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Facile conversion of bis(alkynyl) into diyne ligand on platinum assisted by electrophilic gold phosphine

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Abstract

^{31}P NMR spectroscopy measurements were used to establish the course for the stoichiometric-dependent reactions between $[Au(PPh_3)]^+$ and $[Pt(C{\equiv}CPh)_2(dppf)]$ (**1**), which for equimolar amounts afford as the unique product $[Pt\text{-}\{\eta^3\text{-}C(C{\equiv}CPh){=}C(Ph)Au(PPh_3)\}(dppf)]^+$ (**2**), but any excess of **1** gives also $[Pt(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(dppf)]$ (**3**) [dppf = 1,1′-bis(diphenylphosphine)ferrocene]. Both compounds **2** and **3** were obtained straightforwardly by the reactions of **3** with $[Au(PPh_3)]^+$ and $[Pt(C_2H_4)(dppf)]$ with 1,4-diphenylbutadiyne, respectively. The X-ray crystal structure analysis of **3** confirmed a trigonal-planar coordination geometry about the platinum atom, and a bent η^2-coordinated diyne ligand. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Platinum; Gold; Cross-coupling; Diyne; X-ray

1. Introduction

There has been a growing interest in metal-induced carbon–carbon bond-forming reactions of terminal alkynes [1]. In particular, one of the earliest experimental evidences of coupling reactions, mainly using d^8-metal complexes, has been provided by isolated *trans* and *cis*-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$, $[Pt(\eta^2\text{-}HC{\equiv}CPh)(PPh_3)_2]$, and 1,4-diphenylbuta-1,3-diyne products from the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and phenylacetylene [2]. Theoretical analysis and kinetics studies of oxidative addition and reductive elimination on d^8-metal-centered coupling of organic groups showed that a *cis* orientation or trigonal-planar geometry for the complex is necessary before occurrence of reductive elimination of the coupled product [3,4]. It is well established that the C–C elimination process at platinum(II) center is less favorable than for palladium counterparts, whereas the platinum intermediates are generally substitution-inerts in homogeneous catalysis, being therefore better candidates to carry out mechanistic studies [5,6].

One of our main objectives in the present paper was to find out whether the electrophilic metal reagent $[Au(PR_3)]^+$ behaves toward *cis*-alkynyl groups like its isolobal H^+ in formation of gold–butenynyl ligands [7,8]. This would be in contrast, therefore, to other electrophiles such $[Ag(PR_3)]^+$ and HgX_2 for which the reactions resulted in a coordinated metallic moiety at C≡C bonds of *cis*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ [9]. To ascertain this premise, the reaction of complex **1** with $[Au(PPh_3)]^+$ was used as a model. The chelating dppf ligand was chosen due to its significant steric strain in square planar complexes, which ensures a *cis* configuration for the other two coordination sites. Consequently, it accelerates the formation of the coupling products [10].

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2. Experimental

2.1. General

All manipulations were performed using general Schlenk and high-vacuum techniques. Solvents were appropriately dried and distilled under argon prior to use.

IR spectra were recorded as Nujol mulls on a JASCO IR 700 spectrometer, and calibrated relative to polystyrene at 1601 and 1028 cm^{-1}. The NMR spectra were recorded upon either BRÜKER AC300P (^{1}H 300.13, ^{13}C 75.47, ^{31}P 121.50 MHz) or VARIAN GEMINI 300 (^{1}H 300.08, ^{13}C 75.46, ^{31}P 121.47 MHz) Fourier-transform machines in $CDCl_3$, unless otherwise stated. ^{1}H and ^{13}C-$\{^{1}H\}$ spectra were referenced to internal $SiMe_4$, and ^{31}P-$\{^{1}H\}$ spectra referenced to external 85% H_3PO_4, and locked on the solvent deuterium signal. Reactions monitored by ^{31}P-$\{^{1}H\}$ spectra were recorded in THF with the deuterium lock signal from D_2O, using a concentric glass capillary of this solvent in the 5 mm NMR sample-tube. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyzer. All percentages given are the averages of at least two independent determinations. 1,1′-Bis(diphenylphosphine)ferrocene (dppf) and phenylacetylene were purchased from Aldrich and used as received. $[Ag][O_3SCF_3]$ (Aldrich) was recrystallized from ethyl ether–petroleum ether. 1,4-Diphenylbutadiyne [11] and the complexes $[Pt(C{\equiv}CPh)_2(cod)]$ [11], $[Au(PPh_3)Cl]$ [12] $[PtCl_2(cod)]$ [13] and $[Pt(cod)_2]$ [14] were prepared as described in the literature. Fresh and filtrated solutions of $[Au(PPh_3)(THF)][O_3SCF_3]$ (0.50×10^{-2} mmol ml^{-1}) were used, prepared by an equimolar mixture of $[Ag][O_3SCF_3]$ and $[Au(PPh_3)Cl]$ in THF, which were stirred in the dark for 1 h, and filtered through a pad of diatomaceous earth.

