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Assembly of Symmetrical or Unsymmetrical Cyclometalated Organoplatinum Complexes through a Bridging Diphosphine Ligand[†]

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The cyclometalated complexes [Pt(ppy)Ar(SMe$_2$)] or [Pt(bhq)Ar(SMe$_2$)], where ppyH = 2-phenyl-pyridine, bhqH = benzo[*h*]quinoline, and Ar = 4-tolyl or 4-anisyl, react with bis(diphenylphosphino)-methane, dppm, in a 1:1 ratio to give the corresponding complexes [Pt(ppy)Ar(κ^1-dppm)] and [Pt(bhq)Ar(κ^1-dppm)], in which the dppm ligands are monodentate, or in a 2:1 ratio to give the symmetrical binuclear complexes [{Pt(ppy)Ar}$_2$(μ-dppm)] and [{Pt(bhq)Ar}$_2$(μ-dppm)], in which the dppm ligands are bridging bidentate. Most remarkably, the reaction of [Pt(ppy)Ar(SMe$_2$)] with [Pt(bhq)Ar′(κ^1-dppm)] or of [Pt(bhq)Ar′(SMe$_2$)] with [Pt(ppy)Ar(κ^1-dppm)] occurs selectively to give the unsymmetrical bridged complexes [(ppy)ArPt(μ-dppm)PtAr′(bhq)]. An example of each structural type has been characterized crystallographically, and it is shown that some of the bhq complexes undergo supramolecular self-assembly through π-stacking.

Introduction

The chemistry of cyclometalated organometallic compounds is of great current interest, on the basis of applications of such compounds in stoichiometric or catalytic organic synthesis and in sensing and functional materials.[1] As in other areas of organometallic chemistry,[2] studies of the cyclometalation of platinum complexes have given many interesting complexes as well as new insight into the mechanisms of the reactions.[1,3−6] The cyclometalation reactions can be brought about by using either electrophilic[6] or nucleophilic[3−5] platinum(II) precursor complexes, such as those with formula [PtR$_2$(SMe$_2$)$_2$] or [Pt$_2$R$_4$(μ-SMe$_2$)$_2$].[3−5,7,8] Some typical complexes formed from 2-phenylpyridine or benzo[*h*]quinoline are shown as **A−F** in Chart 1.

There is interest in assembling the cyclometalated complexes to give dimers (**D**, Chart 1),[6n] oligomers, or polymers.[1] In this

regard, it has been shown that the chelate ring in complex **A**[4] can be opened by reaction with a chelating diphosphine, PP = bis(diphenylphosphino)ferrocene, to give the monodentate 2-pyridylphenylplatinum complex **G**.[5] With only a half equivalent of the diphosphine, the symmetrical bridged binuclear complex **H** was formed.[5] This article shows that the short bite diphosphine ligand bis(diphenylphosphino)methane, dppm,[9] does not displace the pyridine donor from complexes analogous to **A** but forms only a monodentate dppm complex, and it will

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Chart 1

A, R = Me, L = SMe$_2$
B, R = Ph, L = Me$_2$SO

C

D

E

F

Scheme 1^a

A

G

H
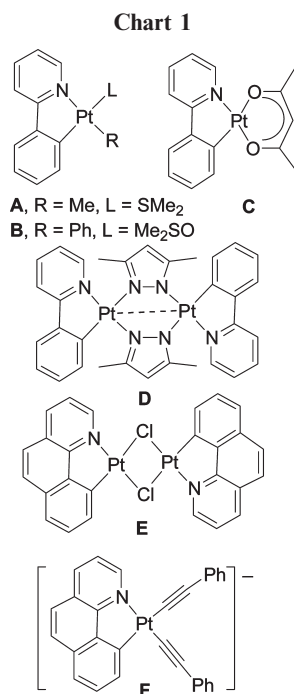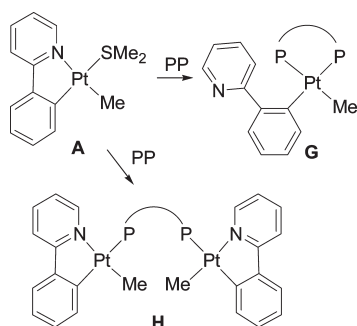
^{a}PP = bis(diphenylphosphino)ferrocene.

be shown that this property can be exploited to form not only symmetrical complexes analogous to **H** (Scheme 1) but also unsymmetrical binuclear complexes containing two different cyclometalated groups.

Results and Discussion

The reaction of 2-phenylpyridine or benzo[*h*]quinoline with [PtAr$_2$(SMe$_2$)$_2$] gave the corresponding complexes [PtAr-(ppy)(SMe$_2$)] (**1a**, Ar = 4-MeC$_6$H$_4$; **1b**, Ar = 4-MeOC$_6$H$_4$) or [PtAr(bhq)(SMe$_2$)] (**2a**, Ar = 4-MeC$_6$H$_4$; **2b**, Ar = 4-MeOC$_6$H$_4$), according to Scheme 2. The formation of the analogous methylplatinum complexes from [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] has been reported previously.[4,5]

The structures of complexes **1** and **2** are readily deduced from the ^{1}H NMR spectra,[4,5] and the structure of complex **2a** has been confirmed by X-ray structure determination (Figure 1). The two aryl groups are mutually *cis* in the square-planar structure (Figure 1a), as expected,[5] and the largest deviation from ideal geometry is the angle C(10)Pt-(1)N(1) = 80.9(3)°, which is associated with the Pt(bhq) chelate ring. There is loose association of the molecules in the
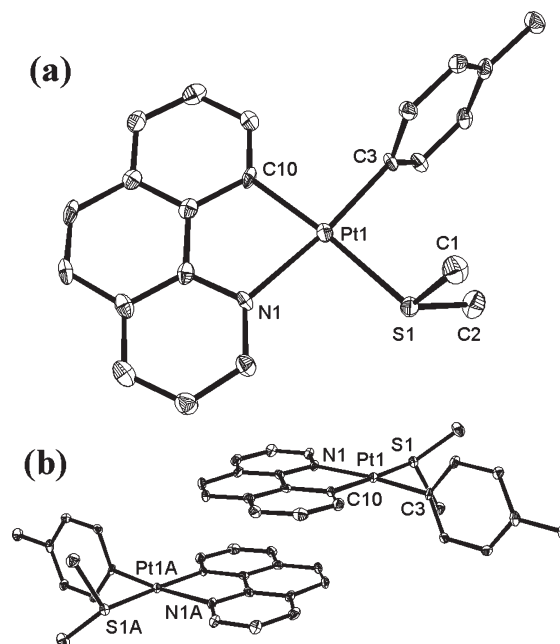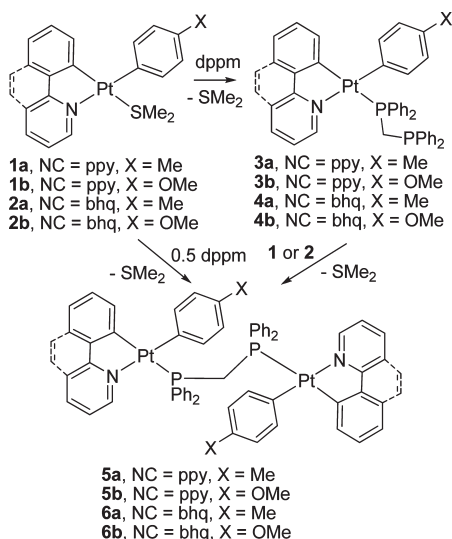

