Cyclometalated organoplatinum(II) complexes: first example of a monodentate benzo[*h*]quinolyl ligand and a complex with bridging *bis*(diphenylphosphino)ethane†

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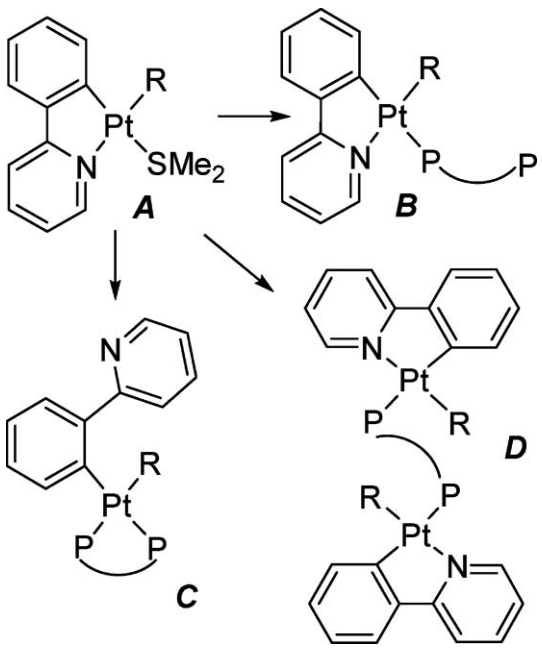
The cyclometalated complexes [Pt(ppy)R(SMe_2)] or [Pt(bhq)R(SMe_2)], where ppyH = 2-phenylpyridine, bhqH = benzo[*h*]quinoline and R = methyl or *p*-tolyl, react with *bis*(diphenylphosphino)ethane, dppe, in a 1 : 1 ratio to give the corresponding complexes [Pt(κ¹-*C*-ppy)R(dppe)] or [Pt(κ¹-*C*-bhq)R(dppe)], in which the ppy or bhq ligands are monodentate and dppe is chelating. The similar reaction in a 2 : 1 ratio gives the binuclear complexes [{Pt(ppy)R}$_2$(μ-dppe)] or [{Pt(bhq)R}$_2$(μ-dppe)], in which the dppe ligands are in the unusual bridging bidentate bonding mode.

Introduction

We and many others have been interested in the assembly of cyclometalated organoplatinum(II) complexes to form more complex structures for potential applications in molecular materials.[1–3] In particular, the reaction of the complexes ***A*** (Scheme 1, R = methyl or aryl)[1,4] with diphosphine ligands in a 1 : 1 molar ratio can give either ***B*** (PP = $Ph_2PCH_2PPh_2$, dppm) or ***C*** (PP = [$(Ph_2PC_5H_4)_2Fe$], dppf).[1] In these complexes, the platinum(II) center remains 4-coordinate with square planar stereochemistry, but there is a competition between chelation by the diphosphine ligand or the C,N-donor ligand derived from 2-phenylpyridine. Complex ***B*** has a free phosphine donor while ***C*** has a free pyridyl group. In either case, reaction in a 2 : 1 molar ratio gives the bridged binuclear complexes ***D*** (Scheme 1).[1]

Based on the above observations, it was not obvious if complexes of type ***C*** would be formed irreversibly by fast ring closing on reaction of ***A*** with strongly chelating diphosphines such as *bis*(diphenylphosphino)ethane, dppe,[5] or if it might still be possible to prepare the bridged binuclear complexes of type ***D*** (Scheme 1).[1] The ligand dppe may often act as a bridging ligand with coinage metals having linear or trigonal stereochemistry, or in transition metal complexes, especially those containing metal-metal bonds.[6–9] However, the tendency for chelation of dppe is very strong in square planar complexes and there are few examples of bridging dppe (Scheme 2).[10,11] It is noteworthy that all contain strongly bound tridentate pincer ligands which leave only one potential coordination site for the diphosphine ligand, so that chelation of dppe is not possible.

This article reports reactions of cyclometalated complexes of type ***A*** (Scheme 1) with the ligand dppe, including characterization of derivatives of type ***C*** and ***D***. The complexes of type ***D*** are unusual examples of square planar complexes with bridging dppe ligands.



Scheme 1 Cyclometalated complexes with diphosphine ligands.

Results and discussion

The new chemistry is shown in Scheme 3. The complexes [PtMe(ppy)(SMe_2)], ppyH = 2-phenylpyridine, **1a**, and [PtMe(bhq)(SMe_2)], **2a**, bhqH = benzo[*h*]quinoline, have been prepared previously by reaction of [Pt_2Me_4(μ-SMe_2)$_2$] with ppyH or bhqH and used *in situ* for further synthesis.[1a,4] In the present study these compounds, and the known precursors [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**, [Pt(*p*-MeC_6H_4)(bhq)(SMe_2)], **2b**, were isolated as pure solids.[1,4,12] They are air-stable solids and complex **1b** was structurally characterized (Fig. 1).

