



REGULAR ARTICLE

Synthesis and characterization of platinum 1,4-bis(ethynyl)benzene complexes

MOHAMMAD EL-KHATEEB^{a,*}, HAYATO MORIYAMA^b, YUKIHIRO YOSHIDA^b and HIROSHI KITAGAWA^b

^aChemistry Department, Jordan University of Science and Technology, Irbid 22110, Jordan

^bDivision of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

E-mail: kateeb@just.edu.jo

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Abstract. The reactions of $(P)_2PtCl_2$ with a large excess of 1,4-bis(ethynyl)benzene catalyzed with copper(I) iodide gave $(P)_2Pt(C\equiv CC_6H_4C\equiv CH)_2$ [$P = PPh_3, \frac{1}{2} (Ph_2PC_5H_4)_2Fe(dppf)$] in high yields. The corresponding 1:2 metal to ligand ratio reaction produced unidentified orange solids. The complexes $(P)_2Pt(C\equiv CC_6H_4C\equiv CH)_2$ have been characterized by IR, 1H -NMR, $^{13}C\{^1H\}$ -NMR, $^{31}P\{^1H\}$ -NMR spectroscopy and elemental analysis. Their crystal structures were determined by X-ray structure determination.

Keywords. Platinum; Complexes; 1,4-Bis(ethynyl)benzene; Structures; Characterization.

1. Introduction

Transition-metal alkynyl complexes have attracted considerable current interest because of their electronic properties.^{1–5} These complexes exhibit a variety of unusual structural, electrical and optical properties.^{6–8} They are considered as linear rigid frameworks which function as molecular wires and are widely used for the fabrication of molecular nanostructures.^{9–11}

Platinum alkynyl complexes were first prepared in the mid-70s and since then many examples have been reported with a variety of alkynes and phosphine or amine supporting ligands.^{12–14} Complexes of the type $L_2Pt(C\equiv CR)_2$ ($L = PPh_3, PEt_3, P^nBu_3, PMePh_2, PMe_2Ph, \frac{1}{2} Ph_2P(CH_2)_2PPh_2$; $R =$ alkyl, aryl, silyl) were synthesized by two major methods.^{15–22} The first method involves chloride displacement of L_2PtCl_2 by the acetylide anions that are generated from acetylenes with weakly acidic hydrogen and an appropriate base. The second major method is a Sonogashira-Hagihara coupling reaction of acetylenes with L_2PtCl_2 catalyzed by copper iodide in the presence of a base. In the case of monophosphine ligands (PR_3), the products are of *trans* geometry even though *cis* starting materials are used. The

cis products may form and quickly rearrange to the more stable *trans* configuration.¹⁸ For chelating diphosphines (e.g. 1,2-bis(diphenylphosphino)ethane; dppe), the products are restricted to the *cis* configuration.¹⁷

The CuI catalyzed reactions of *trans*- $(P^nBu_3)_2PtCl_2$, $(dppe)PtCl_2$ or $(Me_2bipy)PtCl_2$ ($Me_2bipy = 4,4$ -dimethyl-2,2-bipyridine) with the acetylenic sulfide $HC\equiv CSC\equiv CSi^iPr_3$ in the presence of a base produced the corresponding disubstituted alkynyl complexes *trans*- $(P^nBu_3)_2Pt(C\equiv CSC\equiv CSi^iPr_3)_2$, $(dppe)Pt(C\equiv CSC\equiv CSi^iPr_3)_2$ or $(Me_2bipy)Pt(C\equiv CSC\equiv CSi^iPr_3)_2$, respectively.²³ Similar products using the polyyne sulfide $HC\equiv CSC\equiv CC\equiv CSC\equiv CSi^iPr_3$ are obtained from its reactions with the same platinum dichlorides. Dimeric derivatives of the formula *trans*- $[Ph(Et_3P)_2PtC\equiv CSC\equiv CPt(PEt_3)_2Ph]$ and *trans*- $[Ph(Et_3P)_2PtC\equiv CSC\equiv CC\equiv CSC\equiv CPt(PEt_3)_2Ph]$ were also synthesized in moderate yields by reactions of two equivalents of *trans*- $[PtPh(Cl)(PEt_3)_2]$ and the di-terminal acetylenic sulfides in a $CuI/(Me_3Si)_2NH$ system.²³

