Self-Assembly of Polymer and Sheet Structures from Palladium(II) Complexes by Hydrogen Bonding between Carboxamide Substituents

Zengquan Qin, Michael C. Jennings, and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Received June 21, 2001

The self-assembly of supramolecular structures from either neutral or cationic palladium(II) complexes containing primary or secondary carboxamide groups as substituents on pyridine ligands has been explored. The displacement of PhCN in *trans*-[$PdCl_2(PhCN)_2$] by L = *N*-methylnicotinamide (MNA), isonicotinamide (INA), or nicotinamide (NA) gave the corresponding complexes *trans*-[$PdCl_2L_2$] **1**−**3**, respectively. Complex **1**·H_2O forms a 2D sheet network via amide−amide hydrogen bonding supported by chloride ligand-to-water hydrogen-bonding interactions. Several cationic complexes, $[Pd(L'L')L_2]^{2+}$ **4**−**9** and **11**−**16**, containing the above ligands and with PPh_3, dppp, dppm, or bu_2bipy as ancillary ligand(s) were prepared. Complex **4** (L = MNA, L′L′ = dppp) forms dimers through amide−amide hydrogen bonding, forming macrocycles which further propagate to form chains via weak C−H···O═C hydrogen bonding. Complex **6** (L = NA, L′L′ = dppp) forms zigzag chains connected by amide head-to-head hydrogen bonds. Complex **8** (L = INA, L′L′ = dppm) gives interesting double-stranded ribbons linked by two types of amide−amide hydrogen-bonding interactions. Complex **13** (L′ = PPh_3, L = NA) forms an infinite chain via complementary amide−amide hydrogen bonds. Complex **14** (L = MNA, L′L′ = bu_2bipy) forms infinite ribbons via the combination of amide hydrogen bonding mediated by a BF_4 anion and weak C−H···O═C hydrogen bonding. Complex **15** (L = INA, L′L′ = bu_2bipy) gives a ladder polymer formed through amide−amide hydrogen bonds. The structure of *cis*-[$Pd(PPh_3)_2(OH_2)_2$] $(OTf)_2$ (**10**) is also reported.

Introduction

There has been much interest and progress in the study of metal-containing supramolecular systems, partly because of the intellectual challenge in controlling the self-assembly processes and partly because of the potential application of such materials in catalysis, sensing, molecular electronics, magnetic devices, and porous and nanosize materials.[1] Two main strategies, namely, coordination-driven self-assembly and hydrogen bonding, have been used, and the combination of these methods is particularly powerful. The coordination chemistry approach has proven to be powerful for the synthesis of many discrete supramolecular compounds[2] and of highly ordered coordination polymers.[3] The combined coordination chemistry and hydrogen-bonding approach has given particularly interesting supramolecular systems,[7−9] modeled on the pioneering research of organic supramolecular architectures.[4−6]

Because of the relatively strong, directional hydrogen-bonding motifs exhibited by primary and secondary carboxamides as well as the biological relevance, the self-assembly of these compounds to give oligomeric or polymeric structures has been studied extensively.[6] In addition, crystal engineering studies utilizing simple metal ions such as Ag(I) or Pt(II) coordinated to two, three, or four pyridine ligands with carboxamide substituents in hydrogen-bonded supramolecular entities have been reported.[9] There has been little work on complexes containing secondary carboxamide groups or on complexes containing both ancillary ligands and amide-containing ligands, which are the focus of the present report.[10]

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Chart 1. H-bonding Motifs in Carboxamides

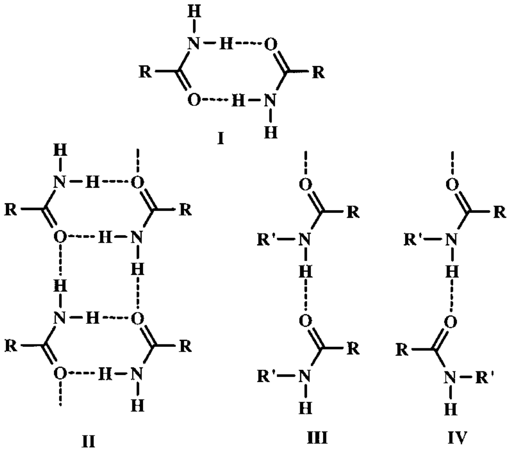
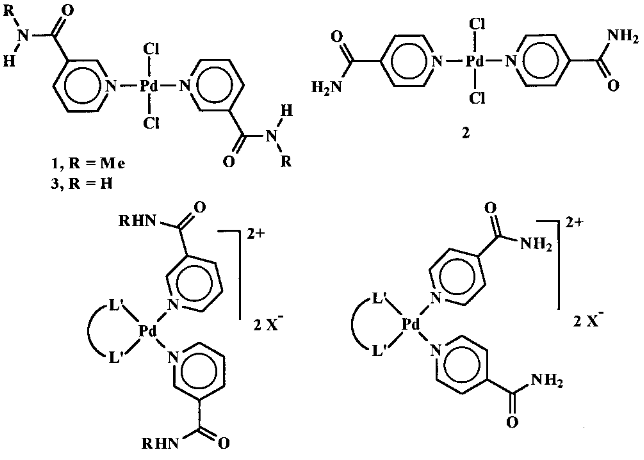


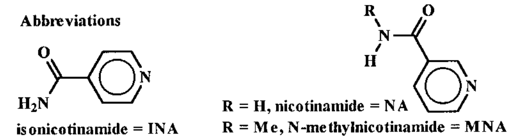
Chart 2



4, L'L' = dppp, R = Me, X = CF$_3$SO$_3$
6, L'L' = dppp, R = H, X = CF$_3$SO$_3$
7, L'L' = dppm, R = Me, X = CF$_3$SO$_3$
9, L'L' = dppm, R = H, X = CF$_3$SO$_3$
11, L' = PPh$_3$, R = Me, X = CF$_3$SO$_3$
13, L' = PPh$_3$, R = H, X = CF$_3$SO$_3$
14, L'L' = bu$_2$bipy, R = Me, X = BF$_4$
16, L'L' = bu$_2$bipy, R = H, X = BF$_4$

5, L'L' = dppp, X = CF$_3$SO$_3$
8, L'L' = dppm, X = CF$_3$SO$_3$
12, L' = PPh3, X = CF$_3$SO$_3$
15, L'L' = bu$_2$bipy, X = BF$_4$

Abbreviations



This work was developed on the basis of earlier studies of palladium(II) complexes containing carboxylic acid groups. It was found that neutral palladium(II) dichloride complexes can give supramolecular structures through intermolecular hydrogen bonding but that, in cationic complexes, the desired hydrogen bonding between carboxylic acid groups did not occur because H bonding of the carboxylic acid groups to the anions or to solvent molecules was generally preferred.[8a,b] Amides form stronger hydrogen bonds, most commonly of the types shown in Chart 1,[6] so there was potential for a more versatile self-assembly system. Primary amides can give ladder structure **II**, whereas secondary amides cannot and tend to give chain structures **III** or **IV** (Chart 1). In the present research, it was planned that pairs of amide groups of both kinds at a square-planar palladium(II) center, with varying stereochemistry and in conjunction with tertiary phosphine or diimine ligands, would be incorporated to investigate the resulting supramolecular chemistry. The successful results of the research are described here.

Results and Discussion

Synthesis and Characterization of Complexes. The neutral complexes *trans*-[PdCl$_2$L$_2$] {**1**, L = *N*-methylnicotinamide (MNA); **2**, isonicotinamide (INA); **3**, L = nicotinamide (NA)} were prepared by the displacement of weakly bound benzonitrile ligands in *trans*-[PdCl$_2$(PhCN)$_2$] with the corresponding ligands (Chart 2). These neutral compounds are yellow, air-stable solids that are insoluble in common organic solvents but soluble in DMF and DMSO, presumably because these solvents are able to break down the hydrogen-bonded network structures.

