

# Organoplatinum(IV) Complexes with Amide Groups: Supramolecular Structure as a Function of Ligand Flexibility

Richard H. W. Au,<sup>[a]</sup> Michael C. Jennings,<sup>[a]</sup> and Richard J. Puddephatt<sup>\*[a]</sup>

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The oxidative addition of the benzyl bromide derivative 4-BrCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>x</sub>C(=O)NH(CH<sub>2</sub>)<sub>y</sub>-4-C<sub>6</sub>H<sub>4</sub>-tBu (**A**),  $x = y = 0$ ; (**B**),  $x = 0$ ,  $y = 1$ ; (**C**),  $x = 1$ ,  $y = 0$ ; (**D**),  $x = y = 1$ , to the dimethylplatinum(II) complex [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)] (**1**), bu<sub>2</sub>bipy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, gave the corresponding amide-substituted benzylplatinum(IV) complexes of the formula [PtBrMe<sub>2</sub>(4-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>x</sub>C(=O)NH(CH<sub>2</sub>)<sub>y</sub>-4-C<sub>6</sub>H<sub>4</sub>-tBu)(bu<sub>2</sub>bipy)], bu<sub>2</sub>bipy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, **2–5**. In the solid state, the complexes **2–5** undergo self-assembly to give the supramolecular polymers **2–4** or the dimers **5**. Intermolecular N-H...Br-Pt hydrogen bonds are fa-

vored over the typical NH...O=C hydrogen bonds found in organic amides. The carbonyl group may be hydrogen-bonded to solvent or not involved in hydrogen bonding. The structures are dependent on the size and flexibility of the amide-substituted benzyl group. In solution, the complexes **3–5** exhibited an equilibrium between the neutral complexes and the bromo-bridged, ionic binuclear complexes [(μ-Br){PtBrMe<sub>2</sub>(4-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>x</sub>C(=O)NH(CH<sub>2</sub>)<sub>y</sub>-4-C<sub>6</sub>H<sub>4</sub>-tBu)(bu<sub>2</sub>bipy)}<sub>2</sub>]<sup>+</sup>Br<sup>-</sup>.

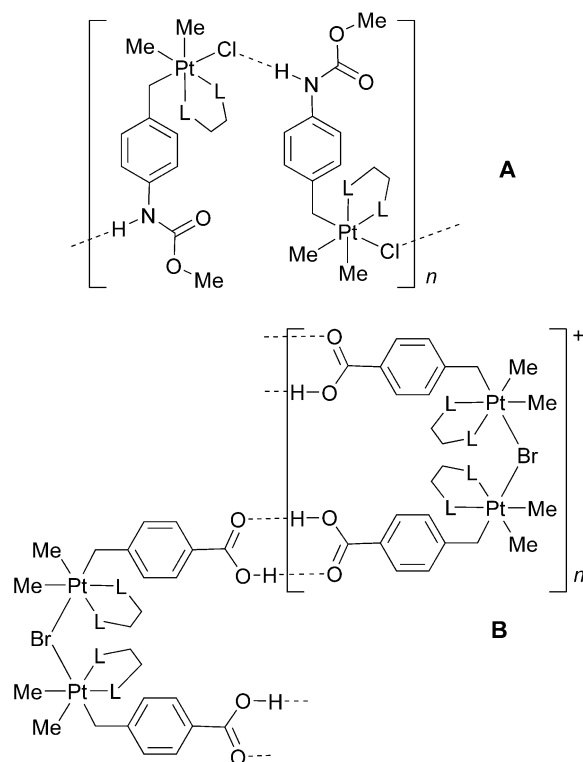
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## Introduction

Coordination complexes or organometallic compounds which contain acid amide groups as substituents can give interesting structures by self-assembly through hydrogen bonding.<sup>[1–3]</sup> They can also act as selective hosts, either by hydrogen bonding of the NH group to an anion or nucleophile or by coordination of the carbonyl group to a cation or electrophile.<sup>[1,4,5]</sup> In developing the field of supramolecular organometallic chemistry, the use of hydrogen bonding has found only limited use because many organometallic compounds are incompatible with protic reagents.<sup>[1]</sup> However, there have been significant advances, and it is known that the classic hydrogen bonding in amides through NH...O=C interactions may be in competition with other types such as M–X...H–N, where M = metal and X = Cl, Br or I.<sup>[1,6]</sup> Alkyl and aryl complexes of platinum have much promise in supramolecular chemistry, because the Pt–C σ-bond is relatively unreactive towards protic reagents.<sup>[7–10]</sup> The alkylplatinum(II) complexes do react with acids to give alkanes but they are tolerant to alcohols and amines, while the alkylplatinum(IV) complexes are typically inert towards cleavage of the Pt–C bonds under mild conditions.<sup>[9]</sup> Platinum complexes may have biological activity, so hydrogen bonding involving the functional groups present in proteins and nucleic acids has broad relevance.<sup>[8a]</sup>

Two supramolecular polymers relevant to the present work are shown in Scheme 1. In the neutral complex **A**, The

NH group of a methylcarbamate unit forms a hydrogen bond NH...ClPt to the Pt–Cl group of a neighboring molecule, in preference to the alternative NH...O=C hydrogen



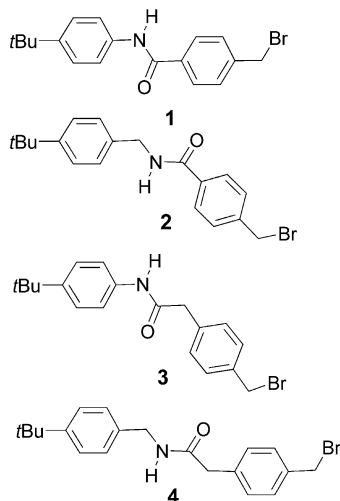
Scheme 1. Two supramolecular organoplatinum(IV) polymers (LL = bu<sub>2</sub>bipy).

[a] Department of Chemistry, University of Western Ontario, London, N6A 5B7, Canada  
Fax: +1-519-661-3022  
E-mail: pudd@uwo.ca

bond motif, and this leads to the formation of the supramolecular polymer.<sup>[10a]</sup> In the binuclear bromo-bridged complex **B**, the hydrogen bonding occurs by the common complementary hydrogen bonding between carboxylic acid groups and gives a different form of supramolecular polymer.<sup>[10d]</sup> The present work describes the syntheses and structures of some related complexes containing acid amide groups as substituents of a benzylplatinum(IV) unit, in complexes of the type  $[\text{PtBrMe}_2(4\text{-CH}_2\text{C}_6\text{H}_4\text{R})(\text{bu}_2\text{bipy})]$ , where  $\text{bu}_2\text{bipy} = 4,4'\text{-di-}t\text{-butyl-2,2'-bipyridine}$ , and focuses on the supramolecular structure as a function of the size and flexibility of the amide-containing group **R**.

