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A Versatile Diphosphine Ligand: cis and trans Chelation or Bridging, with Self Association through Hydrogen Bonding

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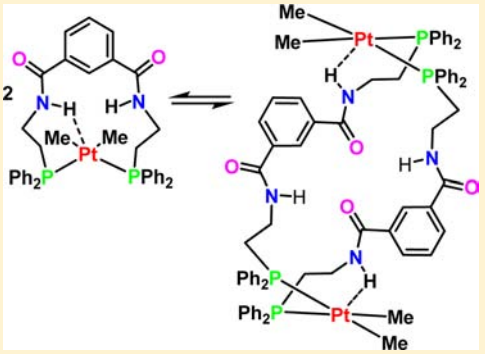
Supporting Information

ABSTRACT: The diphosphine ligand, *N*,*N*′-bis(2-diphenylphosphinoethyl)-isophthalamide, dpipa, contains two amide groups and can form *cis* or *trans* chelate complexes or *cis*,*cis* or *trans*,*trans* bridged complexes. The amide groups are likely to be involved in intramolecular or intermolecular hydrogen bonding. This combination of properties of the ligand dpipa leads to very unusual structural properties of its complexes, which often exist as mixtures of monomers and dimers in solution. In the complex $[Au_2(\mu\text{-dpipa})_2]Cl_2$, the ligands adopt the *trans*,*trans* bridging mode, with linear gold(I) centers, and the amide groups hydrogen bond to the chloride anions. In $[Pt_2Cl_4(\mu\text{-dpipa})_2]$, the ligands adopt the *cis*,*cis* bridging mode, with square planar platinum(II) centers, and the amide groups form intermolecular hydrogen bonds to the chloride ligands to form a supramolecular one-dimensional polymer. Both the monomeric and dimeric complexes $[PtMe_2(dpipa)]$ and $[Pt_2Me_4(\mu\text{-dpipa})_2]$ have *cis*-$PtMe_2$ units with *cis* chelating or *cis*,*cis* bridging dpipa ligands respectively; each forms a supramolecular dimer through hydrogen bonding between amide groups and each contains an unusual NH···Pt interaction. An attempted oxidative addition reaction with methyl iodide gave the complex $[PtIMe(dpipa)]$, which contains *trans* chelating dpipa, while a reaction with bromine gave a disordered complex with approximate composition $[Pt_2Me_3Br_5(\mu\text{-dpipa})_2]$, which contains *trans*,*trans* bridging dpipa ligands.



INTRODUCTION

Diphosphines have played a critical role in the development of coordination chemistry and its applications. They can be designed to act as *cis* or *trans* chelate ligands or as bridging ligands, they may contain additional functional groups such as hydrogen bonding groups or nitrogen donor groups, and they bind strongly to softer metal ions in a wide range of oxidation states.[1,2] Diphosphine-carboxamides in particular have been termed "the inconspicuous gems" and their metal complexes have found roles in catalysis and as potential pharmaceuticals.[3,4] We have been interested in developing the chemistry of diphosphine-dicarboxamides for use in molecular materials.[5] The strategy is to use dynamic coordination chemistry[6] or dynamic ring-opening polymerization,[7] using the phosphine donor groups, to prepare the primary structure, and then to use the carboxamide groups to increase the dimensionality or to engage in host−guest chemistry.[8] This paper reports a new diphosphine ligand, *N*,*N*′-bis(2-diphenylphosphinoethyl)isophthalamide, dpipa, and its complexes with gold(I) and platinum(II). The ligand can be considered as analogous to the previously studied ligands shown in Chart 1, namely, dppbH, which tends to form *cis* or *trans* chelate complexes,[9] and dppeta, which tends to act as a bridging ligand.[5] The new ligand dpipa can adopt any of these binding modes and so promises a particularly rich coordination and supramolecular chemistry.

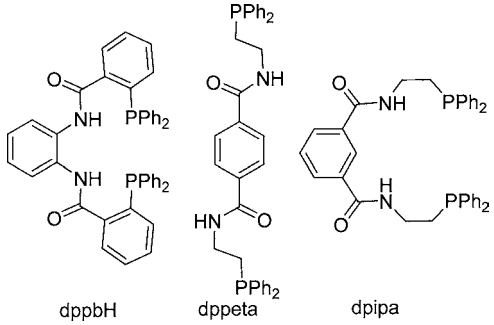
RESULTS

The new ligand *N*,*N*′-bis(2-diphenylphosphinoethyl)isophthalamide, dpipa, was prepared by reaction of isophthaloyl dichloride with 2-(diphenylphosphino)ethylamine in the presence of base (Scheme 1). It was isolated, after flash chromatography, as a white solid. The ligand dpipa was characterized in the ^{1}H NMR spectrum, by well separated NH, CH_2N, and CH_2P resonances at δ 6.35, 3.65, and 2.44 respectively, and, in the ^{31}P NMR spectrum, by a singlet at δ −21.05.

The reaction of dpipa with $[AuCl(SMe_2)]$ in a 1:1 ratio gave complex **1**, which appears to exist in solution as a mixture of the monomer **1a** and dimer **1b**, as shown in Scheme 2.

The equilibrium was most easily monitored by recording the ^{31}P NMR spectrum in $CDCl_3$ at different concentrations, as

Chart 1. Some Diphosphine-Dicarboxamide Ligands



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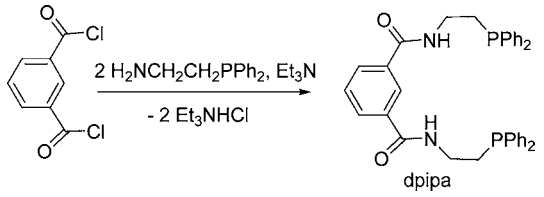
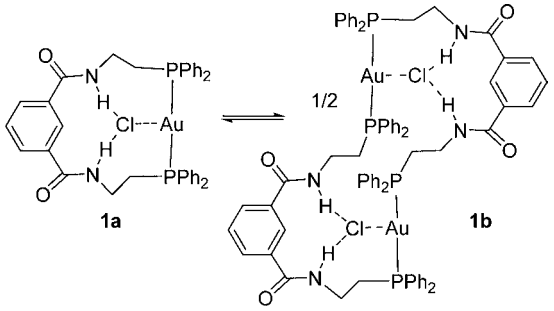
Scheme 1. Synthesis of the Ligand dpipa



Scheme 2. Proposed Equilibrium between Complexes 1a and 1b



shown in Figure 1. At low concentration, the complex was present almost entirely as the monomer **1a**, but at higher

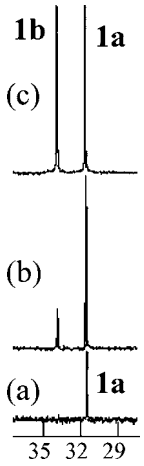


Figure 1. ^{31}P NMR spectrum of complex **1** as a function of concentration in $CDCl_3$ (0.5 mL): (a) 10 mg; (b) 50 mg; (c) 100 mg.

concentrations the dimer **1b** was also observed. The monomer **1a** gave a singlet at $\delta(^{31}P)$ 31.85 while dimer **1b** gave a singlet at $\delta(^{31}P)$ 34.24. The electrospray ionization mass spectrometry (ESI-MS) of complex **1** dissolved in dichloromethane gave two major peaks; one at m/z = 1605.3, which corresponds to the ion $[Au_2(\mu\text{-dpipa})_2]Cl^+$, formed by loss of one chloride ion from **1b**, and another at m/z = 785.2, which corresponds to the ion $[Au(dpipa)]^+$, formed by loss of chloride from **1a**. The data indicate that **1b** is favored by enthalpy and **1a** by entropy effects.