Bi-functional alkynes ($HC\equiv CYC\equiv CH$: $Y =$ pyridine, phenylene, thiophene, 2-(2-thienyl)-pyridine, 2,5-bis(2-thienyl)pyridine, 6,6-bis(2-thienyl)-3,3-bipyridine, 1,4-bis(trimethylsilylethynyl)naphthalene,

*For correspondence

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1,4-bis(ethynyl)naphthalene, 9,10-bis(trimethylsilylethynyl)anthracene, 9,10-bis(ethynyl)anthracene, 2,3-ethynyl-5,7-thieno[3,4-b]pyrazine) undergo coupling reactions with platinum species giving dimeric or polymeric complexes depending on the platinum species.^{24–28} In the case of mono chloro complexes; *trans*-[(R₃P)₂Pt(Ph)Cl] (R= R, ⁿBu), the reaction with dialkynes in a mixture of ¹Pr₂NH/CH₂Cl₂ and in the presence of CuI, afforded the dimers *trans*-[Pt(R₃P)₂Pt-C≡CYC≡C-Pt(PR₃)₂Ph].^{24–28} However, dichloro platinum species (PR₃)₂PtCl₂ reacted with the dialkynes under similar conditions affording the *trans*-[-(PR₃)₂Pt-C≡CYC≡C-]_n polymers.^{29–32} These dimers and polymers are easily cast into thin films. Optical spectroscopic measurements of these materials display varying degrees of donor-acceptor interactions between the metal centers and the conjugated ligands depending on the electronic nature of the Y group. Thermogravimetric analysis showed that the dimers have higher thermal stability than the corresponding polymers. The intra-molecular charge-transfer of the latter materials facilitate manipulation of the electronic structure, leading to small bandgap semi-conducting materials.^{24–32}

The CuI catalyzed interaction of (dppe)PtCl₂ with a large excess of HC≡CYC≡CH (Y= 1,4-C₆H₄, 4,4'-C₆H₄-C₆H₄) afforded the monomeric complexes (dppe)Pt(C≡CYC≡CH)₂ as the major products with the dimeric complexes (HC≡CYC≡C)Pt(dppe)(C≡CYC≡C)Pt(dppe)(C≡CYC≡CH) as the minor products.³³ However, the 1:1 equivalent ratio of (dppe)PtCl₂ with the dialkynes produced oligomeric species [-(dppe)Pt(C≡CYC≡C)-] in reasonable yields.³³

In this contribution, we investigated the reaction of (P)₂PtCl₂ [P= PPh₃, ½ (Ph₂PC₅H₄)₂Fe (dppf)] with different equivalents of 1,4-bis(ethynyl)benzene. Monomers of the type (P)₂Pt(C≡CC₆H₄C≡CH)₂ were obtained when an excess of the dialkyne was used and polymeric unidentified species were produced when one or two equivalents of the dialkyne were used.

2. Experimental

2.1 Materials and methods

Reactions and manipulations were carried out under an inert atmosphere of dinitrogen. Dichloromethane and hexane of super-dry quality were used as received. 1,4-Bis(ethynyl)benzene, di-*iso*-propylamine and copper(I) iodide were purchased from Aldrich or TCI.

