Organoplatinum(IV) Complexes with Hydrogen Bonds: From Monomers to Polymers

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A series of organoplatinum(IV) complexes has been prepared, in which one of the alkyl groups contains a functional group that is capable of taking part in hydrogen bonding. These complexes are formed by oxidative addition of reagents RCH_2X to $[PtMe_2(bu_2bipy)]$ (**1**; bu_2-bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) and have the formula $[PtXMe_2(CH_2R)(bu_2bipy)]$ (**2**, R = CO_2H, X = Br; **3**, R = 4-$C_6H_4CO_2H$, X = Br; **4**, R = 4-$C_6H_4CH_2CO_2H$, X = Br; **5**, R = $C_4N_2H_3O_2$, X = Cl; **6**, R = 4-$C_6H_4NHCO_2Me$, X = Cl; **7**, R = 2,4-$C_6H_3(NHCO_2Me)_2$, X = Cl). These complexes may form dimers through OH···O or NH···O hydrogen bonding or polymers through NH···X hydrogen bonding. Further derivatives were prepared by reaction of the above complexes with $AgBF_4$ in the presence of nicotinic acid or 4,4′-bipyridyl (bipy): namely, $[PtMe_2(CH_2C_6H_4CO_2H)(4\text{-}NC_5H_4CO_2H)(bu_2bipy)][BF_4]$ (**8**) and $[\{PtMe_2(CH_2R)(bu_2bipy)\}_2(\mu\text{-}bipy)][BF_4]_2$ (**9a**, R = $C_6H_4CO_2H$; **10a**, R = $C_6H_4CH_2CO_2H$) Complex **9a** forms a polymer by OH···O hydrogen bonding, whereas **8** and **10a** undergo hydrogen bonding with the solvent and/or the counterion. This work shows that extended structures can be designed with hydrogen bonding in organoplatinum compounds and that there is a fine balance between formation of dimers or polymers through OH···O, NH···O, or NH···Cl bonding forms and formation of simpler structures arising from hydrogen bonding to solvent molecules or counterions.

Introduction

Hydrogen bonding can control the organization of molecules or ions in the solid state and so has been widely used in crystal engineering[1] and supramolecular synthesis.[2] In inorganic complexes, the hydrogen-bonding patterns may be similar to those in organic solids, but there is also the potential for different types, such as M−Cl···H−N bonding.[3] Hydrogen bonding in coordination complexes of platinum has been established in complexes having carboxylic acid substituents, for example in a platinum(II) complex containing the ligand 3-(diphenylphosphino)propanoic acid, but there has been little work on hydrogen bonding in organometallic complexes of platinum.[3−5] The present paper reports the synthesis of organoplatinum(IV) complexes containing substituents that are capable of taking part in hydrogen bonding.[3,5] The aim was to synthesize complexes which exhibit extended polymerization in their solid-state structures, as a result of hydrogen bonding between molecules, and so to advance the broader field of supramolecular organometallic chemistry.[1−3] The approach was to use oxidative addition of alkyl halides, in which the alkyl group contains hydrogen bonding functional groups, to a dimethylplatinum(II) complex. Such reactions are known to be tolerant to the presence of a wide variety of functional groups and have previously been used to prepare covalently bonded oligomers, polymers, and dendrimers.[6] However, the application to synthesis of hydrogen-bonded polymers has not been reported. Indeed, there are few methods known for synthesis of alkyl complexes of transition metals that have functional groups capable of taking part in hydrogen bonding.

Results and Discussion

Several new organoplatinum(IV) complexes were prepared by *trans*-oxidative addition of the corresponding functionalized alkyl bromide to $[PtMe_2(bu_2bipy)]$, bu_2bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine,[7,8] as shown

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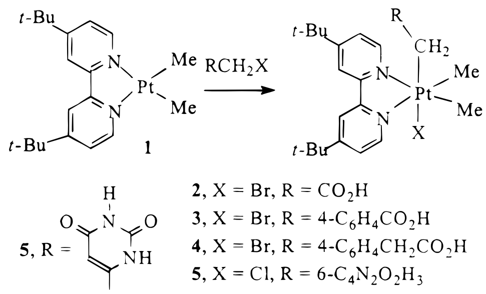
Scheme 1



in Scheme 1. The bu_2bipy ligand is used, instead of the parent 2,2′-bipyridine, to enhance the solubility of the products.[9] The alkyl halides used contained functional groups that could take part in intermolecular hydrogen bonding to give dimeric to polymeric supramolecular architectures in the solid state.

Derivatives with a Single Carboxylic Acid Substituent. The carboxylic acid derived complexes $[PtBrMe_2(bu_2bipy)(CH_2CO_2H)]$ (**2**), $[PtBrMe_2(bu_2bipy)(CH_2C_6H_4CO_2H)]$ (**3**), and $[PtBrMe_2(bu_2bipy)(CH_2C_6H_4CH_2CO_2H)]$ (**4**) were prepared by reaction of complex **1** with bromoacetic acid, α-bromo-4-toluic acid, and 4-(bromomethyl)phenylacetic acid, respectively. In each case, *trans* oxidative addition of the C−Br bond occurs rather than the alternative cleavage of a Pt−Me bond by the carboxylic acid. The complexes were readily characterized in terms of molecular structure by their ^1H NMR spectra by comparison with similar compounds.[5] Each complex gave a single methylplatinum resonance, indicating *trans* oxidative addition, and the coupling constant $^2J(PtMe)$ decreased from 89 Hz in the platinum(II) complex **1** to 65−70 Hz in the platinum(IV) products **2**−**4**. The couplings $^2J(PtCH_2)$ were in the range 90−95 Hz in the products. The infrared spectra as Nujol mulls for **2**−**4** contain peaks due to ν(O−H) in the range 2522−2700 cm^{-1} and ν(C═O) = 1674−1680 cm^{-1}, strongly suggesting that they exist as hydrogen-bonded dimers.[3,10,11]

The presence of a hydrogen-bonded dimer in the solid state for **2** was confirmed by an X-ray structure determination. A view of the structure is given in Figure 1. The O(1A)···O(2B) distance was 2.65 Å, in the normal range of 2.5−2.9 Å for similar hydrogen-bonded dimers.[12] The C═O bond length (1.240(7) Å) was longer and the C−O bond length(1.297(8) Å) shorter than in structures with no hydrogen bonding,[8] as expected for a hydrogen-bonded structure.[13] The conformation of the CH_2CO_2H group is such that the carboxylic acid group is located beneath the flat bu_2bipy ring, presumably to minimize steric hindrance. It has not been possible to obtain X-ray-quality crystals for **3** and **4**, but the IR data are similar to those for **2**; therefore, it is very likely that they adopt a similar solid-state structure.

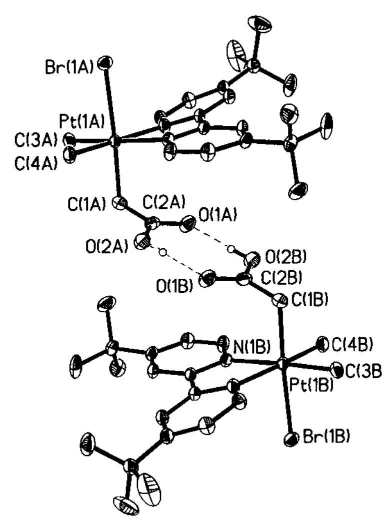


Figure 1. View of the structure of complex **2**, showing a hydrogen-bonded dimer. The OH protons were located in the structure determination but not refined. Selected distances (Å): Pt(1)−C(3) = 2.071(6), Pt(1)−C(4) = 2.084(6), Pt(1)−C(1) = 2.090(6), Pt(1)−N(1) = 2.162(4), Pt(1)−N(2) = 2.169(4), Pt(1)−Br(1) = 2.5394(6), O(1)−C(2) = 1.240(7), O(2)−C(2) = 1.297(8), O(1A)···O(2B) = 2.65(1), H(2B)···O(1A) = 1.80.