The reaction of [Pd(dppp)(OTf)$_2$][11] (dppp = 1,3-bis(diphenylphosphino)propane) and [Pd(dppm)(OTf)$_2$] (dppm = bis(diphenylphosphino)methane) with MNA, INA, and NA gave cationic complexes **4**−**9** (Chart 2). All of these complexes are white, air-stable solids whose characterization data are given in the Experimental Section. These complexes are locked in the cis stereochemistry by diphosphine ligands, and it was planned that related complexes with trans stereochemistry would be prepared by using the complex *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] as the starting material.[12] However, the reaction of *trans*-[Pd(PPh$_3$)$_2$-Cl$_2$] with silver triflate gave a yellow-green product, which was

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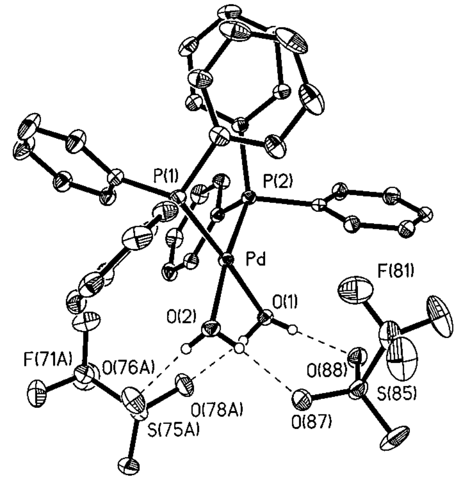

Figure 1. View of the structure of complex **10**, showing the hydrogen bonding between aqua ligands and triflate anions. Selected bond lengths (Å) and angles (deg): Pd−P(1) = 2.2498(6), Pd−P(2) = 2.2772(7), Pd−O(1) = 2.130(2), Pd−O(2) = 2.119(2), O(2)−Pd−O(1) = 87.06(7), O(2)−Pd−P(1) = 91.69(5), O(1)−Pd−P(2) = 86.40(5), P(1)−Pd−P(2) = 94.94(2), O(1)−Pd−P(1) = 177.02(5), O(2)−Pd−P(2) = 173.08(5).

characterized as *cis*-$[Pd(PPh_3)_2(OH_2)_2]$ $(OTf)_2$ (**10**), with the water being derived from an adventitious solvent impurity. This compound is moderately stable at 4 °C, but it decomposed at ambient temperature in several days. There are a few analogous aqua complexes; it is likely that *cis*-$[Pd(PPh_3)_2(OTf)_2]$ is formed first and that aquation occurs during recrystallization.[11b−e] Complex **10** reacted with MNA, INA, and NA to give complexes **11**−**13** (Chart 2) in high yield. These complexes are pale-yellow, air-stable solids.

To investigate complexes with ancillary ligands other than phosphorus donors, the complexes **14**−**16** (Chart 2) were prepared by the reaction of $[Pd(bu_2bipy)Cl_2]$ with silver triflate, followed by a reaction with NA ligands. These products are white, air-stable solids.

Molecular and Supramolecular Structures. 1. Precursor Complex 10. The structure of **10** is shown in Figure 1, and the hydrogen bonding data are in Table 1. The structure is similar to that established earlier for $[Pd(dppp)(OH_2)_2](OTf)_2$,[11c] and the hydrogen bonding between the aqua ligands and triflate anions is similar in the two compounds. The surprising feature is the ease of stereochemical change in the formation of **10** from the precursor that has trans stereochemistry.

2. Neutral Complex 1. The structure of complex **1**·H_2O is shown in Figure 2. The molecular structure is *trans*-$[PdCl_2L_2]$ (L = MNA), and the palladium atom lies on a crystallographic inversion center such that the angles N−Pd−N and Cl−Pd−Cl are 180°. The plane of the pyridine ring is inclined by 61° to the PdN_2Cl_2 coordination plane, giving a conformation similar to that in the analogous complex with L = pyridine-3-carboxylic acid.[8b] The C(═O)NC atoms of the C(O)NHMe substituents are essentially coplanar, as expected and observed for the free compound MNA.[13] In addition, the dihedral angle (23.5°) between the planes of the pyridine ring and that of the *N*-methylamide group is very similar to that in the free ligand (22°); the large deviation from coplanarity is common in compounds of the type ArC(═O)NHR.[14] It follows from the molecular symmetry that the C(═O)NHMe groups are located on opposite sides of the $PdCl_2N_2$ coordination plane.

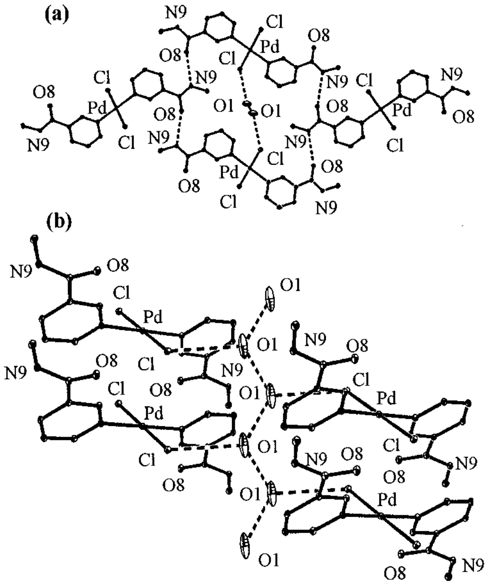

Figure 2. (a) View of the structure of complex **1**·H_2O, showing part of the polymer sheet formed by intermolecular hydrogen bonding as viewed down the *a* axis. (b) Part of the zigzag chain of water molecules that connect the sheets to give a 3D network. Selected bond lengths (Å) and angles (deg): Pd−N(1) = 2.017(3), Pd−Cl = 2.3071(8), N(1)−Pd−Cl = 88.88(8), N(1)−Pd−Cl#1 = 91.12(8). The angles N(1)−Pd−N(1)#1 and Cl−Pd−Cl#1 are 180° by symmetry.

For the *N*-methylamido group, the HN−C═O orientation is anti, so the formation of complementary hydrogen-bond donor−acceptor pairs is not possible. In the structure of **1**, all of the amide groups are involved in C(4) chains[15] via N−H···O hydrogen bonding to form infinite chains of type **IV** (Chart 1), and these are connected by the coordination to palladium(II) to form 2D sheets with cavities, as shown in Figure 2. The hydrogen bonding between individual carboxamide groups is similar to that in the parent ligand structure but with somewhat weaker hydrogen bonds, as indicated by the longer distance of N···O = 3.032(4) Å compared to 2.943 Å for acetanilide.[6] Each cavity in the sheet is occupied by two water molecules. The oxygen atoms of these water molecules appear to be disordered, and this made locating the hydrogen atoms difficult; one hydrogen was found, directed toward a chloride ligand with O···Cl = 3.140 Å, H···Cl = 2.32 Å, and O−H···Cl = 158°. Because there is a short contact O···O = 2.37 Å (there is disorder of the water oxygen atoms over two closely spaced positions, so these distances should be regarded as approximate), it is likely that there is hydrogen bonding to connect these oxygen atoms, but its exact nature could not be determined. These hydrogen bonds reinforce the sheet structure formed by the intermolecular carboxamide hydrogen bonds, as shown in Figure 2a. The sheets shown in Figure 2a are stacked vertically, connected by short contacts Pd···Cl = 3.496 Å and O···O = 2.49 Å. This short O···O contact, again, suggests a hydrogen-bonding interaction, and the alternating contacts with O···O = 2.37 and 2.49 Å give rise to zigzag chains of water molecules, running perpendicular to the sheets, that fill the cavities between the amide ligands, leading to an overall 3D network structure (Figure 2b). A likely overall hydrogen-bonding scheme for the water molecules is shown in Scheme 1.

3. Cationic Cis Complexes $[Pd(dppp)L_2](CF_3SO_3)_2$ (4) and $[Pd(bu_2bipy)L_2](BF_4)_2$ (14) with L = MNA. In the structure of **4**, the coordination geometry is distorted square-planar with

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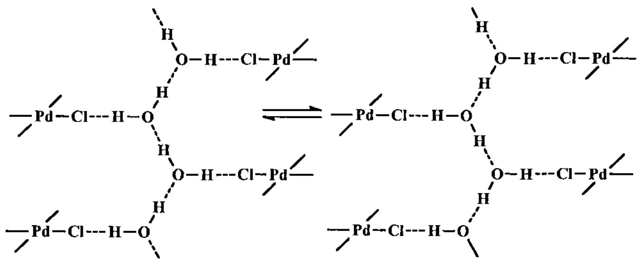
Scheme 1. Proposed H-Bonding and Water Disorder Model in Complex **1**



cis-PdP$_2$N$_2$ coordination. The pyridine rings of the two cis-coordinated MNA molecules lie approximately perpendicular to the PdN$_2$P$_2$ coordination plane of the cation, as indicated by the torsion angles N(2)−Pd−N(1)−C(3) = 90.0° and N(1)−Pd−N(2)−C(17) = 88.7°, and the two amide groups are situated on the same side of the PdN$_2$P$_2$ plane. In this structure, only half of the NH and C=O groups are involved in intermolecular hydrogen bonding between the amide groups (N−H···O=C, with N···O = 2.885(7) Å). This hydrogen bonding links two cations to form a dimer that contains a centrosymmetric $R_2^2(24)$ ring, as shown in Figure 3a. One amide group in each cation serves as a hydrogen-bonding donor, while the other serves as an acceptor. The remaining C=O groups take part in weak hydrogen bonding C−H···O=C (C···O = 3.086 Å, H···O = 2.4 Å, C−H···O = 161°) with phenyl groups of an adjacent dimer, leading to the formation of $R_4^4(32)$ rings. The combination of these two types of hydrogen bonding results in infinite polymeric ribbons, as shown in Figure 3b. All of the triflate anions and acetone solvate molecules are located in channels between adjacent polymeric ribbons. Half of the triflate anions are involved in weak N−H···O hydrogen bonding (N···O = 3.259 Å, H···O = 2.6 Å, N−H···O = 1.36°) with the remaining N−H groups. There is no hydrogen bonding between the polymeric ribbons. This complex hydrogen-bonding motif is aided by the distortion of the C(=O)NHMe substituents. One of these amide groups in each cation is twisted out of the plane of the pyridine ring, with C(17)−C(16)−C(18)−N(4) = −41.0°, while the other is essentially coplanar with the pyridine ring, as shown by C(7)−C(6)−C(8)−N(3) = −1.6°. This arrangement allows the out-of-plane amide group to donate an N−H···O=C hydrogen bond to the in-plane amide group of a second cation and to accept a C−H···O=C hydrogen bond from a phenyl group in a third cation.