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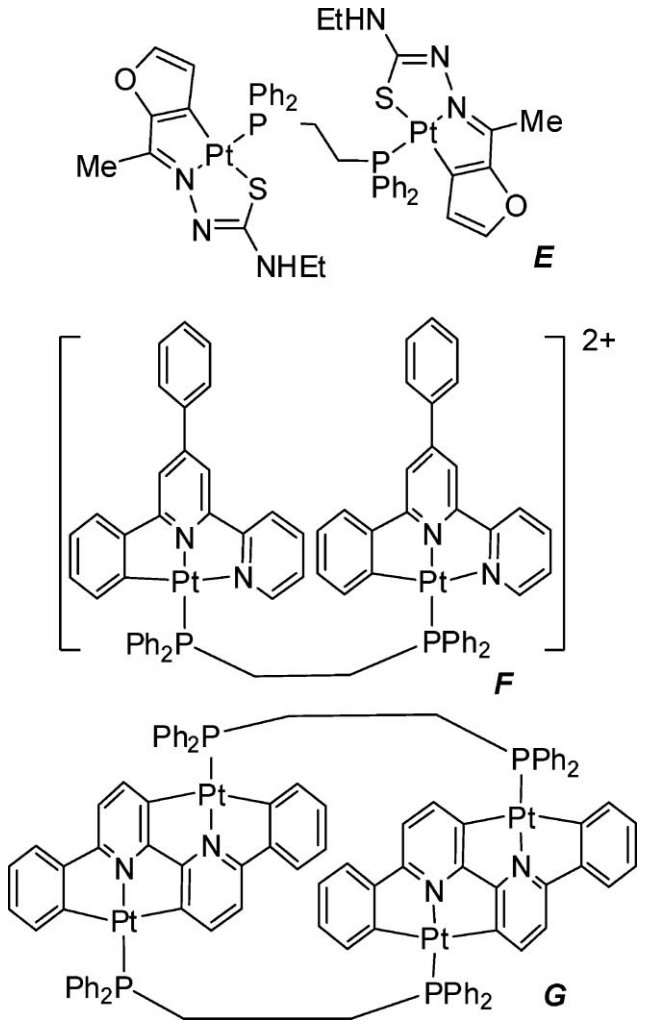
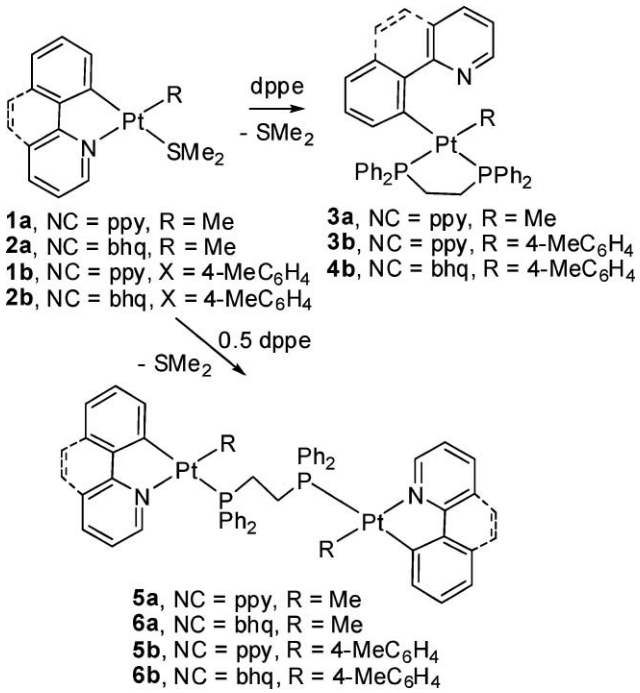


Scheme 2 Platinum complexes with bridging dppe ligands.



Scheme 3 Synthesis of complexes **1–6**.

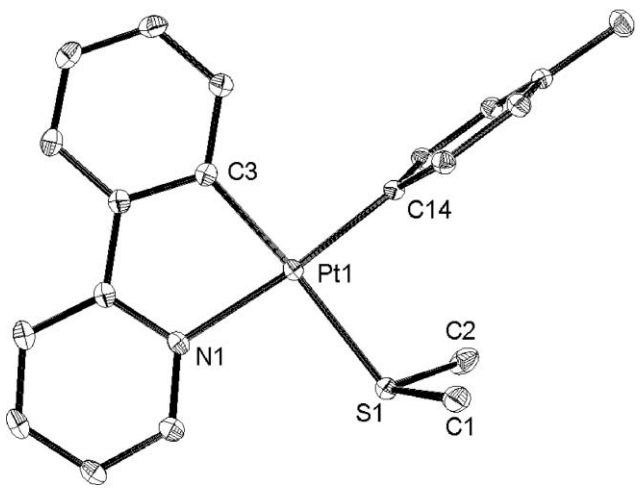


Fig. 1 A view of the structure of complex **1b**. Selected bond parameters (Å, °): Pt1–C14 2.000(2); Pt1–C3 2.006(2); Pt1–N1 2.118(2); Pt1–S1 2.3572(7); C14–Pt1–C3 93.56(10); C3–Pt1–N1 80.48(9); C14–Pt1–S1 90.66(7); N1–Pt1–S1 95.30(6).

The complex [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**, has square planar stereochemistry at platinum, with the greatest distortion associated with the constraints of the chelate Pt(ppy) ring. The *p*-tolyl group lies roughly orthogonal to the square plane and to the ppy ligand, but the two Pt–C distances are approximately equal (Fig. 1).

