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Synthesis of palladium and platinum donor complexes and study of their participation in self-assembly reactions. X-ray crystal structure of [Pt(C$_6$H$_4$C≡CC$_5$H$_4$N)$_2$(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane)

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Abstract

Novel square-planar compounds [M(NC$_5$H$_4$C≡CH)$_2$(dppp)](OTf)$_2$ (M = Pd (**1**), Pt (**2**)), [Pt(C≡CC$_6$H$_4$CN)$_2$(dppp)] (**3**) and [Pt(C$_6$H$_4$C≡CC$_5$H$_4$N)$_2$(dppp)] (**4**) (dppp = 1,3-bis(diphenylphosphino)propane) were prepared and characterised. Their potential as building blocks in the generation of heterobimetallic squares was studied. The reaction of **4** and the ditopic acceptor species [Pd(H$_2$O)$_2$(dppf)](OTf)$_2$ enabled a tetrametallic metallocycle containing two platinum and two palladium atoms to be obtained. The crystal X-ray structure of **4** shows that the Pt···N vectors are nearly perpendicular, and confirm the suitability of the compound to act as a corner unit for the construction of molecular squares.
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Keywords: Supramolecular chemistry; Self-assembly; Metalloligand; Platinum; Palladium; Diphosphine
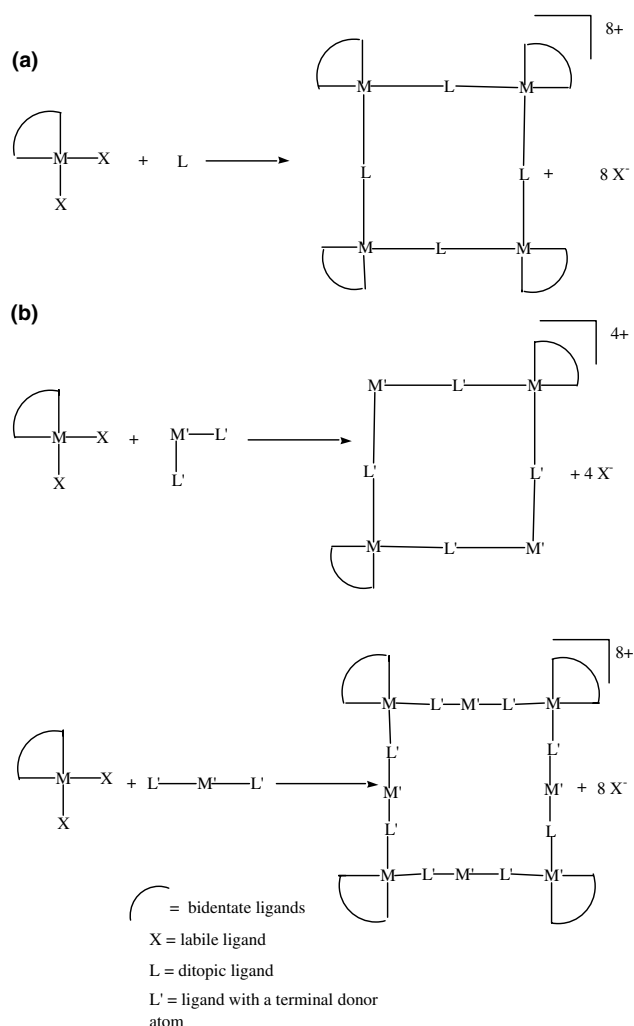
1. Introduction

The preparation of organised nanostructures based on molecular self-assembly, employing coordination as motif, has undergone rapid growth and aroused widespread interest in recent years [1]. In particular, transition-metal directed self-assembly has been used to construct a number of 2D polygons, as well as more complex structures [2].

A general strategy for the construction of palladium- or platinum-containing molecular squares consists of the reaction of a linear ditopic organic ligand L, that contains two reactive sites at a 180° angle from each other, with a *cis*-square planar metal complex having two adjacent weakly labile ligands X, such as triflate or nitrate, as well as a bidentate ligand (Scheme 1(a)). In general, self-assembly reactions to form molecular squares proceed most efficiently under conditions of high dilution since increased concentrations afford polymeric species. Although a huge number of homometallic species prepared by this method have been described so far [3], the synthesis of heterometallic molecular squares requires some modifications. In the latter case, the linker L could be replaced by: (i) a *cis*-square planar or octahedral metal complex with two ligands L′, able to react through a donor atom located at the unbounded end, or (ii) a metal complex having at least two ligands L′ containing reactive sites at a 180° angle from each other. Briefly, two transition metal complexes should be used: one to act as acceptor [MX$_2$(bidentate)], and the other,

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(a)

(b)

= bidentate ligands

X = labile ligand

L = ditopic ligand

L' = ligand with a terminal donor atom

Scheme 1.

either *cis*-[M'L$_2'$ (other ligands)], [M'L$_2'$] or *trans*-[M'L$_2'$ (other ligands)], as donor. The self-assembly of both species will lead to heterobimetallic squares (Scheme 1(b)).

