Synthesis, structures and photophysical properties of luminescent copper(I) and platinum(II) complexes with a flexible naphthyridine-phosphine ligand[†]

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Received 16th November 2007, Accepted 20th March 2008 First published as an Advance Article on the web 30th April 2008 DOI: 10.1039/b71777a

Condensation of Ph₂PH and paraformaldehyde with 2-amino-7-methyl-1,8-naphthyridine gave the new flexible tridentate ligand 2-[*N*-(diphenylphosphino)methyl]amino-7-methyl-1,8-naphthyridine (**L**). Reaction of **L** with [Cu(CH₃CN)₄]BF₄ and/or different ancillary ligands in dichloromethane afforded *N*,*P* chelating or bridging luminescent complexes [(**L**)₂Cu₂](BF₄)₂, [(μ -L)₂Cu₂(PPh₃)₂](BF₄)₂ and [(**L**)Cu(CNN)]BF₄ (CNN = 6-phenyl-2,2'-bipyridine), respectively. Complexes [(**L**)₂Pt]Cl₂, [(μ -L)₂Cl₂ and [(**L**)Pt(CNC)]Cl (CNC = 2,6-biphenylpyridine) were obtained from the reactions of Pt(SMe₂)₂Cl₂ or (CNC)Pt(DMSO)Cl with **L**. The crystal structures and photophysical properties of the complexes are presented.

Introduction

The intriguing structures and bonding properties of 1,8naphthyridine derivative complexes, as well as the spectroscopic properties1-4 associated with this class of compounds, have generated many studies focused on the chemistry of the naphthyridine metal complexes.⁵⁻¹¹ In particular, the diphenylphosphino-1,8-naphthyridine ligand^{12,13} and its derivatives¹⁴ (Scheme 1), which can be regarded as a combination of the bidentate 1,8-naphthyridine (hard Lewis base) and 2-(diphenylphosphino) pyridine (soft Lewis base), exhibit various coordination modes and interesting spectroscopic properties. The complexes of $\text{Cu}(I),^{15}\mbox{ Ag}(I),^{16}\mbox{ Au}(I),^{17}\mbox{ Pt}(II) \mbox{ and }\mbox{ Pd}(II)^{18}\mbox{ with }1,8\mbox{-naphthyridine}$ derivatives containing a phosphorus atom and a chelating aromatic N-donor display a variety of geometries. The ligands I and II in Scheme 1 usually exhibit bridging $P^{\Lambda}N$ or $P^{\Lambda}P$ coordination modes instead of P^N chelating ones, which can be ascribed to the limitation of their rigid structural frameworks.



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† CCDC reference numbers 666202–666207. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717777a

Reports on a *P^N* chelate for rigid ligands are rather scarce. The structures with four-membered chelate rings were only achieved in some metal complexes by coordination of the 2-(diphenylphosphino)pyridine ligand to Rh(II),19 Fe(II),20 W(I)21 and Rh(III),²² whereas the chelated Pd(II) complexes using new flexible P,N pyridylphosphine ligands were recently reported by Long and co-workers.²³ We have focussed on development of a new series of flexible pyrimidine- and naphthyridine-phosphine ligands and their complexes.²⁴ Herein we report on the synthesis, structures and photophysical properties of the copper(I) and platinum(II) complexes with a new flexible 2-[N-(diphenylphosphino)methyl]amino-7-methyl-1,8-naphthyridine (L) ligand (Scheme 1), $[(L)_2Cu_2](BF_4)_2$ (1), $[(\mu-L)_2Cu_2(PPh_3)_2](BF_4)_2$ (2), $[(L)Cu(CNN)]BF_4$ (3) (CNN = 6-phenyl-2,2'-bipyridine), $[(L)_2 Pt[Cl_2 (4), [(L)_2Pt](ClO_4)_2 (5) and [(L)Pt(CNC)]Cl (6) (CNC =$ 2,6-biphenylpyridine). To the best of our knowledge, there are no reports of such work based on a flexible naphthyridine-phosphine ligand.

Results and discussion

The flexible new ligand **L** was easily prepared by the reaction of 2-methyl-7-amino-1,8-naphthyridine with Ph₂PH and $(CH_2O)_n$ refluxing in toluene under a nitrogen atmosphere, according to a previously developed method (Mannich reaction).²⁵ The condensed ligand **L** was isolated with a good yield as a white solid, and was freely soluble in CH_2Cl_2 and $CHCl_3$, but had moderate and poor solubility in MeOH and Et_2O , respectively. The preparation procedures of the **L** ligand and its complexes **1–6** are shown in Scheme 2. (i) HPPh₂/(CH₂O)_n; (ii) [Cu(CH₃CN)₄]BF₄; (iii) [Cu(CH₃CN)₄]BF₄/PPh₃; (iv) [Cu(CH₃CN)₄]BF₄/CNN; (v) Pt(SMe₂)₂Cl₂; (vi) K₂PtCl₄/LiClO₄; (vii) (CNC)Pt(DMSO)Cl.

