# Platinum-catalyzed addition of iodomethane to acetylene\*

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The reaction of iodomethane and acetylene in the presence of  $Pt^{II}$  and NaI in acetone gives (*E*)-1-iodopropene. A possible mechanism involves the intermediate formation of a  $Pt^{IV}$  methyl vinyl derivative by the iodoplatination of acetylene with a reversibly formed a  $Pt^{IV}$  methyl complex and assumes the catalytic character of the process.

Key words: platinum(II) complexes, iodomethane, acetylene, C-C coupling, catalysis.

The C—C cross-coupling reactions catalyzed by transition metal complexes became an important tool of modern organic chemistry, which makes it possible to rather easily obtain complicated molecules from simpler compounds.<sup>1,2</sup> The key intermediates of the cross-coupling are bis(organyl) metal derivatives.<sup>3</sup> We have recently found<sup>4,5</sup> that a combination of the oxidative addition of iodomethane to the Pt<sup>II</sup> iodide complexes followed by alkyne iodoplatination is a simple way to relatively stable methyl vinyl derivatives of Pt<sup>IV</sup>. The purpose of this work is the search for the conditions of the catalytic reaction of  $C(sp^2)-C(sp^3)$  cross-coupling in the  $C_2H_2-MeI-Pt^{II}-$ NaI—acetone system.

### Experimental

Commercial NaI (reagent grade), iodomethane (Aldrich), and acetone- $d_6$  (Merck) were used for solution preparation without additional purification. Salt Na<sub>2</sub>PtCl<sub>4</sub> was synthesized using a known procedure.<sup>6</sup> The platinum iodide complexes were obtained *in situ* in acetone- $d_6$  by the substitution of chloride ligands in the presence of NaI excess.

Salt Na<sub>2</sub>PtCl<sub>4</sub> was dissolved in 0.6 mL of a 1.5 *M* solution of NaI in acetone-d<sub>6</sub>, MeI was added, and the reaction mixture was kept at room temperature for 24 h. A precipitate of sodium chloride was separated by centrifuging, the supernatant was transferred to an NMR tube, and an aliquot of a solution of acetylene and NaI (1.5 *M*) in acetone-d<sub>6</sub> was added. The reaction was carried out at room temperature. The reaction course was monitored by <sup>1</sup>H NMR spectroscopy by the change in the intensity of signals from acetylene and products of its transformation. The concentrations of acetylene, iodomethane, and formed products were determined relative to the internal standard (benzene) by

the integration of the corresponding signals. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Bruker Avance 500, Bruker Avance II 600, and Bruker Avance II 400 spectrometers.

#### **Results and Discussion**

Under the conditions of an excess of  $Pt^{II}$  over acetylene (initial ratio  $[Pt^{II}]_0$ :  $[C_2H_2]_0$ :  $[MeI] \approx 1:0.1:15$ ) in acetone-d<sub>6</sub> in the presence of a high excess of NaI, acetylene predominantly undergoes cross-coupling with iodomethane to give (*E*)-1-iodopropene (1) in ~70% yield (based on reacted acetylene) and some amount of (*E*,*E*)-1,4-diiodobuta-1,3-diene (2) in ~29% yield (Scheme 1, Table 1).

## Scheme 1

Both Pt<sup>II</sup> and iodomethane are necessary for these transformations to occur: the reactions do not take place if at least one of these compounds is absent. In addition to products **1** and **2**, the intermediate formation of the Pt<sup>IV</sup> methyl vinyl derivative (complex **3**) (Scheme 2, Fig. 1) and trace amounts of methane were detected. As the initial concentration of acetylene increases, under other equivalent conditions, the yield of compound **2** increases and that of compound **1** decreases (Table 2, entries 4-6). The ratio of the yields of compounds **1** and **2** increases linearly with an increase in the initial acetylene concentration (Fig. 2).