The complex **3a** was prepared by reaction of complex **1a** with dppe in a 1 : 1 ratio. It was isolated as a stable colorless solid which was characterized by its ^{1}H and ^{31}P NMR spectra. The methylplatinum resonance appeared in the ^{1}H NMR spectrum as a triplet, evidently because the *cis* and *trans* coupling constants to phosphorus are equal with $^3J_{PH}$ = 7 Hz (Fig. 2a). The non-equivalence of the two phosphorus donors was indicated by the observation of two resonances in the ^{31}P NMR spectrum at $\delta(^{31}P)$ = 41.4 [$^1J_{PtP}$ = 1811 Hz] and 44.1 [$^1J_{PtP}$ = 1821 Hz], and the similar magnitudes of the coupling constants $^1J_{PtP}$ indicates that both are *trans* to the carbon donor of an aryl group. The phosphorus-phosphorus coupling constant $^2J_{PP}$ = 2 Hz, is very small and clearly shows that the phosphorus donors are mutually *cis.* Finally, the non-coordination of the pyridyl group is shown by the absence of coupling $^3J_{PtH}$ to the H^6 proton of the pyridyl group. Complexes **3b** and **4b** were prepared and characterized in a similar way from the appropriate precursor complex **1b** and **2b** (Scheme 3). Attempts to prepare the complex [PtMe(η^1-bhq)(dppe)], **4a**, in an analogous way were unsuccessful. Also, complex **4b** was considerably less stable in solution than **3b** and these observations indicate that the rigid ligand bhq is less favored than the more flexible ppy when bound in the η^1 form.

The complexes **5** and **6** were prepared as yellow solids by reaction of the appropriate precursor complex **1** or **2** with dppe in a 2 : 1 ratio (Scheme 3). They were characterized by their ^{1}H and ^{31}P NMR spectra, and complexes **5b** and **6b** were also structurally characterized. The methylplatinum resonance in the ^{1}H NMR

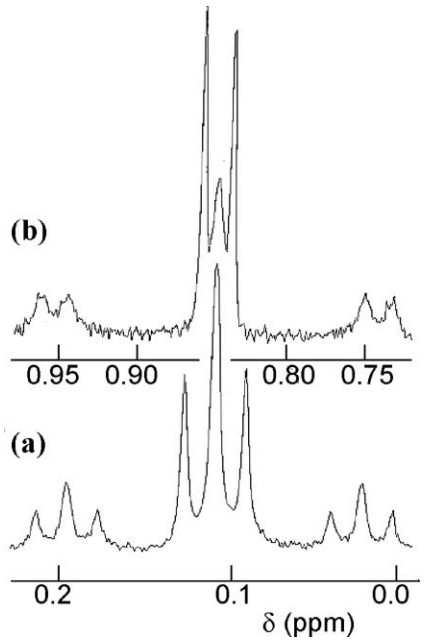


Fig. 2 ^{1}H NMR spectra (Pt–Me region, CD_2Cl_2) of: (a) [PtMe(ppy)-(dppe)], **3a**; (b) [$Pt_2Me_2(bhq)_2$(μ-dppe)], **6a**.

spectrum of [$Pt_2Me_2(bhq)_2$(μ-dppe)], **6a**, is shown in Fig. 2b. The main resonance appears as a second order $A_3A'_3XX'$ spin system through coupling between the ^{1}H and ^{31}P atoms in each $H_3CPtPCCPPtCH_3$ unit. The apparent doublet is separated by ^{3}J(PH) + ^{6}J(PH) and is equal to ^{3}J(PH) because the long range coupling is zero. There is a broad central peak, typical of cases with an intermediate value of ^{3}J(PP).[13] The central resonance in the ^{31}P NMR spectrum (Fig. 3b) appears as a singlet but the satellite resonances display the coupling ^{3}J(PP) = 47 Hz.

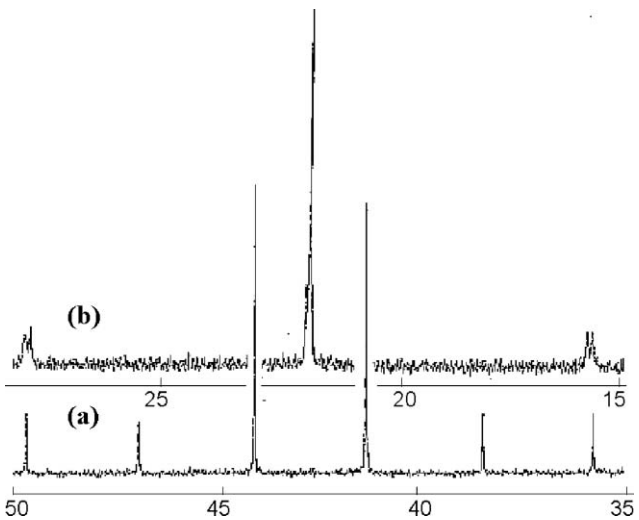


Fig. 3 ^{31}P NMR spectra of: (a) [PtMe(ppy)(dppe)], **3a**; (b) [$Pt_2(p\text{-}MeC_6H_4)_2(bhq)_2$(μ-dppe)], **6b**, in CD_2Cl_2.

