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# Cyclometalated Cluster Complex with a Butterfly-Shaped $Pt_2Ag_2$ Core

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The cyclometalated platinum complex [PtMe(bhq)(dppy)] (**1**), in which bhq = benzo{*h*}quinoline and dppy = 2-(diphenylphosphino)pyridine, was prepared by the reaction of [$PtMe(SMe_2)(bhq)$] with 1 equiv of dppy at room temperature. Complex **1** contains one free pyridyl unit and was readily characterized by multinuclear NMR spectroscopy and elemental microanalysis. The reaction of complex **1** with 1 equiv of [$Ag(CH_3CN)_4$]$BF_4$ gave the cyclometalated cluster complex [$Pt_2Me_2(bhq)_2(\mu\text{-dppy})_2Ag_2(\mu\text{-acetone})$]$(BF_4)_2$ (**2**) in 70% yield. The crystal structure of complex **2** was determined by X-ray crystallography, indicating a rare example of a butterfly cluster with a $Pt_2Ag_2$ core in which the Ag atoms occupy the edge-sharing bond. In solution, the bridging acetone dissociates from the cluster complex **2**, but as shown by NMR spectroscopy, the $Pt_2Ag_2$ core is retained in solution and a dynamic equilibrium is suggested to be established between the planar and butterfly skeletal geometries.

## Introduction

Metal clusters occupy a prominent position in chemistry. In addition to the interest arising from the potential utility of metal clusters in catalysis[1] and the preparation of new materials,[2] there has also been significant interest in exploiting the remarkable structural and bonding properties of these compounds.[3] Metal−metal dative bonds play an important role in the synthesis of metal clusters,[4] and electron-rich platinum(II) complexes can expand opportunities for the formation of metal−metal dative bonds. Examples of the use of anionic (perhalophenyl)platinum(II) complexes in the synthesis of cluster complexes containing Pt−Ag dative bonds have been reported in the literature.[5] Very recently, a self-assembled luminescent octanuclear stellate platinacycle has been constructed via Pt−Ag dative bonds.[6] The electron-donor ability of a $Pt^{II}$ center containing a cyclometalating ligand, e.g., 2-phenylpyridine (ppy) or benzo{*h*}quinoline (bhq), is significantly enhanced, and this would assist in its ability to form Pt−M dative bonds.[7] In this area, a number of cyclometalated platinum(II) complexes have been synthesized in order to study the influence of the Pt−Ag dative bonds on the their physical properties,[7a,b] and helical metal−metal-bonded chains have recently been prepared from the

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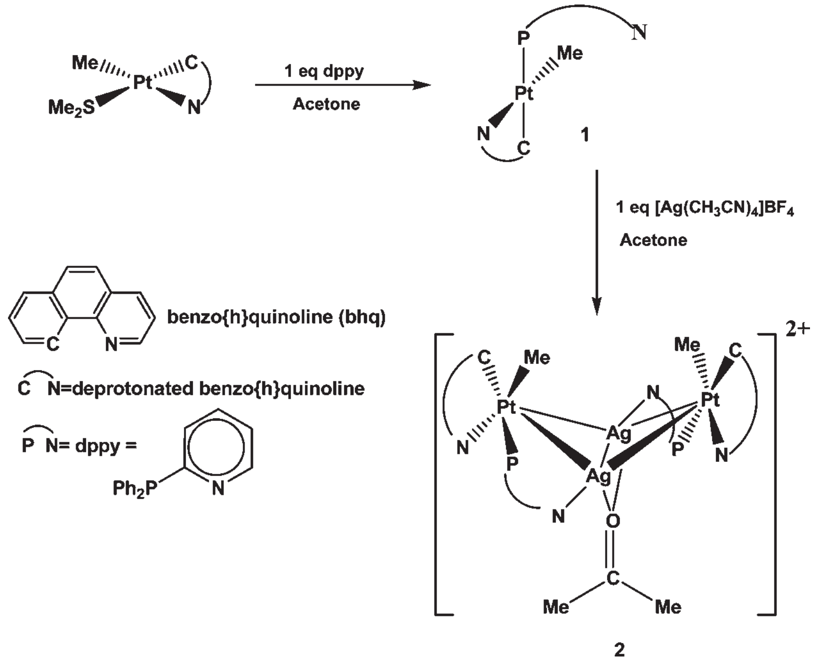
**Scheme 1**



reaction of cyclometalated platinum complexes [Pt(ppy)$_2$] and [Pt(thpy)$_2$] with AgClO$_4$.[8]

