Supramolecular Organoplatinum(IV) Chemistry: Dimers and Polymers Formed by Intermolecular Hydrogen Bonding

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ABSTRACT: The reaction of \([\text{PtMe}_2(6\text{-dppd})]\), 1, where 6-dppd is a 1,4-bis(2-pyridyl)pyridazine derivative, with bromoalkanes \(\text{BrCH}_2\text{R}\), having a hydrogen-bond donor group \(\text{R}\), gave the corresponding chiral products of trans oxidative addition \([\text{PtBrMe}_2(\text{CH}_2\text{R})(6\text{-dppd})]\), \(2a\), \(\text{R} = \text{CO}_2\text{H}\); \(3\), \(\text{R} = 4\text{-C}_6\text{H}_4\text{CO}_2\text{H}\); \(4\), \(\text{R} = 4\text{-C}_6\text{H}_4\text{CH}_2\text{CO}_2\text{H}\); \(7\), \(\text{R} = 2\text{-C}_6\text{H}_4\text{CH}_2\text{OH}\); \(8\), \(\text{R} = 4\text{-C}_6\text{H}_4\text{B(OH)}_2\); and \(10\), \(\text{R} = 2\text{-C}_6\text{H}_4\text{B(OH)}_2\). Complex \(2a\) was formed in equilibrium with two isomers formed by cis oxidative addition, while the reaction of \(1\) with \(\text{BrCH}_2\text{CH}_2\text{CO}_2\text{H}\) gave mostly \([\text{PtBrMe}(6\text{-dppd})]\), \(6\). The supramolecular chemistry was studied by structure determination of six of the platinum(IV) complexes, with emphasis on the preference of the hydrogen bond acceptor \((\text{O, pyridyl N, or Br atom})\), formation of monomer, dimer, or polymer, and self-recognition or self-discrimination in self-assembly. Complex \(7\) formed a monomer with the \(\text{OH} \cdots \text{N}\) hydrogen bond, and complexes \(2a\) and \(10\) formed racemic dimers by complementary hydrogen bonding with self-discrimination between \(\text{CO}_2\text{H}\) or \(\text{B(OH)}_2\) groups, respectively. Complexes \(3\), \(4\), and \(9\) formed polymers by intermolecular hydrogen bonding with self-recognition, with \(4\) containing \(\text{OH} \cdots \text{N}\) and \(3\) and \(9\) containing \(\text{OH} \cdots \text{Br}\) hydrogen bonds. It is concluded that there is no clear preference for the hydrogen bond acceptor group, and that the observed product depends also on the orientation of the hydrogen bond donor group.

INTRODUCTION

The field of supramolecular chemistry, relying on self-assembly through intermolecular secondary bonding, is now well developed and is dominated by the use of intermolecular hydrogen bonding as the secondary bonding force. In both organic and inorganic compounds, the hydrogen bonding groups are easily introduced, and the reversibility and directional nature of the hydrogen bonds has allowed the design of many complex architectures and functional molecular materials.1 The self-assembly of complex structures is less developed in organometallic chemistry because of the incompatibility of the functional groups typically involved as hydrogen bond donors with the metal–carbon bonds, which are often cleaved by protonolysis.2,3 However, alkylplatinum(IV) complexes are stable to protonolysis and many electron-rich alkylplatinum(II) complexes undergo oxidative addition reactions with alkyl halides faster than they undergo Pt–C bond protonolysis.4 This combination of properties has allowed the supramolecular chemistry of platinum(IV) to be developed in a systematic way. Thus, hydrogen bond donors can be introduced by oxidative addition reactions to platinum(II) complexes.5 A typical example, using bromoacetic acid as a reagent, is shown in Scheme 1 \((\text{R} = \text{H, t-Bu, CO}_2\text{Et})\), leading to formation of supramolecular dimers. In contrast, boronic acid derivatives tend to self-associate through intermolecular BOH–BrPt hydrogen bonds to give supramolecular polymers (Scheme 2).6

