

Synthesis, structures and photoluminescence behavior of some group 10 metal alkynyl complexes derived from 3-(*N*-carbazolyl)-1-propyne

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Abstract

A new class of luminescent and thermally stable mononuclear group 10 platinum(II) and palladium(II) acetylides *trans*-[Pt(PR₃)₂(L)₂] (R = Bu, Et) and *trans*-[Pd(PBu₃)₂(L)₂] (LH = 3-(*N*-carbazolyl)-1-propyne) have been successfully synthesized and characterized. The structural properties of these discrete metal complexes have been studied by X-ray crystallography. We report their optical absorption and photoluminescence spectra and interpret the results in terms of the nature of the metal center and the type of phosphines used. Our investigations indicate that they display heavy metal-enhanced phosphorescence bands at 77 K and we find that the platinum complexes afford more intense triplet emission than that for the palladium congener, consistent with the stronger heavy-atom effect of the third row element than the second row neighbor of the same group.

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1. Introduction

Since the discovery of the most sensitive photoconductive organic polymers poly(*N*-vinylcarbazole) (PVK) [1], carbazole-related systems have been extensively studied compared with other aromatic compounds. Carbazole is a well-known hole-transporting and electroluminescent moiety [2]. Polymers containing carbazole units in the main chain or side chain have attracted enormous research efforts because of their unique properties as photoconductive, electroluminescent, and photorefractive materials in various photonic applications [3]. Also, it is well recognized that the thermal stability or glassy-state durability of organic compounds can be greatly improved upon incorporation of a carbazole moiety in the core structure [4]. The carbazole derivatives can be easily functionalized at 3-, 6-, or 9-positions and covalently linked to other molecular moieties [5]. Adding to these features, carbazole has strong

absorptions in the near UV region and a low redox potential. As such, it has been widely used as a functional building block in the fabrication of organic photoconductors, nonlinear optical devices and organic light-emitting devices (OLEDs) [6].

In the past decade, much progress has been made by using transition metal complexes as light emitters in various domains of optoelectronic applications [7]. Because of the strong spin–orbit coupling mediated by heavy transition metals in such complexes, intersystem crossing (ISC) becomes very efficient, leading to an emissive state with high triplet content. For OLEDs, simple spin statistical arguments predict a emissive singlet to nonemissive triplet ratio of 1:3 [8]. Therefore, incorporating heavy metals in such molecular system allows light emission from the triplet excited state of the compound, thus making this energy state spectroscopically assessible. Improved device efficiencies can be anticipated by harvesting the triplet light energy using metal-containing compounds. While developments based on the exploitation of carbazole as the building unit for the synthesis of branched molecules, oligomers, polymers

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or even dendrimers have recently aroused much attention, most of them are limited to organic systems [9]. Carbazole-based coordination/organometallic compounds have been much less explored [10]. To our knowledge, carbazole-containing metal alkynyl compounds are very rare and reported examples are exclusively confined to 2,7-diethylcarbazolediyl-spaced metal complexes and metallopolymers [11]. Although many discrete transition metal bis(arylacetylide) complexes are known [12], there has been no report of (*N*-carbazolyl)propyne-derived metal complexes, and the chemistry of metal compounds of carbazole derivatives is still in its infancy. We envision that a properly derivatized molecule such as 3-(*N*-carbazolyl)-1-propyne could be employed to attach a carbazolyl label to the metal center through an acetylide bridge, which may confer novel optical and photoelectronic properties. Another merit of using 3-(*N*-carbazolyl)-1-propyne in the present study is reflected in its ability to interrupt conjugation by the nitrogen atom in the carbazole unit and the methylene bridge, which may result in materials of high optical gaps and high-energy triplet states. Recent observations demonstrate that the ISC rate from the singlet excited state to the triplet excited state is enhanced when π -conjugation is decreased [13]. On this basis, we report here the synthesis, characterization, crystal structures and photophysical properties of some luminescent group 10 mononuclear platinum(II) and palladium(II) bis(phosphine) complexes functionalized with 3-(*N*-carbazolyl)-1-propyne. The influence of the heavy metal ion and its auxiliary ligands on the photoluminescence behavior will be examined.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization

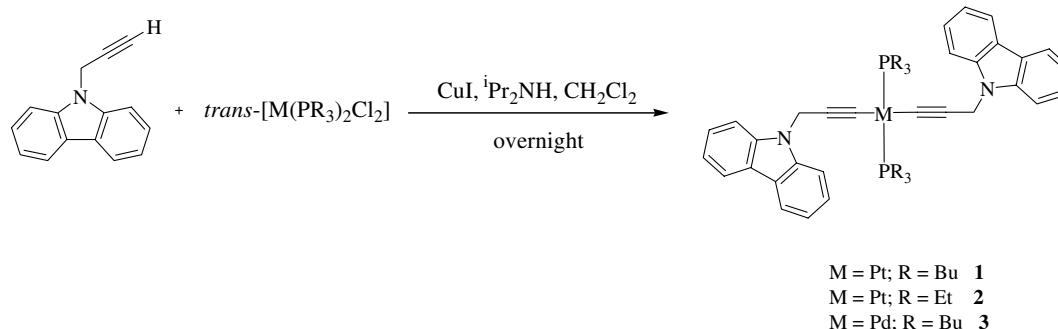
The platinum(II) acetylide complexes **1** and **2** and the palladium(II) complex **3** containing carbazole chromophores were synthesized by CuI-catalyzed dehydrohalogenation reaction of two molar equivalents of 3-(*N*-carbazolyl)-1-propyne (**LH**) with *trans*-[Pt(PR₃)₂Cl₂] (R = Bu and Et) and *trans*-[Pd(PBu₃)₂Cl₂], respectively (Scheme 1). The crude mixture obtained after evaporation of the solvents was subjected to preparative TLC plate on silica with the appropriate eluent and the desired complexes were obtained

as off-white solids in high yields. All the new compounds are soluble in common organic solvents such as CH₂Cl₂, CHCl₃ and THF.

Systematic characterization of these three complexes was achieved by analytical and spectroscopic methods (IR, ¹H, ¹³C and ³¹P NMR, FABMS). The IR spectra of **1–3** display a single sharp $\nu(\text{C}\equiv\text{C})$ absorption at 2122 cm⁻¹ for **1** and **2** and 2116 cm⁻¹ for **3** which indicates a *trans* configuration of the 3-(*N*-carbazolyl)-1-propynyl ligands around the metal center in these square-planar bis(acetylide) species. ³¹P{¹H} NMR spectra of the platinum(II) complexes **1** and **2** exhibit a single resonance with two Pt satellites, further confirming the *trans*-arrangement of the phosphine ligands around Pt. The ¹J_{P-Pt} values in these complexes range from 2351 to 2354 Hz, typical of those for related *trans*-PtP₂ systems [14]. For the palladium analogue **3**, it displays a sharp singlet at δ 10.95 in the room-temperature ³¹P{¹H} NMR spectrum. The ¹H NMR spectra of all compounds exhibit the expected signals for the systems and clearly demonstrate a well-defined structure for each compound. The ¹³C NMR spectral data indicate a highly symmetrical structure in each case and are also consistent with the proposed formulations. The resonances due to the butyl and ethyl groups are clearly identified and the characteristic peak at about δ 34.0 ppm corresponds to the CH₂ carbon atom of the propynyl moiety.

2.2. Thermal analysis

The thermal properties of the complexes were also examined by thermogravimetric analysis (TGA) under nitrogen. Analysis of the TGA curves (heating rate 20 °C/min) showed that complexes **1–3** possess very good thermal stability. Decomposition commences at ca. 340 and 332 °C for the platinum compounds **1** and **2**, respectively. But, the palladium counterpart **3** tends to decompose at a lower onset decomposition temperature of 240 °C. Generally, platinum-containing alkynyl compounds are considerably more air and thermally stable than their palladium and nickel analogues of the group 10 triad [15]. Variation of the PR₃ groups on metal does not seem to alter the onset temperature significantly. We observe a sharp weight loss of 48% between 340 and 362 °C for **1** whereas 66% of the



Scheme 1.

weight was lost for **3** as the temperature rose from 240 to 308 °C. The decomposition step is ascribed to the removal of one L, one PBu_3 and two Bu groups from **1** and one PBu_3 and two Bu groups from **3**.