It has been demonstrated that metal−metal-bonding interactions in cooperation with bridging ligands, such as bis(phosphines),[9] alkynyls,[10] and dithiolates,[11] usually favor the formation of bi- and multinuclear complexes. In this regard, the bridging ligands are usually designed to have a small bite angle, e.g., 2-(diphenylphosphino)pyridine (dppy), in order to bring the metal centers into close proximity and lock them together, thus favoring the formation of metal−metal bonds. For example, cluster complexes [Au$_3$($\mu_3$-E)Ag(dppy)$_3$](BF$_4$)$_2$ (E = O, S, Se) have been prepared by the reaction of AuCl(dppy) with excess Ag$_2$O and NaBF$_4$, and cluster complex [Pt$_2$(dppy)$_4$($\mu_3$-S$_2$)Ag$_3$($\mu_3$-S$_2$)Pt$_2$(dppy)$_4$]PF$_6$ has been prepared by the reaction of dimeric complex [Pt$_2$($\mu$-S)$_2$(dppy)$_4$] with AgPF$_6$.[12] These findings as well as our interest in synthesizing binuclear cyclometalated complexes[13] led us to incorporate appropriate bridging and cyclomtalating ligands into one Pt$^{II}$ center and use them as precursors in the synthesis of new bi- and multiheteronuclear complexes. We report herein the synthesis and crystal structural analysis of the cluster complex [Pt$_2$Me$_2$(bhq)$_2$($\mu$-dppy)$_2$Ag$_2$($\mu$-acetone)][BF$_4$]$_2$ (**2**) containing a Pt$_2$Ag$_2$ core with an unprecedented butterfly skeletal geometry in which the Ag atoms occupy the edge-sharing bond; note that two clusters with planar Pt$_2$Ag$_2$ cores have already been reported.[14]

## Result and Discussion

As summarized in Scheme 1, the reaction of complex [PtMe(bhq)(SMe$_2$)], in which bhq = benzo{*h*}quinoline, with 1 equiv of dppy at room temperature in acetone gave the complex [PtMe(bhq)(dppy)] (**1**) in good yield by replacement of the SMe$_2$ ligand with the P ligating atom of dppy. Complex **1** is a yellow solid that is stable in acetone or chloroform solutions for several hours and fully characterized by multinuclear NMR spectroscopy and elemental microanalysis, and the details are described in the Experimental Section.

In the $^{31}$P NMR spectrum of complex **1**, the observation of a singlet resonance at $\delta$ 33.3 ppm, with satellites due to coupling to the Pt atom ($^1J_{\mathrm{PtP}} = 2096$ Hz), was assigned to the P atom of the dppy ligand connected to the Pt center. Consistently, the $^{195}$Pt NMR spectrum of complex **1** showed a doublet signal at $\delta$ 585 ppm with $^1J_{\mathrm{PtP}} = 2095$ Hz. In the $^1$H NMR spectrum of complex **1**, the Me ligand protons appeared at $\delta$ 0.96 ppm as a doublet due to coupling with the P atom with $^3J_{\mathrm{PH}} = 7.8$ Hz, which is further coupled to the Pt atom with $^2J_{\mathrm{PtH}}$ = 83.5 Hz. The proton of the CH group adjacent to the N atom of the dppy ligand appeared