Scheme 1. Introduction of a Carboxylic Acid Group as a Hydrogen Bond Donor by Oxidative Addition to Platinum(II)

In earlier work, we have described the chemistry of the dimethylplatinum(II) complex \(1\).7 It was not possible to add a second platinum(II) unit to complex \(1\), and the platinum center was shown to be a stronger nucleophile than either of the free nitrogen donors, as illustrated by the oxidative addition of benzyl bromide (Scheme 3).7 A similar oxidative...
addition of alkyl bromides with hydrogen bonding donors as substituents then should allow self-assembly through OH–O (compare Scheme 1), OH–Br (compare Scheme 2), or OH–N hydrogen bonding. This article presents the results of such a study, including examples of each type of the hydrogen bond.

■ RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. The synthesis of some organoplatinum(IV) complexes 2a, 3, and 4, with carboxylic acid groups as substituents and whose structures were determined, is illustrated in Scheme 4. The compounds were isolated as air-stable, yellow solids and were initially characterized by their $^1$H NMR spectra. The square planar platinum(II) complex 1 has an effective plane of symmetry, but the platinum(IV) complexes are chiral. As expected, complex 3 gave two methylplatinum resonances at δ = 1.42 and 1.75 with coupling constants $J_{\text{PtH}} = 70$ and 71 Hz, respectively. The protons of the Pt–CH$_3$ group gave an "AB" multiplet with δ = 2.84 and 2.89 with $J_{\text{PtH}} = 92$ and 83 Hz, respectively. These parameters are typical for organoplatinum(IV) complexes.

The stereochemistry at the platinum(IV) center was defined later by structure determination but is also indicated by the absence of a resonance in the region δ < 1, typical of a methyl group trans to bromide in related compounds.

Complexes 3 and 4 were formed selectively by trans oxidative addition, but the reaction to give 2a was more complex (Scheme 5). When the reaction of 1 with bromoacetic acid in acetone-d$_6$ was monitored by $^1$H NMR spectroscopy, a mixture of the three isomers 2a, 2b, and 2c was formed. Each isomer gave two methylplatinum resonances in the $^1$H NMR spectrum [2a, δ = 1.46, $J_{\text{PtH}} = 70$ Hz, δ = 1.65, $J_{\text{PtH}} = 70$ Hz; 2b, δ = 0.73, $J_{\text{PtH}} = 73$ Hz, δ = 1.49, $J_{\text{PtH}} = 69$ Hz; 2c, δ = 0.75, $J_{\text{PtH}} = 74$ Hz, δ = 1.76, $J_{\text{PtH}} = 70$ Hz], resonances being assigned with the aid of $^1$H–$^1$H NOESY correlations. After 10 min, 24 h, and 72 h reaction time, the ratio 2a/2b/2c was approximately 3:6:1, 3:1:1, and 6:1:1, respectively, showing that 2b was the kinetically controlled product and 2a was the thermodynamically preferred product. The oxidative addition is expected to occur by the $S_{\text{N}2}$ mechanism to give the 16-electron, ionic intermediate A, and bromide addition would be expected to give 2a.$^{1-8}$ However, it is likely that A equilibrates with the more stable 18-electron intermediate B faster than it undergoes bromide addition (perhaps also aided by an interaction of the acid group with the free nitrogen of pyridazine), and that the bromide addition to B gives 2b as the kinetic product. Slower bromide dissociation from 2b then gives back the cationic intermediate B which can equilibrate with A and C to eventually give an equilibrium mixture of the three isomers 2a, 2b, and 2c.