The limitation of the latter method arises from the lack of this kind of donor species or "metalloligands", since in most cases, these complexes have to be specially designed to act as suitable building blocks in self-assembly reactions with the already described bis(triflate) or bis(nitrate) platinum and palladium complexes. As a result, there are far fewer palladium or platinum-containing heterobimetallic molecular squares than homometallic ones. To our knowledge, only a small number of compounds have been used in the preparation of the desired heterobimetallic metallacycles: [Pt(C$_6$H$_4$CN)$_2$(dppp)], [Pt(C≡CC$_5$H$_4$N)$_2$(L)] (L = dppp, DIOP) [4], [Ti(η-C$_5$H$_5$)(O$_2$CC$_5$H$_4$N)$_2$] [5], [Ru-(pyterpy)$_2$(PF$_6$)$_2$] [6], fac-[ReCl(CO)$_3$(N-N)$_2$] [7], [Ru(2,2'-bipy)$_2$(N–N)]Cl$_2$ [8], *trans*-[PtI$_2$(CNC$_6$H$_2$-(*i*-Pr)$_2$-2,6-(C≡CC$_5$H$_4$N-4)-4)$_2$] [9] and *cis*-[Re$_2$Cl$_2$-
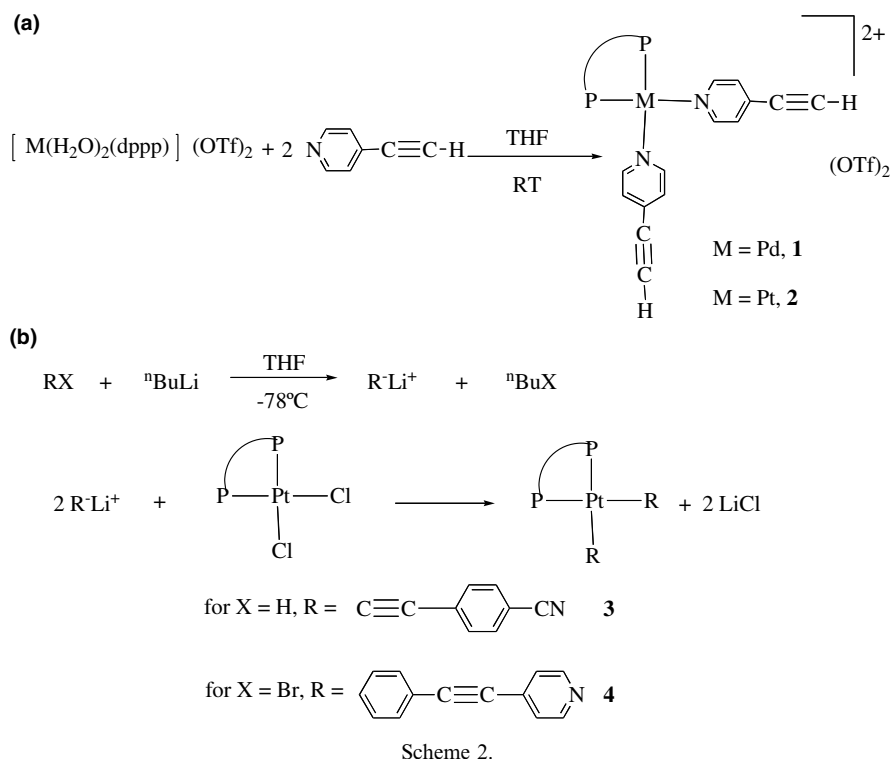
(μ-dppm)$_2$(μ-O$_2$CC$_5$H$_4$N)$_2$] [10]. Interestingly, the obtention of other heterobimetallic square molecular compounds following related strategies has been reported [11]. Given that palladium- or platinum-containing square molecular complexes are relevant to homogeneous catalysis and materials science and processes such as molecular recognition, we undertook our study in order to gain insight into this growing field. Here we report the synthesis of the new "metalloligand" species [M(NC$_5$H$_4$C≡CH)$_2$(dppp)](OTf)$_2$, [Pt(C≡CC$_6$H$_4$CN)$_2$(dppp)] and [Pt(C$_6$H$_4$C≡CC$_5$H$_4$N)$_2$(dppp)] (M = Pd, Pt; dppp = 1,3-bis(diphenylphosphino) propane), and the study of their use as building blocks for the synthesis of new heterobimetallic molecular squares.