Recrystallization of complex **1** from dichloromethane gave single crystals of complex **1b**, whose structure is shown in Figure 2. The stereochemistry at gold is roughly linear, with P(1)−Au(1)−P(2A) 174.82(4)°, and the distance Au(1)···Cl(A) 3.398(2) is too long to represent a gold-chloride covalent bond. This suggests the formulation $[Au_2(\mu\text{-dpipa})_2]Cl_2$ for **1b**. The chloride ions are hydrogen bonded to the NH protons of dpipa ligand, with Cl···N(2) 3.341(4) and Cl···N(1) 3.377(5) Å,

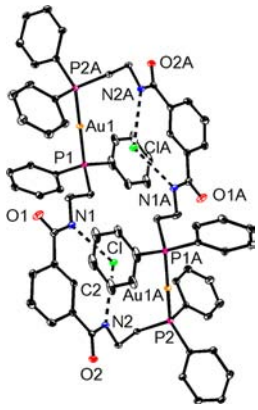
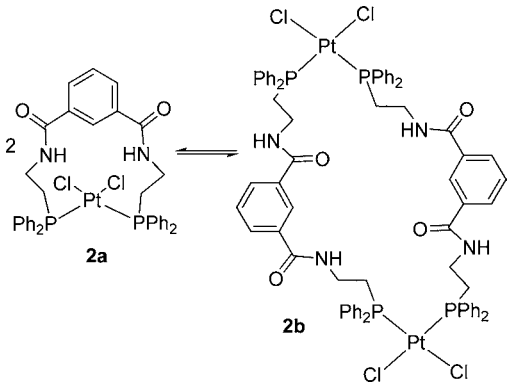


Figure 2. View of the structure of complex **1b**. Selected bond parameters: Au(1)−P(1) 2.308(1), Au(1)−P(2A) 2.313(1), Au(1)···Cl(A) 3.398(2), Cl···N(2) 3.341(4), Cl···N(1) 3.377(5) Å; P(1)−Au(1)−P(2A) 174.82(4), Cl(A)−Au(1)−P(2A) 86.50(3), Cl(A)−Au(1)−P(1) 90.18(3)°. Symmetry equivalent: A, 1−x, 1−y, −z.

which is a common motif for anion binding by isophthalamide derivatives.[7a,10] The positions of the chloride ions, with angles Cl(A)−Au(1)−P(2A) 86.50(3) and Cl(A)−Au(1)−P(1) 90.18(3)°, suggest there may be a weak AuCl interaction, but this is likely to be mostly ionic in character. The gold centers are separated by 9.00 Å. We have not been able to crystallize complex **1a**, and the structure proposed in Scheme 2 is therefore less certain. In addition, it is noted that for **1b** to give a singlet resonance in the ^{31}P NMR spectrum the complex must be fluxional.

The reaction of *cis*/*trans*-$[PtCl_2(SMe_2)_2]$ with dpipa occurred with displacement of dimethylsulfide to give complex **2**, which existed in solution as a mixture of the monomer *cis*-$[PtCl_2$-(dpipa)], **2a**, and dimer *cis*,*cis*-$[Pt_2Cl_4(\mu\text{-dpipa})_2]$, **2b** (Scheme 3).

Scheme 3. Dichloroplatinum(II) Complexes 2a and 2b



As with complex **1**, the relative concentrations of **2a** and **2b** were concentration dependent, with **2b** favored at higher concentrations. For example, in the ^{31}P NMR spectrum, **2a** gave $\delta(^{31}P)$ 1.27, with coupling constant ^1J(PtP) 3608 Hz, while **2b** gave $\delta(^{31}P)$ 1.58, ^1J(PtP) = 3600 Hz. The magnitudes of the values of ^1J(PtP) indicate the stereochemistry with phosphorus *trans* to chloride in each case.[11,12] The *cis*,*cis* stereochemistry of complex **2b** was confirmed crystallographically, and the structure is shown in Figure 3.

The structure of complex **2b** contains a center of symmetry, and the ligand is in a stretched conformation, with the distance between the platinum atoms being 14.28 Å, compared to the

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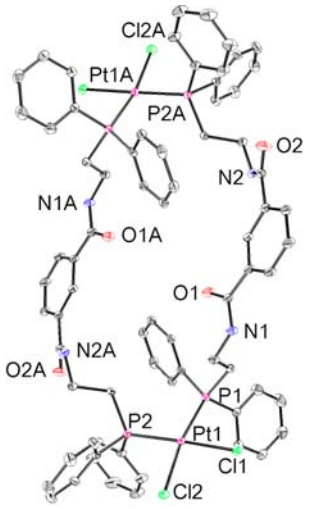


Figure 3. View of the structure of complex **2b**. Selected bond parameters: Pt(1)−Cl(1) 2.389(1), Pt(1)−Cl(2) 2.381(1), Pt(1)−P(2) = 2.284(1), Pt(1)−P(1) = 2.283(1) Å; Cl(1)−Pt(1)−Cl(2) 87.36(4), P(2)−Pt(1)−P(1) 99.80(4)°. Symmetry equivalent: A, 1−*x*, 2−*y*, −*z*.

AuAu distance in **1b** of 9.00 Å (Figure 2). Another difference between the structures of **1b** and **2b** is the conformation of the phthalamide units, which tend to have roughly coplanar $C_6H_4(CONH)_2$ units. In **1b** the symmetrical conformation, which we label the *exo,exo* conformation, is present with torsion angles OCCC = 169 and 172° (Figure 2, the terminal carbon is the C2 atom of the 1,3-phthalamide unit), but in **2b** (Figure 3) the unsymmetrical *exo,endo* conformation is present with corresponding torsion angles of 8 and 149°. The molecules of complex **2b** undergo self-association through complementary NH···Cl hydrogen bonding to give a supramolecular polymer, as shown in Figure 4.

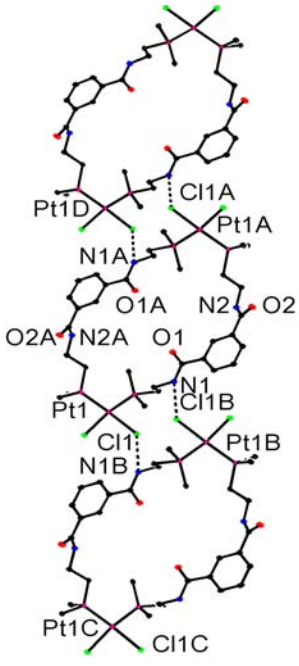
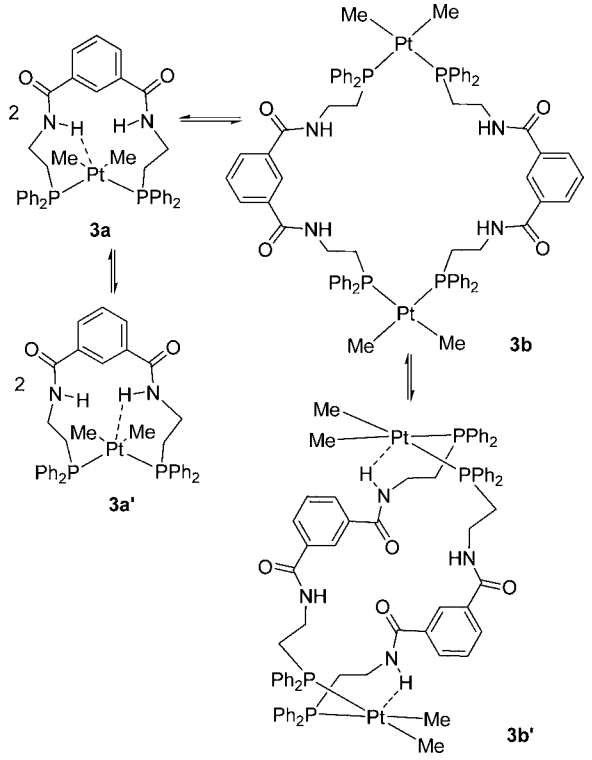


Figure 4. Supramolecular polymeric structure of complex **2b**, formed by intermolecular NH···Cl hydrogen bonding. Only the *ipso* carbon atoms of the phenyl groups are shown, for clarity. Hydrogen bond distance: N(1)···Cl(1B) 3.38(1) Å.