A limitation to this synthetic procedure was found in the reaction of complex 1 with 3-bromopropionic acid, which was expected to give complex 5 by the oxidative addition but which gave mostly the complex [PtBrMe$_2$(6-dppd)], 6 (Scheme 6). The $^1$H NMR spectrum of complex 6 contained a single methylplatinum resonance at δ = 1.44 with $J_{\text{PtH}} = 80$ Hz, in the range expected for a platinum(II) complex.$^7$ A minor product, formed in about 10% yield, was characterized by methylplatinum resonances at δ = 2.03 and 2.29, with $J_{\text{PtH}} = 70$ and 71 Hz respectively, similar to values for complex 2a, suggesting that this complex could be 5. However, it could not be purified and the spectrum was not fully resolved, so the structural assignment is tentative. No intermediates were observed when the reaction was monitored by $^1$H NMR spectroscopy, but it is likely that an intermediate 5-coordinate complex D is formed which can either undergo β-elimination of acrylic acid and reductive elimination of methane to give 6 or bromide coordination to give complex 5 (Scheme 6). The structure of complex 6 was determined and is shown in Figure 1, confirming that the complex is formed selectively with the methyl group trans to pyridine.

The reaction of 2-((bromomethyl)benzyl alcohol with complex 1 occurred very largely by trans oxidative addition to give the platinum(IV) complex [PtBrMe$_2$(C$_{2}$H$_4$–2–C$_6$H$_4$–H)].
CH$_2$OH)(6-dppd), 7, in about 90% yield, as depicted in Scheme 7. Two minor products were formed, each in about 5% yield, based on the integration of their methylplatinum resonances, and are tentatively assigned as isomers of 7. The $^1$H NMR spectrum of 7 contained two methylplatinum resonances at $\delta = 1.40$ and 1.77, each with coupling constant $2J(PtH) = 70$ Hz. The Pt–CH$_2$ group gave an AB multiplet at $\delta = 2.67$ and 2.85, with $2^1J(PtH) = 87$ and 106 Hz, respectively.

The reaction of complex 1 with equimolar amounts of the isomers of (bromomethyl)phenyl boronic acids proceeded according to Scheme 8 to give the corresponding complexes [PtBrMe$_2$(CH$_2$C$_6$H$_4$B(OH)$_2$)(6-dppd)], 8, 9, and 10. The complexes were formed selectively by trans oxidative addition and were characterized by their $^1$H NMR spectra. For example, complex 8 gave methylplatinum resonances at $\delta = 1.39$ and
1.75, with coupling constants \( ^3J(\text{PtH}) = 70 \) and \( 71 \text{ Hz} \), respectively, and PtCH\(_2\) resonances at \( \delta = 2.78 \), \( ^3J(\text{PtH}) = 92 \text{ Hz} \), and 2.84, \( ^3J(\text{PtH}) = 93 \text{ Hz} \).

**Supramolecular Structural Chemistry.** The structures of several of the platinum(IV) complexes with hydrogen bonding substituents were determined to investigate trends in the supramolecular chemistry. The only complex with intramolecular hydrogen bonding was the alcohol derivative 7, whose structure is shown in Figure 2. The benzyl group is oriented above the pyridazine ring of the 6-dppd ligand, allowing a weak \( \pi \)-stacking interaction, and the alcohol group forms a hydrogen bond to the free pyridyl nitrogen atom, with distance O···N(4) 2.79(1) Å. The complex crystallizes as a solvate, including a water molecule which hydrogen-bonds to the alcohol oxygen and to the Pt–Br group of a neighboring molecule to form a supramolecular polymer.

The structure of complex 2a is shown in Figure 3. In this structure, there is typical complementary, intermolecular hydrogen bonding between carboxylic acid groups to form supramolecular dimers, with O(1)···O(2A) = (O1A)–O(2) = 2.63(1) Å. The two molecules in each dimer are related by an inversion center, so they form a racemic pair by self-discrimination.