2.3. Crystal structure analyses

The exact three-dimensional solid state structures of **1–3** were all established by single-crystal X-ray analyses (see Figs. 1 and 2). Selected bond parameters for **1–3** are collectively presented in Table 1. To our knowledge, these molecules represent the first structurally characterized examples of *N*-propynylcarbazole-coordinated metal complexes in the literature. All the three crystals crystallize in the same space group $P2_1/n$ and complexes **1** and **3** are isomorphous to each other. Each of the platinum atoms in **1** and **2** and the palladium atom in **3** sits on a crystallographic center of symmetry, which imposes exact planarity at the metal center, and requires the two alkynyl groups and the two phosphine ligands to occupy mutually *trans* positions. The local coordination geometry at the metal center is square-planar in all of them. The M–P distances compare favorably well with those observed in other *trans*- $\text{M}(\text{PR}_3)_2\text{L}_2$ -type compounds [12e,12i,12j,12k,14]. The Pt–C distance is 2.004(3) and 2.007(3) Å in **1** and **2**, respectively, lying within the range found in other platinum bis(alkynyl) complexes, while the Pd–C bond length in **3** is 2.018(5) Å [12j,14]. The C≡C bond lengths of 1.200(4), 1.186(4) and 1.177(6) Å in **1**, **2** and **3**, respectively, are characteristic of metal-acetylide-bond-

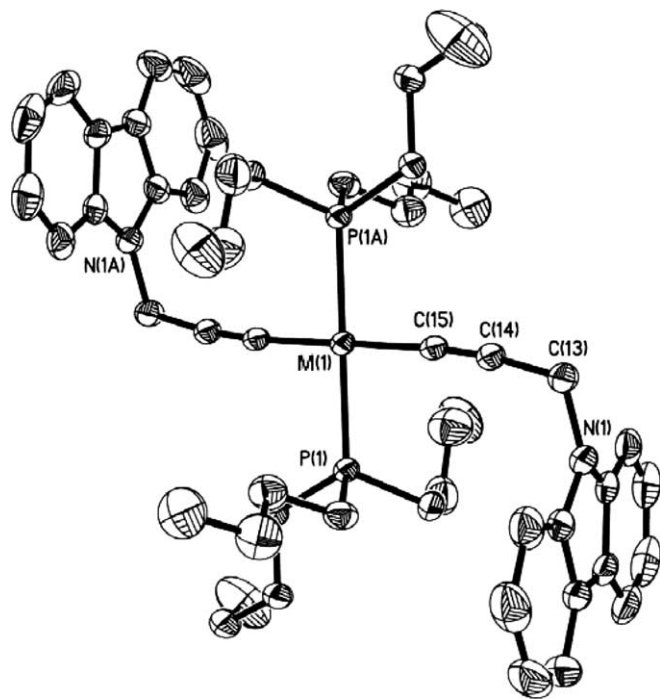


Fig. 1. A perspective view of **1** (M = Pt) and **3** (M = Pd), with the thermal ellipsoids drawn at the 25% probability levels. Carbon atom labels on the butyl and carbazoyl groups and all hydrogen atoms are omitted for clarity.

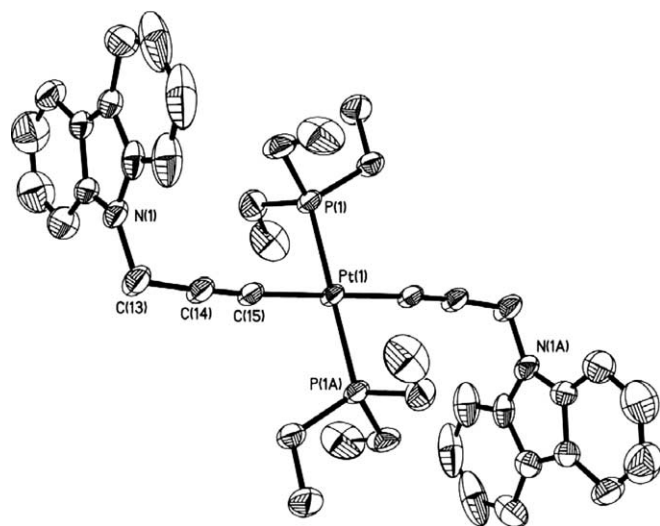


Fig. 2. A perspective view of **2**, with the thermal ellipsoids drawn at the 25% probability levels. Carbon atom labels on the ethyl and carbazoyl groups and all hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **1–3**