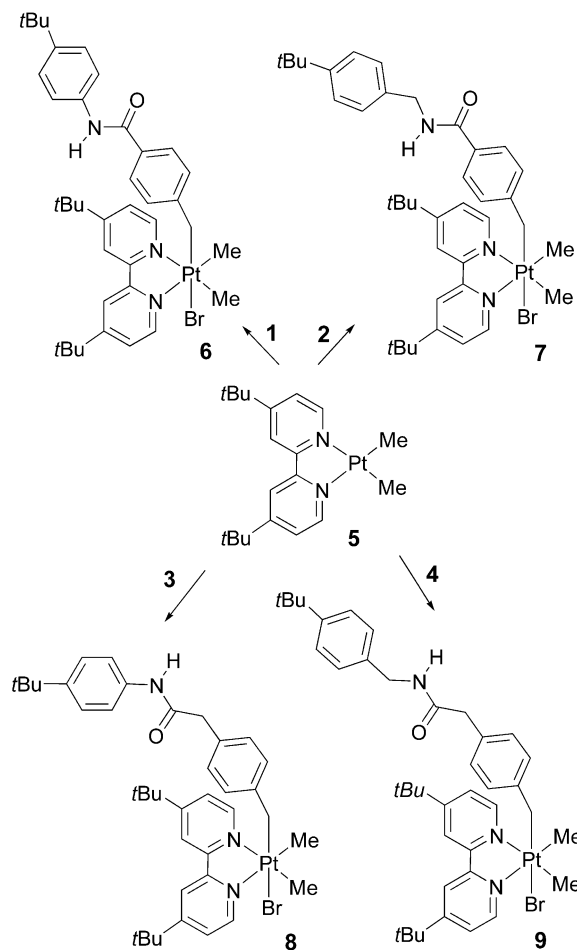
## Results and Discussion

The strategy used to incorporate amide groups into platinum(IV) complexes was to use reagents which contain both a bromobenzyl group and an acid amide group. The bromobenzyl group is used to oxidatively add to a suitable dimethylplatinum(II) complex,<sup>[11]</sup> and the amide group is then available for self-assembly of the product benzylplatinum(IV) complex. Many amides have low solubility in common organic solvents as a result of strong intermolecular hydrogen bonding, and dissolution often requires a polar aprotic solvent or a mixture of an alcohol and a chlorinated solvent. These solvents are able to break the intermolecular hydrogen bonds from the amide functionality.<sup>[12,13]</sup> The reagents **1–4** (Scheme 2) were designed to contain both bulky *tert*-butylphenyl groups and, in the cases of **2–4**, one (**2**, **3**) or two (**4**) additional methylene groups to add flexibility. The addition of bulky and flexible groups is often used to increase solubility of macromolecules.<sup>[14]</sup> The reagents **1–4** were prepared by using known coupling procedures and they were indeed found to have sufficient solubility in solvents such as acetone or dichloromethane to allow easy manipulation and characterization (see experimental section). To further enhance the solubility of the coordinated organoplatinum(IV) complex, the ligand  $\text{bu}_2\text{bipy}$  was used as the supporting ligand in the reagent  $[\text{PtMe}_2(\text{bu}_2\text{bipy})]$ ; **5**, instead of the parent 2,2'-bipyridine.<sup>[15]</sup>



Scheme 2. Bromomethyl amide reagents **1–4**.

The reagents **1–4** reacted easily with  $[\text{PtMe}_2(\text{bu}_2\text{bipy})]$  (**5**), to give the corresponding complexes  $[\text{PtBrMe}_2(4\text{-CH}_2\text{C}_6\text{H}_4(\text{CH}_2)_x\text{C(=O)NH}(\text{CH}_2)_y\text{-4-C}_6\text{H}_4\text{-}t\text{Bu})(\text{bu}_2\text{bipy})]$  (**6**),  $x = y = 0$ ; (**7**),  $x = 0$ ,  $y = 1$ ; (**8**),  $x = 1$ ,  $y = 0$ ; (**9**),  $x = y = 1$ , as shown in Scheme 3. The length and flexibility of the added alkyl group follow the series **6** < **7**, **8** < **9**, and the solubility in organic solvents followed the same trend.



Scheme 3. Synthesis of platinum(IV) complexes **6–9**.

The characterization of complex **6** in solution was straightforward. The  $^1\text{H}$  NMR spectrum contained a single methylplatinum resonance at  $\delta = 1.46$  ppm [ $s$ ,  $^2J_{\text{Pt,H}} = 69$  Hz, 6 H] and a single  $\text{PtCH}_2$  resonance at  $\delta = 2.87$  ppm [ $s$ ,  $^2J_{\text{Pt,H}} = 96$  Hz, 2 H]; as expected for the product of *trans* oxidative addition.<sup>[10]</sup> None of the product of *cis* oxidative addition was detected. Complex **6** has effective  $C_s$  symmetry, with the plane of symmetry containing the  $\text{BrPt}$  axis and bisecting the  $\text{PtMe}_2$  and  $\text{bu}_2\text{bipy}$  groups.

The structure of complex **6** was confirmed crystallographically and is shown in Figure 1. It is typical of the structures of complexes **6–9**.

The platinum(IV) center has the expected octahedral stereochemistry, and the benzyl  $\text{C}_6\text{H}_4$  group is  $\pi$ -stacked with one of the pyridyl groups, while avoiding steric effects of the bulky *tert*-butyl substituent. The amide group has the expected *anti* conformation of the carbonyl and NH units.

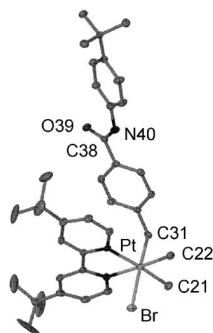


Figure 1. Molecular structure of complex **6**. Selected bond lengths [Å]: Pt–C(21) 2.050(6), Pt–C(22) 2.054(6), Pt–C(31) 2.066(6), Pt–N(1) 2.167(4), Pt–N(12) 2.151(4), Pt–Br 2.5912(6).

The  $C_6H_4$  units of the benzyl and  $tBuC_6H_4$  units are twisted by  $24^\circ$  and  $10^\circ$ , respectively out of the amide plane, allowing conjugation to occur between these groups.

Complex **6** crystallizes as a methanol solvate  $6 \cdot 1.3MeOH$ . The methanol at full occupancy is hydrogen-bonded to the carbonyl oxygen of the amide group [O(39)⋯O(61) 2.783(6) Å]; as shown in Figure 2. The NH group acts as a hydrogen-bond donor to the bromoplatinum group of a neighboring molecule to form an intermolecular N–H⋯Br–Pt structural motif, with N⋯Br 3.552(5) Å (Figure 2). The normal range for N–H⋯Br hydrogen bonding interactions is N⋯Br 3.12–3.69 Å,<sup>[16]</sup> and the value for complex **6** indicates that the hydrogen bond is relatively weak. Propagation of the NH⋯Br interactions leads to formation of the zig-zag supramolecular polymer shown in Figure 2.

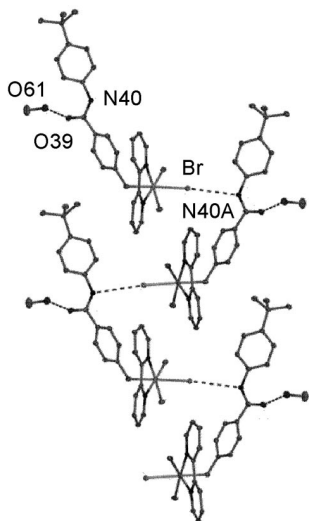


Figure 2. The supramolecular polymeric structure of complex **6**·MeOH. The *tert*-butyl groups of  $bu_2bipy$  are omitted for clarity. Hydrogen bond lengths [Å]: N(40A)⋯Br 3.552(5), O(39)⋯O(61) 2.783(6). Symmetry transformations for neighboring molecules:  $x, 1/2 - y, -1/2 + z$ ;  $x, 1/2 - y, 1/2 + z$ .

The molecular structure of complex **7** is shown in Figure 3. This complex has been crystallized as the solvates  $7 \cdot H_2O \cdot 0.5iPr_2O$  and  $7 \cdot 2C_2H_4Cl_2$ , and Figure 3 shows the

first of these. The molecular structure of the dichloroethane solvate is similar and is not shown. Both solvates form supramolecular polymers through NH⋯BrPt hydrogen bonding, as shown in Figure 4, but the detailed supramolecular structures are different. In the solvate  $7 \cdot H_2O \cdot 0.5iPr_2O$ , neighboring molecules are rotated by  $180^\circ$  with respect to each other and a zig-zag polymer is formed, similar to complex **6**. However, in the solvate  $7 \cdot 2C_2H_4Cl_2$ , neighboring molecules are related by a simple translation and so a more linear polymer is formed (Figure 4). In the solvate  $7 \cdot H_2O \cdot 0.5iPr_2O$ , the bromo ligand is hydrogen-bonded to the water solvate as well as to the NH group of a neighboring molecule. Also, the diisopropyl ether solvent, at 50% occupancy, is hydrogen-bonded to the water solvate (Figure 4).

