Inorg. Chem. **2002**, *41*, 5174–5186

Inorganic Chemistry
Article

Self-Assembly of Polymer and Sheet Structures in Palladium(II) Complexes Containing Carboxylic Acid Substituents

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

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

Kenneth W. Muir

Department of Chemistry, Glasgow University, Glasgow G12 8QQ, U.K.

Received March 28, 2002

A series of complexes *trans*-$[PdCl_2L_2]$ has been prepared by the reaction of $[PdCl_2(PhCN)_2]$ and/or $Na_2[PdCl_4]$ with L = pyridine or quinoline ligands having one or two carboxylic acid groups. These complexes can form 1-D polymers through O–H···O hydrogen bonding between the carboxylic acid groups, as demonstrated by structure determinations of $[PdCl_2(NC_5H_4\text{-}4\text{-}COOH)_2]$, $[PdCl_2(NC_5H_4\text{-}3\text{-}COOH)_2]$, and $[PdCl_2(2\text{-}Ph\text{-}NC_9H_5\text{-}4\text{-}COOH)_2]$. In some cases, solvation breaks down the O–H···O hydrogen-bonded structures, as in the structures of $[PdCl_2(NC_5H_4\text{-}3\text{-}COOH)_2]\cdot 2DMSO$ and $[PdCl_2(2\text{-}Ph\text{-}NC_9H_5\text{-}4\text{-}COOH)_2]\cdot 4DMF$, while pyridine-2-carboxylic acid underwent deprotonation to give the chelate complex $[Pd\{NC_5H_4\text{-}2\text{-}C(O)O\}_2]$. The complexes *trans*-$[PdCl_2L_2]$, L = pyridine-3,5-dicarboxylic acid or 2,6-dimethyl pyridine-3,5-dicarboxylic acid, self-assembled to give 2-D sheet structures, with hydrogen bonding between the carboxylic acid groups mediated by solvate methanol or water molecules. In the cationic complexes $[PdL'_2L_2]^{2+}$ ($L'_2 = Ph_2PCH_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$; L = pyridine carboxylic acid; anions $X^- = CF_3SO_3^-$), hydrogen bonding between the carboxylic acid groups and anions or solvate acetone molecules occurred, and only in one case was a polymeric complex formed by self-assembly.

Introduction

The design of supramolecular architectures by self-assembly of small building blocks has become a major research area.[1] While hydrogen bonding often controls supramolecular organic structures in both natural[2] and synthetic[3] systems, metal complexes are more commonly assembled through coordination chemistry.[4] More recently, the combination of both coordination chemistry and hydrogen bonding has proved to be particularly useful for assembly of complex structures.[5,6] It is well-known that carboxylic acids can take part in hydrogen bonding to give centrosymmetric dimers, and also form other hydrogen bonding motifs in some cases (Chart 1), and the incorporation of carboxylic acid groups into coordination compounds is already known to give interesting supramolecular architectures.[6]

In this paper, the structures arising from supramolecular assembly of complexes *trans*-$[PdCl_2L_2]$ and *cis*-$[Pd(L'L')L_2]^{2+}$ are reported, where L is a ligand containing both a pyridine donor and one or two free carboxylic acid groups that are capable of taking part in hydrogen bonding, and L′L′ is a chelate ligand such as dppm [bis(diphenylphosphino)methane] or dppp [bis(diphenylphosphino)propane] to lock in the cis stereochemistry. The aim was to prepare 1- or 2-D polymers by self-assembly and, in particular, to study systematically the opportunities and limitations in the

---

* Author to whom correspondence should be addressed. E-mail: pudd@uwo.ca.

(1) (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304−1319. (b) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647. (c) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (d) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (e) Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229.

(2) Jeffery, G. A.; Saenger, W. *Hydrogen Bonding in Biological Systems*; Springer-Verlag: Berlin, 1994.

(3) (a) Alcala, R.; Martines-Carrera, S. *Acta Crystallogr.* **1972**, *B28*, 1671. (b) Duchamp, D. J.; Marsh, R. E. *Acta Crystallogr.* **1969**, *B25*, 5. (c) Yang, J.; Marendaz, J.-L.; Geib, S. J.; Hamilton, A. D. *Tetrahedron Lett.* **1994**, *35*, 3665. (d) Zafar, A.; Yang, J.; Geib, S. J.; Hamilton, A. D. *Tetrahedron Lett.* **1996**, *37*, 2327. (e) Kolotuchin, S. V.; Fenlon, E. E.; Wilson, S. R.; Loweth, C. J.; Zimmerman, S. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2654. (f) Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 1330. (g) Ashton, P. R.; Collins, A. N.; Fyfe, M. C. T.; Menzer, S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 735. (h) Zimmerman, S. C.; Zeng, F.; Reichert, D. E. C.; Kolotuchin, S. V. *Science* **1996**, *271*, 1095. (i) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696.

10.1021/ic020239b CCC: $22.00

Chart 1

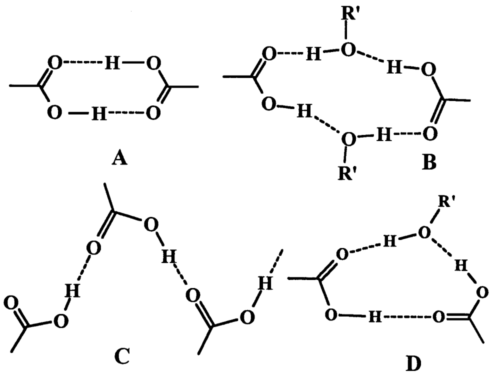
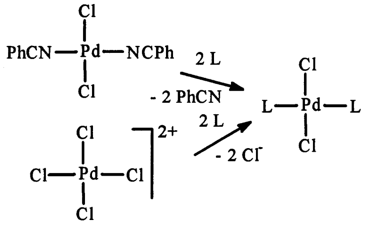


Chart 2



1, L = NC_5H_4-4-COOH
2, L = NC_5H_4-3-COOH
3, L = NC_9H_6-4-COOH
4, L = NC_9H_6-3-COOH
5, L = NC_9H_5-2-Ph-4-COOH
6, L = NC_5H_4-4-CH_2COOH
7, L = NC_5H_4-4-SCH_2COOH

combined use of carboxylic acid units and coordination chemistry of palladium(II) for self-assembly of interesting structures. Some of the results have been communicated,[6a,b] and the hydrogen bonding in related carboxamide derivatives has been described.[6k]