Complex **3** was prepared by displacement of the Me_2S ligands from $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ by the ligand dpipa, and was shown to exist as a mixture of the monomer *cis*-$[PtMe_2(dpipa)]$, **3a**, and dimer *cis,cis*-$[Pt_2Me_4(\mu\text{-dpipa})_2]$, **3b**, illustrated in Scheme 4.

Scheme 4. Equilibrium between Dimethylplatinum(II) Complexes 3a and 3b



The NMR spectra of **3** were broad and contained minor resonances, perhaps suggesting the presence of minor amounts of other isomers or slowly equilibrating conformers. However, the major isomers were clearly identified. In the ^{31}P NMR spectrum, the monomer **3a** gave a sharp singlet at δ 11.23, $^1J(PtP)$ = 1815 Hz, while dimer **3b** gave a broad singlet at δ 10.89, $^1J(PtP)$ = 1800 Hz (Figure 5). The magnitudes of the coupling constants indicate that, in each case, the phosphorus atoms are *trans* to the methyl groups.[11,13] The ESI-MS of complex **3** in dichloromethane, in the presence of NaCl to aid ionization, gave two major peaks; one at m/z = 1649.4, which corresponds to $[Pt_2Me_4(\mu\text{-dpipa})_2]Na^+$ and one m/z = 836.2 which corresponds to $[PtMe_2(dpipa)]Na^+$.

Fortunately, we were able to grow single crystals of both **3a** and **3b** to confirm the structures. The molecular structure of the monomer **3a** is shown in Figure 6. It confirms the expected *cis* square planar stereochemistry at platinum(II), though with the PPtP bond angle at 101.27(4)° significantly distorted from the ideal 90°. An interesting feature of the structure in Figure 6 is that the C(O)NH groups are significantly twisted out of the plane of the C_6H_4 group, in such a way as to give a short intramolecular Pt···HN contact, with Pt···H(1) about 2.63 Å, indicative of the electron rich dimethylplatinum(II) center acting as a hydrogen bond acceptor.[15] The molecules of complex **3a** self-associate to form a hydrogen bonded dimer, as shown in Figure 6. The individual molecules are related by a center of inversion.

The dimer **3b** in the solid state adopts a highly twisted structure (conformation **3b′** in Scheme 4) as shown in Figures 7 and 8.

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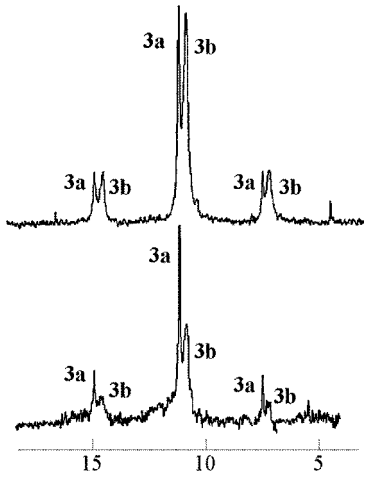

Figure 5. ^{31}P NMR spectra of complex **3** at different concentrations in $CDCl_3$ (0.5 mL), illustrating the equilibrium between **3a** and **3b**: below, 10 mg **3**.; above, 100 mg **3**.

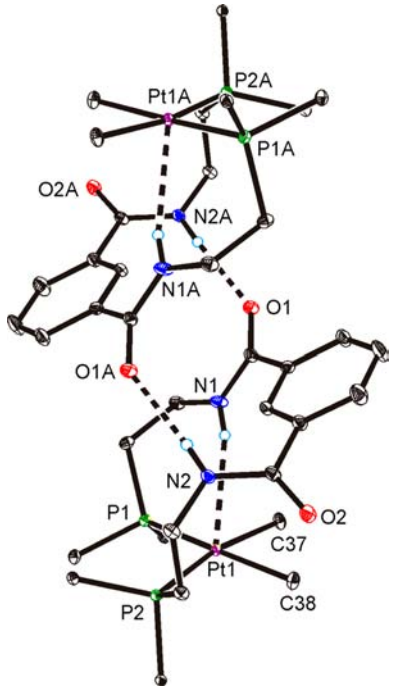

Figure 6. View of the structure of complex **3a**, including the intra- and intermolecular hydrogen bonding. Selected bond parameters: Pt(1)–C(37) 2.100(4), Pt(1)–C(38) 2.101(4), Pt(1)–P(1) 2.309(1), Pt(1)–P(2) 2.319(1), Pt(1)···N(1) 3.461(4) Å; P(1)–Pt(1)–P(2) 101.27(4), C(37)–Pt(1)–C(38) 81.5(2)°. Hydrogen bond distance: O(1)···N(2A) 2.918(5) Å. Torsion: O(1)–C(3)–C(4)–C(24) 148.0(6), O(2)–C(9)–C(8)–C(24) 144.6(6)°. Only the *ipso* carbon atom of the phenyl groups is shown. Symmetry equivalent: A, 1–*x*, 1–*y*, 2–*z*.

There are two independent molecules in the unit cell, but they have similar structures, and only one is shown in Figure 7. Each isophthalamide unit adopts the *exo,endo* conformation observed previously in **2b**, but the overall conformation of each molecule of **3b**′ is helical and quite different from that in **2b** (Figure 3). There is close to a 180° twist in each molecule, as indicated by the typical torsion angle P(1)–Pt(1)–Pt(2)–P(4) of 169°. The lattice contains equal numbers of molecules of **3b**′ in the *P* and *M* helical conformations, related by an inversion center, but

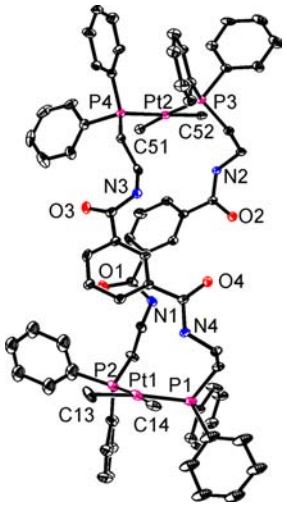

Figure 7. View of the structure of complex **3b**. Selected bond parameters: Pt(1)–P(1) 2.318(2), Pt(1)–P(2) 2.296(3), Pt(2)–P(3) 2.321(2), Pt(2)–P(4) 2.301(2) Å; P(2)–Pt(1)–P(1) 98.53(8), C(14)–Pt(1)–C(13) 82.0(3), C(51)–Pt(2)–C(52) 84.6(3)°. Representative torsion angles: O(1)–C(29)–C(30)–C(35) 153.7, O(2)–C(36)–C(34)–C(35) 24.6°.