2. Results and discussion

2.1. Synthesis and characterisation

The cationic compounds [M(NC$_5$H$_4$C≡CH)$_2$(dppp)] (OTf)$_2$ (M = Pd (**1**), Pt (**2**); dppp = 1,3-bis(diphenyl-phosphino)propane) were synthesised by displacement of the aqua ligands from [M(H$_2$O)$_2$(dppp)](OTf)$_2$ by 4-ethylnylpyridine in THF at room temperature. **1** and **2** were isolated as white solids in excellent yields (Scheme 2(a)). The preparation of [Pt(dppp)(C≡C- C$_6$H$_4$CN)$_2$] (**3**) and [Pt(dppp)(C$_6$H$_4$C≡CC$_5$H$_4$N)$_2$] (**4**) required the prior generation, by treatment with *n*BuLi in THF at −78 °C, of the organolithium derivatives from 4-ethynylbenzonitrile and 4-(4-bromophenylethynyl)pyridine, respectively, followed by the addition of solid [PtCl$_2$(dppp)] (Scheme 2(b)). In both cases, a pale yellow solid was isolated in moderate yields.

Evidence for the proposed structures was obtained from IR, ^{1}H and ^{31}P NMR spectroscopies, ESMS and FABMS spectrometries, elemental analyses and the X-ray crystal structure determination for compound **4**. The IR spectra of **1**–**4** shows a C≡C band (at about 2110 cm^{-1} for **1**–**3** and at 2207 cm^{-1} for **4**) shifted to higher frequencies (10–20 cm^{-1}) than that of the organic ligand. The C≡N stretch for **3** appears within the expected range (2223 cm^{-1}). Interestingly, **1** and **2** show a band at 3233 and 3230 cm^{-1}, respectively, that evidences the presence of a terminal acetylenic proton. In all cases, the ^{31}P NMR spectrum displays, as expected, only one signal, flanked by platinum satellites for **2**–**4**. The ^{1}H NMR spectrum confirms the coordination of 4-ethynylpyridine in **1** and **2** since the H$_\alpha$ of the pyridine ring shifted 0.4 ppm downfield relative to the same signals in the free organic ligand. Curiously, the H$_\beta$ shifted upfield from δ = 7.41 ppm in the free organic molecule to δ = 7.25 ppm in **1** or 7.07 ppm in **2**. In addition, the acetylenic proton appeared at about 4.3 ppm for both compounds. This resonance is not present in the spectrum

(a)

(b)

$$RX + {}^nBuLi \xrightarrow[-78^\circ C]{THF} R^-Li^+ + {}^nBuX$$

for X = H, R = C≡C—⟨ ⟩—CN **3**

for X = Br, R = ⟨ ⟩—C≡C—⟨N⟩ **4**

Scheme 2.

of **3**, confirming the coordination to platinum of the alkynyl ligand through the carbon atom. On the other hand, **4** shows the two signals of the pyridinic protons, H_α ($\delta = 8.47$ ppm) and H_β ($\delta = 7.20$ ppm) shifted slightly upfield from the values found for 4-bromophenyl-4-ethynylpyridine ($\delta = 8.63$, 7.48 ppm). In this case, as both kinds of protons remain far from the metal centre, the coordination process affects them much less.

The ESMS spectra detected the molecular peaks at *m/z* 362.0 for **1** and *m/z* 406.2 for **2**, while those for **3** (*m/z* 859.6 [M + H$^+$]) and **4** (*m/z* 964.2 [M + H$^+$]) were obtained from FABMS experiments. The structure of **4** was confirmed by an X-ray crystal structure determination. Single crystals suitable for X-ray crystallography were grown from dichloromethane/diethylether.

The structure of the platinum complex is shown in Fig. 1; selected bond distances and angles are listed in Table 1.