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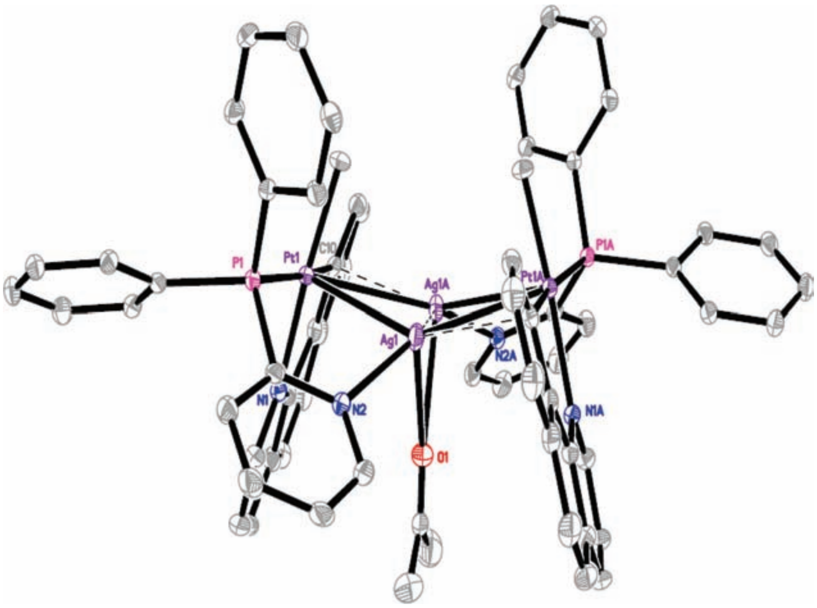

**Figure 1.** Molecular structure of complex **2**, showing 30% probability displacement ellipsoids with selected atom numbering. The anion ($BF_4^-$), acetone solvents of crystallization, and H atoms were omitted for clarity.

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for Complex **2**[a]

| | | | |
|---|---|---|---|
| Pt1−Ag1 | 2.7749(3) | Ag1−Pt1−Ag1A | 58.06(1) |
| Pt1−Ag1A | 3.0311(3) | Pt1−Ag1−Pt1A | 114.68(1) |
| Ag1−Ag1A | 2.8265(5) | N1−Pt1−C1 | 171.81(11) |
| Pt1−P1 | 2.3114(7) | P1−Pt1−C10 | 169.90(8) |
| Pt1−N1 | 2.158(2) | N1−Pt1−C10 | 80.41(10) |
| Pt1−C10 | 2.055(3) | Ag1−Pt1−C10 | 108.65(7) |
| Pt1−C1 | 2.055(3) | | |
| Ag1−N2 | 2.315(3) | | |
| Ag1−O1 | 2.683(3) | | |
| Ag1−C10A | 2.347(3) | | |

[a] The *suffix* A is for the symmetry code: $-x + 1, y, -z + {}^3/_2$.

at $\delta$ 8.70 ppm as a doublet with ${}^3J_{HH} = 4.5$ Hz with no coupling to the Pt center, confirming that the N atom of the pyridyl group is uncoordinated.[15]

As described in Scheme 1, treatment of complex **1** with a stoichiometric amount of $[Ag(CH_3CN)_4]BF_4$ in acetone at room temperature afforded cluster complex **2** in 70% yield.

Red crystals of the complex **2** were obtained by the slow diffusion of ether into an acetone solution of **2** in a refrigerator for 1 week. Cluster complex **2** crystallizes in the monoclinic system, in the space group *C*2/*c*. The asymmetric unit of complex **2** comprises half of the cluster cation complex containing a Pt−Ag dative bond, a tetrafluoroborate counterion, and two acetone molecules as the solvent of crystallization. Each pair of these units is linked together by two Pt−Ag bonds and one Ag−Ag bond to form a tetranuclear cluster with a butterfly $Pt_2Ag_2$ core of alternating Pt and Ag atoms; also, an acetone molecule bridges the two Ag atoms. A view of the molecular structure of **2** is depicted in Figure 1, and the selected bond lengths and angles are listed in Table 1.