Derivative with a Uracil Substituent. Since uracil contains two hydrogen bond donors and acceptors, complexes containing such groups have the potential to form polymers rather than dimers. Oxidative addition of 6-(chloromethyl)uracil to **1** gave the platinum(IV) complex $[PtClMe_2(bu_2bipy)(CH_2C_4H_3N_2O_2)]$ (**5**) (Scheme 1). The IR spectrum for **5** contained peaks due to ν(N−H) at 3410 and 3320 cm^{-1} and four peaks due to ν(C═O) in the region 1710−1620 cm^{-1}, suggesting that there are carbonyl groups involved in hydrogen bonding and some not involved. The structure of **5** was determined crystallographically and is shown in Figure 2.

The structure confirms that **5** is formed by *trans* oxidative addition and shows that intermolecular hydrogen bonding does occur, but only to give dimers. Thus, only one pair of NHCO groups of each uracil substituent takes part in hydrogen bonding. The distance O(8A)···N(9B) = 2.82 Å is in the normal range of 2.81−3.04 Å for NH···O hydrogen bonds.[12] In the dimers formed by hydrogen bonding, the uracil groups align roughly under the bu_2bipy groups. A similar form of hydrogen bonding has recently been observed in the 2-thiouracil complex $[W(CO)_5(SC_4N_2H_3O)]^-$, while uracil gives a sheet structure in the solid state with all NH, C═O, and even CH groups involved in hydrogen bonding.[14] It is likely that the limited hydrogen bonding in complex **5** occurs as a result of steric hindrance to more extensive association. The closest contact of the NHCO groups that are not involved in self-association is to an acetone solvate, with N(7)···O(30) = 3.27 Å and N(7)H···O(30) = 2.45 Å, indicating a very weak interaction.[12]

Complexes with Methyl Carbamate Substituents. The complex $[PtClMe_2(bu_2bipy)(CH_2C_6H_4NHCO_2$-

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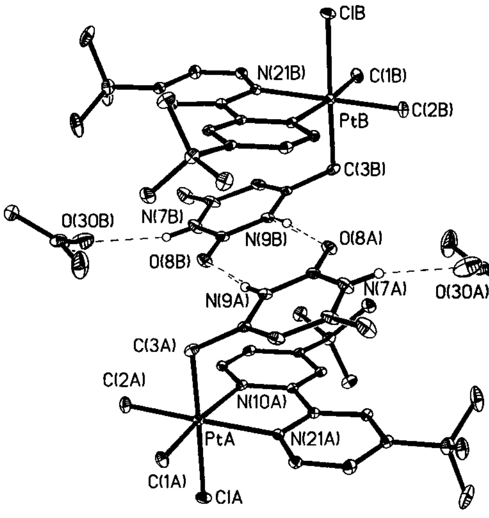
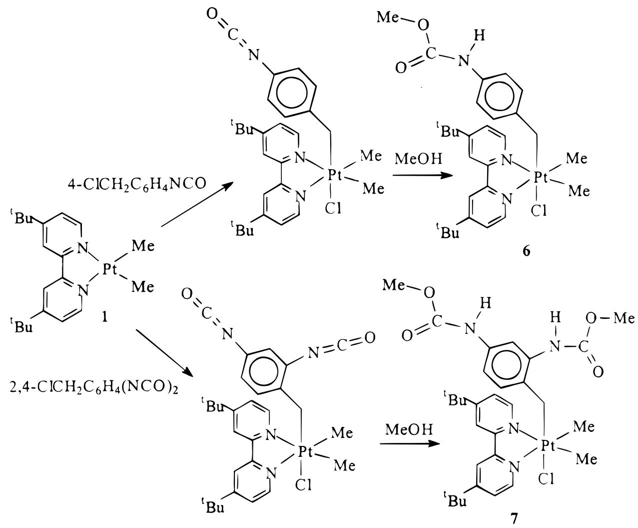


Figure 2. View of the structure of **5**, showing hydrogen bonding of the type C=O···H−N. The hydrogen atoms are omitted for clarity. Selected distances (Å): Pt−C(1) = 2.040(5), Pt−C(2) = 2.063(5), Pt−C(3) = 2.085(5), Pt−N(21) = 2.135(4), Pt−N(10) = 2.158(4), Pt−Cl = 2.431(1), C(6)−O(6) = 1.229(6), C(8)−O(8) = 1.230(6), O(8)···N(B) = 2.82(1), O(8)···H(9A) = 1.95.

Scheme 2



Me)] (**6**) was prepared by oxidative addition of 4-(chloromethyl)phenyl isocyanate to **1** to give [PtClMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$NCO)], followed by addition of methanol to convert the isocyanate group to the corresponding methyl carbamate (Scheme 2). The isocyanate derivative was characterized by a strong peak in the IR spectrum at 2300 cm^{-1}, corresponding to ν(N=C=O),[10] which decays on addition of methanol as the carbamate is formed with ν(C=O) = 1705 cm^{-1}.

Complex **6** was characterized by two structure determinations. The first crystal was grown from THF/pentane solution and crystallized as the THF solvate. There are two independent but similar molecules in the unit cell, and the structure of one of them is shown in Figure 3. Although the molecular structure is as expected, there is only hydrogen bonding between the NH group and a THF solvent molecule (Figure 3), and so there is no supramolecular association of molecules of **6**. In the two independent molecules the N···O(THF) distances were 2.90 and 2.99 Å, in the normal range of 2.81−3.04 Å for NH···O hydrogen-bonded compounds.[12]

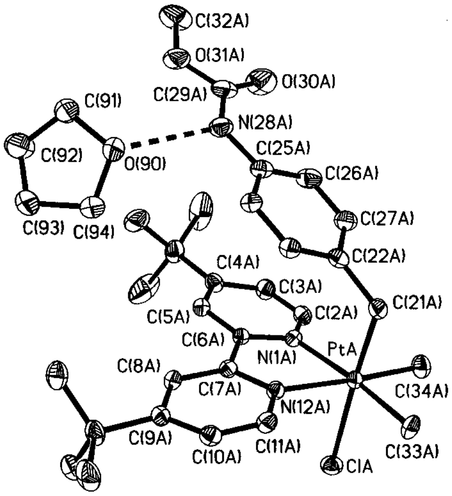


Figure 3. View of the structure of **6**·THF, with NH···O(THF) hydrogen bonding. The hydrogen atoms are omitted for clarity. There is a similar, independent molecule of **6**·THF in the lattice, but it is not shown. Selected distances (Å; the equivalent data for the two independent molecules are given, using the atom labeling for molecule 1 only): Pt−C(33) = 2.044(6), 2.063(8), Pt−C(34) = 2.051(7), 2.052(9), Pt−C(21) = 2.068(6), 2.068(8), Pt−N(1) = 2.157(5), 2.155(6), Pt−N(12) = 2.158(5), 2.143(6), Pt−Cl = 2.473(2), 2.466(2), C(29)−O(30) = 1.18(1), 1.20(1), C(29)−O(31) = 1.37(1), 1.35(1), C(32)−O(31) = 1.45(1), 1.48(1), N(28)···O(90) = 2.90(1), 2.99(1).