The molecule shows the expected *cis*-arrangement for the 4-(4-pyridylethynyl)phenyl ligands (C(1)–Pt–C(1_2) 86.4(7)°; P–Pt–P_2 93.55(18)°), as imposed by the presence of the chelating dppp ligand. The organic ligand is essentially linear (C(4)–C(7)–C(8) 177.5(7)°; C(7)–C(8)–C(9) 177.2(8)°) and the bond angle between the phosphorus and the organic ligand is C(1)–Pt–P 90.0(3)°, as expected for a square-planar Pt(II) centre. The C(7)–C(8) triple bond distance, 1.189(9) Å, compares well with those reported earlier for similar acetylenic moieties [12]. The Pt···N vectors are nearly perpendicular to one another, confirming that this unit
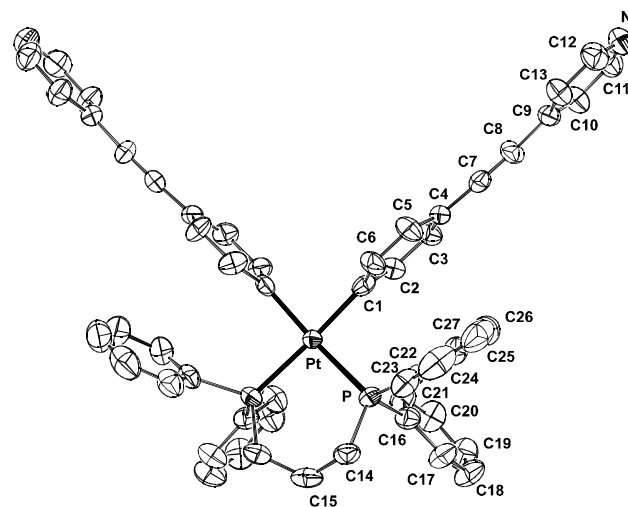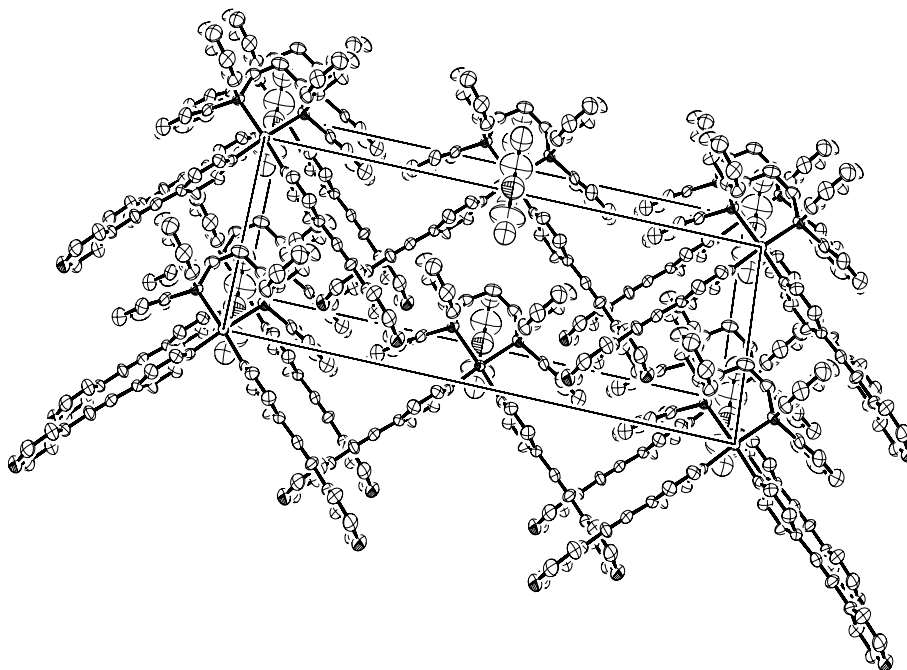

Fig. 1. Molecular structure of **4**.

Table 1
Selected bond distances (Å) and angles (°) for **4**

Pt–C(1)	2.042(13)
Pt–P	2.308(3)
C(7)–C(8)	1.189(9)
P–Pt–P_2	93.55(18)
C(1)–Pt–C(1_2)	86.4(7)
C(1)–Pt–P_2	176.3(4)
C(7)–C(8)–C(9)	177.2(8)
C(4)–C(7)–C(8)	177.5(7)
P–Pt–C(1)	90.0(3)

Fig. 2. Stacking diagram of **4**.

represents a suitable corner for the construction of platinum-containing squares.

Especially interesting is the stacking pattern in the solid state, as shown in Fig. 2. The square-planar molecules of **4** are stacked along the *c*-axis. A platinum atom is located at each of the eight vertices of the unit cell and at the centre of the *bc* faces. The shortest platinum–platinum distance is 9.71 Å, which excludes metal–metal interactions.

It is noteworthy that none of the reported similar compounds [13] shows this type of molecular packing.

2.2. Use of 1–4 as building blocks for the formation of metallacycles

It is well known that acetylide gold complexes can be easily obtained by the reaction of [PPh$_4$][Au(acac)$_2$] with terminal alkyne ligands [14]. Following this strategy we recently published the synthesis of new linear ditopic acetylide gold complexes of the type [PPh$_4$][Au(Alk)$_2$] (Alk = py–C≡C–, py–C≡C–C$_6$H$_4$–C≡C– and others) that were reacted with the acceptor units [M(OTf)$_2$(diphosphine)] (M = Pd, Pt) in an attempt to obtain square molecular polygons containing palladium or platinum and gold [15]. However, in all cases, only intractable and insoluble materials were formed. The formation of polymers, even in high dilution conditions, prevailed over that of metallacycles.

These unsuccessful results together with the report by Bruce et al. [16], who had evidence of the formation of the square [Pt(μ-C≡C–C≡CAuC≡C–C≡C)-(dppe)]$_4^{4-}$ in the reaction between [PPN][Au(acac)$_2$] and [Pt(C≡C–C≡CH)$_2$(dppe)], prompted us to try the "acac" method [14] to synthesise the Pd, Pt/Au heterobimetallic molecules that we were looking for. This strategy required the use of the new cationic complexes **1** and **2**. Thus, **1** and **2** were reacted with [PPh$_4$][Au(acac)$_2$] in dichloromethane. The reaction was monitored by ^{31}P NMR and, after 30 min of stirring, the formation of a new species ($\delta = -10.8$ ppm, $^1J_{(Pt–P)} = 3502$ Hz) that did not contain 4-pyridylacetylene ligand was observed, accompanied by gold deposition. Given that, according to NMR data, the new species was probably [Pt-(acac)(dppp)](OTf), we tried to confirm its nature by reacting **2** with Tl(acac). Indeed, the resulting compound showed the same spectroscopic data, confirming our hypothesis. The use of **1** did not give the desired product.