2.2. Preparations

2.2.1. *[Pt(C_2H_4)(dppf)] [15]*

$[Pt(cod)_2]$ (0.097 g, 0.23 mmol) was added in small portions to 15 ml of petroleum ether saturated with ethylene at 0°C. A solution of dppf (0.133 g, 0.24 mmol) in 15 ml of diethyl ether was then added, and the mixture stirred for 1 h at 25°C in an argon atmosphere. The resulting yellow solution was reduced to a small volume, affording a precipitate by bubbling ethylene through the solution at 0°C, which was washed with cold petroleum ether (3 × 5 ml) saturated with ethylene and dried under reduced pressure for 3 h. Yield of 0.167 g (93%). ^{1}H NMR: δ 2.14 [d, 4H, J(PtH) 60 Hz, J(PH) 2.8 Hz, C_2H_4]; 4.16 (s, 4H, η^5-C_5H_4P); 4.22 (s, 4H, η^5-C_5H_4P); 7.28–7.70 (m, 20H, C*H*, Ph); ^{31}P-$\{^{1}H\}$ NMR: δ 29.1 [s, ^{1}J(PtP) 3684 Hz, Ph_2P]. *Anal.* Found: C, 55.16; H, 4.19. Calc. for $C_{36}H_{32}FeP_2Pt$: C, 55.61; H, 4.15%.

2.2.2. *[Pt(C≡CPh)$_2$(dppf)] (**1**)*

A stirred suspension of $[Pt(C{\equiv}CPh)_2(cod)]$ (0.060 g, 0.12 mmol) in THF (10 ml) was treated with dppf (0.068 g, 0.12 mmol). After stirring for 1 h at 25°C, the resulting orange solution was concentrated under reduced pressure to ca. 2 ml. Addition of diethyl ether afforded a yellow solid, which was washed with diethyl ether and dried in vacuo for 2 h to give 0.089 g (78%). M.p. 225°C (dec.). IR: v(C≡C) 2132 w, 2121 w cm^{-1}. ^{1}H NMR: δ 4.19 (s, 4H, η^5-C_5H_4P); 4.32 (s, 4H, η^5-C_5H_4P); 6.79 [dt, 4H, ^{3}J(HH) 5.4 Hz, ^{4}J(HH) 1.7 Hz, *o*-C*H*, C≡C*Ph]*; 6.4–7.02 (m, 6H, *m*-, *p*-C*H*, C≡C*Ph*); 7.31 [td, 8 H, ^{3}J(HH) 7.5 Hz, ^{4}J(HH) 1.3 Hz, *m*-C*H*, PPh_2]; 7.38 [td, 4H, ^{3}J(HH) 7.5 Hz, ^{4}J(HH) 1.3 Hz, *p*-C*H*, P*Ph*]; 7.85 [m, 8H, ^{3}J(PH) 11.2 Hz, ^{3}J(HH) 7.0 Hz, ^{4}J(HH) 1.3 Hz, *o*-C*H*, P*Ph*]. ^{13}C-$\{^{1}H\}$ NMR: δ 72.82 (s, *C*H, η^5-C_5H_4P); 75.75 (t, *C*H, η^5-C_5H_4P); 75.82 [d, $|^{1}J(CP) + ^{2}J(C\ P')|$ 61 Hz, *C*P, η^5-C_5H_4P]; 103.37 [dd, ^{1}J(PtC) 1132 Hz, $|^{2}J(CP) + ^{2}J(CP')|$ 75 or 133 Hz, Pt*C*≡CPh]; 110.34 [m, ^{2}J(PtC) 308 Hz, $|^{3}J(CP) + ^{3}J(CP')|$ 35.2 Hz, $^{3}J(CP) = \pm(36 \pm 2)$ Hz, $^{3}J(CP') = \pm(0.8 \pm 2)$ Hz, PtC≡*C*Ph]; 125.13 (s, *p*-*C*H, C≡C*Ph*); 127.21 (s, *m*-*C*H, C≡C*Ph*); 128.08 [t, $|^{3}J(CP) + ^{5}J(CP')|$ 10.5 Hz, *m*-*C*H, P*Ph*]; 130.62 (s, *p*-*C*H, P*Ph*); 131.79 (s, *o*-*C*H, C≡C*Ph*); 133.44 [m, ^{2}J(PtC) 27 Hz, $|^{1}J(PC) + ^{3}J(P'C)|$ 57.8 Hz, *ipso*-*C*, P*Ph*]; 135.19 [t, $|^{2}J(CP) + ^{4}J(CP')|$ 11.5 Hz, *o*-*C*H, P*Ph*]. ^{31}P-$\{^{1}H\}$ NMR: δ 15.1 [s, J(PtP) 2372 Hz]. *Anal.* Found: C, 62.70; H, 3.98. Calc. for $C_{50}H_{38}FeP_2Pt$: C, 63.10: H, 4.02%.