In comparison with the previously reported cyclometalated helical chain containing Pt−Ag dative bonds in which every Pt unit is coordinated to the Ag atoms on opposite sides,[8] the Pt−Ag dative bonds in **2** are located on the same side of the coordination plane. Each of the [PtMe(bhq)-($\mu$-dppy)] units, displaying a slightly distorted square-planar geometry [the Pt atom displaced −0.089(1) Å from the coordination plane], is composed of $C_2NP$ donors with bond lengths of Pt−C(bhq) = 2.055(3) Å, Pt−C(Me) = 2.055(3) Å, Pt−P = 2.3114(7) Å, and Pt−N = 2.158(2) Å. The complex contains two different types of Pt−Ag bonds, short and long. Each of the short bonds, either Pt1−Ag1 or Pt1A−Ag1A, is supported by a bridging dppy ligand [with the Ag−N bond distance being 2.315(3) Å], with both bond lengths being 2.7749(3) Å; the bond length is shorter than the sum of the metallic radii of Pt and Ag (2.83 Å), indicating the formation of a strong Pt−Ag dative bond. The bond distance for either of the long bonds, Pt1−Ag1A or Pt1A−Ag1, amounts to 3.0311(3) Å, which is shorter than the sum of the van der Waals radii of Pt and Ag (3.45 Å), demonstrating the presence of a Pt−Ag bonding interaction; note that each bond is also supported by a secondary weak interaction of the Ag atom with the C atom of the bhq ligand that is coordinated to the Pt atom (dashed bonds in Figure 1) with a Ag−C distance of 2.3473(3) Å. The best description for the long bonds will probably be similar to a donor−acceptor ($\pi$ system−metal) interaction as reported previously.[8,16] The Pt−Ag vectors are tilted by 13.02(6)° and 55.15(6)° with respect to the normal line of the platinum coordination plane. The dihedral ("butterfly") angle between the planes Pt1−Ag1−Ag1A and Pt1A−Ag1−Ag1A is 148.55(1)°. The distance between the two Ag atoms in **2** is 2.8265(5) Å, which is significantly shorter than the accepted maximum distance for an argentophilic interaction (3.44 Å, the sum of the van

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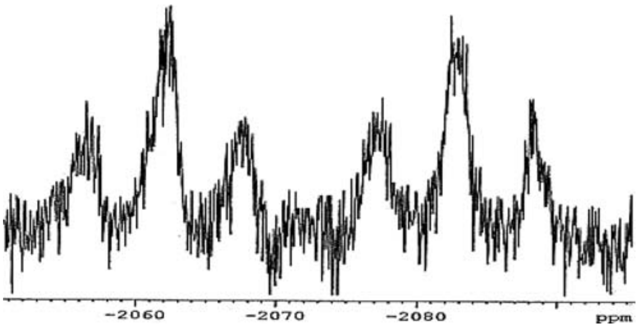

**Figure 2.** $^{195}$Pt NMR spectrum of complex **2** in $CD_2Cl_2$ at room temperature.

der Waals radii of Ag atoms).[17] The Ag−Ag distance in **2** is shorter than that observed in $(NBu_4)_2[Pt_2Ag_2C_{14}(C_6F_5)_4]$ (2.9946 Å),[14b,c] but it is slightly longer than that found in $[(NN)PtMe_2]_2Ag_2(OTf)_2$ [2.6972(2) Å],[14a] in each of which the $Pt_2Ag_2$ core is planar. Finally, the Ag atoms carry a bridging acetone molecule by interacting through the O atom, displaying Ag−O distances of 2.683(3) Å, which is longer than those found in the terminal coordination mode of acetone molecules of $[\{Pt(phpy)_2\}_2\{Ag(acetone)\}_2]_n(ClO_4)_{2n}$ [2.419(9) and 2.373(9) Å] and $[\{Pt\text{-}(thpy)_2\}_3\{Ag(acetone)\}_2](ClO_4)_2$ [2.532(8) and 2.471(7) Å].[8]