Figure 1. (a) View of the structure of complex **2a**. Selected bond parameters (Å and deg): Pt(1)−C(3) 2.030(8); Pt(1)−C(10) 2.052(8); Pt(1)−N(1) 2.142(7); Pt(1)−S(1) 2.358(2); C(3)−Pt(1)−C(10) 93.4(4); C(10)−Pt(1)−N(1) 80.9(3); C(3)−Pt(1)−S(1) 91.7(3); N(1)−Pt(1)−S(1) 93.9(2). (b) Supramolecular structure of complex **2a** formed through π-stacking of the bhq groups.

Scheme 2. The Cyclometalation Reactions

1a, Ar = 4-MeC$_6$H$_4$
1b, Ar = 4-MeOC$_6$H$_4$

2a, Ar = 4-MeC$_6$H$_4$
2b, Ar = 4-MeOC$_6$H$_4$
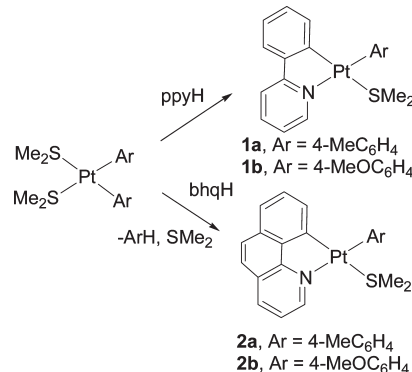
solid state through π-stacking of the planar bhq groups, as shown in Figure 1b (mean interplanar separation 3.3 Å).

The reaction of the dimethylsulfide complex **1** or **2** with the ligand bis(diphenylphosphino)methane, dppm, in a 1:1 or 2:1 ratio gave either the corresponding monodentate dppm complex **3** or **4** or the bridging dppm complex **5** or **6**, respectively, according to Scheme 3. The free phosphorus donor of the dppm ligand in complex **3** or **4** did not displace the nitrogen-donor from complex **3** or **4** to give a complex analogous to **G** (Scheme 1).[5] The complexes **5** and **6** formed according to Scheme 3 have effective C_{2v} symmetry in solution. Thus, the ^{1}H NMR spectra contain a single resonance for the CH$_2$P$_2$ protons of the dppm ligand, and the ^{31}P and ^{195}Pt NMR spectra each contain a single resonance. The dppm-bridged complexes **5** and **6** could be prepared in a single step from **1** or **2**, respectively, or in two separate steps. For example, reaction of **1a** with **3a** gave complex **5a** (Scheme 3).
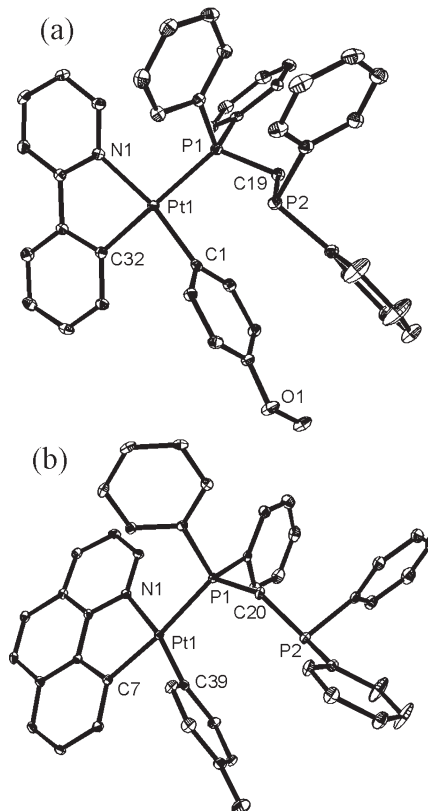
Scheme 3

1a, NC = ppy, X = Me
1b, NC = ppy, X = OMe
2a, NC = bhq, X = Me
2b, NC = bhq, X = OMe

3a, NC = ppy, X = Me
3b, NC = ppy, X = OMe
4a, NC = bhq, X = Me
4b, NC = bhq, X = OMe

5a, NC = ppy, X = Me
5b, NC = ppy, X = OMe
6a, NC = bhq, X = Me
6b, NC = bhq, X = OMe

The structures of the monodentate dppm complexes **3b** and **4a** have been determined and are shown in Figure 2. The key dimensions and conformations within the molecular structures are similar. For example, the nonbonding distances Pt(1)···P(2) are 4.23 and 4.25 Å in **3b** and **4a**, respectively. Although Pt−P bonds are usually favored over Pt−N bonds for the soft platinum(II) metal center,[5] the extra stability of the five-membered chelate ring of the metallacycle, compared to the four-membered ring formed by chelating dppm,[9] evidently favors the observed structures **3** and **4**. The tendency of dppm to act as a bridging or monodentate ligand is well established, and a few complexes with monodentate dppm ligands, or the oxidized form dppmO, have been structurally characterized.[9,10] In contrast to the case with complex **2a** (Figure 1), the bhq groups in complex **4a** do not take part in intermolecular π-stacking.
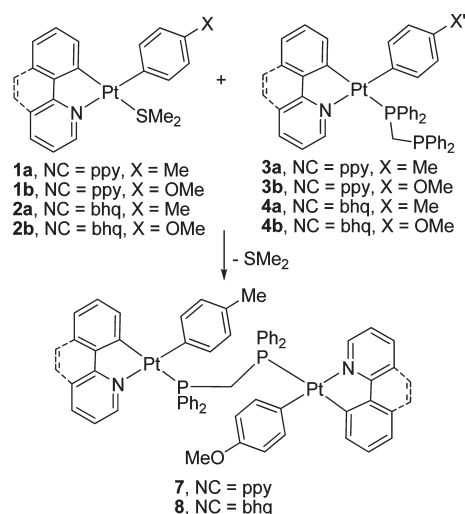
The stepwise formation of complexes **5** and **6** from the monodentate dppm complexes (Scheme 3) suggested that it might be possible to prepare unsymmetrical binuclear complexes. Complexes **7** and **8**, with two different aryl groups, 4-tolyl and 4-anisyl, were successfully prepared according to Scheme 4. Complex **7** could be prepared either by reaction of **1a** with **3b** or by reaction of **1b** with **3a** and contained no detectable impurity of the possible symmetrical complex **5a** or **5b** as determined by the ^{31}P NMR spectrum.