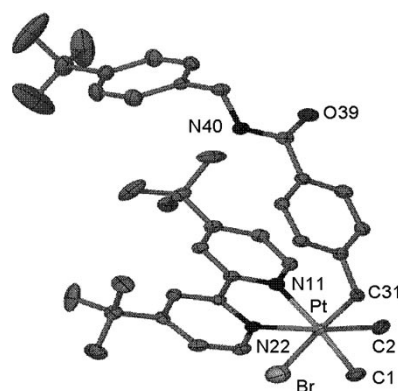


Figure 3. Molecular structure of complex **7** in the solvate  $8 \cdot H_2O \cdot 0.5iPr_2O$ . Selected bond lengths [Å]: Pt–C(1) 2.05(1), Pt–C(2) 2.04(1), Pt–C(31) 2.11(1), Pt–N(11) 2.151(7), Pt–N(22) 2.158(7), Pt–Br = 2.572(2).

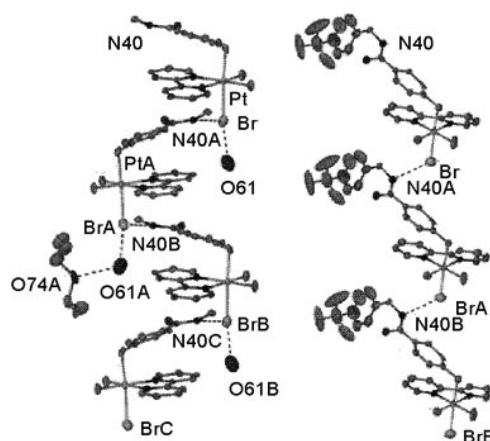


Figure 4. The supramolecular polymeric structures of complex **7**. Left, the solvate  $7 \cdot H_2O \cdot 0.5iPr_2O$  with *tBu* and *tBuC*<sub>6</sub>H<sub>4</sub> groups omitted for clarity. H-bond lengths [Å]: O(61)⋯O(74) 2.98(2), O(61)⋯Br 2.69(1), N(40A)⋯Br 3.384(7). Symmetry transformations for neighboring molecules:  $3/2 - x, 1/2 + y, 1/2 - z$ ;  $3/2 - x, -1/2 + y, 1/2 - z$ . Right, the solvate  $7 \cdot 2C_2H_4Cl_2$ . The *tert*-butyl groups of  $bu_2bipy$  ligands are omitted for clarity. Hydrogen bond length [Å]: N(40A)⋯Br 3.36(1). Symmetry transformations for neighboring molecules:  $x, y + 1, z$ ;  $x, y - 1, z$ .

The structure of complex **8** is shown in Figure 5. The main difference in molecular structure compared to complexes **6** and **7** arises because the carbonyl group is not conjugated to the benzylic C<sub>6</sub>H<sub>4</sub> group, and so is free to rotate. Now the benzyl group  $\pi$ -stacks over the center of the bu<sub>2</sub>bipy ligand, and the amide group lies roughly orthogonal to the C<sub>6</sub>H<sub>4</sub> group. The carbonyl oxygen atom O(40) lies close to intramolecular aromatic C–H groups and forms three weak C–H $\cdots$ O=C hydrogen bonds.<sup>[13]</sup> The amide NH group is directed away from the bu<sub>2</sub>bipy ligand, and this conformation of the amide group is favorable for intermolecular hydrogen bond formation by the NH group, which again occurs through NH $\cdots$ BrPt bond formation. The resulting supramolecular structure is a polymer and neighboring molecules are mirror images. The distance N $\cdots$ Br 3.311(9) Å is somewhat shorter than in complexes **6** and **7**.

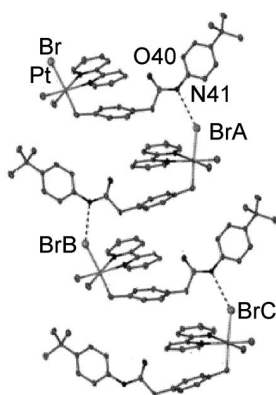


Figure 5. The supramolecular polymeric structure of complex **8**, with *tert*-butyl groups of the bu<sub>2</sub>bipy ligands omitted for clarity. Selected bond lengths [Å]: Pt–C(1) 2.04(1), Pt–C(2) 2.06(1), Pt–C(31) 2.10(1), Pt–N(11) 2.167(8), Pt–N(22) 2.173(9), Pt–Br 2.505(2). Hydrogen bond length [Å]: N(41) $\cdots$ Br(A) 3.311(9). Symmetry transformations for neighboring molecules:  $x + 1, 1/2 + y, 1/2 - z$ ;  $x + 1, -1/2 + y, 1/2 - z$ .

The complex **9** has the longest, most flexible alkyl chain. Its structure is illustrated in Figure 6, and shows the presence of two independent, but similar, molecules in the unit cell. The flexibility leads to minor, unresolved disorder and the atoms are not as precisely located as in the other structures. Now neither C<sub>6</sub>H<sub>4</sub> group is conjugated to the amide and, in contrast to complex **8**, the conformation has the benzyl group  $\pi$ -stacked with just one pyridyl group and with the carbonyl oxygen atom not forming intramolecular CH $\cdots$ O=C hydrogen bonds.

Each independent molecule [containing Pt(1) or Pt(2)] forms a dimer with its equivalent molecule related by inversion. The dimer of molecules containing Pt(2) is shown in Figure 7. The dimers are held together by complementary NH $\cdots$ BrPt hydrogen bonds with N $\cdots$ Br 3.45(3) Å. The way in which the conformation of the amide group adapts to form either a polymer or dimer can be seen by comparison of Figures 5 and 7. The dimer structure is not favoured for complex **8**, probably because conjugation of the NHC<sub>6</sub>H<sub>4</sub> group leads to a preferred conformation with roughly co-

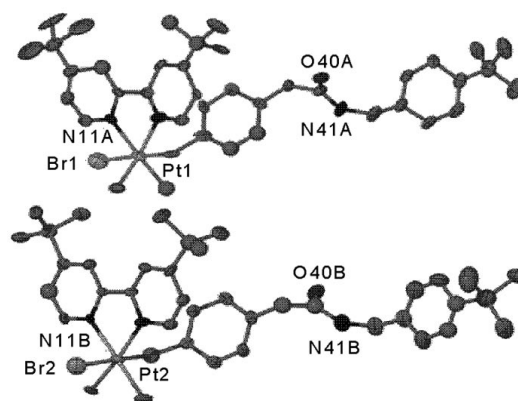


Figure 6. Molecular structure of complex **9**, showing the two independent molecules in the asymmetric unit. Selected bond lengths [Å]: Pt(1)–Br(1) 2.558(5); Pt(2)–Br(2) 2.547(6).

planar C<sub>6</sub>H<sub>4</sub>NHCO atoms and that would lead to steric repulsion between the *ortho* hydrogen atom and bromide in a structure analogous to **9**. The presence of the extra CH<sub>2</sub> group in **9**, although it is present only on the periphery, allows the dimer formation.

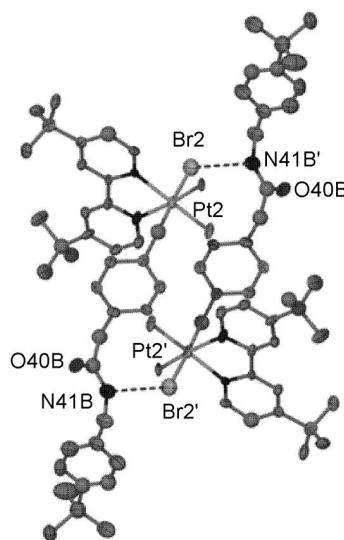


Figure 7. Structure of the dimer of molecules containing Pt(2) in complex **9**. H-bond length [Å]: N(41B) $\cdots$ Br(2)' 3.45(3). Symmetry transformation for neighboring molecules:  $-x, 1 - y, 2 - z$ . The molecules containing Pt(1) form a similar dimer with N(41A) $\cdots$ Br(1)' 3.44(3) Å, related by symmetry transformation  $1 - x, 1 - y, 1 - z$ .