To overcome this problem of hydrogen bonding to solvent, a second structure determination was carried out using a crystal of **6** grown from CH$_2$Cl$_2$/pentane. The structure is shown in Figure 4. In this case, the structure exhibits an extended one-dimensional polymeric structure with a zigzag shape, formed through intermolecular NH···ClPt hydrogen bonding. A recent report has suggested that N−H···Cl−M hydrogen bonding may be generally favorable, but it is not clear why it is preferred over the NH···O hydrogen bonding that is commonly observed in amides.[3,12] For the two independent molecules of **6**, the intermolecular distances N···Cl were 3.22 and 3.27 Å, indicating the presence of the hydrogen bond N−H···Cl.[3] One previously reported example of intermolecular hydrogen bonding to an organoplatinum(II) chloride occurs between ethynyl and chloroplatinum groups, C≡CH···ClPt, giving a linear chain association similar to that in Figure 4.[15]

The reaction of **1** with 1-(chloromethyl)-2,4-diisocyanatobenzene, followed by reaction of the product [PtClMe$_2$(bu$_2$bipy){CH$_2$C$_6$H$_3$(NCO)$_2$}] with methanol, gave the bis(carbamate) derivative [PtClMe$_2$(bu$_2$bipy){CH$_2$C$_6$H$_3$(NHCO$_2$Me)$_2$}] (**7**). The molecular structure of **7** was defined by its ^{1}H NMR spectrum, but it was not possible to grow single crystals for structure determination. However, the IR spectrum as a Nujol mull gave ν(C=O) = 1725 cm^{-1}, which is at a higher wavenumber than expected for a hydrogen-bonded structure. In principle, this complex could form a two- or three-dimensional hydrogen-bonded supramolecular structure, but it is unlikely that such a structure is actually present.

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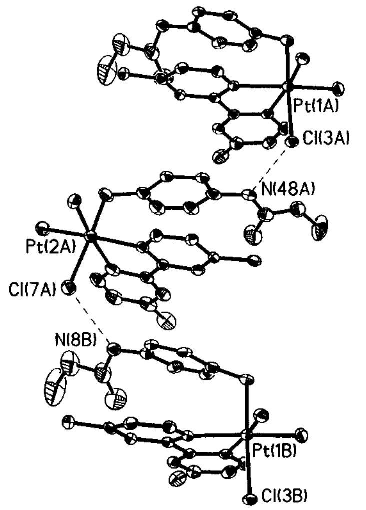
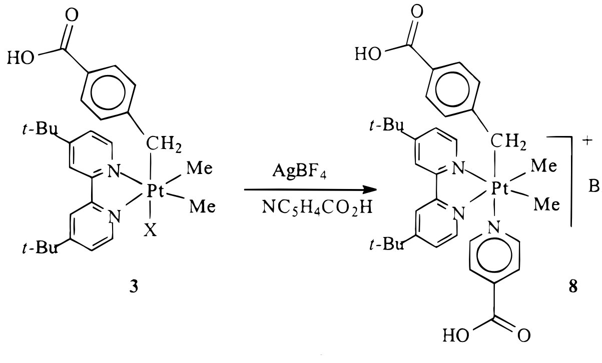


Figure 4. View of the structure of **6**·2CH_2Cl_2, showing part of the polymeric chain formed by NH···Cl hydrogen bonding. The molecules containing Pt(1) and Pt(2) are independent. Solvent molecules are not shown, and only the tertiary carbon atoms of the *tert*-butyl groups are shown for clarity. Selected distances (Å; the equivalent data for the two independent molecules are given, using the atom labeling for molecule 1 only): Pt(1)−C(33) = 2.03(1), 2.04(1), Pt(1)−C(34) = 2.03(1), 2.04(1), Pt(1)−C(1) = 2.09(1), 2.09(1), Pt(1)−N(24) = 2.14(1), 2.13(1), Pt(1)−N(13) = 2.15(1), 2.14(1), Pt(1)−Cl(3) = 2.467(2), 2.478(3), C(9)−O(10) = 1.18(2), 1.23(2), C(9)−O(11) = 1.37(2), 1.31(2), C(12)−O(11) = 1.41(2), 1.54(2), Cl(3)···N(48) = 3.27(1), 3.22(1), Cl(3)−H(48) = 2.40, 2.40.

Scheme 3



Secondary Derivatization. Complexes that are capable of forming extended hydrogen-bonded structures were formed by further derivatization of some of the above complexes. Thus, abstraction of the bromide ligand from complex **3** by use of $AgBF_4$ in the presence of isonicotinic acid gave the ionic complex [$PtMe_2$(bu_2-bipy)($CH_2C_6H_4CO_2H$)($NC_5H_4CO_2H$)][BF_4] (**8**) according to Scheme 3. In this way an organoplatinum(IV) complex containing two carboxylic acid substituents is readily formed.

The structure of **8** was determined as the acetone solvate, and the structure is illustrated in Figure 5. The molecular structure of the cation is confirmed by the structure determination, but no interesting supramolecular structure is present. Thus, the toluic acid substituent takes part in hydrogen bonding to an acetone solvent molecule (OH···O=CMe_2), while the isonicotinic acid substituent takes part in hydrogen bonding to a BF_4^- counterion (OH···FB), as shown in Figure 5. The corresponding distances O(39)···O(63) = 2.61 Å and O(29)···F(54) = 2.64 Å support the presence of strong hydrogen bonding in each case, since the accepted ranges for such bonds are 2.48−2.90 and 2.65−2.72 Å, respectively.[12] Clearly these secondary bonding effects compete well with the expected self-association through hydrogen bond formation between carboxylic acid groups that had been anticipated. Attempts to grow crystals from several other organic solvents were unsuccessful.

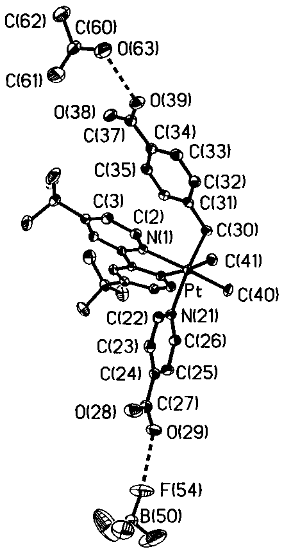
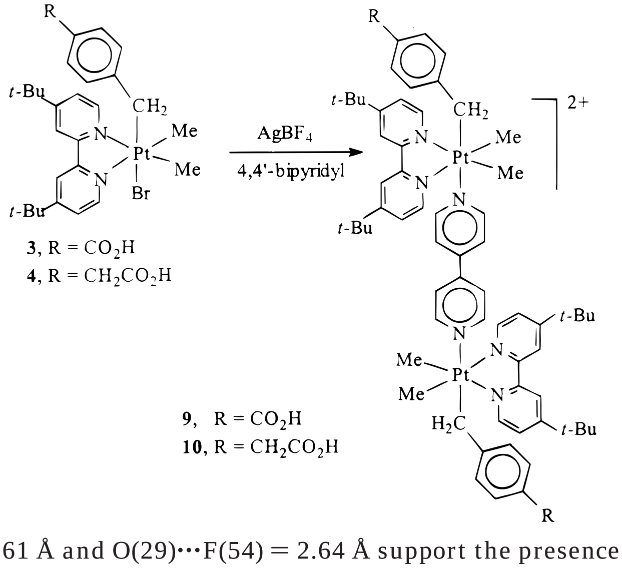