Finally, unsymmetrical binuclear complexes **9** containing two different cyclometalated groups could be prepared selectively according to Scheme 5. These complexes could contain the same (**9a**, **9b**) or different (**9c**, **9d**) aryl groups.

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Figure 2. Views of the structures of (a) complex **3b** and (b) complex **4a**. Selected bond parameters (Å and deg): **3b**: Pt(1)−C(1) 2.008(3); Pt(1)−C(32) 2.042(3); Pt(1)−N(1) 2.127(3); Pt(1)−P(1) 2.3118(8); C(1)−Pt(1)−C(32) 89.3(1); C(32)−Pt(1)−N(1) 79.9(1); C(1)−Pt(1)−P(1) 91.87(8); N(1)−Pt(1)−P(1) 98.98(7); **4a**: Pt(1)−C(39) 2.003(2); Pt(1)−C(7) 2.038(2); Pt(1)−N(1) 2.139(2); Pt(1)−P(1) 2.3095(6); C(39)−Pt(1)−C(7) 90.12(9); C(39)−Pt(1)−P(1) 92.29(7); C(7)−Pt(1)−N(1) 80.37(8); N(1)−Pt(1)−P(1) 97.24(5).

Scheme 4

1a, NC = ppy, X = Me
1b, NC = ppy, X = OMe
2a, NC = bhq, X = Me
2b, NC = bhq, X = OMe

3a, NC = ppy, X = Me
3b, NC = ppy, X = OMe
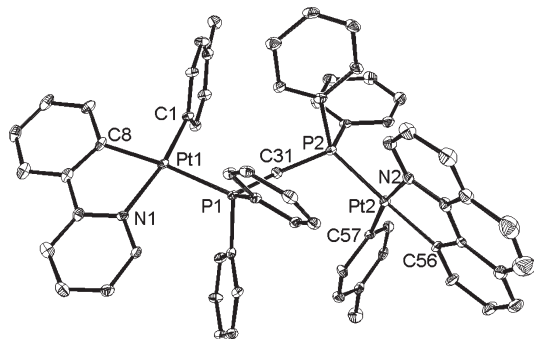4a, NC = bhq, X = Me
4b, NC = bhq, X = OMe

7, NC = ppy
8, NC = bhq

Again there are two routes to each complex. For example, complex **9c** could be prepared either from **1a** and **4b** or from **2b** and **3a** (Scheme 5).

The structure of complex **9a** is shown in Figure 3. It can be seen that the dppm ligand adopts an *anti* conformation such

Figure 3. View of the structure of complex **9a**. Selected bond parameters (Å and deg): Pt(1)−C(1) 2.042(7); Pt(1)−C(8) 2.058(7); Pt(1)−N(1) 2.151(6); Pt(1)−P(1) 2.3191(19) ; Pt(2)−C(57) 2.039(7); Pt(2)−C(56) 2.046(7); Pt(2)−N(2) 2.149(6); Pt(2)−P(2) 2.309(2); C(1)−Pt(1)−C(8) 88.8(3); C(8)−Pt(1)−N(1) 79.3(3); C(1)−Pt(1)−P(1) 93.9(2); N(1)−Pt(1)−P(1) 97.3(2); C(57)−Pt(2)−C(56) 88.8(3); C(56)−Pt(2)−N(2) 79.5(3); C(57)−Pt(2)−P(2) 88.6(2); N(2)−Pt(2)−P(2) 103.5(2).

Scheme 5

9a, X = X' = Me
9b, X = X' = OMe
9c, X = Me, X' = OMe
9d, X = OMe, X' = Me
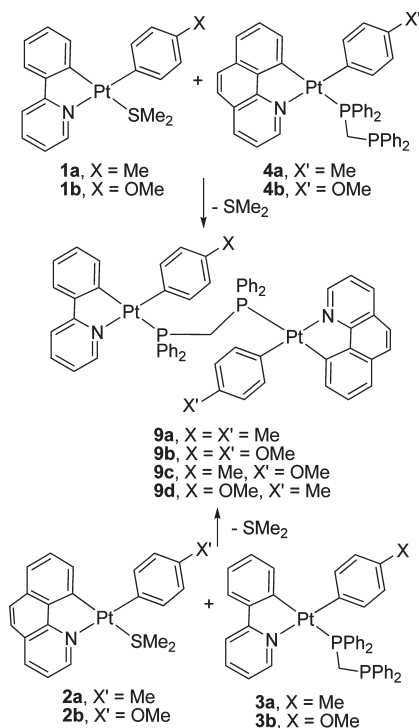
that the two square-planar platinum(II) centers are well separated [Pt(1)···Pt(2) = 6.73 Å]. The 4-tolyl groups lie roughly orthogonal to the planes of the respective platinum centers [angles between the mean tolyl and platinum planes are 84° and 85° for Pt(1) and Pt(2), respectively]. The angle between the square planes of Pt(1) and Pt(2) is 92°, as a result of different conformations arising from rotation about the Pt−P bonds. This conformation allows intermolecular π-stacking of bhq groups to form supramolecular dimers, in a similar way to that found in complex **2a** (Figure 1b), as illustrated in Figure 4.

The structures of the dppm complexes in solution were deduced from the ^{1}H, ^{31}P, and ^{195}Pt NMR spectra, and selected ^{31}P NMR spectra are illustrated in Figure 5. The complex **4a** is typical of the complexes with monodentate dppm ligands. Its ^{31}P NMR spectrum (Figure 5a) contains
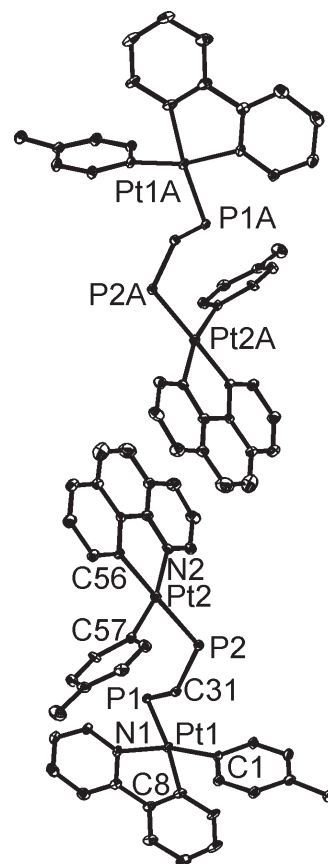