The molecular structure of the cation [Pt(bu$_2$bipy)(MNA)$_2$]$^{2+}$ in complex **14** is similar to that in complex **4**, with the amide groups located on the same side of the PdN$_4$ plane as shown in Figure 4. However, in this case, there is no amide−amide hydrogen bonding. The supramolecular association occurs through weak hydrogen bonding of the type C=O···H−C, involving an aryl C−H group of a bu$_2$bipy ligand and one of the C(=O)NHMe groups leading to the formation of an $R_2^2(18)$ cationic dimer (Figure 4a). All of the NH groups act as hydrogen-bond donors to the tetrafluoroborate anions to form links of the type NH···FBF···HN, as shown in Figure 4b, so the tetrafluoroborate anions form bridges between the dimers, thus giving infinite chains.[16]

4. NA Complexes [Pd(dppp)(NA)$_2$](CF$_3$SO$_3$)$_2$ (6) and *cis*-[Pd(PPh$_3$)$_2$(NA)$_2$](CF$_3$SO$_3$)$_2$ (13). In the NA complexes, there are NH groups both syn and anti to the C=O vector in each C(=O)NH$_2$ group. Hence, there is a difference from the MNA complexes in that the complementary hydrogen-bonding pairs are possible and that they are observed in both **6** and **13**. The structure of **6** is shown in Figure 5. There is the expected *cis*-PdP$_2$N$_2$ coordination, and the pyridine rings lie roughly orthogonal to the coordination plane. The amide groups are located on the same side of the coordination plane. The orientation of the amide groups relative to the pyridine rings is different. One amide group is roughly coplanar with the pyridyl ring to which it is connected, as shown by the pyridyl−amide dihedral angle of 3.8°, while the other is twisted out of the plane of the pyridine ring by 29.7°. The anti N−H groups take part in hydrogen bonding, one with a solvate acetone molecule and the other with a triflate anion (illustrated in Figure 5a); the triflate is further bound by weak CH···O and Pd···O interactions (Figure 5a). The molecules of **6** associate through intermolecular complementary pairwise hydrogen bonding between C(=O)NH$_2$ groups of type **I** (Chart 1) to form infinite zigzag polymeric chains (Figure 5b) using the syn NH groups and carbonyl groups. Similar hydrogen-bonded chains are formed in [Pt(PEt$_3$)$_2$-(NC$_5$H$_4$-4-CONH$_2$)$_2$](NO$_3$)$_2$,[10a] but this then forms a 2D structure by connecting adjacent chains via water and nitrate anions.

The structure of complex **13** is shown in Figure 6. This structure is similar to that of **6** in containing the *cis*-PdP$_2$N$_2$ coordination and with the pyridine rings oriented essentially

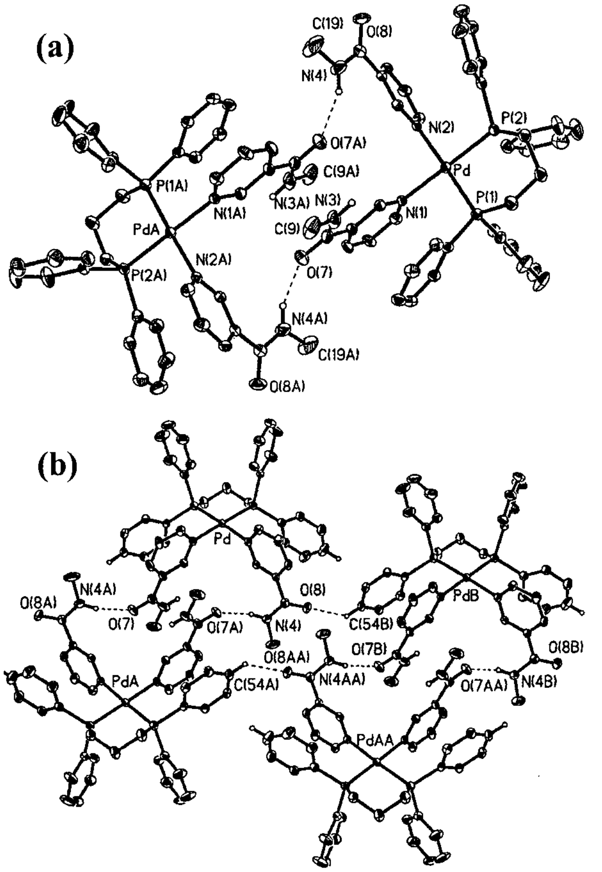


Figure 3. (a) View of a cation dimer of complex **4**·acetone, formed by intermolecular N−H···O hydrogen bonding. (b) View of part of the polymeric ribbon formed by N−H···O and C−H···O hydrogen bonding, as viewed down the *b* axis. All of the triflate anions and solvate acetone molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−N(1) = 2.104(3), Pd−N(2) = 2.125(3), Pd−P(1) = 2.286(1), Pd−P(2) = 2.279(1), N(1)−Pd−N(2) = 88.7(1), N(1)−Pd−P(1) = 89.8(1), N(2)−Pd−P(2) = 90.4(1), P(1)−Pd−P(2) = 91.02(5), N(1)−Pd−P(2) = 179.1(1), N(2)−Pd−P(1) = 178.2(1).

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(16) Bondy, C. R.; Gale, P. A.; Loeb, S. J. *J. Chem. Soc., Chem. Commun.* **2001**, 729.

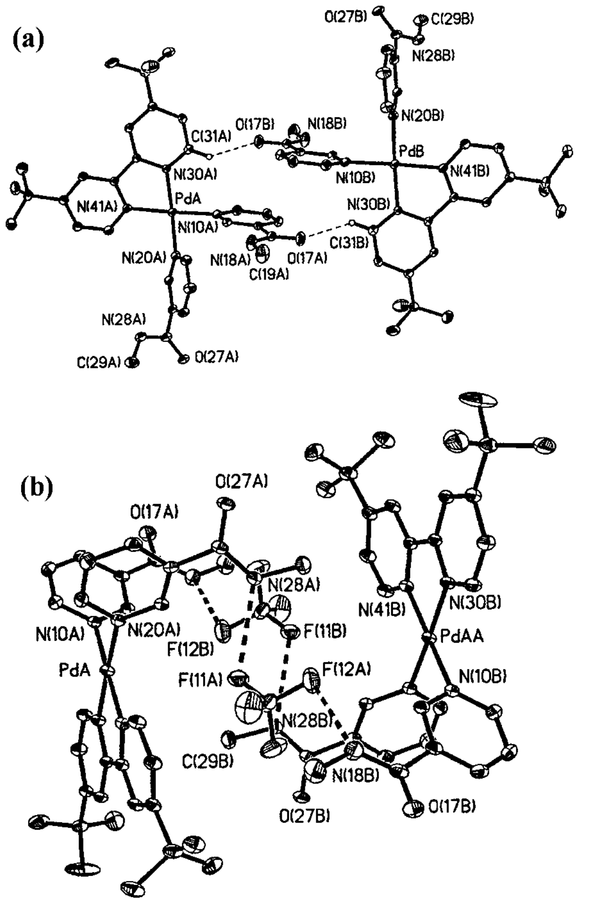

Figure 4. Views of the structure of complex **14**·2.5acetone: (a) dimer formed by C−H···O=C hydrogen bonding and (b) dimer formed by N−H···F hydrogen bonds. Most of the hydrogen atoms, some of the anions, and some of the solvate molecules are omitted for clarity. The combination of the association in a and b gives rise to a 1D polymeric structure. Selected bond lengths (Å) and angles (deg): Pd−N(10) = 2.033(4), Pd−N(20) = 2.032(4), Pd−N(30) = 2.009(4), Pd−N(41) = 2.004(4), N(20)−Pd−N(10) = 86.6(1), N(30)−Pd−N(10) = 96.1(1), N(41)−Pd−N(30) = 80.8(1), N(41)−Pd−N(20) = 96.5(1), N(30)−Pd−N(20) = 177.2(1), N(41)−Pd−N(10) = 176.2(2).

