Note

Stable Pt(IV) vinylic complexes with unusual regioselectivity formed in the reaction of methylpropiolate triple bond activation

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Abstract

An unusual fact of $HC\equiv C-COOMe$ triple bond activation by Pt(IV) iodide leading to the formation of new bis-σ-vinyl complexes $[Pt(CH=CI-COOMe)(CIH=C-COOMe)(Sol)_{3-n}I_n]^{2-n}$ (where $n = 2, 3$) with different regioselectivity in vinyl ligands is reported. The isolated complex can be involved in C–C coupling reaction resulting in a head-to-tail connection of vinyl groups in a substituted diene unit. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Triple bond activation is a very important process from both industrial (conversion of natural alkynes) and synthetic (convenient route to unsaturated systems) points of view. The main progress in this area was achieved with an active development of transition metal catalyzed processes as the most reliable way to accomplish high stereo- and regioselectivity under mild reaction conditions [1,2]. It has been shown that alkyne insertion into a metal–X bond and external nucleophile addition to coordinated alkyne are the two most often occurring triple bond activation mechanisms [1–4]. The former transformation in most cases leads to *cis*-substituted olefin compounds, while the latter predominantly results in products with *trans*-conformation.

Recently, we have reported a simple system based on Pt(IV) iodide complexes ($PtI_6^{2-}/I^-/I_3^-$, methanol or water solutions) for highly stereo- and regioselective conversion of alkynes ($HC\equiv CR$) into *E,E*-1,4-diiodosubstituted dienes ($ICR=CH-CH=CIR$) at room tempera-

ture [5,6]. For R = H and CH_2OH the reaction can be carried out under catalytic conditions [5,6]. The detailed elucidation of the mechanism (Scheme 1, R = CH_2OH) has shown that the reaction proceeds through the subsequent triple bond activation via the nucleophile addition pathway of two alkyne molecules with intermediate formation of bis-σ-vinyl Pt(IV) derivatives, which were isolated and studied with X-ray [5] and NMR [7] methods. The C–C reductive elimination from complex **4** leads to the formation of the final product **5**, mainly after preliminary breaking of one of the chelate rings [8]. By varying substrates we have found that only acetylene and substituted alkynes with chelating –OR group take part in the reaction.

To enhance the scope of the reaction we have investigated the behavior of the triple bond activation system developed by us using an electron acceptor substituted alkyne (R = COOMe) as a substrate. The question is also very intriguing from another point of view, since the recent triple bond activation procedures reported for $HC\equiv C-COOMe$ were shown to proceed through the insertion mechanism [9–11], while in our system external nucleophile addition is expected, thus, providing a synthetic route for products with opposite stereochemistry.

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2. Results and discussion

In this article we describe the triple bond activation reaction of methylpropiolate by Pt(IV) iodide complexes and the synthesis of new $[Pt(CH=CI–COOMe)(CIH=C–COOMe)(Sol)_{3-n}I_n]^{2-n}$ (where $n = 2$, 3) compounds. The formation of these complexes is very interesting, since these are the products of subsequent

triple bond activation via nucleophile addition to terminal and internal C≡C carbon atoms carried out on a single metal center. A detailed 2D (two-dimensional) multinuclear ^1H-, ^{13}C-, ^{195}Pt-NMR investigation is reported as well.