Results and Discussion

Neutral Palladium(II) Complexes with Pyridine or Quinoline Carboxylic Acid Ligands. Several new complexes *trans*-[$PdCl_2L_2$] (**1**−**7**, Chart 2) were prepared by displacement of the weakly bound benzonitrile ligands in *trans*-[$PdCl_2(PhCN)_2$] by corresponding ligands L or by the displacement of two chloride ligands from $Na_2[PdCl_4]$ by ligands L. All new complexes are yellow, air-stable solids. These complexes have very limited solubility in most common organic solvents, but high solubility in dimethyl sulfoxide (DMSO) which can both break down hydrogen-bonded polymers and, in some cases, displace the pyridine ligands from palladium. For example, complex **4** reacted on dissolution in DMSO with displacement of the pyridyl ligands, as monitored by the ^{1}H NMR spectra. Complexes **5**−**7** which either contain bulky organic substituents (**5**) or relatively flexible pyridyl groups (**6**, **7**) are also soluble in dimethyl formamide (DMF). The complexes were characterized by elemental analysis, by their IR and ^{1}H NMR (when soluble) spectra, and, in some cases, by X-ray structure determinations. The IR spectra as Nujol mulls for the complexes contain peaks due to ν(OH) = 2568−3226 cm^{-1} and ν(C=O) = 1697−1735 cm^{-1}, as expected if the carboxylic groups are involved in hydrogen bonding.[7]

Structure determinations were carried out for the complexes [$PdCl_2(NC_5H_4$-4-$COOH)_2$] (**1**), [$PdCl_2(NC_5H_4$-3-$COOH)_2$] (**2**), **2**·2DMSO, [$PdCl_2$(2-Ph-NC_9H_5-4-$COOH)_2$] (**5**), and **5**·4DMF. Views of their structures are shown in Figures 1−6, and selected bond distances and angles are listed in Tables 1−6. As expected, all three unsolvated complexes **1**, **2**, and **5**, which were grown by very slow diffusion of the reagents together (see Experimental Section), self-assembled into infinite 1-D polymeric chains through pairwise, intermolecular hydrogen bonding between carboxylic acid groups of the type $\mathbf{R}^2_2(8)$ (Type A, Chart 1).[8] In each case, the palladium atom lies on a crystallographic inversion center so that the angles N−Pd−N and Cl−Pd−Cl are 180°. In the case of complex **1** (Figure 1), the two pyridine rings are coplanar in the complex molecule because of crystallographic symmetry, but they twist from the PdN_2Cl_2 coordination plane, with torsion angle C(1)−N(1)−Pd(1)−Cl(1) = 125° (Figure 1). The carboxylic acid group is essentially coplanar with the pyridine ring to which it is bonded, with torsion angle C(2)−C(3)−C(4)−O(2) = −4.5°, suggesting conjugation between them. Infinite linear chains were formed because of $\mathbf{R}^2_2(8)$ intermolecular carboxylic acid hydrogen bonding with O···H = 1.71 Å, O···H−O = 179°, O···O = 2.637(3) Å, typical of such bond parameters in carboxylic acid derivatives (Figure 1, Table 2).[6] The polymeric chains pack parallel to one another, and there is some evidence of weak interaction between each chloride ligand and the pyridyl C(2)−H group of a molecule in an adjacent chain (Table 2). In addition, the centroid distances

---

(4) (a) Lehn, J.-M. *Supramolecular Chemistry-Concepts and Perspectives*; VCH: New York, 1995. (b) Puddephatt, R. J. *Chem. Commun.* **1998**, 1055. (c) Kickham, J. E.; Loeb, S. J. *Inorg. Chem.* **1995**, *34*, 5656. (d) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.

(5) (a) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375. (b) Burrows, A. D.; Chan, C. W.; Chowdhry, M. M.; McGrady, J. E.; Mingos, D. M. P. *Chem. Soc. Rev.* **1995**, 329. (c) Aakeröy, C. B.; Beatty, A. M. *Chem. Commun*. **1998**, 1067. (d) Chowdhry, M. M.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 899. (e) Huch, W. T. S.; Hulst, R.; Timmerman, P.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1006. (f) Munakata, M.; Wu, L.-P.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Am. Chem. Soc.* **1996**, *118*, 3117. (g) Kumar, R. K.; Balasubramanian, S.; Goldberg, I. *Inorg. Chem*. **1998**, *37*, 541. (h) Aakeröy, C. B.; Beatty, A. M.; Leinen. D. S. *Angew. Chem., Int. Ed.*. **1999**, *38*, 1815.

(6) (a) Qin, Z.; Jenkins, H. A.; Coles, S. J.; Muir, K. W.; Puddephatt, R. J. *Can. J. Chem.* **1998**, *77*, 155. (b) Qin, Z.; Jennings, M. C.; Puddephatt, R. J.; Muir, K. W. *CrystEngComm* **2000**, 11. (c) Braga, D.; Maini, L.; Grepioni, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2240. (d) Stepnicka, P.; Podlaha, J.; Gyepes, R.; Polasek, M. *J. Organomet. Chem.* **1998**, *552*, 293. (e) Bishop, P.; Marsh, P.; Brisdon, A. K.; Brisdon, B. J.; Mahon, M. F. *J. Chem. Soc., Dalton Trans*. **1998**, 675. (f) Desmartin, P. G.; Willianms, A. F.; Bernardinelli, G. *New J. Chem*. **1995**, *19*, 1109. (g) Fraser, C. S. A.; Jenkins, H. A.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 1635. (h) Gianneschi, N. C.; Tiekink, E. R. T.; Rendina, L. M. *J. Am. Chem. Soc.* **2000**, *122*, 8474. (i) Schneider, W.; Bauer, A.; Schmidbaur, H. *Organometallics* **1996**, *15*, 5445. (j) Wilton-Ely, J. D. E. T.; Schier, A.; Mitzel, N. W.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans*. **2001**, *7*, 1058. (k) Qin, Z.; Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **2001**, *40*, 6220.

(7) Lambert, J. B.; Shurvell, H. F.; Lightner, D.; Cooks, R. G. *Structural Spectroscopy*; Prentice Hall: Englewood Cliffs, NJ, 1998.

(8) Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1555.

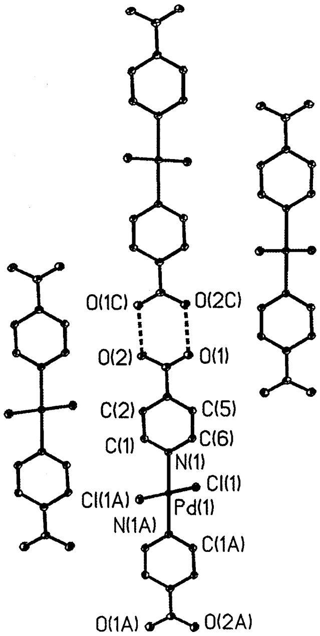


Figure 1. View of part of the 1-D polymeric chain formed by hydrogen bonding between carboxylic acid substituents in complex **1**, and of molecules in two neighboring chains.

