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Note

The mechanism of C–C bond formation on the Pt(IV) center involving chelate metallocycle ligands

Valentine P. Ananikov [a,*], Sergey A. Mitchenko [b], Irina P. Beletskaya [c]

[a] *N.D. Zelinsky Institute of Organic Chemistry, Leninsky Prospect 47, Moscow 117913, Russia*
[b] *A.N. Nesmeyanov Institute of Organoelemental Compounds, Moscow 117813, Russia*
[c] *M.V. Lomonosov Moscow State University, Moscow 119899, Russia*

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Abstract

An unusual fact of C–C reductive elimination reaction in bis-chelated Pt(IV) complexes under mild conditions was studied. It has been shown that breaking at least one of the chelate rings is required to promote a carbon–carbon bond formation reaction. An intermediate complex, which resulted from a chelate ligand breaking process, was detected directly in the reaction mixture using 2D $^{1}H-^{195}Pt$ heteronuclear NMR spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recently we have reported a new Pt(IV) catalyzed alkyne conversion reaction [1,2] providing a convenient route to diiodosubstituted dienes (Scheme 1). Outstanding features of the reaction is high stereo- and regioselectivity in formation of the diene system: nucleophile (I^-) attack occurs only as a *trans*-addition reaction to the most substituted carbon atom [1,2]. It has been shown, that catalytic reactions proceed through the intermediate formation of Pt(IV) bis-σ-vinyl derivatives. Corresponding bis-σ-vinyl derivatives synthesized from substituted alkynes HC≡CR ($R = CH_2OH$, CH_2OCH_3) were isolated and studied in detail by X-ray [2] and NMR [3] methods. Intramolecular vinyl and vinyl C–C coupling reaction from these complexes lead to the final products (Scheme 2).

$$HC{\equiv}CR \xrightarrow[H_2O/CH_3OH]{Pt(IV)/\,I^-/I_3^-} E,E\text{-}\ IRC{=}CH{-}CH{=}CRI$$

Scheme 1.

In the previous investigations [1,2], we have assumed the same C–C reductive elimination mechanism for decomposition of all intermediate divinyl complexes **1**–**3** (Scheme 2). Reductive elimination is a well known way of C–C bond formation between monodentant σ-bonded ligands from both experimental [4,5] and theoretical [6,7] points of view. However, in contrast to the former, carbon–carbon bond formation on the metal center with chelate ligands is a significantly less studied phenomenon. In addition, we have found, that reductive elimination from complexes **2** and **3** requires significant heating (80 and 95°C, respectively), while the catalytic synthesis of **5** is carried out at 15°C [1,2]. The questions arose whether the same C–C bond formation mechanism may be proposed for both non-cyclic (**1**) and chelate (**2**, **3**) intermediate complexes and, since the complexes **2** and **3** are relatively thermally stable compounds, whether they can be really considered as intermediates of the catalytic process.

In the present article we report a mechanistic study of C–C bond formation reaction on the Pt(IV) center involving chelate-vinyl ligands. The work deals with a very important question of the carbon–carbon bond formation between chelate ligands (C–ligand with supported group) in organotransition metal complexes.

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* Corresponding author. Fax: +7-95-1355328.
E-mail address: val@cacr.ioc.ac.ru (V.P. Ananikov).

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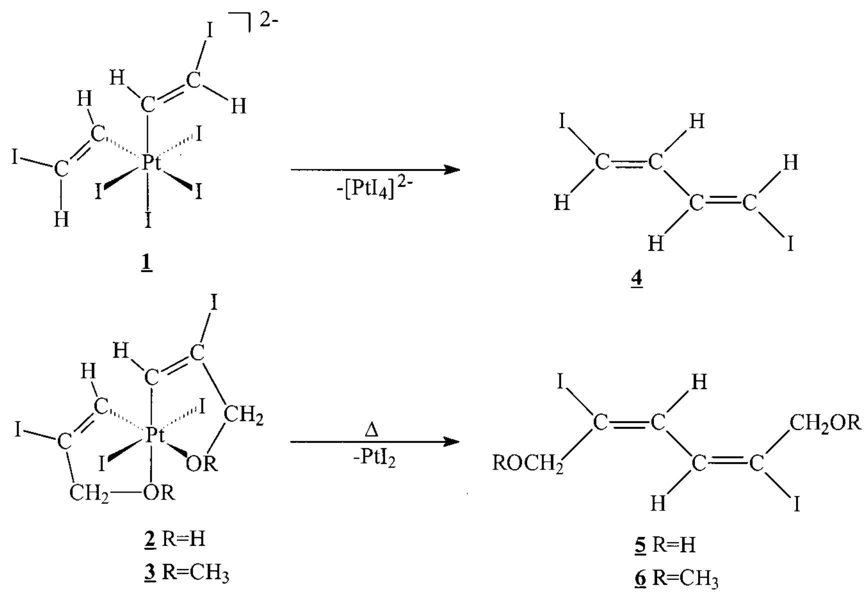