Triple bond activation in HC≡C–COOMe by PtI_6^{2-} in 2 M NaI solution in methanol leads to the formation of complex **7** at room temperature (Scheme 2). The
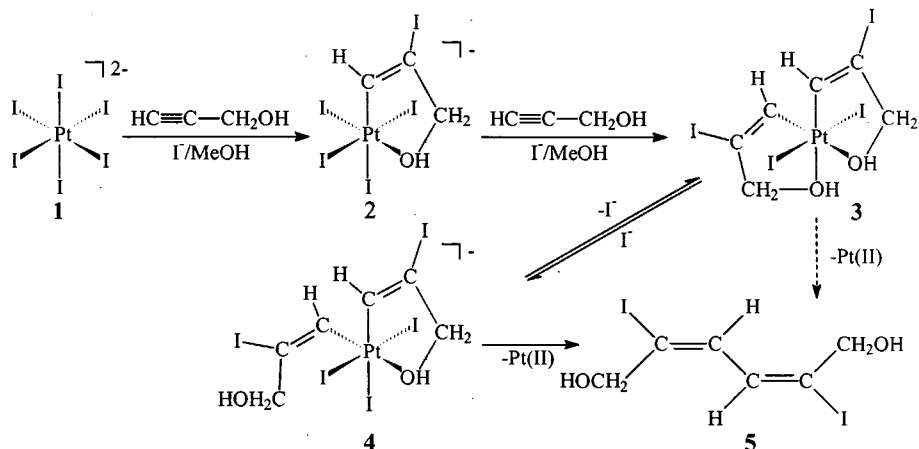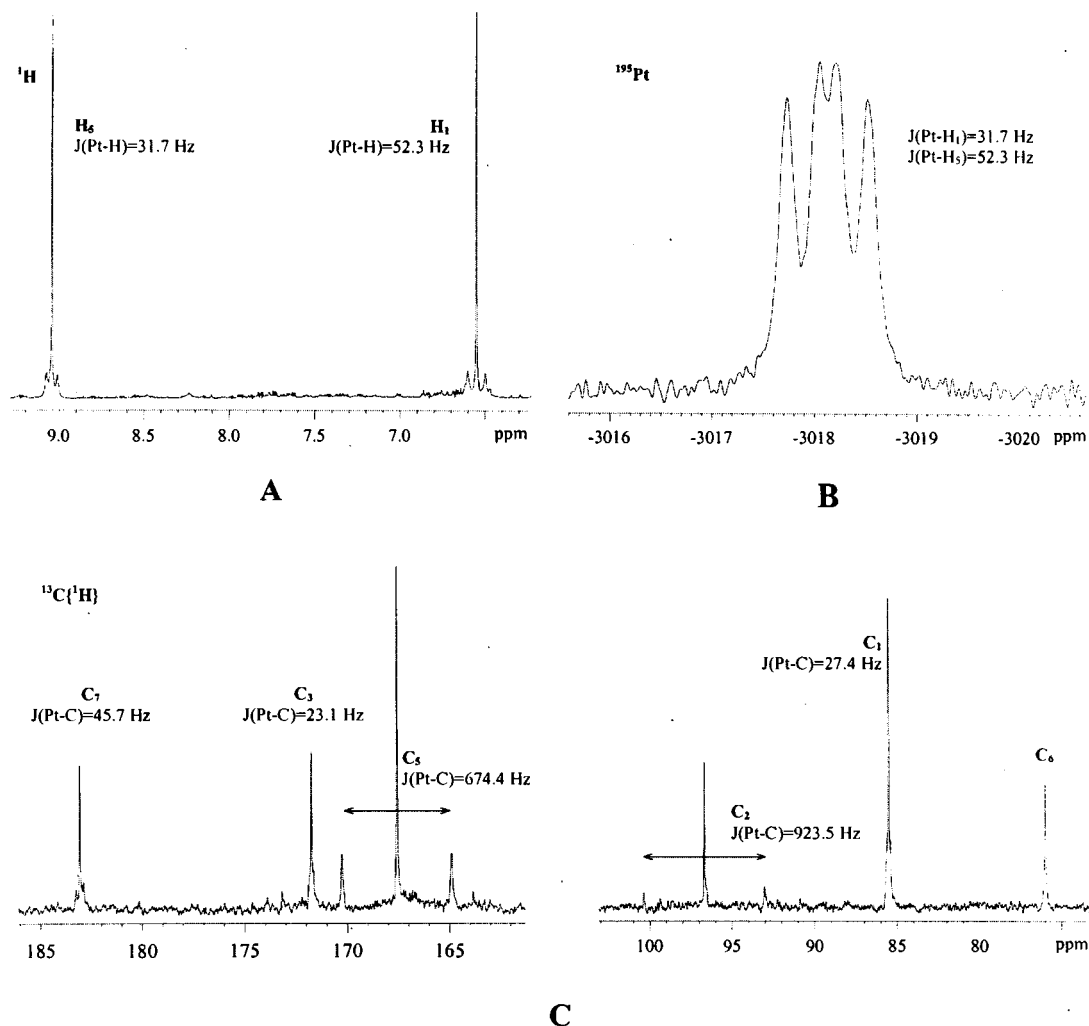