2.2.3. *[Pt{η^3-C(C≡CPh)=C(Ph)AuPPh$_3$}(dppf)][O$_3$SCF$_3$] (**2**)*

A stirred solution of **3** (0.075 g 0.078 mmol) in THF (5 ml) was treated with $[Au(PPh_3)][O_3SCF_3]$ (0.080 mmol) in THF (16 ml) at °C. The resulting orange solution was stirred for 5 min at 5°C, and 10 min at r.t. The volume was reduced to 5 ml under vacuum, and fast addition of diethyl ether (10 ml) afforded yellow precipitate, which was washed with diethyl ether (3 × 5 ml) and dried under reduced pressure for 10 h. Yield of 0.106 g (87%). IR: v(C≡C) not observed; v(CF) 1270 vs, br; v(SO) 1154 s, br; 1028 s, br cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 2H, η^5-C_5H_4P); 4.28 (s, 2H, η^5-C_5H_4P); 4.50 (s, 4H, η^5-C_5H_4P); δ 6.75–6.88 (m, 9H, Ph) 6.90–6.97 [td, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 1.9 Hz, 4 H, Ph]; 7.14–7.33 (m, 12 H, Ph); 7.40 [t, ^{3}J(HH) 7.8 Hz, 3 H, Ph]; 7.47–7.57 (m, 9 H, Ph); 7.59 (m, 4 H, *o*-CH, Ph, dppf); 7.81 [m, ^{3}J(PH) 11.3 Hz, ^{3}J(HH) 7.8 Hz, ^{4}J(HH) 1.4 Hz, 4 H, *o*-CH, Ph, dppf]. ^{31}P-$\{^{1}H\}$ NMR ($CDCl_3$): δ 20.48 [dd, ^{1}J(PtP) 3036 Hz, J(PP′) 16.5 Hz, J(PP″) 8.9 Hz, Pt(dppf)]; 23.58 [t, ^{1}J(PtP) 4364 Hz, ^{2}J(PP) 18.9 Hz, J(PP′) 16.5 Hz, Pt(dppf)]; 35.15 [dd, J(PtP) 209 Hz, J(P′P″) 18.9 Hz, J(PP″) 8.9 Hz, $Au(PPh_3)$]. *Anal.* Found: C, 53.04: H, 3.13. Calc. for $C_{69}H_{53}AuF_3O_3FeP_3PtS$: C, 53.11; H, 3.43%.

*2.2.4. [Pt(η^2-PhC≡CC≡CPh)(dppf)] (**3**)*

Method A. [Pt(cod)$_2$] (0.060 g, 0.15 mmol) was added in small portions to 15 ml of petroleum ether saturated with ethylene at 0°C. A solution of dppf (0.081 g, 0.15 mmol) in 15 ml of diethyl ether was added, and the mixture stirred for 1 h at 25°C in an argon atmosphere. 1,4-Diphenylbutadiyne (0.041 g, 0.203 mmol) was then added, and the solution stirred further for 1 h. The volatiles were evaporated, and the residue extracted from benzene (3 ml). Addition of 15 ml of petroleum ether gave a yellow solid, which was washed with petroleum ether (3 × 10 ml) and dried under reduced pressure. Yield of 0.107 g (77%). IR: ν(C≡C)$_{\mathrm{uncoord}}$ 2166 m, ν(C≡C)$_{\mathrm{coord}}$ 1720 m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.95 (q, 2H, η^5-C$_5$H$_4$P); 4.14 (t, *J* 1.6 Hz, 2H, η^5-C$_5$H$_4$P); 4.32 (m, 2H, *J* 1.4 Hz, η^5-C$_5$H$_4$P); 4.37 (dd, *J* 3.8 Hz, *J* 1.9 Hz, 2H, η^5-C$_5$H$_4$P); 6.88–7.00 (m, 1H, *p*-C*H*, 2H, *m*-C*H*, PhC≡C); 7.15–7.38 (m, 19H, Ph); 7.71 [m, 4H, ^3J(PH) 11.3 Hz, ^3J(HH) 7.8 Hz, ^4J(HH) 1.9 Hz, *o*-C*H*, PPh$_2$]; 7.90 [m, 4H, ^3J(PH) 11.2 Hz, ^3J(HH) 8.0 Hz, ^4J(HH) 1.5 Hz, *o*-C*H*, PPh$_2$]. NMR ^{13}C {^{1}H} (CDCl$_3$): δ 71.02 [d, *J*(CP) 5.7 Hz, η^5-C$_5$H$_4$P]; 72.08 [d, *J*(CP) 6.3 Hz, η^5-C$_5$H$_4$P]; 74.29 [m, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 9.5 Hz, η^5-C$_5$H$_4$P]; 75.03 [q, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 10.7 Hz, η^5-C$_5$H$_4$P]; 80.07 [d, ^1J(CP) 51.4 Hz, CP, η^5-C$_5$H$_4$P]; 82.77 [dd, *J*(CP) 12.99 Hz, *J*(CP′) 6.93 Hz, *C*≡CPh free]; 82.81 [dd, ^1J(CP) 50.8 Hz, ^3J(CP) 3.2 Hz, CP, η^5-C$_5$H$_4$P]; 103.83 [d, *J*(PtC) 17.5 Hz, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 7.4 Hz, C≡*C*Ph free]; 109.19 [dd, ^1J(PtC) 289 Hz, ^2J(CP) 78.0 Hz, ^2J(CP′) 5.5 Hz, η^2-C≡C]; 125.52 [d, *J*(PtC) 12 Hz, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 2.2 Hz, probably *ipso*-C, C≡C*Ph* free]; 126.40 (s, *p*-CH, C≡C*Ph*); 126.81 (s, *p*-CH, C≡C*Ph*); 127.77 (s, *m*-CH, C≡C*Ph*); 127.78 [d, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 10.0 Hz, *m*-CH, PPh]; 127.95 (s, *m*-CH, C≡C*Ph*); 128.04 [d, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 10.4 Hz, *m*-CH, PPh]; 129.34 [d, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 1.4 Hz, *p*-CH, PPh); 129.90 [d, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 1.0 Hz, *p*-CH, PPh]; 130.62 [d, ^4J(PtC) 37.3 Hz, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 5.5 Hz, *o*-CH, η^2-C≡C*Ph*]; 130.79 [d, *J*(PtC) 8.6 Hz, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 1.9 Hz, *o*-CH, C≡C*Ph* free]; 132.36 [t, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 19.0 Hz, *J*(PtC) 6.6 Hz, probably *ipso*-C, η^2-C≡C*Ph*]; 134.00 [d, *J*(PtC) 20.4 Hz, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 13.7 Hz, *o*-CH, P*Ph*]; 134.56 [d, *J*(PtC) 27.6 Hz, $|J(\mathrm{CP})+J(\mathrm{CP'})|$ 14.4 Hz, *o*-CH, P*Ph*]; 135.90 [dd, ^2J(CP) 79.1 Hz, ^2J(CP′) 6.3 Hz, probably η^2-C≡C]; 136.25 [d, *J*(PtC) 44.2 Hz, ^1J(CP) 44.6 Hz, ^3J(CP) 2.8 Hz, *ipso*-C, P*Ph*]; 136.90 [d, *J*(PtC) 36.7 Hz, ^1J(CP) 46.3 Hz, ^3J(CP) 2.5 Hz, *ipso*-C, P*Ph*]. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 22.1 [d, ^1J(PtP) 3630 Hz, ^2J(PP) 10.7 Hz, Ph$_2$*P*Pt]; 22.9 [d, ^1J(PtP) 3371 Hz, ^2J(PP) 10.7 Hz, Ph$_2$*P*Pt]. *Anal.* Found: C, 63.17; H, 4.00. Calc. for C$_{50}$H$_{38}$FeP$_2$Pt: C, 63.10; H, 4.02%.