Scheme 2.

2. Results and discussion

First of all, unambiguous confirmation of the metallocycle structure must be obtained. X-ray analysis [2] provides strong evidence, however solvent molecules could, in principal, substitute oxygen atoms of the chelate ligands in the coordination sphere of the metal. Our study indicates that the substitution process does not take place and that both complexes **2** and **3** keep metallocycle structure in solution.

For complex **3** an analysis of indirect spin–spin coupling network in 2D $^{1}H-^{195}Pt$ HMQC spectrum shows very close values of platinum–proton interactions in methyl and methylene groups signals (Fig. 1). These can only result from the metallocycle structure (**3**) and $^{3}J(^{1}H-^{195}Pt)$ coupling pathways rather than open structure (**3A**) with equal ^{4}J and ^{6}J couplings. In addition, the presence of $^{1}H-^{195}Pt$ spin–spin interaction with methyl group protons, as confirmed clearly with 2D heteronuclear correlation experiment (Fig. 1), suggests metallocycle as the only possible structure. In other cases, one has to assume a spin–spin interaction through the six bonds, which is very unlikely and has never been observed, while $^{3}J = 4.8$ Hz is the expected value (see reviews [8,9]).

Complex **2** has a hydroxyl group coordinated to the metal and a chelate structure may not be derived directly from NMR data. Of course, rather similar NMR parameters [1,2] for both complexes and similar chemical behavior makes an assumption of metallocycle structure reasonable for this complex as well. An additional confirmation was obtained after iodide to chloride ligand substitution in the coordination sphere of the metal. The reaction was carried out using AgCl as a mild I^{-} acceptor [10], and under the reaction conditions leads to the substitution of only one iodide ligand (Scheme 3). It should be noted, that Na_2PtCl_6 may be used as a chloride ligand donor instead of AgCl to perform the synthesis of compound **7** in homogeneous conditions. In this case the process can be monitored using ^{1}H-NMR spectroscopy[1], disappearance of the signals corresponding to compound **2** was accompanied with complex **7** formation. No other signals, excepting those of **7**, were detected in the final solution. As expected, adding NaI causes the reverse **7** → **2** conversion.

In contrast to **2**, complex **7** has no symmetry point group and methylene protons became unequivalent (H_a lies in upper direction from the chelate plane at the shorter distance to the chloride ligand, while H_b in the bottom is closer to the iodide ligand). As a result, methylene group signals in the ^{1}H spectrum of **7** give typical ABX splitting (X-vinyl proton) with $J(H_A-H_b) = 14.2$ Hz. In the case of the open structure, A_2X splitting should be expected due to internal rotation. It should be noted that in **7** the Pt center is chiral and could, in principle, be an alternative reason for the methylene protons inequivalence in the open form of the ligand. However, in this case, the chiral center is located far enough and no chirality induced NMR changes in the ^{13}C spectra were observed, therefore we think that chirality can not be the only real reason for the AB structure appearance in the ^{1}H-NMR spectrum.

A variable temperature study of reductive elimination process from complex **2** (Scheme 2) showed rela-

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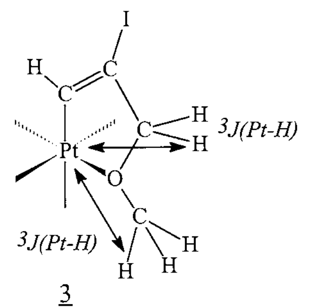
[1] Time evolution ^{1}H-NMR spectra for complex **7** formation in homogeneous conditions are available from authors upon request.