Crystal structures

All of the complexes reported here are air-stable and have been structurally characterized by X-ray crystal analysis. Selected bond lengths and angles are listed in Table 1. Reaction of L with $[Cu(CH_3CN)_4]BF_4$ in dichloromethane yielded the binuclear



Scheme 2 Synthesis of 1-6.

copper(I) complex 1. In contrast to the linear trinuclear copper(I) complex¹⁵ with rigid diphenylphosphino-naphthyridine ligands, the complex cation of 1 comprises a dicopper center wrapped around by two L ligands displaying P,N(2)-chelating and P,N(1)-bridging coordination modes (Fig. 1). Each copper(I) atom is coordinated by two nitrogen atoms from two L ligands and one phosphorus atom from the phosphine group, finishing its T-shaped CuN₂P geometry at the Cu atoms. The copper(I) to naphthyridine-N bond distance Cu(1)–N(1A) is 1.944(8) Å, shorter than the bond length for Cu(1)–N(2) of 2.287(8) Å, and



Fig. 1 Perspective drawing (30% thermal ellipsoids) of the cation in complex 1 on a crystallographic twofold axis with phenyl rings and the hydrogen atoms removed for clarity.

the Cu(1)–P(1) distance is 2.177(3) Å. These coordinated N(2) and P(1) atoms in the chelating ring are all afforded by another L ligand. Corresponding N(1A)–Cu(1)–P(1), N(1A)–Cu(1)–N(2) and P(1)–Cu(1)–N(2) bond angles are 155.2(3), 104.6(3) and 94.2(2)°, respectively. The intramolecular Cu(1) ··· Cu(2) distance is 2.908(3) Å. These data are all comparable to those observed for other Cu(I) analogues,¹¹ and also confirm the distorted planar trigonal coordination geometry of the copper(I) center.

Complex 2 was obtained as a yellow solid by reacting equimolar [Cu(CH₃CN)₄]BF₄, PPh₃ and L under a nitrogen atmosphere in dichloromethane solution. Unlike the chelating mode found in the structure of complex 1, the crystal structure of 2 indicates that ligand L bridges two Cu(I) metal centers through the naphthyridine-N atoms and the phosphine group to form a bimetallic sixteen-membered ring that can be divided into two CuNCN four-membered rings and a twelve-membered ring having a boat conformation (Fig. 2). Each copper atom has a distorted tetrahedral geometry in which the metal center is coordinated to two chelating naphthyridine-N atoms of one L ligand and one phosphorus atom of another L ligand, leaving the fourth coordinating point occupied by the independent PPh₃. The two tridentate L ligands bridge the two copper atoms in a head-to-tail configuration. The average Cu-N and Cu-P bond lengths are 2.159(4) and 2.256(2) Å, respectively, similar to those in $[Cu_2(dpnapy)_3][ClO_4]_2$ (dpnapy = 7-diphenylphosphino-2,4dimethyl-1,8-naphthyridine).¹⁵ The bond angles at the copper atoms vary from 61.5(1) to $131.59(6)^{\circ}$. The non-bonding Cu · · · Cu separation in this compound is 5.218 Å, which is longer than that in twelve-membered ring dipalladium complexes linked by nonrigid ligands phosphine-pyridine (4.594 Å) and phosphine-pyrimidine (4.921 Å).²⁴ The two naphthyridine (N1–C9–N2 and N4–C31–N5) planes are not parallel to each other showing a dihedral angle of 8.6°.