Scheme 1.
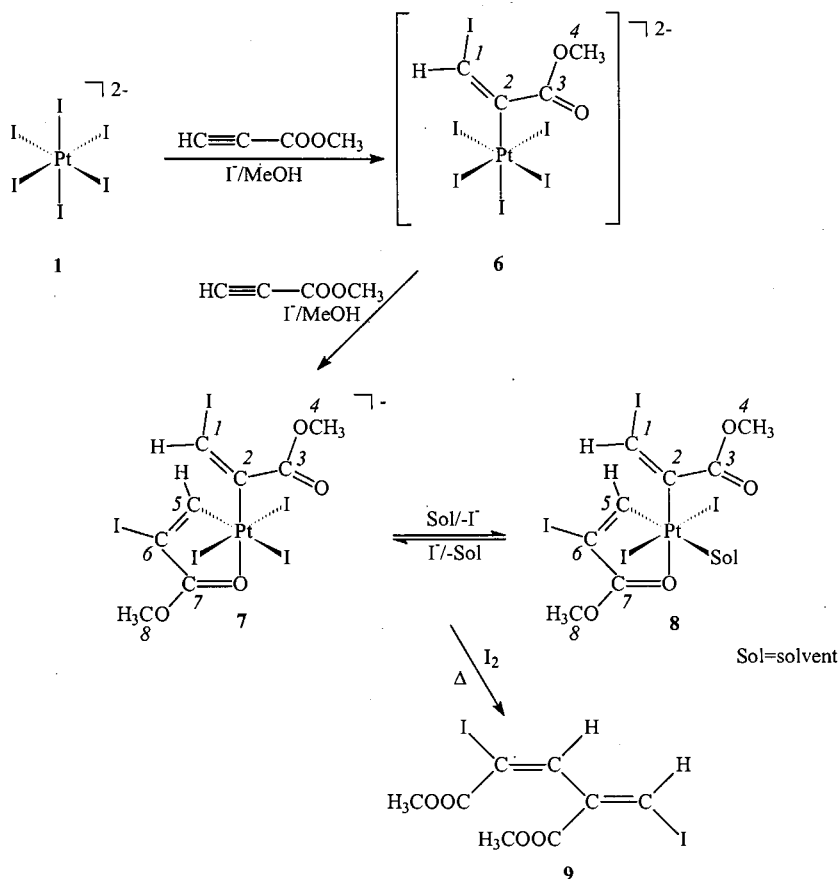
Scheme 2.

Fig. 1. (A) Vinyl region of ^{1}H spectrum (500 MHz). (B) ^{195}Pt spectrum (107 MHz). (C) ^{13}C{^{1}H} spectrum (125 MHz; OMe resonances are not shown) of complex **7** in CD$_3$OD–2 M NaI solution.

probable mechanism of the reaction would start with the triple bond activation via nucleophile addition to the terminal carbon atom (C$_1$) and Pt–C$_2$ σ-bond formation. The first activation step results in the formation of the intermediate complex **6**, in agreement with the regioselectivity expected for the COOR substituted alkyne. However, in the second activation step an opposite regioselectivity is observed. Nucleophile addition occurs at the terminal carbon atom (C$_6$) and C$_5$ binds to the metal. The former case corresponds to the triple bond activation in formal agreement with Markovnikov's rule, while in the latter an opposite type of substitution type was detected possibly due to the sterical reasons. If the reaction is performed in NaI solution in methanol only complex **7** has been found as a final product.