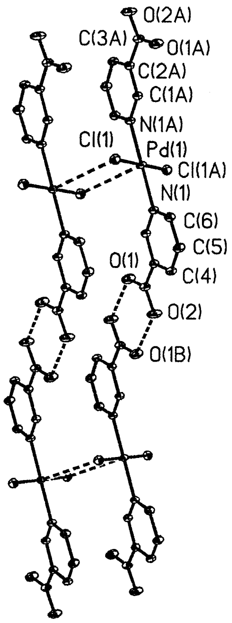


Figure 2. View of part of the 1-D zigzag chain formed by hydrogen bonding between carboxylic acid substituents in complex **2**, with pairwise Cl···Pd interactions connecting them to give a sheet structure.

between neighboring pyridyl rings in different polymeric chains are 3.955 Å, allowing weak π-stacking interactions. These intermolecular secondary bonding effects lead to a compact structure in the solid state, with no large cavities or channels (Figure 1).

The structure of complex **2** is given in Figure 2, with data in Table 3. It follows from the molecular symmetry that the COOH groups are located on opposite sides of the $PdCl_2N_2$ coordination plane. Thus, zigzag chains are naturally formed through the intermolecular hydrogen bonding between the carboxylic acid groups with O···H = 1.94 Å, O···H−O = 173°, O···O = 2.634(3) Å (Figure 2). The conformation of the pyridine ring with regard to the coordination plane PdN_2Cl_2 is similar to that in complex **1**, with torsion angle C(1)−N(1)−Pd(1)−Cl(1) = 124.5°. Also as in **1**, the carboxylic acid group is approximately coplanar with the pyridyl ring, as shown by the torsion angle C(1)−C(2)−C(3)−O(1) = −5.1°. However, the packing motif in **2** is different from that in **1**. There are sheets in which polymeric chains pack parallel to one another, with weak secondary Pd···Cl bonds (Pd···Cl = 3.42 Å), as shown in Figure 2. However, the chains in adjacent sheets run crosswise as shown in Figure 3, and there are weak pyridyl C−H···ClPd hydrogen bonding interactions that cross-link the sheets. The overall structure is compact (note the high density) with very small cavities.

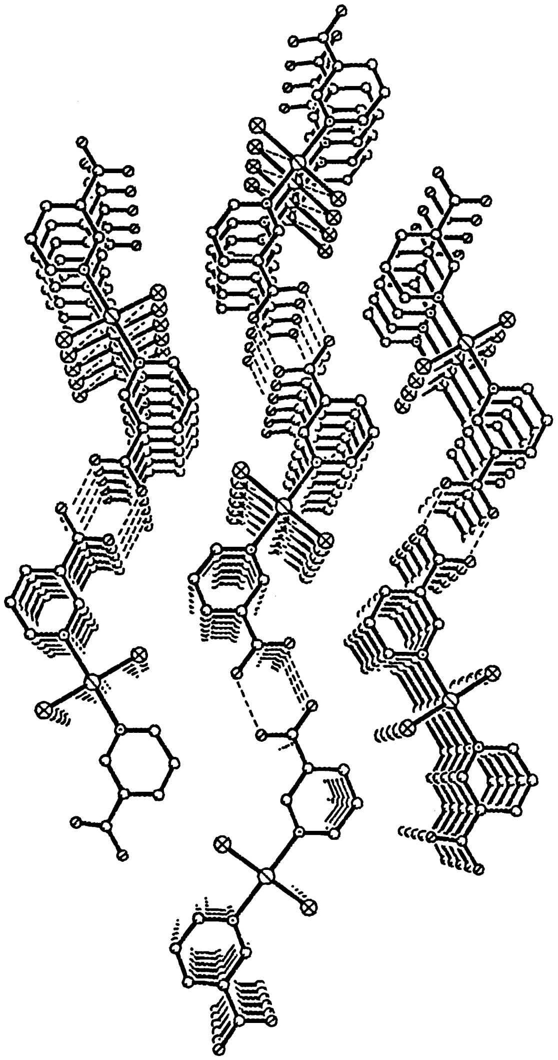


Figure 3. Different orientations of molecules of complex **2** in neighboring sheets, as required to maximize intersheet CH···ClPd or CH···OC hydrogen bonding.

As would be expected, the hydrogen-bonded polymeric chains that exist in complex **2** are not present in the structure of **2**·2DMSO because the DMSO molecules hydrogen bond to each of the carboxyl groups as shown in Figure 4. DMSO serves as a strong hydrogen bond acceptor, as indicated by the hydrogen bonding between the OH groups in the complex and the S=O groups in DMSO with H···O = 1.74 Å, O−H···O = 171°, O···O = 2.550(3) Å (Tables

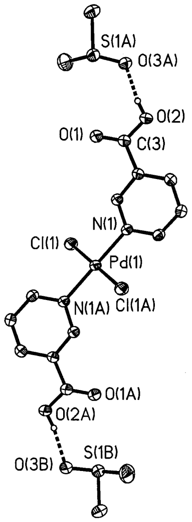


Figure 4. View of the structure of complex **2**·2DMSO, showing the hydrogen bonding OH···O to DMSO molecules. There is also weak C−H···O and O−H···S hydrogen bonding that is not illustrated.

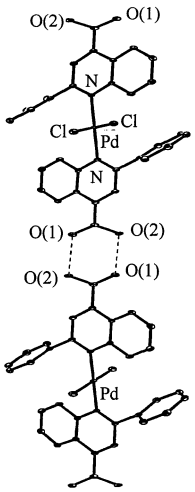


Figure 5. View of the part of the polymeric structure of **5** showing hydrogen bonding between carboxylic groups.