Table 1 Selected bond lengths (Å) and angles (°) for 1–6							
Complex 1 ^a							
Cu(1)-N(1)#	1.944(8)	Cu(1) - P(1)	2.177(3)				
Cu(1) - N(2)	2 287(8)	Cu(1) = Cu(1) #	2.908(3)				
N(1) - Cu(1) #	1.943(8)	Cu(1) Cu(1)#	2.900(5)				
N(1)-Cu(1)#	1.745(0)						
$N(1)#_Cu(1)_P(1)$	155 2(3)	$N(1) = C_{11}(1) = N(2)$	104 6(3)				
$P(1) = C_{11}(1) = N(2)$	94.2(2)	$N(1) #_Cu(1) = Cu(1) #$	82 6(2)				
P(1) = Cu(1) = N(2) P(1) = Cu(1) = Cu(1) = Cu(1)	120.0(0)	N(1) = Cu(1) = Cu(1) = U(1)	62.0(2)				
$\Gamma(1) = Cu(1) = Cu(1) #$	120.0(9)	N(2) = Cu(1) = Cu(1)#	07.7(2)				
Complex 2							
$C_{\rm H}(1)$ N(1)	2 170(4)	$C_{\rm H}(1)$ $\mathbf{P}(4)$	2 218(1)				
Cu(1) = N(1) Cu(1) = N(2)	2.179(4)	Cu(1) - I(4) Cu(1) - D(1)	2.210(1)				
Cu(1) = N(2) Cu(2) = N(4)	2.239(4)	Cu(1) = P(1)	2.293(2)				
Cu(2) = IN(4)	2.033(4)	Cu(2)-P(2)	2.225(1)				
Cu(2)-P(3)	2.288(2)						
$N(1) = C_{11}(1) = P(4)$	125 9(1)	$N(1) = C_{11}(1) = N(2)$	61 5(1)				
$P(4) C_{11}(1) N(2)$	123.9(1) 124.9(1)	N(1) Cu(1) P(1)	100.4(1)				
P(4) = Cu(1) = N(2) P(4) = Cu(1) = D(1)	124.9(1) 126.2(5)	N(1) = Cu(1) = I(1) N(2) = Cu(1) = D(1)	100.4(1)				
$\Gamma(4) = Cu(1) = \Gamma(1)$ N(4) Cu(2) D(2)	120.3(3)	N(2) = Cu(1) = F(1) N(4) = Cu(2) = D(2)	90.0(1) 10(0(1)				
N(4) - Cu(2) - P(2)	119.9(1)	N(4) - Cu(2) - P(3)	106.9(1)				
P(2) = Cu(2) = P(3)	131.6(6)						
Complex 3							
$C_{\rm H}(1)$ N(2)	2.040(6)	$C_{\rm H}(1)$ N(1)	2.055(6)				
Cu(1) = N(2) Cu(1) = D(1)	2.040(0) 2.162(2)	Cu(1) = N(1) Cu(1) = N(2)	2.055(0)				
$\operatorname{Cu}(1) - \operatorname{P}(1)$	2.102(2)	Cu(1)-IN(3)	2.203(3)				
N(2)-Cu(1)-N(1)	80.4(3)	N(2)-Cu(1)-P(1)	130.0(2)				
N(1)-Cu(1)-P(1)	133.9(2)	N(2)-Cu(1)-N(3)	95.1(2)				
N(1)-Cu(1)-N(3)	117.2(2)	P(1)-Cu(1)-N(3)	96.2(2)				
Complex 4							
Pt(1)-N(4)	2.126(4)	Pt(1)-N(1)	2.139(4)				
Pt(1) - P(2)	2.204(2)	Pt(1)-P(1)	2.209(2)				
$N(4) P_{t}(1) N(1)$	92.5(2)	$N(A) P_{f}(1) P(2)$	83 5(1)				
N(4) = I(1) = N(1) N(1) = Dt(1) = D(2)	$\frac{92.3(2)}{167.4(1)}$	N(4) = I(1) = I(2) N(4) = P(1) = P(1)	167.2(1)				
$N(1) - \Gamma(1) - \Gamma(2)$ N(1) - D(1)	107.4(1)	P(4) = P(1) = P(1)	107.5(1)				
N(1) - r(1) - r(1)	83.9(1)	r(2) - r(1) - r(1)	102.3(8)				
Complex 5							
Pt(1) = N(4)	2 126(4)	Pt(1) = N(1)	2 126(4)				
$P_{t}(1) = P(1)$	2.120(4) 2.202(2)	$P_{t}(1) = P(1)$	2.120(4) 2.213(2)				
1 ((1) - 1 (1))	2.202(2)	1 ((1) - 1 (2))	2.213(2)				
N(4)-Pt(1)-N(1)	90.6(2)	N(4)-Pt(1)-P(1)	166.5(1)				
N(1)-Pt(1)-P(1)	84.0(1)	N(4)-Pt(1)-P(2)	85.0(1)				
N(1)-Pt(1)-P(2)	166.0(1)	P(1)-Pt(1)-P(2)	103.06(7)				
Complex 6							
	1.000	R (1) R (1)					
Pt(1)-C(1)	1.991(3)	Pt(1)-N(1)	2.118(3)				
Pt(1)-N(3)	2.183(3)	Pt(1)-P(1)	2.1878(9)				
$C(1)_{Pt}(1) N(1)$	80.0(1)	C(1) = Pt(1) N(3)	163.0(1)				
$N(1)_Pt(1)_N(3)$	99 7(1)	C(1) = Pt(1) = P(1)	101 6(1)				
N(1) - Pt(1) - P(3)	164 67(8)	N(3) - Pt(1) - P(1)	83 27(8)				
r(1) = 1 ((1) = r(1)	104.07(0)	$1 (3) - 1 ((1) - \Gamma(1))$	05.27(0)				
" Atoms marked with	a # are relat	ed by C_2 symmetry.					