Method B. A stirred solution of [Pt(C$_2$H$_4$)(dppf)] (0.160 g, 0.21 mmol) in THF (15 ml) was treated with 1,4-diphenylbutadiyne (0.050 g, 0.25 mmol) at r.t. After being stirred for 1 h, the resulting yellow solution was filtered through an alumina column and concentrated to 2 ml. Addition of diethyl ether and petroleum ether (1:1) afforded a yellow solid, which was washed with petroleum ether and dried under vacuum. Yield: 0.180 g (92%). *Anal.* Found: C, 63.17; H, 3.81. Calc. for C$_{50}$H$_{38}$FeP$_2$Pt: C, 63.10; H, 4.02%. The spectral data were identical with that of **3** prepared from the method A.

*2.2.5. Both **2** and **3** from the same reaction*

A solution of [Pt(C≡CPh)$_2$(dppf)] (0.033 g, 0.035 mmol) in THF (10 ml) was treated with [Au(PPh$_3$)(thf)][O$_3$SCF$_3$] (0.030 mmol) in THF (6 ml). After 3 h of stirring, the yellow solution was concentrated under reduced pressure, and diethyl ether added to the solution to give an orange precipitate, which was washed with diethyl ether (3 × 5 ml), and dried under vacuum for 2 h. This product was identified as **2**. Yield of 0.013 g (23%). *Anal.* Found: C, 53.00; H, 3.24. Calc. for C$_{69}$H$_{53}$AuF$_3$O$_3$FeP$_3$PtS: C, 53.11; H, 3.43%.

The supernatant liquid and washings were passed through an alumina column. Addition of 5 ml of petroleum ether yielded yellow crystalline solids, after leaving the solution stand overnight at −20°C. The crystals were washed with petroleum ether (3 × 5 ml), dried under reduced pressure, and identified as **3**. Yield of 0.010 g (30%). *Anal.* Found: C, 52.81; H, 2.98. Calc. for C$_{69}$H$_{53}$AuF$_3$O$_3$FeP$_3$PtS: C, 53.11; H, 3.43%. The spectral data were identical with those of **2** and **3** prepared before.

2.3. X-ray crystallography

Single crystals of **3** were grown from diethyl ether–petroleum ether 1:1 mixture. A yellow crystal (0.45 × 0.30 × 0.15 mm) of the compound was mounted on a glass fiber and used for intensity data collection. For data collection the unit cell dimensions and the orientation matrix were obtained from a least square fit of 25 reflections in the range $8.78 \leq \theta \leq 13.42°$. The automatic intensity search and indexing method indicated a cell belonging to the monoclinic crystal system with a P lattice. X-ray intensity data were recorded on an Enraf–Nonius CAD4 diffractometer employing the ω–2θ scan method with a scan speed of 45 sec/reflection. Every 60 min, the intensity and orientation of three standard reflections were confirmed; the observed intensity decay was less than 1.4% over the data collection. From the Bravais lattice and observed reflections, the space group was chosen to be $P2_1/n$. Lorentz and polarization corrections were made on the intensity data; due to the linear absorption coefficient of 3.96 mm^{-1} a semi-empirical absorption correction based on psi-scans was performed [16].

The structure was solved using the heavy-atom Patterson method employing SHELXS-97 [17] program and all non-hydrogen atoms were located by subsequent Fourier difference synthesis. For structure refinement the SHELXL-97 [18] program was employed and the full-matrix least-squares method minimized on $\Sigma w(F_o^2 - F_c^2)^2$ where w is a weighting scheme indicated below. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atom sites were obtained geometrically and their displacement parameters were refined isotropically on a groupwise basis. For the final refinement of the structure, an isotropic extinction correction was included. The final refinements including 510 parameters converge to $R = 4.15$ and $R_w = 7.32\%$ with the weighting scheme, $w = 1/[s^2(F_o^2) + (0.0291P)^2 + 4.3290P]$ where $P = (F_o^2 + 2F_c^2)/3$.