The compounds (P)₂PtCl₂ [P= PPh₃, ½ dppf] were prepared according to reported procedures.^{34,35}

The NMR spectra were measured with JEOL JNM-ECA 600 MHz spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) for ¹H NMR, the solvent peak for ¹³C{¹H} NMR and relative to external H₃PO₄ for ³¹P{¹H} NMR. The Fourier transform infrared (FT-IR) spectra were recorded with KBr pellet on a Thermo Nicolet Nexus 670 FT-IR spectrometer. Elemental analyses were performed at the Elemental Analysis Center of the Faculty of Pharmaceutical Science, Kyoto University. The intensity data of X-ray diffraction peaks were collected on a Rigaku XtaLAB P200 diffractometer using Mo K α radiation (λ = 0.71073 Å) fitted with SHELXTL for structure determination.³⁶ Direct method using SHELXS-2014 was employed to solve the structure and Fourier transformation was carried out using SHELXL-2014 employing full-matrix least-square refinement calculations.³⁷

2.2 General procedure for the preparation

of (P)₂Pt(C≡CC₆H₄C≡CH)₂ [P= PPh₃ (**1**), ½ dppf (**2**)]

Platinum complex (PPh₃)₂PtCl₂ or (dppf)PtCl₂ (0.20 g, 0.25 mmol) and the 1,4-bis(ethynyl)benzene (0.19 g, 1.50 mmol) were dissolved in a mixture of 20 mL di-*iso*-propylamine and 40 mL of dichloromethane. A catalytic amount of copper iodide (4 mg) was added and the resulting mixture was stirred overnight under nitrogen gas. The volatiles were removed under vacuum. The residual solid was extracted with dichloromethane (3 × 5 mL), filtered and layered with hexane. The mixture was kept at -4 °C overnight resulting in the formation of crystals of the products.

2.2a (PPh₃)₂Pt(C≡CC₆H₄C≡CH)₂, **1**: Yellow (85%). IR (KBr, cm⁻¹): ν_{C-H} 3290 (m); $\nu_{C\equiv C}$ 2099 (m). ¹H-NMR (600 MHz, CDCl₃): δ 2.99 (s, 2H, CH); 6.19 (m, 4H, C₆H₄, J_{HH} = 6 Hz); 7.05 (m, 4H, C₆H₄, J_{HH} = 6 Hz); 7.34 (m, 18H, PPh₃); 7.76 (m, 12H, PPh₃). ³¹P{¹H}-NMR (243 MHz, CDCl₃): 19.26 (J_{P-P} = 2705 Hz). ¹³C{¹H}-NMR (150 MHz, CDCl₃): δ 64.32 CH; 117.60 C≡C; 127.94-135.11 Ph. Anal. Calc. for C₅₆H₄₀P₂Pt·½CH₂Cl₂: C, 67.03; H, 4.08%. Found: C, 66.24; H, 4.59%.

2.2b (dppf)Pt(C≡CC₆H₄C≡CH)₂, **2**: Yellow (90%). IR (KBr, cm⁻¹): ν_{C-H} 3282 (m); $\nu_{C\equiv C}$ 2102 (m). ¹H-NMR (600 MHz, CDCl₃): δ 3.00 (s, 2H, CH); 4.17 (d, 4H, C₅H₄, J_{HH} = 9 Hz); 4.31 (d, 4H, C₅H₄, J_{HH} = 9 Hz);

6.68 (d, 4H, C₆H₄, J_{HH} = 6 Hz); 7.18 (m, 4H, C₆H₄, J_{HH} = 6 Hz); 7.29 (m, 8H, PPh₃); 7.37 (m, 4H, PPh₃); 7.61 (m, 8H, PPh₃). ³¹P{¹H}-NMR (243 MHz, CDCl₃): 15.22 (J_{PtP} = 2391 Hz). ¹³C{¹H}-NMR (150 MHz, CDCl₃): δ 64.39 CH; 118.22 C≡C; 72.69, 75.70 C₅H₄; 128.00–134.88 Ph. Anal. Calc. for C₅₄H₃₈FeP₂Pt·½CH₂Cl₂: C, 62.81; H, 3.77%. Found: C, 62.81; H, 4.04%.