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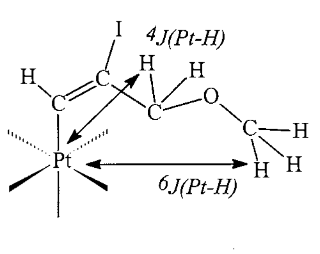

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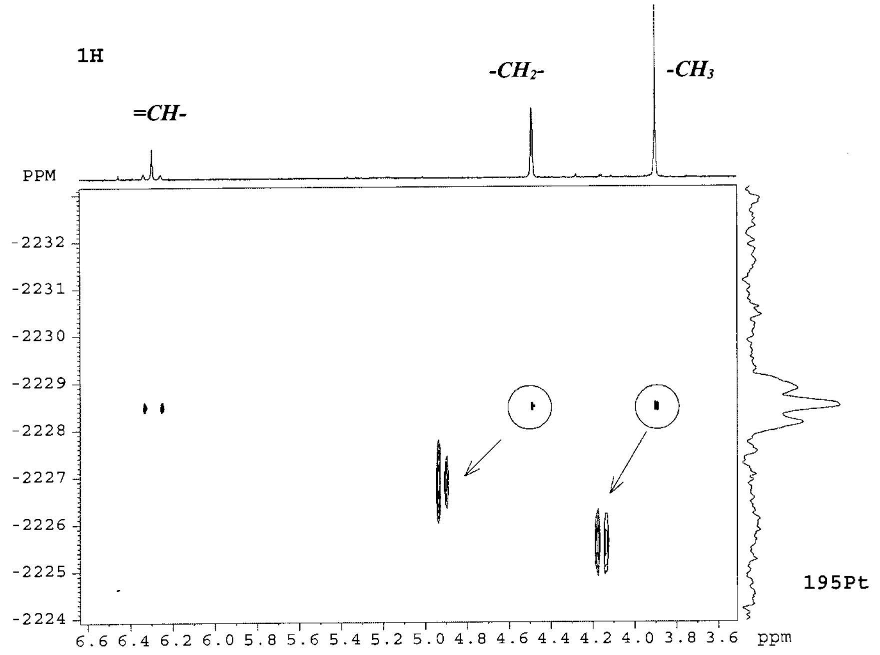
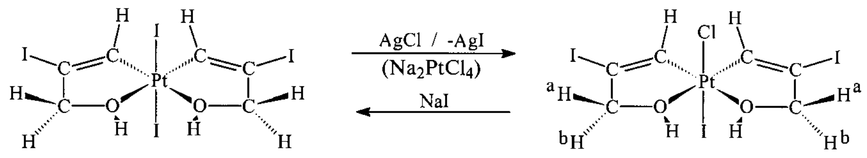


Fig. 1. 2D $^{1}H-^{195}Pt$ HMQC spectrum of complex **3** in $CDCl_3$; $^{1}H-^{195}Pt$ coupling constants are 410.0 Hz for $-CH=$ and about 4.8 Hz for $-CH_2-$ and $-CH_3$ protons.



Scheme 3.

tively slow reaction in agreement with an earlier observation [1]. Activation energy of 127 ± 5 kJ mol^{-1} and pre-exponential factor of $A = 5.8 \times 10^{14}$ s^{-1} were calculated from Arrhenius relationship[2] in the temperature range 72–116°C. Rather high activation energy indicates that the process is unlikely to take place at room temperature. Surprisingly, the catalytic synthesis of diiodosubstituted diene **5** may be performed at 15°C [2]. The difference in reaction conditions is in the presence of 2.5 M $[I^-]$ in solution in the last case. Thus, one may conclude that iodide may somehow interact with the metal complex and increase the reaction rate.