2, 4). A weak O−H···S hydrogen bond is also possible (Figure 4) though the associated parameters indicate that it is weak [OH···S = 2.69 Å, O−H···S = 158°]. The most interesting feature is that the centrosymmetric $\boldsymbol{R}^2_2(10)$ rings formed by weak C−H···O−C hydrogen bonding between neighboring molecules give rise to polymeric chains. The C−H···O−C hydrogen bond's parameters, H···O = 2.51 Å, C−H···O = 138°, O···C = 3.263(4) Å, are consistent with Desiraju's criteria for the presence of C−H···O hydrogen bonding.[9] The structural parameters of the complex molecule are comparable to those of solvate-free molecule **2** except that the C−O bond (1.308(4) vs 1.263(4) Å in **2**) is longer and the C=O bond (1.194(4) vs 1.261(4) Å in **2**) is shorter, as expected for the different hydrogen bonding motifs (the presence of almost equal CO distances in **2** could be a result of disorder, but the H atoms were located in reasonable positions so this is considered unlikely; it is an expected result of strong H-bonding). The polymeric chains in **2**·2dmso pack parallel to one another to form a compact structure. In addition, CH bonds of DMSO take part in weak C−H···Cl−Pd hydrogen bonds involving the Cl−Pd groups of neighboring chains (not shown).

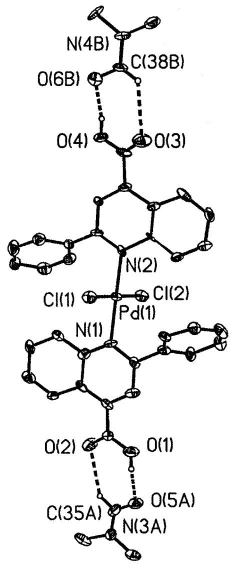


Figure 6. View of the structure of **5**·4DMF showing hydrogen bonding between carboxylic acid groups and DMF solvate molecules. The other two DMF molecules which are not involved in hydrogen bonding are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex **1**

Pd(1)−N(1)	2.021(2)	Pd(1)−Cl(1)	2.3051(7)
C(4)−O(1)	1.245(4)	C(4)−O(2)	1.280(4)
N(1)−Pd(1)−Cl(1)	90.48(7)	O(1)−C(4)−C(3)	120.0(3)
O(1)−C(4)−O(2)	123.6(3)	O(2)−C(4)−C(3)	116.4(3)

Table 2. Hydrogen Bonding Interactions and Close Contacts in the Complexes

complex	D−H···A	H···A (Å)	D···A (Å)	D−H···A (deg)
1	O−H···O	1.71	2.637(4)	179
	C(2B)−H···Cl(1)	2.77	3.535(4)	142
2	O−H···O	1.94	2.634(3)	173
	C(4B)−H···Cl(1)	2.89	3.467(3)	128
2·2DMSO	O(2)−H···O(3A)(DMSO)	1.74	2.550(3)	171
	C(4)−H···O(2B)	2.51	3.263(4)	138
5	O−H···O	1.83	2.655(3)	168
5·4DMF	O(1)−H···O(5)(DMF)	1.79	2.600(2)	172
	C(35)−H···O(2)	2.48	3.214(2)	136
	O(4)−H···O(6)(DMF)	1.73	2.538(2)	169
	C(38)−H···O(3)	2.47	3.159(2)	131
8	C(4B)−H···O(8)	2.49	3.408(3)	164
9	O(12)−H···O(21)(MeOH)	1.71	2.526(5)	169
	O(12)−H···O(21)	1.87	2.665(3)	161
	O(9)−H···Cl	2.27	3.087(3)	168
10	O(2)−H···O(3)	1.62	2.579(3)	174
	O(3)−H···O(1)	2.01	2.795(3)	174
	O(3)−H···Cl		3.273(3)	
11	O(29)−H···O(36)(Otf)	1.91	2.724(6)	162
	O(19)−H···O(w)	1.71	2.538(6)	169
	O(37)···O(w)		2.862(6)	
13	O(2B)−H···O(43A)	1.85	2.689(7)	173
	O(4B)−H···O(11B)	1.87	2.708(7)	176
	O(2A)−H···O(22A)	1.88	2.722(6)	175
14	O(12)−H···O(96)(Me_2CO)	1.85	2.68(1)	167
	O(24)−H···O(102)(Me_2CO)	1.88	2.68(1)	160
17	O(19)−H···O(47)	1.86	2.660(6)	159
	O(29)−H···O(37)	1.86	2.672(4)	161

---

[9] Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **2**

Pd(1)–N(1)	2.022(2)	Pd(1)–Cl(1)	2.3048(7)
O(1)–C(3)	1.263(4)	O(2)–C(3)	1.261(4)
N(1)–Pd(1)–Cl(1)	90.07(7)	O(1)–C(3)–C(2)	119.3(3)
O(1)–C(3)–O(2)	123.9(3)	O(2)–C(3)–C(2)	116.8(3)

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **2**·2DMSO

Pd(1)–N(1)	2.018(2)	Pd(1)–Cl(1)	2.2989(9)
C(3)–O(1)	1.194(4)	C(3)–O(2)	1.308(4)
N(1)–Pd(1)–Cl(1)	90.00(7)	O(1)–C(3)–C(2)	122.6(3)
O(1)–C(3)–O(2)	124.6(3)	O(2)–C(3)–C(2)	112.8(3)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex **5**

Pd–N	2.035(2)	Pd–Cl	2.3078(7)
O(1)–C(10)	1.219(3)	O(2)–C(10)	1.312(3)
N–Pd–Cl	91.79(6)	O(1)–C(10)–C(3)	121.8(2)
O(1)–C(10)–O(2)	125.1(2)	O(2)–C(10)–C(3)	113.1(2)

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complex **5**·4DMF

Pd(1)–N(2)	2.006(9)	O(1)–C(8)	1.34(2)
Pd(1)–N(1)	2.074(9)	O(2)–C(8)	1.15(2)
Pd(1)–Cl(1)	2.308(4)	O(3)–C(24)	1.24(2)
Pd(1)–Cl(2)	2.315(3)	O(4)–C(24)	1.27(2)
N(2)–Pd(1)–Cl(1)	89.6(3)	N(1)–Pd(1)–Cl(2)	89.4(3)
N(1)–Pd(1)–Cl(1)	90.7(3)	N(2)–Pd(1)–N(1)	179.6(5)
N(2)–Pd(1)–Cl(2)	90.3(3)	Cl(1)–Pd(1)–Cl(2)	179.8(2)
O(2)–C(8)–O(1)	125.3(11)	O(3)–C(24)–O(4)	122.3(10)
O(2)–C(8)–C(7)	124.1(11)	O(3)–C(24)–C(23)	122.7(11)
O(1)–C(8)–C(7)	110.3(11)	O(4)–C(24)–C(23)	114.5(10)

The structure of complex **5** is shown in Figure 5, with data in Table 5. This complex gives a structure that is remarkably similar to that of complex **1**, with linear chains assembled through hydrogen bonding and with O···H = 1.83 Å, O···H–O = 168°, O···O = 2.655(3) Å. In contrast to the ligand orientation in complexes **1** and **2**, the quinoline ring is close to perpendicular to the coordination plane PdN_2Cl_2, as indicated by the Cl–Pd–N–C torsion angles of −108° and 81°. The dihedral angle between the phenyl and pyridine rings is 59.2(1)°. The C–C–C(10)–O(1) torsion angle of 34.8° in **5** indicates that the carboxylic acid group deviates significantly from the quinoline ring plane. All these differences probably arise in order to minimize steric contacts between the two large ligands. It is clear from Figure 5 that there are intramolecular edge-to-face π-stacking interactions [centroid distance 4.851 Å] between orthophenylene and phenyl groups in the complex. There are also intermolecular π-stacking interactions [centroid distance 3.62 Å] between quinoline rings and intermolecular π-stacking interactions between phenyl rings (not shown).