The structure of complex **6a** is shown in Fig. 4. There are two independent molecules in the unit cell, one less symmetrical conformer (Fig. 4a) and one having a center of symmetry (Fig. 4b). In the centrosymmetric molecule the dppe ligand has the ideal anti conformation with dihedral angle PCCP = 180° and

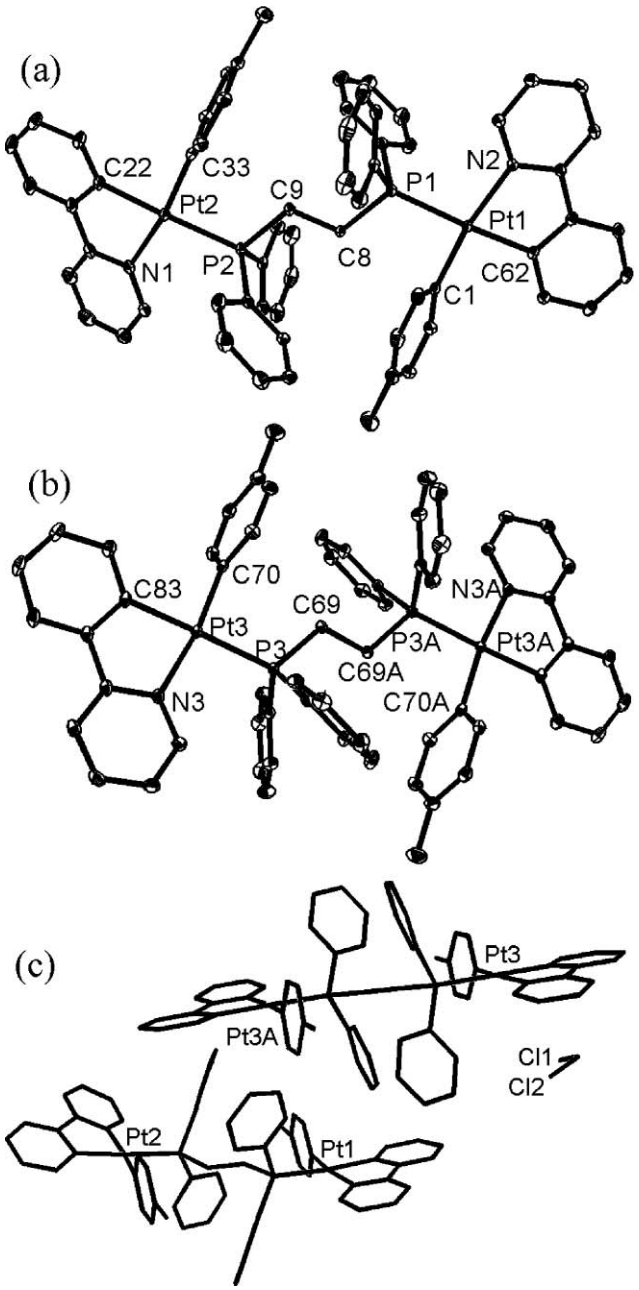


Fig. 4 Views of the structure of complex **5b**: (a) the non-centrosymmetric molecule; (b) the centrosymmetric molecule; (c) two adjacent molecules showing some aryl-aryl interactions and a dichloromethane solvate molecule. Selected bond parameters (Å, °): Pt1–C1 2.012(3); Pt1–C62 2.041(3); Pt1–N2 2.110(2); Pt1–P1 2.3206(7); Pt2–C33 2.009(3); Pt2–C22 2.033(3); Pt2–N1 2.122(2); Pt2–P2 2.3190(7); Pt3–C70 2.015(3); Pt3–C83 2.045(3); Pt3–N3 2.124(2); Pt3–P3 2.3106(7); C62–Pt1–N2 79.83(10); C22–Pt2–N1 79.70(11); C83–Pt3–N3 79.47(10).

the ppy ligands perfectly parallel to one another. However, the unsymmetrical molecule has PCCP = 175° and the angle between the mean planes of the ppy ligands is 143°. Fig. 4c shows two adjacent molecules, in which secondary bonding occurs through a series of edge-to-face and vertex-to-face aryl · · · aryl attractions.

The structure of complex **6b** is shown in Fig. 5. The molecule is centrosymmetric (Fig. 5a) and is similar to the centrosymmetric conformer of complex **5b** (Fig. 4b). The main difference between

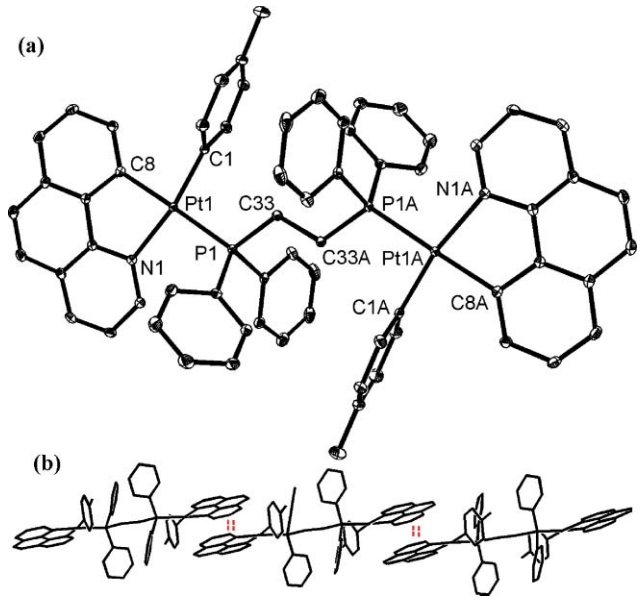
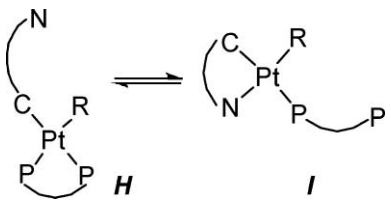


Fig. 5 Views of the structure of complex **6b**: (a) the centrosymmetric molecule; (b) the packing of molecules through π-stacking of bhq groups. Selected bond parameters (Å, °): Pt1–C1 2.010(2); Pt1–C8 2.046(2); Pt1–N1 2.1318(17); Pt1–P1 2.3106(5); C1–Pt1–C8 88.81(8); C8–Pt1–N1 80.60(7); C1–Pt1–P1 91.79(6); N1–Pt1–P1 98.91(5).