The way in which the dimers are arranged with respect to each other is shown in Figure 8. The orientation of the carbonyl group with respect to a bu<sub>2</sub>bipy ligand is remarkably similar in complexes **8** and **9**, as seen by comparison of Figure 5 and Figure 8, but in complex **9** the interaction is intermolecular whereas in **8** it is intramolecular. The effect in **9** is to form a loose supramolecular polymer of dimers.



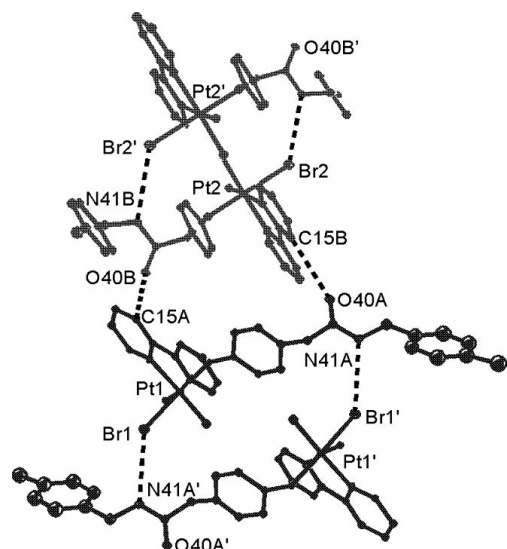
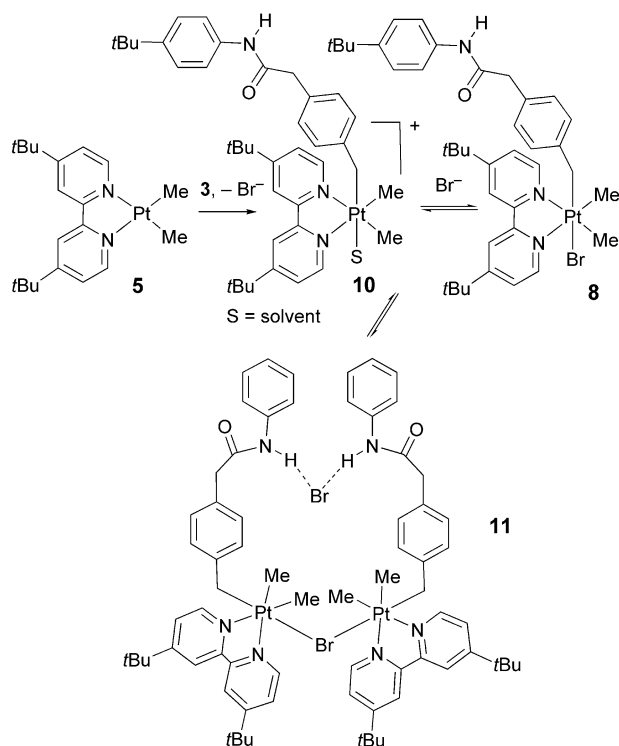
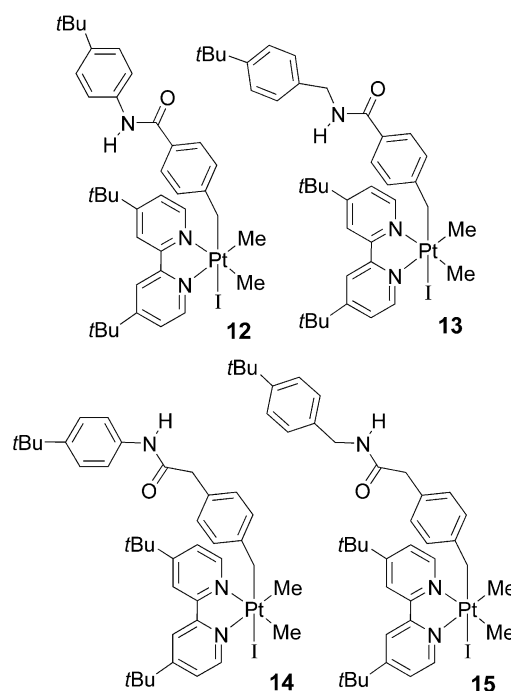


Figure 8. The loose polymer of dimers in the structure of complex **9**, formed through weak  $\text{CH}\cdots\text{O}=\text{C}$  hydrogen bonding with shortest contact  $\text{O}(40\text{A})\cdots\text{C}(15\text{B})$  3.34 Å.

An unexpected feature in the  $^1\text{H}$  NMR spectra of complexes **7–9**, was the presence of two sets of resonances of unequal intensity, with each displaying the peaks expected for a product of *trans* oxidative addition (effective  $C_s$  symmetry). The ESI-MS of the solution of complex **8** in acetone contained key peaks assigned to  $[\text{PtMe}_2\text{R}(\text{bu}_2\text{bipy})(\text{acetone})]^+$  at  $m/z = 831$  and to  $[\{\text{PtMe}_2(\text{bu}_2\text{bipy})\text{R}\}_2(\mu\text{-Br})]^+$  at  $m/z = 1625$  ( $\text{R} = \text{CH}_2\text{-4-C}_6\text{H}_4\text{CH}_2\text{CONH-4-C}_6\text{H}_4\text{-tBu}$ ). On this basis, it is suggested that the second complex present in solution is complex **11**, which can be formed reversibly by dissociation of bromide from complex **8** to give **10**, followed by combination of **10** and **8** with loss of acetone as shown in Scheme 4. There are precedents for formation of bridging halide complexes on oxidative addition of alkyl halides to platinum(II), but the binuclear complexes are not usually thermodynamically stable unless the precursor is a bridged binuclear platinum(II) complex.<sup>[17]</sup> With mononuclear precursor complexes such as **5** it is possible to form the  $\mu$ -bromo complexes, such as **B** in Scheme 1, but a bromide abstraction step is needed. We suggest that the reversible bromide abstraction from complex **8** is aided kinetically by formation of  $\text{NH}\cdots\text{BrPt}$  hydrogen bonds in solution, and favoured thermodynamically by hydrogen bonding of the dissociated bromide by the two NH groups, as shown in **11**, Scheme 4.<sup>[4]</sup> This chelation of the bromide ion must overcome the unfavourable entropy effect of forming the binuclear complex **11**. Note that no binuclear complex was detected in solutions of complex **6**, which contains the most rigid benzyl-amide group. In terms of Pearson's Hard-Soft Acid-Base theory, the hydrogen-bond donor is a hard acid whereas platinum is a soft acid. The ionization should therefore be relatively less favourable for the softer iodide compared to bromide. The iodide complexes **12–15** (Scheme 5) were prepared by halide exchange from the corresponding bromoplatinum complexes **6–9**. In solution, they all existed as a single form as determined by their  $^1\text{H}$  NMR spectra, in accord with expectation.



Scheme 4. The proposed equilibrium present in solutions of complex **8** ( $\text{S} = \text{acetone}$ ).



Scheme 5. The iodide complexes **12–15**.

## Conclusions

This study of the supramolecular chemistry of organo-platinum(IV) complexes containing amide groups has established several principles. There is a general preference for  $\text{NH}\cdots\text{Br-Pt}$  over  $\text{NH}\cdots\text{O}=\text{C}$  hydrogen bonding, so the

analogy to organic amides, in which  $\text{NH}\cdots\text{O}=\text{C}$  bonding dominates, is limited. The inorganic component plays a pivotal role. In most of the complexes studied, the hydrogen bonding leads to formation of supramolecular polymers but, in one case, a dimer is formed. The nature of the hydrogen bonding, and hence the supramolecular structure, depends on the length and flexibility of the alkyl group containing the amide functionality. When an aryl group is adjacent to either the carbonyl or the amine group, it tends to lie very roughly coplanar with the amide group and this limits the hydrogen bonding. Introduction of a methylene group between the aryl and amide units both increases the length of the alkyl group and increases the flexibility. Both features are important and only the complex with the longest and most flexible alkyl group forms a dimer by complementary hydrogen bonding. The involvement of solvent molecules in the crystalline products is common; it may simply be present to fill cavities in the lattice or it may play a more significant role by taking part in hydrogen bonding. Finally, the hydrogen bonding is shown to be important in aiding bromide ligand dissociation.