There is no interesting supramolecular association in the structure of **5**·4DMF (Figure 6, Table 6). Two of the four solvate DMF molecules take part in hydrogen bonding with the carboxylic groups of the complex molecule to form $R^2_2(7)$ rings, which include O–H···O and C–H···O hydrogen bonds, as shown in Figure 6, while the third DMF is located above the $\mathbf{R}^2_2(7)$ rings and has contact with an OH group of the COOH substituent (not shown). The hydrogen bonds formed by each of the carboxylic acid groups with DMF are also different, as shown by the hydrogen bond parameters (H-atoms were located for this structure, Table 2). The dihedral angle between the phenyl and quinoline rings (51.4°) and that between the carboxyl group and the quinoline ring (16.6°) are smaller than those in unsolvated complex **6**.

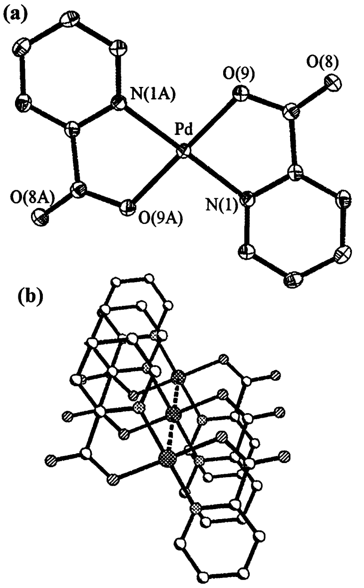
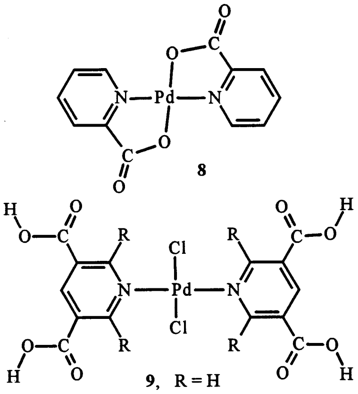


Figure 7. (a) Molecular structure of complex **8**. (b) View of part of the offset columnar structure; each level is part of a sheet structure formed via weak C–H···O hydrogen bonding (not shown).

Chart 3



8

9, R = H
10, R = Me

Pyridine Carboxylate Complex. The reaction of pyridine-2-carboxylic acid with $[PdCl_2(PhCN)_2]$ or with $Na_2[PdCl_4]$ yielded a white, insoluble product, $[Pd(NC_5H_4\text{-}2\text{-}C\{O\}O)_2]$ (**8**) (Chart 3). The IR spectrum of **8** displayed two absorption bands due to $\nu(CO_2)$ at 1676 and 1606 cm^{-1}, and there was no band for ν(O–H), indicating that deprotonation of the carboxylic acid group had occurred with formation of a palladium carboxylate unit. Crystals of complex **8** were obtained over a period of several months by diffusion of an acetone solution of $[PdCl_2(PhCN)_2]$ into an aqueous solution of the ligand. The molecular structure of complex **8** is shown in Figure 7, with selected bond parameters in Table 7. The coordination sphere around the palladium atom is approximately square planar with two pyridine-2-carboxylate ligands coordinated in a bidentate N,O fashion to give a planar neutral molecule (Figure 7a). The five-membered

Table 7. Selected Bond Distances (Å) and Angles (deg) for Complex **8**

Pd−N(1)	1.998(2)	C(7)−O(8)	1.213(3)
Pd−O(9)	2.003(2)	C(7)−O(9)	1.310(4)
N(1)−Pd−O(9)	82.36(9)	O(8)−C(7)−C(6)	120.5(3)
O(8)−C(7)−O(9)	124.5(3)	O(9)−C(7)−C(6)	115.0(3)

chelate ring had a bite angle N−Pd−O = 82.36(9)°, similar to values in other pyridine-2-carboxylate complexes.[10] The palladium atom lies at a crystallographic inversion center so that the angles N−Pd−N and O−Pd−O are 180°. The C=O bond length (1.213(3) Å) and the C−O bond length (1.310(4) Å) are typical.[10] The molecules stack into columns with Pd···Pd = 3.71 Å (Figure 7b), and with π-stacking attractions between unsaturated groups.[11] There are also weak intermolecular C=O···H−C hydrogen bonds, with the distances O···H = 2.49 Å and O···C = 3.408(3) Å and angle O−H···C = 164°, that cross-link the columns to give an infinite 3-D network. The intermolecular attractions that give rise to the overall network structure are presumably responsible for the complex being insoluble. Clearly, the easy deprotonation of the carboxylic acid group to give a chelated carboxylate group is a limitation on the use of *ortho* substituted carboxylic acid groups in supramolecular chemistry.

Neutral Palladium(II) Complexes with Pyridine Dicarboxylic Acid Ligands. Two complexes, $[PdCl_2\{NC_5H_3\text{-}3,5\text{-}(COOH)_2\}]$ (**9**) and $[PdCl_2\{2,6\text{-}Me_2{-}NC_5H_3\text{-}3,5\text{-}(COOH)_2\}]$ (**10**), (Chart 3) were synthesized by displacement of the weakly bound benzonitrile ligands of *trans*-$[PdCl_2(PhCN)_2]$ in THF by the corresponding ligand. Both are pale yellow, air-stable solids. Unlike complexes **1** and **2**, which are insoluble in most organic solvents, both complexes **9** and **10** are soluble in THF, methanol, and ethanol, although the ligands have very limited solubility in these solvents.