The ortho boronic acid derivative 10 also forms a supramolecular dimer, illustrated in Figure 4. The benzyl group is trans to the bromine atom as expected, and the benzyl group is positioned directly over the pyridazine ring, probably to allow \( \pi \)-stacking. Of the two protons of the boronic acid group, that on O(1) is oriented toward O(2) of a neighbor to form an intermolecular hydrogen bond, with O(1)···O(2A) = O(1A)···O(2) = 2.74(1) Å, while that on O(2) forms a hydrogen bond to a tetrahydrofuran solvate molecule, with O(2)···O(4) = 2.64(1) Å. The two molecules of the dimer are again related by an inversion center, so they form a racemic dimer by self-discrimination. The hydrogen bond pairs in both 2a and 10 are described using a graph set notation as \( R_2^2(8) \).

Three of the complexes studied form supramolecular polymers, two (complexes 3 and 9) by forming intermolecular OH···Br bonds and one (complex 4) by forming intermolecular OH···N(py) bonds. The molecular structure of complex 4 is shown in Figure 5. It can be seen that the carboxylic acid and the nitrogen atom of the free pyridyl group are oriented away from one another. This conformation is suited to the formation of a supramolecular polymer through OH···N hydrogen bonding, as illustrated in Figure 6, with intermolecular distances O(2)···N(4A) = N(4)···O(2B) = 2.75(1) Å. All platinum centers in a polymer chain have the same chirality, and so the polymer is formed by self-recognition between units of 4. The space group is not chiral, so there are equal numbers of polymer chains with the individual platinum centers in clockwise (C) or anticlockwise (A) configurations.

The molecular structure of complex 3 (Figure 7) is similar to that of complex 4 (Figure 5), except for the orientation of the carboxylic acid group. This difference arises because complex 4 has an extra methylene spacer group. This change leads to a different supramolecular polymeric structure formed by...
intermolecular OH···BrPt hydrogen bonding in 3 (Figure 8, O1···Br(1) = 3.19(1) Å) compared to OH···N(py) hydrogen bonding in 4 (Figure 6). Individual molecules in each polymer chain lie on a 2-fold screw axis and, as for complex 3, they have the same chirality.

The molecular structure of the 3-benzylboronic acid derivative 9 is shown in Figure 9. One proton of the B(OH)₂ groups acts as a weak hydrogen bond donor to an acetone solvate molecule, with O(2)···O(3) = 3.20(2) Å. Similar bonding has been observed in the self-association of several other boronic acid derivatives. The second BOH group in complex 9 forms a weak, intermolecular hydrogen bond to the PtBr group of a neighboring molecule, with distance O(1)···Br(1) = 3.37(1) Å, and propagation of this motif gives a supramolecular polymer, as illustrated in Figure 10. As for the supramolecular polymers of 3 and 4, all platinum centers in a given polymer chain have the same chirality.

CONCLUSIONS

The dimethylplatinum(II) complex, 1, typically undergoes trans oxidative addition reactions with alkyl and benzyl bromide derivatives with hydrogen bonding substituents to

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**Figure 5.** Structure of complex 4, showing 30% probability ellipsoids. Bond distances: Pt(1)–N(1) 2.153(4), Pt(1)–N(2) 2.140(4), Pt(1)–C(21) 2.103(6), Pt(1)–C(30) 2.068(6), Pt(1)–C(31) 2.062(5), Pt(1)–Br(1) 2.5826(9) Å.

**Figure 6.** Supramolecular polymeric structure of complex 4. H-bond distance: O(2)···N(4A) = N(4)···O(2B) = 2.75(1) Å. Symmetry equivalent atoms: x, y, z; x, y, z; 1 + x, 1/2 + y, 1/2 – z; 1/2 + x, 1/2 – y, 1/2 – z.

**Figure 7.** Molecular structure of complex 3. Bond distances: Pt(1)–N(1) 2.144(6), Pt(1)–N(2) 2.127(5), Pt(1)–C(21) 2.091(6), Pt(1)–C(22) 2.050(7), Pt(1)–C(23), 2.098(7), Pt(1)–Br(1) 2.5830(8) Å.