In the $^{31}$P NMR spectrum of complex **2** in the $CDCl_3$ solvent, although on the basis of its crystal structure (vide supra) the two P atoms are equivalent, two unequal intensity singlet signals at $\delta$ 35.9 ppm (with $^1J_{PtP} = 2206$ Hz) and $\delta$ 35.6 ppm (with $^1J_{PtP} = 2214$ Hz) were observed. It is therefore probable that in solution complex **2** is present as a mixture of two skeletal isomers. The $^{195}$Pt NMR spectrum of complex **2** is particularly informative and proves that the $Pt_2Ag_2$ core, observed in the solid state, is retained in solution. Thus, the $^{195}$Pt NMR spectrum of a $CD_2Cl_2$ solution of complex **2** (Figure 2) showed a doublet of triplets at $\delta$ −2072 ppm due to coupling with the P atom with $^1J_{PtP} = 2203$ Hz, which is further coupled to two spin-active $^{107,109}$Ag atoms with $^1J_{^{195}Pt-^{107,109}Ag} = 580$ Hz. The strength of the spin−spin coupling depends on the magnetogyric ratios of the nuclei, and because the difference in the magnetogyric ratios of the silver isotopes is small $[\gamma(^{107}Ag)/\gamma(^{109}Ag) = 1.15]$, it is assumed that there is a small difference in the coupling constants of $^1J(Pt-^{107}Ag)$ and $^1J(Pt-^{109}Ag)$. Similar coupling constants of isotopes $^{107}$Ag and $^{109}$Ag have been reported previously.[18] The peaks due to the two skeletal isomers, suggested above on the basis of the $^{31}$P NMR spectrum, seem to have overlapped considering that the observed signal is significantly broadened.

In the $^1$H NMR spectrum of a $CDCl_3$ solution of complex **2** at 295 K (see Figure 3, spectrum on the bottom), the two unequal intensity resonances at $\delta$ 0.30 ppm (with $^2J_{PtH} = 67.0$ Hz and $^3J_{PH} = 9.4$ Hz) and 1.26 ppm (with $^2J_{PtH} = 73.0$ Hz and $^3J_{PH} = 7.6$ Hz) in a 1:1.6 ratio, respectively, were assigned to the protons of the methyl ligands of the two isomers and a sharp singlet signal (with relative intensity approximately equal to the sum of the methyl intensities, i.e., $1 + 1.6 = 2.6$) at $\delta$ 2.17 ppm was assigned to the free acetone molecule in $CDCl_3$.[19] Reduction of the coupling constant $^2J_{PtH}$ of the methyl ligands from the value of 83.5 Hz in the $^1$H NMR spectrum of complex **1** to the values of 67.0 and 73.0 Hz in the $^1$H NMR spectrum of complex **2** confirms the persistence of the Pt−Ag bonds in solution.[20,14a]

**Scheme 2**

The $^1$H NMR spectrum of complex **2** was monitored as a function of the temperature in the $CDCl_3$ solution (see the high-field region spectra, shown in Figure 3). A change in the relative intensities was observed upon cooling from room temperature to −50 °C. As the temperature is lowered, the methyl resonance at $\delta$ 0.30 ppm becomes more broadened and its intensity decreases, while the intensity of the methyl resonance at $\delta$ 1.26 ppm increases. We therefore suggest that the two skeletal isomers in solution are in dynamic equilibrium. Considering the butterfly structure of **2** in the solid state and previous planar structures reported for $Pt_2Ag_2$ clusters, we propose that the equilibration involves conversion between planar and butterfly arrangements of the metal atoms (see Scheme 2).

It is possible that the crystal packing in conjunction with the acetone molecule being coordinated to Ag atoms in the solid state has strongly encouraged the butterfly arrangements. Note that it has been described that for the tetranuclear cluster complexes there are six possible skeletal isomers; the butterfly geometry is the most frequently reported metal core geometry.[21] Among these six possibilities, there are only four (as demonstrated in Scheme 3) in which the metal core has a "closed" arrangement. As mentioned before, the $^{195}$Pt NMR spectrum of complex **2** represents that each Pt atom bonds to two Ag atoms. As such, only the four geometries described in Scheme 3, i.e., tetrahedral (a), butterfly (b), or planar (c or d), are possible for complex **2** in solution. If the complex adapts a tetrahedral geometry (a), then a Pt−Pt edge and so a P−Pt−Pt−P arrangement, which can be characterized by the superimposition of the spectra of the three isotopomers P−Pt−Pt−P, $P-^{195}Pt-Pt-P$, and $P-^{195}Pt-^{195}Pt-P$, are required to be present. Analyses of these spin systems for tetrahedral and other core geometries have been carried out previously,[22] and they are clearly not consistent with the $^{31}$P and $^{195}$Pt NMR patterns discussed above for complex **2**. Besides, it is very unlikely that the strong argentophilic interaction between the

