# **ORGANOMETALLICS**

# Organoplatinum Chemistry with a Dicarboxamide–Diphosphine Ligand: Hydrogen Bonding, Cyclometalation, and a Complex with Two Metal–Metal Donor–Acceptor Bonds

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**Supporting Information** 

**ABSTRACT:** The chemistry of the ligand bis(2-diphenylphosphinoethyl)phthalamide, dpppa, with platinum(II) is described. The reaction of dpppa with  $[Pt_2Me_4(\mu-SMe_2)_2]$ , 1, in a 2:1 ratio gave a mixture of  $[PtMe_2(dpppa)]$  and  $[Pt_2Me_4(\mu-dpppa)_2]$ , both of which contain  $Pt\cdots H-N$  hydrogen bonds. However, reaction in a 1:1 ratio gave a remarkable tetraplatinum complex,  $[Pt_4Me_6(\mu-dpppa-H)_2]$ , which is shown to contain two Pt-Pt donor-acceptor bonds and in which one arm of the dpppa ligand has been cyclometalated. The reaction of  $[PtCl_2(dpppa)]$  with silver trifluoroacetate, to abstract chloride, and triethylamine as base has given



the bis(cyclometalated) complex [Pt(dpppa-2H)], and this has been crystallized in three different forms, in which one or both of the carbonyl groups act as donors to a proton or to silver(I). The complex [Pt(dpppa-2H)]·AgO<sub>2</sub>CCF<sub>3</sub>·dmso forms a dimer and [Pt(dpppa-2H)]·(AgO<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> forms a coordination polymer in the solid state.

## ■ INTRODUCTION

Ligands that contain both a phosphine and an amine or carboxamide group are proving to be useful in catalysis or molecular materials for sensing and other applications.<sup>1</sup> The phosphine groups are typically used to bind to transition metal ions, while the carboxamide groups engage in hydrogen bonding, with the role of recognizing substrates for catalysis or sensing or to increase dimensionality in molecular materials.<sup>1,2</sup> Some typical examples are shown in Chart 1. The simplest ligands contain one phosphine and one carboxamide, as in dpb and bdp.<sup>3</sup> However, more complex examples, such as dpfca (Chart 1), which contains two phosphines and one carboxamide group, have also been used.<sup>1,3</sup> Diphosphine dicarboxamide ligands, such as dppbH,<sup>4</sup> have been studied, and chiral analogues, such as the Trost and Morimoto ligands (Chart 1), have proved to be particularly useful in catalysis.<sup>5</sup> The application of the related para-, meta-, and ortho-substituted dicarboxamide ligands dppeta, dpipa, and dpppa (Chart 1) in the synthesis of coordination and supramolecular polymers has also been reported.<sup>6</sup> All of these diphosphine dicarboxamide ligands can act as cis or trans chelating ligands or as bridging diphosphine ligands, while the carbonyl group can also coordinate, and the NH groups can act as hydrogen bond donors or can be deprotonated to give amido complexes.<sup>1-6</sup>

The versatility of the ligands dpipa and dppeta (Chart 1) in organometallic chemistry has been established earlier.<sup>6</sup> For example, some chemistry of dpipa with the dimethylplatinum-(II) complex  $[Pt_2Me_4(\mu-SMe_2)_2]$ , 1, is illustrated in Scheme 1. The reaction with stoichiometry dpipa:  $\mathbf{1} = 2:1$  gave an equilibrium mixture of monomeric and dimeric dimethylplatinum(II) complexes A and B, each of which contained an unusual NH··Pt hydrogen bond. Heating this

#### Chart 1. Examples of Phosphine-Carboxamide Ligands



mixture caused loss of methane with formation of the PNCpincer complex C, in which each ligand is doubly cyclometalated by activation of an N-H bond and an aromatic C-H

Received: August 2, 2013 Published: September 13, 2013 Scheme 1. Some Organometallic Chemistry of the Ligand dpipa $^a$ 



<sup>a</sup>Stoichiometry dpipa:1 is 2:1 to form A, B, C and 1:1 to form D, E.

bond. On the other hand, the reaction with stoichiometry dpipa:  $\mathbf{1} = 1:1$  in dmso solution gave an intermediate, tentatively identified as D, which eliminated methane on heating to give the bis-PNC-pincer complex E, in which each dpipa ligand has been quadruply cyclometalated by activation of both N–H bonds and two aromatic C–H bonds.<sup>6</sup>

This paper reports a study of related organoplatinum chemistry of the ligand dpppa (Chart 1). Its dimethylplatinum-(II) complexes feature similar NH···Pt hydrogen bonding to that in complexes A and B (Scheme 1), but the cyclometalation chemistry involves only the N–H bonds, and an unexpected complex containing two platinum–platinum donor–acceptor bonds was formed.

#### RESULTS AND DISCUSSION

The reaction of dpppa with *cis/trans*-[PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>], **2a**, in 1:1 ratio gave the complex [PtCl<sub>2</sub>(dpppa)], **3**, according to Scheme 2. In the <sup>31</sup>P NMR spectrum, complex **3** gave a singlet resonance at  $\delta$ (<sup>31</sup>P) = 1.69, with <sup>1</sup>J(PtP) = 3630 Hz in the range expected for a complex with phosphorus *trans* to chloride.<sup>4,7</sup> In the <sup>1</sup>H NMR spectrum, the NH resonance was at  $\delta$  = 7.94, significantly shifted from the value for free dpppa of



6.89, consistent with a hydrogen-bonded structure.<sup>2-4,6,8</sup> The ESI-MS of complex 3 dissolved in dichloromethane gave a major peak at m/z = 818.1, which corresponds to the ion [PtCl(dpppa)]<sup>+</sup>, formed by loss of chloride from complex 3.