In the vinyl protons region in the ^{1}H-NMR spectrum of **7** two resonances were detected (Fig. 1A), both with well-resolved ^{195}Pt satellites (^{195}Pt nucleus, $I = 1/2$, natural abundance 34%) showing the presence of both vinyl ligands. The multiplet in the ^{195}Pt spectrum (Fig. 1B) indicates the presence of two ligands asymmetrically bound to the metal. Unambiguous confirmation of the bonding scheme of the vinyl ligands comes from the analysis of the ^{13}C{^{1}H} spectrum, since for the Pt–C σ-bond ^{1}J coupling constants of several hundreds of Hertz are expected, while ^{2}J couplings for these type of complexes are as much as 20–30 times smaller (see reviews [12,13] and our previous reports [5–8]). Thus, ^{1}J(Pt–C$_5$) = 674.4 Hz and ^{1}J(Pt–C$_2$) = 923.5 Hz clearly indicate the binding points to the metal (Fig. 1C). The complete line assignment in the ^{1}H and ^{13}C spectra has been made through the analysis of heteronuclear ^{1}J and ^{n}J ($n > 1$) spin–spin coupling network provided with HMQC and HMBC spectra, respectively (Fig. 2). Independent confirmation of different types of substitution in the ligands comes from the analysis of ^{1}J(C–H) couplings. The coupling constant ^{1}J(C$_5$–H) = 181.0 Hz is close to the typical value for the σ-vinyl carbon atom bound to platinum [7], while a larger value ^{1}J(C$_1$–H) =

203.9 Hz agrees well with the expected value for the halogen substituted sp^2 carbon.

We were not able to isolate complex **7** synthesized in the methanol solution of NaI. The problem can be overcome by carrying out the reaction under mild conditions in water; however, in this case a mixture of complexes **7** and **8** is formed. In the ^1H-NMR spectrum in methanol two pairs of resonances were detected approximately in the **8:7** = 1:4 ratio. The 2D $^1H-^{195}Pt$ HMQC spectrum of the system clearly indicates the mixture of two complexes (Fig. 3). The ^{195}Pt signal at -2350.0 ppm correlates to ^1H resonances at 6.36 and 8.49 ppm corresponding to complex **7**, while the ^{195}Pt nuclei with the signal at -3018.1 ppm has spin–spin interactions with ^1H signals at 6.58 and 9.15 ppm representing complex **8**. A more than 500 ppm ^{195}Pt signal high field shift very well describes the expected behavior for I^- coordination to the platinum center [8,12,13]. Iodide to solvent exchange induces the high field shift of vinyl signals in both ^1H and ^{13}C spectra (oxygen has much smaller *trans*-influence compared to iodide), not surprisingly, the largest 24.2 ppm effect is detected for C_5.

In the previous article [8] we have reported iodide ion mediated equilibrium between **3** and **4** (Scheme 1), which has resulted in a similar $^1H-^{195}Pt$ 2D heteronuclear correlation spectrum. Moreover, in the present case using 2D NOESY technique ($\tau_{mix} = 2$ s) a dynamic nature of the process has been confirmed and the corresponding exchange cross-peaks $H_1(\mathbf{7})-H_1(\mathbf{8})$ and $H_5(\mathbf{7})-H_5(\mathbf{8})$ were observed (Fig. 3). As one may ex-

pect, adding NaI to the mixture of complexes in methanol solution results in the quantitative conversion of $\mathbf{8} \rightarrow \mathbf{7}$.

The presence of internal dynamics in the coordination sphere of the metal and the solvent exchange reaction made it difficult to separate the complexes and grow single crystals suitable for X-ray study. Nevertheless, using modern multinuclear NMR methods we were able to perform structural elucidation for the new type of complexes directly in the mixture.

Heating the mixture of complexes **7** and **8** in methanol solution at 60 °C in the presence of I_2 promotes C–C coupling reaction and the formation of conjugated diene **9** (Scheme 2). The process is similar to reductive vinyl plus vinyl coupling we have reported earlier [5,6,8]. However, in contrast to the former, head-to-tail connection of vinyl groups is observed in the present case, thus providing a new synthetic route to 1,3-substituted 1,4-diiodobuta-1,3-diene unit.