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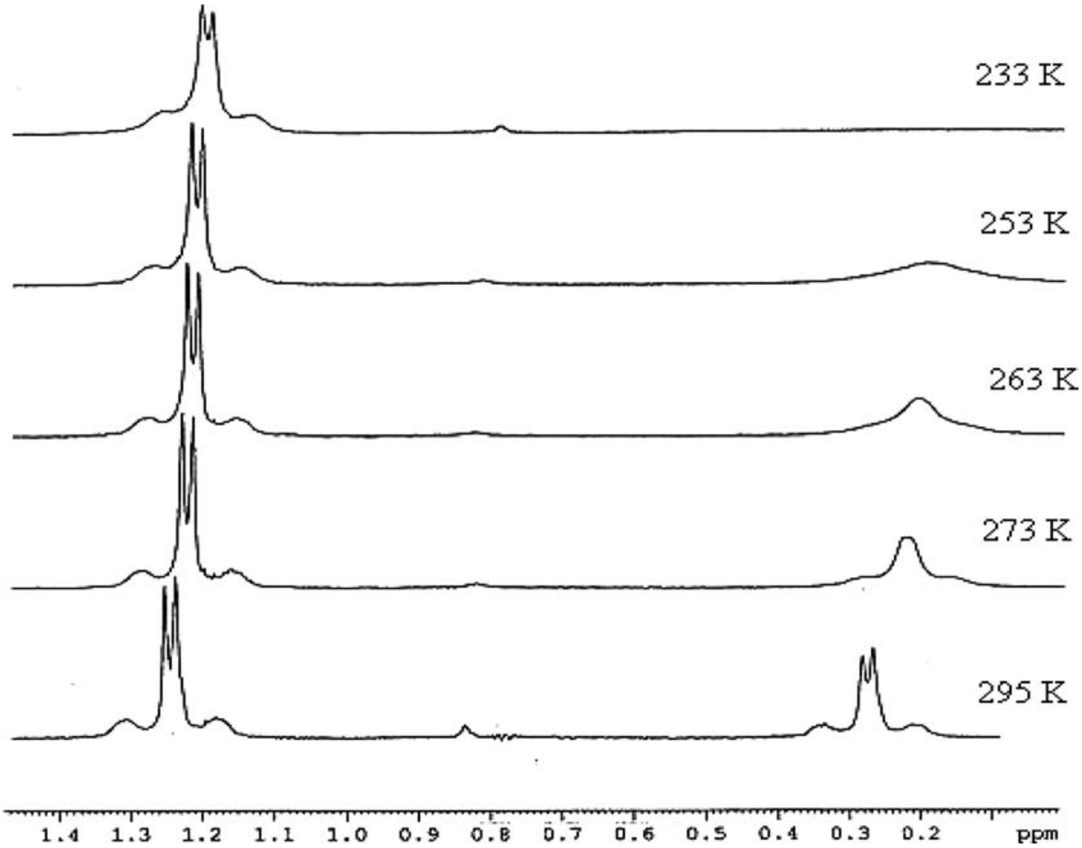
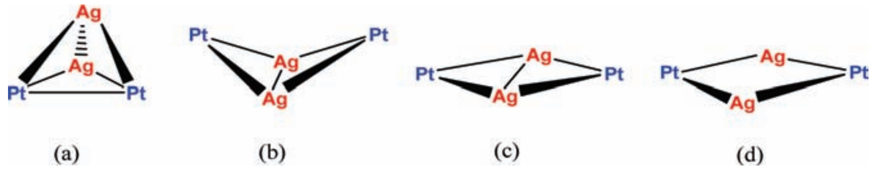


**Figure 3.** $^1$H NMR spectra (methyl region) of complex **2** at different temperatures.

**Scheme 3**



two Ag atoms of the $Pt_2Ag_2$ core in the solid state of **2** would break up in solution, and this most probably eliminates the possibility of an alternative geometry (d). Therefore, the above assumption that the metal core of **2** is retained in solution as an equilibrium mixture of the butterfly (b) and planar(c) geometries seems to be reasonable, although there may be alternative mechanisms that are also consistent with the observed NMR data.