The structure of complex 3 is shown in Figure 1. It confirms the cis chelate structure in which each phosphine is *trans* to



Figure 1. View of the structure of complex 3, with 30% probability ellipsoids. Selected bond parameters (Å and deg): Pt(1)-Cl(1) 2.3623(9), Pt(1)-Cl(2) 2.362(1), Pt(1)-P(2) 2.258(1), Pt(1)-P(1) 2.2534(9); Cl(1)-Pt(1)-Cl(2) 86.35(3), Cl(1)-Pt(1)-P(2) 88.20(3), P(2)-Pt(1)-P(1) 97.82(3), P(1)-Pt(1)-Cl(2) 87.59(3). Hydrogen bond distances:  $Cl(1)\cdots N(2)$  3.157(3),  $Cl(2)\cdots N(1)$  3.358(3) Å. The estimated hydrogen bond angles are N(1)H(1)Cl(2) 148° and N(2)H(2)Cl(1) 128°.

chloride. The P–Pt–P angle of P(2)–Pt(1)–P(1) 97.82(3)° is not greatly distorted from the ideal 90°, considering the large 13-membered ring resulting from chelation. The conformation of the ligand is such that the NH groups are directed toward the chloride ligands, with distances  $Cl(1)\cdots N(2)$  3.157(3) Å and  $Cl(2)\cdots N(1)$  3.358(3) Å. These distances are clearly different, but both are in the accepted range of 3.1–3.4 Å for NH…Cl hydrogen bonds.<sup>9</sup>

The reaction of dpppa with  $[Pt_2Me_4(\mu-SMe_2)_2]$  in a 2:1 ratio gave a mixture of products, from which the monomeric and dimeric dimethylplatinum(II) complexes **4a** and **4b** were crystallized and structurally characterized (Scheme 3, Figures 2 and 3). Both complexes have *cis*-PtMe\_2P<sub>2</sub> coordination, but the monomer **4a** has chelating dpppa (Figure 2) and the dimer **4b** has bridging dpppa ligands (Figure 3). The two halves of the Scheme 3. Reaction of dpppa with  $[Pt_2Me_4(\mu-SMe_2)_2]$  in 2:1 Ratio





Figure 2. View of the structure of complex 4a, with 30% probability ellipsoids. Selected bond parameters (Å and deg): Pt(1)-C(1) 2.106(4), Pt(1)-C(2) 2.110(3), Pt(1)-P(2) 2.300(1), Pt(1)-P(1) 2.306(1),  $Pt(1)\cdots N(1)$  3.599(3),  $Pt(1)\cdots N(2)$  3.463(3); P(1)-Pt(1)-P(2) 98.31(3), C(1)-Pt(1)-C(2) 82.4(1), P(1)-Pt(1)-C(1) 90.6(1), P(2)-Pt(1)-C(2) 88.75(9)°.

dimer 4b are related by a center of inversion. Both complexes 4a and 4b have one NH…Pt hydrogen bond for each dimethylplatinum(II) unit, and the ligand must twist to allow the short NH---Pt contact (compare Figures 2 and 3). In complex 4a (Figure 2) the two Pt...N distances are similar [Pt(1)...N(1) 3.599(3), Pt(1)...N(2) 3.463(3) Å], but the estimated Pt…H distances are not [Pt(1)…H(1) 3.57, Pt(1)… H(2) 2.65 Å] since only H(2) is oriented toward the platinum center. In complex 4b (Figure 3), the NH…Pt bond appears somewhat stronger, with  $Pt(1) \cdots N(1)$  3.258(4) Å and estimated  $Pt(1)\cdots H(1)$  2.47 Å. In complex 4a, the only hydrogen bond is the NH···Pt bond, but, in complex 4b, there are also two intramolecular NH…O=C hydrogen bonds, with O(1)...N(2) and O(1A)...N(2A) 2.772(4) Å, and also a weaker hydrogen bond to a chloroform solvate molecule with O(1)... C(1S) 3.12 Å. The NH…Pt hydrogen bonding in the dpppa complexes 4a and 4b is directly comparable to that in the related dpipa complexes A and B (Scheme 1).

The <sup>31</sup>P NMR spectrum for the initial mixture of products of reaction of dpppa with  $[Pt_2Me_4(\mu-SMe_2)_2]$  in 2:1 ratio is shown in Figure 4a and was initially difficult to interpret. However, recrystallization gave two batches of crystals, one containing only 4a (Figure 4b) and one containing crystals of



**Figure 3.** View of the structure of complex **4b**, with 30% probability ellipsoids. Selected bond parameters (Å and deg): Pt(1)-P(1) 2.310(1), Pt(1)-P(2) 2.297(1), Pt(1)-C(2) 2.083(6), C(1)-Pt(1) 2.109(4),  $Pt(1)\cdots N(1)$  3.258(4),  $Pt(1)\cdots N(2)$  5.329(3); P(2)-Pt(1)-C(2) 90.1(1), P(2)-Pt(1)-P(1) 99.56(4), P(1)-Pt(1)-C(1) 89.0(1), C(1)-Pt(1)-C(2) 81.2(2). Symmetry equivalent: 1-x, -y, -z.



Figure 4. <sup>31</sup>P NMR spectra (162 MHz, CDCl<sub>3</sub> solution, 298 K) of (a) the initial mixture obtained in the reaction of Scheme 3; (b) the crystals of 4a; (c) the crystal mixture of 4a and 4b.

both 4a and 4b (Figure 4c). Thus 4a gives a sharp singlet resonance at  $\delta({}^{31}\text{P}) = 7.08$ ,  ${}^{1}J(\text{PtP}) = 1814$  Hz, while 4b gives a broad singlet resonance at  $\delta({}^{31}\text{P}) = 10.28$ ,  ${}^{1}J(\text{PtP}) = 1760$  Hz. The isomers interconvert only slowly at room temperature. The low values of  ${}^{1}J(\text{PtP})$  are characteristic of platinum(II) complexes with the phosphine *trans* to a methyl group.<sup>7</sup> In the initial  ${}^{31}\text{P}$  NMR spectrum (Figure 4a), the resonances for 4a and 4b are observed, but two additional singlet resonances are also present, labeled  $F[\delta({}^{31}\text{P}) = 11.18$ ,  ${}^{1}J(\text{PtP}) = 1790$  Hz] and  $G[\delta({}^{31}\text{P}) = 11.80$ ,  ${}^{1}J(\text{PtP}) = 1800$  Hz], for which the coupling constants also indicate phosphine *trans* to methyl, but these peaks could not be assigned and the compounds could

not be obtained in pure form. The ESI-MS of the initial reaction mixture dissolved in dichloromethane gave two major peaks at m/z = 798.2, which corresponds to the ion [PtMe(dpppa)]<sup>+</sup>, and at m/z = 1649.4, which corresponds to the ion [Pt<sub>2</sub>Me<sub>4</sub>(dpppa)<sub>2</sub>]Na<sup>+</sup>. These peaks are consistent with the presence of a mixture of **4a** and **4b**, but they give no insight into the structures of *F* and *G*.