The structure of **9**·2MeOH is shown in Figure 8, and selected bond distances and angles are given in Table 8. Each molecule of **9** lies on an inversion center and displays the expected *trans*-$[PdCl_2L_2]$ structure (Figure 8a). The two pyridine rings are approximately perpendicular to the PdN_2Cl_2 square coordination plane, as indicated by the torsion angle Cl−Pd−N−C = 88.1°. The two carboxylic acid groups in each ligand lie in the plane of the pyridine ring, but they are oriented so that their hydroxyl groups are respectively syn and anti with respect to the palladium atom. The anti carboxylic acid groups are related by the inversion center, and they take part in hydrogen bonding mediated by methanol molecules. This hydrogen bonding forms planar centrosymmetric $R^4_4(12)$ rings (Type B, Chart 1) and gives a zigzag chain structure. The zigzag chains pack parallel to one another, and pairs of Pd atoms in adjacent chains are interlinked by hydrogen bonding between the syn carboxylic acid groups and chloride ligands [O···Cl 3.087(3) Å, H···Cl 2.27 Å, O−H···Cl 168°]. Centrosymmetric $R^2_2(16)$ rings containing pairs of palladium atoms are formed (Figures 8a, 8b). Because the chloride ligands of each $PdCl_2$ group hydrogen bond to the carboxylic groups of different zigzag chains, the combination of the two hydrogen bonding schemes leads to the corrugated 2-D structure shown in Figure 8b. The overall structure is compact, and there are no cavities which might give rise to further solvent inclusion.

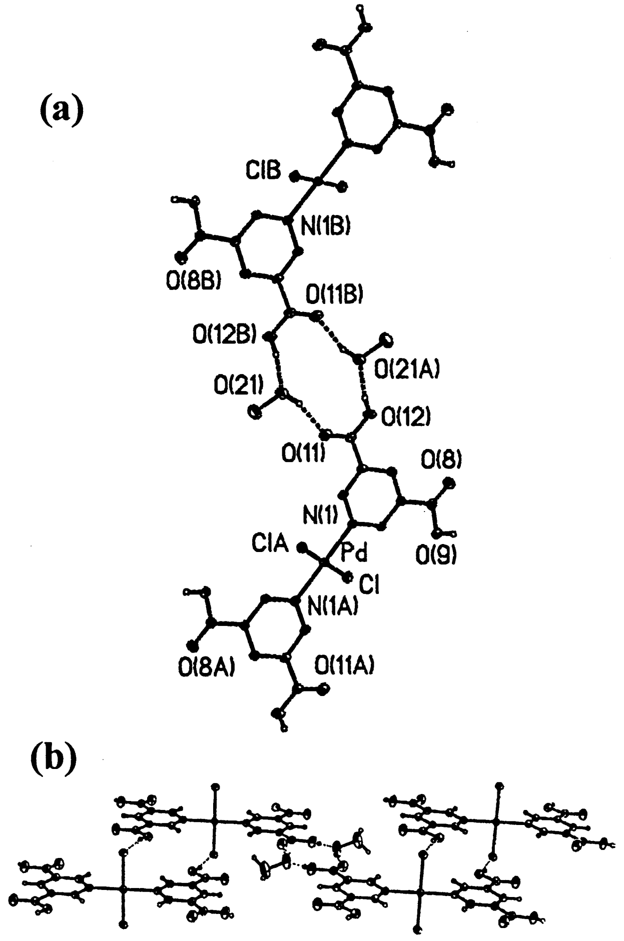


Figure 8. (a) View of the structure of **9**·2MeOH, showing the hydrogen bonding to methanol solvate molecules. (b) View of part of the sheet structure formed by combination of hydrogen-bonded $R^4_4(12)$ rings and O−H···Cl units.

Table 8. Selected Bond Distances (Å) and Angles (deg) for Complex **9**

Pd−N(1)	2.005(3)	Pd−Cl	2.301(1)
C(7)−O(8)	1.192(5)	C(10)−O(11)	1.210(5)
C(7)−O(9)	1.330(4)	C(10)−O(12)	1.288(5)
N(1)−Pd−Cl	91.66(9)	O(9)−C(7)−C(5)	112.0(3)
O(8)−C(7)−O(9)	125.2(4)	O(11)−C(10)−O(12)	125.5(4)
O(8)−C(7)−C(5)	122.7(3)	O(11)−C(10)−C(3)	120.7(4)
O(12)−C(10)−C(3)	113.8(4)		

Complex **10** was recrystallized from acetone by slow evaporation to give the solvate **10**·$4H_2O$, whose structure is shown in Figure 9. There is also evidence for disordered acetone molecules in the crystals. The molecules of **10** display crystallographic **2**/*m* (C_{2h}) symmetry. In the molecules of **10**, the pyridine rings are tilted by only 6° from orthogonality with the PdN_2Cl_2 coordination plane despite the steric crowding that results from the two extra *o*-methyl groups in each pyridine ring. The Pd−N bonds (Table 9) in

---

(10) (a) Hoare, J. L.; Cavell, K. J.; Hecker, R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 2197. (b) Jin, H.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1995**, 2159.

(11) (a) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525. (b) Hunter, C. A. *Chem. Soc. Rev.* **1994**, *23*, 101.