When ligand L was reacted with $[Cu(CH_3CN)_4]BF_4$ in a 1 : 1 molar ratio in the presence of an ancillary ligand 6-phenyl-2,2'-bipyridine (CNN) in dichloromethane, the mononuclear copper(1) complex 3 using P,N(3)- and CN,N-chelation was obtained with a nathphyridine-N remaining uncoordinated to the Cu center (Fig. 3). An attempt to prepare the $[(CNN)Cu(L)_2]BF_4$ *via*



Fig. 2 Perspective drawing (30% thermal ellipsoids) of the cation in complex 2 with the hydrogen atoms removed for clarity.



Fig. 3 Perspective drawing (30% thermal ellipsoids) of the cation in complex 3 with the hydrogen atoms removed for clarity.

CN,N-chelating and P-coordinating, leaving free naphthyridine-N atoms was unsuccessful. This indicated that the L ligand more favorably adopts the P,N-chelating coordination and forms a stable six-membered ring structure.

The copper atom in **3** is four-coordinated with a distorted tetrahedral geometry in which the **L** ligand and the CNN ligand chelate the metal center through *P*,*N* and *N*,*N* atoms, respectively. Compared with the copper(1) to naphthyridine-N bond length Cu(1)–N(3) of 2.205(5) Å, the average bond distance of copper(1) to nitrogen atoms of the CNN ligand is much shorter (2.048(6) Å). The bond length Cu–P of 2.162(2) Å falls within the normal ranges for copper phosphine complexes. The bond angles at the copper atom vary from 80.4(3) to 133.6(2)°.

A *P*-coordinated platinum(II) complex [Pt{Ph₂PCH₂N(H)-C₅H₃(OH)N}₂Cl₂] obtained from the reaction of Ph₂PCH₂-N(H)C₅H₃(OH)N and [PtCl₂(cod)] (cod = cycloocta-1,5-diene) in a 2 : 1 molar ratio has been reported by Smith and co-workers,²⁶ in which the chloride atom had not been abstracted by the nitrogen

atom of pyridine. However, in the present study, the reaction of L and $Pt(SMe_2)_2Cl_2$ in a 2 : 1 molar ratio in dichloromethane gave only the complex *cis*-[(L)_2Pt]Cl_2·2CH_2Cl_2 (4·2CH_2Cl_2) with a high yield (70%). The L ligand of 4 adopted the same coordinating mode as that of 3, which further proved that L prefers the *P*, N(1)-chelating mode.

Addition of an excess of LiClO₄ to the solution of 4 in CH₃CN generated the complex $[(L)_2Pt](ClO_4)_2 \cdot CH_2Cl_2$ (5 · CH₂Cl₂). Complex [(L)Pt(CNC)]Cl (6) was prepared following a procedure similar to that described for 4, but using (CNC)Pt(DMSO)Cl as a starting material, and in chloroform at room temperature. Complexes 4 and 5 have similar crystal structures. The bis-chelate dicationic complex has a near square-planar environment around the Pt center and forms the cis isomer exclusively (Fig. 4 and 5). The L ligand chelates the platinum center through the P atom and the N(1)/N(4) atom of the naphthyridine group, and the average bond lengths of Pt-P and Pt-N are 2.207(2) and 2.129(4) Å, respectively. The N(2)/N(5) atom of the naphthyridine group is uncoordinated with an average Pt-N distance of 2.931 Å. The least-squares plane through the atoms Pt(1), P(1), P(2), N(1) and N(2) has a mean deviation of 0.17 Å. The plane defined by Pt and the coordinated P and N(3) atoms makes a dihedral angle of 15.5° With the PtN_2 mean plane.



Fig. 4 Perspective drawing (30% thermal ellipsoids) of the complex **4** with the hydrogen atoms removed for clarity.

Compared to complexes **4** and **5**, in **6** the four-coordinated platinum(II) is bonded to an adjacent *ortho*-carbon atom, the nitrogen atom of the CNC ligand and *P*,*N* atoms of **L** (Fig. 6). The least-squares plane through the atoms Pt(1), P(1), N(1), N(2) and C(1) shows a mean deviation of 0.24 Å. The plane defined by Pt(1)–P(1)–N(1) atoms has a dihedral angle of 24.7° with the Pt(1)–N(2)–C(1) mean plane. The Pt–P, Pt–C and average Pt–N bond lengths are 2.1878(9), 1.991(3) and 2.150(8) Å, respectively. The bite angles C(1)–Pt(1)–N(1) and N(3)–Pt(1)–P(1) are 80.0(1) and 83.27(8)°, respectively.