	1 (M = Pt)	2 (M = Pt)	3 (M = Pd)
M(1)–P(1)	2.2995(7)	2.2941(10)	2.3035(12)
C(14)–C(15)	1.200(4)	1.186(4)	1.177(6)
C(13)–N(1)	1.459(4)	1.461(4)	1.463(6)
M(1)–C(15)	2.004(3)	2.007(3)	2.018(5)
C(13)–C(14)	1.475(4)	1.482(5)	1.489(7)
P(1)–M(1)–C(15)	85.95(8)	86.62(9)	93.62(13)
C(13)–C(14)–C(15)	172.8(3)	176.1(4)	173.9(5)
M(1)–C(15)–C(14)	175.2(2)	177.0(3)	173.2(4)
N(1)–C(13)–C(14)	112.2(3)	112.2(3)	111.9(4)

ing. The Pt(1)–C(15)–C(14) (for **1** and **2**) and Pd(1)–C(15)–C(14) (for **3**) fragments are essentially linear such that each molecule affords a rigid C–C–Pt–C–C–C linear chain. By virtue of symmetry, the two carbazoyl rings are positioned on the opposite side and each of them is almost planar. There are no unusual bond parameters in the organic moieties of all complexes.

2.4. Absorption and photoluminescence spectroscopies

The photophysical properties of our complexed chromophores **1–3** have been studied (Tables 2 and 3). All the group 10 metal complexes exhibit similar absorption bands in the near UV region that can be ascribed to the ligand-centered π – π^* transitions, possibly with some admixture of metal d orbitals which may change the overall energy of the transition. We associate the lowest energy peak with the $S_0 \rightarrow S_1$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), which are mainly delocalized π and π^* orbitals. The absorption energies are relatively insensitive to the nature of transition metal and its auxiliary phosphine ligands. As compared to the band peaking at 339 nm for 3-(*N*-carbazoyl)-1-propyne, we find that the position of

Table 2
Absorption data for compounds **1–3** in CH₂Cl₂ at 290 K

Complex	λ_{\max} (nm) ^a	λ_{\max} (nm)	E_g (eV) ^b
	CH ₂ Cl ₂	Thin film	
1	237 (9.3), 263 (5.3), 295 (4.0), 331 (1.03), 346 (1.07)	229, 263, 298, 333, 348	3.47
2	237 (11.6), 262 (6.4), 295 (4.8), 308 (2.2), 331 (1.2), 345 (1.2)	232, 263, 297, 307, 332, 347	3.47
3	237 (16.7), 263 (8.7), 295 (5.5), 331 (1.3), 345 (1.4)	239, 262, 285, 296, 331, 346	3.51

^a Extinction coefficients ($\epsilon \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) are shown in parentheses.

^b Estimated from the onset wavelength of the solid-state optical absorption.

Table 3
Emission data for compounds **1–3** in CH₂Cl₂^a

Complex	λ_{em} (nm)	Quantum yield Φ_F ^b (%)	λ_{em} (nm)	Lifetime	
	CH ₂ Cl ₂ (290 K)		CH ₂ Cl ₂ (77 K)	290 K (ns) ^c	77 K (μs) ^d
1	346, 363	3.27	346, 362, 408, 436, 459	0.79	4.00
2	346, 362	1.36	347, 361, 410, 437, 463	0.62	4.54
3	345, 361	15.8	347, 363, 408, 436, 458	4.13	3.67

^a Excitation wavelength = 325 nm.

^b Fluorescence quantum yield relative to quinine sulphate in 1.0 N H₂SO₄ ($\Phi_F = 0.54$).

^c Lifetime for the fluorescence band.

^d Lifetime for the phosphorescence band.

the lowest absorption band is slightly red-shifted when the metal group is introduced. However, the small shift of only a few nanometers (e.g., from 339 in **LH** to 346 nm in **1**) reveals that π -conjugation of the ligands into and through the metal center is, to a certain extent, disrupted due to the presence of non- π -conjugated CH₂ group adjacent to the C \equiv C unit in the alkyne ligand. In energy terms, the HOMO–LUMO energy gap (E_g) as measured from the onset wavelength in solid film state is 3.47 eV for **1** and **2** and 3.51 eV for **3**, which appear larger than those in other 3,6-diethynylcarbazole-linked compounds [11]. This observation attests to the importance of designing high-energy gap materials through the use of non- π -conjugated interrupter along the main chain.