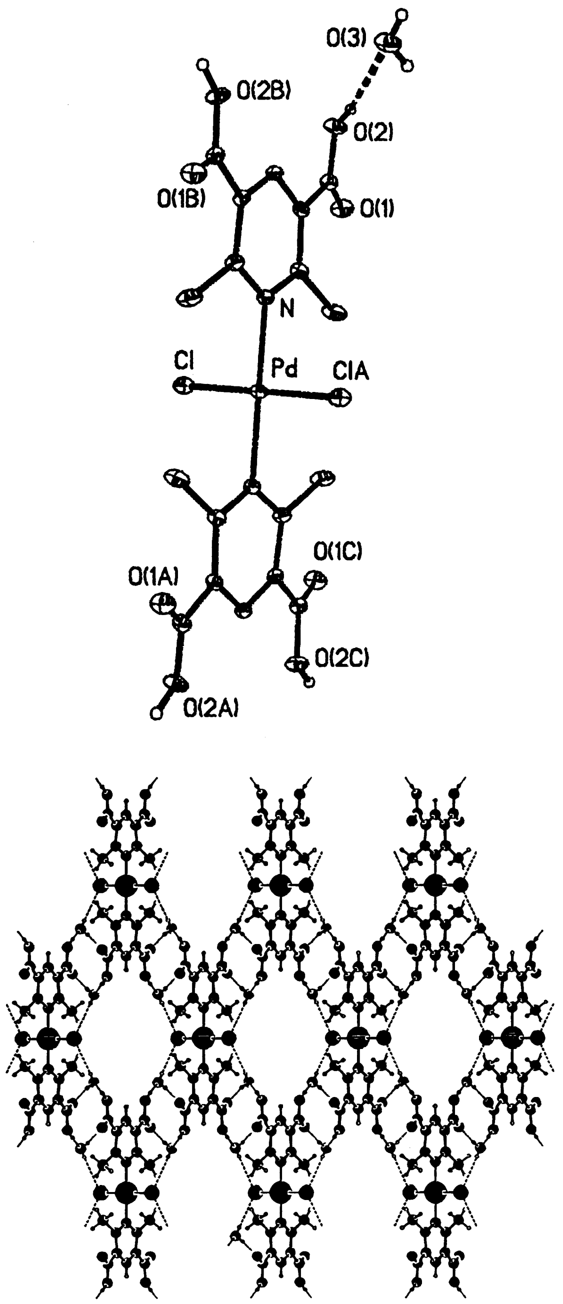


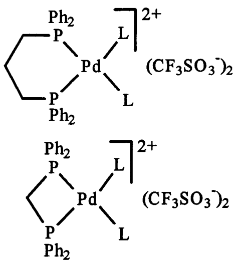
Figure 9. (a) View of the structure of **10**·$4H_2O$ and (b) view of part of the sheet structure formed by hydrogen bonding with a cross section of the porous channel structure.

Table 9. Selected Bond Distances (Å) and Angles (deg) for Complex **10**

Pd−N	2.063(3)	Pd−Cl	2.311(1)
O(1)−C(5)	1.213(4)	O(2)−C(5)	1.310(4)
N−Pd−Cl	90.0	O(1)−C(5)−C(2)	124.1(3)
O(1)−C(5)−O(2)	123.6(3)	O(2)−C(5)−C(2)	112.3(2)

10 are 0.06 Å longer than those in **9**, thereby helping to relieve short intramolecular H···H and H···Pd contacts involving the three hydrogen atoms of the methyl group. Crystallographic symmetry requires the four carboxylic acid groups in a molecule to be equivalent. The OH groups in **10** therefore are all anti to the Pd atom, as is shown by the C(1)−C(2)−C(5)−O(2) torsion angle of −169.1(3)°. Each carboxylic acid group takes part in hydrogen bonding mediated by water molecules, thereby forming slightly puckered, centrosymmetric $R^4_4(12)$ rings (Type B, Chart 1), similar to those formed in 2-benzoylbenzoic acid.[12] The water molecules also take part in weak hydrogen bonding to the chloride ligands. The final outcome of the self-assembly process is the formation of stacks of molecules related by translation along the *c*-axis. Adjacent molecules of **10** within each stack are held together by Cl···H−O(water) and C=O···H−O(water) hydrogen bonds from the same water molecule, while $R^4_4(12)$ rings link each stack to its four nearest neighbors (Figure 9b). Channels running parallel to *c* are thereby formed which are large enough (144 Å^3 per cell) to accommodate disordered molecules of acetone.[13] The nature of the hydrogen bonding network in **10** suggests that the solid should be resistant to degradation by heating. This expectation is fulfilled: thermogravimetric analysis indicated no weight loss on heating to 200 °C, and only ~4% weight loss at 260 °C; the decomposition temperature was 264 °C. This high thermal stability suggests the potential use of complex **10** as a functional porous material.

Chart 4



11, L = NC_5H_4-4-COOH
12, L = NC_5H_4-3-COOH
13, L = NC_5H_4-4-SCH_2COOH
14, L = NC_5H_3-3,5-$(COOH)_2$
15, L = NC_5H-2,6-Me_2-3,5-$(COOH)_2$

16, L = NC_5H_4-4-COOH
17, L = NC_5H_4-3-COOH
18, L = NC_5H_4-4-SCH_2COOH
19, L = NC_5H_3-3,5-$(COOH)_2$

Cationic Palladium(II) Complexes with Pyridine Carboxylic Acid Ligands. A great number of cationic palladium(II) supramolecules, including squares, cages, and catenanes, have been synthesized using chelated *cis*-palladium(II) precursors,[4d] and several cationic palladium(II) complexes containing two or four carboxylic acid groups (Chart 4), which have the potential to self-assemble by supramolecular association via hydrogen bonding, were prepared similarly. The reactions of $[Pd(dppp)(OTf)_2]$ (OTf = triflate)[14] or $[Pd(dppm)(OTf)_2]$ with carboxylic acid or dicarboxylic acid pyridyl ligands gave the compounds **11**−**19** in high yields (Chart 4). All complexes are air-stable, colorless solids, albeit hygroscopic. The complexes were characterized by elemental analysis and IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR spectra. Those with dppp as chelate ligand give ^{31}P NMR signals in the range $\delta = 9.15-10.15$, with the exception of **15** whose ^{31}P resonance is at 16.26 ppm. In the case of the dppm chelated complexes, their ^{31}P signals ranged from −36.99 to −38.97 ppm.

X-ray crystal structure determinations were carried out for four of the cationic palladium(II) complexes. Views of their

---

(12) Lalancette, R. A.; Vanderhoff, P. A.; Thompson, H. W. *Acta Crystallogr.* **1990**, *C46*, 1682.

(13) (a) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34. (b) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht: The Netherlands, 1998.

(14) (a) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216. (b) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

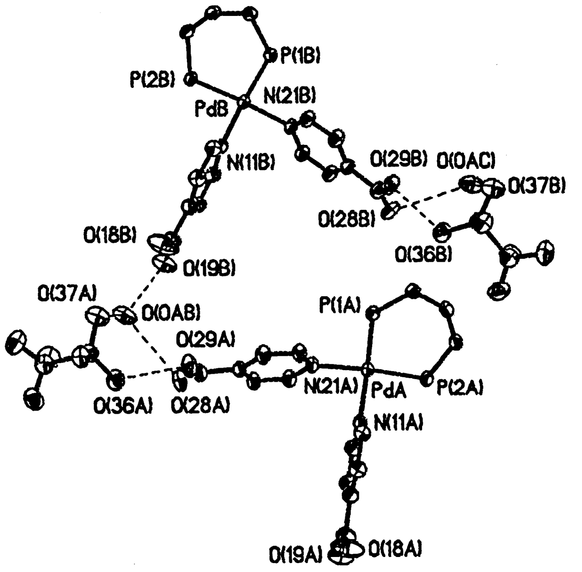


Figure 10. View of the structure of complex **11** showing hydrogen bonding between carboxylic acid groups and water molecule as well as triflate anion, leading to a polymeric structure. Phenyl groups are omitted for clarity.

