = 27.4], 76.0 s (C^6), 56.8 s (C^8), 51.6 s (C^4); HMQC: $^1J(C^5,H)$ = 181.0, $^1J(C^8,H)$ = 150.7, $^1J(C^1,H)$ = 203.9, $^1J(C^4,H)$ = 145.1; [195]Pt: –3018.1 d.d [$J(Pt,1\text{-H})$ = 31.3, $J(Pt,5\text{-H})$ = 52.4).

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