In view of these results, we investigated the possibility of forming heterobimetallic polygons using **3** and **4**. The topology of these molecules makes them appropriate for carrying out reactions with acceptor corner units. **3**, for which an alternative synthetic strategy was reported in the course of this work [3m], was reacted with [Pd(H$_2$O)$_2$(dppp)](OTf)$_2$ in dichloromethane at room temperature. However, we were unable to isolate the expected molecular square in spite of numerous changes in reaction conditions involving solvents, reaction times, solution concentrations and temperatures. On the other hand, the use of **4** gave better results. Indeed, **4** was reacted with [Pd(H$_2$O)$_2$(dppf)](OTf)$_2$ in CH$_2$Cl$_2$ at room temperature Eq. (1).

$$(1)$$
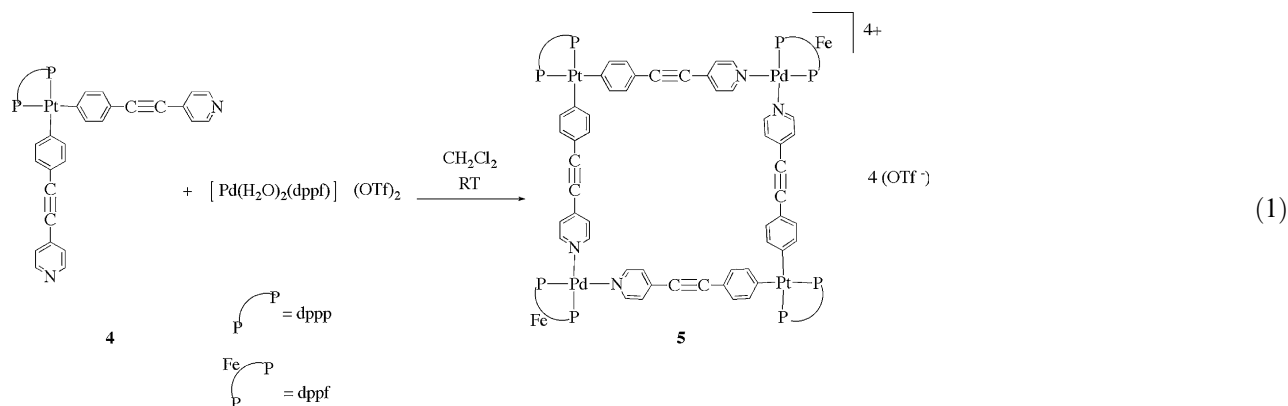
The process was monitored by ^{31}P NMR spectroscopy. After 1 h of stirring, the solution was concentrated and the addition of diethylether gave compound **5** as a red solid, which was spectroscopically characterised. The ^{31}P NMR spectrum (Fig. 3) showed unambiguously the formation of **5**: the signal at δ [31]P = 31.1 ppm is assigned to the phosphorus atoms coordinated to palladium; while the resonance at -3.4 ppm, flanked by [195]Pt satellites ($J_{(Pt–P)}$ = 1719 Hz), is due to the phosphorus atoms linked to platinum.

It should be noted that the phosphorus resonance of the palladium complex shifts about 15 ppm upfield on coordination (δ [31]P = 45.6 ppm for [Pd(H$_2$O)$_2$(dppf)]-(OTf)$_2$); in contrast, the signal due to the platinum complex only shifts 1 ppm relative to the starting complex because the platinum environment is scarcely modified after coordination. As observed in the spectrum, the reaction is very clean and yields the product in excellent yields. On the other hand, the ^{1}H NMR spectrum showed the signals of the protons of both phosphine ligands with their expected integration, as well as the protons of the organic ligand (see Section 3). The two expected resonances for the Cp protons of dppf appear at 4.73 and 4.58 ppm. Again, the H$_\alpha$ of the pyridine ligand (δ = 8.55 ppm) shifted downfield about 0.1 ppm from the values of **4** and can be used as a diagnostic tool for confirming the coordination of the metalloligand. FABMS spectrum of **5** contains the molecular peak at m/z 811.9 [(M $-$ 4OTf)$^{4+}$], providing further evidence of the formation of the molecular square.