An extensive investigation of C–C coupling reaction in the presence of iodide has shown, that such interaction does take place in the studied system. Upon coordination, I^- substitutes an oxygen atom of δ-vinyl ligand leading to the mixed complex **8** with chelate and open ligands (Scheme 4). Low temperature (0°C) 2D-NMR spectroscopy allowed us to detect both com-

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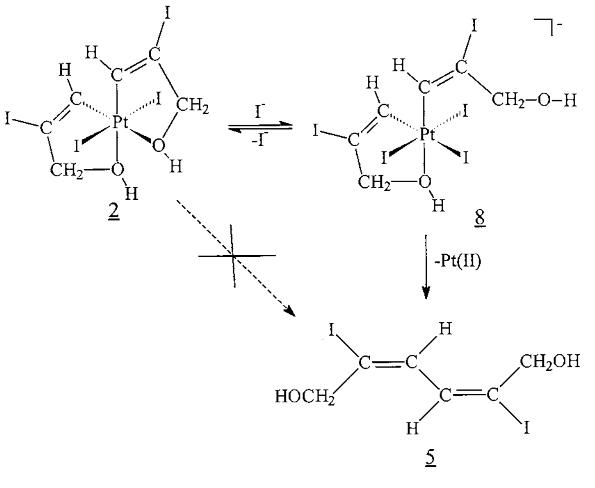
[2] Arrhenius plot and the rate constants for complex **2** decomposition are available from the authors upon request.



Scheme 4.

plexes **2** and **8** directly in the reaction mixture (Fig. 2). The cross-peak between the vinyl proton at 6.4 ppm and the platinum signal at $\delta = -2380$ ppm corresponds to complex **2**; only one signal for vinyl protons is detected due to internal symmetry. I^- coordination breaks the symmetry, two vinyl resonances appear at 7.9 and 6.7 ppm, both correlated to the ^{195}Pt signal at $\delta = -2960$ ppm. More than a 500-ppm high field shift of platinum signal is in very good agreement with an earlier finding concerning iodide ligand coordination to platinum [8,9]. With varying the concentration of iodide in solution, the equilibrium constant $K = 1.8 \pm 0.1$ M^{-1} has been determined at 0°C according to equation $K = [\mathbf{8}]/([\mathbf{2}][I^-]_0)$.

Coordination of I^- breaks one of the chelate cycles and the appearance of the flexible non-cyclic ligand facilitates reductive elimination. The final experiment in 2 M $[I^-]$ solution in methanol showed the complete decomposition of complex **2** at 55°C for 2 h, while extrapolation, according to activation parameters measured in the absence of added iodide ions, gives decomposition half life time about $t_{1/2} = 60$ h at the same temperature. Thus, it is absolutely clear that I^- coordination has a tremendous effect on the reaction rate and it is the destruction of one of the chelate rings that made the C–C coupling reaction possible under mild conditions.

One could expect that a complex with both vinyl groups in the open form would be more reactive in the C–C coupling reaction. However, we were not able to detect a product of two iodide ions coordination to the metal in the wide range of $[I^-]$ and temperature conditions. Even at the highest possible concentration of the iodide ion in methanol, the approximate ratio **2**:**8** = 1:5 were observed and full conversion of **2** into **8** was not achieved.

3. Conclusions

To the best of our knowledge, we report here the first example where the equilibrium between initial bis-