Figure 4. π-Stacking of the bhq groups of complex **9a** to form a supramolecular dimer. The phenyl groups of the dppm ligands are omitted for clarity.
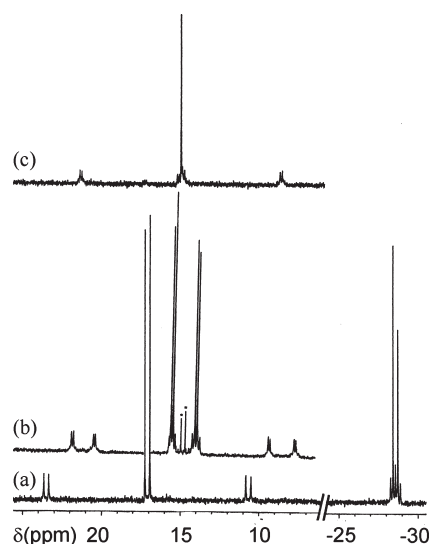
Figure 5. ^{31}P NMR spectra of selected complexes: (a) [Pt(*p*-Me-C$_6$H$_4$)(bhq)(η^1-dppm)], **4a**; (b) [(*p*-MeC$_6$H$_4$)(ppy)Pt(*μ*-dppm)Pt-(*p*-MeC$_6$H$_4$)(bhq)], **9a** (trace impurities indicated by * are assigned to the symmetrical complexes **5a** and **6a**); (c) [Pt$_2$(*p*-MeC$_6$H$_4$)$_2$-(bhq)$_2$(*μ*-dppm)], **6a**.

two doublet resonances with coupling $^2J_{PP}$ = 51 Hz for the coordinated [δ = 17.1, $^1J_{PtP}$ = 2082 Hz] and free [δ = −28.6, $^3J_{PtP}$ = 50 Hz] phosphorus atoms. The ^{31}P NMR spectra of the symmetrical dppm-bridged complexes contained a single resonance, illustrated for complex **6a** in

Scheme 6[a]
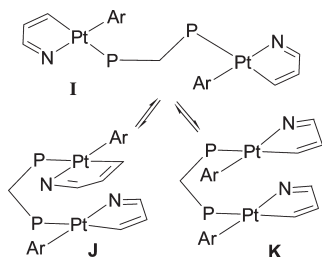
[a] Only the core atoms of the dppm and ppy or bhq groups are shown, for clarity.

Figure 5c [δ = 14.6, $^1J_{PtP}$ = 2060 Hz, $^3J_{PtP}$ = 52 Hz, $^2J_{PP}$ = 21 Hz]. There are satellite spectra arising from coupling to ^{195}Pt, with both $^1J_{PtP}$ and $^3J_{PtP}$ couplings resolved, and the coupling $^2J_{PP}$ is resolved in these satellite spectra. The unsymmetrical dppm-bridged complexes give similar ^{31}P NMR parameters to those for **6a**, but two separate resonances are resolved in the spectra. For example, complex **9a** (Figure 5b) gave peaks at δ = 15.5 [d, $^1J_{PtP}$ = 1996 Hz, $^2J_{PP}$ = 20 Hz, $^3J_{PtP}$ = 46 Hz, P *trans* to ppy] and 14.1 [d, $^1J_{PtP}$ = 2055 Hz, $^2J_{PP}$ = 20 Hz, $^3J_{PtP}$ = 56 Hz, P *trans* to bhq]. Minor impurity peaks marked with an asterisk in Figure 5b are assigned to the symmetrical compounds **5a** and **6a**, which are formed by disproportionation of complex **9a**. They are present in < 5% abundance, indicating high selectivity in the formation of **9a**. In all complexes studied, the phosphorus *trans* to ppy occurred at higher δ and with lower $^1J_{PtP}$ compared to phosphorus *trans* to bhq.

The ^{1}H NMR spectra do not indicate restricted rotation about the P−C bonds of the dppm ligands, so there is probably easy conformational change of the bridged complexes in solution. In some square-planar platinum(II) complexes bridged by dppm ligands, the *syn* conformation has been observed (analogous to **J** or **K** in Scheme 6), and this allows a metallophilic Pt···Pt interaction to occur.[11] The preference for conformation **I** (Scheme 6) for complex **9a** is probably a result of the aryl groups (Ar in Scheme 6) being roughly orthogonal to the square plane of the platinum center. The close approach of the platinum atoms to one another is thus prevented by steric effects involving these aryl groups in either the C_2 (staggered) or C_{2h} (eclipsed) conformation, **J** or **K**, respectively.

The ^{195}Pt chemical shifts for the monodentate dppm complexes **3a**−**4b** lie in the range δ = −2393 to −2418, and those for the bridging dppm complexes **5a**−**9d** in the range δ = −2332 to −2393. In general, the chemical shifts are more negative for the monodentate dppm complexes and, in most cases, more negative for the bhq compared to ppy complexes. For the binuclear complexes, the symmetrical complexes **5a**−**6b** give a single ^{195}Pt resonance, while the unsymmetrical complexes **7**−**9d** give two resonances. The ^{195}Pt chemical shifts are in the expected range for organoplatinum(II) complexes.[5,14]

Conclusions

Several platinum(II) complexes containing both a bidentate cyclometalated ppy or bhq ligand and an aryl group were prepared in high yields. For the first time, it has been possible to assemble pairs of these units in any combination by using dppm as the assembling agent. This short bite diphosphine ligand acts as a monodentate ligand only in forming the complexes [PtAr(κ^2-*C,N*-ppy)(κ^1-*P*-dppm)] and [PtAr(κ^2-*C,N*-bhq)(κ^1-*P*-dppm)] and not [PtAr(κ^1-*C*-ppy)(κ^2-*P,P'*-dppm)] and [PtAr(κ^1-*C*-bhq)(κ^2-*P,P'*-dppm)]. The monodentate dppm ligand can then be used as a metalloligand to bind a second platinum unit.[9−13] Binuclear platinum(II) complexes, including examples such as [Pt(4-tolyl)(κ^2-*C,N*-ppy)(μ-dppm)Pt(4-anisyl))(κ^2-*C,N*-bhq)] with two different aryl groups and two different cyclometalated groups, can be prepared in a selective way by using this simple methodology.