## Experimental Section

**General:** All reactions were performed under nitrogen using standard Schlenk techniques.  $[\text{PtMe}_2(\text{bu}_2\text{bipy})]$  was prepared using the literature method.<sup>[15]</sup> 1D and 2D  $^1\text{H}$  NMR spectra were recorded with a Varian Mercury 400 NMR or a Varian Inova 400 NMR spectrometer at room temperature unless specified otherwise. Mass spectra were recorded with an Electrospray PE-Sciex API 365 spectrometer or a Micromass LCT spectrometer. Exact molecular masses were determined by using a Finnigan MAT 8400 mass spectrometer.

**$\text{BrCH}_2\text{-4-C}_6\text{H}_4\text{CONH-4-C}_6\text{H}_4\text{-}t\text{Bu}$  (1):** 4-(Bromomethyl)benzoyl bromide (560 mg, 2.01 mmol) was dissolved in dry THF (6 mL), and the solution was cooled to  $0^\circ\text{C}$ . Triethylamine (150 mg, 1.46 mmol) and 4-*tert*-butylaniline (220 mg, 1.46 mmol) in dry THF (6 mL) were added dropwise to the solution over 15 min. The reaction mixture was warmed to ambient temperature and stirred for 2 h. The product precipitated out from the solution as a white solid and was filtered and washed with THF, 1 M HCl, saturated aqueous  $\text{NaHCO}_3$ ,  $\text{H}_2\text{O}$  and heptane to give a 95% yield (480 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.32 (s, 9 H, *t*Bu); 4.52 (s, 2 H,  $\text{BrCH}_2$ ); 7.40 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.51 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.55 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.74 (br. s, 1 H, NH), 7.84 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ) ppm. MS:  $m/z$  calcd: 345.0728; found 345.0726.

**$\text{BrCH}_2\text{-4-C}_6\text{H}_4\text{CONHCH}_2\text{-4-C}_6\text{H}_4\text{-}t\text{Bu}$  (2):** This was prepared similarly from 4-(bromomethyl)benzoyl bromide (560 mg, 2.01 mmol), triethylamine (150 mg, 1.46 mmol) and 4-*tert*-butylbenzylamine (220 mg, 1.46 mmol). A white solid was produced. Yield 97% (510 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.32 (s, 9 H, *t*Bu), 4.49 (s, 2 H,  $\text{BrCH}_2$ ), 4.61 (d,  $^3J_{\text{H,H}} = 5$  Hz, 2 H,  $\text{NCH}_2$ ), 6.33 (br. s, 1 H, NH), 7.29 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.39 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.45 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.84 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ) ppm. MS:  $m/z$  calcd: 359.0885, found 359.0880.

**$\text{BrCH}_2\text{-4-C}_6\text{H}_4\text{CH}_2\text{CONH-4-C}_6\text{H}_4\text{-}t\text{Bu}$  (3):** 4-(Bromomethyl)phenylacetic acid (540 mg, 2.34 mmol) was dissolved in 1:1 DMF/ $\text{CH}_2\text{Cl}_2$  (6 mL), and the solution was cooled to  $0^\circ\text{C}$ . 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 450 mg,

2.34 mmol) was added, and the reaction mixture was stirred for 10 min. A solution of 4-*tert*-butylaniline (350 mg, 2.34 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (5 mL) was then added dropwise to the mixture over 15 min. The reaction mixture was warmed to ambient temperature, stirred for 1 h, and then diluted with EtOAc (25 mL) and washed with 1 M HCl (25 mL), saturated aqueous  $\text{NaHCO}_3$  (25 mL) and brine (25 mL). The organic layer was dried with  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. Recrystallization from EtOAc/heptane gave a light brown crystalline solid in 45% yield (380 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.28 (s, 9 H, *t*Bu), 3.73 (s, 2 H,  $\text{O}=\text{CCH}_2$ ), 4.50 (s, 2 H,  $\text{BrCH}_2$ ), 6.98 (br. s, 1 H, NH), 7.32 (m, 6 H,  $\text{C}_6\text{H}_4$ ), 7.42 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ) ppm. MS:  $m/z$  calcd. 359.0885; found 359.0880.

**$\text{BrCH}_2\text{-4-C}_6\text{H}_4\text{CH}_2\text{CONHCH}_2\text{-4-C}_6\text{H}_4\text{-}t\text{Bu}$  (4):** This was prepared similarly from 4-(bromomethyl)phenylacetic acid (540 mg, 2.34 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 450 mg, 2.34 mmol) and 4-*tert*-butylbenzylamine (380 mg, 2.34 mmol). A white solid was produced. Yield 25% (220 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.30 (s, 9 H, *t*Bu), 3.61 (s, 2 H,  $\text{O}=\text{CCH}_2$ ), 4.39 (d,  $^3J_{\text{H,H}} = 6$  Hz, 2 H,  $\text{NCH}_2$ ), 4.48 (s, 2 H,  $\text{BrCH}_2$ ), 5.65 (br. s, 1 H, NH), 7.13 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.27 (t,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.33 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.37 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ) ppm. MS:  $m/z$  calcd. 373.1041; found 373.1032.

**$[\text{PtBrMe}_2(\text{bu}_2\text{bipy})(\text{CH}_2\text{-4-C}_6\text{H}_4\text{CONH-4-C}_6\text{H}_4\text{-}t\text{Bu})]$  (6):** A mixture of  $[\text{PtMe}_2(\text{bu}_2\text{bipy})]$  (25.0 mg, 0.05 mmol) and compound **1** (17.5 mg, 0.05 mmol) in acetone (5 mL) was stirred for 5 h at room temperature. The solvent was evaporated under vacuum and the resulting solid was washed with water and then pentane. The product was isolated as a yellow solid, which was dried in vacuo. Yield 95% (39.9 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.31 (s, 9 H, *t*Bu), 1.41 (s, 18 H, bipy-bu), 1.46 (s,  $^2J_{\text{Pt,H}} = 69$  Hz, 6 H, PtMe), 2.87 (s,  $^2J_{\text{Pt,H}} = 96$  Hz, 2 H, PtCH<sub>2</sub>), 6.43 (d,  $^3J_{\text{H,H}} = 8$ ,  $^4J_{\text{Pt,H}} = 18$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.12 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.36 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.44 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.49 (d,  $^3J_{\text{H,H}} = 6$  Hz, 2 H, bipy( $\text{H}^5$ ,  $\text{H}^{5'}$ )), 7.54 (s, 1 H, NH), 7.99 [s, 2 H, bipy( $\text{H}^3$ ,  $\text{H}^{3'}$ )], 8.53 [d,  $^3J_{\text{H,H}} = 6$ ,  $^3J_{\text{Pt,H}} = 19$  Hz, 2 H, bipy( $\text{H}^6$ ,  $\text{H}^{6'}$ )] ppm.  $\text{C}_{38}\text{H}_{50}\text{BrN}_3\text{OPt}$  (839.83): calcd. C 54.35, H 6.00, N 5.00; found C 54.55, H 6.02, N 4.99.