2.3 Crystal structure determination of **1** and **2**

2.3a Crystallographic data for 1: C₅₆H₄₀P₂Pt, Mr = 969.91 g mol⁻¹, yellow plate, monoclinic, space group *I*2/*m*, *a* = 11.2146(3), *b* = 8.3836(2), *c* = 23.1286(7) Å, β = 102.426(3)°, *V* = 2123.59(11) Å³, *T* = -173(2) °C, *Z* = 2, ρ_{calcd.} = 1.517 g cm⁻³, μ (Mo K_α) = 3.418 mm⁻¹, *F*(000) = 968, 3057 independent reflections 323 refined parameters, *R*₁ = 0.0271 [for *I* > 2σ(*I*)], *wR*₂ = 0.0630 (for all data), GOF = 1.081, largest difference peak and hole: 2.42 / -1.44 e Å⁻³, CCDC 2046541.

2.3b Crystallographic data for 2: C₅₆H₃₈FeP₂Pt, Mr = 999.72 g mol⁻¹, yellow block, triclinic, space group *P*-1, *a* = 10.6721(3), *b* = 13.7177(4), *c* = 15.3174(4) Å, α = 85.458(2)°, β = 72.986(3)°, γ = 87.065(2)°, *V* = 2136.61(11) Å³, *T* = -173(2) °C, *Z* = 2, ρ_{calcd.} = 1.554 g cm⁻³, μ (Mo K_α) = 3.721 mm⁻¹, *F*(000) = 992, 11485 independent reflections, 744 refined parameters, *R*₁ = 0.0273 [for *I* > 2σ(*I*)], *wR*₂ = 0.0655 (for all data), GOF = 1.049, largest difference peak and hole: 2.40 / -1.73 e Å⁻³, CCDC 2046542.