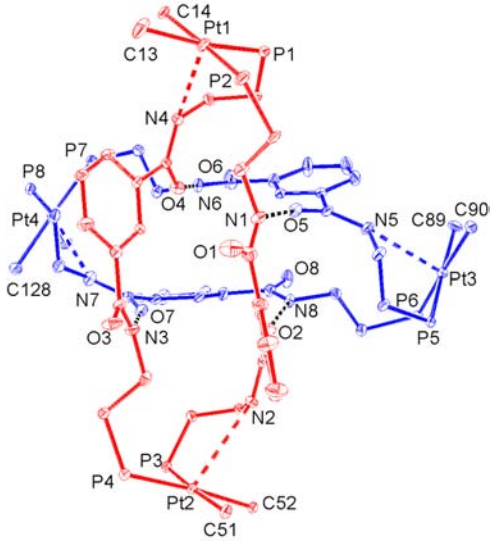

Figure 8. Dimer of dimers formed by hydrogen bonding in complex **3b**. Hydrogen bond distances: N(1)···O(5) 2.784(8), O(4)···N(6) 2.770(8), N(3)···O(7) 2.803(9), O(2)···N(8) 2.759(8), Pt(1)···N(4) 3.348(5), Pt(2)···N(2) 3.334(5), Pt(3)···N(5) 3.304(5), Pt(4)···N(7) 3.371(5) Å. The phenyl groups have been omitted for clarity.

individual molecules have no crystallographically imposed symmetry (Figure 7). There is a short NH···Pt contact for each dimethylplatinum(II) center (Figure 8), and this hydrogen bond, which is similar to that observed in the monomer **3a**, appears to control the unusual conformation of the complex. There is no such NH···Pt hydrogen bond in complex **2b**, which contains less nucleophilic dichloroplatinum(II) centers. In each independent pair of dimers, four of the NH groups are directed inward, and these are involved in the intramolecular NH···Pt hydrogen bonds, while four are directed outward and form intermolecular NH···O═C hydrogen bonds to the neighboring dimer. This gives rise to a dimer of dimers structure (Figure 8), which can be considered to have a "swastika" conformation. If the Pt(1)Pt(2) and Pt(3)Pt(4) dimers are considered to have

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P, *M* and *P*′, *M*′ conformations respectively, each dimer contains a *P*,*M*′ or *M*,*P*′ pair. Figure 8 illustrates a *P*,*M*′ dimer of dimers.

The twisted structures observed for **3a** and **3b** should give more complex NMR spectra than those observed (Figure 5), which suggest that the complexes have effective mirror symmetry in solution. For complex **3a**, a relatively simple twisting motion is required to exchange the Pt··HN hydrogen bond between the N(1)H and N(2)H donors, as indicated in Scheme 4, leading to effective C_s symmetry. However, if the conformation of the dimer **3b**′ is retained in solution, to the *P* and *M* conformers would need to interchange rapidly to give a single ^{31}P NMR resonance, and this would require passing through a symmetrical intermediate such as **3b** in Scheme 4. To study the potential dynamic exchange, a variable temperature NMR study was carried out, with interesting results. Figure 9 shows the

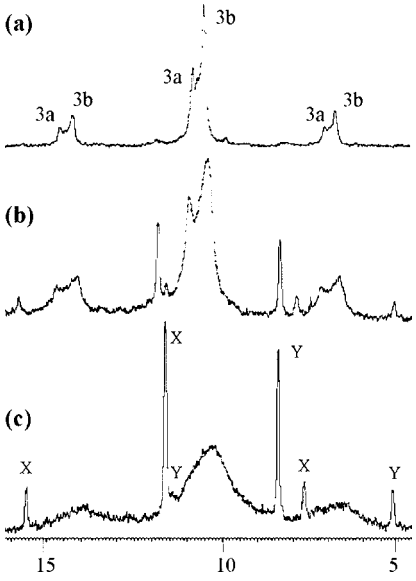
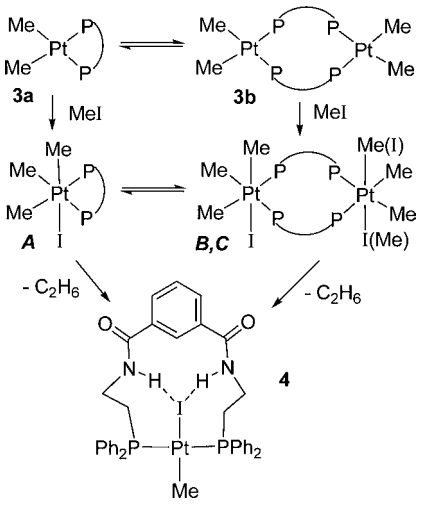


Figure 9. Variable temperature ^{31}P NMR spectra (243 MHz) of complex **3** in CD_2Cl_2 solution: (a) 25 °C; (b) 0 °C; (c) −20 °C.

^{31}P NMR spectra as a function of temperature. As the temperature decreases, the singlet resonances for the monomer **3a** and dimer **3b** broaden, but they do not split to give separate resonances at the lowest temperature studied (−80 °C). However, two new resonances (labeled X and Y in Figure 9) appear and grow in intensity as the temperature is decreased. The parameters [δ(P^X) 11.6, ^1J(PtP) 1920 Hz, ^2J(PP) 15 Hz, and δ(P^Y) 8.4, ^1J(PtP) 1590 Hz, ^2J(PP) 15 Hz] indicate an unsymmetrical arrangement *cis*-(PtMe$_2$P^{X}P^Y) as expected for the twisted structure **3b**′. The most likely explanation of this observation is that the dimer is present in solution at room temperature mostly as a more symmetrical conformer (**3b** in Scheme 4), or a conformer (such as one analogous to that in the dichloroplatinum(II) derivative **2b**) which can very easily equilibrate with **3b**. The rigid twisted structure **3b**′, which is likely to be disfavored by entropy effects, increases in concentration at lower temperatures but equilibrates only relatively slowly on the NMR time scale with the more symmetrical conformer **3b**. The low temperature ^{1}H NMR spectra are consistent with this interpretation. At −20 °C, two new methylplatinum resonances [δ(Me^X) 0.67, ^2J(PtH) 64 Hz, ^3J(PH) 6 Hz; δ(Me^Y) 0.20, ^2J(PtH) 68 Hz, ^3J(PH) 8 Hz] and two new NH resonances [δ(NH^X) 10.13; δ(NH^Y) 9.32] appear and are assigned to **3b**′. The resonance at δ(NH^X) 10.13 is tentatively assigned as the hydrogen bonded Pt··HN group in **3b**′, based on the downfield chemical shift, but no coupling to ^{195}Pt was resolved.[15]

The reaction of complex **3** with methyl iodide gave a new platinum(II) complex *trans*-[PtIMe(dpipa)], **4** (Scheme 5). In

Scheme 5. Possible Routes to Complex 4[a]



[a]P−P represents the dpipa ligand.

the ^{1}H NMR spectrum, complex **4** gave a triplet methylplatinum resonance at δ 0.15, with ^3J(PH) = 7 Hz and with ^2J(PtH) = 80 Hz, and in the ^{31}P NMR spectrum it gave a singlet at δ(^{31}P) = 16.12, with ^1J(PtP) = 2946 Hz. The magnitude of ^1J(PtP) suggests the presence of mutually *trans* phosphine donors.[11,14] The ESI-MS of complex **4** in dichloromethane, with NaCl present, gave a major peak at m/z = 948.1, which corresponds to the ion [PtIMe(dpipa)]Na$^+$. Some possible routes to complex **4** by oxidative addition of methyl iodide followed by reductive elimination of ethane are shown in Scheme 5.

The structure of complex **4** is shown in Figure 10. It shows that the ligand dpipa is acting as a *trans* chelate ligand. The carboxamide groups are in the *exo*,*exo* conformation, which allows formation of two NH···I hydrogen bonds. The complex crystallized with a water molecule, which bridges between monomeric units of complex **4** by hydrogen bonding, to form a supramolecular dimer.