**$[\text{PtBrMe}_2(\text{bu}_2\text{bipy})(\text{CH}_2\text{-4-C}_6\text{H}_4\text{CONHCH}_2\text{-4-C}_6\text{H}_4\text{-}t\text{Bu})]$  (7):** This was prepared similarly from  $[\text{PtMe}_2(\text{bu}_2\text{bipy})]$  (25.0 mg, 0.05 mmol) and compound **2** (18.0 mg, 0.05 mmol). A yellow solid was produced. Yield 96% (41.0 mg). Two sets of resonance, (a) and (b), were found in the spectrum. (a)  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 1.31 (s, 9 H, *t*Bu), 1.39 (s, 18 H, bipy-bu), 1.35 (s, 6 H,  $^2J_{\text{Pt,H}} = 69$  Hz, PtMe), 2.80 (s, 2 H,  $^2J_{\text{Pt,H}} = 96$  Hz, PtCH<sub>2</sub>), 4.44 (d, 2 H,  $^3J_{\text{H,H}} = 6$  Hz,  $\text{NCH}_2$ ), 6.15 (t, 1 H,  $^3J_{\text{H,H}} = 6$  Hz, NH), 6.37 (d, 2 H,  $^3J_{\text{H,H}} = 8$  Hz,  $^4J_{\text{Pt,H}} = 15$  Hz,  $\text{C}_6\text{H}_4$ ), 7.02 (d, 2 H,  $^3J_{\text{H,H}} = 8$  Hz,  $\text{C}_6\text{H}_4$ ), 7.22 (d, 2 H,  $^3J_{\text{H,H}} = 8$  Hz,  $\text{C}_6\text{H}_4$ ), 7.37 (d, 2 H,  $^3J_{\text{H,H}} = 8$  Hz,  $\text{C}_6\text{H}_4$ ), 7.46 [d, 2 H,  $^3J_{\text{H,H}} = 6$  Hz, bipy( $\text{H}^5$ ,  $\text{H}^{5'}$ )], 7.96 [s, 2 H,  $^4J_{\text{H,H}} = 2$  Hz, bipy( $\text{H}^3$ ,  $\text{H}^{3'}$ )], 8.49 [d, 2 H,  $^3J_{\text{H,H}} = 6$  Hz,  $^3J_{\text{Pt,H}} = 19$  Hz, bipy( $\text{H}^6$ ,  $\text{H}^{6'}$ )] (b)  $\delta$  = 1.31 (s, 9 H, bu), 1.39 (s, 18 H, bipy-bu), 1.43 (s,  $^2J_{\text{Pt,H}} = 69$  Hz, 6 H, PtMe), 2.84 (s,  $^2J_{\text{Pt,H}} = 96$  Hz, 2 H, PtCH<sub>2</sub>), 4.44 (d,  $^3J_{\text{H,H}} = 6$  Hz, 2 H,  $\text{NCH}_2$ ), 6.15 (t,  $^3J_{\text{H,H}} = 6$  Hz, 1 H, NH), 6.38 (d,  $^3J_{\text{H,H}} = 8$ ,  $^4J_{\text{Pt,H}} = 15$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.02 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.22 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.37 (d,  $^3J_{\text{H,H}} = 8$  Hz, 2 H,  $\text{C}_6\text{H}_4$ ), 7.46 [d,  $^3J_{\text{H,H}} = 6$  Hz, 2 H, bipy( $\text{H}^5$ ,  $\text{H}^{5'}$ )], 7.97 [s, 2 H, bipy( $\text{H}^3$ ,  $\text{H}^{3'}$ )], 8.51 [d,  $^3J_{\text{H,H}} = 6$ ,  $^3J_{\text{Pt,H}} = 19$  Hz, 2 H, bipy( $\text{H}^6$ ,  $\text{H}^{6'}$ )] ppm.  $\text{C}_{39}\text{H}_{52}\text{BrN}_3\text{OPt}$  (853.85): calcd. C 54.86, H 6.14, N 4.92; found C 54.58, H 6.40, N 5.05. ESI-MS:  $m/z$  = 773  $[\text{PtMe}_2(\text{bu}_2\text{bipy})\text{R}]^+$ , 831  $[\text{PtMe}_2(\text{bu}_2\text{bipy})-(\text{CH}_3)_2\text{CO}]^+$ , 876  $[\text{PtBrMe}_2(\text{bu}_2\text{bipy})\text{R} + \text{Na}]^+$ , 1625  $[\{\text{PtMe}_2-$

(bu<sub>2</sub>bipy)R)<sub>2</sub>(μ-Br)]<sup>+</sup> where R = CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CONHCH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu.

**[PtBrMe<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CONH-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)] (8):** This was prepared similarly from [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)] (50.0 mg, 0.10 mmol) and ligand **4** (36.0 mg, 0.10 mmol). A yellow solid was produced. Yield 95% (81.1 mg). Two sets of resonance, (a) and (b), were found in the spectrum. (a) <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.27 (s, 9 H, *t*Bu), 1.39 (s, 18 H, bipy-bu), 1.34 (s, <sup>2</sup>J<sub>Pt,H</sub> = 68 Hz, 6 H, PtMe), 2.77 (s, <sup>2</sup>J<sub>Pt,H</sub> = 94 Hz, 2 H, PtCH<sub>2</sub>), 3.31 (m, 2 H, O=CCH<sub>2</sub>), 6.31 (d, <sup>3</sup>J<sub>H,H</sub> = 8, <sup>4</sup>J<sub>Pt,H</sub> = 18 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 6.52 (m, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.01 (br. s, 1 H, NH), 7.29 (m, 4 H, C<sub>6</sub>H<sub>4</sub>), 7.46 [d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, bipy(H<sup>5</sup>, H<sup>5'</sup>)], 8.00 [s, 2 H, bipy(H<sup>3</sup>, H<sup>3'</sup>)], 8.52 [d, <sup>3</sup>J<sub>H,H</sub> = 6, <sup>3</sup>J<sub>Pt,H</sub> = 17 Hz, 2 H, bipy(H<sup>6</sup>, H<sup>6'</sup>)] ppm. (b) δ = 1.27 (s, 9 H, *t*Bu), 1.39 (s, 18 H, bipy-bu), 1.43 (s, <sup>2</sup>J<sub>Pt,H</sub> = 68 Hz, 6 H, PtMe), 2.80 (s, <sup>2</sup>J<sub>Pt,H</sub> = 94 Hz, 2 H, PtCH<sub>2</sub>), 3.31 (m, 2 H, O=CCH<sub>2</sub>), 6.32 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, <sup>4</sup>J<sub>Pt,H</sub> = 18 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 6.52 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.01 (br. s, 1 H, NH), 7.29 (m, 4 H, C<sub>6</sub>H<sub>4</sub>), 7.46 [d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, bipy(H<sup>5</sup>, H<sup>5'</sup>)], 8.00 [s, 2 H, bipy(H<sup>3</sup>, H<sup>3'</sup>)], 8.55 [d, 2 H, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, <sup>3</sup>J<sub>Pt,H</sub> = 17 Hz, bipy(H<sup>6</sup>, H<sup>6'</sup>)]. C<sub>39</sub>H<sub>52</sub>BrN<sub>3</sub>O<sub>2</sub>Pt (853.85): calcd. C 54.86, H 6.14, N 4.92; found C 54.94, H 6.23, N 5.14. ESI-MS: *m/z* = 773 [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)L]<sup>+</sup>, 831 [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)((CH<sub>3</sub>)<sub>2</sub>CO)R]<sup>+</sup>, 876 [PtBrMe<sub>2</sub>(bu<sub>2</sub>bipy)L + Na]<sup>+</sup>, 1625 [{PtMe<sub>2</sub>(bu<sub>2</sub>bipy)R]<sub>2</sub>(μ-Br)]<sup>+</sup> where R = CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CONH-4-C<sub>6</sub>H<sub>4</sub>C(CH<sub>3</sub>)<sub>3</sub>.