3. Results and Discussion

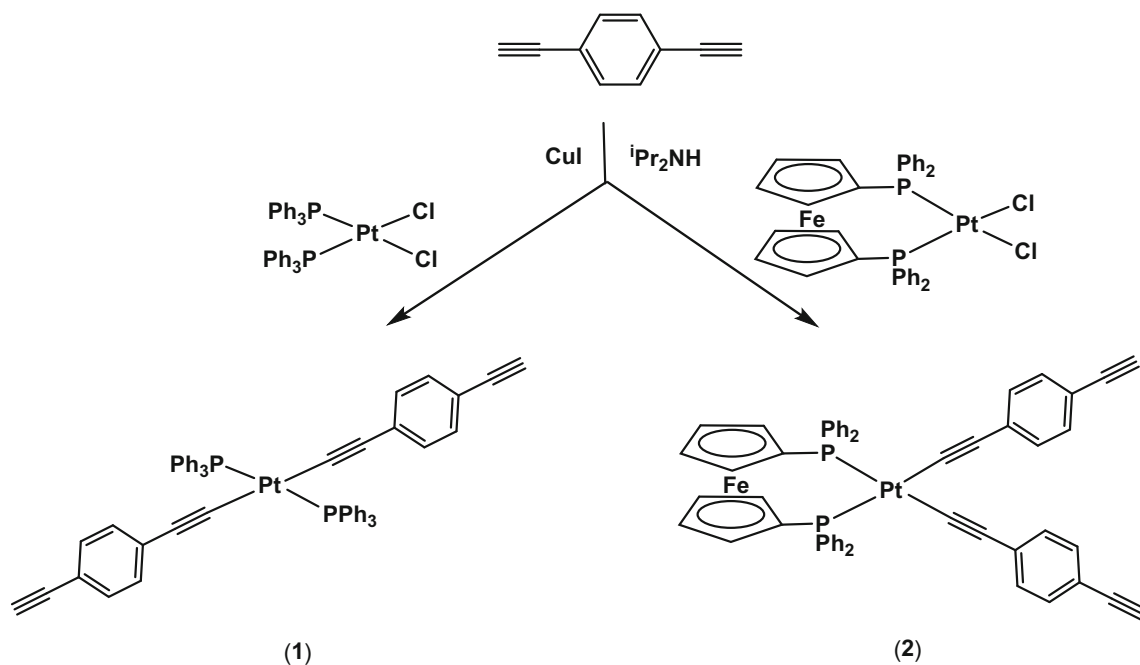
3.1 Synthesis of complexes

The coupling reactions of (P)₂PtCl₂ with a large excess of 1,4-bis(ethynyl)benzene are catalyzed by copper iodide and gave (P)₂Pt(C≡CC₆H₄C≡CH)₂ [P = PPh₃ (**1**), ½ dppf (**2**)] in high yield as shown in Scheme 1. A plausible mechanism for the formation of the products is presented in Scheme 2. Copper iodide is added as a catalyst to activate the C(sp)-H bond *via* the oxidative addition step. Then, the transmetalation step of the Cu-acetylide with the platinum dichloride occurred generating the products and Cu(II) salt. The latter losses chloride regenerating the Cu(I) catalyst.^{38,39} If the metal to ligand ratio is reduced to 1:2, the only orange polymeric material is obtained.

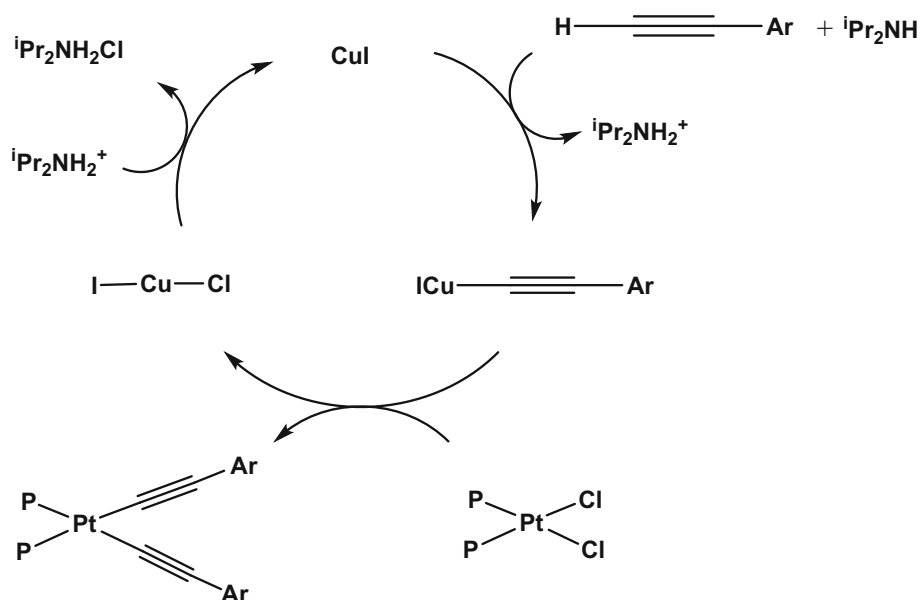
The yellow complexes **1** and **2** were identified based on their IR, ¹H-NMR, ³¹P{¹H}-NMR, ¹³C{¹H}-NMR spectroscopies, elemental analysis as well as X-ray structure determination. The complexes are soluble in common organic solvents and insoluble in hydrocarbons. They are air-stable solids and also stable in solution. Their IR spectra exhibited a band for the stretching frequency of the acetylenic C-H group in the range of 3282–3290 cm⁻¹ and another band in the range of 2099–2102 cm⁻¹ for the C≡C groups. These two bands are very comparable to those observed for the corresponding dppe complex (dppe)Pt(C≡CC₆H₄C≡CH)₂.³³ The ¹H-NMR spectra of complexes **1** and **2** displayed a singlet peak for the acetylenic protons at 2.99 and 3.00 ppm, respectively. These values are also comparable to those of (dppe)Pt(C≡CArC≡CH)₂ (Ar = C₆H₄, biphenyl).³³ The phenyl protons of the acetylenic group are present in the spectra as two doublets (**1**: 6.19, 7.05 and **2**: 6.68, 7.18 ppm). In addition to these peaks, the spectrum of **2** presented additional two doublets (4.17, 4.31 ppm) for the two proton types of the Cp-rings of the dppf ligand. Both spectra indicated the presence of the aromatic protons of the phosphine ligands in the expected region and multiplicity. The ³¹P{¹H}-NMR spectrum of **1** showed a singlet at 19.26 ppm with Pt-satellites (J_{PtP} = 2705 Hz). This singlet is at a higher value compared to that of **2** at 15.22 (J_{PtP} = 2391 Hz) indicating more electron density around Pt in **2**. These chemical shift values are higher than those of the corresponding values of the dithiolate complexes (P)₂Pt(SR)₂.^{35,36} The platinum-phosphorus compiling indicated that complex **1** is in a *trans* geometry while that of **2** is in a *cis* geometry. In the ¹³C{¹H}-NMR spectra of **1** and **2**; the peaks in the 64.32–64.39 and 117.6–118.22 ppm ranges are due to the acetylenic carbons, while the peaks in the range 127.99–135.88 ppm are due to the phenyl protons of the acetylenic and phosphine ligands. The spectrum of **2** showed additional two peaks at 72.69 and 75.70 ppm for the carbon atoms of the Cp-rings of the dppf ligand.