6b and **5b** is in the packing of the molecules. Molecules of complex **6b** assemble to give a supramolecular polymer structure through π-stacking between parallel bhq groups, as shown in Fig. 5b, while complex **5b** does not give π-stacking between the smaller ppy groups (Fig. 4c).

Conclusions

The cyclometalated platinum(II) complexes derived from 2-phenylpyridine or benzo[*h*]quinoline have already given a wide range of interesting compounds.[1–4] The range is now extended to give rare examples of square planar complexes containing bridging dppe ligands,[10,11] as illustrated by the structures of complexes **5b** and **6b** (Scheme 3, Figs. 4 and 5). It is now also possible to discuss the relative stabilities of the isomers ***H*** and ***I*** (Scheme 4) as a function of the diphosphine and C,N-donor ligand. For the complexes studied so far, there is no dependence on whether R = methyl or aryl or whether C–N = ppy or bhq, but there is a dependence on the ligand P–P = $Ph_2PCH_2PPh_2$ (dppm), $(Ph_2PC_5H_4)_2Fe$ (dppf), or $Ph_2P(CH_2)_2PPh_2$ (dppe).[1] Only with dppm is the isomer ***I*** favoured, while both dppf and dppe favour isomer ***H***.



Scheme 4 The potential conversion between isomers [Pt(κ¹-C–N)-(κ²-P–P)], ***H***, and [Pt(κ²-C–N)(κ¹-P–P)], ***I***.

It is well known that the 4-membered Pt(dppm) chelate ring is strained whereas the 5-membered Pt(dppe) chelate ring is not,[14] and so this can rationalize the observation of isomer ***I*** when P–P = dppm, even though platinum(II) is a soft metal center which normally favors phosphorus over nitrogen coordination.[15] It should also be noted that the chelate Pt(bhq) is expected to be relatively favoured compared to the chelate Pt(ppy) ring, based on the fact that bhq is more rigid. Several monodentate ppy complexes are known, including ***I*** (Scheme 4, C–N = ppy, P–P = dppf, R = Me),[1a] but we are not aware of any precedents for the monodentate form of bhq which is established for complex **4b** (Scheme 3).[1–3] There is a strong analogy to the coordination chemistry of 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen), for which bipy forms more monodentate complexes than the more rigid ligand phen.[16]

The lowest energy structures of the complexes [PtPh(κ¹-*C*-bhq)(dppe)] and [PtPh(κ¹-*C*-ppy)(dppe)], as calculated by Density Functional Theory (DFT), are shown in Fig. 6.[17] In the complex [PtPh(κ¹-*C*-bhq)(dppe)], the nitrogen donor is held close to the platinum centre (Pt..N = 2.70 Å, Fig. 6a), very close to the distances observed in monodentate phen complexes,[16] as required by the rigid bhq skeleton. The Pt..N interaction appears to be weakly antibonding in nature, with the HOMO having the character of the antibonding combination of filled platinum $5d_{z^2}$ and nitrogen lone pair orbitals (Fig. 6c). In the complex [PtPh(κ¹-*C*-ppy)(dppe)], the nitrogen donor is anti to platinum and rotation about the pyridyl-phenyl bond allows the *ortho*-CH group to twist away from the platinum centre (Fig. 6b) and the HOMO has weakly antibonding character with contributions from Pt $5d_{z^2}$, **σ** (CH) and nitrogen lone pair orbitals (Fig. 6d).

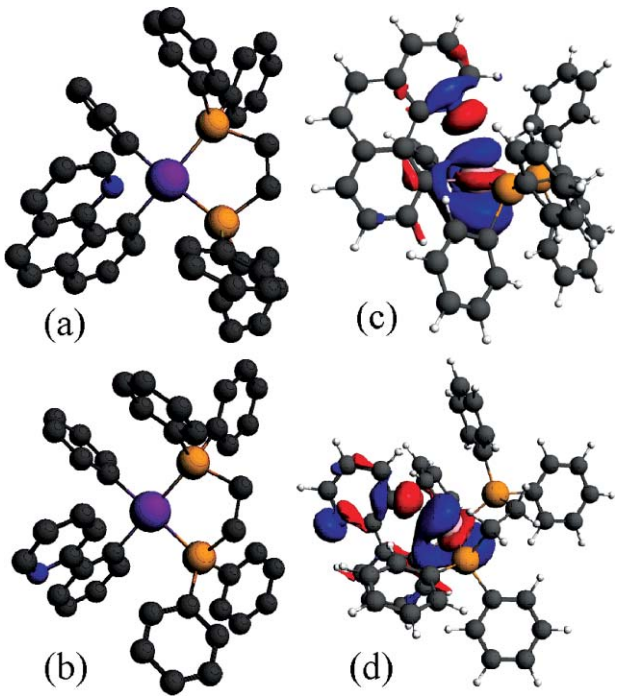


Fig. 6 Views of the DFT calculated structure and the HOMO of (a), (c) [PtPh(κ¹-*C*-bhq)(dppe)] and (b), (d) [PtPh(κ¹-*C*-ppy)(dppe)].