## Experimental Section

The $^1$H and $^{31}$P NMR spectra were recorded on a Bruker Avance DRX 500-MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: $^1$H (500 MHz, tetramethylsilane, $SiMe_4$), $^{31}$P (202 MHz, 85% $H_3PO_4$), and $^{195}$Pt (107 MHz, aqueous $Na_2PtCl_4$). The chemical shifts and coupling constants are in parts per million and hertz, respectively. Benzo{*h*}quinoline and $[Ag(CH_3CN)_4]BF_4$ were purchased from commercial sources, and a yellow solution of [PtMe(bhq)($SMe_2$)] in acetone was prepared in situ as described previously.[13a,23] Crystal data and refinement parameters for **2** are given in Table 2.

**[PtMe(bhq)(dppy)] (1).** To a solution of the complex [PtMe(bhq)($SMe_2$)] (100 mg, 0.22 mmol) in acetone (15 mL) was added 1 equiv of dppy (59 mg, 0.22 mmol) at room temperature. The mixture was stirred at this condition for 1 h, then the solvent was removed under reduced pressure, the residue was triturated with ether (2 × 3 mL), and the product as a yellow solid was dried under vacuum. Yield: 65%. NMR data in $CDCl_3$: $\delta(^1H)$ 0.96 (3H, d, $^2J_{PtH} = 83.5$ Hz, $^3J_{PH} = 7.8$ Hz, PtMe), 6.00 (m, 1H, H atom adjacent to the coordinated C atom of the bhq ligand), 7.0−8.0 (m, 19 H, aryl protons), 8.4 (m, 1H, H atom adjacent to the coordinated N atom of the bhq ligand), 8.7 (d, 1H, $^3J_{HH} = 4.5$ Hz, H atom adjacent to the N atom of the free pyridine ring); $\delta(^{31}P)$ 33.3 (s, $^1J_{PtP} = 2096$ Hz); $\delta(^{195}Pt)$ 585 (d, $^1J_{PtP} = 2095$ Hz). Anal. Calcd for $C_{31}H_{25}N_2PPt$: C, 57.1; H, 3.8; N, 4.3. Found: C, 57.4; H, 3.9; N, 4.1.

**[$Pt_2Me_2(bhq)_2(\mu$-dppy$)_2Ag_2(\mu$-acetone$)](BF_4)_2$ (2).** To a solution of complex **1** (200 mg, 0.31 mmol) in acetone (20 mL) at room temperature under an argon atmosphere was added 1 equiv of $[Ag(CH_3CN)_4]BF_4$ (111 mg, 0.31 mmol). The mixture was stirred at this condition for 1.5 h in the dark, and then the solvent was removed under reduced pressure. The residue was washed with ether (2 × 3 mL), and the product was dried under vacuum. Yield: 70%. NMR data in $CDCl_3$: for the first isomer,

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**Table 2.** Crystal Data and Structure Refinement Parameters of Complex **2**