Experimental Section

The ^{1}H NMR spectra were recorded by using either a Bruker Avance DPX 250 spectrometer (in CDCl$_3$) or a Varian Mercury 400 spectrometer (in CD$_2$Cl$_2$), with TMS as reference. The labels H^o, H^m refer to the *ortho* and *meta* protons of the aryl group, while H^6 refers to the N═CH proton of the ppy or bhq group, and H^5 refers to the adjacent hydrogen. The ^{31}P NMR spectra were recorded either on a Bruker Avance DRX 500 spectrometer (in CDCl$_3$) or on a Varian Mercury 400 spectrometer (in CD$_2$Cl$_2$), with 85% H$_3$PO$_4$ as reference, and ^{195}Pt NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (in CDCl$_3$), with aqueous Na$_2$PtCl$_4$ as reference. The microanalyses were performed using a Thermo Finnigan Flash EA-1112 CHNSO rapid elemental analyzer. The monomeric precursors *cis*-[PtR$_2$(SMe$_2$)$_2$], R = *p*-MeC$_6$H$_4$ and *p*-MeOC$_6$H$_4$, were prepared by the literature methods.[7]

[Pt(*p*-MeC$_6$H$_4$)(ppy)(SMe$_2$)], 1a. To a solution of *cis*-[Pt(*p*-MeC$_6$H$_4$)$_2$(SMe$_2$)$_2$] (150 mg, 0.3 mmol) in acetone (30 mL) was added 2-phenylpyridine (43 μL, 0.3 mmol), and the reaction mixture was refluxed for 4 h. A light green solution was formed; then the solvent was removed under reduced pressure, and the residue was triturated with cold acetone (2 × 2 mL). The product as a light green solid was dried under vacuum. Yield: 141 mg, 70%; mp 225 °C (dec). Anal. Calcd for C$_{20}$H$_{21}$NPtS: C, 47.8; H, 4.2; N, 2.8. Found: C, 48.1; H, 4.3; N, 2.9. NMR in CDCl$_3$: δ(^{1}H) = 2.20 [s, 6H, $^3J_{PtH}$ = 25 Hz, MeS]; 2.30 [s, 3H, MeC]; 6.93 [d, 2H, $^3J_{H^mH^o}$ = 7.5 Hz, H^m]; 7.46 [d, 2H, $^3J_{PtH^o}$ = 64 Hz, $^3J_{H^oH^m}$ = 7.5 Hz, H^o]; 8.87 [d, 1H, $^3J_{PtH^6}$ = 19 Hz, $^3J_{H^6H^5}$ = 5.5 Hz, H^6 of ppy].

The following complexes were prepared similarly by using the appropriate starting complexes [PtAr$_2$(SMe$_2$)$_2$] and the related ligand 2-phenylpyridine or benzo[*h*]quinoline:

[Pt(*p*-MeOC$_6$H$_4$)(ppy)(SMe$_2$)], 1b. Yield: 65%; mp 234 °C (dec). Anal. Calcd for C$_{20}$H$_{21}$NOPtS: C, 46.0; H, 4.0; N, 2.7. Found: C, 45.8; H, 4.0; N, 2.3. NMR in CDCl$_3$: δ(^{1}H) = 2.20 [s, 6H, $^3J_{PtH}$ = 25 Hz, MeS]; 3.85 [s, 3H, OMe]; 6.75 [d, 2H, $^3J_{H^mH^o}$ = 7.5 Hz, H^m]; 7.46 [d, 2H, $^3J_{PtH^o}$ = 64 Hz, $^3J_{H^oH^m}$ = 7.5 Hz, H^o]; 8.87 [d, 1H, $^3J_{PtH^6}$ = 19 Hz, $^3J_{H^6H^5}$ = 5.5 Hz, H^6].

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[Pt(*p*-MeC$_6$H$_4$)(bhq)(SMe$_2$)], 2a. Yield: 65%; mp 217 °C (dec). Anal. Calcd for C$_{22}$H$_{21}$NPtS: C, 50.1; H, 4.0; N, 2.7. Found: C, 50.1; H, 4.0; N, 2.6. NMR in CDCl$_3$: δ(^{1}H) = 2.29 [s, 6H, $^3J_{PtH}$ = 24 Hz, MeS]; 2.34 [s, 3H, MeC]; 6.98 [d, 2H, $^3J_{H^mH^o}$ = 7 Hz, H^m]; 7.57 [d, 2H, $^3J_{PtH^o}$ = 63 Hz, $^3J_{H^oH^m}$ = 7 Hz, H^o]; 9.13 [d, 1H, $^3J_{PtH^6}$ = 18 Hz, $^3J_{H^6H^5}$ = 6 Hz, H^6].

[Pt(*p*-MeOC$_6$H$_4$)(bhq)(SMe$_2$)], 2b. Yield: 76%; mp 210 °C (dec). Anal. Calcd for C$_{22}$H$_{21}$NOPtS: C, 48.7; H, 3.9; N, 2.6. Found: C, 48.7; H, 3.7; N, 2.6. NMR in CDCl$_3$: δ(^{1}H) = 2.28 [s, 6H, $^3J_{PtH}$ = 22 Hz, MeS]; 3.84 [s, 3H, MeO]; 6.82 [d, 2H, $^3J_{H^mH^o}$ = 8 Hz, H^m]; 7.56 [d, 2H, $^3J_{PtH^o}$ = 65 Hz, $^3J_{H^oH^m}$ = 8 Hz, H^o]; 9.13 [d, 1H, $^3J_{PtH^6}$ = 17 Hz, $^3J_{H^6H^5}$ = 5 Hz, H^6].

[Pt(*p*-MeC$_6$H$_4$)(ppy)(η^1-dppm)], 3a. To a solution of [Pt(*p*-MeC$_6$H$_4$)(ppy)(SMe$_2$)], **1a** (52 mg, 0.1 mmol), in acetone (20 mL) was added dppm (40 mg, 0.1 mmol). The mixture was stirred at room temperature for 1 h. After removal of the solvent by evaporation, a residue was obtained, which was washed several times with ether and then with cold acetone and dried under vacuum. It was isolated as a green-yellow microcrystalline powder. Yield: 58 mg, 71%; mp 231−233 °C (dec). Anal. Calcd for C$_{43}$H$_{37}$NP$_2$Pt: C, 62.6; H, 4.5; N, 1.7. Found: C, 62.2; H, 4.4; N, 2.1. NMR in CD$_2$Cl$_2$: δ(^{1}H) = 2.13 [s, 3H, MeC]; 2.58 [dd, 2H, $^2J_{PH}$ = 9 and 2 Hz, $^3J_{PtH}$ = 19 Hz, CH$_2$P$_2$]; 6.52 [ddd, 1H, $^3J_{H^5H^3}$ = 6 Hz, $^3J_{H^5H^4}$ = 7 Hz, $^4J_{H^5H^3}$ = 1 Hz, H^5]; δ(^{31}P) = 17.6 [d, $^1J_{PtP}$ = 2015 Hz, $^2J_{PP}$ = 50 Hz, 1 P], δ = −28.6 [d, $^3J_{PtP}$ = 48 Hz, $^2J_{PP}$ = 50 Hz, 1 P]; ^{195}Pt NMR (in CDCl$_3$) δ = −2395 [dd, $^1J_{PtP}$ = 2010 Hz, $^3J_{PtP}$ = 53 Hz, Pt].