**[PtBrMe<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CONHCH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)] (9):** This was prepared similarly, from [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)] (50.0 mg, 0.10 mmol) and ligand **5** (37.0 mg, 0.10 mmol). A yellow solid was produced. Yield 92% (79.8 mg). A mixture of product was generated as discussed previously [i.e. platinum(IV) complex together with either the acetone-solvated complex or the bromo-bridged dimer]. Two sets of resonance, (a) and (b), were found in the spectrum. (a) <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.27 (s, 9 H, *t*Bu), 1.33 (s, <sup>2</sup>J<sub>Pt,H</sub> = 69 Hz, 6 H, PtMe), 1.41 (s, 18 H, bipy-bu), 2.74 (s, <sup>2</sup>J<sub>Pt,H</sub> = 95 Hz, 2 H, PtCH<sub>2</sub>), 3.19 (m, 2 H, O=CCH<sub>2</sub>), 4.27 (d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, NCH<sub>2</sub>), 5.55 (t, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 1 H, NH), 6.26 (d, <sup>3</sup>J<sub>H,H</sub> = 8, <sup>4</sup>J<sub>Pt,H</sub> = 17 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 6.46 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.07 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.30 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.45 [d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, bipy(H<sup>5</sup>, H<sup>5'</sup>)], 7.99 [s, 2 H, bipy(H<sup>3</sup>, H<sup>3'</sup>)], 8.50 [d, <sup>3</sup>J<sub>H,H</sub> = 6, <sup>3</sup>J<sub>Pt,H</sub> = 19 Hz, 2 H, bipy(H<sup>6</sup>, H<sup>6'</sup>)] ppm. (b) δ = 1.27 (s, 9 H, *t*Bu), 1.41 (s, <sup>2</sup>J<sub>Pt,H</sub> = 69 Hz, 6 H, PtMe), 1.41 (s, 18 H, bipy-bu), 2.77 (s, <sup>2</sup>J<sub>Pt,H</sub> = 95 Hz, 2 H, PtCH<sub>2</sub>), 3.19 (m, 2 H, O=CCH<sub>2</sub>), 4.27 (d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, NCH<sub>2</sub>), 5.55 (t, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 1 H, NH), 6.27 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, <sup>4</sup>J<sub>Pt,H</sub> = 17 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 6.46 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.07 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.30 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.45 (d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, bipy(H<sup>5</sup>, H<sup>5'</sup>)), 8.00 (s, 2 H, bipy(H<sup>3</sup>, H<sup>3'</sup>)), 8.52 [d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, <sup>3</sup>J<sub>Pt,H</sub> = 19 Hz, 2 H, bipy(H<sup>6</sup>, H<sup>6'</sup>)]. C<sub>40</sub>H<sub>54</sub>BrN<sub>3</sub>O<sub>2</sub>Pt (867.88): calcd. C 55.36, H 6.27, N 4.84; found C 55.63, H 6.51, N 4.84. ESI-MS: *m/z* = 787 [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)R]<sup>+</sup>, 846 [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)((CH<sub>3</sub>)<sub>2</sub>CO)R]<sup>+</sup>, 890 [PtBrMe<sub>2</sub>(bu<sub>2</sub>bipy)R + Na]<sup>+</sup>, where R = CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CONH-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu.

**[PtI Me<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CONH-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)] (12):** This was prepared by the same synthetic procedures as **13**, with complex **7** (93.0 mg, 0.11 mmol) and excess lithium iodide (44.0 mg, 0.33 mmol). A yellow solid was produced. Yield 80% (92.4 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.31 (s, 9 H, *t*Bu), 1.42 (s, 18 H, bipy-bu), 1.46 (s, <sup>2</sup>J<sub>Pt,H</sub> = 70 Hz, 6 H, PtMe), 2.90 (s, <sup>2</sup>J<sub>Pt,H</sub> = 94 Hz, 2 H, PtCH<sub>2</sub>), 6.40 (d, <sup>3</sup>J<sub>H,H</sub> = 8, <sup>4</sup>J<sub>Pt,H</sub> = 19 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.10 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.36 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.43 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.48 [d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, bipy(H<sup>5</sup>, H<sup>5'</sup>)], 7.53 (s, 1 H, NH), 7.98 [s, 2 H, bipy(H<sup>3</sup>, H<sup>3'</sup>)], 8.58 [d, <sup>3</sup>J<sub>H,H</sub> = 6, <sup>3</sup>J<sub>Pt,H</sub> = 19 Hz, 2 H, bipy(H<sup>6</sup>, H<sup>6'</sup>)] ppm. C<sub>38</sub>H<sub>50</sub>IN<sub>3</sub>O<sub>2</sub>Pt (886.83): calcd. C 51.47, H 5.68, N 4.74; found C 51.71, H 5.55, N 4.59.

**[PtI Me<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CONHCH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)] (13):** This was prepared by the same synthetic procedures as **13**, with complex **8** (91.0 mg, 0.11 mmol) and excess lithium iodide (44.0 mg, 0.33 mmol). A yellow solid was produced. Yield 87% (90.5 mg). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.31 [s, 9 H, *t*Bu], 1.39 [s, 18 H, bipy-bu], 1.56 [s, <sup>2</sup>J<sub>Pt,H</sub> = 70 Hz, 6 H, PtMe], 2.87 [s, <sup>2</sup>J<sub>Pt,H</sub> = 94 Hz, 2 H, PtCH<sub>2</sub>], 4.44 [d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, NCH<sub>2</sub>], 6.15 [t, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 1 H, NH], 6.34 [d, <sup>3</sup>J<sub>H,H</sub> = 8, <sup>4</sup>J<sub>Pt,H</sub> = 19 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>], 7.01 [d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>], 7.22 [d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>], 7.37 [d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>], 7.45 [d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, bipy(H<sup>5</sup>, H<sup>5'</sup>)], 7.95 [s, 2 H, bipy(H<sup>3</sup>, H<sup>3'</sup>)], 8.55 [d, <sup>3</sup>J<sub>H,H</sub> = 6, <sup>3</sup>J<sub>Pt,H</sub> = 19 Hz, 2 H, bipy(H<sup>6</sup>, H<sup>6'</sup>)] ppm. C<sub>39</sub>H<sub>52</sub>IN<sub>3</sub>O<sub>2</sub>Pt (900.85): calcd. C 52.00, H 5.82, N 4.66; found C 52.38, H 5.75, N 4.37.

**[PtI Me<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CONH-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)] (14):** This was prepared by the same synthetic procedures as **13**, with complex **9** (91.0 mg, 0.11 mmol) and excess lithium iodide (44.0 mg, 0.33 mmol). A yellow solid was produced. Yield 86% (77.7 mg). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.27 (s, 9 H, *t*Bu), 1.39 (s, 18 H, bipy-bu), 1.56 (s, <sup>2</sup>J<sub>Pt,H</sub> = 70 Hz, 6 H, PtMe), 2.82 (s, <sup>2</sup>J<sub>Pt,H</sub> = 92 Hz, 2 H, PtCH<sub>2</sub>), 3.30 (m, 2 H, O=CCH<sub>2</sub>), 6.27 (d, <sup>3</sup>J<sub>H,H</sub> = 8, <sup>4</sup>J<sub>Pt,H</sub> = 20 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 6.50 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 6.94 (br. s, 1 H, NH), 7.29 (m, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.32 (m, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.46 [d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, bipy(H<sup>5</sup>, H<sup>5'</sup>)], 7.99 [s, 2 H, bipy(H<sup>3</sup>, H<sup>3'</sup>)], 8.60 [d, <sup>3</sup>J<sub>H,H</sub> = 6, <sup>3</sup>J<sub>Pt,H</sub> = 19 Hz, 2 H, bipy(H<sup>6</sup>, H<sup>6'</sup>)] ppm. C<sub>39</sub>H<sub>52</sub>IN<sub>3</sub>O<sub>2</sub>Pt (900.85): calcd. C 52.00, H 5.82, N 4.66; found C 51.95, H 5.79, N 4.48.