The calculated structure of [PtPh(κ²-*C*,*N*-ppy)(κ¹-*P*-dppe)] and the HOMO, which has mostly platinum $5d_{z^2}$ character, are shown

in Fig. 7. The calculated energy is 62 kJ mol-1 higher than for its isomer shown in Fig. 6b, while the corresponding energy for [PtPh(κ²-*C*,*N*-bhq)(κ¹-*P*-dppe)] is calculated to be 26 kJ mol-1 higher than for its isomer [PtPh(κ¹-*C*-bhq)(κ²-dppe)] shown in Fig. 6a. Thus, the theory correctly predicts the preferred isomer and also predicts a greater preference for the κ¹-*C*-isomer for the pph compared to the bhq complex.

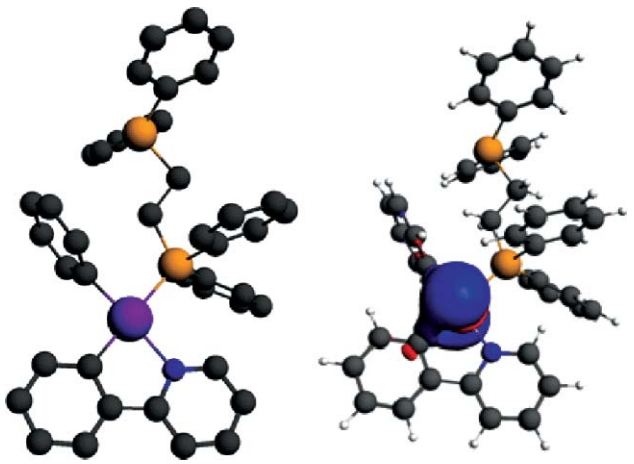


Fig. 7 The calculated structure of [PtPh(κ²-*C*,*N*-ppy)(κ¹-*P*-dppe)] (left, H-atoms omitted for clarity) and the HOMO (right).

Similar calculations for the dppm complexes give the predicted structures shown in Fig. 8, and predict that the complex [PtPh(κ²-*C*,*N*-bhq)(κ¹-*P*-dppm)] (Fig. 8a) is more stable than its isomer [PtPh(κ¹-*C*-bhq)(κ²-*P*,*P*-dppm)] (Fig. 8b) by 46 kJ mol^{-1}, in accord with experiment.[1b]

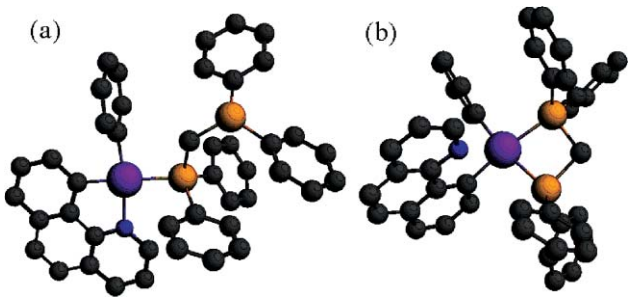


Fig. 8 The calculated structures of (a) [PtPh(κ²-*C*,*N*-bhq)(κ¹-*P*-dppm)] and (b) [PtPh(κ¹-*C*-bhq)(κ²-*P*,*P*-dppm)] (H-atoms omitted for clarity).

Thus, in these monomeric complexes, there are two potentially bidentate ligands and one of them must be monodentate because the platinum(II) centre prefers square-planar stereochemistry. There is a fine balance such that the complexes with P–P = dppe and dppf prefer the isomeric form ***H*** whereas the complexes with P–P = dppm prefer the form ***I***.[1] Both isomers can react with more platinum complex precursor to give the unusual diphosphine-bridged binuclear complexes, even when P–P = dppe.

Experimental

The ^{1}H NMR spectra were recorded using either a Bruker Avance DPX 250 spectrometer (in $CDCl_3$), or a Varian Mercury 400 spectrometer (in CD_2Cl_2), with TMS as reference. The ^{31}P NMR spectra were recorded using either a Bruker Avance DRX 500 spectrometer (in $CDCl_3$), or a Varian Mercury 400 spectrometer (in CD_2Cl_2), with 85% H_3PO_4 as reference. The microanalyses were performed using a Thermofinigan Flash EA-1112 CHNSO rapid elemental analyzer. The complexes [PtMe(ppy)(SMe_2)], ppy = 2-phenylpyridine, **1a**,[4a] and [PtMe(bhq)(SMe_2)], **1b**, bhq = benzo[*h*]quinoline,[1a,4a] have been prepared and used *in situ*. However in the present study they were prepared as pure solids and characterized as described below. Other precursor complexes [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1c**,[1b] [Pt(*p*-MeC_6H_4)(bhq)(SMe_2)], **1d**,[1b] and [$PtMe_2$(μ-SMe_2)]$_2$,[12a] were made by the known methods.