The following complexes were prepared similarly by using the appropriate starting material **1**:

[Pt(*p*-MeOC$_6$H$_4$)(ppy)(η^1-dppm)], 3b. Yield: 73%; mp 203 °C (dec). Anal. Calcd for C$_{43}$H$_{37}$NP$_2$Pt: C, 61.4; H, 4.4; N, 1.7. Found: C, 60.9; H, 4.5; N, 1.8. NMR in CDCl$_3$: δ(^{1}H) = 3.70 [s, 3H, MeO]; 2.70 [m, 2H, CH$_2$P$_2$]; 6.45 [m, 1H, $^3J_{PtH}$ = 8 Hz, H^5]; δ(^{31}P) = 19.8 [d, 1P, $^1J_{PtP}$ = 2000 Hz, $^2J_{PP}$ = 43 Hz, PtP]; −26.8 [d, 1P, $^3J_{PtP}$ = 34 Hz, $^2J_{PP}$ = 43 Hz, P]; δ(^{195}Pt) = −2393 [dd, $^1J_{PtP}$ = 1995 Hz, $^3J_{PtP}$ = 31 Hz, Pt].

[Pt(*p*-MeC$_6$H$_4$)(bhq)(η^1-dppm)], 4a. Yield: 93%; mp 261 °C (dec). Anal. Calcd for C$_{45}$H$_{37}$NP$_2$Pt: C, 63.7; H, 4.4; N, 1.6. Found: C, 63.4; H, 4.4; N, 1.6. NMR in CD$_2$Cl$_2$: δ(^{1}H) = 2.17 [s, 3H, MeC]; 2.60 [dd, 2H, $^2J_{PH}$ = 9 and 1 Hz, $^3J_{PtH}$ = 20 Hz, CH$_2$P$_2$]; 8.12 [dd, 1H, $^3J_{H^6H^5}$ = 8 Hz, $^4J_{H^6}$H^4 = 1 Hz, H^6]; δ(^{31}P) = 17.1 [d, 1P, $^2J_{PP}$ = 51 Hz, $^1J_{PtP}$ = 2082 Hz, PtP); −28.6 [d, 1P, $^2J_{PP}$ = 51 Hz, $^3J_{PtP}$ = 50 Hz, P]; NMR in CDCl$_3$: δ(^{195}Pt) = −2418 [br d, $^1J_{PtP}$ = 2080 Hz, Pt].

[Pt(*p*-MeOC$_6$H$_4$)(bhq)(η^1-dppm)], 4b. Yield: 75%; mp 233 °C (dec). Anal. Calcd for C$_{45}$H$_{37}$NOP$_2$Pt: C, 62.5; H, 4.2; N, 1.6. Found: C, 61.4; H, 4.3; N, 1.6. NMR in CDCl$_3$: δ(^{1}H) = 3.76 [s, 3H, MeO]; 2.73 [m, 2H, CH$_2$P$_2$]; 8.12 [d, 1H, $^3J_{H^6H^5}$ = 8 Hz, H^6]; δ(^{31}P) = 17.3 [d, 1P, $^2J_{PP}$ = 46 Hz, $^1J_{PtP}$ = 2059 Hz, PtP); −27.9 [d, 1P, $^2J_{PP}$ = 46 Hz, P]; δ(^{195}Pt) = −2415 [br d, $^1J_{PtP}$ = 2065 Hz, Pt].

[Pt$_2$(*p*-MeC$_6$H$_4$)$_2$(ppy)$_2$(μ-dppm)], 5a. This was prepared by two methods:

(a) To a solution of [Pt(*p*-MeC$_6$H$_4$)(ppy)(SMe$_2$)], **1a** (50 mg, 0.1 mmol), in acetone (20 mL) was added dppm (19 mg, 0.05 mmol). The mixture was stirred at room temperature for 1 h. The solvent was removed and the residue was purified to a yellow microcrystalline powder by treatment with cold acetone and ether and dried under vacuum.

(b) To a solution of [Pt(*p*-MeC$_6$H$_4$)(ppy)(η^1-dppm)], **3a** (82 mg, 0.1 mmol), in CH$_2$Cl$_2$ (20 mL) was added [Pt(*p*-MeC$_6$H$_4$)(ppy)-(SMe$_2$)], **1a** (50 mg, 0.1 mmol). The mixture was stirred at room temperature for 5 h. The solvent was removed and the residue was purified to a yellow microcrystalline powder by treatment with cold acetone and ether and drying under vacuum. Yield: 87 mg, 69%; mp 236 °C (dec). Anal. Calcd for C$_{61}$H$_{52}$N$_2$P$_2$Pt$_2$: C, 57.9; H, 4.1; N, 2.2. Found: C, 57.8; H, 4.1; N, 2.4. NMR in CDCl$_3$: δ(^{1}H) = 2.25 [s, 6H, MeC]; 3.07 [m, 2H, $^3J_{PtH}$ = 17 Hz, CH$_2$P$_2$]; 6.49 [t, $^3J_{H^5H^6}$ = $^3J_{H^5H^4}$ = 6 Hz, H^5]; δ(^{31}P) = 15.5 [s, $^1J_{PtP}$ = 1994 Hz, $^3J_{PtP}$ = 47 Hz, $^2J_{PP}$ = 20 Hz, PtP]; δ(^{195}Pt) = −2342 [dd, $^1J_{PtP}$ = 1990 Hz, $^3J_{PtP}$ = 47 Hz, Pt].

The following complexes were prepared similarly by using the appropriate starting materials:

[Pt$_2$(*p*-MeOC$_6$H$_4$)$_2$(ppy)$_2$(μ-dppm)], 5b. Yield: 63%; mp 241 °C (dec). Anal. Calcd for C$_{61}$H$_{52}$N$_2$O$_2$P$_2$Pt$_2$: C, 56.4; H, 4.0; N, 2.2. Found: C, 56.4; H, 3.8; N, 2.4. NMR data in CDCl$_3$: ^{1}H NMR δ(^{1}H) = 3.70 [s, 6H, MeO]; 3.10 [m, 2H, CH$_2$P$_2$]; 6.62 [m, 2H, H^5]; δ(^{31}P) = 16.5 [br s, $^1J_{PtP}$ = 1970 Hz, PtP]; δ(^{195}Pt) = −2393 [br d, $^1J_{PtP}$ ≈ 1980 Hz, Pt].

[Pt$_2$(*p*-MeC$_6$H$_4$)$_2$(bhq)$_2$(μ-dppm)], 6a. Yield: 63%; mp 263 °C (dec). Anal. Calcd for C$_{65}$H$_{52}$N$_2$P$_2$Pt$_2$: C, 59.4; H, 4.0; N, 2.1. Found: C, 59.4; H, 4.0; N, 2.2. NMR in CD$_2$Cl$_2$: δ(^{1}H) = 2.23 [s, 6H, MeC]; 3.17 [t, 2H, $^2J_{PH}$ = 9 Hz, CH$_2$P$_2$]; 8.13 [dd, 2H, $^3J_{H^6H^5}$ = 8 Hz, $^4J_{H^6H^4}$ = 2 Hz, H^6]; δ(^{31}P) = 14.6 [s, $^1J_{PtP}$ = 2060 Hz, $^3J_{PtP}$ = 52 Hz, $^2J_{PP}$ = 21 Hz, PtP]; NMR in CDCl$_3$: δ(^{195}Pt) = −2370 [br d, $^1J_{PtP}$ = 2055 Hz, 2Pt].