3.2 Crystal structures of **1** and **2**

The molecular structure of **1** is shown in Figure 1 and has a *trans* geometry as expected for (PPh₃)₂Pt containing complexes. The structure is highly disordered and only one orientation of the disordered atoms is shown in Figure 1 while Figure S9 (Supplementary Information) showed the disordered structure. The complex displayed a square planar configuration around the Pt coordinated with two P and two



Scheme 1. Synthesis of platinum acetylide complexes **1** and **2**.



Scheme 2. Mechanism of the formation of **1** and **2** from the corresponding chlorides showing the role of CuI.

C-atoms. The P-Pt-P and C-Pt-C angles ($\approx 180^\circ$) prove the *trans* geometry of the molecule. The Pt-P bond distance (2.297(7) Å) and the Pt-C bond length (2.000(6) Å) are similar to those of **2** (*vide infra*) and to the corresponding lengths of analogous complexes.^{33,35} The acetylenic C≡C bond distance of the coordinate group is 1.217(8)° slightly longer than the uncoordinated one of 1.179(8)°.

Single crystals of **2** suitable for X-ray diffraction analysis were obtained from a mixed solvent (CH₂Cl₂/hexane). The structure is highly disordered and only one orientation of the disordered atoms is shown in Figure 2 while Figure S10 (Supplementary Information) showed the disordered structure. The complex displayed a square planar configuration at Pt as indicated from the P-Pt-P (100.17(2)°), P-Pt-C (84.62(7),