[PtMe(ppy)(SMe_2)], 1a

Pure 2-phenylpyridine (100 μL, 0.7 mmol) was added dropwise *via* syringe to a solution of [$PtMe_2$(μ-SMe_2)]$_2$ (200 mg, 0.35 mmol) in acetone (20 mL) at room temperature. The solution immediately turned yellow, and small bubbles formed. The solution was stirred for 20 h and then the solvent was evaporated from the resulting solution to give a solid that was washed with cold ether and acetone and dried under vacuum. Yield 110 mg; 75%, mp = 176 °C (decomp). NMR in $CDCl_3$: δ(^{1}H) = 1.07 [s, 3H, $^2J_{PtH}$ = 83 Hz, MePt]; 2.45 (s, 6H, $^3J_{PtH}$ = 25 Hz, MeS]; 8.90 [d, 1H, $^3J_{PtH^6}$ = 15 Hz, $^3J_{H^6H^5}$ = 6 Hz, H^6 of ppy].

[PtMe(bhq)(SMe_2)], 2a

This was prepared similarly using benzo[*h*]quinoline. Yield 183 mg; 58%, mp = 185 °C (decomp). Anal. Calcd d. for $C_{16}H_{17}NPtS$: C, 42.7; H, 3.8; N, 3.1; Found: C, 42.4; H, 3.7; N, 2.9. NMR in $CDCl_3$: δ(^{1}H) = 1.25 [s, 3H, $^2J_{PtH}$ = 83 Hz, MePt]; 2.56 [s, 6H, $^3J_{PtH}$ = 26 Hz, MeS]; 9.14 [d, 1H, $^3J_{PtH^6}$ = 18 Hz, $^3J_{H^6H^5}$ = 6 Hz, H^6 of bhq].

[PtMe(ppy)(dppe)], 3a

Dppe (40 mg, 0.1 mmol) was added to a solution of [Pt(Me)(ppy)(SMe_2)], **1a**, (42 mg, 0.1 mmol) in acetone (20 ml). The mixture was stirred at room temperature for 20 h. After removal of the solvent by evaporation, a residue was obtained which was further purified by repeated washing with ether. The product, as a white solid, was dried under vacuum. Yield 49 mg; 64%, mp = 195 °C (decomp). Anal. Calcd. for $C_{35}H_{35}NP_2Pt$: C, 59.8; H, 4.6; N, 1.8; Found: C, 59.3; H, 4.6; N, 2.1. NMR in CD_2Cl_2: δ(^{1}H) = 0.11 [t, 3H, $^2J_{PtH}$ = 72 Hz, $^3J_{PH}$ = 7 Hz, MePt]; 1.70 [br, 2H, CH_2P]; 2.11 [br, 2H, CH_2P]; 8.02 [d, 1H, $^3J_{H^6H^5}$ = 4 Hz, H^6 of ppy]; δ(^{31}P) = 41.4 [d, 1P, $^2J_{PP}$ = 2 Hz, $^1J_{ptP}$ = 1811 Hz, PtP]; 44.1 [d, 1P, $^2J_{pP}$ = 2 Hz, $^1J_{ptP}$ = 1821 Hz, PtP].

The following complexes were made similarly by using the appropriate starting complex **1b** or **2b** and dppe:

[Pt(*p*-MeC_6H_4)(ppy)(dppe)], 3b

Yield 60%, mp = 224 °C (decomp). Anal. Calcd for $C_{44}H_{39}NP_2Pt$: C, 63.0; H, 4.7; N, 1.7. Found: C, 62.7; H, 4.5; N, 1.5. NMR in $CDCl_3$: δ(^{1}H) = 2.34 [s, 3H, MeC]; 2.58 [br, 2H, CH_2P]; 2.68 [br, 2H, CH_2P]; 8.28 [d, 1H, $^3J_{H^6H^5}$ = 4 Hz, H^6 of ppy]; δ(^{31}P) = 39.6 [s, 1P, $^1J_{ptP}$ = 1786 Hz, PtP]; 40.7 [s, 1P, $^1J_{ptP}$ = 1726 Hz, PtP].

Table 1 Crystal and refinement data for the complexes

Complex	**1b**	**5b**·2/3CH_2Cl_2	**6b**·2CH_2Cl_2
Formula	$C_{20}H_{21}NPtS$	$C_{62.67}H_{55.33}Cl_{1.33}N_2P_2Pt_2$	$C_{68}H_{58}Cl_4N_2P_2Pt_2$
fw	502.53	1335.81	1497.08
T/K	150(2)	150(2)	150(2)
λ/Å	0.71073	0.71073	0.71073
cryst. syst.	Monoclinic	Monoclinic	Monoclinic
Space gp.	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	9.9851(5)	14.4438(5)	13.5252(9)
b/Å	9.4255(5)	33.6884(12)	14.6944(10)
c/Å	18.8056(11)	17.0228(6)	15.0201(10)
α (°)	90	90	90
β (°)	97.461(3)	105.626(2)	100.079(3)
γ (°)	90	90	90
V/Å^3	1754.9(2)	7977.0(5)	2939.1(3)
Z	4	6	2
d(c)/Mg m^{-3}	1.902	1.668	1.692
μ/mm^{-1}	8.113	5.425	5.035
data/restr./param	4908/0/211	22381/0/949	6751/0/353
R_1 [$I > 2\sigma(I)$]	0.0202	0.0250	0.0161
wR_2 [all data]	0.0386	0.0484	0.0359