[Pt$_2$(*p*-MeOC$_6$H$_4$)$_2$(bhq)$_2$(μ-dppm)], 6b. Yield: 65%; mp 216 °C (dec). Anal. Calcd for C$_{65}$H$_{52}$N$_2$O$_2$P$_2$Pt$_2$: C, 58.0; H, 3.9; N, 2.1. Found: C, 58.2; H, 4.1; N, 2.2. NMR in CDCl$_3$: δ(^{1}H) = 3.72 [s, 6H, MeO]; 3.20 [t, 2H, $^2J_{PH}$ = 8.5 Hz, CH$_2$P$_2$]; 8.05 [d, $^3J_{HH}$ = 8 Hz, H^6]; δ(^{31}P) = 14.9 [s, $^1J_{PtP}$ = 2046 Hz, $^2J_{PP}$ = 20 Hz, $^3J_{PtP}$ = 70 Hz, PtP]; δ(^{195}Pt) = −2365 [br d, $^1J_{PtP}$ = 2050 Hz, Pt].

[(*p*-MeC$_6$H$_4$)(ppy)Pt(μ-dppm)Pt(*p*-MeC$_6$H$_4$)(bhq)], 9a. This complex was prepared by the two following methods:

(a) To a solution of [Pt(*p*-MeC$_6$H$_4$)(ppy)(η^1-dppm)], **3a** (82 mg, 0.1 mmol), in CH$_2$Cl$_2$ (20 mL) was added [Pt(*p*-MeC$_6$H$_4$)(bhq)-(SMe$_2$)], **2a** (53 mg, 0.1 mmol). The mixture was stirred at room temperature for 1 h, and then the solvent was evaporated from the resulting solution and the residue was washed with ether and cold acetone and dried under vacuum to give a yellow microcrystalline powder.

(b) To a solution of [Pt(*p*-MeC$_6$H$_4$)(ppy)(SMe$_2$)], **1a** (50 mg, 0.1 mmol), in CH$_2$Cl$_2$ (20 mL) was added [Pt(*p*-MeC$_6$H$_4$)-(bhq)(η^1-dppm)], **4a** (85 mg, 0.1 mmol). The mixture was stirred at room temperature for 1 h, and then the solvent was evaporated from the resulting solution and the residue was washed with ether and cold acetone and dried under vacuum to give the product as a yellow powder. Anal. Calcd for C$_{63}$H$_{52}$N$_2$P$_2$Pt$_2$: C, 58.7; H, 4.1; N, 2.2. Found: C, 58.1; H, 4.1; N, 2.2. NMR in CD$_2$Cl$_2$: δ(^{1}H) = 2.15 [s, 6H, MeC]; 3.16 [t, 2H, $^3J_{PH}$ = 9 Hz, CH$_2$P$_2$]; 6.51 [dt, 1H, $^3J_{H^5H^6}$ = $^3J_{H^5H^4}$ = 6 Hz, $^4J_{H^5}$H^3 = 1 Hz, H^5]; 8.15 [dd, 1H, $^3J_{H^6H^5}$ = 8 Hz, $^4J_{H^6H^4}$ = 1 Hz, H^6]; δ(^{31}P) = 15.5 [d, $^1J_{PtP}$ = 1996 Hz, $^2J_{PP}$ = 20 Hz, $^3J_{PtP}$ = 46 Hz, PtP]; 14.1 [d, $^1J_{PtP}$ = 2055 Hz, $^2J_{PP}$ = 20 Hz, $^3J_{PtP}$ = 56 Hz, PtP].

The following complexes were prepared similarly by both methods using the appropriate starting materials:

[(*p*-MeOC$_6$H$_4$)(ppy)Pt(μ-dppm)Pt(*p*-MeC$_6$H$_4$)(ppy)], 7. Yield: 68%; mp 234 °C (dec). Anal. Calcd for C$_{61}$H$_{52}$N$_2$OP$_2$Pt$_2$: C, 53.2; H, 4.0; N, 2.1. Found: C, 52.4; H, 4.0; N, 2.0. NMR in CDCl$_3$: δ(^{1}H) = 2.30 [s, 3H, MeC]; δ = 3.70 [s, 3H, MeO]; 3.10 [t, 2H, $^3J_{PH}$ = 9 Hz, CH$_2$P$_2$]; 6.52 [m, 2H, H^5]; δ(^{31}P) = 16.9 [d, $^1J_{PtP}$ = 1979 Hz, $^2J_{PP}$ = 32 Hz, PtP]; 16.6 [d, $^1J_{PtP}$ = 1994 Hz, $^2J_{PP}$ = 32 Hz, PtP]; δ(^{195}Pt) = −2332 [br d, $^1J_{PtP}$ = 1985 Hz, Pt]; −2351 [br d, $^1J_{PtP}$ = 2000 Hz, Pt].

[(*p*-MeC$_6$H$_4$)(bhq)Pt(μ-dppm)Pt(*p*-MeOC$_6$H$_4$)(bhq)], 8. Yield: 82%; mp 253−255 °C (dec). Anal. Calcd for C$_{65}$H$_{52}$N$_2$OP$_2$Pt$_2$: C, 58.7; H, 3.9; N, 2.1. Found: C, 58.4; H, 3.8; N, 2.0. NMR in CDCl$_3$: δ(^{1}H) = 2.32 [s, 3H, MeC]; 3.80 [s, 3H, MeO]; 3.28 [t, 2H, $^3J_{PH}$ = 9 Hz, CH$_2$P$_2$]; 8.03 [d, 2H, $^3J_{H^6}$H^5 = 8 Hz, H^6]; δ(^{31}P) = 15.1 [d, $^1J_{PtP}$ = 2061 Hz, $^2J_{PP}$ = 21 Hz, PtP]; 14.7 [d, $^1J_{PtP}$ = 2043 Hz, $^2J_{PP}$ = 21 Hz, PtP]; δ(^{195}Pt) = −2362 [br d, $^1J_{PtP}$ ≈ 2040 Hz, Pt]; −2374 [br d, $^1J_{PtP}$ ≈ 2035 Hz, Pt].