Figure 5. View of the structure of **8**[BF_4]·2(acetone), showing hydrogen bonding to the acetone solvent molecule (OH···O, H···O = 1.81 Å) and to the BF_4^- counterion (OH···F, H···F = 1.85 Å). The second acetone is not shown. Selected distances (Å): Pt−C(40) = 2.056(4), Pt−C(41) = 2.069(4), Pt−C(30) = 2.084(4), Pt−N(12) = 2.143(3), Pt−N(1) = 2.159(3), Pt−N(21) = 2.190(4), C(27)−O(28) = 1.189(7), C(27)−O(29) = 1.310(7), C(37)−O(38) = 1.210(6), C(37)−O(39) = 1.298(7), O(29)···F(54) = 2.64(1), F(54)···H(29) = 1.85, O(39)···O(63) = 2.61(1), O(63)···H(39) = 1.81.

Scheme 4



An alternative synthesis of complexes containing two hydrogen-bonding donors is to couple 2 equiv of the complex **3** or **4** by abstraction of bromide using $AgBF_4$ in the presence of the bridging ligand 4,4′-bipyridyl = bipy, as shown in Scheme 4. In this way, the complexes [{$PtMe_2$(bu_2bipy)($CH_2C_6H_4CO_2H$)}$_2$(μ-bipy)][BF_4]$_2$ (**9a**) and [{$PtMe_2$(bu_2bipy)($CH_2C_6H_4CH_2CO_2H$)}$_2$(μ-bipy)]-

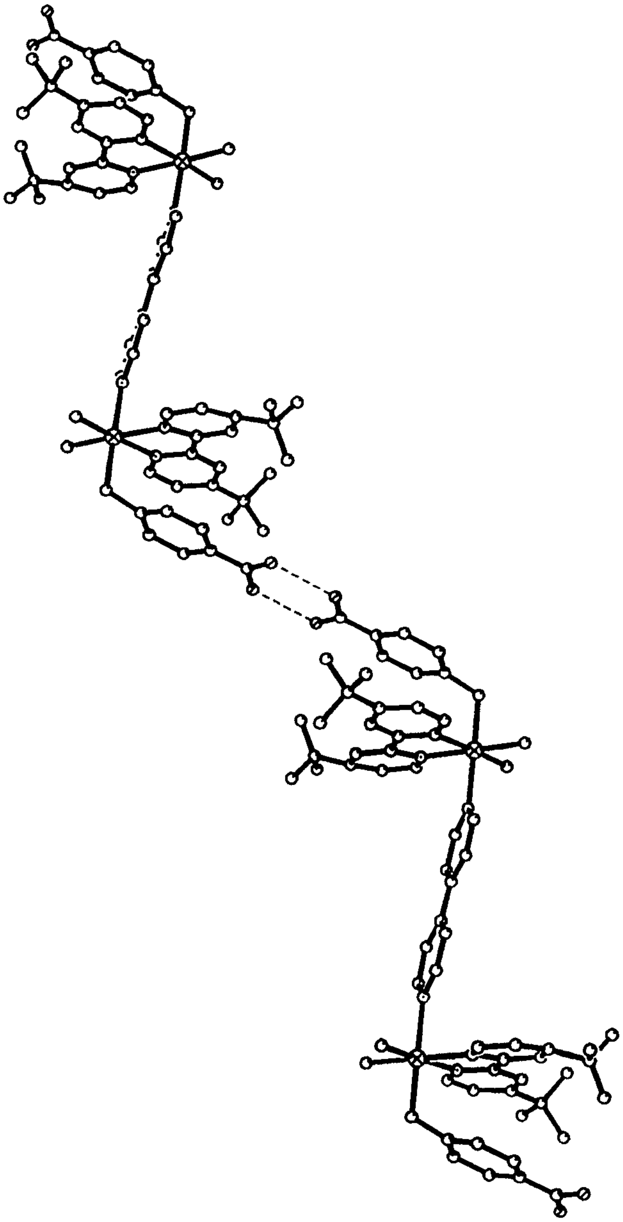


Figure 6. View of part of the polymeric chain formed by hydrogen bonding between carboxylic acid substituents in the cation present in complex **9**$[BF_4]_2\cdot Et_2O$. There is a center of symmetry at the midpoint of the central C−C bond of the bridging bipyridine ligand. Selected distances (Å): Pt−C(22) = 2.054(6), Pt−C(21) = 2.064(6), Pt−C(23) = 2.094(6), Pt−N(1) = 2.139(4), Pt−N(12) = 2.146(4), Pt−N(33) = 2.173(5), C(30)−O(31) = 1.23(1), C(30)−O(32) = 1.29(1), C(51)−O(52) = 1.30(1), O(52)−C(53) = 1.36(2), C(61)−O(62) = 1.50(2), O(62)−C(63) = 1.33(1), O(31A)···O(32D) = 2.65(1), O(31)···H(32B) = 1.81.

$[BF_4]_2$ (**10a**) were prepared. The IR spectra for **9a** and **10a** contained peaks due to ν(C=O) and ν(O−H) in the range expected for hydrogen-bonded complexes.

The structure of complex **9a** is shown in Figure 6. There is a crystallographic center of symmetry at the midpoint of the C(36)−C(36A) bond of **9a**. Complex **9a** adopts a polymeric structure through intermolecular hydrogen bonding between carboxylic acid groups, giving the zigzag chain structure shown in Figure 6. Although the BF_4^- counterion has the ability to be involved in hydrogen bonding to the carboxylic group substituents in organoplatinum(IV) complexes, as was demonstrated in the structure of complex **8**, this did not occur in this case and the desired polymeric structure was obtained. The intermolecular separation O(31A)···O(31D) = 2.65 Å is in the range expected for a hydrogen-bonded association.[12]

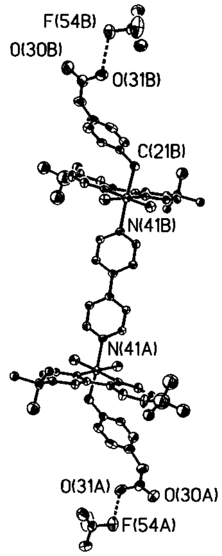


Figure 7. View of the structure of complex **10**$[BF_4]_2$, showing the weak hydrogen bonding OH···F to the tetrafluoroborate anions. The hydrogen atoms are omitted for clarity. Selected distances (Å): Pt−C(33) = 2.05(1), Pt−C(32) = 2.07(1), Pt−C(21) = 2.07(1), Pt−N(1) = 2.150(7), Pt−N(12) = 2.155(6), Pt−N(41) = 2.210(8), C(29)−O(30) = 1.27(2), C(29)−O(31) = 1.27(2), O(31A)···F(54A) = 2.86(1).