**Figure 8.** Supramolecular polymeric structure of complex 3. H-bond distance: O(1)···Br(1B) = O(1A)···Br(1) = 3.19(1) Å. Symmetry-equivalent atoms: x, y, z; x, y, z; 1/2 – x, 1/2 + y, 1/2 – z; 1/2 + x, 1/2 – y, 1/2 – z.
yield the corresponding chiral organoplatinum(IV) complexes as racemates. The only complications arose with 3-bromopropionic acid, which contains β-hydrogen atoms and which gave mostly the platinum(II) product expected if the oxidative addition is followed by β-elimination and reductive elimination, and with bromoacetic acid, which gave products of both cis and trans oxidative addition.

The structures of six platinum(IV) complexes were determined. The aim was to study selectivity of hydrogen bonding which might occur between the hydrogen bond donor and any of three acceptor groups, namely, an oxygen atom of the hydrogen bonding group itself, the free pyridyl nitrogen atom or the bromide ligand. The hydrogen bonding might occur intramolecularly or intermolecularly, and the intramolecular hydrogen bonding might occur to give supramolecular dimers or polymers and might involve self-recognition or self-discrimination. The broad conclusion is that there is a fine balance and that all outcomes are possible. For the one monomer, complex 7, there is a good fit to bring the alcohol and free pyridine groups in close proximity to form an intramolecular hydrogen bond (Figure 2). The only other complex that has sufficient flexibility to allow a similar interaction is complex 4, but here the spacer group is too long and the intermolecular OH···N(pyridyl) hydrogen bond is formed instead to yield a supramolecular polymer (Figures 5 and 6). Two complexes 2a (Figure 3) and 10 (Figure 4) form complementary hydrogen bonds between pairs of CO₂H or B(OH)₂ groups, respectively. These therefore form supramolecular dimers, and both by self-discrimination to give racemic dimers. Two complexes 3 (Figures 7 and 8) and 9 (Figures 9 and 10) form supramolecular polymers through COH···Br or BOH···Br hydrogen bonding, and both form by self-recognition to form chiral polymer chains.

An illustrative density functional theory calculation for complex 3 gives the filled orbital energies Br, −5.1 eV, N(py) −6.8 eV, O(C=O) −7.0 eV, and Hirshfeld atomic charges Br, −0.32 e, O(C=O) −0.28 e, N(py) −0.13 e. On the basis of both orbital energy and atomic charge, hydrogen bonding to bromide might be predicted, but hydrogen bonds are strongest with small electronnegative atoms and bromide is large. The orbital energy favors nitrogen over oxygen as an acceptor, but the atomic charge favors oxygen over nitrogen. It is therefore understandable that, overall, the three potential acceptors have about equal affinity for the hydrogen bond donor. The preferred supramolecular structure depends on the orientation of the hydrogen bonding group and probably on other weak bonding forces in forming the solid state lattice.\(^5\)\(^,\)\(^10\)

### EXPERIMENTAL SECTION

**Reagents and General Procedures.** All reactions were carried out in an inert atmosphere of dry nitrogen using standard Schlenk techniques at room temperature, unless otherwise specified. All solvents used for air and moisture sensitive materials were purified using an Innovative Technology Inc. PURE SOLV solvent purification system (SPS). Complex 1 was prepared as previously reported.\(^7\) NMR spectra were recorded using Varian Mercury 400 or Varian Inova 400 or 600 spectrometers. Complete assignment of each compound was aided by the use of \(^1\)H--\(^1\)H NOESY, \(^1\)H--\(^13\)C-\(^{1}{\text{H}}\)-HSQC, and \(^1\)H--\(^1\)H gCOSY experiments as required. The standard labeling scheme for aromatic rings is used when labeling NMR resonances, with rings a and b referring to coordinated and free pyridyl groups, respectively, and ring c to other aryl rings (Chart 1). Mass spectrometric analysis was carried out using an electrospray PE-Sciex mass spectrometer (ESI-MS) coupled with a TOF detector.