The slow reaction of the mixture of isomers **3a**/**3b** with excess methyl iodide was monitored by ^{31}P NMR spectroscopy in $CDCl_3$ solution (Figure 11). After 30 min, about 60% of the reagent had reacted and three major new singlet resonances were observed, namely, a sharp resonance at δ −25.46, ^1J(PtP) 996 Hz, tentatively assigned to the monomer ***A*** (Scheme 5), and two broader resonances at δ −25.96, ^1J(PtP) 1060 Hz, and δ −26.66, ^1J(PtP) 974 Hz, tentatively assigned to the *syn* and *anti* dimers ***B***, ***C***. After 2 h, a new unassigned resonance was observed at δ −23.59, ^1J(PtP) 1119 Hz, and the first appearance of the resonance for complex **4**. After 2 days, the reaction was complete, and complex **4** was formed almost quantitatively. The singlet resonances in the region δ −23 to −27, with coupling constants ^1J(PtP) in the range 974−1119 Hz, are characteristic of complexes with the fac-[PtIMe$_3$P$_2$] stereochemistry.[11,16] The reductive elimination of ethane from complexes ***A***−***C*** is likely to occur by partial dissociation of a dpipa ligand, and a common 5-coordinate intermediate [PtIMe$_3$(κ^1-dpipa)] could be formed, which then gives ethane and a shortlived

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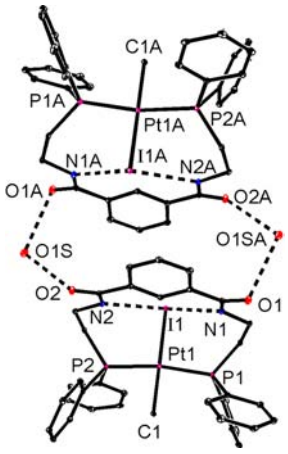


Figure 10. View of the structure of complex **4**. Selected bond parameters: Pt(1)−C(1) 2.093(5), Pt(1)−I(1) 2.7035(5), Pt(1)−P(1) 2.296(2), Pt(1)−P(2) 2.309(2) Å; P(1)−Pt(1)−I(1) 94.38(4), P(2)−Pt(1)−I(1) 93.29(4), P(2)−Pt(1)−C(1) 85.1(2), C(1)−Pt(1)−P(1) 86.4(2)°. Hydrogen bond distances: N(1)···I(1) 3.699(5), N(2)···I(1) 3.703(5), O(2)···O(1S) 2.953(8), O(1)···O(1S) 2.913(8) Å.

3-coordinate [PtIMe(κ^1-dpipa)], which would then give *trans*-[PtIMe(κ^2-dpipa)], **4**.[17] None of the possible *cis* isomer, which should contain nonequivalent phosphorus atoms and hence give a pair of doublets in the ^{31}P NMR spectrum, was observed at any stage of the reaction (Figure 11).

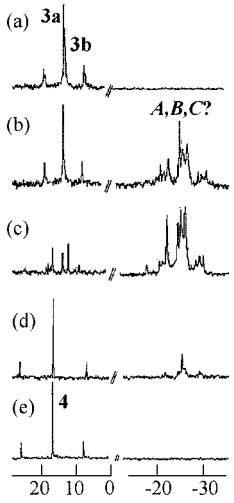
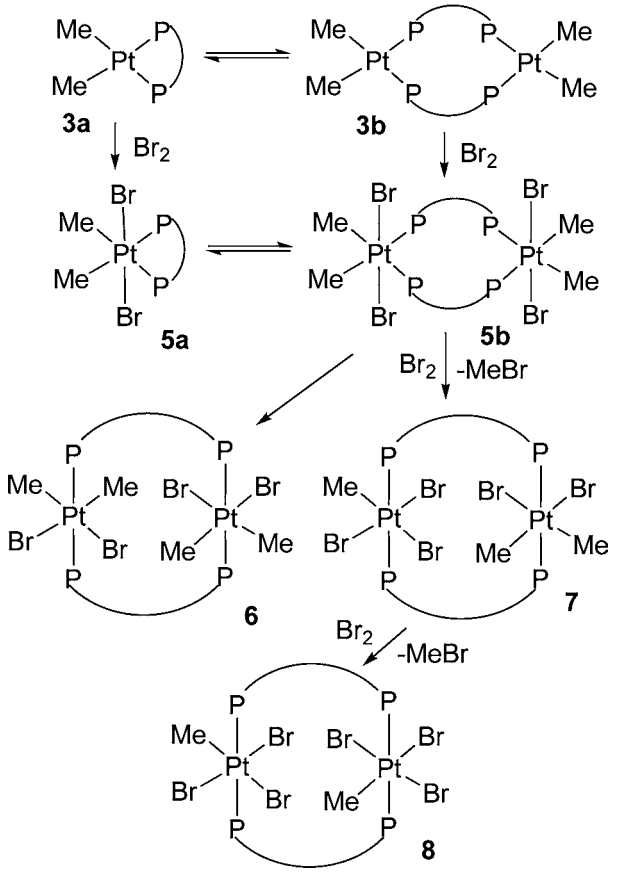


Figure 11. ^{31}P NMR spectra for the reaction of **3a**, **3b** with excess MeI in $CDCl_3$: (a) before addition of MeI; (b) after 30 min; (c) after 2 h; (d) after 24 h; (e) after 2 days.

The chemistry of complexes **3a**/**3b** with bromine is depicted in Scheme 6. The reaction was expected to give complexes **5a** and **5b** by *trans* oxidative addition of bromine to **3a** and **3b** respectively, but, although a reaction occurred rapidly using several different stoichiometries, it proved difficult to characterize the product. Eventually, crystals of a product, formed using about 4-fold excess of bromine, were grown from a complex mixture of solvents, and the resulting structure is shown in Figure 12.

There are several surprising features of the structure in Figure 12. Most obviously, the product is a diplatinum complex with *trans*-PtP_2 stereochemistry at each octahedral platinum-

Scheme 6. Possible Route to Complexes 5, 6, 7 (and Possibly 8) (PP = dpipa)



(IV) center, whereas both monomeric **3a** and dimeric **3b** starting materials contained the *cis*-PtP_2 stereochemistry. Each platinum center contains four anionic ligands, of which two refined well as bromide ions. However, the other two, labeled C(1X) and C(2X) in Figure 12, could only be refined as disordered CH_3/Br units with occupancies of Br:C 29:71 and 25:75 in the two sites. This leads to a formula [$Pt_2Br_{5.08}Me_{2.92}(dpipa)_2$], approximating to [$Pt_2Br_5Me_3(dpipa)_2$], thus suggesting that about equal numbers of the platinum(IV) centers have [$PtBr_2Me_2P_2$] and [$PtBr_3MeP_2$] coordination. This might suggest complex **7**, with intramolecular disorder of the $PtBr_2Me_2$ and $PtBr_3Me$ groups, but it is also consistent with a disordered mixture of complexes [$Pt_2Br_4Me_4(dpipa)_2$], **6**, [$Pt_2Br_5Me_3(dpipa)_2$], **7**, and [$Pt_2Br_6Me_2(dpipa)_2$], **8** (Scheme 6). The two halves of the molecule in Figure 12 are related by a center of symmetry, and the two platinum atoms are separated by 12.0 Å. The isophthalamide units adopt a distorted *exo,endo* conformation. The NH groups are not involved in hydrogen bonding to either the carbonyl groups or the bromide ligands, but may hydrogen bond to solvent molecules which could not be identified and refined.