perpendicular to the coordination plane (dihedral angles of 85.5° and 76.5°). However, there is a significant difference because the two amide groups in **13** lie on opposite sides of the coordination plane while they lie on the same side in complex **6** (Figure 5). Both $C(=O)NH_2$ groups are twisted out of the plane of the pyridine rings, and this orientation makes it possible for intermolecular complementary hydrogen bonding (distorted type **I** in Chart 1) to give roughly linear chains as shown in Figure 6b. Hydrogen bonds between the remaining anti N−H groups, triflate anions, and solvate acetone molecules serve to link adjacent chains, resulting in an overall 2D structure. The binding of one triflate anion is shown in Figure 6a and involves N(28)H···O(38) binding, along with three weak CH···O hydrogen bonds with two bonds to O(38) and one to O(37). In the overall layer structure, all of the amide groups lie on one side and all of the phenyl groups on the other. The sheets then pack back-to-back so that further intersheet interactions between phenyl groups are maximized on one side and the polar amide−triflate−solvent interactions are possible on the other.

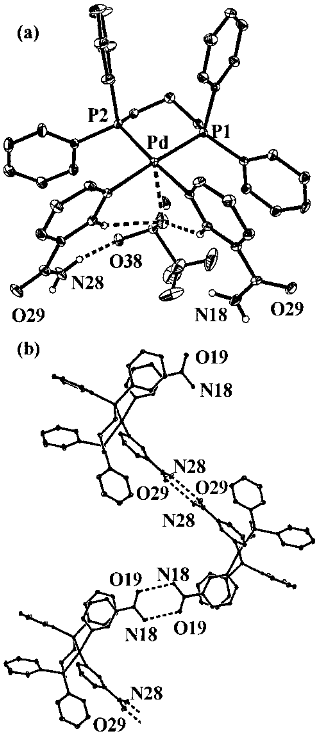

Figure 5. Views of the structure of complex **6**·2acetone: (a) binding of a triflate anion and (b) part of a zigzag polymeric ribbon connected by complementary carboxamide hydrogen bonds. All of the triflate anions and solvate acetone molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−N(11) = 2.105(4), Pd−N(21) = 2.128(4), Pd−P(1) = 2.276(1), Pd−P(2) = 2.274(1), N(11)−Pd−N(21) = 87.1(1), N(11)−Pd−P(1) = 91.0(1), N(21)−Pd−P(2) = 93.2(1), P(1)−Pd−P(2) = 88.90(5), N(11)−Pd−P(2) = 173.2(1), N(21)−Pd−P(1) = 177.3(1).

5. INA Complexes $[Pd(dppm)(INA)_2](CF_3SO_3)_2$ (8) and *cis*-$[Pd(bu_2bipy)(INA)_2](BF_4)_2$ (15). In the structure of complex **8** shown in Figure 7, each palladium atom, again, has *cis*-PdP_2N_2 coordination. One $C(=O)NH_2$ substituent in each molecule takes part in complementary pairwise hydrogen bonding to a neighboring molecule to form a dimer. An important feature of the structure is the anti arrangement of the other two INA ligands within these dimers. One NH group of each of these INA ligands takes part in hydrogen bonding to the carbonyl group of an INA ligand in a neighboring dimer that is already involved in pairwise hydrogen bonding (Figure 7). The combination of these two types of amide−amide hydrogen bonds leads to an infinite ladder-type (double-stranded) chain, as indicated in Figure 7a. The remaining amide N−H groups are hydrogen bonded to oxygen atoms from a triflate counterion, as shown in Figure 7b, and this reinforces the hydrogen-bonded structure and occupies the space between the rungs of the ladder. The combination of the hydrogen bonds and the amide−amide hydrogen bonds results in the formation of $R_4^3(10)$ rings, as shown by Figure 7b. There is no hydrogen bonding between the chains.

In the structure of **15** shown in Figure 8, the asymmetric unit contains two independent complex cations [abbreviated as Pd(1) and Pd(2)], which differ slightly in conformational details but have the same square-planar PdN_4 coordination. The pyridine rings are approximately perpendicular to the coordination plane in each cation. The amide groups twist from the pyridine planes by 29° and 31° in one cation and by 40° and 40° in the other. There are no complementary pairwise intermolecular hydrogen bonds in this case, but each Pd(1) cation is linked to two Pd(2) cations through hydrogen bonding (involving *anti*-N−H···O=C interactions), leading to an infinite zigzag polymeric chain. In addition, neighboring Pd(1) cations are connected by hydrogen bonding mediated by water molecules of the form C=O···HO···HN, and neighboring Pd(2) cations are similarly connected, as

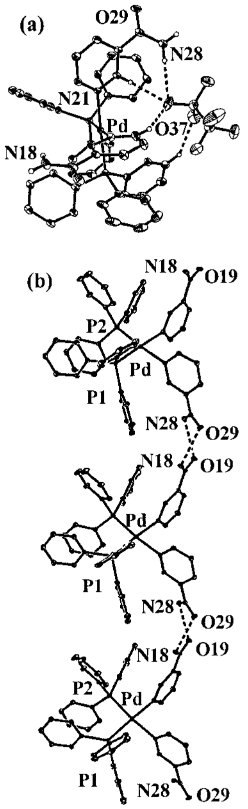

Figure 6. Structure of complex **13**·acetone: (a) view showing the binding of a triflate anion through H bonding [N(28)−H···O(38), two C−H···O(38), one C−H···O(37)] and (b) part of the polymeric ribbon structure formed by complementary hydrogen bonding. All of the triflate anions, solvate acetone molecules, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−N(11) = 2.082(8), Pd−N(21) = 2.128(8), Pd−P(1) = 2.322(3), Pd−P(2) = 2.297(3), N(11)−Pd−N(21) = 84.7(3), N(11)−Pd−P(1) = 92.1(2), N(11)−Pd−P(2) = 89.1(3), P(1)−Pd−P(2) = 94.1(1), N(11)−Pd−P(1) = 176.7(3), N(21)−Pd−P(2) = 173.8(2).

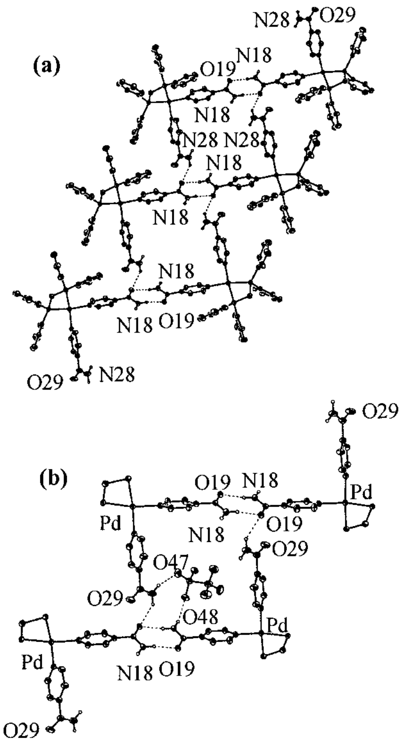

Figure 7. (a) View of the structure of complex **8**·acetone, showing part of the polymeric ladder formed by two types of N−H···O intermolecular hydrogen bonds. All of the hydrogen atoms, with the exception of those involved in hydrogen bonding, are omitted for clarity. All of the triflate anions and solvate acetone molecules are also omitted. (b) View of the structure of **8**·acetone showing the motif of hydrogen bonding between triflate anions and N−H groups. Selected bond lengths (Å) and angles (deg): Pd−N(11) = 2.099(3), Pd−N(21) = 2.109(3), Pd−P(1) = 2.249(1), Pd−P(2) = 2.253(1), N(11)−Pd−N(21) = 88.5(1), N(11)−Pd−P(1) = 97.6(1), N(21)−Pd−P(2) = 102.1(1), P(1)−Pd−P(2) = 71.72(5), N(11)−Pd−P(2) = 169.3(1), N(21)−Pd−P(1) = 170.2(1).

shown in Figure 8. The combination of these two types of hydrogen bonding gives a ladder-type polymer (Figure 8).

Concluding Discussion

This work has shown that both neutral and cationic palladium(II) complexes containing carboxamide groups are readily prepared and that they self-assemble to form interesting supramolecular arrays. The neutral complex *trans*-[PdCl$_2$(NC$_5$H$_4$-3-CONHMe)$_2$] forms an infinite 2D sheet structure in the solid state, and both amide−amide and chloride−water hydrogen-bonding interactions are important in linking neighboring molecules. The sheets are further connected by weaker Pd···Cl bonds and O···H−O hydrogen bonds to form a 3D network.