Complexes **1–3** were shown to exhibit luminescence in fluid solutions and their photoluminescence spectra recorded at 290 and 77 K are illustrated in Figs. 3 and 4, respectively. There is little change in the emission spectra upon variation of the excitation wavelength, indicating that a single emissive state or multiple states in equilibrium is (are) responsible for the observed emission. At 290 K, the emission energy for each complex does not vary much with respect to the substituent R of the phosphine and the type of metal ion. The striking similarity of the emission peak shapes of these metalated σ -alkynyl complexes and that of the free ligand are suggestive of a ligand-dominating emissive state, and the lowest emissive states in these complexes can tentatively be assigned as metal-perturbed intraligand π - π^* transitions (or ligand-based fluorescence). Photoluminescence quantum yields (Φ_F) are similar for **1** and **2**, but they are lower than that of **3**. With reference to previous work on other metal acetylide systems or alike [16], we can possibly attribute the lower Φ_F values for the fluorescence band in **1** and **2** to the greater heavy-atom ef-

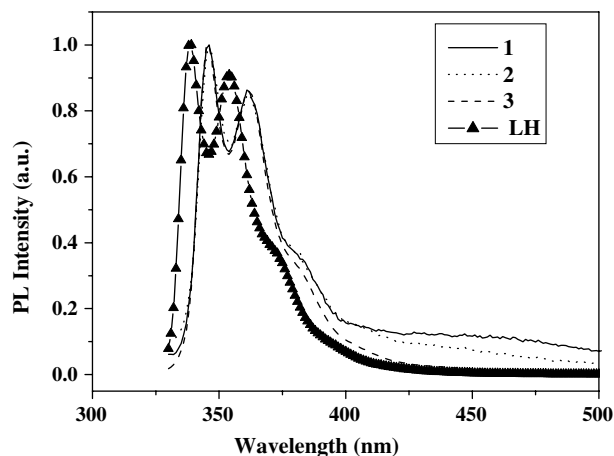


Fig. 3. Photoluminescence spectrum of complexes **1–3** and 3-(*N*-carbazoyl)-1-propyne (**LH**) at 290 K.

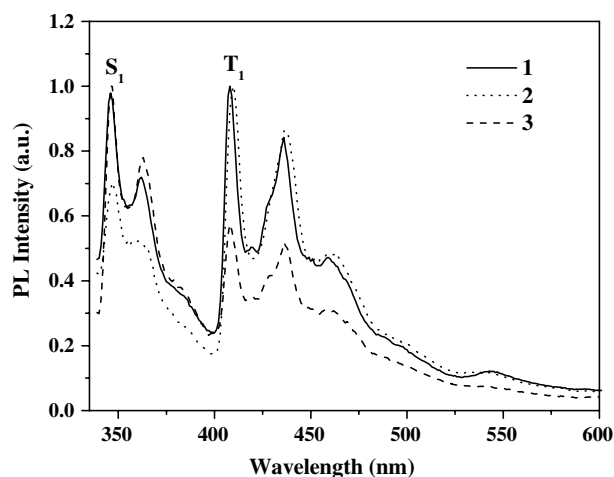


Fig. 4. Photoluminescence spectrum of complexes **1–3** at 77 K.

Table 4
Triplet energies and intersystem crossing efficiencies of **1–3**

Complex	$E(T_1-S_0)$ (eV)	$\Delta E(T_1 \rightarrow S_0, S_1 \rightarrow S_0)^a$
1	3.04	1.1
2	3.02	1.4
3	3.04	0.5

^a Ratio of the intensities of triplet emission to singlet emission at 77 K.