3. Conclusions

To summarize, in the system studied two types of activation processes with opposite regioselectivity occur on a single metal center and lead to the formation of a stable bis-σ-vinyl transition metal complex. To the best of our knowledge, we report here the first example of regioselectivity switching upon the triple bond activation reaction, since it is clear that the mono-σ-vinyl intermediate reacts with opposite regioselectivity com-
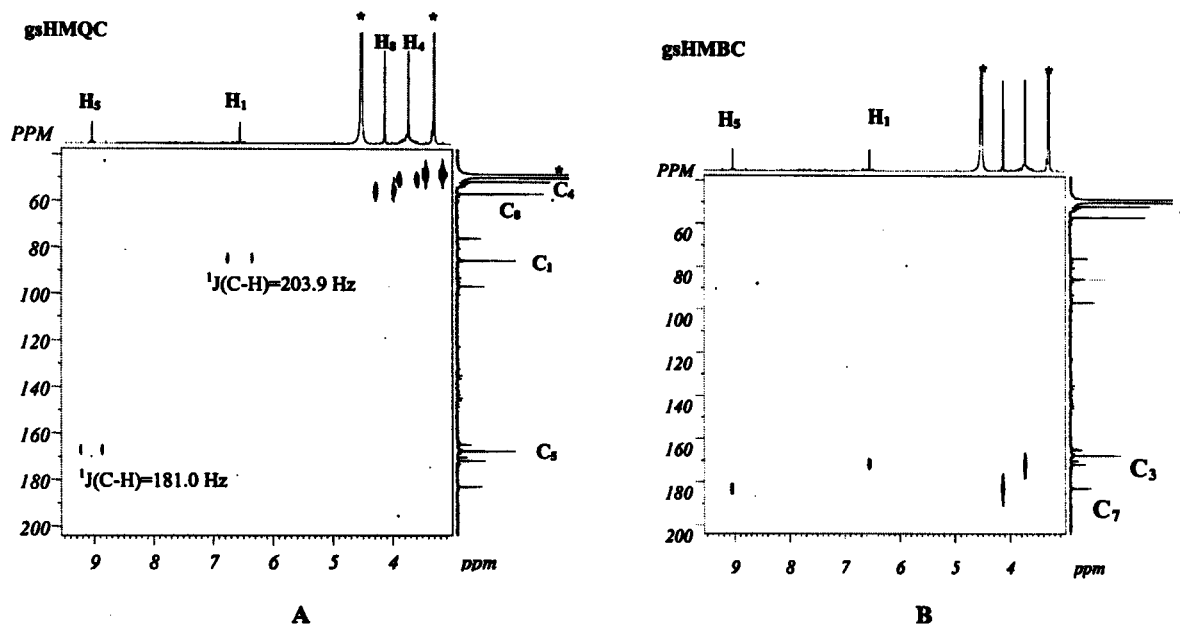