In conclusion, although attempts to prepare heterobimetallic square complexes of palladium or platinum using the new donor corners **1**, **2** and **3** have been unsuccessful to date, the coordination ability of the pyridinic nitrogen atoms in compound **4**, together with its suitable topology, enabled us to synthesise a tetrametallic square containing two platinum and two palladium atoms. This promising result encourage us to extend our investigations to other transition metal building blocks in order
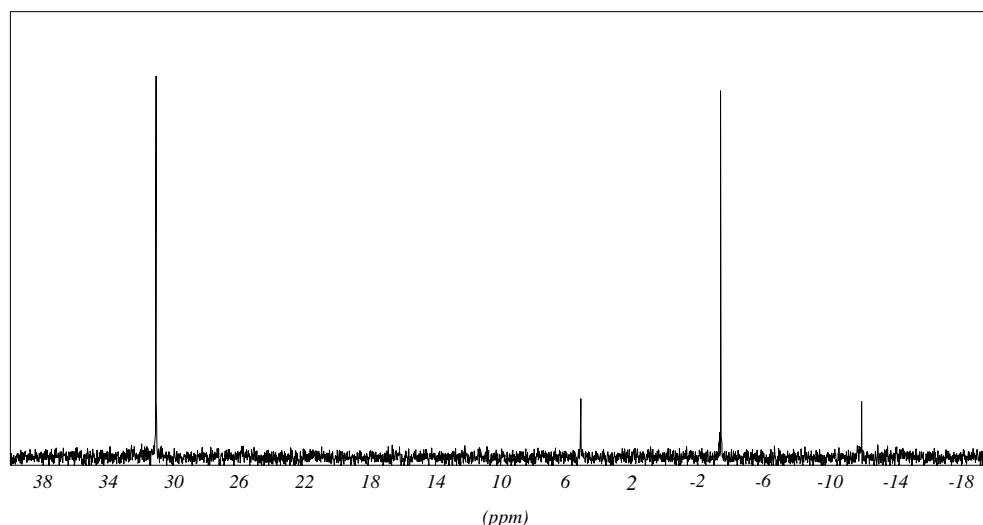

Fig. 3. ^{31}P NMR spectrum of **5**.

to construct new heterobimetallic assemblies with potentially wide applications.

3. Experimental

All manipulations were performed under prepurified N_2 using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. Infrared spectra were recorded on a FT-IR 520 Nicolet spectrophotometer. $^{31}P\{^1H\}$ NMR (δ(85% H_3PO_4) = 0.0 ppm) and ^1H NMR (δ(TMS) = 0.0 ppm) spectra were obtained on a Bruker DXR 250 and Varian Gemini 200 spectrometers. Elemental analyses of C, H, N and S were carried out at the Serveis Científico-Tècnics in Barcelona. FAB(+) and Electrospray mass spectra were recorded on a Fisions VG Quattro spectrometer. The compounds [PtCl₂(dppp)] [17], [Pt(H₂O)₂(dppp)](OTf)₂ [18], [Pd(H₂O)₂(dppp)](OTf)₂ [18], [Pd(H₂O)₂(dppf)]-(OTf)₂ [19], 4-ethynylpyridine [20], 4-ethynylbenzonitrile [21] and 4-(4-bromophenylethynyl)pyridine [22] were prepared as described elsewhere.

3.1. Synthesis of [Pd(dppp)(4-ethynylpyridine)₂](OTf)₂ (1)

Solid 4-ethynylpyridine (6 mg, 0.06 mmol) was added to a THF (10 ml) solution of [Pd(H₂O)₂(dppp)](OTf)₂ (23 mg, 0.03 mmol) at room temperature. After 1 h of stirring the solution was concentrated to 3 ml under vacuum. The addition of pentane (35 ml) caused the precipitation of the product (1) as a white solid, which was filtered and vacuum-dried. Yield: 98%. IR (KBr, cm⁻¹): 3233 m, v(C–H); 2115 m, v(C≡C); 1260 vs, 1157 m, 1101 m, 1029 vs, (OTf⁻). $^{31}P\{^1H\}$ NMR (298 K, THF, inset acetone-d_6 with 1% POMe₃): 6.0 (s). ^1H NMR (298 K, acetone-d_6): 9.05 (m, 4H, H$_{\alpha–pyr}$), 7.85–7.33 (m, 20H, Ph), 7.25 (m, 4H, H$_{\beta–pyr}$), 4.35 (s, 2H, C≡CH), 3.43 (s, br, 4H, P–CH₂), 2.32 (m, 2H, PCH₂CH₂). ES(+) m/z; [M²⁺]: Calc.: 362.0; Found: 362.1. Anal. Calc.: C, 50.46; H, 3.50; N, 2.70. Found: C, 49.88; H, 3.52; N, 2.67.