fect of platinum, which catalyzes the nonradiative deactivation of the excited states of the fluorophoric ligand. Due to the lack of available low-lying metal-localized excited states in these complexes, it is unlikely to see energy or electron-transfer quenching mechanism operational here [16,17]. Two major emission bands were detected for each of the compounds **1–3** at 77 K. The higher-lying emission peaks are again attributed to the fluorescence transitions ($S_1 \rightarrow S_0$), similar to the room-temperature spectra. We consider that the intense feature at the low-energy regime at around 436 nm of the emission spectrum is due to emission from a triplet excited state (i.e., phosphorescence $T_1 \rightarrow S_0$). The large energy shift observed between the absorption and emission features ascertains this emitting state as a T_1 excited state. This spectral assignment can be further interpreted in terms of the lifetime measurements. Lifetime data for the lower-lying emission in the microsecond range (~ 4.0 , 4.5 and 3.7 μs for **1–3**, respectively) suggest that the luminescence band is rather long-lived, typical of the phosphorescent triplet state in other similar organometallic complexes [14,18]. Vibronic fine structure is also seen for the triplet emission at 77 K and the vibrational progression of ca. $1509\text{--}1570\text{ cm}^{-1}$ for **1–3** corresponds to the aromatic stretching of the organic ligands that is usually diagnostic of the involvement of the intraligand $\pi\text{--}\pi^*$ transitions in the emission [12i,12j]. In addition, the emissions do not change in dilute solutions, which exclude an excimer origin. Apparently, all these phosphorescent metal-organic compounds containing the conjugation-interrupting CH_2 unit can show high T_1 levels of about 3.04 eV and the corresponding S_1 levels are ~ 3.58 eV. The T_1 state is one of the highest for Pt(II) alkynyl complexes [14]. To evaluate the relative ISC efficiency triggered by the heavy metal in our systems, the peak height ratio from triplet emission to singlet emission at 77 K ($\Delta E(T_1 \rightarrow S_0, S_1 \rightarrow S_0)$) was taken as a good indicator (Table 4). Clearly, the order of $S_1\text{--}T_1$ crossover efficiency is $\mathbf{1} \approx \mathbf{2} > \mathbf{3}$, a fact that can be ascribed to the stronger heavy-atom effect of the third-row Pt element than the second-row Pd neighbor.

3. Concluding remarks

This report describes the successful use of 3-(*N*-carbazolyl)-1-propyne (**LH**) as a synthetic reagent for the preparation of a new class of luminescent carbazole-containing metalated molecular systems. A series of four-coordinate bis(alkynyl) complexes of group 10 transition metals of

the general formula $\text{trans-}[M(\text{PR}_3)_2(\text{L})_2]$ ($M = \text{Pd, Pt}$; $R = \text{Bu, Et}$) were synthesized in good yields by complexation of **LH** with suitable metal chloride precursors and complete characterization was achieved by both spectroscopic and crystallographic methods. All the metal complexes are organic-soluble and thermally stable. Our investigations show that these new complexes are all emissive in solutions and the transition metals (viz., palladium and platinum) can exert heavy-atom effect in the enhancement of intersystem crossing efficiency to render the phosphorescent emissions observable at 77 K. The emission wavelengths of the complexes are insensitive to the nature of M and R units. The phosphorescence intensity generally increases down the group from Pd to Pt but remains almost invariant of the type of phosphine ligands used.

4. Experimental

4.1. General procedures

All reactions were carried out under nitrogen atmosphere with the use of standard Schlenk techniques, but no special precautions were taken to exclude oxygen during workup. Solvents were predried and distilled from appropriate drying agents under an inert nitrogen atmosphere prior to use. Glasswares were oven-dried at about $120\text{ }^\circ\text{C}$. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources and used without further purification. Preparative TLC ($20\text{ cm} \times 20\text{ cm}$) was performed in air on 0.7 mm silica plates (Merck Kieselgel 60 GF₂₅₄) prepared in our laboratory. The starting complexes $\text{trans-}[Pt(\text{PR}_3)_2\text{Cl}_2]$ ($R = \text{Bu}$ and Et) [19] and $\text{trans-}[Pd(\text{P}^i\text{Bu}_3)_2\text{Cl}_2]$ [20] were prepared by the literature methods. 3-(*N*-carbazolyl)-1-propyne was obtained from Wako Pure Chemical Industries. Infrared spectra were recorded as CH_2Cl_2 solutions using a Nicolet Magna 550 Series II FT-IR spectrometer, using CaF_2 cells with a 0.5 mm path length. NMR spectra were measured in appropriate deuterated solvents as lock signal on a JEOL EX270 or a Varian Inova 400 MHz FT NMR spectrometer, with ^1H NMR chemical shifts quoted relative to SiMe_4 and ^{31}P chemical shifts relative to an 85% H_3PO_4 external standard. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 mass spectrometer in *m*-nitrobenzyl alcohol matrices. Electronic absorption spectra were obtained with a HP 8453 UV-Vis spectrometer. Photoluminescence data were obtained by the LS50B fluorescent spectrophotometer. Elemental analyses were carried out by Butterworth Laboratories, UK. Thermal analysis was performed with the Perkin-Elmer TGA6 thermal analyser at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$.