Fig. 2. (A) $^1H-^{13}C$ gsHMQC (left) and (B) $^1H-^{13}C$ gsHMBC (right) spectra of complex **7** in CD_3OD–2 M NaI solution, both recorded without ^{13}C decoupling (^1J(C–H) for OMe groups are not shown, see Section 4); residual solvent signals are marked with '*'.
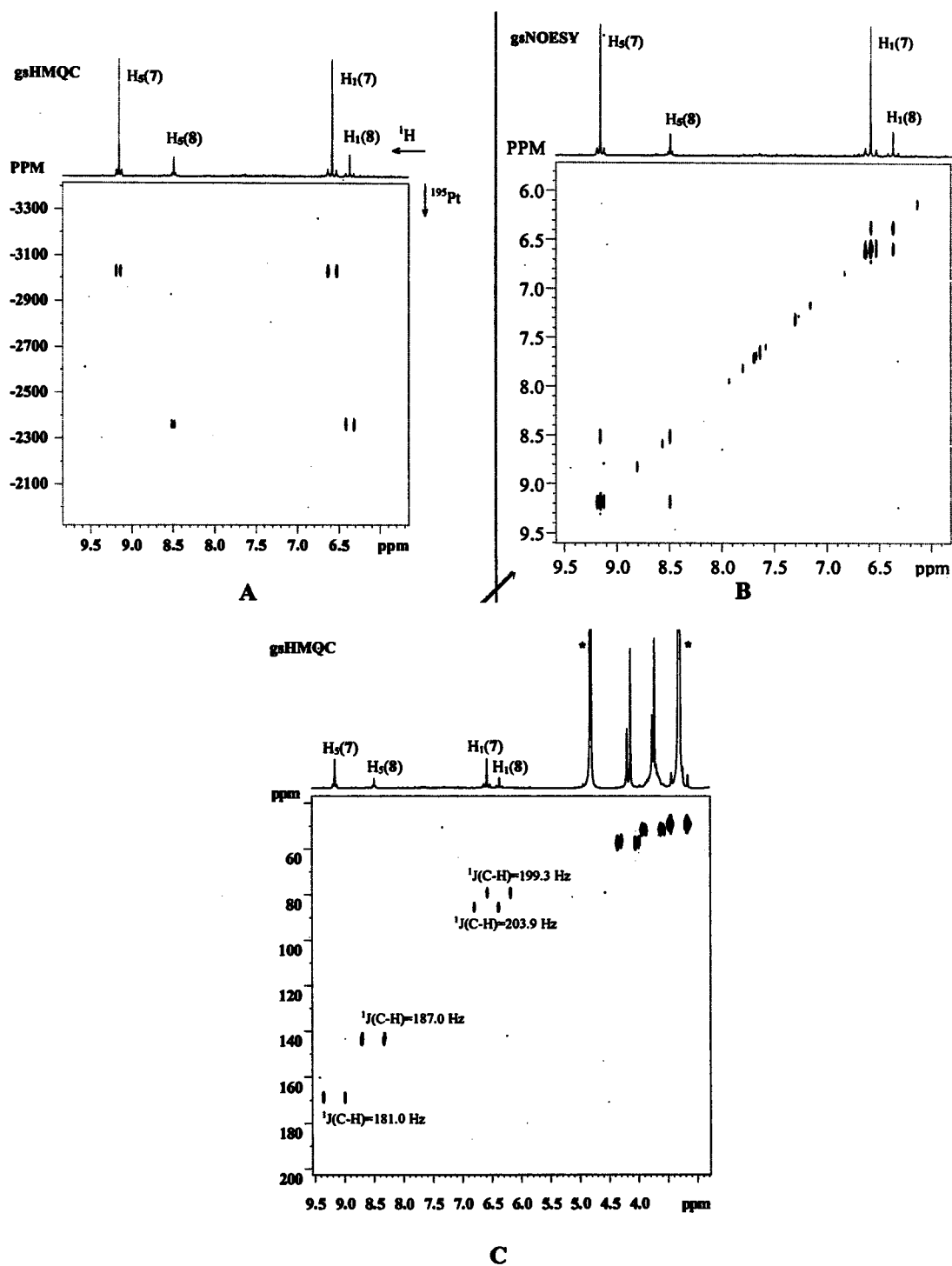
Fig. 3. (A) $^1H-^{195}Pt$ gsHMQC spectrum; (B) gsNOESY spectra ($\tau_{mix} = 2$ s, only cross-peaks of the same sign as diagonal are shown); (C) $^1H-^{13}C$ gsHMQC spectrum (OMe assignment is not shown) of the mixture of complexes **7** and **8** in CD_3OD; residual solvent signals are marked with '*'.

pared to the initial platinum(IV) iodide. The synthesized complex can be involved in the C–C bond formation reaction giving a conjugated diene unit as a final product.

The further investigations related to reactivity and possible catalytic activity of the complexes synthesized are the subject of ongoing work in our group and will be reported elsewhere.

4. Experimental

4.1. Materials and methods

All NMR measurements were performed in a three channel Bruker DRX500 spectrometer operating at 500, 125 and 107 MHz for ^1H, ^{13}C and ^{195}Pt nuclei, respectively. The spectra were processed in a Silicon Graphics workstation using the XWINMR 2.0 software package. All 2D spectra were recorded on the inverse triple resonance probe-head with active shielded Z-gradient coil.

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

2D heteronuclear correlations were recorded using pulse field gradient versions of HMQC and HMBC experiments.

4.2. NMR monitoring of the triple bond activation reaction

The saturated PtI_6^{2-} solution was prepared by dissolving 20 mg of $Na_2PtCl_6\cdot6H_2O$ in 0.5 ml of 2 M NaI solution in CD_3OD. An excess of the platinum salt was filtered out and the solution was placed in the NMR tube. A stoichiometric amount of $HC\equiv C-COOMe$ was added to the solution and stirred at room temperature (r.t.). ^1H-NMR monitoring of the triple bond activation reaction was performed during 6–8 h.

4.3. Preparation of complexes 7 and 8

$Na_2PtCl_6\cdot6H_2O$ (45 mg) was dissolved in 2 ml of 5 M NaI solution in H_2O. $HC\equiv C-COOMe$ (30 μl) was added to the resulting mixture and stirred for 12 h at r.t. A dark-brown precipitate was isolated, washed out with water (3×10 ml) and extracted with 10 ml of MeOH. After MeOH evaporation 60 mg of the final product was obtained (estimated yield 85% based on initial Pt^{IV}).