In order to observe a single <sup>31</sup>P NMR resonance, each complex **4a** and **4b** must undergo dynamic exchange of the hydrogen bond between the N(1)H and N(2)H donors. At -80 °C, the monomer (**4a**) still showed a single resonance in the <sup>31</sup>P NMR spectrum, but the dimer (**4b**) gave two broad resonances  $[\delta(^{31}P) = 14.6, ^{1}J(PtP) \approx 1920$  Hz and 3.9,  $^{1}J(PtP) \approx 1670$  Hz], with a coalescence temperature of about -60 °C, giving, from the Eyring equation, an approximate activation energy of 9 kcal mol<sup>-1</sup>. The fluxionality for **4b** involves breaking both NH···Pt and both NH··O=C hydrogen bonds and then twisting the ligands to form the symmetry-equivalent hydrogen bonds, whereas for **4a** it only involves twisting of the ligand to replace one NH···Pt hydrogen bond by another. It is not surprising therefore that fluxionality is more difficult for **4b**.

The reaction of dpppa with  $[Pt_2Me_4(\mu-SMe_2)_2]$ , 1, in 1:1 ratio again gave a mixture of products, including 4a and 4b, but the <sup>31</sup>P NMR spectrum indicated the formation of a new complex, 5, which gave two resonances at  $\delta(^{31}P) = 23.63$ , <sup>1</sup>J(PtP) = 3230 Hz, <sup>2</sup>J(PtP) = 1380 Hz, <sup>3</sup>J(PP) = 8 Hz, and  $\delta(^{31}P) = 2.87$ , <sup>1</sup>J(PtP) = 926 Hz, <sup>3</sup>J(PP) = 8 Hz, and  $\delta(^{31}P) = 2.87$ , <sup>1</sup>J(PtP) = 926 Hz, <sup>3</sup>J(PP) = 8 Hz. Recrystallization gave a mixture of colorless crystals of 4a and yellow crystals of 5. The ESI-MS of the isolated crystals of complex 5 dissolved in dichloromethane, with NaI added, gave a major peak at m/z = 2067.4, which corresponds to the ion  $[Pt_4Me_6(dpppa-H)_2]Na^+$ . Complex 5 was finally characterized to be  $[\{Me_2Pt(\mu_3-\kappa^4-P,O,N,P-Ph_2PCH_2CH_2NHCOC_6H_4CON-CH_2CH_2PPh_2)PtMe\}_2]$  by a structure determination. The formation of 5 is depicted in Scheme 4. It involves activation





of one N-H bond of each dpppa ligand and one methylplatinum bond of 1, with elimination of methane, and displacement of the dimethylsulfide ligands from 1.

The remarkable structure of complex 5, which crystallized as a chloroform solvate, is shown in Figure 5. There are four platinum atoms in the molecule, two having square pyramidal  $PtMe_2POPt$  coordination and two having square planar PtMePNPt coordination. Each Pt-Pt bonded unit can be considered as a "T-over-square" complex containing a donor-



Figure 5. Structure of complex 5, with 30% probability ellipsoids. The phenyl groups are not shown, for clarity. Selected bond parameters (Å and deg): Pt(1)-Pt(2) 2.6491(7), Pt(1)-P(1) 2.164(3), Pt(1)-N(1) 2.098(8), Pt(1)-C(1) 2.06(1), Pt(2)-P(3) 2.327(3), Pt(2)-O(1) 2.149(7), Pt(2)-C(2) 2.03(1), Pt(2)-C(3) 2.07(1), Pt(3)-Pt(4) 2.6495(9), Pt(3)-P(4) 2.159(3), Pt(3)-N(4) 2.105(9), Pt(3)-P(4) 2.325(3), Pt(4)-O(4) 2.150(7), Pt(4)-C(5) 2.03(1), Pt(4)-C(6) 2.08(1), N(1)-C(9) 1.30(1), O(1)-C(9) 1.31(1), N(2)-C(16) 1.34(1), O(2)-C(16) 1.24(1), N(3)-C(45) 1.34(1), O(3)-C(45) 1.24(1), N(4)-C(52) 1.28(4), O(4)-C(52) 1.30(1),  $N(2)\cdotsO(4) 2.77$ ,  $N(3)\cdotsO(1) 2.76$ ; P(1)-Pt(1)-Pt(2) 168.08(8), P(4)-Pt(3)-Pt(4) 168.00(8).

acceptor metal—metal bond, with the dimethylplatinum center as donor and the monomethylplatinum center as acceptor.<sup>11</sup> Each platinum(II) center then has the favored 16-electron configuration. Some related examples (H, I, J) are shown in Chart 2, but the formation of the donor—acceptor bond during cyclometalation and the presence of two donor—acceptor bonds in the same molecule appear to be unprecedented.<sup>11</sup>

Chart 2. Compounds H, I, and J with Donor-Acceptor Bonds, and a Diplatinum(III) Complex K (ON = amidate)



While the coordination of the amide nitrogen in 5 was not unexpected,<sup>4,6</sup> the coordination of the carbonyl group to the soft platinum center was a surprise. Each Pt-Pt donoracceptor bond is supported by the bridging amidate N-C=O unit. Bridging amidates are well known in inorganic complexes, including diplatinum(III) complexes (complex K, Chart 2) and related platinum blues, but they are uncommon in organoplatinum chemistry.<sup>12</sup> In the bridging amidate groups, the NC bonds [N(1)-C(9) 1.30(1), N(4)-C(52) 1.28(1) Å] are on average slightly shorter than the CO bonds [O(1)-C(9)]1.31(1), O(4)–C(52) 1.30(1) Å], whereas in the amide groups the CO bonds are shorter [N(2)-C(16) 1.34(1), O(2)-C(16)]1.25(1), N(3)-C(45) 1.28(1), O(3)-C(45) 1.24(1) Å], indicating that both resonance forms shown in Scheme 4 are significant. The Pt–Pt distances [Pt(1)-Pt(2) 2.6491(7)], Pt(3)-Pt(4) 2.6495(9) Å] are comparable to those in related complexes [2.769(1) Å in *H*; 2.6491(4) Å in *I*, Chart 2].<sup>11</sup> The distance Pt(1)-P(1) 2.164(3) Å is short, and comparison with distances in 3, 4a, and 4b indicates that the trans-influence series is Me<sup>-</sup> (4a, 4b) > Cl<sup>-</sup> (3), NR<sub>2</sub><sup>-</sup> (7, 8, 9, see below) > PtMe<sub>2</sub>PO (5), and thus that the platinum donor has a particularly low trans-influence. This is consistent with the large value of the coupling constant  ${}^{1}J(PtP) = 3230$  Hz for the P(1) atom in 5.7 The two remaining NH groups in 5 are hydrogen bonded to carbonyl groups  $[N(2)\cdots O(4) 2.77, N(3)\cdots O(1)]$ 2.76 Å], and the other two carbonyl groups are weakly hydrogen bonded to chloroform solvate molecules [O(2)... C(1X) 3.17, O(3)…C(1Y) 3.13 Å]. The NH…O=C hydrogen bonds are intramolecular but interligand, in contrast to 4b, in which intraligand hydrogen bonding is observed (Figure 3).