If the reaction of **3a**/**3b** with bromine was carried out in dichloromethane solution, much of the product precipitated as an orange solid. Recrystallization of this solid gave the single crystals, from which the structure was determined. The ^{1}H NMR spectrum of this initial orange complex in dmso-d_6 contains broad peaks, probably due to restricted rotations, but clearly indicates that the product contains a mixture of complexes **6** and **7** in about a 3:1 ratio. The symmetrical complex **6** gives a single methylplatinum resonance [$\delta(^1H)$ 0.55, $^2J_{PtH}$ = 65 Hz] and a

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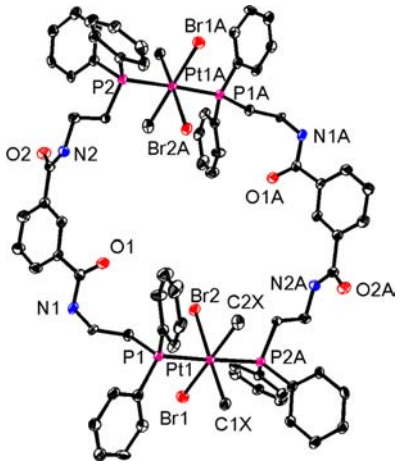

Figure 12. View of the structure of complex **7**, showing only the carbon atoms C(1X) and C(2X) of the disordered Me/Br groups. Selected bond parameters: Pt(1)−Br(1) 2.557(1), Pt(1)−Br(2) 2.589(1), Pt(1)−P(1) 2.384(3), Pt(1)−P(2) 2.373(2) Å; Br(1)−Pt(1)−Br(2) 91.08(4), P(1)−Pt(1)−P(2) 177.54(8)°. Symmetry equivalent: A, $1-x$, $1-y$, $-z$.

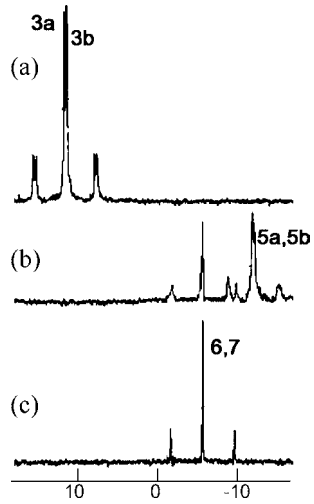

Figure 13. ^{31}P NMR spectra for the reaction of complexes **3a** and **3b** in $CDCl_3$ with Br_2: (a) before the addition of Br_2; (b) after 3 h; (c) after 4 days.

single set of resonances for the $NHCH_2CH_2P$ protons, whereas the unsymmetrical complex **7** gave two sets of resonances for the $NHCH_2CH_2P$ protons, and two methylplatinum resonances [$\delta(^1H)$ 1.08, $^2J_{PtH}$ = 68 Hz, for the $PtMeBr_3$ group and 0.59, $^2J_{PtH}$ = 65 Hz, for the $PtMe_2Br_2$ group], with the $PtMeBr_3$ resonance shifted to higher δ, as expected from comparison with related complexes.[18] The surprising feature was that the ^{31}P NMR spectrum contained only one resolved resonance at $\delta(^{31}P) = -5.59$, $^1J_{PtP}$ = 2050 Hz, whereas three resonances are expected for a mixture of **6** and **7**. The ESI-MS of the sample, as a dilute solution in dichloromethane with NaCl added to promote ionization, gave peaks, with masses reported for the ^{195}Pt,^{79}Br isotopomer, at m/z = 994.0, 1965.1, and 2029.0 which correspond to the ions $[PtBr_2Me_2(dpipa)]Na^+$, $[Pt_2Br_4Me_4(\mu\text{-dpipa})_2]Na^+$, and $[Pt_2Br_5Me_3(\mu\text{-dpipa})_2]Na^+$, respectively. It is likely that the ion $[PtBr_2Me_2(dpipa)]Na^+$ arises from fragmentation of **6**, because there was no evidence for the monomeric complex in either the ^{1}H or the ^{31}P NMR spectra. The combined spectra support the assignment of the initial orange product as a mixture of complexes **6** and **7**.

To gain further insight, the reaction of **3a**/**3b** with bromine was carried out in both $CDCl_3$ and dmso-d_6, with monitoring by ^{1}H and ^{31}P NMR spectroscopy at room temperature. In $CDCl_3$, some orange precipitate formed even at room temperature, and low temperature experiments were not possible because of the limited solubility of the complexes. Immediately after addition of bromine, a methylplatinum resonance was observed at δ 0.68, $^2J_{PtH}$ = 64 Hz, with second order ($A_3A'_3XX'$) appearance expected for a *cis*-$PtMe_2P_2$ grouping, as expected in complexes **5a**,**5b** .[13,16,18] Over a period of about an hour, this resonance was replaced by a triplet resonance assigned to complex **6**, with weaker resonances due to **7**. A resonance for methyl bromide [δ 2.69] grew during this period, but no further growth in the resonance occurred. The ^{31}P NMR spectrum at intermediate stages contained a resonance at δ −13.6, $^1J_{PtP}$ = 1585 Hz, assigned to **5a**,**5b**, and two closely spaced resonances at δ −4.8 and −5.1, each with $^1J_{PtP}$ = 2050 Hz, assigned to **6** and **7**, respectively. Three peaks are expected for a mixture of **6** and **7** and so two are presumed to overlap. Better ^{31}P NMR spectra were obtained in dmso-d_6 solution, as illustrated in Figure 13, because the solubility was improved. Immediately after addition of bromine, the resonances of **3a**,**3b** disappeared, and resonances assigned to **5a**,**5b** [δ −11.1, $^1J_{PtP}$ = 1585 Hz] and **6**,**7** [δ −5.59, $^1J_{PtP}$ = 2050 Hz] were observed. Over time, the resonance for **5a**,**5b** decayed, and the resonance for **6**,**7** (again with accidental degeneracy of the chemical shifts) increased in intensity.

Once formed, the complexes **6** and **7** were unreactive to bromine, so it is likely that the formation of methyl bromide occurs at an early stage. One possibility is that there is a competition between isomerization of **5** to **6** and reductive elimination of methyl bromide from **5** followed by further reaction with bromine to give **7** (Scheme 6), but there may be other potential routes.

■ CONCLUSIONS

The new diphosphine-dicarboxamide ligand dpipa is shown to be remarkably versatile in its coordination chemistry, with the carboxamide groups playing an important role in several cases. Ligand dpipa can act as a *trans* chelate ligand in the complex *trans*-[PtIMe(dpipa)], **4**, and probably in the gold complex [Au(dpipa)]Cl, **1a**. In complex **4**, and probably in **1a**, the carboxamide groups are hydrogen bonded to the halide ligand or anion. The ligand acts as a *cis* chelate ligand in the complexes *cis*-[$PtCl_2$(dpipa)], **2a**, and *cis*-[$PtMe_2$(dpipa)], **3a**. In complex **3a** the carboxamide groups are bifunctional, forming an intramolecular NH···Pt hydrogen bond and taking part in intermolecular NH···O═C hydrogen bonding to form supramolecular dimers. The *trans*,*trans* bridging mode of binding is found in the gold(I) complex $[Au_2(\mu\text{-dpipa})_2]Cl_2$, **1b**, and the platinum(IV) complexes $[Pt_2Br_4Me_4(\mu\text{-dpipa})_2]$, **6**, and $[Pt_2Br_5Me_3(\mu\text{-dpipa})_2]$, **7**. Figures 2 and 12 illustrate how the flexible dpipa ligand adapts to accommodate the 2-coordinate gold(I) center or the more sterically demanding octahedral platinum(IV) center. The *cis*,*cis* bridging mode of binding is found in the platinum(II) complexes $[Pt_2Cl_4(\mu\text{-dpipa})_2]$, **2b**, and $[Pt_2Me_4(\mu\text{-dpipa})_2]$, **3b**, and in the intermediate platinum(IV) complex $[Pt_2Br_4Me_4(\mu\text{-dpipa})_2]$, **5b**. Complex **3b** adopts a more twisted conformation than **2b**, apparently to allow formation of intramolecular NH···Pt hydrogen bonds, and the carboxamide groups in both complexes also take part in intermolecular NH···O═C hydrogen bonding.