4.2. Preparations of complexes

4.2.1. Synthesis of $\text{trans-}[Pt(\text{P}^i\text{Bu}_3)_2(\text{L})_2]$ (**1**)

The reaction of $\text{trans-}[Pt(\text{P}^i\text{Bu}_3)_2\text{Cl}_2]$ (100 mg, 0.149 mmol) with two equivalents of 3-(*N*-carbazolyl)-1-propyne (**LH**,

61.2 mg, 0.298 mmol), in the presence of CuI (5 mg), in $i\text{Pr}_2\text{NH}/\text{CH}_2\text{Cl}_2$ (40 cm³, 1:1, v/v) afforded the complex **1** as a white solid in 75% yield after purification on preparative TLC silica plate using a CH_2Cl_2 /hexane mixture (1:2, v/v) as eluent ($R_f = 0.58$). IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2122 cm⁻¹. ¹H NMR (CDCl_3): δ 0.69–0.73 (m, 18H, CH₃), 1.00–1.18 (m, 24H, CH₂), 1.54–1.58 (m, 12H, CH₃), 4.98 (s, 4H, CH₂), 7.16 (t, 4H, $J_{\text{H-H}} = 8.0$ Hz, Ar), 7.37 (t, 4H, $J_{\text{H-H}} = 4.0$ Hz, Ar), 7.47 (d, 4H, $J_{\text{H-H}} = 8.0$ Hz, Ar) and 8.02 (d, 4H, $J_{\text{H-H}} = 8.0$ Hz, Ar). ¹³C NMR (CDCl_3): δ 13.72, 23.01, 23.97, 25.98 (Bu), 34.91 (CH₂), 98.91, 99.97 (C≡C) and 109.23, 118.55, 119.99, 122.86, 125.26, 140.15 (Ar). ³¹P{¹H} NMR (CDCl_3): δ 3.59 ($J_{\text{P-Pt}} = 2351$ Hz). FABMS: m/z 1008 (M⁺). Anal. Calc. for C₅₄H₇₄N₂P₂Pt: C, 64.33; H, 7.40; N, 2.78. Found: C, 64.05; H, 7.12; N, 2.54%.

4.2.2. Synthesis of *trans*-[Pt(PEt₃)₂(L)₂] (**2**)

A mixture of *trans*-[Pt(PEt₃)₂Cl₂] (80.0 mg, 0.159 mmol) and **LH** (65.4 mg, 0.319 mmol) in $i\text{Pr}_2\text{NH}/\text{CH}_2\text{Cl}_2$ (40 cm³, 1:1, v/v) was allowed to react in the presence of CuI (5 mg) at room temperature overnight. The resulting solution was evaporated to dryness. The residue was redissolved in CH_2Cl_2 and subjected to preparative TLC silica plates using a CH_2Cl_2 /hexane (2:1, v/v) mixture as the eluent ($R_f = 0.48$) to obtain the product as a white powder in 89% yield. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2122 cm⁻¹. ¹H NMR

(CDCl_3): δ 0.63–0.71 (m, 18H, CH₃), 1.55 (m, 12H, CH₂), 4.97 (s, 4H, CH₂), 7.15 (t, 4H, $J_{\text{H-H}} = 16.0$ Hz, Ar), 7.37 (t, 4H, $J_{\text{H-H}} = 16.0$ Hz, Ar), 7.45 (d, 4H, $J_{\text{H-H}} = 8.0$ Hz, Ar) and 8.02 (d, 4H, $J_{\text{H-H}} = 8.0$ Hz, Ar). ¹³C NMR (CDCl_3): δ 7.75, 15.64 (Et), 34.83 (CH₂), 98.56, 100.75 (C≡C) and 109.29, 118.60, 119.98, 122.97, 125.26, 140.22 (Ar). ³¹P{¹H} NMR (CDCl_3): δ 11.25 ($J_{\text{P-Pt}} = 2354$ Hz). FABMS: m/z 838 (M⁺). Anal. Calc. for C₄₂H₅₀N₂P₂Pt: C, 60.06; H, 6.00; N, 3.34. Found: C, 59.88; H, 5.74; N, 3.40%.