Fig. 5 Perspective drawing (30% thermal ellipsoids) of the complex **5** with the hydrogen atoms removed for clarity.



Fig. 6 Perspective drawing (30% thermal ellipsoids) of the cation in complex 6 with the hydrogen atoms removed for clarity.

Absorption and emission spectra

The spectroscopic and photophysical data of **1–6** are summarized in Table 2. Their UV-vis absorption spectra are characterized by an absorption band at 350–356 nm with tails extending to *ca.* 450 nm, which is assigned to a metal-to-ligand charge transfer (MLCT): d(Cu) $\rightarrow \pi^*$ (naphthyridine/CNN) for **1–3** and d(Pt) $\rightarrow \pi^*$ (naphthyridine) for **4–6**.^{15,27–29} In comparison, the absorption at <350 nm is attributed to originate from the intraligand (IL) $\pi \rightarrow \pi^*$ transition.⁴

Upon excitation at 350–360 nm, complexes 1–6 exhibit a photoluminescence with λ_{max} at 390–425 nm in dichloromethane

 Table 2
 Photophysical spectra data for complexes 1–6

Complex	Medium	$\lambda_{abs}/nm (\epsilon/dm^3 mol^{-1} cm^{-1})$	$\lambda_{\rm em}/\rm{nm}$ ($\lambda_{\rm ex}/\rm{nm}$)	τ/ns	$\phi_{ m em}$
1	CH_2Cl_2	273 (26 650), 355 (18 550) 375 (13 700)	423(350)	5.1	0.077
	Solid	575 (15 700)	525(350)	1341	
2	CH ₂ Cl ₂ Solid	270 (41 650), 350 (13 450)	425(350) 540(350)	4.9 609	0.217
3	CH_2Cl_2	270 (34 534), 308 (26 657) 355 (13 157)	390(350)	2.9	0.014
	Solid		450(350)		
4	CH ₂ Cl ₂	275 (21 190), 335 (22 488) 350 (24 833) 370 (20 143)	420(370)	1.3	0.307
	Solid	220 (21 022), 270 (20 112)	490(370)	29500	
5	CH_2Cl_2	270 (20.260), 328 (18 490) 342 (21557) 357 (21 773)	420(360)	5.1	0.114
	Solid		480(370)	2160	
6	CH ₂ Cl ₂ Solid	270 (37 856), 350 (19 695)	395(360) 530/370	1.5	0.024

solution $(2.0 \times 10^{-5} \text{ M})$ at room temperature, with measured emission quantum yields of 0.077, 0.217, 0.014, 0.307, 0.114 and 0.024, respectively. The short excited-state lifetimes (<10 ns) and small Stokes shifts of these complexes indicate that the emissions are the intraligand fluorescence. However, complexes 2 and 4 display intense solid-state emissions at 540 and 490 nm, respectively. The emissions have relatively long lifetimes of 0.6 and 29.5 µs implying that these emissions originate from a triplet excited state. In addition, time-resolved emission measurements of solid samples of 2 and 4 revealed that the emissions follow a single-exponential decay with microsecond lifetime magnitudes (Fig. 7 and 8).



Fig. 7 Time-resolved emission spectra of 2 with excitation at 355 nm in the solid state at room temperature.

Conclusions

A new flexible N,P ligand 2-[N-(diphenylphosphino)methyl]amino-7-methyl-1,8-naphthyridine and its six types of



Fig. 8 Time-resolved emission spectra of 4 with excitation at 355 nm in the solid state at room temperature.

photoluminescent mono- or binuclear Cu(I) and Pt(II) complexes were prepared. X-Ray crystal analysis showed that complex $[(L)_2Cu_2](BF_4)_2$ exhibits both P,N-chelating and -bridging coordination modes, and has crystallographic C_2 symmetry. But when one coordinating point is occupied, ligand L bridges two Cu(I) centers to form the binuclear complex 2. However, one bidentate 6-phenyl-2,2'-bipyridine ligand was chelated to a copper(I), resulting in a *P*,*N*-chelating mononuclear complex. In comparison with the structures of copper(I) the ligand L in the reported platinum(II) complexes having a square-planar array adopts only a chelating mode to coordinate to metal in a cis configuration, and the bonding mode is unaffected in the presence of ancillary ligand. Spectroscopic investigations suggest that solution emissions of these compounds at room temperature are derived from an intraligand singlet excited state, whereas relatively solid-state low-energy emissions are assigned to ³MLCT transition. This study provides novel information for the development of flexible 1,8-naphthyridine-phosphine derivatives with promising applications.