| | |
|---|---|
| empirical formula | $[C_{65}H_{56}Ag_2N_4OP_2Pt_2](BF_4)_2 \cdot 4C_3H_6O$ |
| fw | 1982.91 |
| cryst size (mm) | 0.25 × 0.30 × 0.60 |
| cryst syst | monoclinic |
| space group | *C*2/*c* |
| $\theta_{max}$ (deg) | 32.2 |
| *a* (Å) | 23.2342(13) |
| *b* (Å) | 18.1759(12) |
| *c* (Å) | 17.5809(12) |
| β (deg) | 96.314(10) |
| *V* (Å$^3$) | 7379.4(8) |
| *Z* | 4 |
| $D_{calcd}$ (Mg/m$^3$) | 1.785 |
| *M* (mm$^{-1}$) | 4.420 |
| *F*(000) | 3888 |
| index ranges | $-34 \leq h \leq 33$<br>$-26 \leq k \leq 26$<br>$-26 \leq l \leq 25$ |
| no. of mead reflns | 44 537 |
| no. of indep reflns/$R_{int}$ | 12 091/0.027 |
| no. of obsd reflns [$I > 2\sigma(I)$] | 8982 |
| no. of param/restraints | 467/52 |
| GOF | 0.95 |
| R1 (obsd data) | 0.0288 |
| wR2 (all data)[a] | 0.0676 |

[a] $w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

$\delta(^1H)$ 0.30 (3H, d, $^2J_{PtH} = 67.0$ Hz and $^3J_{PH} = 9.4$ Hz, PtMe); for the other isomer $\delta(^1H)$ 1.26 (3H, d, $^2J_{PtH} = 73.0$ Hz, $^3J_{PH} = 7.6$ Hz, PtMe), 2.17 (s, Me groups of dissociated acetone); for one isomer, $\delta(^{31}P)$ 35.9 (s, $^1J_{PtP} = 2206$ Hz); for the other isomer, $\delta(^{31}P)$ 35.6 ($^1J_{PtP} = 2214$ Hz); both isomers in $CD_2Cl_2$, $\delta(^{195}Pt)$ −2072 (d of t, $^1J_{PtP} = 2203$ Hz, $^1J_{^{195}Pt-^{107,109}Ag} = 580$ Hz). Anal. Calcd for $C_{65}H_{56}N_4P_2Pt_2Ag_2O$: C, 44.5; H, 3.2; N, 3.2. Found: C, 44.7; H, 3.1; N, 3.4.

**Crystal Structure Determinations.** X-ray intensity data were collected on the Oxford Diffraction Xcalibur CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at a temperature of 295(2) K. The data reduction, including the analytical numerical absorption correction,[24a] was performed using the *CrysAlis* software package.[24b] The structures were solved by direct methods (*SHELXS97*) and refined by full-matrix least squares (*SHELXL-97*) on $F^2$.[25] The non-H atoms were refined anisotropically. All of the H atoms were positioned geometrically and refined with the riding model approximation, with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$. All calculations were carried out using *PLATON*.[26] For molecular graphics, the program *SHELXTL* was used.[25]

## Conclusion

The complex [PtMe(bhq)(dppy)] (**1**), in which bhq = benzo{*h*}quinoline and dppy = 2-(diphenylphosphino)pyridine, has an electron-rich Pt center and an uncoordinated pyridyl group, and this creates the possibility of synthesizing new bi- and multinuclear complexes containing cyclometalated platinum units. In the present work, complex **1** has been coupled with 1 equiv of $[Ag(CH_3CN)_4]BF_4$ to form a Pt−Ag dative bond, which is accompanied by a bridging dppy ligand, and the cyclometalated cluster complex $[Pt_2Me_2(bhq)_2(\mu\text{-dppy})_2Ag_2(\mu\text{-acetone})](BF_4)_2$ (**2**) is, in fact, an association formed by rather strong intermolecular interactions between Pt and Ag atoms of two of the coupled species, each supported by a secondary weak interaction of the Ag atom with the C atom of the bhq ligand, followed by the formation of a strong Ag−Ag bond. Complex **2** is a tetranuclear cluster with a butterfly $Pt_2Ag_2$ core of alternating Pt and Ag atoms [the angle between the wings of the butterfly core is 148.55(1)°], in which an acetone molecule has also bridged between the two Ag atoms. Dissociation of the bridging acetone molecule has probably been responsible for the establishment of a dynamic equilibrium in solution between two possible skeletal isomers of complex **2**, shown by NMR experiments to be planar (c) and butterfly (b), as described in Schemes 2 and 3.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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