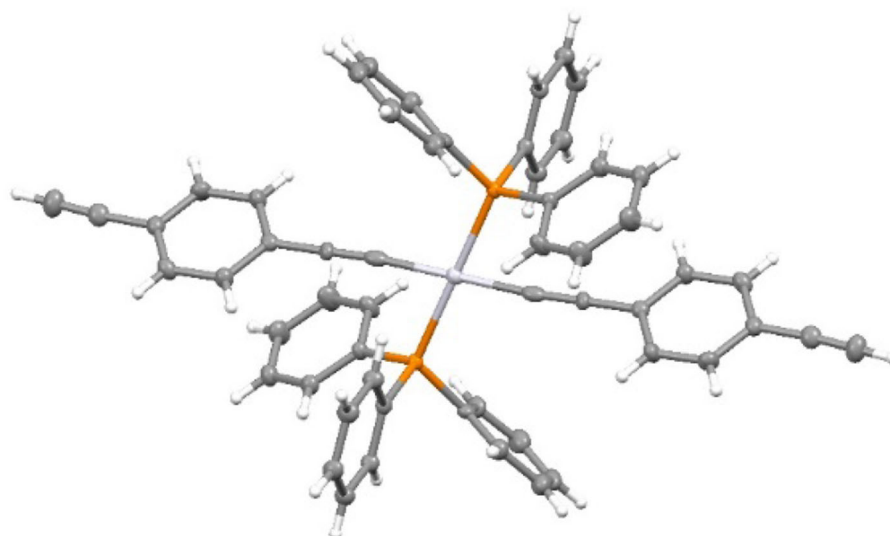


Figure 1. Molecular structure of **1** determined by X-ray diffraction (gray: C, white: H, orange: P, silver: Pt). Only one orientation of the disordered 1,4-bis(ethynyl)benzene and triphenylphosphine groups is shown.

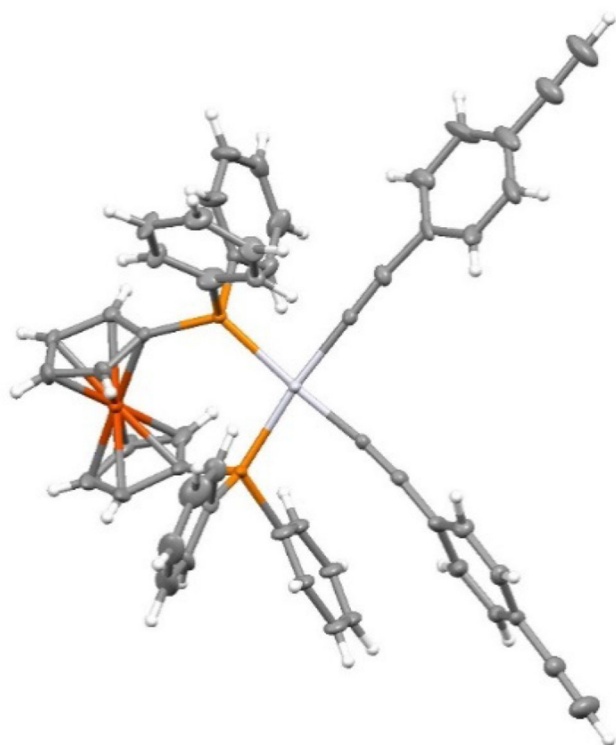


Figure 2. Molecular structure of **2** determined by X-ray diffraction (gray: C, white: H, red: Fe, orange: P, silver: Pt). Only one orientation of the disordered 4-ethynylphenyl groups and phenyl rings is shown.

85.76(7)° and C-Pt-C (89.77(10)°) angles. The P-Pt-P angle is quite higher than that of the dithiolates (dppf)Pt(SR)₂ (95.96-98.25) which may be due to a larger size of the alkyne ligand.³⁵ The Pt-P bond

distances are 2.2985(7) and 2.3165(6) Å while the Pt-C bond lengths are 2.001(3) and 2.010(3) Å. These bond lengths are similar to the corresponding lengths of analogous complexes.³³ The Fe-C(Cp) bond distances ranging from 2.010(3)-2.061(3) Å are similar to the corresponding lengths of analogous complexes.

4. Conclusions

In summary, the coupling reactions of (P)₂PtCl₂ with 1,4-bis(ethynyl)benzene produced (P)₂Pt(C≡CC₆H₄-C≡CH)₂ when an excess of the alkyne was used and orange unidentified materials when equivalent amounts of the reactants were used. The products displayed a square planar geometry around the Pt in which **1** displayed a *trans* geometry while **2** has a *cis* one. The spectroscopic data for the monomeric complexes were reported and found to be similar to those reported for analogous complexes.

Supplementary Information (SI)

Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC-2046541 for **1** and 2046542 for **2** contain the supplementary crystallographic data excluding structure factors; this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Figures S1-S10 are available at www.ias.ac.in/chemsci.

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