**[PtI Me<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CONHCH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)] (15):** This was prepared by the same synthetic procedures as **13**, with complex **10** (92.0 mg, 0.10 mmol) and excess lithium iodide (40.0 mg, 0.30 mmol). A yellow solid was produced. Yield 78% (77.7 mg). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.27 (s, 9 H, *t*Bu), 1.42 (s, 18 H, bipy-bu), 1.54 (s, <sup>2</sup>J<sub>Pt,H</sub> = 70 Hz, 6 H, PtMe), 2.80 (s, <sup>2</sup>J<sub>Pt,H</sub> = 92 Hz, 2 H, PtCH<sub>2</sub>), 3.18 (m, 2 H, O=CCH<sub>2</sub>), 4.27 (d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, NCH<sub>2</sub>), 5.55 (t, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 1 H, NH), 6.22 (d, <sup>3</sup>J<sub>H,H</sub> = 8, <sup>4</sup>J<sub>Pt,H</sub> = 19 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 6.44 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.07 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.30 (d, <sup>3</sup>J<sub>H,H</sub> = 8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.44 [d, <sup>3</sup>J<sub>H,H</sub> = 6 Hz, 2 H, bipy(H<sup>5</sup>, H<sup>5'</sup>)], 7.98 [s, 2 H, bipy(H<sup>3</sup>, H<sup>3'</sup>)], 8.57 [d, <sup>3</sup>J<sub>H,H</sub> = 6, <sup>3</sup>J<sub>Pt,H</sub> = 19 Hz, 2 H, bipy(H<sup>6</sup>, H<sup>6'</sup>)] ppm. C<sub>40</sub>H<sub>54</sub>IN<sub>3</sub>O<sub>2</sub>Pt (914.88): calcd. C 52.51, H 5.95, N 4.59; found C 52.64, H 5.75, N 4.42.

**X-ray Structure Determinations:** A crystal suitable for X-ray analysis was mounted on a glass fibre. Data were collected with a Nonius-Kappa CCD diffractometer using COLLECT (Nonius, B.V. 1997–2002) software. The unit-cell parameters were calculated and refined from the full data set. Crystal-cell refinement and data reduction was carried out using the HKL2000 DENZO-SMN (Otwinowski & Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The SHELXTL/PC V6.14 for Windows NT (G. M. Sheldrick, 2001) program package was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon, nitrogen and oxygen atoms. Details of the data collection and refinement are given in Table 1.

CCDC-715919 (for **6**·1.3MeOH), -715920 (for **7**·H<sub>2</sub>O·0.5iPr<sub>2</sub>O), -715921 (for **7**·2C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>), -715922 (for **8**), -715923 (for **9**·0.5CH<sub>2</sub>Cl<sub>2</sub>) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/



Table 1. X-ray data and structure refinement.

|                                                 | 6·1.3MeOH                                                                             | 7·H <sub>2</sub> O·0.5 <i>i</i> Pr <sub>2</sub> O                     | 7·2C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>                     | 8                                                    | 9·0.5CH <sub>2</sub> Cl <sub>2</sub>                      |
|-------------------------------------------------|---------------------------------------------------------------------------------------|-----------------------------------------------------------------------|----------------------------------------------------------------------|------------------------------------------------------|-----------------------------------------------------------|
| Formula                                         | C <sub>39.50</sub> H <sub>56</sub> BrN <sub>3</sub> O <sub>2.50</sub> Pt <sub>2</sub> | C <sub>42</sub> H <sub>61</sub> BrN <sub>3</sub> O <sub>2.50</sub> Pt | C <sub>43</sub> H <sub>60</sub> BrCl <sub>4</sub> N <sub>3</sub> OPt | C <sub>39</sub> H <sub>52</sub> BrN <sub>3</sub> OPt | C <sub>40.50</sub> H <sub>55</sub> BrClN <sub>3</sub> OPt |
| <i>F</i> <sub>w</sub>                           | 887.87                                                                                | 922.94                                                                | 1051.74                                                              | 853.84                                               | 910.32                                                    |
| Temperature [K]                                 | 150(2)                                                                                | 150(2)                                                                | 150(2)                                                               | 150(2)                                               | 150(2)                                                    |
| $\lambda$ [Å]                                   | 0.71073                                                                               | 0.71073                                                               | 0.71073                                                              | 0.71073                                              | 0.71073                                                   |
| Crystal system                                  | monoclinic                                                                            | monoclinic                                                            | orthorhombic                                                         | monoclinic                                           | triclinic                                                 |
| Space group                                     | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                    | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                    | <i>Pbca</i>                                                          | <i>P</i> 2 <sub>1</sub> / <i>c</i>                   | <i>P</i> 1̄                                               |
| <i>a</i> [Å]                                    | 13.4236(5)                                                                            | 18.0300(4)                                                            | 24.5624(5)                                                           | 11.3904(4)                                           | 12.1947(9)                                                |
| <i>b</i> [Å]                                    | 21.2226(7)                                                                            | 12.7859(3)                                                            | 10.2379(2)                                                           | 13.7507(5)                                           | 19.987(2)                                                 |
| <i>c</i> [Å]                                    | 13.5954(3)                                                                            | 18.3151(5)                                                            | 35.9093(7)                                                           | 23.4710(7)                                           | 21.137(1)                                                 |
| $\alpha$ [°]                                    | 90                                                                                    | 90                                                                    | 90                                                                   | 90                                                   | 111.398(5)                                                |
| $\beta$ [°]                                     | 94.287(2)                                                                             | 98.658(2)                                                             | 90                                                                   | 96.118(2)                                            | 99.947(5)                                                 |
| $\gamma$ [°]                                    | 90                                                                                    | 90                                                                    | 90                                                                   | 90                                                   | 95.133(5)                                                 |
| <i>V</i> [Å <sup>3</sup> ]                      | 3862.3(2)                                                                             | 3955.0(2)                                                             | 9030.0(3)                                                            | 3655.2(2)                                            | 4659.0(6)                                                 |
| <i>Z</i>                                        | 4                                                                                     | 4                                                                     | 8                                                                    | 4                                                    | 4                                                         |
| <i>d</i> <sub>calcd.</sub> [Mg/m <sup>3</sup> ] | 1.527                                                                                 | 1.469                                                                 | 1.547                                                                | 1.552                                                | 1.298                                                     |
| $\mu$ [mm <sup>−1</sup> ]                       | 4.705                                                                                 | 4.357                                                                 | 4.264                                                                | 4.965                                                | 3.955                                                     |
| <i>F</i> (000)                                  | 1788                                                                                  | 1868                                                                  | 4224                                                                 | 1712                                                 | 1828                                                      |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>  | 0.0429, 0.0945                                                                        | 0.0672, 0.1797                                                        | 0.0821, 0.2288                                                       | 0.0710, 0.1946                                       | 0.1166, 0.2940                                            |

data\_request/cif. Brief comments on unusual features are given below.

**[PtBrMe<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CONH-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)]·1.3MeOH (6·1.3MeOH):** Crystals were grown by slow diffusion of hexane into a solution of **7** in carbon tetrachloride and methanol. One methanol molecule of solvation was well ordered, the other was modeled isotropically at 0.3 occupancy with C–O constrained to be 1.40 Å.

**[PtBrMe<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CONHCH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)]·H<sub>2</sub>O·*i*Pr<sub>2</sub>O (7·H<sub>2</sub>O·*i*Pr<sub>2</sub>O):** Crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>/isopropyl ether. There was evidence of unresolved disorder and soft constraints (SIMU and DELU) were used. The 0.5 occupancy isopropyl ether was located on a symmetry site. Crystals of 7·2C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexane. The C–Cl bonds of solvate molecules were restrained to be equal (1.75 Å).

**[PtBrMe<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CONH-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)] (8):** Crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexane.

**[PtBrMe<sub>2</sub>(bu<sub>2</sub>bipy)(CH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CONHCH<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>-*t*Bu)]·0.5CH<sub>2</sub>Cl<sub>2</sub> (9·0.5CH<sub>2</sub>Cl<sub>2</sub>):** Crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexane. The crystal diffracted weakly and showed evidence of twinning. A single Twin Law was suggested by ROTAX, and confirmed by improved refinement. The bond lengths in the CH<sub>2</sub>Cl<sub>2</sub> molecule were fixed. Some weak high angle data were discarded in the refinement.

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