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Several of the complexes exhibit facile monomer−dimer isomerization. In one case, it was possible to determine the structures of both of the isomers, monomer **3a** and dimer **3b**. In other cases, the equilibria between **1a**, **1b** or **2a**, **2b** could be studied by NMR spectroscopy and so clearly established. The ability to form such facile monomer−dimer isomerization when the stereochemistry at the metal is either *cis* or *trans* appears to be unique to the ligand dpipa. Often chelate complexes are relatively inert, but the very large ring sizes formed by chelating or bridging dpipa (14- or 28-membered rings respectively) evidently confer little kinetic inertness or thermodynamic stability toward reversible dissociation of the metal−phosphorus bonds. Facile monomer−dimer equilibria are more commonly observed for short chain diphosphine ligands such as *bis*(diphenylphosphino)methane, dppm, for which the 4-membered chelate is strained. For example, there is a facile equilibrium between [$PtMe_2$(dppm)] and [$Pt_2Me_4(\mu$-dppm)$_2$].[13] There is potential for applications of the ligand dpipa in catalysis or host−guest chemistry based on its unique coordination chemistry

EXPERIMENTAL SECTION

Reagents and General Procedures. All reactions were carried out in 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 (SPS). 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. ^{1}H chemical shifts are reported relative to TMS, and ^{31}P chemical shifts relative to 85% H_3PO_4. Mass spectrometric analysis was carried out using an electrospray PE-Sciex Mass Spectrometer (ESI-MS) coupled with TOF detector.

X-ray Crystallography.[19] 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 with ω and φ scans using a Bruker Smart Apex II diffractometer and Bruker SMART software or Nonius Kappa-CCD diffractometer with COLLECT software, using graphite-monochromated $Mo_{K\alpha}$ radiation(λ = 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 and refined by full-matrix least−square techniques against F^2 using SHELXL. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined using the riding model. Crystal data are summarized in the Supporting Information, cif files. Unusual features are as follows. The structures **1b**, **2b**, and **7** contained regions of disordered solvent molecule(s) which eluded sensible modeling. The data and model were subjected to the SQUEEZE procedure as implemented in PLATON.[19] Complex **1b**: there was a chloroform molecule and an unidentifiable solvent molecule in the lattice. Complex **3b**: there was a chloroform and a dichloromethane molecule for each pair of dimers. Complex **4**: the crystal was nonmerohedrally twinned and the twinning was successfully treated. Complex **7**: there was disorder of the CH_3/Br atoms over two sites, and the occupancies were refined with free variables, and there were large voids containing disordered solvent.

1,3-C_6H_4(CONHCH$_2$CH$_2$PPh$_2$)$_2$, dpipa. To a solution of 2-(diphenylphosphino)ethylamine (4.0 g, 17.44 mmol) and triethylamine (10 mL) in $CHCl_3$ (20 mL) was added dropwise a solution of isophthaloyl dichloride (1.771 g, 8.723 mmol) in CH_2Cl_2 (20 mL). After stirring for 12 h, the reaction mixture was washed with water (3 × 30 mL), the organic layer was separated, dried over $MgSO_4$, then filtered, and the solvent was evaporated under vacuum to give an oily product. The product was purified by flash chromatography using 70:30 ethyl acetate and hexane as eluent. The solvent was evaporated to give dpipa as a white solid, which was dried under vacuum. Yield: 4.5 g, 88%. NMR in $CDCl_3$: δ(^{1}H) = 7.95 [s, 1H, C_6H_4]; 7.72 [dd, 2H, J = 8, 2 Hz, C_6H_4]; 7.26−7.5 [m, 21H, Ph and C_6H_4]; 6.35 [t, 2H, J = 6 Hz, NH]; 3.65 [m, 4H, CH_2N]; 2.44 [t, 4H, J = 7 Hz, CH_2P]; δ(^{31}P) = −21.05 [s]. Anal. Calcd. for $C_{36}H_{34}N_2O_2P_2$: C, 73.46; H, 5.82; N, 4.76. Found: C, 73.44; H, 5.89; N, 4.74%.

*[Au(dpipa)]Cl, **1a**, and [Au$_2$(μ-dpipa)$_2$]Cl$_2$, **1b**.* A solution of [$AuCl(SMe_2)$] (0.05 g, 0.1697 mmol) in CH_2Cl_2 (5 mL) was added to a stirring solution of dpipa (0.099 g, 0.1697 mmol) in CH_2Cl_2 (10 mL). The resulting solution was allowed to stir overnight, then the solvent was evaporated under vacuum to give the product as a white solid, which was collected, washed with ether (3 × 5 mL) and pentane (3 × 5 mL) and then dried under high vacuum. Yield: 0.1 g, 72%. NMR in $CDCl_3$: **1a**, δ(^{1}H) = 9.35 [m, 2H, NH]; 9.12 [s, 1 H, C_6H_4]; 7.95 [dd, 2H, J = 7, 2 Hz, C_6H_4]; 7.30−7.71 [m, 21H, Ph and C_6H_4]; 3.82 [br, 2H, NCH_2CH_2P]; 3.44−3.68 [m, 4H, NCH_2CH_2P]; 2.96 [br, 2H, NCH_2CH_2P]; δ (^{31}P) = 31.85[s]; **1b**, δ(^{1}H) = 9.18 [m, 4H, NH]; 8.78 [s, 2H, C_6H_4]; 8.02 [dd, 4H, J = 7, 2 Hz, C_6H_4]; 7.30−7.87 [m, 42H, Ph and C_6H_4]; 3.82 [br, 8H, NCH_2]; 3.26 [br, 8H, CH_2P]; δ(^{31}P) = 34.24 [s]. Anal. Calcd. for $C_{72}H_{68}Au_2Cl_2N_4O_4P_4$: C, 52.66; H, 4.17; N, 3.41%. Found: C, 52.59; H, 4.12; N, 3.30%. Single crystals of complex **1b** were grown by slow diffusion of *n*-pentane into a solution of the compound **1a**/**1b** dissolved in dichloromethane.

*[PtCl$_2$(dpipa)], **2a**, and [Pt$_2$Cl$_4$(μ-dpipa)$_2$], **2b**.* To a solution of dpipa (0.10 g, 0.17 mmol) in CH_2Cl_2 (10 mL) was added *cis*/*trans*-[$PtCl_2(SMe_2)_2$] (0.0612 g, 0.170 mmol) in CH_2Cl_2 (10 mL). A white precipitate was formed immediately. After allowing the reaction contents to stir for 6 h, the solvent was decanted and the white solid was washed with ether (3 × 5 mL) and pentane (3 × 5 mL) and then dried under high vacuum. Yield: 0.12 g, 83%. NMR in DMSO-d_6: **2a**, δ(^{1}H) = 8.99 [m, 2H, NH]; 8.49 [s, 1H, C_6H_4]; 8.03 [d, 2H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.19−7.68 [m, 21H, Ph and C_6H_4]; 3.61 [br, 4H, NCH_2]; 2.62 [br, 4H, CH_2P]; δ(^{31}P) = 1.27 [s, $^1J_{PtP}$ = 3608 Hz]. **2b**, δ(^{1}H) = 8.82 [m, 4H, NH]; 8.33 [s, 2H, C_6H_4]; 7.94 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.22−7.68 [m, 42H, Ph and C_6H_4]; 3.61 [br, 8H, NCH_2]; 2.62 [br, 8H, CH_2P]; δ(^{31}P) = 1.58 [s, $^1J_{PtP}$ = 3600 Hz]. Anal. Calcd. for $C_{72}H_{68}Cl_4N_4O_4P_4Pt_2$: C, 50.60; H, 4.01; N, 3.28%. Found: C, 50.40; H, 3.97; N, 3.15%. Single crystals of complex **2b** were grown by slow diffusion of *n*-pentane into a solution of **2a**/**2b** dissolved in a mixture of equal volumes of benzene, DMSO, MeOH, acetone, CH_2Cl_2, and $CHCl_3$.