In contrast to the analogous complexes containing carboxylic acid groups,[8a,b] most of the cationic complexes reported here also self-assemble to give amide−amide hydrogen-bonded supramolecular architectures, which are of several different types. The supramolecular structures can be described as chains, ladders, or sheets. Both of the NA complexes that were structurally characterized exist as chain structures with complementary hydrogen bonding between carboxamide groups (Figures 5 and 6), but the structures are very different. In complex **13** (Figure 6), the segregation between nonpolar triphenylphosphine and polar carboxamide regions is particularly clearly defined; the linear chains align to give sheets with all of the phenyl groups on one side and all of the amide groups on the other side. Both of the INA complexes that were structurally characterized give ladder structures (**8** in Figure 7 and **15** in Figure 8), and a ladder structure was also observed for the MNA complex (**4** in Figure 3). In all of these cases, the outer sections contain the nonpolar phenyl or *tert*-butyl substituents while the ladder rungs and the inner section contain the more polar groups, including the carboxamide, anionic, and any solvent molecules. It must be noted that the hydrogen-bonding motifs are different in all of the cases. Overall, the structures described in this paper, combined with those reported by other research groups,[9,10] demonstrate that carboxamide groups have great potential in the combined coordination chemistry-plus-hydrogen bonding approach to the formation of supramolecular arrays of different types. At this point, the detailed supramolecular structures are still difficult to predict, but it is already clear that both of the specific carboxamide groups used (primary vs secondary), its position on the pyridine ligand used, and, in the cationic complexes, the nature of the supporting ligands and the anions can all be influential factors.[9,10] It is still too early to predict the supramolecular structures, but it is clear from this work that, in complexes with bulky organic ligands, the tendency to segregate the hydrophilic and hydrophobic regions in the supramolecular association is an important factor. This contribution adds several new features to the fast-developing field of supramolecular chemistry and aids in the fundamental understanding of molecular recognition and the systematic rationalization of molecular aggregation in inorganic crystal engineering.

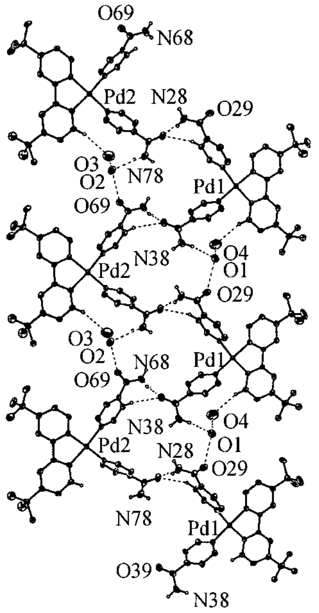

Figure 8. View of the structure of complex **15**$\cdot$Me$_2$CO$\cdot$2H$_2$O, showing part of the polymeric ladder structure formed by intermolecular N−H$\cdots$O and water-mediated amide hydrogen bonds. All of the triflate anions, solvate acetone molecules, and hydrogen atoms, except those taking part in hydrogen bonding, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−N(1) = 2.005(7), Pd(1)−N(12) = 2.011(7), Pd(1)−N(21) = 2.029(8), Pd(1)−N(31) = 2.031(8), N(1)−Pd(1)−N(12) = 80.4(3), N(12)−Pd(1)−N(21) = 95.4(3), N(1)−Pd(1)−N(31) = 97.8(3), N(21)−Pd(1)−N(31) = 86.4(3), N(1)−Pd(1)−N(21) = 172.7(3), N(12)−Pd(1)−N(31) = 178.2(3), Pd(2)−N(41) = 2.007(7), Pd(2)−N(52) = 2.005(7), Pd(2)−N(71) = 2.030(8), Pd(2)−N(61) = 2.033(8), N(41)−Pd(2)−N(52) = 80.4(3), N(41)−Pd(2)−N(71) = 97.8(3), N(52)−Pd(2)−N(61) = 95.7(3), N(71)−Pd(2)−N(61) = 86.1(3), N(41)−Pd(2)−N(61) = 173.0(3), N(52)−Pd(2)−N(71) = 178.2(3).

Experimental Section

All of the reactions were conducted under a dry nitrogen atmosphere using Schlenk techniques; however, the products may be handled in air, and water was not rigorously excluded during recrystallizations. NMR spectra, including 2D spectra, were recorded using a Varian Mercury-400 spectrometer. ^{1}H, ^{31}P, and ^{19}F chemical shifts were reported relative to TMS, external 85% H_3PO_4, and external $CFCl_3$, respectively. IR spectra were recorded as Nujol mulls using a Perkin-Elmer 2000 FTIR spectrometer.

[PdCl$_2$(NC$_5$H$_4$-3-CONHMe)$_2$] (1). To a solution of [Pd(PhCN)$_2$Cl$_2$] (76.7 mg, 0.200 mmol) in THF (10 mL) was added a solution of MNA (54.9 mg, 0.400 mmol) in THF (10 mL). After 2 h, the yellow precipitate that formed was separated by filtration, washed with acetone, and dried in vacuo. Yield: 84.0 mg, 93%. Anal. Calcd for $C_{14}H_{16}Cl_2N_4O_2Pd$: C, 37.40; H, 3.59; N, 12.46. Found: C, 37.15; H, 3.69; N, 12.00. IR (Nujol): $\nu_{C=O}$ 1644 cm^{-1} (s), ν_{NH} 3477, 3323 cm^{-1} (s). NMR in DMSO: δ (^{1}H) = 9.14 [s, 2H, H^2], 8.87 [d, $^3J_{HH}$ = 6 Hz, 2H, H^6], 8.37 [dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 2H, H^4], 7.67 [dd, $^3J_{HH}$ = 6, 8 Hz, 2H, H^5], 8.91 [br, 2H, NH], 2.80 [d, $^3J_{HH}$ = 4 Hz, 6H, CH$_3$]; δ (^{13}C) = 162.95, 154.84, 151.86, 137.78, 131.42, 125.29, 26.40. Mp: >300 °C. Single crystals of **1**$\cdot$H$_2$O were obtained in several weeks by the slow diffusion of a solution of [PdCl$_2$(PhCN)$_2$] in acetone into a solution of MNA in water.

[PdCl$_2$(NC$_5$H$_4$-4-CONH$_2$)$_2$] (2). This complex was prepared similarly to **1** with the exception that INA was used, and the product was isolated as a yellow powder. Yield: 80 mg, 95%. Anal. Calcd for $C_{12}H_{12}Cl_2N_4O_2Pd$: C, 34.19; H, 2.87; N, 13.29. Found: C, 33.78; H, 2.55; N, 12.72. IR (Nujol): $\nu_{C=O}$ 1699, 1625 cm^{-1}, ν_{NH} 3407, 3172 cm^{-1} (s). NMR in DMSO: δ (^{1}H) = 8.88 [d, $^3J_{HH}$ = 5 Hz, 4H, H^{2,6}], 7.85 [d, $^3J_{HH}$ = 5 Hz, 4H, H^{3,5}], 8.40 [s, 2H, NH], 7.94 [s, 2H, NH]. Mp: >300 °C.

Table 1. Selected Hydrogen-Bonding Interactions

complex	D−H$\cdots$A	H$\cdots$A (Å)	D$\cdots$A (Å)	D−H$\cdots$A (deg)
1	N−H$\cdots$O	2.2	3.032(4)	163
	Ow−H$\cdots$Cl	2.3	3.140(8)	158
	Ow−H$\cdots$Ow	*a*	2.37[b]	*a*
	Ow−H$\cdots$Ow	*a*	2.49[c]	*a*
4	N(4)−H$\cdots$O(7A)	2.1	2.885(7)	149
	C(54A)−H$\cdots$O(8)	2.4	3.086(6)	129
	N(3)−H$\cdots$O(1A)(OTf)	2.6	3.259(7)	136
6	N(18A)−H$\cdots$O(19)	2.0	2.888(6)	160
	N(28B)−H$\cdots$O(29)	2.0	2.865(6)	173
	N(18)−H$\cdots$O(54)$_s$	2.3	3.053(7)	143
	N(28)−H$\cdots$O(38)(OTf)	2.2	3.016(6)	153
8	N(18)−H$\cdots$O(19A)	2.0	2.834(6)	167
	N(28)−H$\cdots$O(19B)	2.2	2.969(6)	145
	N(18)−H$\cdots$O(48D)(OTf)	2.0	2.819(6)	149
	N(28)−H$\cdots$O(47A)	2.1	2.978(6)	162
10	O(1)−H(1A)$\cdots$O(88)	1.9	2.682(2)	178
	O(1)−H(1B)$\cdots$O(78A)	1.9	2.682(2)	170
	O(2)−H(2A)$\cdots$O(87)	1.9	2.716(2)	174
	O(2)−H(2B)$\cdots$O(86A)	1.9	2.713(2)	170
13	N(18)−H$\cdots$O(29A)	2.1	2.97(2)	168
	N(28a)−H$\cdots$O(19)	2.1	2.98(2)	168
14	C(31C)−H$\cdots$O(17A)	2.3	3.094(6)	144
	N(28C)−H$\cdots$F(11A)	2.0	2.896(8)	173
	N(18B)−H$\cdots$F(12A)	2.5	3.339(9)	157
15	N(28A)−H$\cdots$O(79A)	2.0	2.85(1)	165
	N(68A)−H$\cdots$O(39B)	2.0	2.86(1)	163
	N(38B)−H$\cdots$O(1A)(H$_2$O)	2.1	2.92(1)	162
	O(1A)$\cdots$O(29A)	*a*	2.77(1)	*a*
	O(1A)$\cdots$O(4A)(H$_2$O)	*a*	2.83(1)	*a*
	N(78B)−H$\cdots$O(2A)(H$_2$O)	2.1	2.93(1)	164
	O(2A)$\cdots$O(69A)	*a*	2.76(1)	*a*
	O(2A)$\cdots$O(3A)(H$_2$O)	*a*	2.81(1)	*a*