The formation of complex 5 (Scheme 4) involves elimination of methane, by combination of N-H and Pt-Me groups. In principle, elimination of methane from 4a, 4b, or 5 could give further amidoplatinum(II) complexes. However, heating complex 4a/4b to 140 °C in dmso gave only partial reaction, and no pure products could be obtained. Greater success was achieved by reaction of [PtCl<sub>2</sub>(dpppa)], 3, with silver trifluoroacetate and triethylamine, as shown in Scheme 5. The reaction gives derivatives of the complex  $[Pt{\kappa^4-PNNP C_6H_4$ -1,2-(CONCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>], 6. However, although 6 has been isolated in pure form after addition of LiCl to remove silver ions, it has not been possible to crystallize 6 in its simple form. The complex binds to silver, and the adducts 7 = 6.  $AgO_2CCF_3$ ·dmso·0.5C<sub>6</sub>H<sub>6</sub>, when dmso was present in the recrystallization solvent mixture, or  $8 = 6 \cdot (AgO_2CCF_3)_2$ , when no dmso was present, were formed instead (Scheme 5). When the reaction was carried out as in Scheme 5, but with lithium chloride added to precipitate the remaining silver compounds as AgCl, crystals of the adduct  $9 = 6_2 \cdot \text{Et}_3 \text{NOH}^+ \text{CF}_3 \text{CO}_2^- \cdot \text{H}_2 \text{O} \cdot$ CHCl<sub>3</sub> (Figure 6) could be obtained. It seems that the carbonyl groups in complex 6 are basic and tend either to bind to  $Ag^+$  in 7 and 8 or to engage in hydrogen bonding in 9. The Et<sub>3</sub>NOH<sup>+</sup> ion in 9 is identified crystallographically and is presumed to be formed by oxidation of triethylamine during recrystallization in the presence of  $Et_3NH^+CF_3CO_2^-$ . Single crystals of the pure complex 6 could not be obtained, but it and its derivatives 7, 8, and 9 have very similar NMR spectra. For example, the <sup>31</sup>P NMR spectra for 9 and 8 in CDCl<sub>3</sub> solution gave  $\delta(^{31}P) =$ 31.27,  ${}^{1}J(PtP) = 3100$  Hz, and  $\delta({}^{31}P) = 30.80$ ,  ${}^{1}J(PtP) = 3110$ Hz, respectively, while complex 7 in dmso- $d_6$  gave  $\delta(^{31}P) =$ 31.04,  ${}^{1}J(PtP) = 3090$  Hz. In the ESI-MS, complexes 7, 8, and 9 all gave a major peak at m/z = 782.2, which corresponds to 6+H<sup>+</sup>, complexes 7 and 8 gave a peak at m/z = 1783.2, which

Scheme 5. Synthesis of Complex 6 and Its Silver(I) Adducts



corresponds to  $\mathbf{6}_2$ +AgO<sub>2</sub>CCF<sub>3</sub>+H<sup>+</sup>, and complex 7 gave a peak at m/z = 2003.1, which corresponds to  $\mathbf{6}_2$ +(AgO<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>+H<sup>+</sup>.

In the adduct 9, Figure 6, there is a molecule of 6 (Figure 6a) and a molecule of  $[6 \cdot \text{Et}_3 \text{NOH}]^+$  (Figure 6b), in which the Pt(1) molecule of 6 is strongly hydrogen bonded to the Et<sub>3</sub>NOH<sup>+</sup> cation  $[O(1A) \cdots O(1XA) 2.603(8) \text{ Å}]$ . The structure confirms that the complex has the diamido-diphosphine-platinum(II) coordination observed previously in related compounds.<sup>4</sup> The structure contains two five-membered rings and one seven-membered ring in the boat conformation, and this structure is also observed in the silver(I) adducts 7 and 8.

The structure of complex 7 is shown in Figure 7. It can be considered to contain a  $Ag_2(\mu$ -dmso)<sub>2</sub> core,<sup>13</sup> with each silver ion coordinated by a trifluoroacetate ion on one side and by a carbonyl group from a molecule of complex **6** on the other.

In the structure of complex **8**, there are two crystallographically independent molecules of **6**, each of which is coordinated first to an  $Ag_2(O_2CCF_3)_2$  unit using both carbonyl groups as ligands (Figure 8). In the Pt(1) molecule, which is also depicted in Scheme 5, one trifluoroacetate ligand bridges between silver(I) ions, with Ag(1)-O(5A) 2.247(4) and Ag(2)-O(6A) 2.227(3) Å, while the other bridges and also chelates to Ag(2), with Ag(1)-O(3A) 2.405(4), Ag(2)-O(3A) 2.572(5), and Ag(2)-O(4A) 2.536(4) Å. In the Pt(2) molecule, one trifluoroacetate bridges between silver(I) ions, with Ag(3)-O(5B) 2.434(5) and Ag(4)-O(6B) 2.392(5) Å, while the other bridges through a single oxygen donor, with Ag(3)-O(3B) 2.333(5) and Ag(4)-O(3B) 2.308(4) Å.

The building blocks of  $[6 \cdot (AgO_2CCF_3)_2]$ , which are illustrated in Figure 8, undergo self-association to give coordination polymers, as shown for the Pt(1) molecules in Figure 9. Each carbonyl oxygen donor bridges between



Figure 6. Views of the two platinum compounds in 9: (a) the Pt(2) molecule of 6 and (b) the Pt(1) molecule of  $[6 \cdot Et_3NOH]^+$ , with 30% probability ellipsoids. Selected bond parameters (Å and deg): Pt(1)–P(1A) 2.235(1), Pt(1)–P(2A) 2.236(1), Pt(1)–N(2A) 2.071(3), Pt(1)–N(1A) 2.049(3), N(1X)–O(1X) 1.414(7); N(1A)–Pt(1)–N(2A) 92.6(1), N(1A)–Pt(1)–P(1A) 79.72(9), P(2A)–Pt(1)–N(2A) 83.91(9), P(2A)–Pt(1)–P(1A) 103.14(4). For the Pt(2) molecule, which has no strong H-bonds: Pt(2)–P(1B) 2.242(1), Pt(2)–P(2B) 2.241(1), Pt(2)–N(1B) 2.048(3), Pt(2)–N(2B) 2.051(3); N(1B)–Pt(2)–N(2B) 93.3(1), N(1B)–Pt(2)–P(1B) 79.91(9), P(1B)–Pt(2)–P(2B) 102.84(4), N(2B)–Pt(2)–P(2B) 83.2(1).