IR (KBr pellet, cm^{-1}): 3060 (vw), 2950 (vw), 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).

4.3.1. NMR data for complex 7 in 2 M NaI solution in CD_3OD

^1H (δ, ppm; J, Hz): 9.15 (s with ^{195}Pt satellites, $J(Pt-H) = 31.3$, H_1), 6.58 (s with ^{195}Pt satellites, $J(Pt-H) = 52.4$, H_5), 4.13 (s, H_4), 3.72 (s, H_8).

$^{13}C\{^1H\}$ (δ, ppm; J, Hz): 183.0 (s with ^{195}Pt satellites, $J(Pt-C) = 45.7$, C_7), 171.8 (s with ^{195}Pt satellites, $J(Pt-C) = 23.1$, C_3), 167.6 (s with ^{195}Pt satellites, $J(Pt-C) = 674.4$, C_5), 96.7 (s with ^{195}Pt satellites,

$J(Pt-C) = 923.5$, C_2), 85.5 (s with ^{195}Pt satellites, $J(Pt-C) = 27.4$, C_1), 76.0 (s, C_6), 56.8 (s, C_8), 51.6 (s, C_4).

HMQC (Hz): $^1J(C_5-H) = 181.0$, $^1J(C_8-H) = 150.7$, $^1J(C_1-H) = 203.9$, $^1J(C_4-H) = 145.1$.

^{195}Pt (δ, ppm; J, Hz): -3018.1 (dd, $J(Pt-H_1) = 31.3$, $J(Pt-H_5) = 52.4$).

4.3.2. NMR data for complex 8 in CD_3OD

^1H (δ, ppm; J, Hz): 8.49 (s with ^{195}Pt satellites, $J(Pt-H) = 18.9$, H_1), 6.36 (s with ^{195}Pt satellites, $J(Pt-H) = 49.3$, H_5), 4.19 (s, H_4), 3.76 (s, H_8).

HMQC (δ, ppm; J, Hz, only protonated carbon atoms): 143.4 ($^1J(C-H) = 187.0$, C_5), 79.4 ($^1J(C-H) = 199.3$, C_1), 57.3 ($^1J(C-H) = 151.2$, C_8), 51.6 ($^1J(C-H) = 147.8$, C_4).

^{195}Pt (δ, ppm; J, Hz): -2350.0 (dd, $J(Pt-H_1) = 18.9$, $J(Pt-H_5) = 49.3$).

4.4. Structure determination of complexes 7 and 8

4.4.1. $^1H-^{195}Pt$ 2D HMQC experiment

4.4.1.1. The mixture of complexes 7 and 8 (Fig. 3A). The spectrum was collected with ^1H and ^{195}Pt 90° pulses of 12.5 and 17.0 μs, respectively, a relaxation delay of 2 s, $\Delta = (2 \times {}^2J_{H-Pt})^{-1} = 10$ ms (optimized for a coupling constant of 50 Hz), a 0.2 s acquisition time and 2000 and 160 000 Hz spectral windows for the $^1H(F2)$ and $^{195}Pt(F1)$ dimensions, respectively. Eight transients were averaged for each of the 256 increments on t_1. The data were zero filled to a 2048×2048 matrix and processed with QSINE (SSB = 2) and SINE (SSB = 2) window functions for the F2 and F1 dimensions, respectively. In the case of the pulse field gradient experiment 1 ms sine shaped gradient pulses with the ratio 50:30:40 (%) followed with 100 μs recovery delay were applied.

4.4.2. $^1H-^{13}C$ 2D HMQC experiment

4.4.2.1. Complex 7 and the mixture of complexes 7 and 8 (Figs. 2a and 3c). The spectrum was collected with ^1H and ^{13}C 90° pulses of 12.5 and 13.0 μs, respectively, a relaxation delay of 2 s, $\Delta = (2 \times {}^1J_{H-C})^{-1} = 2.6$ ms (optimized for the average coupling constant of 190 Hz), a 0.2 s acquisition time and 3400 and 25 000 Hz spectral windows for the $^1H(F2)$ and $^{13}C(F1)$ dimensions, respectively. Eight transients were averaged for each of the 256 increments on t_1 for the mixture of complexes 7 and 8 (Fig. 3C), while two transients and 512 increments were used for complex 7 (Fig. 2A). The data were zero filled to a 2048×2048 matrix and processed with QSINE (SSB = 2) and SINE (SSB = 2) window functions for F2 and F1 dimensions, respectively. In the case of the pulse field gradient experiment 1 ms sine shaped gradient pulses with the ratio 50:30:40 (%) followed with 100 μs recovery delay were applied.