[a] H atom(s) of water not located. [b] Intralayer O$\cdots$O. [c] Interlayer O$\cdots$O.

[PdCl$_2$(NC$_5$H$_4$-3-CONH$_2$)$_2$] (3). This complex was prepared similarly to **1** except that NA was used, and it was isolated as a yellow powder. Yield: 81 mg, 96%. Anal. Calcd for $C_{12}H_{12}Cl_2N_4O_2Pd$: C, 34.19; H, 2.87; N, 13.29. Found: C, 33.85; H, 2.57; N, 12.85. IR (Nujol): $\nu_{C=O}$ 1704, 1624 cm^{-1}, ν_{NH} 3394, 3154 cm^{-1} (s). NMR in DMSO: δ (^{1}H) = 9.18 (s, 2H, H^2), 8.87 (d, $^3J_{HH}$ = 6.0 Hz, 2H, H^6), 8.40 (d, $^3J_{HH}$ = 8 Hz, 2H, H^4), 7.67 (dd, $^3J_{HH}$ = 6, 8 Hz, 2H, H^5), 8.39 (s, 2H, NH), 7.87 (s, 2H, NH). Mp: >300 °C.

[Pd(dppp)(NC$_5$H$_4$-3-CONHMe)$_2$](CF$_3$SO$_3$)$_2$ (4). A mixture of [Pd(dppp)(CF$_3$SO$_3$)$_2$][11a] (81.7 mg, 0.100 mmol) and MNA (27.3 mg, 0.200 mmol) in THF (15 mL) was stirred for 3 h, then the solution was concentrated to 5 mL, and pentane (40 mL) was added to give a white precipitate that was separated by filtration, washed with pentane, and dried in vacuo. Yield: 91 mg, 84%. Anal. Calcd for $C_{43}H_{42}F_6N_4O_8P_2PdS_2$: C, 47.41; H, 3.89; N, 5.14. Found: C, 47.30; H, 3.75; N, 5.00. IR (Nujol): $\nu_{C=O}$ 1673 cm^{-1} (s), ν_{NH} 3373 cm^{-1} (s), 3525 cm^{-1}, $\nu_{SO_3CF_3}$ 1030 cm^{-1} (s), 1162 cm^{-1} (s). NMR in acetone: δ (^{1}H) = 9.34 [br, s, 2H, H^2], 9.05 [br, s, 2H, H^6], 8.20 [d, $^3J_{HH}$ = 8 Hz, 2H, H^4], 7.2−8.0 [m, 34H, H^5 − Py + CONH + H − Ph], 2.86 [d, $^3J_{HH}$ = 5 Hz, 6H, CH$_3$], 3.36 [br, PC*H*$_2$], 2.85 [br, PCH$_2$C*H*$_2$]; δ (^{31}P) = 8.56 (s); δ (^{19}F) = −79.19 (s). Mp: 258 °C. Single crystals of **4**$\cdot$acetone were obtained from an acetone/pentane solution by slow diffusion.

[Pd(dppp)(NC$_5$H$_4$-4-CONH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (5). This was prepared similarly to **4** except that INA was used. Yield: 82.5%. Anal. Calcd for $C_{41}H_{38}F_6N_4O_8P_2PdS_2$: C, 46.40; H, 3.61; N, 5.28. Found: C, 45.80; H, 3.40; N, 5.15. IR (Nujol): $\nu_{C=O}$ 1686, 1612 cm^{-1}, ν_{NH} 3397, 3340, 3205 cm^{-1}. NMR in acetone: δ (^{1}H) = 9.13 [d, $^3J_{HH}$ = 4 Hz, 4H, H^{2,6}], 7.53 [d, $^3J_{HH}$ = 4 Hz, 2H, H^{3,5}], 7.75 [s, 2H, NH], 7.12 [s, 2H, CONH], 7.80 [m, 8H, H^{3,5} − Ph], 7.47 [m, 4H, H^4 − Ph], 7.39 [m, 8H, H^{2,6} − Ph], 3.38 [br, s, 4H, PC*H*$_2$], 2.60 [br, m, 2H PCH$_2$C*H*$_2$]; δ (^{31}P) = 8.35 (s); δ (^{19}F) = −79.2 (s). Mp: 198 °C.

[Pd(dppp)(NC$_5$H$_4$-3-CONH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (6). This was prepared similarly to **4** except that NA was used. Yield: 91%. Anal. Calcd for $C_{41}H_{38}F_6N_4O_8P_2PdS_2$: C, 46.40; H, 3.61; N, 5.28. Found: C, 46.11;

Table 2. Crystallographic Data, Data Collection, and Refinement Parameters

	1·H_2O	**4**·Me_2CO	**6**·$2Me_2CO$	**8**·Me_2CO
formula	$C_{14}H_{20}Cl_2N_4O_4Pd$	$C_{46}H_{48}F_6N_4O_9P_2PdS_2$	$C_{47}H_{50}F_6N_4O_{10}P_2PdS_2$	$C_{42}H_{40}F_6N_4O_9P_2PdS_2$
fw	485.64	1147.34	1177.37	1091.24
temp (K)	200(2)	150(2)	200(2)	200(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P2(1)/c$	$P\bar{1}$	$Pbcn$	$P\bar{1}$
a (Å)	4.0558(3)	13.444(3)	14.1456(4)	10.7013(3)
b (Å)	10.1814(8)	13.553(3)	21.0391(5)	12.1564(3)
c (Å)	21.7453(14)	14.578(3)	35.0323(9)	20.2002(5)
α (deg)	90	81.14(3)	90	101.8430(10)
β (deg)	93.832(4)	84.18(3)	90	98.5680(10)
γ (deg)	90	77.70(3)	90	102.6280(10)
vol (Å^3)	895.94(11)	2557.9	10426.0(5)	2457.44(11)
Z	2	2	8	2
D_{calcd} (g cm^{-3})	1.800	1.490	1.500	1.475
μ (mm^{-1})	1.361	0.585	0.578	0.605
$F(000)$	488	1172	4816	1108
θ range (deg)	2.74−27.49	4.11−26.40	2.61−25.03	2.59−27.48
range h	−5 to 5	0 to 16	−16 to 16	−13 to 13
range k	−13 to 12	−16 to 16	−23 to 24	−15 to 15
range l	−28 to 28	−18 to 18	−41 to 41	−26 to 26
reflns collected	5812	21 992	38 100	28 248
unique reflns	2041	10 021	9094	11 242
max and min transm	0.9630, 0.7018	0.0524	0.9717, 0.9032	0.9094, 0.7600
R indices [$I > 2\sigma(I)$]^a				
R1	0.0362	0.1208	0.0561	0.0600
wR2	0.0752		0.1237	0.1701