equivalent silver(I) ions to give four-membered  $Ag_2(\mu-6)_2$ rings, with Ag(1)-O(1A) 2.410(4) and Ag(1A)-O(1A)2.429(4) Å on one side and Ag(2)-O(2A) 2.310(3) and Ag(2B)-O(2A) 2.472(4) Å on the other side. There is a center of symmetry at the middle of each four-membered ring. Repetition of this self-assembly gives rise to the polymer, and the Pt(2) molecules undergo the same type of self-assembly to give a very similar polymer. Overall, in the Pt(1) polymer, the Ag(1) centers are four-coordinate [Ag(1)O(1A)O(1AA)O-(3A)O(5A)] and the Ag(2) centers are five-coordinate [Ag(2)O(2A)O(2AB)O(3A)O(4A)O(6A)], while in the Pt(2) polymer, both silver ions are four-coordinate [Ag(3)O-(1B)O(1BA)O(3B)O(5B) and Ag(4)O(2B)O(2BB)O(3B)O-(6B)].

The analogous diamido-diphosphine complex of platinum-(II), L, Chart 3, appears to be much less basic than 6. Thus complex L forms spontaneously by reaction of  $[PtCl_2(1,5-$ 



Figure 7. View of the structure of complex 7, with 30% probability ellipsoids. Phenyl groups attached to phosphorus atoms are omitted for clarity. Selected bond parameters (Å and deg): Pt(1)-P(1) 2.2483(9), Pt(1)-P(2) 2.2340(9), Pt(1)-N(1) 2.044(2), Pt(1)-N(2) 2.059(2), Ag(1)-O(3) 2.314(3), Ag(1)-O(2) 2.212(2), Ag(1)-O(5) 2.573(5), Ag(1)-O(5A) 2.342(4) Å; P(1)-Pt(1)-P(2) 102.45(2), P(1)-Pt(1)-N(1) 83.88(6), N(1)-Pt(1)-N(2) 92.99(8), N(2)-Pt(1)-P(2) 79.91(6), O(2)-Ag(1)-O(3) 120.1(1), O(5)-Ag(1)-O(3) 104.5(1), O(5)-Ag(1)-O(3) 94.7(1), O(5)-Ag(1)-O(2) 96.7(1), Ag(1)-O(5)-Ag(1) 98.0(1), O(5)-Ag(1)-O(5) 82.0(1)°.

cyclooctadiene)] with dppbH (Chart 1), without the need for added base, and it is not easily protonated.<sup>4</sup> Complex 6 contains two five-membered and one seven-membered chelate ring, while L contains one five-membered and two sixmembered rings. Both 6 and L contain essentially planar nitrogen atoms, and more extensive delocalization of the  $p_{\pi}$ lone pair is possible in L, which has extra phenylene groups compared to  $6.^4$  Structural data suggest that hydrogen bonding or coordination of 6 to  $E^+$  (Chart 3, E = H or Ag) gives resonance forms M and N, with significant contribution from the imine form N. Thus in the Pt(1) molecule of 9 (E =  $Et_3NOH^+$ , Figure 6), the distance N(1A)–C(3A) = 1.312(6) Å is shorter than N(2A)-C(10A) = 1.347(6) Å and O(1A)-C(3A) = 1.262(6) Å is longer than O(2A) - C(10A) = 1.242(5)Å, and in complex 7 (E = Ag<sup>+</sup>, Figure 7), N(2)-C(10) =1.321(3) Å is shorter than N(1)-C(3) = 1.337(3) Å and O(2)-C(10) = 1.267(3) Å is longer than O(1)-C(3) =1.245(3) Å.

A feature of the chemistry of the dimethylplatinum complexes is that the electron-rich platinum(II) center tends to act as a nucleophile in forming hydrogen bonds in complexes 4a and 4b or in forming donor-acceptor metal-metal bonds in complex 5. Some DFT calculations were carried out, using the Becke-Perdew (BP) functional, with scalar relativistic correction, to gain some insight into these unusual bonds. The Pt…HN hydrogen bonds in 4a and 4b were modeled by using *cis*-[PtMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] as the platinum center and Nmethylformamide as the amide. The calculation predicts that, in the model adduct (Figure 10c),  $Pt \cdots H = 2.39$  Å and  $Pt \cdots N =$ 3.43 Å, which are similar to the distances Pt - H = 2.65, 2.47 Å and Pt…N = 3.46, 3.26 Å in 4a and 4b, respectively. The bonding energy is calculated to be 8 kcal mol<sup>-1</sup> in the model complex, in the usual range for a hydrogen bond.  $^{\rm 8}$  The key frontier orbitals are the filled  $5d_{z^2}$  orbital of platinum (Figure 10e) as nucleophile and the  $\sigma^*(NH)$  orbital of the amide (Figure 10d) as electrophile. The calculated HOMO of the



Figure 8. Views of the structure of complex 8, with 30% probability ellipsoids. Above, the Pt(1) molecule and, below, the Pt(2) molecule. Selected bond distances (Å): Pt(1)–P(1A) 2.244(2), Pt(1)–P(2A) 2.249(1), Pt(1)–N(1A) 2.071(4), Pt(1)–N(2A) 2.055(5), Ag(1)–O(3A) 2.405(4), Ag(1)–O(5A) 2.247(4), Ag(1)–O(1A) 2.410(4), Ag(1)–O(1AA) 2.429(4), Ag(2)–O(4A) 2.536(4), Ag(2)–O(3A) 2.572(5), Ag(2)–O(2A) 2.310(3), Ag(2)–O(2AB) 2.472(4), Ag(2)–O(6A) 2.227(3); Pt(2)–P(1B) 2.249(2), Pt(2)–P(2B) 2.250(1), Pt(2)–N(1B) 2.058(3), Pt(2)–N(2B) 2.057(5), Ag(3)–O(3B) 2.333(5), Ag(3)–O(5B) 2.434(5), Ag(3)–O(1B) 2.432(4), Ag(3)–O(1BA) 2.381(4), Ag(4)–O(6B) 2.392(5), Ag(4)–O(3B) 2.308(4), Ag(4)–O(2B) 2.450(3), Ag(4)–O(2BB) 2.302(5).



Figure 9. Part of the polymeric structure of complex 8, showing the Pt(1) molecules only. The Pt(2) molecules form a very similar polymer.