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Compound	npound <sup>1</sup> H NMR, δ ( <i>J</i> /Hz)	
Complex 3	8.18 (d, 1 H, H(1), $J_{H-H} = 13.0$ with <sup>195</sup> Pt satellites, ${}^{2}J_{Pt-H} = 51.5$ ), 5.61 (d, 1 H, H(2), $J_{H-H} = 13.0$ with <sup>195</sup> Pt satellites, ${}^{2}J_{Pt-H} = 39.1$ ), 3.16 (s, 3 H, Me, with <sup>195</sup> Pt satellites, ${}^{2}J_{Pt-H} = 76.6$ )	_
<i>E</i> -1-iodopropene (1)	6.53 (m, 1 H, H(2)); 6.22 (d, 1 H, H(1), $J_{H-H} = 13.0$ ); 1.73 (dq, 3 H, Me, $J_{H-H} = 6.8$ , $J_{H-H} = 1.6$ )	141.1 (C(2)), 75.3 (C(1)), 18.4 (Me)
(E,E)-1,4-diiodobuta- 1,3-diene ( <b>2</b> )	7.23 (m, 2 H, H(2), H(2 <sup>'</sup> )); 6.96 (m, 2 H, H(1), H(1 <sup>'</sup> ))	145.9 (C(2), C(2´)), 82.3 (C(1), C(1´))
(E)-but-2-ene	5.41 (m, 2 H, CH); 1.59 (m, 6 H, Me)	125.2 (CH), 17.3 (Me)
( <i>E</i> , <i>E</i> )-1,4-diiodopenta- 1,3-diene	7.05 (dd, 1 H, H(2), $J_{H-H} = 14.3$ , $J_{H-H} = 10.3$ ); 6.43 (d, 1 H, H(1), $J_{H-H} = 14.3$ ); 6.15 (m, 1 H, H(3)); 5.84 (m, 1 H, H(4)); 1.69 (m, 3 H, Me)	145.1 (C(2)), 131.5 (C(3)), 130.4 (C(4)), 76.6 (C(1)), 21.1 (Me)
(E,E)-hexa-2,4-diene	6.01 (m, 2 H, H(2), H(2')); 5.55 (m, 2 H, H(1), H(1')); 1.68 (m, 6 H, Me) 13.3 (Me)	125.7 (C(1), C(1')), 131.6 (C(2), C(2')),

Table 1. NMR spectra data for the products and intermediate of the reaction of acetylene and iodomethane in the  $C_2H_2$ -MeI-Pt<sup>II</sup>-NaI-acetone-d<sub>6</sub> system



HC≡CH, I⁻

At the initial concentrations  $[Pt^{II}]_0 = 0.01 \text{ mol } L^{-1}$ ,  $[C_2H_2]_0 = 0.32 \text{ mol } L^{-1}$ , and  $[MeI]_0 = 1.3 \text{ mol } L^{-1}$ , the concentration of (*E*)-1-iodopropene (1) formed within 20 days reaches 0.034 mol  $L^{-1}$ , indicating the catalytic character of the reaction and corresponding to the value of TON 3.4. Note that at prolonged reaction times the following by-products are formed: (*E*)-but-2-ene, (*E*,*E*)-1-iodopenta-1,3-diene, and (*E*,*E*)-hexa-2,4-diene (see Table 1).

Identification of the reaction products. Complex 3. A rather high value of spin-spin coupling constant  $J_{H-H}$  (see Table 1) indicates the *trans*-arrangement of the H(1) and H(2) protons. The position of the signal from the H(1) proton and the value of spin-spin coupling constant  $J_{Pt-H}$  are characteristic of protons at the **3** 



Fig. 1. Typical kinetics of acetylene consumption (1) and accumulation of (E)-1-iodopropene 1 (2), (E,E)-1,4-diiodobuta-1,3-diene 2 (3), and complex 3 (4); initial concentration  $[Pt^{II}]_0 = 0.05 \text{ mol } L^{-1}.$ 



Fig. 2. Ratio of products 1 and 2 extrapolated to the beginning of the reaction vs initial acetylene concentration  $[C_2H_2]_0$ .

sp<sup>2</sup>-hybridized C atom  $\sigma$ -bonded to the platinum atom. The chemical shift of the signal from the protons of the methyl group and the value of spin-spin coupling constant  $J_{\rm Pt-H}$  correspond<sup>7</sup> to the methyl ligand of Pt<sup>IV</sup>. The ratio of integral intensities of signals from the H(1) and H(2)protons and the protons of the Me group is 1:1:3, which corresponds to a complex including the vinyl and methyl group.