	10	**13**·Me_2CO	**14**·$2.5Me_2CO$	**15**·Me_2CO·$2H_2O$
formula	$C_{38}H_{34}F_6O_8P_2PdS_2$	$C_{53}H_{48}F_6N_4O_9P_2PdS_2$	$C_{39.50}H_{53.50}B_2F_8N_6O_{4.50}Pd$	$C_{33}H_{42}B_2F_8N_6O_5Pd$
fw	965.11	1231.41	964.40	882.75
temp (K)	200(2)	200(2)	200(2)	200(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.5132(3)	12.4775(7)	12.3417(9)	11.6074(7)
b (Å)	19.5022(7)	12.870 75(5)	12.4393(9)	13.9377(8)
c (Å)	20.2079(4)	17.5888(6)	16.1222(11)	24.6962(11)
α (deg)	90	71.835(2)	70.494(4)	89.994(3)
β (deg)	97.011(2)	88.993(3)	86.609(3)	88.272(3)
γ (deg)	90	86.174(3)	88.409(4)	90.002(3)
vol (Å^3)	4112.3(2)	2677.9(2)	2328.9(3)	3993.5(4)
Z	4	2	2	4
D_{calcd} (g cm^{-3})	1.559	1.527	1.375	1.468
μ (mm^{-1})	0.707	0.565	0.475	0.548
$F(000)$	1952	1256	993	1800
θ range (deg)	2.84−27.47	2.80−27.49	2.07−26.32	2.79−24.11
range h	−13 to 13	−16 to 16	0 to 15	−13 to 11
range k	−23 to 25	−16 to 15	−15 to 15	−15 to 14
range l	−26 to 26	−22 to 22	−19 to 20	−25 to 28
reflns collected	37 926	24 135	17 560	18 383
unique reflns	9402	12 139	9337	11 049
max and min transm	0.9489, 0.8175	0.9302, 0.7851	0.9906, 0.8864	0.9272, 0.8106
R indices [$I > 2\sigma(I)$]^a				
R1	0.0359	0.146	0.0708	0.0814
wR2	0.0797	0.388	0.1666	0.2071

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

H, 3.56; N, 5.06. IR (Nujol): $\nu_{C=O}$ 1694, 1631 cm^{-1}, ν_{NH} 3403, 3164 cm^{-1}. NMR in acetone: δ (^{1}H) = 9.39 [s, 2H, H^2], 9.11 [s, 2H, H^6], 8.16 [d, $^3J_{HH}$ = 8.0 Hz, 2H, H^4], 7.00 [s, 2H, NH], 7.79 [br, 8H, H^{2,6} − Ph + CONH], 7.40 [br, 18H, H^5 and H^{3,4,5} − Ph], 3.37 [s, 4H, PCH_2], 2.89 [br, s, 2H PCH$_2$CH_2]; δ (^{31}P) = 8.44 (s); δ (^{19}F) = −79.16 (s). Mp: 255 °C. Single crystals of **6**·2acetone were obtained from an acetone/hexane solution by slow diffusion.

[Pd(dppm)(NC$_5$H$_4$-3-CONHCH$_3$)$_2$](CF$_3$SO$_3$)$_2$ (7). A mixture of [Pd(dppm)(CF$_3$SO$_3$)$_2$] (78.9 mg, 0.100 mmol) and MNA (27.3 mg, 0.200 mmol) in THF (15 mL) was stirred for 2 h, then the solution was concentrated to 5 mL, and pentane (40 mL) was added to give the product as a white precipitate, which was separated by filtration, washed with pentane, and dried in vacuo. Yield: 85.0 mg, 80%. Anal. Calcd for $C_{41}H_{38}F_6N_4O_8P_2PdS_2$: C, 46.40; H, 3.61; N, 5.28. Found: C, 45.90; H, 3.55; N, 5.13. IR (Nujol): $\nu_{C=O}$ 1674 cm^{-1} (s), ν_{NH} 3364 cm^{-1} (s), $\nu_{SO_3CF_3}$ 1029 cm^{-1} (s), 1156 cm^{-1} (s). NMR in acetone: δ (^{1}H) = 9.27 [br, s, 2H, H^6], 9.18 [s, 2H, H^2], 8.39 [dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 2H, H^4], 7.82 [br, 2H, CONH], 7.51 [m, 8H, H^{3,5} − Ph], 7.64 [m, 6H, H^5 − Py + H^4 − Ph], 7.92 [m, 8H, H^{2,6} − Ph], 2.82 [d, $^3J_{HH}$ = 4 Hz, 6H, CH$_3$], 5.20 [t, $^2J_{PCH}$ = 12 Hz, 2H, PCH$_2$]; δ (^{31}P) = −36.54 (s); δ (^{19}F) = −79.24. Mp: 212 °C. Single crystals were obtained from an acetone/hexane solution by slow diffusion.

[Pd(dppm)(NC$_5$H$_4$-4-CONH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (8). This was prepared similarly to **7** except that INA was used. Yield: 81%. Anal. Calcd for $C_{39}H_{34}F_6N_4O_8P_2PdS_2$: C, 45.34; H, 3.32; N, 5.42. Found: C, 44.81; H, 3.07; N, 5.16. IR (Nujol): $\nu_{C=O}$ 1681, 1613 cm^{-1}, ν_{NH} 3409, 3324, 3214 cm^{-1}. NMR in acetone: δ (^{1}H) = 9.19 [d, $^3J_{HH}$ = 5 Hz, 4H, H^{2,6}], 7.88 [d, $^3J_{HH}$ = 5 Hz, 2H, H^{3,5}], 7.20 [s, 2H, CONH], 7.93 [m, 10H, CONH + H^{3,5} − Ph], 7.67 [m, 4H, H^4 − Ph], 7.54 [m, 8H, H^{2,6} − Ph], 5.23 [t, $^2J_{PCH}$ = 12 Hz, 2H, PCH_2]; δ (^{31}P) = −38.17 (s);

δ (^{19}F) = −79.22 (s). Mp: 228 °C. Single crystals of **8**·acetone were obtained from an acetone/hexane solution by slow diffusion.

[Pd(dppm)(NC$_5$H$_4$-3-CONH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (9). This was prepared similarly to **7** except that NA was used. Yield: 85%. Anal. Calcd for $C_{39}H_{34}F_6N_4O_8P_2PdS_2$: C, 45.34; H, 3.32; N, 5.42. Found: C, 44.82; H, 3.18; N, 5.34. IR (Nujol): $\nu_{C=O}$ 1685, 1624 cm^{-1}, ν_{NH} 3399, 3211 cm^{-1}. NMR in acetone: δ (^{1}H) = 9.29 [br, s, 4H, H^{2,6}], 8.47 [d, $^3J_{HH}$ = 7 Hz, 2H, H^4], 6.99 [s, 2H, CONH], 7.92 [m, 8H, H^{2,6} − Ph], 7.51 [m, 8H, H^{3,5} − Ph], 7.65 [m, 8H, H^5 − Py + CONH + H^4 − Ph], 5.21 [t, $^2J_{PCH}$ = 12 Hz, 2H, PC*H$_2$*]; δ (^{31}P) = −36.82 (s); δ (^{19}F) = −79.22 (s). Mp: 190 °C.

[Pd(PPh$_3$)$_2$(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$ (10). To a stirred suspension or solution of *trans*-[PdCl$_2$(PPh$_3$)$_2$] (0.523 mmol, 0.366 g) in CH$_2$Cl$_2$ (50 mL) was added AgOTf (0.269 g, 1.05 mmol), and the mixture was stirred for 24 h. The solution was filtered to remove AgCl, the filtrate was concentrated to 3 mL, and diethyl ether was added to give a yellow-green precipitate, which was collected, washed with ether, and dried in vacuo. Yield: 0.42 g, 88%. IR (Nujol): ν_{O-H} 3168 cm^{-1} (s), $\nu_{SO_3CF_3}$ 1026 cm^{-1} (s), 1165 cm^{-1} (s). NMR in acetone: δ (^{1}H) = 7.49 [m, 12H, H^{3,5} − Ph], 7.65 [m, 18H, H^{2,4,6} − Ph]; δ (^{31}P) = −39.05 (s); δ (^{19}F) = −79.16 (s). Mp: 128 °C. Single crystals of **10** were grown from a CH$_2$Cl$_2$/hexane solution by slow diffusion.

[Pd(PPh$_3$)$_2$(NC$_5$H$_4$-3-CONHCH$_3$)$_2$](CF$_3$SO$_3$)$_2$ (11). A mixture of complex **10** (93 mg, 0.100 mmol) and MNA (27.3 mg, 0.200 mmol) in THF (20 mL) was stirred for 2 h, then the solution was concentrated to 5 mL, and pentane (50 mL) was added to give the product as a pale-yellow precipitate. This was separated by filtration, washed with pentane, and dried in vacuo. Yield: 66 mg, 55%. Anal. Calcd for $C_{52}H_{46}F_6N_4O_8P_2PdS_2$: C, 51.99; H, 3.86; N, 4.66. Found: C, 51.80; H, 3.79; N, 4.50. IR (Nujol): $\nu_{C=O}$ 1668 cm^{-1} (s), ν_{NH} 3355 cm^{-1} (s), 3520 cm^{-1}. NMR in acetone: δ (^{1}H) = 9.41 [d, $^3J_{HH}$ = 6 Hz, 2H, H^6], 8.91 [s, 2H, H^2], 8.12 [d, $^3J_{HH}$ = 8 Hz, 2H, H^4], 7.35 [dd, $^3J_{HH}$ = 8, 6 Hz, 2H, H^5], 7.4−7.8 [m, 30H, H − Ph], 2.83 [d, $^3J_{HH}$ = 5 Hz, 6H, CH$_3$]; δ (^{31}P) = 27.19 (s); δ (^{19}F) = −79.16 (s). Mp: 149 °C dec.