**Figure 10.** Calculated structures and some frontier orbitals for (a, d) structure and  $\sigma^*(NH)$  orbital of HCONHMe; (b, e) structure and HOMO of *cis*-[PtMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>]; (c, f) structure and HOMO of the H-bonded complex.

adduct (Figure 10f) and electron transfer of 0.05e from platinum donor to amide acceptor are consistent with the formulation of the Pt…HN interaction as a hydrogen bond, but not as an agostic interaction, and this is supported by the calculated linear Pt…H–N geometry (Figure 10c).<sup>10</sup>

The formation of one of the PtPt donor-acceptor bonds in complex 5 has been modeled in terms of the combination of fragments  $PtMe(Me_2PCH_2CH_2NCOMe)$ , O, and  $PtMe_2(PMe_3)$ , P, to give the amidate-bridged PtPt bond in model complex Q, in which each fragment acts as both donor

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and acceptor in forming the Pt–Pt and Pt–O bonds (Scheme 6).

Scheme 6. Model for Formation of One of the PtPt Donor-Acceptor Bonds in Complex 5



Some of the frontier orbitals involved are shown in Figure 11. while an orbital correlation energy diagram is shown in Figure 12. The HOMO in both O and Q has the character of N and O  $p_{\pi}$  and platinum  $d_{\pi}$  orbitals and is primarily nonbonding in both (Figures 11a,b 12). The HOMO in **P** is the platinum  $5d_{z^2}$ orbital (Figure 11d), which interacts with the LUMO of the 14electron fragment O, which is a 5d6s6p hybrid orbital (Figure 11c), to form the PtPt donor-acceptor bond, with associated bonding and antibonding MOs (Figure 11e,f). The complementary Pt-O bond is formed by donation from the HOMO-1 orbital of O (Figure 11g) to the LUMO of P, which is a 5d6s6p hybrid orbital (Figure 11h), with the resulting bonding MO illustrated in Figure 11i. There are also interactions between filled  $d_{\pi}$  orbitals of the two fragments, but these are mostly nonbonding overall (Figure 12). The overall bonding energy, which is the sum of the Pt-Pt and Pt-O bonding energies, is calculated to be 64 kcal mol<sup>-1</sup>. The yellow color of complex 5 arises from the transition from the HOMO (Figure 11b) to the low-lying Pt–Pt  $\sigma^*$  molecular orbital (Figures 11f and 12).

#### CONCLUSIONS

The chemistry described illustrates the nucleophilic character of the platinum(II) center in dimethylplatinum(II) complexes by formation of hydrogen bonds in the complexes [PtMe<sub>2</sub>(dpppa)], **4a**, and [Pt<sub>2</sub>Me<sub>4</sub>( $\mu$ -dpppa)<sub>2</sub>], **4b**, and Pt-Pt donor-acceptor bonds in [Pt<sub>4</sub>Me<sub>6</sub>( $\mu$ -dpppa-H)<sub>2</sub>], **5**. The isolation of complex **5** also illustrates how the cyclometalation of dpppa occurs in a stepwise manner, though the doubly cyclometalated complex [Pt(dpppa-2H)] can be isolated only from the chloride precursor [PtCl<sub>2</sub>(dpppa)]. [Pt(dpppa-2H)] is also electron rich and forms interesting complexes with silver(I) through coordination of one or both of the carbonyl groups.

### EXPERIMENTAL SECTION

**Reagents and General Procedures.** All reactions were carried out in an inert atmosphere of dry nitrogen using standard Schlenk techniques, unless otherwise specified. All solvents used for air- and moisture-sensitive materials were purified using an Innovative Technology Inc. PURE SOLV solvent purification system. NMR spectra were recorded at ambient temperature, unless otherwise noted (ca. 25 °C), by using Varian Mercury 400 or Varian Inova 400 or 600 spectrometers. <sup>1</sup>H chemical shifts are reported relative to TMS, and <sup>31</sup>P chemical shifts relative to 85% H<sub>3</sub>PO<sub>4</sub>. Mass spectrometric analysis was carried out using an electrospray PE-Sciex mass spectrometer (ESI-MS) coupled with a TOF detector. Analyses were performed at Laboratoire d'Analyse Élémentaire, Montreal. The ligand dpppa and complexes [PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>] and [Pt<sub>2</sub>Me<sub>4</sub>( $\mu$ -SMe<sub>2</sub>)<sub>2</sub>] were prepared as described previously.<sup>6,14</sup> DFT calculations were carried out by using the Amsterdam Density Functional program based on the BLYP functional, with double- $\zeta$  basis set and first-order scalar relativistic



**Figure 11.** Frontier orbitals for model reagents and product in Scheme 6: (a, b) the HOMO in O, Q; (c, d) the acceptor orbital in O and donor orbital in P in forming the PtPt bond; (e, f) the resulting bonding and antibonding orbitals in Q; (g, h) the donor orbital in O and acceptor orbital in P in forming the PtO bond; (i) the resulting bonding orbital in Q.

corrections.<sup>15</sup> The energy minima were confirmed by vibrational frequency analysis in each case.

 $\bar{X}$ -ray Crystallography (ref 16). The sample was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. X-ray data were collected at 110 K with  $\omega$  and  $\varphi$  scans using a Bruker Smart Apex II diffractometer and Bruker SMART software or a Nonius Kappa-CCD diffractometer with COLLECT software, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Unit cell parameters were calculated and refined from the full data set. Reflections were scaled and corrected for absorption effects using SADABS. All structures were solved by either Patterson or direct methods with SHELXS or the SIR2011 program and refined by full-matrix least-squares techniques against  $F^2$  using SHELXL. All non-hydrogen atoms were refined anistropically. The hydrogen atoms, including the NH hydrogen atoms, were not located but were placed

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Figure 12. Energy correlation diagram for formation of model complex Q.

in calculated positions and refined using the riding model; the hydrogen atoms are not usually shown in the figures. Crystal data are summarized in the cif files. Unusual features are as follows. The asymmetric unit of complex 5 contains four CHCl<sub>3</sub> molecules, one of which is disordered. The disorder was successfully modeled. For complex 5, CheckCIF gives an A level alert due to high-amplitude motion in one of the phenyl rings. The difference map did not give any peaks in this region that could be used to model a possible disorder, so there was no way to address this alert. Complex 7 exhibits both positional and compositional disorders. The Ag atom was disordered over three sites, denoted as Ag1, Ag1', and Ag1". The occupancies were refined until they were stable in the least-squares. To prevent high correlation with ADPs, they were normalized to 1.0 and fixed for subsequent refinement cycles. The occupancies were 0.83533, 0.08734, and 0.07733 for Ag1, Ag1', and Ag1", respectively. In addition, the ADP parameters for the silver atoms were constrained to be equal. In addition to the positional disorder, the complex exhibits compositional disorder wherein a dmso and a SMe2 molecule occupy the same region of the asymmetric unit. The methyl groups of the dmso and the SMe<sub>2</sub> were coincident. The SMe2 is bonded to Ag1', and therefore the occupancy of that moiety was set equal to the occupancy of the Ag1' site. Similarly, the dmso-bridged Ag1 sites, which were related by a crystallographic inversion center, and the occupancy of the dmso molecule were set equal to the occupancy of the Ag1 site. Because the silver is disordered over three sites and the sulfurs are disordered over two sites, the occupancies for the DMSO and the SMe<sub>2</sub> do not sum to 1.0. This is why the formula contains fractional numbers for C, H, and S.