Experimental

Materials

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. The compounds [Cu(CH₃CN)₄]BF₄, Pt(SMe₂)₂Cl₂,³⁰ (CNC)Pt(DMSO)Cl³¹ and 6-phenyl-2,2'-bipyridine³² as well as starting material 2-methyl-7-amino-1,8-naphthyridine³³ were prepared according to previously published methods. Reagent grade solvents were dried by standard procedures, and freshly distilled prior to use. Solvents used in spectroscopic measurements were HPLC grade, and solutions were degassed by employing at least four freeze–pump–thaw cycles. All other chemicals were obtained from commercial sources and used directly without further purification.

Instrumentation

¹H, ¹³C and ³¹P NMR spectra were recorded on a DPX-400 Bruker spectrometer and chemical shifts (δ , ppm) were obtained relative to tetramethylsilane (Me₄Si) for ¹H. Elemental analyses were performed with a Carlo Erba 1106 element analysis instrument. The UV-vis spectra were taken on a HITACHI U-3010 spectrophotometer, and the corrected emission spectra of solutions and solids were obtained on a HITACHI F-4500 fluorescence spectrophotometer adapted to a right-angle configuration at room temperature. Time-resolved emission spectra and emission lifetimes of the samples were performed with Single Photon Count Technology on a FL920 Spectrometer (Edinburgh). Time-resolved spectra were developed by measurement of the decays at individual wavelengths.

Synthesis of 2-[*N*-(diphenylphosphino)methyl]amino-7-methyl-1,8naphthyridine, L

Diphenylphosphine, 4.65 g (0.025 mol), and paraformaldehyde, 0.75 g (0.025 mol), were added to a suspension of 3.98 g (0.025 mol) 2-methyl-7-amino-1,8-naphthyridine in toluene (100 ml). The mixture was refluxed with stirring for 12 h under a nitrogen atmosphere. The resulting solution was then cooled slowly to -20 °C. A pale yellow crystalline solid was isolated by suction filtration, and then washed with small portions of diethyl ether and dried in vacuo. Yield: 5.47 g (61%). The crystalline solid was characterized by ¹H, ¹³C and ³¹P NMR. ¹H NMR (400 MHz, CDCl₃): δ 2.70 (s, 3H, CH₃), 4.42 (t, J = 4.8 Hz, 2H, CH₂), 4.82 (broad, 1H, NH), 6.52 (d, J = 8.7 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H). ¹³C NMR (CDCl₃): δ 25.0 (CH₃), 39.8 (d, CH₂), 111.7, 115.0, 118.1, 128.2, 128.3, 128.7, 132.4, 132.6, 135.8, 136.7, 158.5, 161.4. ³¹P NMR (CDCl₃): δ –17.21.

Synthesis of complex (L)₂Cu₂(BF₄)₂, 1

L, 100 mg (0.28 mmol), and $[Cu(CH_3CN)_4]BF_4$, 88.5 mg (0.28 mmol), were mixed in dichloromethane (30 ml) under a nitrogen atmosphere. After stirring for 15 h at room temperature,

the mixture was evaporated until dry *in vacuo*, leaving a yellow solid. Light yellow crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into a dichloromethane solution. Yield: 88 mg (62%). ¹H NMR (400 MHz, DMSO-d₆): δ 2.50 (s, 6H, CH₃), 3.33 (s, 4H, CH₂), 4.74 (broad, 2H, NH), 6.98 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 7.36 (t, J = 7.2 Hz, 8H), 7.45 (t, J = 7.2 Hz, 4H), 7.67 (broad, 8H), 7.89 (d, J = 8.9 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H). Anal. Calc. for C₄₄H₄₀B₂Cu₂F₈N₆P₂: C, 52.04; H, 3.97; N, 8.28. Found: C, 51.92; H, 3.93; N, 8.24%.

Synthesis of complex (µ-L)₂Cu₂(PPh₃)₂(BF₄)₂, 2

L, 100 mg (0.28 mmol), was added to an overnight stirred solution of PPh₃, 73 mg (0.28 mmol), and $[Cu(CH_3CN)_4]BF_4$, 88.5 mg (0.28 mmol), in dichloromethane (30 ml), under a nitrogen atmosphere at ambient temperature. After stirring the solution for 4 h, the solvent was removed. Yield: 116 mg (54%). Yellow single crystals were obtained by diffusion of diethyl ether into a dichloromethane solution. ¹H NMR (400 MHz, CDCl₃): δ 2.15 (s, 6H, CH₃), 3.48 (s, 4H, CH₂), 4.34 (broad, 2H, NH), 7.03 (broad, 20H), 7.17 (m, 20H), 7.33 (m, 10H), 7.48 (m, 2H), 7.53 (m, 4H), 7.64–7.73 (m, 2H). Anal. Calc. for C₈₀H₇₀B₂Cu₂F₈N₆P₄: C, 62.39; H, 4.58; N, 5.46. Found: C, 62.28; H, 4.54; N, 5.37%.