The structure of complex **10a** is shown in Figure 7. The molecular structure is similar to that of **9a**, but any hydrogen bonding was between the carboxylic acid groups and the BF_4^- counterion (OH···FB; O(31A)···F(54A) = 2.86 Å, suggesting very weak association[12]); therefore, no polymeric supramolecular structure was observed in this case. It is remarkable that the minor structural difference between **9a** and **10a** should lead to this switch in preferred hydrogen bonding of the carboxylic acid substituents.

The derivatives $[\{PtMe_2(bu_2bipy)(CH_2C_6H_4CO_2H)\}_2(\mu\text{-bipy})][BPh_4]_2$ (**9b**) and $[\{PtMe_2(bu_2bipy)(CH_2C_6H_4CH_2CO_2H)\}_2(\mu\text{-bipy})][BPh_4]_2$ (**10b**) were prepared by anion exchange from **9a** and **10a**, respectively. Since the counterion BPh_4^- is less likely than BF_4^- to take part in hydrogen bonding, it was hoped that these salts might form polymeric supramolecular structures. The IR spectra for **9b** and **10b** contained peaks due to ν(C=O) stretching and ν(O−H) in the region expected for hydrogen-bonded structures, but it has not been possible to grow crystals for structure determinations to confirm the expected polymeric structures.

Conclusions

The oxidative addition reaction gives a very simple, high-yield synthesis of organoplatinum(IV) complexes containing a wide range of functional groups that are capable of taking part in hydrogen bonding. When the product complex contains only one hydrogen bond donor/acceptor pair, as in the carboxylic acid derivatives **2**−**4**, only dimerization can occur by association between them, and this pattern is illustrated by the structure of complex **2**, shown in Figure 1. Two other possible patterns are illustrated by the carbamate ester complex **6**, which can form a hydrogen bond to solvent when crystallized from THF, and so exist as a monomer, or can form a polymer by intermolecular N−H···Cl−Pt hydrogen bonding, when crystallized from dichloromethane. Association of **6** by intermolecular NH···O hydrogen bonding between carbamate groups was not observed.

When the product complex contains two hydrogen bond donor/acceptor pairs, polymer formation might occur. However, in complex **5**, only one such pair within the uracil group takes part in intermolecular hydrogen bonding; therefore, only a dimer is formed. This lack of polymer formation is probably due to steric hindrance to formation of the maximum number of hydrogen bonds in **5**; as seen in Figure 2, the remaining free NH and CO groups in **5** are protected by the *tert*-butyl groups of the supporting ligands. To overcome such effects, two routes were developed to place hydrogen-bonding groups on opposite ends of the complexes. Displacement of bromide from **3** or **4** by nicotinic acid gave bis(carboxylic acid) derivatives, but the structure of **8** displayed hydrogen bonding to acetone and tetrafluoroborate anion only, and thus, no supramolecular structure was observed. Displacement of bromide from **3** or **4** by 4,4′-bipyridine gave the binuclear dicationic complexes **9a** and **10a**, which each contain two carboxylic acid groups. While **10a** gave very weak hydrogen bonding only to the tetrafluoroborate anions, complex **9a** gave the desired form of intermolecular hydrogen bonding, leading to formation of a polymer in the solid state.

In conclusion, the synthetic strategies developed here allow synthesis of both neutral and cationic organoplatinum(IV) complexes having hydrogen-bonding substituents, and self-association can lead to structures from dimers to polymers. The greatest difficulty is in predicting in advance which form of hydrogen bonding will be preferred. There is a fine balance between the predicted form of self-assembly and structures arising from hydrogen bonding to Pt−Cl groups, to solvent molecules, or, in the ionic complexes, to the counterions. It is likely that, in at least some cases, the presence of the bulky, hydrophobic *tert*-butyl substituents disfavor tighter hydrogen-bonded structure formation. These groups are useful for modifying the complex solubility, thus allowing crystals to be grown for characterization purposes, but they are not ideal for maximizing the intermolecular hydrogen-bonding interactions. While the prediction of preferred hydrogen-bonding patterns for crystal engineering has proved to be difficult, the complexes described here provide rare examples of self-assembly through hydrogen bonding in alkyl derivatives of transition metals[1] and indicate that it is a fruitful area for further study.

Experimental Section

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. NMR and IR spectra were recorded by using a Varian Gemini 300 NMR and a Perkin-Elmer FT-IR 2000 spectrometer, respectively. Compound **1** was prepared using the literature method.[7] Several of the hydrogen-bonded complexes formed as hydrates or solvates on crystallization from some solvents; in each case the presence of H_2O was confirmed by a resonance in the ^1H NMR in the range δ 2.8−3 or solvent from its characteristic ^1H NMR spectrum.

[PtBrMe$_2$(bu$_2$bipy)(CH$_2$CO$_2$H)] (2). A mixture of complex **1** (100 mg) and bromoacetic acid (28 mg) in acetone (10 mL) was stirred for 5 h at room temperature. The solvent was removed under vacuum, and the product was recrystallized using acetone/pentane to give a yellow product. Yield: 74%. Anal. Calcd for $C_{22}H_{33}BrN_2O_2Pt$: C, 41.78; H, 5.25; N, 4.43. Found: C, 42.31; H, 5.36; N, 4.18. NMR in acetone-d_6 ($\delta(^1H)$): 1.42 (s, 18H, bu); 1.46 (s, 6H, $^2J(PtH) = 70$ Hz, PtMe); 3.00 (s, 2H, $^2J(PtH) = 96$ Hz, PtCH$_2$); 7.82 (dd, 2H, $^3J(H^5H^6) = 6$ Hz, $^4J(H^3H^5) = 2$ Hz, bipy H^5); 8.62 (d, 2H, $^4J(H^3H^5) = 2$ Hz, bipy H^3); 9.18 (d, 2H, $^3J(H^5H^6) = 6$ Hz, $^3J(PtH^6) = 18$ Hz, bipy H^6). IR (Nujol mull): ν(CO) 1674 cm^{-1}; ν(OH) = 2700, 2545 cm^{-1}.

[PtBrMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CO$_2$H)] (3). This was prepared similarly from complex **1** and α-bromo-4-toluic acid. Yield: 87%. Anal. Calcd for $C_{28}H_{37}BrN_2O_2Pt$: C, 47.46; H, 5.26; N, 3.95. Found: C, 47.04; H, 5.40; N, 3.73. NMR in acetone-d_6 ($\delta(^1H)$): 1.41 (s, 18H, bu); 1.43 (s, 6H, $^2J(PtH) = 70$ Hz, PtMe); 2.80 (s, 2H, $^2J(PtH) = 96$ Hz, PtCH$_2$); 6.34 (d, 2H, $^3J(H^2H^3) = 6$ Hz, $^4J(PtH) = 19$ Hz, H^2); 7.22 (d, 2H, $^3J(H^2H^3) = 6$ Hz, H^3); 7.22 (dd, 2H, $^3J(H^5H^6) = 6$ Hz, $^4J(H^3H^5) = 2$ Hz, bipy H^5); 8.42 (d, 2H, $^4J(H^3H^5) = 2$ Hz, bipy H^3); 8.60 (d, 2H, $^3J(H^5H^6) = 6$ Hz, $^3J(PtH^6) = 18$ Hz, bipy H^6). IR (Nujol mull): ν(CO) = 1674 cm^{-1}; ν(OH) = 2630, 2522 cm^{-1}.

[PtBrMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CH$_2$CO$_2$H)] (4). This was prepared similarly from complex **1** and (4-(bromomethyl)-phenyl)acetic acid. Yield: 85%. Anal. Calcd for $C_{29}H_{39}N_2O_2BrPt\cdot H_2O$: C, 47.00; H, 5.58; N, 3.78. Found: C, 47.50; H, 5.43; N, 3.81. NMR in acetone-d_6: $\delta(^1H)$ = 1.40 (s, 6H, $^2J(PtH) = 70$ Hz, PtMe); 1.42 (s, 18H, bu); 2.70 (s, 2H, $^2J(PtH) = 93$ Hz, PtCH$_2$); 3.25 (s, 2H, CH$_2$); 6.16 (d, 2H, $^3J(H^2H^3) = 6$ Hz, $^4J(PtH) = 19$ Hz, H^2); 6.44 (d, 2H, $^3J(H^2H^3) = 6$ Hz, H^3), 7.66 (dd, 2H, $^3J(H^5H^6) = 6$ Hz, $^4J(H^3H^5) = 2$ Hz, bipy H^5), 8.32 (d, 2H, $^4J(H^3H^5) = 2$ Hz, bipy H^3); 8.60 (d, 2H, $^3J(H^5H^6) = 6$ Hz, $^3J(PtH^6) = 18$ Hz, bipy H^6). IR (Nujol mull): ν(CO) = 1680 cm^{-1}; ν(OH) = 2668, 2545 cm^{-1}.

[PtClMe$_2$(bu$_2$bipy)(CH$_2$C$_4$N$_2$O$_2$H$_3$)] (5). This was prepared similarly from complex **1** (100 mg) and 6-(chloromethyl)-uracil (33 mg) in dry THF (30 mL). Yield: 86%. Anal. Calcd for $C_{25}H_{35}N_4O_2ClPt$: C, 45.90; H, 5.39; N, 8.56. Found: C, 46.17; H, 5.50; N, 7.81. NMR in acetone-d_6 ($\delta(^1H)$): 1.35 (s, 6H, $^2J(PtH) = 68$ Hz, MePt); 1.44 (s, 18H, bu); 2.33 (s, 2H, $^2J(PtH) = 98$ Hz, PtCH$_2$); 4.38 (s, 1H, $^4J(PtH) = 15$ Hz, uracil H^2); 7.78 (dd, 2H, $^3J(H^5H^6) = 6$ Hz, $^4J(H^3H^5) = 2$ Hz, bipy H^5); 8.59 (d, 2H, $^4J(H^3H^5) = 2$ Hz, bipy H^3); 8.72 (d, 2H, $^3J(H^5H^6) = 6$ Hz, $^3J(PtH^6) = 18$ Hz, bipy H^6). IR (Nujol mull): ν(CO) = 1711, 1682, 1662, 1623 cm^{-1}; ν(NH) = 3410, 3320 cm^{-1}.

[PtClMe$_2$(bu$_2$bipy){CH$_2$C$_6$H$_4$NHCO$_2$Me}] (6). A mixture of complex **1** (100 mg) and 4-(chloromethyl)phenyl isocyanate (34 mg) in dry THF (50 mL) was stirred under N$_2$ overnight. The solvent was removed under vacuum, and methanol (30 mL) was added. The solution was stirred for 5 h under N$_2$. The solvent was evaporated under vacuum, and the product was recrystallized from acetone/pentane. Yield: 82%. Anal. Calcd for $C_{29}H_{40}ClN_3O_2Pt\cdot H_2O$: C, 48.97; H, 5.95; N, 5.91. Found: C, 49.07; H, 5.83; N, 6.00. NMR in acetone-d_6 ($\delta(^1H)$): 1.30 (s, 6H, $^2J(PtH) = 70$ Hz, MePt); 1.40 (s, 18H, bu); 2.62 (s, 2H, $^2J(PtH) = 92$ Hz, PtCH$_2$); 3.60 (s, 3H, −OMe); 6.13 (s, 2H, $^3J(H^2H^3) = 8$ Hz, $^4J(PtH^2) = 14$ Hz, H^2); 6.72 (s, 2H, $^3J(H^2H^3) = 8$ Hz, H^3); 7.63 (dd, 2H, $^3J(H^5H^6) = 6$ Hz, $^4J(H^3H^5) = 2$ Hz, bipy H^5); 8.35 (d, 2H, $^4J(H^3H^5) = 2$ Hz, bipy H^3); 8.58 (d, 2H, $^3J(H^5H^6) = 6$ Hz, $^3J(PtH^6) = 19$ Hz, bipy H^6). IR (Nujol mull): ν(CO) = 1705 cm^{-1}; ν(NH) = 3400 cm^{-1}.

[PtClMe$_2$(bu$_2$bipy){CH$_2$C$_6$H$_3$(NHCO$_2$Me)$_2$}] (7). This was prepared similarly from complex **1** and 1-(chloromethyl)-2,4-diisocyanatobenzene. Yield: 81%. Anal. Calcd for $C_{31}H_{43}ClN_4O_4Pt$: C, 48.59; H, 5.66; N, 7.31. Found: C, 48.83; H, 5.67; N, 7.54. NMR in acetone-d_6 ($\delta(^1H)$): 1.36 (s, 6H, $^2J(PtH) = 68$

Table 1. Crystallographic Data for 2, 5, 6, 8, 9a, and 10a

	2	**5**	**6**·THF	**6**·2CH$_2$Cl$_2$	**8**[BF$_4$]·2Me$_2$CO	**9**[BF$_4$]$_2$·Et$_2$O	**10**[BF$_4$]$_2$
formula	$C_{22}H_{33}BrN_2O_2Pt$	$C_{31}H_{47}ClN_4O_4Pt$	$C_{33}H_{48}ClN_3O_3Pt$	$C_{31}H_{44}Cl_5N_3O_2Pt$	$C_{40}H_{54}BF_4N_3O_6Pt$	$C_{37}H_{51}BF_4N_3O_3Pt$	$C_{68}H_{86}B_2F_8N_6O_4Pt_2$
fw	632.50	770.27	765.25	863.03	954.76	867.71	1615.23
temp (K)	293(2)	100(2)	293(2)	200(2)	292(2)	200(2)	296(2)
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	6.787(1)	12.647(3)	22.1988(3)	13.9808(2)	17.0747(2)	14.5655(7)	12.4406(4)
b (Å)	11.384(1)	20.008(4)	14.4142(2)	23.6523(5)	14.7560(2)	15.1038(7)	22.708(1)
c (Å)	31.124(1)	13.675(3)	24.3526(4)	24.3279(4)	17.3898(2)	19.4029(8)	13.4517(5)
β (deg)	90.470(1)	104.72(3)	116.757(1)	103.257(1)	103.678(1)	93.965(3)	90.304(2)
V (Å^3)	2404.7(4)	3347(1)	6957.9(2)	7830.3(2)	4257.18(9)	4258.3(3)	3800.1(3)
Z	4	4	8	8	4	4	2
d_{calcd} (Mg/m^3)	1.747	1.529	1.453	1.464	1.490	1.353	1.412
abs coeff (mm^{-1})	7.515	4.311	4.144	3.954	3.360	3.347	3.742
F(000)	1232	1552	3056	3440	1928	1748	1612
R1, wR2	0.0381, 0.0834	0.0618, 0.0874	0.0742, 0.1381	0.1303, 0.2475	0.0466, 0.1075	0.1039, 0.1616	0.1047, 0.1840