2.3.1. Crystal data: complex *3*

$C_{50}H_{38}FeP_2Pt$, $M = 951.68$, monoclinic, $a = 14.8059(2)$, $b = 17.6930(3)$, $c = 15.8196(2)$ Å, $\beta = 104.590(2)°$, space group $P2_1/n$, $Z = 4$, $V = 4010.48(10)$ Å^3.

3. Results and discussion

3.1. Synthesis and properties of complexes

Complex $[Pt(C\equiv CPh)_2(dppf)]$ **1** is readily prepared in good yield from $[Pt(C\equiv CPh)_2(cod)]$ [19] with the displacement of cod by dppf ligand (cod = 1,5-cyclooctadiene). Treatment of **1** with less of than 1 equiv. of $[Au(thf)(PPh_3)][O_3SCF_3]$ in THF affords a mixture of $[Pt\{\eta^3\text{-}C(C\equiv CPh){=}C(Ph)AuPPh_3\}(dppf)]^+$ (**2**) and $[Pt(\eta^2\text{-}PhC\equiv CC\equiv CPh)(dppf)]$ (**3**). Concentration of the reactional solution, the less soluble complex **2** is selectively precipitated with diethyl ether. Crystallization of **3** is performed by adding petroleum ether into the supernatant and cooling. An increase in the relative amount of **1** towards two-fold excess in the reaction with $[Au(PPh_3)]^+$ favors the yield of **3**, as the main product. Complex **3** is reasonably stable in the solid state and in solution. Pure **2**, isolated as triflate salt, is stable as a solid, but is thermally unstable for prolonged periods in THF and $CHCl_3$ solutions. An authentic sample of **3** is prepared either by reaction of $[Pt(cod)_2]$ with dppf and 1,4-diphenylbutadiyne in petroleum ether saturated with ethylene or by treatment of $[Pt(C_2H_4)(dppf)]$ with diphenylbutadiyne. An alternative route for a rapid preparation of **2** in good yields is by treatment of **3** with $[Au(PPh_3)]^+$ in a 1:1 ratio.

3.2. Spectroscopic characterization

The IR spectrum of **1** exhibits two weak absorptions at 2132 and 2121 cm^{-1}, which correspond to the stretching frequencies of the *cis*-$Pt(C\equiv CPh)_2$ moiety. Compound **3** shows one band at 2166 cm^{-1} assignable to an uncoordinated alkyne, and another at 1720 cm^{-1}, owing to a carbon–carbon triple bond order is significantly reduced because of the coordination of the alkyne at the platinum atom.

A comparison between the ^1H NMR spectra of **1** (δ 4.19, and 4.32, 1:1) and **2** (δ 4.50, 4.28, and 3.79, 2:1:1) in the region of the cyclopentadienyl ring suggests a decrease in the symmetry of **2**. Whereas the spin system of **2** is AA′BB′CC′DD′, the single peak with double intensity is indeed two unresolved resonances [20]. The ^1H NMR spectrum of **3** exhibits four resonances with equal intensity for the chemically non-equivalent cyclopentadienyl protons and well-solved multiplets in the phenyl proton regions. Quaternary carbon resonances of the alkynyl ligands of **1** are observed at δ 103.4 [J(PtC) 1132 Hz] for C_α and at δ 110.3 [J(PtC) 308 Hz] for C_β in the $^{13}C\text{-}\{^1H\}$ NMR spectrum. These carbons appear as the A part of AXX′ and AMXX′ spin system (M = ^{195}Pt, and X = ^{31}P) of a second-order spectrum, owing to the presence of chemically equivalent but magnetically non-equivalent ^{31}P nuclei.

^{31}P NMR data proved to be very useful for a better characterization of the complexes. Complex **1** displays only a singlet at high field (δ 15.1) with ^1J(PtP) of 2372 Hz, assigned to the phosphorus nuclei of the ligand dppf bound at the platinum atom. The presence of three sets of doublets in the spectrum of **2** reveals three distinct phosphorus nuclei environments. Two of these sets at δ 20.48 and 23.58, with very large platinum coupling constants ^1J(PtP) of 3036 and 4364 Hz, belong to the two P of the dppf. The smallest J(PtP) value is typical of a P atom lying *trans* to the stronger-field vinyl that is structurally well recognized, while the largest J(PtP) value shows a P atom *trans* to the weaker-field coordinated alkyne [21]. Interestingly, **2** has chemical shifts and ^1J(PtP) values near those observed for $[Pt(\eta^3\text{-allyl})(PR_3)_2]^+$ [22], η^3-propargyl–allenyl $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]$ [23], and butadienyl $[Pt(\eta^3\text{-}CH_2CRCCH_2)(dppf)]^+$ [24] complexes. Of particular relevance is the third set at lower field (δ 35.15) with a large J(PtP) 209 Hz, which is tentatively assigned to the P of the spacious $Au(PPh_3)$ moiety bound at the vinyl group of the buta-1,3-diynyl ligand. However, we must bear in mind that we cannot rule out the possibility of an interaction between platinum and gold atoms. Additionally, a coupling constant of this magnitude is compared to those found for sp^3 carbon-bound P in complexes of the type $[Pt\{\sigma{:}\eta^2\text{-}C_8H_{12}(PR_3)\}(dppe)]^+$ (^3J(PtP) 223 Hz) [25], but is larger than in the bridged complex $[Pt_2(\mu\text{-}\eta^2,\eta^2\text{-butadiyne})(PPh_3)_4]$ (^4J(PtP) 34 Hz) [26]. Unfortunately, no single-crystal of **2** was obtained for X-ray analysis. The basic structure of **2** appears analogous to $[Ru(CO)_2\{C(C\equiv CPh){=}C(Ph)HgCl\}Cl(PMe_2Ph)_2]$, which has the HgCl sub-