**X-ray Crystallography.**\(^11\) A suitable crystal of each compound was coated in Paratone oil and mounted on a glass fiber loop. X-ray data were collected at 150 K using either a Bruker Smart APEX II diffractometer or a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo (Kα) radiation (\(\lambda = 0.71073 \text{ Å}\)). Unit cell parameters were calculated and refined from the full data set. Reflections were scaled and corrected for absorption effects. Structures were solved by

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**Figure 9.** Molecular structure of complex 9, showing 30% probability ellipsoids. Bond distances: Pt(1)−N(1) 2.167(7), Pt(1)−N(2) 2.135(6), Pt(1)−C(21) 2.055(8), Pt(1)−C(22) 2.047(9), Pt(1)−C(23) 2.045(10), Pt(1)−Br(1) 2.620(1) Å. Symmetry-related atoms: N(1) 2.135(6), Pt(1)−Br(1) 2.620(1) Å. Bond distances: O(2)−O(3) = 3.20(2), O(1)−Br(1A) = O(1B)−Br(1) = 3.37(1) Å. Symmetry-related atoms: x, y, z; x − l, y − l, z; x + l, y + l, z.

**Figure 10.** Supramolecular polymeric structure of complex 9. H-bond distances: O(2)···O(3) = 3.20(2), O(1)−Br(1A) = O(1B)−Br(1) = 3.37(1) Å. Symmetry-related atoms: x, y, z; x − l, y − l, z; x + l, y + l, z.
Chart 1. Scheme for NMR Labels

![Diagram]

either Patterson or direct methods and refined by full-matrix least-squares techniques. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined using the riding model.

The cyclooctane ring showed disorder in complexes 3 and 4, leading to apparent intramolecular H contacts. There is a water molecule of solvation for complex 6.

**[PtBrMe2(CH2CO2H)(6-dppd)], 2** To a solution of complex 1 (0.100 g, 0.0184 mmol) in acetone (2 mL) was added bromoacetic acid (0.026 g, 0.184 mmol). An immediate color change from red to yellow was observed. The solvent was evaporated under vacuum to give the product as a yellow solid, which was washed with ether and dried under vacuum. Yield: 0.011 g, 87%. NMR analysis indicated that 2 was a mixture of three isomers 2a, 2b, and 2c. The complex was treated as a 1:1:1 ratio. Partial NMR data in CD2Cl2 for complex 2: δ (1H) 2.05 (m, 8H, 4CH2 of cyclooctene ring), 7.27 (d, 1H, J(PtH) = 8 Hz, J(CH3) = 95 Hz, CH3H5), 8.15 (d, 1H, J(PtH) = 97 Hz, CHAHB), 3.24 (d, 1H, J(PtH) = 90 Hz, CHAHB), 2.81 (d, 1H, J(HH) = 9 Hz, J(PtH) = 88 Hz, CHH5), 2.90 (m, 2H, CH3 ring), 3.09 (m, 2H, CH2 ring), 3.25 (d, 2H, CHH5), 6.25 (2H, J(HH) = 8 Hz, J(PtH) = 91 Hz, H2c), 6.48 (d, 2H, J(HH) = 8 Hz, H3c), 7.54 (m, 1H, H5a), 7.62 (m, 1H, H5b), 8.05 (m, 2H, H4b/H4a), 8.09 (m, 2H, H3a/H3b), 8.78 (d, 1H, H6b), 8.96 (d, 1H, J(PtH) = 20 Hz, H6a). ESI-MS(ToF): calcd for C31H35BrN4O2PtNa+: m/z = 793.1454; found: m/z = 793.1454. Anal. Calcd for C31H35BrN4O2PtNa+: C, 47.91; H, 4.93; N, 6.85. Found: C, 47.94; H, 4.23; N, 6.95%.