[PtCl<sub>2</sub>(dpppa)], **3**. To a stirred solution of dpppa (0.10 g, 0.17 mmol) in acetone (10 mL) was added a solution of *cis/trans*-[PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>] (0.061 g, 0.17 mmol) in acetone (10 mL). The precipitate of complex **3** was collected, washed with pentane ( $3 \times 5$  mL) and ether ( $3 \times 5$  mL), and dried under high vacuum. Yield: 0.12

g, 83%. NMR in dmso- $d_6$ :  $\delta(^{1}\text{H}) = 7.94$  [br, 2H, NH]; 7.72–7.82 [m, 4H, C<sub>6</sub>H<sub>4</sub>]; 7.17–7.58 [m, 20H, Ph]; 3.72 [m, 4H, NCH<sub>2</sub>]; 2.99 [m, 4H, CH<sub>2</sub>P];  $\delta(^{31}\text{P}) = 1.69$  [s,  $^{1}J_{\text{PtP}} = 3630$  Hz]. Single crystals of complex 3 were grown by slow diffusion of *n*-pentane into a solution of the compound dissolved in a mixture of solvents: benzene, dimethylsulfoxide, methanol, acetone, dichloromethane, and chloroform (0.1 mL of each). Anal. Calcd for C<sub>36</sub>H<sub>34</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Pt: C, 50.60; H, 4.01; N, 3.28. Found: C, 50.87; H, 3.76; N, 3.02.

[PtMe<sub>2</sub>(dpppa)], 4a, and [Pt<sub>2</sub>Me<sub>4</sub>( $\mu$ -dpppa)<sub>2</sub>], 4b. To a solution of dpppa (0.10 g, 0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added a solution of  $[Pt_2Me_4(\mu-SMe_2)_2]$  (0.0488 g, 0.085 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solution was allowed to stir for 12 h., and the solvent was removed under vacuum to give a white solid product, which was washed with ether  $(3 \times 5 \text{ mL})$  and pentane  $(3 \times 5 \text{ mL})$  and then dried under high vacuum. Yield (4a+4b): 0.12 g, 87%. NMR in CDCl<sub>3</sub>: 4a,  $\delta(^{1}\text{H}) = 7.61$  [br s, 2H, NH]; 7.42 -7.60 [m, 4H, C<sub>6</sub>H<sub>4</sub>]; 7.30-7.09 [m, 20H, Ph]; 3.92 [m, 4H, NCH<sub>2</sub>]; 2.70 [m, 4H, CH<sub>2</sub>P]; 0.21 [m, 6H,  ${}^{2}J_{\text{PtH}} = 66$  Hz,  ${}^{3}J_{\text{PH}} = 6$  Hz, PtCH<sub>3</sub>];  $\delta$  ( ${}^{31}\text{P}$ ) = 7.08 [s,  ${}^{1}J_{\text{PtP}} = 1814$ Hz]. 4b,  $\delta({}^{1}\text{H}) = 8.11$  [br s, 4H, NH]; 7.70–7.79 [m, 4H, C<sub>6</sub>H<sub>4</sub>]; 7.36-7.03 [m, 44H, Ph and C<sub>6</sub>H<sub>4</sub>]; 3.68 [br m, 8H, NCH<sub>2</sub>]; 2.52 [br m, 8H,  $CH_2P$ ]; 0.46 [m, 12H,  ${}^{2}J_{PtH} = 67$  Hz,  ${}^{3}J_{PH} = 7$  Hz,  $PtCH_3$ ];  $\delta(^{31}\text{P}) = 10.28 \text{ [s, }^{1}J_{\text{PtP}} = 1760 \text{ Hz]}$ . Anal. Calcd for  $C_{76}H_{80}N_4O_4P_4Pt_2$ : C, 56.09; H, 4.95; N, 3.44. Found: C, 56.22; H, 4.75; N, 3.15. Single crystals of both complexes 4a and 4b were grown by slow diffusion of *n*-pentane into a solution of the compound dissolved in chloroform; typically, single crystals of both 4a and 4b were present in a given batch of crystals with the ratio dependent on concentration used.

[*Pt<sub>4</sub>Me<sub>6</sub>(μ-dpppa-H)<sub>2</sub>*], **5**. To a solution of dpppa (0.10 g, 0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added a solution of [Pt<sub>2</sub>Me<sub>4</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>] (0.10 g, 0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). A mixture of yellow and white precipitates was obtained after allowing the solution to stir for ca. 10 h. The yellow precipitate was isolated by crystallization. Yield: 0.078 g, 45%. Single crystals of complex **5** were grown by slow diffusion of *n*-pentane into a solution of the impure compound dissolved in chloroform. NMR in CDCl<sub>3</sub>:  $\delta$ (<sup>1</sup>H) = 8.37 [br s, 2H, NH]; 7.70–7.21 [m, 48H, Ph and C<sub>6</sub>H<sub>4</sub>]; 4.17 [m, 4H, NCH<sub>2</sub>]; 3.10 [m, 4H, NCH<sub>2</sub>]; 2.70 [m, 4H, PCH<sub>2</sub>]; 2.27 [m, 4H, PCH<sub>2</sub>]; 0.79 [d, 6H, <sup>2</sup>J<sub>PtH</sub> = 50 Hz, <sup>3</sup>J<sub>PH</sub> = 9 Hz, PtMe *trans* to P]; 0.63 [s, 6H, <sup>2</sup>J<sub>PtH</sub> = 82 Hz, PtMe *trans* to N]; 0.08 [s, 6H, <sup>2</sup>J<sub>PtH</sub> = 1380 Hz, <sup>3</sup>J<sub>PP</sub> = 8 Hz]; 2.87 [d, <sup>1</sup>J<sub>PtP</sub> = 926 Hz, <sup>3</sup>J<sub>PP</sub> = 8 Hz]. Anal. Calcd for C<sub>78</sub>H<sub>84</sub>N<sub>4</sub>O<sub>4</sub>P<sub>4</sub>Pt<sub>4</sub>: C, 45.79; H, 4.14; N, 2.74. Found: C, 45.69; H, 4.31; N, 2.52.