[Pd(PPh$_3$)$_2$(NC$_5$H$_4$-4-CONH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (12). This was prepared similarly to **11** except that INA was used. Yield: 100 mg, 86%. Anal. Calcd for $C_{50}H_{42}F_6N_4O_8P_2PdS_2$: C, 51.18; H, 3.61; N, 4.77. Found: C, 50.79; H, 3.42; N, 4.62. IR (Nujol): $\nu_{C=O}$ 3339, 3191 cm^{-1}, ν_{NH} 1674, 1611 cm^{-1}. NMR in acetone: δ (^{1}H) = 9.15 [d, $^3J_{HH}$ = 4 Hz, 4H, H^{2,6}], 7.13 [s, 2H, NH], 7.47 [m, 16H, H^{3,5} − Py + H^{3,5} − Ph], 7.60 [m, 6H, H^4 − Ph], 7.78 [m, 12H, 2NH + H^{2,6} − Ph]; δ (^{31}P) = 27.13 (s); δ (^{19}F) = −79.15 (s). Mp: 178 °C.

[Pd(PPh$_3$)$_2$(NC$_5$H$_4$-3-CONH$_2$)$_2$] (CF$_3$SO$_3$)$_2$ (13). This was prepared similarly to **11** except that NA was used. Yield: 100 mg, 86%. Anal. Calcd for $C_{50}H_{42}F_6N_4O_8P_2PdS_2$: C, 51.18; H, 3.61; N, 4.77. Found: C, 50.78; H, 3.43; N, 5.10. IR (Nujol): $\nu_{C=O}$ 3397, 3201 cm^{-1}, ν_{NH} 1693, 1623 cm^{-1}. NMR in acetone: δ (^{1}H) = 9.40 [d, $^3J_{HH}$ = 5 Hz, 2H, H^6], 9.07 [s, 2H, H^2], 8.17 [d, $^3J_{HH}$ = 8 Hz, 2H, H^4], 7.38 [dd, $^3J_{HH}$ = 8, 5 Hz, 2H, H^5], 7.4−7.8 [m, 30H, H − Ph], 6.97 [s, 2H, CONH], 7.51 [s, 2H, CONH]; δ (^{31}P) = 27.09 (s); δ (^{19}F) = −79.14 (s). Mp: 185 °C. Single crystals of **13**·acetone were grown from an acetone/hexane solution by slow diffusion.

[Pd(bu$_2$bipy)(NC$_5$H$_4$-3-CONHMe)$_2$](BF$_4$)$_2$ (14). A mixture of [PdCl$_2$(bu$_2$bipy)] (44.5 mg, 0.100 mmol) and AgBF$_4$ (38.9 mg, 0.200 mmol) in THF (15 mL) was stirred for 2 h. The solution was filtered through Celite (to remove AgCl) into a solution of MNA (27.3 mg, 0.20 mmol) in THF (10 mL). The mixture was stirred for 2 h and then concentrated to about 5 mL, and ether (30 mL) was added to give the product as an off-white precipitate, which was collected by filtration, washed with ether and pentane, and dried under vacuo. Yield: 78 mg, 95%. Anal. Calcd for $C_{32}H_{40}B_2F_8O_2N_6Pd$: C, 46.83; H, 4.91; N, 10.24. Found: C, 45.89; H, 4.91; N, 10.00. IR (Nujol): $\nu_{C=O}$ 1662 cm^{-1} (s), ν_{NH} 3407 cm^{-1} (s), 3615 cm^{-1} (m), ν_{BF_4} 1062 cm^{-1} (s). NMR in acetone: δ (^{1}H) = 9.78 [s, 2H, H^2 − Py], 9.55 [br, m, 2H, H^6 − Py], 8.60 [dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, H^4 − Py], 7.98 [br, m, 4H, H^5 − Py + CONH], 8.79 [d, $^4J_{HH}$ = 2 Hz, 2H, H^3 − bu$_2$bipy], 7.69 [dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, H^5 − bu$_2$bipy], 7.54 [d, $^3J_{HH}$ = 6 Hz, 2H, H^6 − bu$_2$bipy], 2.91 [d, $^3J_{HH}$ = 3 Hz, 6H, NCH$_3$], 1.43 [s, 18H, CH$_3$]; δ (^{19}F) = −151.0 (s). Mp: 194 °C. Single crystals of **14**·2.5acetone were obtained from an acetone/pentane solution by slow diffusion.

[Pd(bu$_2$bipy)(NC$_5$H$_4$-4-CONH$_2$)$_2$] (BF$_4$)$_2$ (15). This was prepared similarly to **14** except that INA was used. Yield: 65 mg, 82%. Anal. Calcd for $C_{30}H_{36}B_2F_8N_6O_2Pd$: C, 45.46; H, 4.58; N, 10.60. Found: C, 45.12; H, 4.59; N, 10.32. IR (Nujol): $\nu_{C=O}$ 1685 cm^{-1} (s), ν_{NH} 3345 cm^{-1}, 3417 cm^{-1} (s), 3609 cm^{-1} (m), ν_{BF_4} 1064 cm^{-1} (s). NMR in acetone: δ (^{1}H) = 9.57 [d, $^3J_{HH}$ = 6 Hz, 4H, H^{2,6} − Py], 8.20 [d, $^3J_{HH}$ = 6 Hz, 4H, H^{3,5} − Py], 7.96 [s, 2H, CONH], 7.33 [s, 2H, CONH], 8.79 [d, $^4J_{HH}$ = 2 Hz, 2H, H^3 − bu$_2$bipy], 7.70 [dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, H^5 − bu$_2$bipy], 7.56 [d, $^3J_{HH}$ = 6 Hz, 2H, H^6 − bu$_2$bipy], 1.42 [s, 18H, CH$_3$]; δ (^{19}F) = −151.01 (s). Mp: 216 °C. Single crystals of **15**·acetone·H$_2$O were obtained from an acetone/pentane solution by slow diffusion.

[Pd(bu$_2$bipy)(NC$_5$H$_4$-3-CONH$_2$)$_2$](BF$_4$)$_2$ (16). This was prepared similarly to **14** except that NA was used. Yield: 77 mg, 94%. Anal. Calcd for $C_{30}H_{36}B_2F_8N_6O_2Pd$: C, 45.46; H, 4.58; N, 10.60. Found: C, 44.95; H, 4.48; N, 10.13. IR (Nujol): $\nu_{C=O}$ 1685, 1621 cm^{-1}, ν_{NH} 3467, 3368, 3212 cm^{-1}. NMR in acetone: δ (^{1}H) = 9.85 [s, 2H, H^2 − Py], 9.58 [br, s, 2H, H^6 − Py], 8.66 [d, $^3J_{HH}$ = 8 Hz, 2H, H^4 − Py], 7.99 [m, 2H, H^5 − Py], 7.78 [s, 2H, CONH], 7.23 [s, 2H, CONH], 8.78 [d, $^4J_{HH}$ = 2 Hz, 2H, H^3 − bu$_2$bipy], 7.69 [dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, H^5 − bu$_2$bipy], 7.54 [d, $^3J_{HH}$ = 6 Hz, 2H, H^6 − bu$_2$bipy], 1.43 [s, 18H, CH$_3$]; δ (^{19}F) = −150.80 (s). Mp: 208 °C.

X-ray Structure Determinations. Data were collected using a Nonius κ-CCD diffractometer using COLLECT (Nonius 1997 or 1998) software. The unit cell parameters were calculated and refined from the full data set, and crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius 1997 or 1998), and no other absorption corrections were applied. The SHELXTL 5.1 (Sheldrick, G. M., Madison, WI) program package was used to solve and refine the structures. Anisotropic thermal parameters were applied to all non-hydrogen atoms. A summary of the crystallographic data can be found in Table 2.

The structure of complex **13** was of low quality. Analysis of the $e^2 - 1$ statistics and variance indicated that the crystal was twinned, but a good model for this could not be found. As a result, there was large residual electron density close to the palladium atom. Despite the poor agreement factors, the atoms of the complex cation, the anions, and the solvent molecule are well defined.

Acknowledgment. We thank the NSERC (Canada) for financial support, and R.J.P. thanks the Government of Canada for a Canada Research Chair.

Supporting Information Available: Tables of crystal data, atomic positions and thermal parameters, anisotropic thermal parameters, bond distances, and bond angles have been deposited as CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0106625