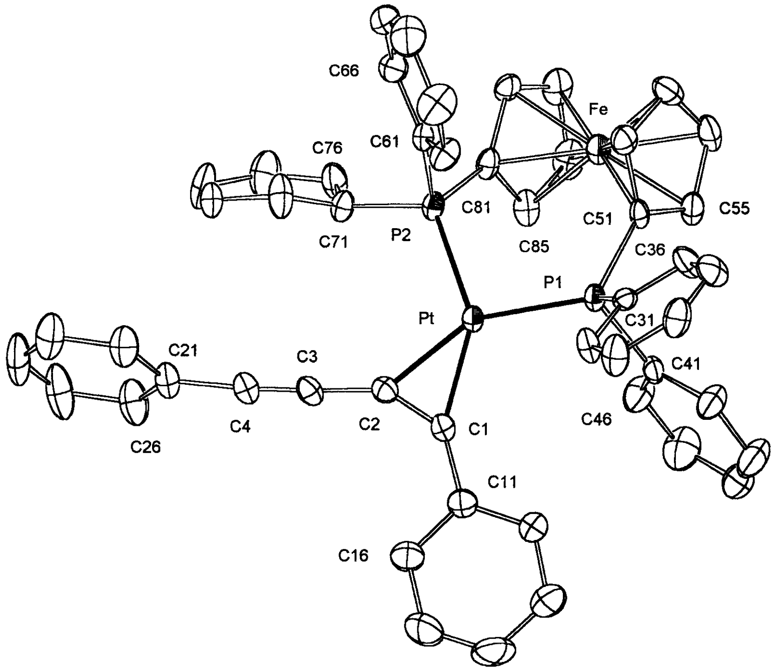


Fig. 1. ZORTEP plot with atom-labeling scheme of the structure of **3**; displacement ellipsoids at the 30% probability level.

stituent at 1-position of the η^1-but-1-en-3-yn-2-yl ligand, and also decomposes slowly in solution releasing $Me_3CC{\equiv}CC{\equiv}CCMe_3$ [27]. Taking into account a comparison between spectroscopic and reactivity data of **2** with known enynyl analogues [28], the compound **2** would be better described as an η^3-enynyl ligand rather than the alternate η^2,η^2 description. On the other hand, the assignment is unambiguous in complex **3**. The two near doublets at 22.1 and 22.9 ppm with large ^1J(PtP) of 3630 and 3371 Hz are typical of complexes $[Pt(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)L_2]$ (L = phosphine ligands) [20]. The identity of **3** is supported by X-ray study and an analogy with early data of η^2-coordinated diyne ligands, in which the complexes have been prepared and in some case structurally characterized by X-ray diffraction studies [29].

3.2.1. *Crystal structure of 3*

The ZORTEP [30] drawing of the molecular structure of **3** is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The list of the observed and calculated structure factors is available from the authors upon request.

The neutral complex shows a trigonal coordination of platinum by the η^2-coordinated Ph–C≡CC≡CPh ligand [Pt–C(1) = 2.050(7), Pt–C(2) = 2.040(7) Å], and the dppf ligand [Pt–P(1) = 2.2714(16), Pt–P(2) = 2.2679(18) Å]. Atoms P(1), P(2), C(2) and C(1) forms a plane (RMS deviation 0.021 Å), from which the Pt atom is moved away by 0.010(2) Å. The Pt atom is distanced 1.94 Å from the center of the C(1)–C(2) bond, and the Pt–C1 and Pt–C2 distances compare well with those reported earlier for acetylene platinum compounds [31]. The P1–Pt–P2 angle of 101.32(2)° is one the most striking feature of this bidentate ligand (95–103° range) [32].

Table 1
Selected bond lengths (Å) and angles (°) for **3** with e.s.d.s in parenthesis

Pt–C(2)	2.040(7)
Pt–C(1)	2.050(7)
Pt–P(2)	2.2679(18)
Pt–P(1)	2.2714(16)
C(1)–C(2)	1.293(9)
C(1)–C(11)	1.432(10)
C(2)–C(3)	1.394(9)
C(3)–C(4)	1.176(9)
C(2)–Pt–C(1)	36.9(2)
C(2)–Pt–P(2)	108.7(2)
C(1)–Pt–P(2)	145.50(19)
C(2)–Pt–P(1)	150.0(2)
C(1)–Pt–P(1)	113.14(19)
P(2)–Pt–P(1)	101.32(6)
C(2)–C(1)–C(1)	138.6(7)
C(2)–C(1)–Pt	71.2(5)
C(11)–C(1)–Pt	150.2(5)
C(1)–C(2)–C(3)	147.0(7)
C(1)–C(2)–Pt	72.0(4)
C(3)–C(2)–Pt	141.0(5)
C(4)–C(3)–C(2)	177.0(9)
Torsion angles	
C(1)–C(2)–P(2)–P(1)	3.0(5)
C(1)–P(1)–P(2)–C(2)	1.08(17)
C(12)–C(11)–C(1)–C(2)	175.7(9)
P(1)–C(51)–C(81)–P(2)	33.8(4)

