A novel stereoselective and catalytic C–C coupling reaction: acetylene dimerization accompanied by addition of iodine to yield (*E*,*E*)-1,4-diiodobuta-1,3-diene in the $Pt^{IV}–I^{–}–I_2–MeOH$ system

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A new catalytic reaction – dimerization of acetylene accompanied by addition of iodine to yield (*E*,*E*)-1,4-diiodobuta-1,3-diene at 30 °C in a methanolic solution of NaI, Pt^{IV} and I_2 – has been found; a plausible reaction mechanism involves intermediate formation of a *cis*-divinyl derivative of platinum(IV) through two subsequent triple bond iodoplatination steps followed by reductive elimination of the final product.

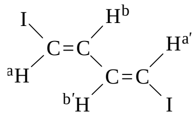
Metal complex catalysis of acetylene hydrocarbon conversions usually involves[1–2] an intermediate π-complex of alkyne and metal centre formation. Probably due to the inability of platinum(IV) to form a stable π-complex with alkynes,[3] for a long time Pt^{IV} has been considered to be inert toward alkynes. Recently it has been shown[4] that Pt^{IV} is a rather effective catalyst for acetylene hydroiodation in aqueous acidic (HI) solutions. This reaction involves intermediate platinum(IV) σ-vinyl derivative formation through a triple bond iodoplatination step. Now we have found a new reaction of alkynes with Pt^{IV} complexes in the absence of acid but in the presence of iodine. In the case of acetylene the reaction proceeds under catalytic conditions giving (*E*,*E*)-1,4-diiodobuta-1,3-diene.

Acetylene selectively and quantitatively converts into (*E*,*E*)-1,4-diiodobuta-1,3-diene at 30 °C in a methanolic solution of NaI (0.3–3.0 M), Pt^{IV} ([$Na_2PtCl_6 \cdot 6H_2O$] = 0.002–0.02 M), and I_2 (0.2 M):[†]

$$HC{\equiv}CH \xrightarrow[I^{-},\ I_2/MeOH]{Pt^{IV}} (E,E)\text{-}(ICH{=}CH)_2$$

The yield[‡] of product based on consumed acetylene is close to 100%, and the highest value of the yield is about 5000% based on the catalyst involved.

The *E*,*E*-diene configuration is in accordance with the AA′BB′ pattern in the ^1H NMR spectrum (Figure 1). An iteration procedure leads to the following parameters (Figure 2):

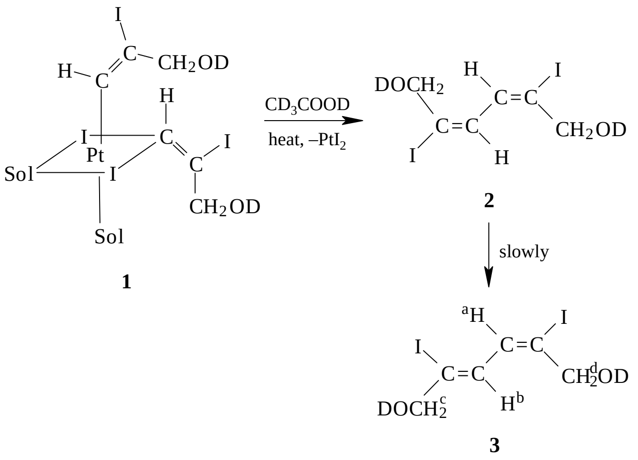


$\delta(a) = 7.13$ ppm
$\delta(b) = 6.82$ ppm
$J(ab) = 14.39$ Hz, $J(ab') = –0.60$ Hz
$J(aa') = 0.50$ Hz, $J(bb') = 10.19$ Hz

The data obtained corresponds to an *E*,*E*-product configuration [*cf.* the spectrum[5] of (*E*,*E*)-1,4-dichlorobuta-1,3-diene]. $^{13}C\{^1H\}$ (CD_3OD): δ = 145.5 (–CH=), 83.1 (–CI=).

IR spectrum (cm^{-1}, pellet with KBr): 3020 vw ($\nu_{H–C=}$), 1620 m ($\nu_{C=C}$), 1530 s, 1380 m, 1280 s, 1140 s, 1010 m, 960 vs ($\delta_{H–C=}$). The last band is typical[6] of conjugated *trans*-double bonds.