Synthesis of complex [(L)Cu(CNN)]BF₄, 3

mg mmol), 6-phenyl-2,2'-bipyridine, 40 (0.17)and [Cu(CH₃CN)₄]BF₄, 56 mg (0.17 mmol), were mixed with stirring in dichloromethane (30 ml) under a nitrogen atmosphere. After 30 min, L, 62 mg (0.17 mmol), was added. The resulting mixture was stirred overnight and concentrated to ~ 2 ml. Subsequent diethyl ether diffusion into the solution afforded orange crystals in a 75% yield. ¹H NMR (400 MHz, CDCl₃): δ 1.66 (s, 3H, CH₃), 4.23 (s, 2H, CH₂), 6.65 (d, J = 7.2 Hz, 1H), 6.99-7.10 (m, 5H), 7.20 (t, J = 7.2 Hz, 4H), 7.26-7.32 (m, 7H),7.45–7.57 (m, 3H), 7.77 (s, 1H), 7.87 (d, J = 6.8 Hz, 1H), 8.08 (s, 1H), 8.15 (s, 1H), 8.22 (d, J = 6.5 Hz, 1H), 8.54 (s, 1H). Anal. Calc. for C₃₈H₃₂BCuF₄N₅P: C, 61.68; H, 4.36; N, 9.46. Found: C, 61.53; H, 4.32; N, 9.57%.

Synthesis of complex [(L)₂Pt]Cl₂, 4

A mixture of L, 92 mg (0.26 mmol), and Pt(SMe₂)₂Cl₂, 50 mg (0.13 mmol), in dichloromethane (30 ml) was stirred under a nitrogen atmosphere at room temperature for 2 h. The mixture gradually turned from yellow to clear colorless. The solvent was removed *in vacuo*. The pale yellow crystals in 70% yield were obtained by diffusion of diethyl ether into a dichloromethane solution. ¹H NMR (400 MHz, DMSO-d₆): δ 2.77 (s, 6H, CH₃), 3.33 (s, 4H, CH₂), 4.75 (broad, 2H, NH) 6.78 (d, J = 8.8 Hz, 2H) 7.04–7.08 (m, 10H), 7.29 (t, J = 8.0 Hz, 2H), 7.45 (t, J = 7.2 Hz, 4H), 7.57 (t, J = 7.2 Hz, 2H), 7.62 (d, J = 8.9 Hz, 2H), 7.73 (d, J = 7.9 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 7.9 Hz, 2H). Anal. Calc. for C₄₄H₄₀Cl₂N₆P₂Pt: C, 53.88; H, 4.11; N, 8.57. Found: C, 53.85; H, 4.16; N, 8.59%.

Synthesis of complex [(L)₂Pt](ClO₄)₂, 5

A mixture of 4, 100 mg (0.10 mmol), and excess $LiClO_4$ ·3H₂O, 160 mg (1.00 mmol), in acetonitrile (30 ml) was stirred under a

	1	2	3	$\textbf{4}{\cdot}\textbf{2}\textbf{C}\textbf{H}_{2}\textbf{C}\textbf{l}_{2}$	$5 \cdot CH_2Cl_2$	6
Formula	$C_{44}H_{40}B_2Cu_2F_8N_6P_2$	$C_{80}H_{70}B_2Cu_2F_8N_6P_4$	$C_{38}H_{32}BCuF_4N_5P$	$C_{46}H_{44}Cl_6N_6P_2Pt$	$C_{45}H_{42}Cl_4N_6O_8P_2Pt \\$	$C_{39}H_{32}N_4PClPt$
Formula weight	1015.46	1540.00	740.01	1150.60	1193.68	818.23
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P\overline{1}$	C2/c	$P2_1/n$	$P2_1/c$	C2/c
Crystal size/mm	$0.21 \times 0.14 \times 0.12$	$0.22 \times 0.18 \times 0.14$	$0.66 \times 0.20 \times 0.18$	$0.40 \times 0.380.35$	$0.32 \times 0.18 \times 0.16$	$0.24 \times 0.20 \times 0.18$
a/Å	17.790(2)	13.046(2)	49.300(11)	16.299(13)	14.624(11)	37.565(8)
b/Å	16.382(2)	13.073(2)	12.055(3)	16.892(14)	17.326(12)	10.6978(19)
c/Å	15.468(3)	22.398(4)	25.150(5)	19.458(16)	20.341(15)	22.217(5)
$a/^{\circ}$	90	88.669(3)	90	90	90	90
β/°	97.821(3)	88.968(4)	109.728(5)	113.498(9)	110.453(7)	132.471(2)
y/°	90	74.638(3)	90	90	90	90
$V/Å^3$	4466.0(11)	3682.3(11)	14069(5)	4913(7)	4829(6)	6586(2)
Ζ	4	2	16	4	4	8
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.510	1.389	1.397	1.556	1.642	1.650
F(000)	2064	1584	6080	2288	2376	3232
μ/mm^{-1}	1.098	0.734	0.723	3.286	3.251	4.426
θ range/°	1.70-25.01	0.91-25.02	1.65-25.01	1.39-28.80	1.49-25.01	1.47-27.89
Reflections collected	11353	18971	36058	30802	23953	30213
$R_{\rm int}$	0.1425	0.0507	0.1226	0.0536	0.0460	0.0422
Parameters	352	921	957	550	639	420
Goodness of fit	0.979	1.028	1.006	1.015	1.019	1.078
$R1^a$	0.0737	0.0569	0.0618	0.0424	0.0321	0.0288
$wR2^a$	0.1732	0.1026	0.1294	0.0887	0.0766	0.0659
Δho /e Å ⁻³	0. 69, -0.546	0.660, -0.460	0.508, -0.394	2.862, -1.476	1.61, -0.693	2.135, -1.120
^{<i>a</i>} $I > 2\sigma(I), R_1 = \sum H$	$ F_{o} - F_{c} \sum F_{o} ; wR$	$P_2 = \{\sum [w(F_o^2 - F_c^2)^2]$	$]/\sum [w(F_o^2)^2]\}^{1/2}.$			