Hz, MePt); 1.42 (s, 18H, bu); 2.54 (s, 2H, ^2J(PtH) = 90 Hz, PtCH$_2$); 3.63 (s, 3H, −OMe), 3.69 (s, 3H, −OMe); 5.85 (d, 1H, ^3J(H^{2}H^3) = 6 Hz, ^4J(PtH^2) = 18 Hz, H^2); 6.60 (dd, 1H, ^3J(H^{2}H^3) = 6 Hz, ^4J(H^{3}H^5) = 2 Hz, H^3); 7.30 (d, 1H, ^4J(H^{3}H^5) = 2 Hz, H^5); 7.66 (dd, 2H, ^3J(H^{5}H^6) = 6 Hz, ^4J(H^{3}H^5) = 2 Hz, bipy H^5); 8.27 (d, 2H, ^4J(H^{3}H^5) = 2 Hz, bipy H^3); 8.67 (d, 2H, ^3J(H^{5}H^6) = 6 Hz, ^3J(PtH^6) = 20 Hz, bipy H^6). IR (Nujol mull): ν(CO) = 1725 cm^{-1}; ν(NH) = 3380 cm^{-1}.

[PtMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CO$_2$H)(NC$_5$H$_4$CO$_2$H)][BF$_4$] (8). A solution of complex **3** was prepared by reaction of complex **1** (100 mg) with α-bromo-4-toluic acid (44 mg) in acetone (10 mL) as above. To this solution was added dropwise a solution of AgBF$_4$ (40 mg) in acetone (5 mL) to precipitate AgBr. After 30 min, the mixture was filtered through Celite into a solution of isonicotinic acid (25 mg) in acetone (10 mL). The solvent was evaporated under vacuum, and the product was recrystallized from CH$_2$Cl$_2$/pentane to give a white solid. Yield: 84%. Anal. Calcd for $C_{34}H_{42}BF_4N_3O_4Pt\cdot H_2O$: C, 47.67; H, 5.17; N, 4.90. Found: C, 47.94; H, 5.08; N, 5.01. NMR in acetone-d_6 (δ(^{1}H)): 1.39 (s, 18H, bu); 1.44 (s, 6H, ^2J(PtH) = 67 Hz, PtMe); 3.06 (s, 2H, ^2J(PtH) = 93 Hz, PtCH$_2$); 6.48 (d, 2H, ^3J(H^{2}H^3) = 8 Hz, ^4J(PtH) = 16 Hz, toluic H^2); 7.28 (d, 2H, ^3J(H^{2}H^3) = 8 Hz, toluic H^3); 7.86 (d, 2H, ^3J(H^{2}H^3) = 8 Hz, isonicotinic H^3); 7.88 (dd, 2H, ^3J(H^{5}H^6) = 6 Hz, ^4J(H^{3}H^5) = 2 Hz, bipy H^5); 8.50 (d, 2H, ^4J(H^{3}H^5) = 2 Hz, bipy H^3); 8.64 (d, 2H, ^3J(H^{2}H^3) = 7 Hz, ^3J(PtH^2) = 20 Hz, isonicotinic H^2); 8.95 (d, 2H, ^3J(H^{5}H^6) = 6 Hz, ^3J(PtH^6) = 18 Hz, bipy H^6). IR (Nujol mull): ν(CO) = 1694 cm^{-1}; ν(OH) = 3380 cm^{-1}.

[{PtMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CO$_2$H)}$_2$(μ-bipy)][BF$_4$]$_2$ (9a). A solution of complex **3** was prepared from complex **1** (100 mg) and α-bromo-4-toluic acid (44 mg) in acetone (10 mL) as above. A solution of AgBF$_4$ (40 mg) in acetone (5 mL) was added dropwise. After 30 min, during which time AgBr precipitated, this solution was filtered through Celite into a solution of 4,4′-bipyridyl (16 mg) in acetone (5 mL). After 5 h, the solvent was evaporated and the product was recrystallized from CH$_2$Cl$_2$/pentane to give a pale yellow solid. Yield: 86%. Anal. Calcd for $C_{66}H_{82}B_2F_8N_6O_4Pt_2\cdot H_2O$: C, 49.38; H, 5.27; N, 5.23. Found: C, 49.42; H, 5.22; N, 5.08. NMR in acetone-d_6 (δ(^{1}H)): 1.39 (s, 36H, bu); 1.44 (s, 12H, ^2J(PtH) = 67 Hz, PtMe); 3.06 (s, 4H, ^2J(PtH) = 96 Hz, PtCH$_2$); 6.46 (d, 4H, ^3J(H^{2}H^3) = 6 Hz, ^4J(PtH) = 17 Hz, H^2); 7.27 (d, 4H, ^3J(H^{2}H^3) = 6 Hz, H^3), 7.86 (dd, 4H, ^3J(H^{5}H^6) = 6 Hz, ^4J(H^{3}H^5) = 2 Hz, bipy H^5); 7.88 (d, 4H, ^3J(H^{2}H^3) = 8 Hz, ^3J(PtH) = 18 Hz, m-bipy H^3); 8.50 (d, 4H, ^4J(H^{3}H^5) = 2 Hz, bipy H^3); 8.63 (d, 4H, ^3J(H^{2}H^3) = 8 Hz, ^4J(PtH) = 17 Hz, m-bipy H^2); 8.95 (d, 4H, ^3J(H^{5}H^6) = 6 Hz, ^3J(PtH^6) = 19 Hz, bipy H^6). IR (Nujol mull): ν(CO) = 1694 cm^{-1}; ν(OH) = 2668, 2555 cm^{-1}.

[{PtMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CH$_2$CO$_2$H)}$_2$(μ-bipy)][BF$_4$]$_2$ (10a). A solution of complex **4** was prepared by reaction of complex **1** (100 mg) and (4-(bromomethyl)phenyl)acetic acid (44 mg) in acetone (10 mL) as above. A solution of AgBF$_4$ (40 mg) in acetone (5 mL) was added dropwise. After 30 min, during which time AgBr precipitated, the solution was filtered through Celite into a solution of 4,4′-bipyridyl (16 mg) in acetone (5 mL). After 5 h, the solvent was evaporated under vacuum and the product was recrystallized from CH$_2$Cl$_2$/pentane to give a pale yellow solid. Yield: 84%. Anal. Calcd for $C_{67}H_{84}B_2F_8N_6O_4Pt_2\cdot CH_2Cl_2$: C, 48.75; H, 5.22; N, 4.94. Found: C, 48.61; H, 5.52; N, 5.00. NMR in acetone-d_6 (δ(^{1}H)): 1.35 (s, 12H, ^2J(PtH) = 67 Hz, PtMe); 1.38 (s, 36H, bu); 2.93 (s, 4H, ^2J(PtH) = 89 Hz, PtCH$_2$); 3.28 (s, 4H, CH$_2$); 6.23 (d, 4H, ^3J(H^{2}H^3) = 6 Hz, ^4J(PtH) = 17 Hz, H^2); 6.47 (d, 4H, ^3J(H^{2}H^3) = 6 Hz, H^3); 7.78 (dd, 4H, ^3J(H^{5}H^6) = 6 Hz, ^4J(H^{3}H^5) = 2 Hz, bipy H^5); 7.85 (d, 4H, ^3J(H^{2}H^3) = 8 Hz, ^3J(PtH) = 18 Hz, μ-bipy H^3); 8.37 (d, 4H, ^4J(H^{3}H^5) = 2 Hz, bipy H^3); 8.48 (d, 4H, ^3J(H^{2}H^3) = 8 Hz, ^4J(PtH) = 17 Hz, μ-bipy H^2); 8.92 (d, 4H, ^3J(H^{5}H^6) = 6 Hz, ^3J(PtH^6) = 19 Hz, bipy H^6). IR (Nujol mull): ν(CO) = 1686 cm^{-1}; ν(OH) = 2647, 2548 cm^{-1}.