3.2. Synthesis of [Pt(dppp)(4-ethynylpyridine)₂]-(OTf)₂ (2)

Details of synthesis of 1 also apply to 2. IR (KBr, cm⁻¹): 3230 m, v(C–H), 2109 m, v(C≡C); 1260 vs, 1159 m, 1100 m, 1030 vs, (OTf⁻). $^{31}P\{^1H\}$ NMR (298 K, THF, inset acetone-d_6 with 1% POMe₃): −16.1 (s, $^1J_{Pt–P}$ = 3064 Hz). ^1H NMR (298 K, acetone-d_6): 9.01 (d, $J_{H–H}$ = 6.4 Hz, 4H, H$_{\alpha–pyr}$), 7.81–7.31 (m, 20H, Ph), 7.07 (d, 4H, H$_{\beta–pyr}$), 4.33 (s, 2H, C≡CH), 3.42 (s, br, 4H, P–CH₂), 2.17 (m, 2H, PCH₂CH₂). ES(+) m/z; [M²⁺]: Calc: 406.7; Found: 406.2. Anal. Calc.: C, 46.44; H, 3.24; N, 2.52. Found: C, 46.53; H, 3.51; N, 2.29.

3.3. Synthesis of [Pt(4-cyanophenylethynyl)₂(dppp)] (3)

To a precooled (−78 °C) solution of 4-ethynylbenzonitrile (58 mg, 0.44 mmol) in THF (15 ml), ^{n}BuLi (0.28 ml, 0.44 mmol) was added dropwise. The solution turned pale yellow immediately. After 1 h of stirring, solid [PtCl₂(dppp)] (100 mg, 0.14 mmol) was added and the solution was allowed to warm slowly to room temperature. The solution was concentrated to dryness. The pale green residue was extracted with toluene (3 × 10 ml) and the resulting filtrates were combined, evaporated to dryness and washed with diethylether. A pale yellow solid was obtained in 65% yield after recrystallisation with dichloromethane/diethylether. IR (KBr, cm⁻¹): 2223 m, v(C≡N); 2113 m, v(C≡C). $^{31}P\{^1H\}$ NMR (298 K, THF, inset acetone-d_6 with 1% POMe₃): −7.2 (s, $^1J_{Pt–P}$ = 2173 Hz). ^1H NMR (298 K, CDCl₃): 7.59 (d, $J_{H–H}$ = 8.5 Hz, 4H, CN–C₆H$_{2,o}$H$_{2,m}$), 7.40–7.36 (m, 20H, Ph), 6.81 (d, 4H, CN–C₆H$_{2,o}$H$_{2,m}$), 2.53 (s, br, 4H, P–CH₂), 2.24 (m, 2H, P–CH₂–CH₂). FAB(+) m/z; [M + H⁺]: Calc.: 859.1; Found: 859.6; [(M − 4-ethynylbenzonitrile)⁺]: Calc.: 733.1; Found: 733.8. Anal. Calc.: C, 62.86; H, 3.95; N, 3.26. Found: C, 62.90; H, 3.97; N, 3.28.

3.4. Synthesis of [Pt(4-(4-pyridylethynyl)phenyl)₂-(dppp)] (4)

To a precooled (−78 °C) solution of 4-(4-bromophenylethynyl)pyridine (114 mg, 0.44 mmol) in THF (15 ml), ^{n}BuLi (0.28 ml, 0.44 mmol) was added dropwise and the pale yellow solution turned dark green immediately. After 1 h of stirring at −78 °C, solid [PtCl₂(dppp)] (100 mg, 0.15 mmol) was added and the solution was allowed to warm slowly to room temperature. After 3 days of stirring, the solution was concentrated to dryness and extracted with hot toluene (3 × 10 ml). A pale yellow solid was obtained in 13% yield after recrystallisation with dichloromethane/diethylether. IR (KBr, cm⁻¹): 2207 s, 2151 w, v(C≡C). $^{31}P\{^1H\}$ NMR (298 K, THF, inset acetone-d_6 with 1% POMe₃): −2.4 (s, $^1J_{Pt–P}$ = 1717 Hz). ^1H NMR (298 K, CDCl₃): 8,46 (d, $J_{H–H}$ = 6.1 Hz, 4H, H$_{\alpha–pyr}$), 7.45–7.26 (m, 20H, Ph), 7.22 (d, 4H, H$_{\beta–pyr}$), 7.10 (m, 4H, PtC₆H$_{2,o}$H$_{2,m}$), 6.69 (d, $J_{H–H}$ = 7.7 Hz, 4H, PtC₆H$_{2,o}$H$_{2,m}$), 2.61 (s, br, 4H, P–CH₂), 1.88 (m, 2H, PCH₂CH₂). FAB(+) m/z; [M + H⁺]: Calc.: 964.1; Found: 964.2. Anal. Calc.: C, 58.82; H, 4.25; N, 2.59. Found: C, 58.87; H, 4.29; N, 2.62.