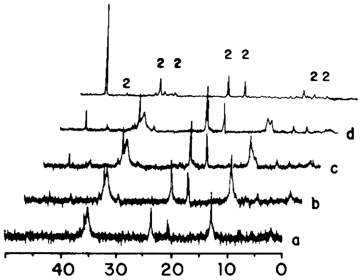


Fig. 2. Monitored ^{31}P-{^{1}H} NMR spectra (ppm) of the reaction mixture obtained by reaction between **1** and $[Au(PPh_3)]^+$ (1:1) in THF at times: (a) 15; (b) 30; (c) 45; (d) 90; (e) 300 min. The numbers **2** are the peaks due to this complex.

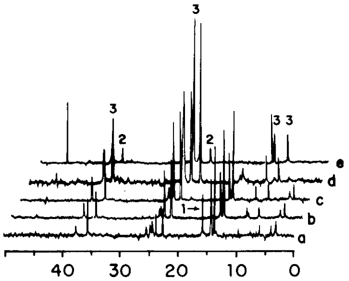


Fig. 3. Monitored ^{31}P-{^{1}H} NMR spectra (ppm) of the reaction between **1** and $[Au(PPh_3)]^+$ (2:1) in THF at times: (a) 15; (b) 30; (c) 45 min; (d) 3; (e) 12 h. The numbers **1**, **2**, and **3** are peaks due to these complexes.

Due to the η^2-coordination, the C(1)–C(2) distance is elongated to 1.293(9) compared with 1.176(9) Å for the alkynyl fragment C(3)–C(4) with C–C-triple bond character, and C(1) becomes sp^2-character [C(2)–C(1)–C(11) = 138.6(7)°].

The ferrocenyl group deviates slightly from the local D_{5d} point symmetry demonstrated by the torsion angle P(1)–C(51)–C(81)–P(2) of 33.8(4)° and the observed angle of 2.7(2)° between both cyclopentadienyl rings. These five membered rings are essentially planar: C(51)–C(52)–C(53)–C(54)–C(55) (RMS deviation 0.0035 Å) and C(81)–C(82)–C(83)–C(84)–C(85) (RMS deviation 0.0014 Å), from which the Fe(II) ion is moved away by 1.640(3) and 1.642(3) Å, respectively.

All phenyl rings are almost planar with an average RMS deviation of 0.0201 Å. One of these phenyl rings is partially disordered in that atoms C(74), C(75) and C(76) split over to the alternative positions of atoms C(74A), C(75A) and C(76A) hawing complementary occupancy factors of 43, 45 and 47%, respectively.

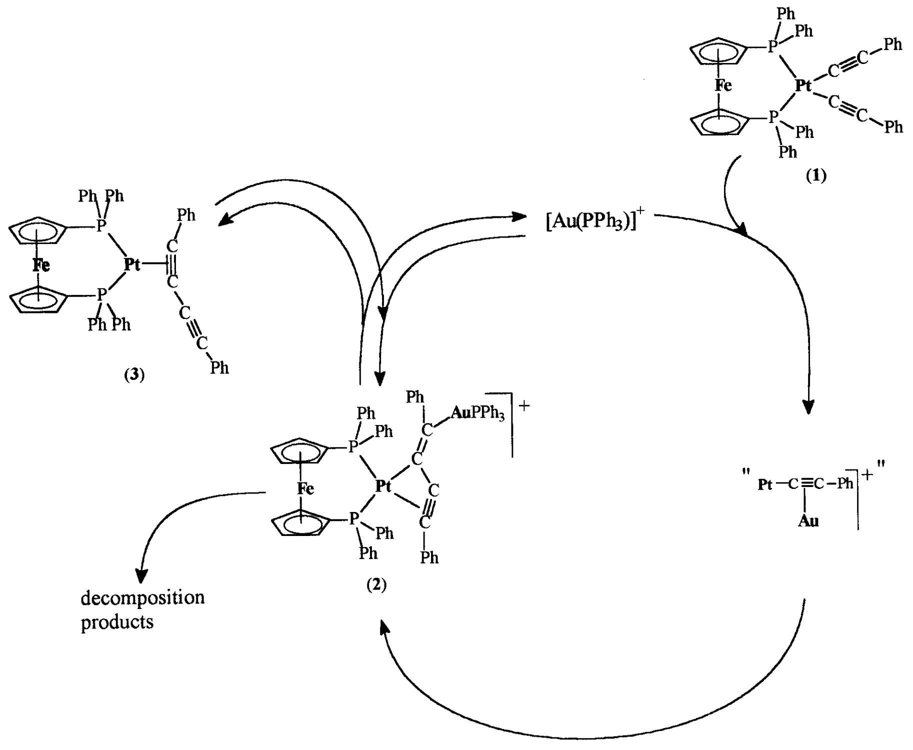
3.2.2. The course of the reactions followed by ^{31}P NMR

One characteristic of the reactional system is the formation of species that resonate in different regions of the ^{31}P NMR spectrum, allowing the stages of the reactions to be monitored. Moreover, the previous spectroscopic data of the isolated species **1**–**3** have supported the assignments (see under Section 2). Decomposition products of **2**, detected in the solution by ^{31}P NMR data in Figs. 2 and 3, were an unidentified phosphine–gold product of $[Au(PPh_3)]^+$, which resonates at 45.5 ppm in the expected high-frequency region of gold complexes [33] and $[Pt(dppf)(H_2O)_2]^{2+}$ at 9.7 ppm [34].