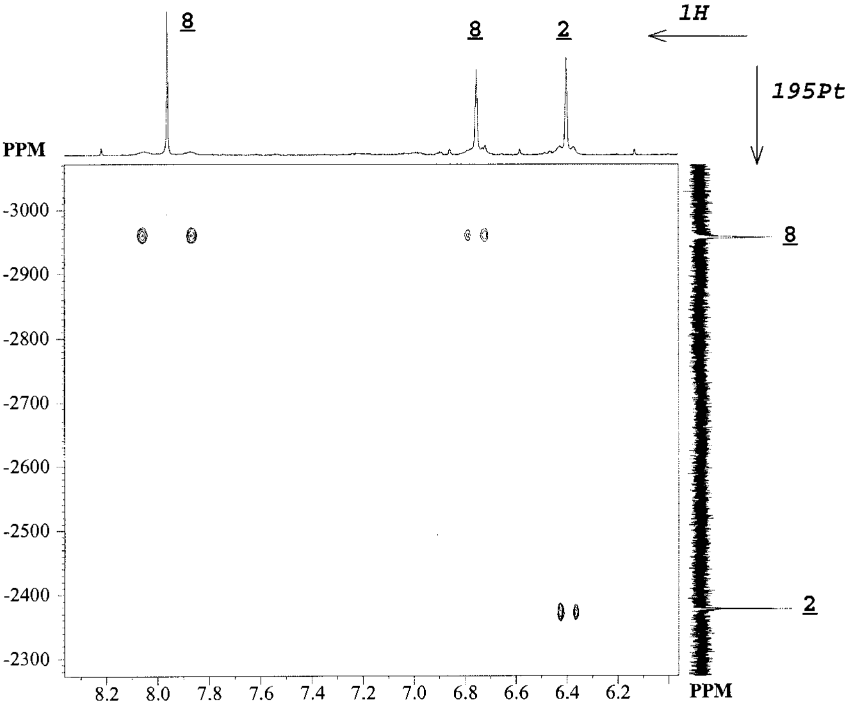


Fig. 2. 2D ^{1}H–^{195}Pt HMQC spectrum of the **2** and **8** mixture in 1 M NaI–CD_3OD solution at 0°C; ^{1}H–^{195}Pt coupling constants are 95.0 and 33.0 Hz for **8** and 31.0 Hz for **2**.

chelate and mono-chelate derivative for Pt(IV) complexes were detected directly in the reaction mixture and it has been shown clearly, that breaking at least one of the chelating rings is the necessary condition to involve bis-chelate metallocycle complexes in the C–C reductive elimination reaction.

We have found that the coordination of external ligands to the metal center accompanied with one of the chelate rings breaking, increases the rate of reductive C–C coupling reaction from bis-chelate Pt(IV) complexes greatly. This is in total agreement with an earlier finding [1,2], and explains the catalytic synthesis of diiodosubstituted dienes unusually easy. The results also suggest the same carbon–carbon bond formation mechanism for both non-cyclic and cyclic organoplatinum complexes.

In this case, the most probable origin of facilitating reductive elimination reaction is due to the removal of sterical difficulties. According to the X-ray structure [1], C–C distance in the bis-chelate divinyl complex is about 2.9 Å, which is obviously too large to reach carbon–carbon bond formation transition state without breaking at least one of the chelate cycles. However, the electronic factor can not be neglected also, since the charge of the complex changes from 0 to -1 upon iodide ligand coordination. Thus, the system studied here represents a good model for studying different aspects of the C–C bond formation reaction from cyclic organometallic complexes. The further detailed study on the topic is the subject of ongoing work in our group.

4. Experimental

4.1. Material and methods

Complexes **2** and **3** were synthesized according to procedures described earlier [1,2]. All NMR measurements were performed on Bruker DRX500 spectrometer operating at 500, 125 and 107 MHz for ^{1}H, ^{13}C and ^{195}Pt nuclei, respectively. The spectra were processed on a Silicon Graphics workstation using XWINNMR 2.0 software package. UV spectra were obtained on Specord UV–vis instrument.

^{1}H and ^{13}C chemical shifts are reported relative to corresponding solvent signals used as an internal reference; ^{195}Pt chemical shift is relative to external Na_2PtCl_6–D_2O.

2D heteronuclear ^{1}H–^{195}Pt correlations were recorded using pulse field gradient version [11,12] of the HMQC experiment [13].

4.2. ^{1}H–^{195}Pt 2D HMQC experiment

4.2.1. The mixture of complexes **2** and **8** (Fig. 2)

The spectrum was collected with ^{1}H and ^{195}Pt 90° pulses of 15.0 and 8.5 μs, respectively, a relaxation delay of 2 s, $\Delta = (2^2J_{H-Pt})^{-1} = 10$ ms (optimized for average coupling constant of 50 Hz), a 0.210 s acquisition time and 1200 and 100 000 Hz spectral windows for the ^{1}H(F2) and ^{195}Pt(F1) dimensions, respectively. Eight transients were averaged for each of 256 increments on t_1. The data was zero filled to a 2048 × 2048 matrix and processed with QSIN(SSB = 2) and SINE(SSB = 2) window functions for F2 and F1 dimensions, respectively. In the case of pulse field gradient experiments, a 1 ms sine shaped gradient pulses with the ratio 50:30:40 (%) followed with 100 μs recovery delay were applied.