(E)-1-Iodopropene (1). The spin-spin coupling between the H(1), H(2) protons and the protons of the methyl group appears as cross-peaks in the 2D COSY NMR spectrum, which indicates that these protons belong to one molecule. Upon an additional irradiation at the frequency of the signal from the Me group protons, two multiplets corresponding to the H(1) and H(2) protons are simplified to doublets with the spin-spin coupling constant equal to 14.3 Hz. This value is characteristic of the trans-arrangement of the H(1) and H(2) protons. By irradiating at the frequency of the signal of the H(1) proton,

Table 2. Yields of products 1 and 2  $(\eta_1, \eta_2)$  vs initial concentrations of acetylene, iodomethane, and Pt<sup>II\*</sup>

Entry	$[Pt^{II}]_0$	[MeI] <sub>0</sub>	$[C_2H_2]_0$	$\eta_1$	$\eta_2$
		mol L-			
1	0.000	1.30	0.1300	0	0
2	0.050	0.00	0.1000	0	0
3	0.015	0.68	0.1300	$0.18 {\pm} 0.03$	$0.75 {\pm} 0.08$
4	0.050	1.00	0.0056	$0.70 {\pm} 0.06$	$0.29 {\pm} 0.03$
5	0.050	1.00	0.0270	$0.51 {\pm} 0.05$	$0.56 {\pm} 0.06$
6	0.050	1.00	0.1000	$0.26 {\pm} 0.02$	$0.73 {\pm} 0.06$
7	0.100	0.90	0.0016	$0.81 {\pm} 0.06$	$0.19 {\pm} 0.04$
8	0.110	1.30	0.0020	$0.75{\pm}0.06$	$0.18{\pm}0.03$

\* The yields of products 1 and 2 are extrapolated to the beginning of the reaction when acetylene consumption was relatively low.

the multiplicity of the signal corresponding to the H(2)protons decreased: the doublet of quadruplets becomes a quadruplet.

(E,E)-1,4-Diiodobuta-1,3-diene (2) and (E)-but-2ene. The signals in the spectra of these compounds were assigned according to the published data,<sup>8,9</sup> respectively.



(E,E)-1-Iodopenta-1,3-diene. In the 2D COSY NMR spectrum, the H(1) proton couples with the H(2) proton, which results in the splitting of their signals in the <sup>1</sup>H NMR spectrum into

a doublet with a high spin-spin coupling constant value of 14.3 Hz characteristic of the mutual trans-arrangement of these protons. The H(2) proton cou-



ples with the H(1) and H(3) protons, due to which its signal in the <sup>1</sup>H NMR spectrum is split into a doublet of doublets. A more complicated pattern is observed for the H(3), H(4) protons and protons of the Me group. In the 2D COSY spectrum, the H(3) proton couples with the H(4) proton, and the latter couples with the methyl group protons; however, their signals in the <sup>1</sup>H NMR spectrum are complicated multiplets because of close spin-spin coupling constant values.

(E,E)-Hexa-2,4-diene. The coupling between the H(1) and H(2) protons and between them and protons of the

methyl groups follows from the 2D COSY NMR spectrum. Upon the irradiation at the frequency of the signal corresponding to the protons of the Me group, the multiplicity of this



spectrum becomes similar to that of the spectrum of compound 2. Upon the irradiation at the frequency of the signal of the H(1) and H(1') protons, signals of the H(2), H(2') protons and the protons of the methyl group are reduced to singlets. Irradiating at a frequency of the signal from the H(2) and H(2') protons, the signal from the H(1) and H(1<sup>'</sup>) protons is transformed into a quadruplet with the spin-spin coupling constant equal to 6 Hz and the signal from the protons of the methyl group is simplified to a doublet with the same spin-spin coupling constant value. The  ${}^{13}C{}^{1}H{}$  NMR spectrum is consistent with the published data.<sup>10</sup>

**Reaction mechanism.** The effects observed can be explained by the staged mechanism presented in Scheme 2.

The equilibrium oxidative addition of MeI to Pt<sup>II</sup> (under the studied conditions, equilibrium (1) is rapid<sup>4</sup>) gives the  $Pt^{IV}$  methyl derivative (stage (1)). The iodoplatination of the triple C=C bond by the latter (stage (2)) leads to the intermediate formation of the PtIV methyl vinyl derivative (complex 3), whose decomposition via reductive elimination gives  $C(sp^2) - C(sp^3)$  cross-coupling product 1 and regenerates the catalyst (stage (3)). At stage (4), the second molecule of acetylene is iodoplatinated by complex 3 with the intermediate formation of the methyl divinyl derivative. Under the same conditions, a similar iodoplatination of alkyne with the PtIV methyl vinyl complex with the formation of the methyl divinyl derivative was observed<sup>5</sup> for methyl propiolate. The subsequent fast reductive elimination of two vinyl ligands of complex 4 (stage (5)) affords product 2 and the Pt<sup>II</sup> methyl derivative. Under the action of water traces, the Pt<sup>II</sup> methyl complex partially undergoes protolysis with methane evolution and also can be oxidized with oxygen<sup>11</sup> to MePt<sup>IV</sup>.