[Pt(*p*-MeC$_6$H$_4$)(bhq)(dppe)], 4b

Yield 62%, mp = 230 °C (decomp). Anal. Calcd for $C_{45}H_{37}NP_2Pt$: C, 57.4; H, 4.2; N, 1.4; Found: C, 57.5; H, 4.3; N, 1.5. NMR in $CDCl_3$: δ(^{1}H) = 2.14 [s, 3H, MeC]; 2.35 [br, 2H, CH_2P]; 2.74 [br, 2H, CH_2P]; 6.02 [br. s, 1H, $^3J_{PtH}$ = 8 Hz, H^1 of bhq]; 8.50 [br. s, 1H, $^3J_{PtH}$ = 7.4 Hz, H^6 of bhq]; δ(^{31}P) = 39.2 [s, 1P, $^1J_{PtP}$ = 1946 Hz, PtP]; 41.3 [d, 1P, $^1J_{PtP}$ = 1964 Hz, PtP].

[Pt$_2$Me$_2$(ppy)$_2$(μ-dppe)], 5a

Dppe (20 mg, 0.05 mmol) was added to a solution of [Pt(Me)(ppy)(SMe$_2$)], **1a**, (43 mg, 0.1 mmol) in acetone (20 ml). The mixture was stirred at room temperature for 24 h. After removal of the solvent by evaporation, a yellow residue was obtained which was further purified by repeated washing with ether and cold acetone. Yield 34 mg; 30%, mp = 220 °C (decomp). Anal. Calcd. for $C_{50}H_{46}N_2P_2Pt_2$: C, 53.3; H, 4.1; N, 2.5; Found: C, 53.6; H, 4.0; N, 2.2. NMR in $CDCl_3$: δ(^{1}H) = 0.80 [m, 6H, $^2J_{PtH}$ = 79 Hz, $^3J_{PH}$ = 5 Hz, MePt]; 2.81 [br, 4H, CH_2P]; 6.50 [br. s, 2H, $^3J_{PtH}$ = 6 Hz, H^1 of ppy]; 7.94 [br. s, 2H, H^6 of ppy]; δ(^{31}P) = 24.5 [s, $^1J_{ptP}$ = 2085 Hz, $^3J_{PP}$ = 44 Hz, $^4J_{ptP}$ = 2 Hz, PtP].

The following complexes were made similarly by using the appropriate precursor complexes **2a**, **1b** or **2b** and dppe:

[Pt$_2$Me$_2$(bhq)$_2$(μ-dppe)], 6a

Yield 21%, mp = 285 °C (decomp). Anal. Calcd. for $C_{54}H_{46}N_2P_2Pt_2$: C, 55.2; H, 3.9; N, 2.4; Found: C, 55.5; H, 3.9; N, 2.2. NMR data in CD_2Cl_2: δ(^{1}H) = 0.85 [m, 6H, $^3J_{PH}$ = 8 Hz, $^2J_{PtH}$ = 83 Hz, MePt]; 2.92 [br, 4H, CH_2P]; 6.75 [dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 5 Hz, H^1 of ppy]; δ(^{31}P) = 24.4 [s, $^3J_{PP}$ = 47 Hz, $^1J_{ptP}$ = 2084 Hz, $^4J_{ptP}$ ≈ 0 Hz, PtP].

[Pt$_2$(*p*-MeC$_6$H$_4$)$_2$(ppy)$_2$(μ-dppe)], 5b

Yield 35%, mp = 230 °C (decomp). Anal. Calcd for $C_{64}H_{54}N_2P_2Pt_2$: C, 58.2; H, 4.3; N, 2.2; Found: C, 58.8; H, 4.7; N, 2.6. NMR in $CDCl_3$: δ(^{1}H) = 2.30 [s, 3H, MeC]; 1.60 [br, 4H, CH_2P]; 6.47 [br. s, 2H, $^3J_{PtH}$ = 6 Hz, H^1 of ppy]; δ(^{31}P) = 22.1 [s, $^1J_{PtP}$ = 2000 Hz, $^3J_{PP}$ = 20 Hz, $^4J_{ptP}$ ≈ 0 Hz, PtP).

[Pt$_2$(*p*-MeC$_6$H$_4$)$_2$(bhq)$_2$(μ-dppe)], 6b

Yield 47%, mp = 285 °C (decomp). Anal. Calcd for $C_{66}H_{54}N_2P_2Pt_2$: C, 59.7; H, 4.1; N, 2.1; Found: C, 59.3; H, 3.8; N, 2.0. NMR in $CDCl_3$: δ(^{1}H) = 2.31 [s, 3H, MeC]; 1.79 [br, 4H, CH_2P]; 8.08 [d, $^3J_{HH}$ = 2 Hz, $^3J_{PtH}$ = 8 Hz, H^6 of bhq]; δ(^{31}P) = 21.8 [s, $^3J_{PP}$ = 21 Hz, $^1J_{PtP}$ = 2059 Hz, $^4J_{ptP}$ ≈ 0 Hz, PtP].

X-ray structure determinations

Data were collected using a Bruker diffractometer. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). The structures were solved by direct methods and refined using the Bruker SHELXTL Software Package. Details are given in Table 1. CCDC-784480–784482 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

DFT calculations

Calculations were made using the Amsterdam Density Functional program based on the Becke–Perdew functional, with first-order scalar relativistic corrections.[17]

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