*[PtMe$_2$(dpipa)], **3a**, and [Pt$_2$Me$_4$(μ-dpipa)$_2$], **3b**.* To a solution of dpipa (0.10 g, 0.17 mmol) in CH_2Cl_2 (10 mL) was added a solution of [$Pt_2Me_4(\mu$-$SMe_2)_2$] (0.0488 g, 0.0849 mmol) in CH_2Cl_2 (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 × 5 mL) and pentane (3 × 5 mL) and then dried under high vacuum. Yield: 0.11 g, 80%. NMR in $CDCl_3$: **3a**, δ(^{1}H) = 8.35 [s, 1H, C_6H_4]; 8.04 [d, 2H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.94 [br s, 2H, NH]; 7.54 [t, 1H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.30−7.35 [m, 20H, Ph]; 3.74 [br, 4H, NCH_2]; 2.48 [br, 4H, CH_2P]; 0.56 [m, 6H, $PtCH_3$]; δ (^{31}P) = 11.23 [s, $^1J_{PtP}$ = 1815 Hz]. **3b**, δ(^{1}H) = 8.35 [s, 2H, C_6H_4]; 8.04 [d, 4 H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.98 [br, 4H, NH]; 7.54 [t, 2H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.30−7.35 [m, 40H, Ph]; 3.60 [br, 8H, NCH_2]; 2.24 [br, 8H, CH_2P]; 0.50 [m, 12H, $PtCH_3$]; δ (^{31}P) = 10.89 [s, $^1J_{PtP}$ = 1800 Hz]. Anal. Calcd. for $C_{76}H_{80}N_4O_4P_4Pt_2$: C, 56.09; H, 4.95; N, 3.44%. Found: C, 55.94; H, 4.92; N, 3.27%. Single crystals of both complexes **3a** and **3b** were grown by slow diffusion of *n*-pentane into a solution of the compound dissolved in a mixture of equal volumes of benzene, dimethylsulfoxide, methanol, acetone, dichloromethane, and chloroform. NMR of **3b**′ in CD_2Cl_2 at −20 °C: δ(^{1}H) = 10.13, 9.32 [each s, 2H, NH]; 6.4−9.1 [48H, Ph and C_6H_4]; 1.8−4.1 [br, 16H, CH_2]; 0.67 [m, 6H, ^2J(PtH) 64 Hz, ^3J(PH) 6 Hz, $PtCH_3$]; 0.20 [m, 6H, ^2J(PtH) 68 Hz, ^3J(PH) 8 Hz, $PtCH_3$]; δ (^{31}P) = 11.6 [d, ^1J(PtP) 1920 Hz, ^2J(PP) 15 Hz, PtP]; 8.4 [d, ^1J(PtP) 1590 Hz, ^2J(PP) 15 Hz, PtP].

*[PtIMe(dpipa)], **4**.* To a stirred solution of complexes **3a**/**3b** (0.10 g, 0.123 mmol) in dry CH_2Cl_2 (15 mL) was added a solution of MeI (100 μL, 1.61 mmol) in CH_2Cl_2 (5 mL). After 18 h, the solvent was removed under vacuum, and a white solid was obtained which was washed with pentane (3 × 5 mL) and ether (3 × 5 mL) and then dried under high vacuum. Yield: 0.105 g, 92%. NMR in $CDCl_3$: δ(^{1}H) = 8.17 [d, 2H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.75 [s, 1H, C_6H_4]; 7.65−7.27

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[m, 21H, Ph and C_6H_4]; 7.34 [m, 2H, NH]; 4.15 [m, 4H, NCH_2]; 3.31 [m, 4H, CH_2P]; 0.15 [t, $^2J_{PtH}$ = 80 Hz, $^3J_{PH}$ = 7 Hz, 3H, PtMe]; $\delta(^{31}P)$ = 16.12 [s, $^1J_{PPt}$ = 2946 Hz]. Anal. Calcd. for $C_{37}H_{37}IN_2O_2P_2Pt$: C, 48.01; H, 4.03; N, 3.03%. Found: C, 47.84; H, 4.08; N, 2.88%. Single crystals of complex **4** were grown by slow diffusion of *n*-pentane into a solution of the compound dissolved in a mixture of equal volumes of benzene, acetone, methanol, dichloromethane, tetrahydrofuran, and chloroform.

*[$Pt_2Br_4Me_4(dpipa)_2$], **6**, and[$Pt_2Br_5Me_3(dpipa)_2$], **7**.* To a stirred solution of **3a**/**3b** (0.10 g, 0.123 mmol) in dry CH_2Cl_2 (15 mL) was added a solution of Br_2 (30 μL, 0.54 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 12 h, then the orange precipitate which formed was separated, washed with pentane (3 × 5 mL) and ether (3 × 5 mL) and dried under high vacuum. Yield: 0.105 g. NMR in DMSO-d_6: **6**, $\delta(^1H)$ = 8.78 [br, 4H, NH]; 8.23 [s, 2H, C_6H_4]; 8.0−7.2 [m, 46H, Ph and C_6H_4]; 3.57 [br, 8H, NCH_2]; 2.94 [br, 8H, CH_2P]; 0.55 [br, 12H, $^2J_{PtH}$ = 65 Hz, $PtMe_2Br_2$]; $\delta(^{31}P)$ = −5.59 [s, $^1J_{PPt}$ = 2050 Hz]. **7**, $\delta(^1H)$ = 8.80 [br, 2H, NH]; 8.63 [br, 2H, NH]; 8.15 [s, 2H, C_6H_4]; 8.0−7.2 [m, 46H, Ph and C_6H_4]; 3.67 [br, 4H, NCH_2]; 3.42 [br, 4H, NCH_2]; 2.89 [br, 4H, CH_2P]; 2.66 [br, 4H, CH_2P]; 1.08 [br, 3H, $^2J_{PtH}$ = 68 Hz $PtMeBr_3$]; 0.59 [t, 6H, $^3J_{PH}$ = 5 Hz, $^2J_{PtH}$ = 65 Hz, $PtMe_2Br_2$]; $\delta(^{31}P)$ = −5.59 [s, $^1J_{PPt}$ = 2050 Hz]. Single crystals of complex **7** were grown by slow diffusion of *n*-pentane into a solution of the compound dissolved in a mixture of equal volumes of benzene, dimethylsulfoxide, methanol, acetone, dichloromethane, and chloroform. Anal. Calcd. for $C_{75}H_{77}Br_5N_4O_4P_4Pt_2$: C, 44.77; H, 3.86; N, 2.78%. Found: C, 44.54; H, 3.90; N, 2.59%.

From the in situ formation of **5a**/**5b** in $CDCl_3$: $\delta(^1H)$ = 8.68 [br, 4H, NH]; 8.1−6.9 [m, 48H, Ph and C_6H_4]; 3.75 [br, 8H, CH_2P]; 3.60 [br, 8H, NCH_2]; 0.66 [br m, 12H, $^3J_{PH}$ + $^3J_{P'H}$ = 4 Hz, $^2J_{PtH}$ = 65 Hz, $PtMe_2Br_2$]; $\delta(^{31}P)$ = −13.6 [s, $^1J_{PtP}$ = 1585 Hz].

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the X-ray data collection, solution, and refinement in electronic CIF form. This material is 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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