[(*p*-MeOC$_6$H$_4$)(ppy)Pt(μ-dppm)Pt(*p*-MeOC$_6$H$_4$)(bhq)], 9b. Yield: 60%; mp 212−216 °C (dec). Anal. Calcd for C$_{63}$H$_{52}$N$_2$P$_2$Pt$_2$: C, 57.3; H, 4.0; N, 2.2. Found: C, 58.4; H, 4.2; N, 2.2. NMR in CDCl$_3$: δ(^{1}H) = 3.70 [s, 6H, MeO]; 3.09 [t, 2H, $^3J_{PH}$ = 9 Hz, CH$_2$P$_2$]; 6.38 [t, 1H, $^3J_{H^5H^6}$ = $^3J_{H^5H^4}$ = 7 Hz, H^5]; 8.00 [d, $^3J_{H^6H^5}$ = 7 Hz, H^6]; δ(^{31}P) = 15.9 [d, $^1J_{PtP}$ = 1985 Hz, $^2J_{PP}$ = 21 Hz, $^3J_{PtP}$ = 48 Hz, PtP]; 14.5 [d, $^1J_{PtP}$ = 2041 Hz, $^2J_{PP}$ = 21 Hz, PtP];

Table 1. Crystal Data and Structure Refinement for the Complexes

	2a	**3b**	**4a**	**9a**
formula	$C_{22}H_{21}NPtS$	$C_{43}H_{37}NOP_2Pt$	$C_{90}H_{74}N_2P_4Pt_2$	$C_{63}H_{52}N_2P_2Pt_2$
fw	526.55	840.77	1697.57	1289.19
T/K	150(2)	150(2)	150(2)	150(2)
$\lambda/\text{Å}$	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic	triclinic
space gp	$P1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
cell dimens/mm	$0.18 \times 0.17 \times 0.13$	$0.03 \times 0.05 \times 0.06$	$0.08 \times 0.11 \times 0.13$	$0.13 \times 0.07 \times 0.04$
$a/\text{Å}$	8.705(2)	8.9759(4)	9.2470(3)	11.595(2)
$b/\text{Å}$	10.154(2)	9.9660(4)	9.8227(4)	13.699(3)
$c/\text{Å}$	11.044(2)	19.4068(9)	19.3364(7)	18.152(4)
α/deg	69.73(3)	89.980(3)	90.239(2)	96.83(3)
β/deg	80.06(3)	89.733(2)	90.210(2)	108.61(3)
γ/deg	88.40(3)	88.706(2)	93.781(2)	111.59(3)
$V/\text{Å}^3$	901.4(3)	1735.5(1)	1752.5(1)	2447(1)
Z	2	2	1	2
d(calc)/Mg m^{-3}	1.940	1.609	1.609	1.749
μ/mm^{-1}	7.903	4.170	4.129	5.819
data/rest/params	4135/0/226	7376/0/434	6199/0/442	11 232/0/622
$R_1[I > 2\sigma(I)]$	0.051	0.021	0.016	0.046
wR_2[all data]	0.152	0.047	0.044	0.162

$\delta(^{195}\text{Pt}) = -2345$ [br d, $^1J_{\text{PtP}} \approx 1970$ Hz, Pt]; -2360 [br d, $^1J_{\text{PtP}} \approx 2020$ Hz, Pt].

[(*p*-MeOC$_6$H$_4$)(bhq)Pt(*μ*-dppm)Pt(*p*-MeC$_6$H$_4$)(ppy)], 9c. Yield: 86%; mp 230–235 °C (dec). Anal. Calcd for $C_{63}H_{52}N_2P_2Pt_2$: C, 58.0; H, 4.0; N, 2.1. Found: C, 57.5; H, 4.1; N, 2.0. NMR in CD$_2$Cl$_2$: $\delta(^1\text{H}) = 2.24$ [s, 3H, MeC]; 3.89 [s, 3H, MeO]; 3.18 [t, 2H, $^2J_{\text{PH}} = 8$ Hz, CH$_2$P$_2$]; 6.50 [dt, 1H, $^3J_{\text{H}^5\text{H}^6} = {}^3J_{\text{H}^5\text{H}^4} = 7$ Hz, $^4J_{\text{H}^5\text{H}^3} = 1$ Hz, H^5]; 8.16 [dd, $^3J_{\text{H}^6\text{H}^5} = 8$ Hz, $^4J_{\text{H}^6\text{H}^4} = 1$ Hz, H^6]; $\delta(^{31}\text{P}) = 15.7$ [d, $^1J_{\text{PtP}} = 1998$ Hz, $^2J_{\text{PP}} = 21$ Hz, $^3J_{\text{PtP}} = 40$ Hz, PtP]; 14.2 [d, $^1J_{\text{PtP}} = 2041$ Hz, $^2J_{\text{PP}} = 21$ Hz, $^3J_{\text{PtP}} = 57$ Hz, PtP]; NMR in CDCl$_3$: $\delta(^{195}\text{Pt}) = -2356$ [br d, $^1J_{\text{PtP}} \approx 2015$ Hz, Pt]; -2352 [br d, $^1J_{\text{PtP}} \approx 2000$ Hz, Pt].

[(*p*-MeC$_6$H$_4$)(bhq)Pt(*μ*-dppm)Pt(*p*-MeOC$_6$H$_4$)(ppy)], 9d. Yield: 79%, mp 205–209 °C (dec). Anal. Calcd for $C_{63}H_{52}N_2P_2Pt_2$: C, 58.0; H, 4.0; N, 2.1. Found: C, 57.8; H, 4.2; N, 2.0. NMR data in CDCl$_3$: ^{1}H NMR: $\delta(^1\text{H}) = 2.35$ [s, 3H, MeC]; 3.80 [s, 3H, MeO]; 3.24 [t, $^3J_{\text{PH}} = 9$ Hz, CH$_2$P$_2$]; 6.47 [t, 1H, $^3J_{\text{H}^5\text{H}^6} = {}^3J_{\text{H}^5\text{H}^4} = 6$ Hz, H^5 of ppy]; 8.05 [d, $^3J_{\text{H}^6\text{H}^5} = 8$ Hz, H^6 of bhq]; $\delta(^{31}\text{P}) = 15.7$ [d, $^1J_{\text{PtP}} = 1987$ Hz, $^2J_{\text{PP}} = 21$ Hz, $^3J_{\text{PtP}} = 51$ Hz, PtP]; 14.6 [d, $^1J_{\text{PtP}} = 2055$ Hz, $^2J_{\text{PP}} = 21$ Hz, $^3J_{\text{PtP}} = 43$ Hz, PtP]; $\delta(^{195}\text{Pt}) = -2340$ (br d, $^1J_{\text{PtP}} \approx 1950$ Hz, Pt]; -2367 [br d, $^1J_{\text{PtP}} \approx 2070$ Hz, Pt].

Structure Determinations. Data were collected using a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997–2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski and Minor, 1997). The absorption corrections were applied using HKL2000 DENZO-SMN (SCALEPACK). The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G. M., 2001) suite of programs was used to solve the structures by direct methods. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Details are given in Table 1.

Supporting Information Available: Tables of X-ray data for the complexes in cif format This material is available free of charge via the Internet at http://pubs.acs.org.