**[PtBrMe2(CH2OCH2CH2CO2H)(6-dppd)], 5**, and **[PtBrMe2(CH2OCH2CO2H)(6-dppd)], 6** To a solution of complex 1 (0.010 g, 0.0184 mmol) in acetone (2 mL) was added 3-bromopropionic acid (0.011 g, 0.0184 mmol). An immediate color change from red to yellow was observed. The solvent was removed under vacuum, and the yellow solid product was washed with diethyl ether and dried under vacuum. NMR analysis indicated that there was a mixture of two complexes 5 and 6 in an approximately 1:1 ratio. Partial NMR data in CD2Cl2 for 5: δ (1H) 2.03 (3H, 3J(PtH) = 70 Hz, CH3), 2.29 (3H, 3J(PtH) = 70 Hz, CH3), 1.90−3.10 (12H, CH2 of cyclooctene ring), 7.60 (m, 1H, H5a), 7.78 (m, 1H, H5b), 8.03 (d, 1H, H3a), 8.15 (m, 1H, H4b), 8.30 (t, 1H, H4a), 8.35 (d, 1H, H3b), 9.03 (d, 1H, H6b), 9.80 (d, 1H, H6a). Crystals of complex 6 were obtained from acetone/pentane. Yield: 0.005 g, 44%. NMR in CD2Cl2 for 6: δ (1H) 1.44 (3H, 3J(PtH) = 80 Hz, CH3), 1.55 (m, 2H, CH2), 1.70 (m, 2H, CH2), 2.08 (m, 2H, CH2), 3.00 (m, 2H, CH2), 3.33 (m, 2H, CH2), 7.46 (m, 1H, H5a), 7.73 (m, 1H, H5b), 7.96 (d, 1H, H4b), 8.10 (d, 1H, H3b), 8.18 (dd, 1H, H4a), 8.23 (d, 1H, H3a), 8.74 (d, 1H, H6b), 10.00 (d, 1H, J(PtH) = 24 Hz, H6a). Anal. Calcd for C31H35BrN4O2Pt: 13627
collected, washed with pentane, and dried under vacuum. Yield: 0.011 g, 80%. NMR in CDCl3: δ(H) 1.40 (s, 3H, 3(Ph) = 70 Hz, CH3), 1.77 (s, 3H, 3(Ph) = 70 Hz, CH3), 1.20–3.10 (m, 12H, CH3 of cyclooctene ring), 2.67 (d, 1H, 3(Ph) = 87 Hz, CH3H3), 2.85 (d, 1H, 3(Ph) = 9 Hz, 3(Ph) = 106 Hz, CH3H3), 2.67 (d, 1H, 3(Ph) = 15 Hz, CH3H3), 4.48 (d, 1H, 3(Ph) = 15 Hz, CH3H3), 5.86 (d, 1H, 3(Ph) = 7 Hz, 3(Ph) = 18 Hz, H6c), 6.39 (t, 1H, 3(Ph) = 7 Hz, H5c), 6.78 (t, 1H, 3(Ph) = 7 Hz, H4c), 6.96 (d, 1H, 3(Ph) = 7 Hz, H3c), 7.56 (m, 1H, H5a), 7.59 (d, 1H, H3b), 7.76 (m, 1H, H5b), 7.95 (dd, 1H, H4b), 7.99 (dd, 1H, H3a), 8.13 (dd, 1H, H4a), 8.80 (d, 1H, H6b), 9.21 (d, 1H, 3(Ph) = 17 Hz, H6a). Anal. Calcd for C30H35BrN4OPt: C, 46.25; H, 4.56; N, 6.87%.

**ASSOCIATED CONTENT**

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01860.

CCDC 1851107–1851113 contain the supplementary crystallographic data for this paper (CIF)

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We thank the NSERC (Canada) for financial support.

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ACS Omega 2018, 3, 13621–13629
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