4.2.2. Complex **3** (Fig. 1)

The same parameters as above, excepting smaller spectral window of 1500 Hz on ^{195}Pt(F1) dimension, smaller number of t_1 increments (64) and $\Delta = 12$ ms.

4.3. Synthesis of [Pt(CH=CI–CH$_2$OH)$_2$ICl]

$AgNO_3$ (160 mg) was added to NaCl solution in water, the formed AgCl precipitate was washed thoroughly by water to remove excess NaCl. $[Pt(CH{=}CI{-}CH_2OH)_2I_2]$ (80 mg) was dissolved in 10 ml of methanol and added to the AgCl prepared freshly. The resulting solution was stirred for 3 h in a dark place, during which time solution color changed from dark to light brown. The mixture filtered and the filtrate were evaporated to dryness. Yield 50 mg (70%) of light brown powder.

^{1}H (CD_3OD): $\delta = 6.64$ (t with ^{195}Pt satellites, ^4J(H–H) = 1.9, J(Pt–H) = 23.5, –CH=), 4.56 (center of dd-AB splitting, ^4J(H–H) = 1.9, ^2J(H^a–H^b) = 14.2, –CH$_2$–).

^{13}C{^{1}H} (CD_3OD): $\delta = 105.6$ (s with ^{195}Pt satellites, J(Pt–C) = 808.3, –CH=), 83.4 s with ^{195}Pt satellites, J(Pt–C) = 20.9, –CH$_2$–), 72.8 (s with ^{195}Pt satellites, J(Pt–C) = 28.0, =CI–).

^{195}Pt (CD_3COCD_3): $\delta = -1813.2$ (t, J(Pt–H) = 23.5).

Anal. Calc. for $C_6H_8O_2I_3ClPt$: C, 9.95; H, 1.11; Pt, 26.95, (I + Cl), 57.57. Found: C, 10.1; H, 1.2; Pt, 23.6; (I + Cl), 57.4%.

4.4. NMR monitoring of iodide to chloride ligand substitution reaction

Saturated Na_2PtCl_4 solution (0.5 ml) in CD_3COCD_3 was prepared and an excess of the platinum salt was filtered out. $[Pt(CH{=}CI{-}CH_2OH)_2I_2]$ (10 mg) was added to the solution and the mixture was placed in NMR tube. The iodide to chloride ligand substitution reaction (see Scheme 3) was monitored according to ^{1}H spectra. Data points were collected after each 10–15 min, full conversion time ca. 4 h.

*4.5. Kinetics of reductive elimination reaction from complex **2***

Complex **2** (10 mg) were dissolved in 0.6 ml of butanol. A total of 50 l of solution were added to 2.5 ml of the preliminary thermostated butanol in 1 cm quartz cuvet in the thermostated cuvet holder of the spectrometer. The measurements were performed by following absorption peak at 375 nm and the data was treated according to the first-order rate law. Kinetic studies were also carried out by NMR using approximately 0.03 M solution of **2** in butanol-d_{10}. NMR tubes were placed in a water bath and the spectra recorded periodically after cooling the solution to ambient temperature. Progress of the reaction was followed by monitoring the disappearance of methylene signals at 4.5 ppm. The reaction rates determined with NMR agreed with those obtained from UV spectroscopy.

*4.6. Equilibrium constant of I^- coordination to **2***

The equilibrium constant has been measured in NMR tube using complex **2** solution in CD_3OD with initial concentration of 0. M. NaI concentration was varied in the range 0.50–3.10 M. Six data points were measured at 0.50, 1.00, 1.55, 2.10, 2.61 and 3.10 M. The ratio **8**:**2** was determined from the integration of corresponding vinyl protons signals in the ^{1}H-NMR spectra. All measurements were performed at 0°C. Equilibrium constant $K = 1.8 \pm 0.1\ M^{-1}$ has been calculated from linear regression plot according to equation $K = [\mathbf{8}]/([\mathbf{2}][I^-]_0)$ (taking into account that $[I^-]_0 \gg [\mathbf{2}]_0$).

Acknowledgements

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