3.5. Synthesis of [{Pt(μ-4-(4-pyridylethynyl)phenyl)₂-(dppp)}₂{Pd(dppf)}₂](OTf)₄ (5)

A dichloromethane (1 ml) solution of [Pd(H₂O)₂-(dppf)](OTf)₂ (12 mg, 0.01 mmol) was added dropwise

to a dichloromethane (2 ml) solution of [Pt(4-(4-pyridyle-thynyl)phenyl)$_2$(dppp)] (**4**) (10 mg, 0.01 mmol). After 1 h of stirring at room temperature, the resulting mixture turned orange. The solution was concentrated to 1 ml under vacuum and the addition of diethylether (5 ml) caused the precipitation of the product in 90% yield. IR (KBr, cm^{-1}): 2209 s, 2150 w, ν(C≡C); 1258 vs, 1157 m, 1101 m, 1029 vs, (OTf$^-$). ^{31}P{^{1}H} NMR (298 K, CH$_2$Cl$_2$, inset acetone-d_6 with 1% POMe$_3$): 31.1 (s, Pd–PPh$_2$), −3.4 (s, $^1J_{Pt–P}$ = 1719 Hz, Pt–P Ph$_2$). ^{1}H NMR (298K, CDCl$_3$): 8.55 (m, 8H, H$_{\alpha–pyr}$), 7.80–6.72 (m, 96H, Ph + PtC$_6$H$_{2,o}$H$_{2,m}$ + H$_{\beta–pyr}$), 6.47 (m, 8H, PtC$_6$H$_{2,o}$H$_{2,m}$), 4.73 (s, 4H, H$_{\alpha–ferr}$), 4.58 (s, 4H, H$_{\beta–ferr}$), 2.57 (s, br, 8H, P–CH_2–), 1.79 (m, 4H, P–CH$_2$–CH_2–). ES(+) m/z; [[Pt(4-(4-pyridylethynyl)phenyl)$_2$(dppp)] + H$^+$]: Calc.: 964.1; Found: 962.3; [(M − 4OTf$^-$)$^{4+}$]: Calc.: 811.9; Found: 811.0. Anal. Calc.: C, 29.37; H, 2.03; N, 0.73. Found: C, 29.40; H, 2.07; N, 0.71.

3.6. X-ray structure determination of **4**

A prismatic crystal (0.01 × 0.07 × 0.48 mm) was selected and mounted on a Bruker SMART-CCD area diffractometer with graphite monochromatised Mo Kα radiation using φ scan-technique. 7502 reflections were measured in the range 2.27 ⩽ Θ ⩽ 28.30°, 4354 of which were non-equivalent by symmetry (R_{int}(on I) = 0.044). 3926 reflections were taken as observed and the condition $I > 2\sigma(I)$ was used. Lorentz-polarisation occurred, but no absorption corrections were made. Numerical details are shown in Table 2.

The structure was solved by Patterson synthesis, using the SHELXS computer program [23], and refined by full-matrix least-squares method with the SHELXL computer program [24], using 4354 reflections. The function minimised was $\Sigma w||F_o|^2 − |F_c|^2|^2$, where $w = \sigma^{-2}(I)$, f, f' and f'' were taken from the International Tables of X-Ray Crystallography [25]. The chirality of structure was defined from the Flack coefficient, which was equal to 0.021(9) for the given results [26]. The position of 22 H atoms was computed and refined using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent of the linked C atom. The final R(on F) factor was 0.042, wR(on $|F|^2$) = 0.068 and Goodness-of-fit = 0.964 for all observed reflections. Number of refined parameters was 299. Max. shift/esd = 0.001, Mean shift/esd = 0.000. Max. and min. peaks in final difference synthesis were 0.605 and −0.398 e Å^{-3}, respectively.

Crystallographic data for the structural analysis were deposited with the Cambridge Crystallographic Data Centre, CCDC No. 255640 for compound **4**. 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; deposit@ccdc.cam.ac.uk or e-mail: http://www.ccdc.cam.ac.uk).

Table 2
Crystal data and details of the structural determination of **4**

Empirical formula	C$_{57}$H$_{52}$N$_2$OP$_2$Pt
Formula weight	1038.04
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C_m
Unit cell dimensions	
a (Å)	11.3140(12)
b (Å)	25.359(3)
c (Å)	9.7065(11)
α (°)	90
β (°)	121.99(4)
γ (°)	90
V (Å^3)	2362.0(5)
Z	2
D_{calc} (mg/m^3)	1.460
Absorption coefficient (mm^{-1})	3.080
$F(000)$	1048
Crystal size (mm^3)	0.01 × 0.07 × 0.48
Theta range for data collection (°)	2.27–28.30°
Index ranges	−15 ⩽ h ⩽ 13, −23 ⩽ k ⩽ 33, −12 ⩽ l ⩽ 12
Reflections collected/unique	7502/4354 [R_{int} = 0.0441]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4354/2/299
Goodness-of-fit on F^2	0.964
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0415, wR_2 = 0.0684
R indices (all data)	R_1 = 0.0529, wR_2 = 0.0733
Largest diff. peak and hole (e Å^{-3})	1.005 and −0.798

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