Scheme 2 explains why iodomethane is necessary for the transformation of acetylene into diene 2 in the Pt<sup>II</sup>—NaI—acetone system. It is known<sup>12</sup> that in acetylene iodoplatination, the Pt<sup>II</sup> complexes are substantially less reactive compared to Pt<sup>IV</sup>. The oxidative addition of iodomethane to Pt<sup>II</sup> gives the Pt<sup>IV</sup> methyl derivative, thus generating the active form of the catalyst: it has earlier been shown<sup>8</sup> that Pt<sup>IV</sup> iodides catalyze the transformation of acetylene into compound 2, and this reaction includes two consecutive stages of iodoplatination of the triple bond of acetylene with the intermediate formation of the mono- and divinyl derivatives of Pt<sup>IV</sup>.

According to Scheme 2, under the quasi-stationary conditions with respect to intermediate complex 3, the ratio of the yields of compounds 2 and 1 extrapolated to the beginning of the reaction is described by Eq. (1)

$$\eta_2 / \eta_1 = (k_4 / k_3) [C_2 H_4], \tag{1}$$

which agrees with the experimental data (see Fig. 2) at  $k_4/k_3 = (29\pm2)$  L mol<sup>-1</sup>. The fulfillment of dependence (1) means that the reductive elimination during the decomposition of complex **4** results in the formation of diene **2** rather than iodopropene **1**; *i.e.*, complex **4** decomposes predominantly by C—C cross-coupling of two vinyl ligands rather than one of the vinyl ligands with the methyl one. It can be concluded that the C(sp<sup>2</sup>)—C(sp<sup>2</sup>) reductive elimination is considerably easier than C(sp<sup>2</sup>)—C(sp<sup>3</sup>) cross-coupling, which is consistent with the published data.<sup>13,14</sup>

The above obtained value of  $k_4/k_3$  makes it possible to estimate the upper limit of the rate constants  $k_5/k_3$ . Even under the most favorable conditions, namely, the maximum concentration of acetylene equal to 0.13 mol L<sup>-1</sup>, no formation of noticeable amounts of the Pt<sup>IV</sup> methyl divinyl derivative (complex **4**) was detected. Therefore, under these conditions, the stationary concentration of complex **4** is substantially lower than the stationary concentration of complex **3**. Therefore, 0.13  $\cdot k_4 \ll k_5$  and, correspondingly,  $k_5/k_3 \gg 4$ ; *i.e.*, complex **4** is significantly less stable than complex **1**.

Unlike complexes 3 and 4, their earlier obtained analogs, *viz.*, methyl vinyl derivatives 5, 6, <sup>5</sup> and 7<sup>4</sup> (Scheme 3), do not give cross-coupling products: the indicated reactions do not occur with a noticeable rate. The first three of them do not take place, evidently, because of the bidentate character of one of the vinyl ligands. It has previously been shown<sup>15</sup> that the preliminary chelate opening is necessary for C—C cross-coupling to occur. Steric factors prevent the occurrence of other reactions.





The kinetics and mechanism of the reactions in the  $C_2H_2$ -MeI-Pt<sup>II</sup>-NaI-acetone system and the routes of formation of other products will be studied elsewhere.

Thus, the new catalytic reaction of iodomethane addition to the triple bond of acetylene with the formation of (E)-1-iodopropene in acetone solutions in the presence of Pt<sup>II</sup> and NaI was found. The probable mechanism includes three stages, namely, the equilibrium oxidative addition of iodomethane to Pt<sup>II</sup>, the iodoplatination of acetylene with the Pt<sup>IV</sup> methyl complex and the intermediate Pt<sup>IV</sup> methyl vinyl derivative, and subsequent decomposition of the latter *via* reductive elimination to give the C(sp<sup>2</sup>)–C(sp<sup>3</sup>) cross-coupling product. The data obtained suggest that the C(sp<sup>2</sup>)–C(sp<sup>2</sup>) reductive elimination is substantially easier than the C(sp<sup>2</sup>)–C(sp<sup>3</sup>) crosscoupling.

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