[{PtMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CO$_2$H)}$_2$(μ-bipy)][BPh$_4$]$_2$ (9b). A mixture of complex **9a** (100 mg) and NaBPh$_4$ (44 mg) in acetone (10 mL) was stirred for 5 h. The solvent was evaporated under vacuum, and the product was recrystallized using CH$_2$Cl$_2$/pentane to give a pale yellow solid. Yield: 80%. Anal. Calcd for $C_{114}H_{122}B_2N_6O_4Pt_2\cdot CH_2Cl_2$: C, 64.64; H, 5.85; N, 3.93. Found: C, 64.83; H, 5.68; N, 4.00. NMR in acetone-d_6 (δ(^{1}H)): as for **9a** + peaks due to anions. IR (Nujol mull): ν(CO) = 1694 cm^{-1}; ν(OH) = 2668, 2555 cm^{-1}.

[{PtMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CH$_2$CO$_2$H)}$_2$(μ-bipy)][BPh$_4$]$_2$ (10b). This was prepared similarly from complex **10a** (100 mg) and NaBPh$_4$ (42 mg) in acetone (10 mL). Yield: 79%. Anal. Calcd for $C_{116}H_{126}B_2N_6O_4Pt_2\cdot CH_2Cl_2$: C, 64.91; H, 5.96; N, 3.88. Found: C, 64.60; H, 5.90; N, 4.13. NMR in acetone-d_6 (δ(^{1}H)): as for **10a** + peaks due to anions. IR (Nujol mull): ν(CO) = 1686 cm^{-1}; ν(OH) = 2647, 2548 cm^{-1}.

X-ray Structure Determinations. A crystal suitable for X-ray analysis was mounted on a glass fiber. Data were collected using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied. The SHELXTL (G. M. Sheldrick, Madison, WI) program package was used to solve and refine the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. A summary of the X-ray determinations is given in Table 1, and individual descriptions are given below. The accuracy of bond distances was low in some cases as a result of disorder, but the structures are all well-defined.

[PtBrMe$_2$(bu$_2$bipy)(CH$_2$CO$_2$H)] (2). Crystals of [PtBrMe$_2$(bu$_2$bipy)(CH$_2$CO$_2$H)] were grown from methylene chloride. The crystal size was 0.30 × 0.20 × 0.20 mm, and data were collected over the range 1.9−25.0°. Systematic absences were consistent with the monoclinic space group $P2_1/n$, and this was borne out by successful refinement of the structure. One of the *tert*-butyl groups was disordered over two positions, and each carbon atom was modeled with 50% occupancy. The largest residual peak was found to be associated with the Pt atom (1.044 e/Å^3).

[PtClMe$_2$(bu$_2$bipy)(CH$_2$C$_4$N$_2$O$_2$H$_3$)] (5). Crystals of PtClMe$_2$(bu$_2$bipy)(CH$_2$C$_4$N$_2$O$_2$H$_3$)·2(acetone) were grown by slow diffusion of pentane into an acetone solution. The crystal size was 0.20 × 0.15 × 0.14 mm, and data were collected over the range 4.1−26.4°. The reflection data and systematic absences were consistent with a monoclinic system, $P2_1/c$. The two acetone molecules were well-behaved. The largest residual electron density peak (1.236 e/Å^3) was associated with an acetone of solvation.

[PtClMe$_2$(bu$_2$bipy){CH$_2$C$_6$H$_4$NHCO$_2$Me}] (6). Crystals of PtClMe$_2$(bu$_2$bipy)[CH$_2$C$_6$H$_4$NHCO$_2$Me]·THF were grown by slow diffusion of pentane into a THF solution. The crystal size was 0.47 × 0.31 × 0.17 mm, and data were collected over the range 1.7−26.4°. The reflection data and systematic absences were consistent with a monoclinic system, $P2_1/n$. The THF molecules of solvation were well-behaved. The largest residual electron density peak (0.946 e/Å^3) was associated with the atom C(23A).

Crystals of [PtClMe$_2$(bu$_2$bipy){CH$_2$C$_6$H$_4$NHCO$_2$Me}]·2CH$_2$Cl$_2$ were grown from methylene chloride solution by diffusion of pentane. The crystal size was 0.64 × 0.59 × 0.25 mm, and data were collected over the range 2.6−30.1°. The reflection data and systematic absences were consistent with a monoclinic system, $P2_1/c$. The four solvent molecules in the asymmetric unit were poorly behaved. Each one was refined as two independent molecules with occupancies of 50%. Three could be refined well anisotropically, but the fourth could not and was kept isotropic. The largest residual electron density peak (2.178 e/Å^3) was associated with one of the platinum atoms.

[PtMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CO$_2$H)(NC$_5$H$_4$CO$_2$H)][BF$_4$] (8). Crystals of **8**[BF$_4$]·2(acetone) were grown by slow diffusion of pentane into an acetone solution. The crystal size was 0.36 × 0.23 × 0.11 mm, and data were collected over the range 3.6−27.1°. The reflection data and systematic absences were consistent with a monoclinic space group, $P2_1/n$. The largest residual electron density peak (1.591 e/Å^3) was associated with an acetone of solvation.

[{PtMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CO$_2$H)}$_2$(*μ*-bipy)][BF$_4$]$_2$ (9a). Crystals of **9a**·(ether) were grown from slow diffusion of diethyl ether into an acetonitrile solution. The crystal size was 0.38 × 0.23 × 0.07 mm, and data were collected over the range 2.7−30.5°. The reflection data and systematic absences were consistent with a monoclinic space group, $P2_1/n$. There was disorder in the methyl substituents of the *tert*-butyl groups; they were modeled at half-occupancy, and the carbons were kept isotropic. The diethyl ether of solvation was disordered over two positions at half-occupancy, the O and C atoms were also kept isotropic, and the bond lengths were fixed at standard values. The largest residual electron density peak (1.529 e/Å^3) was associated with the platinum atom.

[{PtMe$_2$(bu$_2$bipy)(CH$_2$C$_6$H$_4$CH$_2$CO$_2$H)}$_2$(*μ*-bipy)][BF$_4$]$_2$ (10a). Crystals of **10**[BF$_4$]$_2$ were grown by slow diffusion of pentane into a methylene chloride solution. The crystal size was 0.32 × 0.26 × 0.08 mm, and data were collected over the range 2.2−26.1°. The reflection data and systematic absences were consistent with a monoclinic system, $P2_1/n$. Both of the *tert*-butyl groups were disordered, with methyl groups in two positions (occupancy ratios of 50/50 and 60/40 for the two *tert*-butyl groups). The 12 Me−C distances were constrained to be the same. The largest residual electron density peak was 1.777 e/Å^3 and was not close to another atom.

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Supporting Information Available: Tables of X-ray data for **2**, **5**, **6**, **8**, **9a**, and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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