It should be noted that reaction of the acetylene derivative propargyl alcohol with Pt^{IV} in an aqueous iodide solution at 5 °C leads to the formation of a bis(β-iodovinyl) Pt^{IV} derivative isolated as $[Pt(CH{=}CI–CH_2OH)_2I_2](CH_3OH)$ **1**.[§] The NMR and IR data as well as elemental analysis confirm the structure proposed. The large value of J(Pt–C) = 801.4 Hz clearly

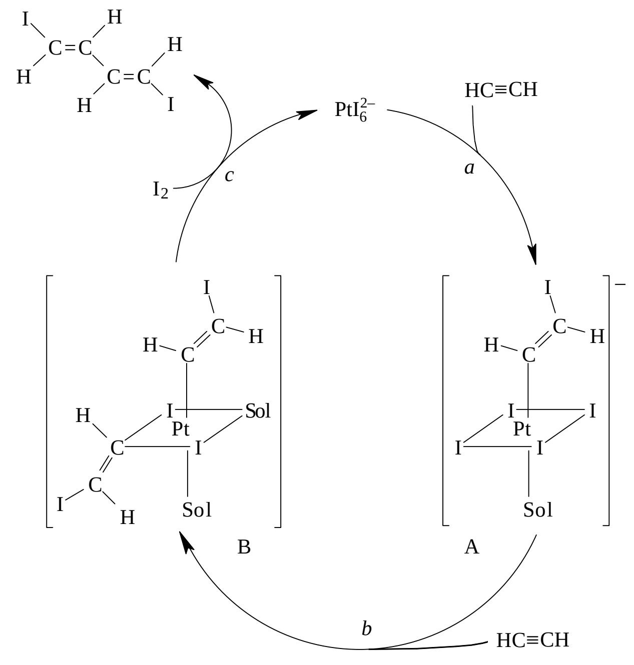


Scheme 1

[†] *Synthesis of* (*E*,*E*)-1,4-*diiodobuta*-1,3-*diene*. Anhydrous NaI (0.6 g) was dissolved in methanol (5 ml) and the solution was saturated with acetylene. Iodine (0.36 g) and $Na_2PtCl_6 \cdot 6H_2O$ (27 mg, 0.048 mmol) were added to the resulting solution. The reaction proceeds at room temperature. After 6 h the product was precipitated by adding water to the solution. The precipitate was separated, washed out by water, then by a saturated aqueous solution of NaI, and after that repeatedly by water up to the absence of iodide ions in the washings. The product was extracted by methanol. The extract solution was evaporated at room temperature and the residue obtained was dried in vacuum. A white crystalline product was obtained (60 mg, 0.196 mmol). MS (EI), *m*/*z*: 306 (M^+), 179 ($CHI{=}CH–CH{=}CH^+$), 127 (I^+). Found (%): C 16.2, H 1.5; calc. for $C_4H_4I_2$ (%): C 15.69, H 1.31.

[‡] The values of the product yield were determined by ^1H NMR spectroscopy.

[§] *Synthesis of* $[Pt(CH{=}CI–CH_2OH)_2I_2](CH_3OH)$ **1**. K_2PtCl_6 (0.2 g, 0.412 mmol) was suspended in 10 ml of an aqueous solution of KI (5 M) and stirred for 1 h. The precipitate of K_2PtI_6 was isolated and dissolved in 10 ml of H_2O. To suppress the possible reduction of platinum(IV) iodide complexes[8] a solution (0.15 ml) of I_2 (1 M, 0.15 mmol) and NaI (5 M) was added to K_2PtI_6 dissolved in water. Propargyl alcohol (1.39 mmol) was added dropwise during 2 h to the resulting solution at 5 °C. After 6 h the precipitate formed was isolated, twice washed out by water, then twice by a 1 M aqueous solution of KI and finally repeatedly by water up to the absence of I^- in the washings. Extraction by methanol of the washed precipitate gives after solvent evaporation a dark brown product (95 mg, yield based on Pt^{IV} is 28%). Found (%): C 9.8, H 1.4, Pt 23.0; calc. for $C_7H_{12}O_3I_4Pt$ (%): C 9.92, H 1.42, Pt 23.02. ^1H NMR (CD_3OD): δ 6.44 [triplet accompanied by ^{195}Pt satellites, 2H, J(HH) = 2.0 Hz, J(PtH) = 31.1 Hz], 4.50 [doublet accompanied by ^{195}Pt satellites, 4H, J(HH) = 2.0 Hz, J(PtH) = 2.5 Hz]; $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 100.9 [J(CPt) = 801.4 Hz, –CH=], 82.3 [J(CPt) = 24.4 Hz, –CI=], 72.6 [J(CPt) = 30.2 Hz, $–CH_2–$]. IR (cm^{-1}, pellet with KBr): 3030 vw ($\nu_{H–C=}$), 2920, 2860 w (ν_{CH_2}), 1630 m ($\nu_{C=C}$), 1430 w ($\nu_{H_2C–C=}$), 1000, 940 m ($\delta_{H–C=}$).



Scheme 2

indicates the presence of a metal–carbon σ-bond. Decomposition of **1** leading to (*E*,*E*)-2,5-diiodohexa-2,4-dien-1,6-diol[¶] **2** (Scheme 1) was monitored by ^{1}H NMR spectroscopy. Complex **1** in CD_3COOD solution almost completely decomposes into **2** and PtI_2 during 3 h at 80 °C. Slow isomerization of the product **2** into the (*Z*,*E*)-2,5-diiodohexa-2,4-dien-1,6-diol **3** takes place in CD_3OD solution. An equilibrium mixture (1:1) of **2** and **3** is formed within 3 months at room temperature. Assignment of the NMR spectrum for compound **3** due to the intrinsic asymmetry of **3** can be easily made.[††] The observed isomerization of **2** into **3** may be considered as independent evidence for the *E*,*E*-conformation of the product **2**.