45.79; H, 4.14; N, 2.74. Found: C, 45.69; H, 4.31; N, 2.52.  $[Pt\{\kappa^{4}-N,N,P,P-C_{6}H_{4}-1,2-(CONCH_{2}CH_{2}PPh_{2})]_{2}, \mathbf{6}, and \mathbf{9} = \mathbf{6}_{2}.$   $Et_{3}NOH^{+}CF_{3}CO_{2}^{-}\cdot H_{2}O\cdot CHCI_{3}. \text{ To a solution of } 3 (0.10g, 0.11)$ mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), acetone (2 mL), and methanol (2 mL) was added a solution of silver trifluoroacetate (0.052 g, 0.23 mmol) in THF (5 mL). After allowing the reaction to stir for 1 h, triethylamine (33  $\mu$ L, 0.23 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added to the reaction contents. Two hours after the triethylamine addition, lithium chloride (0.02 g, 0.47 mmol) in methanol (5 mL) was added. The reaction was allowed to stir overnight (ca. 16 h). AgCl precipitate was removed by filtration, the filtrate was collected, solvents were evaporated, and the product 6 was isolated as a colorless solid, washed with pentane  $(3 \times 5 \text{ mL})$  and ether  $(3 \times 5 \text{ mL})$ , and dried under high vacuum. Yield: 0.08 g, 87%. NMR in CDCl<sub>3</sub>:  $\delta$ (<sup>1</sup>H) = 7.53 [m, 2H, C<sub>6</sub>H<sub>4</sub>]; 7.05-7.25 [m, 22H, Ph and C<sub>6</sub>H<sub>4</sub>]; 3.02 [m, 4H, NCH<sub>2</sub>]; 2.31 [m, 4H, CH<sub>2</sub>P];  $\delta(^{31}P) = 31.27$  [s,  $^{1}J_{PPt} = 3100$  Hz]. Anal. Calcd for C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Pt: C, 55.32; H, 4.13; N, 3.58. Found: C, 55.08; H, 4.10; N, 3.32. Single crystals of complex 9 were grown by slow diffusion of *n*-pentane into a solution of a similar reaction mixture dissolved in chloroform.

[ $Pt \{\kappa^4 - N, N, P, P - C_6H_4 - 1, 2 - (CONCH_2CH_2PPH_2)\}]_2$ .  $Ag_2(OCOCF_3)_2(OSMe_2)_2$ , 7. To a solution of 3 (0.10g, 0.12 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), acetone (2 mL), methanol (2 mL), and dmso (0.2 mL) was added a solution of silver trifluoroacetate (0.16 g, 0.70 mmol) in THF (5 mL). After allowing the reaction to stir for 1 h, triethylamine (0.10 mL, 0.70 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added to the reaction contents. The reaction was allowed to stir overnight (ca. 10 h.). The formed AgCl precipitate was removed by filtration. The filtrate was collected, solvents were evaporated, and the product was isolated as a colorless solid. The product was washed with pentane (3 × 5 mL) and ether (3 × 5 mL) and dried under high vacuum. Yield: 0.11 g, 86%. NMR in dmso- $d_6$ :  $\delta(^{1}\text{H}) = 6.94-7.59$  [m, 48H, Ph and C<sub>6</sub>H<sub>4</sub>]; 3.11 [m, 8H, NCH<sub>2</sub>]; 2.50 [m, 12H, (CH<sub>3</sub>)<sub>2</sub>SO]; 2.17 [m, 8H, CH<sub>2</sub>P];  $\delta(^{31}\text{P}) = 31.04$  [s,  $^{1}J_{\text{PPt}} = 3090$  Hz]. Single crystals of complex 7 were grown by slow diffusion of *n*-pentane into a solution of the compound dissolved in dichloromethane, chloroform, and benzene (0.1 mL of each). Anal. Calcd for C<sub>80</sub>H<sub>76</sub>Ag<sub>2</sub>F<sub>6</sub>N<sub>4</sub>O<sub>10</sub>P<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>: C, 44.46; H, 3.54; N, 2.59. Found: C, 44.64; H, 3.80; N, 2.50.

 $[Pt{\kappa^4-N,N,P,P-C_6H_4-1,2-(CONCH_2CH_2PPh_2)_2}Ag_2(OCOCF_3)_2]_n, 8.$ To a solution of 3 (0.10 g, 0.12 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), acetone (2 mL), and methanol (2 mL) was added a solution of silver trifluoroacetate (0.16 g, 0.70 mmol) in THF (5 mL). After allowing the reaction to stir for 1 h, triethylamine (0.1 mL, 0.70 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added to the reaction contents. The reaction was allowed to stir overnight (ca. 10 h). The formed AgCl precipitate was removed by filtration. The filtrate was collected, solvents were evaporated, and the product was isolated as a colorless solid. The product was washed with pentane  $(3 \times 5 \text{ mL})$  and ether  $(3 \times 5 \text{ mL})$ and dried under high vacuum. Yield: 0.12 g, 83%. NMR in CDCl3:  $\delta({}^{1}\text{H}) = 8.02 \text{ [t, } {}^{3}J_{\text{HH}} = 6 \text{ Hz}, 2\text{H}, C_{6}\text{H}_{4}\text{]}; 6.85-7.77 \text{ [m, 22H, Ph and }$  $C_6H_4$ ]; 4.86 [m, 4H, NCH<sub>2</sub>]; 2.60 [m, 4H, CH<sub>2</sub>P];  $\delta$ <sup>(31</sup>P) = 30.80 [s,  ${}^{1}J_{PPt}$  = 3110 Hz]. Single crystals of complex 5 were grown by slow diffusion of *n*-pentane into a solution of the compound dissolved in dichloromethane and chloroform (0.1 mL of each). Anal. Calcd for C<sub>80</sub>H<sub>64</sub>Ag<sub>4</sub>F<sub>12</sub>N<sub>4</sub>O<sub>12</sub>P<sub>4</sub>Pt<sub>2</sub>: C, 39.27; H, 2.64; N, 2.29. Found: C, 39.02; H, 2.78; N, 2.54.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

CIF files in electronic form only are available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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