4.2.3. Synthesis of *trans*-[Pd(PBu₃)₂(L)₂] (**3**)

Complex **3** was obtained by the reaction of *trans*-[Pd(PBu₃)₂Cl₂] (100 mg, 0.172 mmol) with two equivalents of **LH** (70.5 mg, 0.344 mmol), in the presence of CuI (5 mg), in $i\text{Pr}_2\text{NH}/\text{CH}_2\text{Cl}_2$ (40 cm³, 1:1, v/v). The title product was purified on preparative TLC plates eluting with CH_2Cl_2 /hexane (1:4, v/v) and isolated as a pale yellow solid ($R_f = 0.24$, 68.9 mg, 44%). IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2116 cm⁻¹. ¹H NMR (CDCl_3): δ 0.69–0.75 (m, 18H, CH₃), 0.99–1.19 (m, 24H, CH₂), 1.46–1.56 (m, 12H, CH₂), 4.96 (s, 4H, CH₂), 7.15 (t, 4H, $J_{\text{H-H}} = 16.2$ Hz, Ar), 7.37 (t, 4H, $J_{\text{H-H}} = 16.2$ Hz, Ar), 7.47 (d, 4H, $J_{\text{H-H}} = 8.1$ Hz, Ar) and 8.02 (d, 4H, $J_{\text{H-H}} = 8.1$ Hz, Ar). ¹³C NMR (CDCl_3): δ 13.77, 22.41, 24.01, 26.22 (Bu), 34.49 (CH₂), 101.74, 102.90 (C≡C) and 109.19, 118.86, 120.17, 122.84, 125.26, 140.09 (Ar). ³¹P{¹H} NMR (CDCl_3):

Table 5
Summary of crystal structure data for complexes **1**, **2** and **3**

	1	2	3
Empirical formula	C ₅₄ H ₇₄ N ₂ P ₂ Pt	C ₄₂ H ₅₀ N ₂ P ₂ Pt	C ₅₄ H ₇₄ N ₂ P ₂ Pd
Molecular weight	1008.18	839.87	919.49
Crystal size (mm)	0.30 × 0.22 × 0.20	0.28 × 0.25 × 0.22	0.33 × 0.16 × 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.2000(5)	8.932(2)	13.1729(12)
<i>b</i> (Å)	12.5112(5)	12.696(3)	12.5146(11)
<i>c</i> (Å)	15.2495(6)	17.572(5)	15.2671(14)
α (°)	90	90	90
β (°)	90.3550(10)	93.662(5)	90.306(2)
γ (°)	90	90	90
<i>U</i> (Å ³)	2518.37(17)	1988.4(9)	2516.8(4)
μ (Mo K α) (mm ⁻¹)	2.885	3.638	0.468
<i>D</i> _{calc} (g cm ⁻³)	1.330	1.403	1.213
<i>Z</i>	2	2	2
<i>F</i> (000)	1040	848	976
θ range (°)	2.05–28.27	1.98–28.26	2.05–25.00
Reflections collected	14,514	11,567	12,278
Unique reflections	5767	4577	4421
<i>R</i> _{int}	0.0251	0.0244	0.0608
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	4241	3006	2409
Number of parameters	268	214	268
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0255, 0.0660	0.0243, 0.0570	0.0474, 0.1085
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0392, 0.0747	0.0481, 0.0674	0.1146, 0.1391
Goodness-of-fit on <i>F</i> ²	1.022	1.004	0.985
Residual extrema in final diff. map (e Å ⁻³)	0.816 to -0.714	0.537 to -0.269	0.414 to -0.471

δ 10.95. FABMS: m/z 920 (M^+). Anal. Calc. for $C_{54}H_{74}N_2-P_2Pd$: C, 70.53; H, 8.11; N, 3.05. Found: C, 70.37; H, 7.98; N, 2.87%.

5. Crystallography

Single crystals of **1–3** suitable for X-ray crystallographic analyses were grown by slow evaporation of their respective solutions in CH_2Cl_2 /hexane at room temperature. The crystals were chosen and mounted on a glass fiber using epoxy resin. Crystal data, data collection parameters and refinement results of the analyses are listed in Table 5. The diffraction experiments were carried out at 290 K on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The raw intensity data frames were integrated with the SAINT+ program using a narrow-frame integration algorithm [21]. Corrections for Lorentz and polarization effects were also applied by SAINT. For each analysis, an empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS [22]. The structures were solved by direct methods, and expanded by difference Fourier syntheses using the software SHELXTL [23]. Structure refinements were made on F^2 by the full-matrix least-squares technique. In each case, all the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in their ideal positions but not refined.

6. Supplementary material

Crystallographic data (comprising hydrogen atom coordinates, thermal parameters and full tables of bond lengths and angles) for the structural analysis have been deposited with the Cambridge Crystallographic Centre (Deposition Nos. 281486–281488). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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