The catalytic reaction mechanism can be rationalised within the framework of Scheme 2. By analogy with the above-mentioned reactions of propargyl alcohol we may assume that the catalytic transformation of acetylene proceeds through two subsequent acetylene triple bond iodoplatination reactions (steps *a* and *b*) leading to intermediate formation of a *cis*-divinyl derivative of platinum(IV). Decomposition of the latter organoplatinum compound through a reductive elimination route (step *c*) should give [*cf.* reaction (1), Scheme 1] the final product. The latter reaction can proceed due to oxidative assistance by iodine in the reductive elimination step (*cf.* ref. 7); in this case the platinum oxidation state does not change. If this oxidative assistance is not necessary for the reductive elimination flow, oxidation by iodine[8] of platinum(II) which should be formed in the step *c* will regenerate the initial catalyst.

Exploring the generality of this reactivity, particularly with respect to its implications for alkyne activation by Pt^{IV}, as well as elucidation of the reaction mechanism, are the subjects of ongoing studies in our laboratories.

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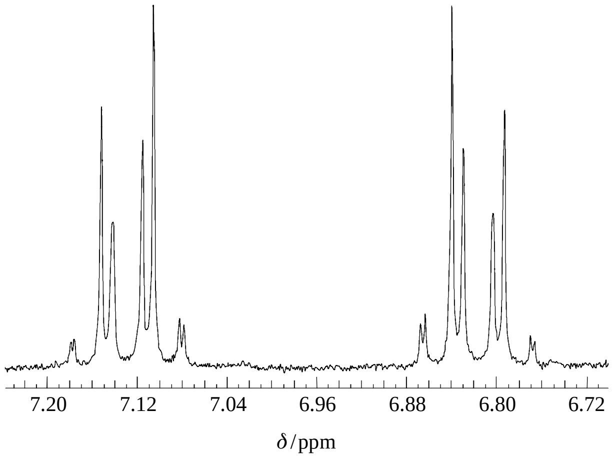

Figure 1 Experimental ^{1}H NMR spectrum of (*E*,*E*)-1,4-diiodobuta-1,3-diene; CD_3OD, Bruker AM-300 (300 MHz).

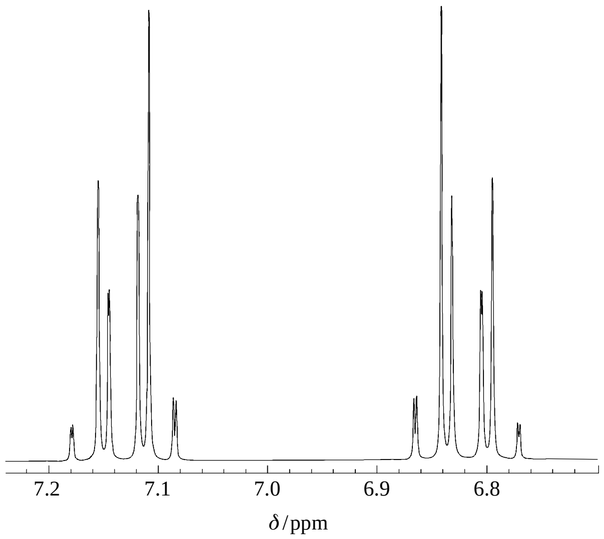

Figure 2 Simulated (see the text) ^{1}H NMR spectrum of (*E*,*E*)-1,4-diiodobuta-1,3-diene.

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[¶] ^{1}H NMR: δ 7.16 (s, 2H), 4.41 (s, 4H); $^{13}C\{^1H\}$ (CD_3OD): δ 137.6 (–CH=), 109.8 (–CI=), 66.4 ($-CH_2-$); IR (cm^{-1}, pellet with KBr): 3210 vs (ν_{O-H}), 3050 vw ($\nu_{H-C=}$), 2920, and 2840 m (ν_{CH_2}), 1630 m and 1570 s ($\nu_{C=C}$), 1430 s ($\nu_{H_2C-C=}$), 1370 s, 1300 m, and 1240 s (δ_{CH_2}), 1040 vs (ν_{C-O}), 1010 vs, and 970 s ($\delta_{H-C=}$).

[††] ^{1}H NMR: δ 7.06 [dt, 1H, $J(H^aH^d)$ = 1.0 Hz, $J(H^aH^b)$ = 10.4 Hz], 6.92 [dt, 1H, $J(H^bH^c)$ = 1.5 Hz, $J(H^bH^a)$ = 10.4 Hz], 4.37 [d, 2H, $J(H^dH^a)$ = 1.0 Hz], 4.25 [d, 2H, $J(H^cH^b)$ = 1.5 Hz].