 Table 3
 Summary of X-ray crystallographic data for complexes 1–6

nitrogen atmosphere at room temperature for 1 h. Next, the solvent was concentrated down to ~2 ml, excess diethyl ether was added and a pale yellow solid was obtained. Recrystallization of the crude product from a dichloromethane and diethyl ether solution afforded pale yellow single crystals of **5**·CH₂Cl₂ in 80% yield. ¹H NMR (400 MHz, DMSO-d₆): δ 2.77 (s, 6H, CH₃), 3.32 (s, 4H, CH₂), 4.80 (broad, 2H, NH), 6.72 (d, J = 8.9 Hz, 2H), 7.05–7.14 (m, 10H), 7.30 (t, J = 7.2 Hz, 2H), 7.43–7.51 (m, 4H), 7.56 (t, J = 7.2 Hz, 2H), 7.62 (d, J = 8.9 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 8.14 (dd, J = 7.7 Hz, 4H). Anal. Calc. for C₄₄H₄₀Cl₂N₆O₈P₂Pt: C, 47.66; H, 3.64; N, 7.58. Found: C, 47.58; H, 3.57; N, 7.66%.

Synthesis of complex [(L)Pt(CNC)]Cl, 6

A mixture of (CNC)Pt(DMSO)Cl, 108 mg (0.20 mmol), and L, 71 mg (0.20 mmol), in chloroform (30 ml) was stirred overnight under a nitrogen atmosphere at room temperature. The solvent was concentrated down to ~2 ml *in vacuo*. Addition of diethyl ether gave a yellow solid. Yellow crystals (65% yield) were obtained by diffusion of diethyl ether into a chloroform solution. ¹H NMR (400 MHz, CDCl₃): δ 2.78 (s, 3H, CH₃), 3.47 (s, 2H, CH₂), 4.67 (broad, 1H, NH), 6.70 (d, J = 7.8 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.90–7.14 (m, 4H), 7.30 (m, 4H), 7.43–7.55 (m, 8H), 7.68 (m, 2H), 7.76–7.93 (m, 4H), 7.97 (d, J = 7.8 Hz, 1H), 8.12 (d, J =7.8 Hz, 1H). Anal. Calc. for C₃₉H₃₂ClN₄PPt: C, 57.25; H, 3.94; N, 6.85. Found: C, 57.38; H, 3.96; N, 6.77%.

X-Ray crystallography

Crystal data, details of data collection as well as refinement of the structures of **1–6** are summarized in Table 3. Diffraction data were collected at 298 K with graphite-monochromated Mo-K α radiation ($\lambda = 0.071073$ nm) on a Rigaku R-AXIS RAPID

IP X-ray diffractometer. The diffraction data were corrected for absorption correction using the ABSCOR program. The structures were determined by direct methods using the program SHELXS 97 and refined by full-matrix least squares on F^2 using the SHELXL 97 program package.³⁴ The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically, assigned appropriate isotropic thermal parameters and included in structure factor calculations.

CCDC reference numbers 666202-666207.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717777a

Acknowledgements

The work was supported by the National Basic Research Program of China (973 program 2005CCA06800, 2007CB613304), the National Natural Science Foundation of China (NSFC Grant No. 20761006, 20671094, 90610034). We thank the foundation (50418010) for NSFC/RGC Joint Research.

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