Reaction between $[Au(PPh_3)]^+$ and **1** in equimolar amounts in THF, shown in Fig. 2, is accompanied by immediate growth of the resonances assigned to **2** [δ 20.4, 23.6 (P_2Pt), and 35.1 (PAu)]. The set of resonances observed at δ 35 (PAu), and at δ 13 (P_2Pt, ^1J(PtP) 2620 Hz), which disappears completely within 3–5 h, is assigned to the intermediate with gold π-coordinated at C≡C bonds of the $(dppf)Pt(C{\equiv}CPh)_2$ moiety. The assignment is in line with data for analogous systems, whereas the addition of electrophiles to the electron-rich β-carbon of metal acetylides is the best entry into vinylidene and enynyl complexes [35]. The activation of C≡C bonds by $Au(PPh_3)^+$ would allow further rearrangements, as shown in Scheme 1. The signals associated with **1** (15.1 ppm), $[Au(PPh_3)]^+$ (30.2 ppm), and **3** (22.1, and 22.9 ppm) were not detected in all these spectra. Therefore, the product **2**, without the participation of **1**, does not rearrange into butadiyne complex **3**.

The time evolution of the ^{31}P-{^{1}H} NMR spectra recorded for the reaction between **1** and $[Au(PPh_3)]^+$ in 2:1 molar ratio in THF are shown in the Fig. 3. Transient resonances of the precursor complex **1** remain for more than 30 min, while increase the characteristic signals of **3**. The extra set of close signals that arises at 13.5 ppm (^1J(PtP) = 2585 Hz) and 14.0 ppm (^1J(PtP) = 2504 Hz), and a unique singlet at 35.5 ppm (PAu) may now be attributed to two intermediates. Probably, an intermediate has a gold atom coordinated at C≡C bonds of two *cis*-$Pt(C{\equiv}C)_2$ moieties, because there is no signal for bonded PPh_3. Signals of **2** appear only after 45 min of reaction, and remain approximately constant during the measurements, while resonances of **3** grow significantly until becoming predominant at the end of the reaction. Subsequent spectra, registered over 1 day, reveal a nearly complete conversion of the precursors into the major complex **3**. Occasionally, such spectra exhibited an extra resonance at 34.2 ppm from residual $[Au(PPh_3)Cl]$, which eliminates the presence of silver derivatives of **1** in solution. Therefore, when **1** is initially employed in excess, a second reaction between **2** and **1** occurs to produce **3**.

A reaction of **1** with **2** (1:1 ratio) has been carried out in THF to better understand the contribution of **2** to the overall-reaction. ^{31}P NMR spectra show immediate formation of **3** and the usual intermediates (at 13.5, 14.0, and 35.5 ppm), which converts into **2** during reaction (Fig. 4). As the signal of $[Au(PPh_3)]^+$ (30.2



Scheme 1. Pathways to the reaction between **1** and $[Au(PPh_3)]^+$ in THF.

ppm) is not present in all spectra, such results provide a diagnostic indication that the rapid rearrangement step of **2** to **3** depends strongly on the presence of **1** for sequestering $[Au(PPh_3)]^+$ from **2**. Inversely, since $[Au(PPh_3)]^+$ also promptly reacts with **3**, any trace of unreacted $[Au(PPh_3)]^+$ in solution is consumed by available **1** or **3**, closing the formal reaction cycle. This emergent result reinforces the conclusion that the reaction of **3** by $[Au(PPh_3)]^+$ leads to the gold derivative of a but-1-en-3-yn-2-yl ligand. Therefore, the reduction/oxidation occurs reversibly in these two stages under mild condition as a very facile process (see Scheme 1). Particularly interesting for the comprehension this reaction process with electrophilic gold was the protonation at a coordinated carbon of 1,4-diphenylbutadiyne ligand of the zerovalent complex $[Ru(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_2(PPh_3)_2]$ [36]. Moreover, reactions of hydrides $[RuH(O_2CCF_3C)(CO)(PPh_3)_2]$ [5b] and $[(PP_3)Ru(H)(H_2)][BPh_4]$ [37] with 1,4-diphenylbutadiyne also have provided an alternate synthetic method for 1,4-diphenylbut-1-en-3-yn-2-ylruthenium(II) complexes.

Considering these facts, the proposed reaction pathways for formation of products are now outlined in Scheme 1.

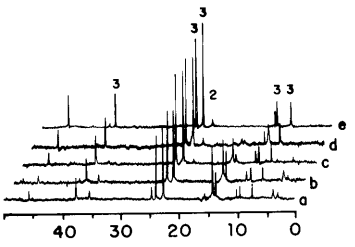


Fig. 4. Monitored $^{31}P\text{-}\{^1H\}$ NMR spectra (ppm) of the reaction between **1** and **2** (1:1) in THF at times: (a) 15; (b) 30 min; (c) 1.50; (d) 5; (e) 12 h. The numbers **2** and **3** are the peaks due to these complexes.

4. Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 133546. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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