4.4.3. ^1H–^{13}C 2D HMBC experiment

4.4.3.1. Complex **7** (Fig. 2B).
The spectrum was collected with ^1H and ^{13}C 90° pulses of 12.5 and 13.0 μs, respectively, a relaxation delay of 2 s, a 0.3 s acquisition time and 3400 and 31 000 Hz spectral windows for the ^1H(F2) and ^{13}C(F1) dimensions, respectively. Thirty-two transients were averaged for each of the 128 increments on t_1. For the low pass filter a delay $\Delta = (2 \times {}^1J_{H-C})^{-1} = 2.6$ ms (optimized for the average coupling constant of 190 Hz) was used, while a 150 ms delay was applied for the evolution of long range couplings. The data were zero filled to a 2048×2048 matrix and processed with QSINE (SSB = 2) and QSINE (SSB = 2) window functions for the F2 and F1 dimensions, respectively. In the case of the pulse field gradient experiment 1 ms sine shaped gradient pulses with the ratio 50:30:40 (%) followed with 100 μs recovery delay were applied.

4.4.4. 2D NOESY experiment

4.4.4.1. Mixture of complexes **7** and **8** (Fig. 3B).
The spectrum was recorded using the following bipolar gradients pulse sequence:

$$90-t_1-90-\tau_{mix}/2-G1-180-G2-\tau_{mix}/2-90-acq$$

where the ^1H 90° pulse is 12.5 μs and gradients ratio $G1/G2 = 40: -40$ (%). In both cases 1 ms sine shaped gradient pulses followed with 100 μs recovery delay were applied. A 0.3 s acquisition time, 2 s relaxation delay, and mixing time $\tau_{mix} = 2$ s were used. Thirty-two transients were averaged for each of the 128 increments on t_1, 3400 Hz spectral windows were used for both dimensions. The data were zero filled to a 2048×2048 matrix and processed with SINE (SSB = 2) and SINE (SSB = 2) window functions for the F2 and F1 dimensions, respectively.

4.5. C–C coupling reaction and diene **9** formation

Ten milligrams of the mixture of complexes **7** and **8** obtained as described above were dissolved in 0.5 ml of CD_3OD, then 30 mg of I_2 was added and the resulting solution was placed in the NMR tube. The reaction was monitored using ^1H-NMR and 50% conversion was detected after ca. 3 h heating at 60 °C. The structure of the final product **9** was established using 2D HMQC, HMBC, NOESY and long-range COSY methods with the experimental conditions similar to that described above. Particularly, 1.5 s mixing time was used in 2D NOESY, 300 ms delay for evolution of long-range homonuclear couplings in 2D LR-COSY and 90 ms delay for the evolution of long-range heteronuclear couplings in 2D HMBC.

4.5.1. NMR data for compound **9** in CD_3OD

The numbering of carbon atoms is the same as in **7** and **8**: $^8CH_3$–O^7CO–^6CI=^5CH–$^2C(^3COO^4CH_3)$=^1CHI.

^1H (δ, ppm; J, Hz): 7.67 (d, ^4J(H–H) = 0.9, ^1CHI), 7.34 (d, ^4J(H–H) = 0.9, ^5CH), 4.17 (s, $^8CH_3$), 3.74 (s, $^4CH_3$).

$^{13}C\{^1H\}$ (δ, ppm; J, Hz, protonated carbon atoms assigned from HMQC, carbonyl atoms from HMBC): 182.1 (^7C), 165.1 (^3C), 145.2 (^1J(C–H) = 167.5, ^5C), 95.2 (^1J(C–H) = 189.4, ^1C), 57.0 (^1J(C–H) = 150.3, ^8C), 53.1 (^1J(C–H) = 149.0, ^4C).

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