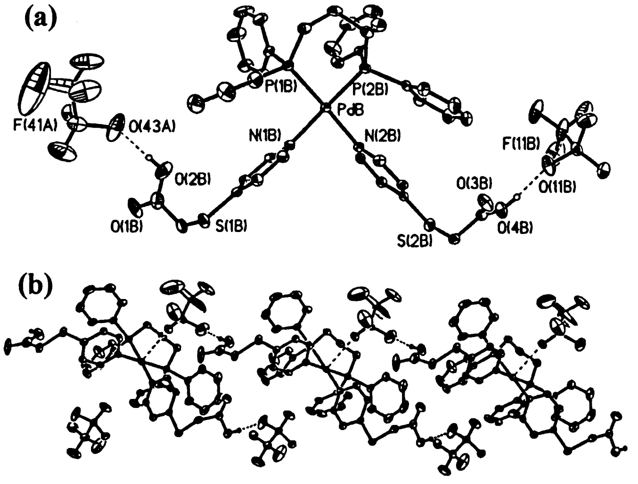


Figure 11. (a) View of the molecular structure of **17** showing hydrogen bonding between COOH groups and triflate counter ions. (b) View of part of the chain structure (all phenyl groups are omitted for clarity) formed by H-bonding and O···Pd interactions.

structures are shown in Figures 10−13. The coordination geometry about the cationic palladium(II) metal centers is roughly square planar in each case. The potential intermolecular hydrogen bonding between carboxyl groups was not present in any case, but the carboxylic acid groups take part in hydrogen bonding with either triflate anions or solvate acetone molecules.

The structure of [Pd(dppp)(NC_5H_4-4-COOH)$_2$](CF_3SO_3)$_2$ (**11**) is shown in Figure 10, while selected bond distances and angles are given in Table 10. There is *cis*-PdP_2N_2 coordination, and the pyridine rings lie roughly orthogonal to the coordination plane. The two carboxylic acid groups are approximately coplanar to the pyridine rings to which they are connected. One carboxylic acid group takes part in hydrogen bonding O(19)−H(19A)···O(w) [O(19)···O = 2.54 Å] with a solvate water molecule, while the other carboxylic acid group forms hydrogen bonding O(29)−H(29A)···O(36) (OTf) [O(29)···O(36) = 2.72 Å] with a triflate anion (Figure 10). The second oxygen atom of the triflate anion hydrogen bonds to the water molecule [O(37)···O = 2.86 Å]. The combination of the hydrogen bonding interactions leads to an infinite polymeric chain, as shown in Figure 10. The adjacent polymeric chains further aggregate to give a 2-D sheet structure through the contacts Pd···O(38) = 3.11 Å.

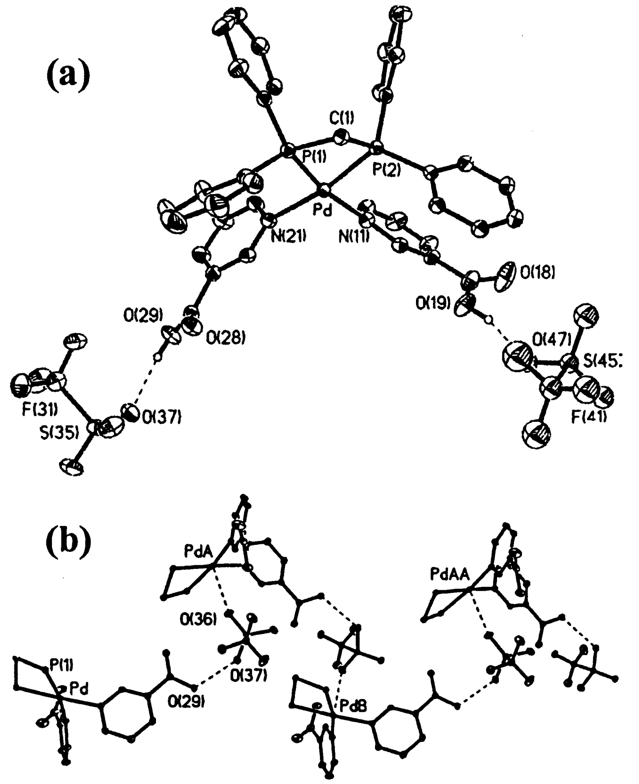


Figure 12. (a) View of the molecular structure of **13** showing hydrogen bonding between COOH groups and triflate counter ions. (b) View of part of the chain structure formed via hydrogen bonding and O···Pd interactions. Only one of the two independent molecules is shown.

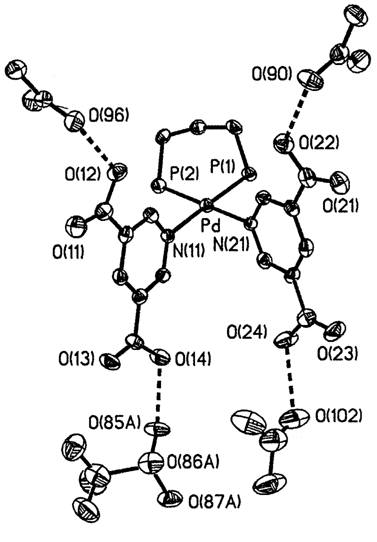


Figure 13. View of the molecular structure of complex **14** showing hydrogen bonding between COOH groups and solvate acetone molecules and O···Pd interaction. The other solvates and phenyl groups are omitted for clarity.

In the structure of complex **17** shown in Figure 11 (see also Table 11), both carboxylic acid groups in the complex

Table 10. Selected Bond Distances (Å) and Angles (deg) for Complex **11**

Pd−N(11)	2.098(3)	Pd−P(2)	2.2734(10)
Pd−N(21)	2.103(3)	Pd−P(1)	2.2806(11)
C(17)−O(18)	1.176(6)	C(27)−O(28)	1.197(6)
C(17)−O(19)	1.305(6)	C(27)−O(29)	1.329(6)
N(11)−Pd−N(21)	83.90(14)	P(2)−Pd−P(1)	91.12(4)
N(11)−Pd−P(2)	91.43(9)	N(21)−Pd−P(1)	93.53(10)
N(11)−Pd−P(1)	177.24(10)	N(21)−Pd−P(2)	175.22(10)
O(18)−C(17)−O(19)	124.1(5)	O(28)−C(27)−O(29)	125.0(4)
O(18)−C(17)−C(14)	123.6(5)	O(28)−C(27)−C(24)	122.8(4)
O(19)−C(17)−C(14)	112.2(4)	O(29)−C(27)−C(24)	112.2(4)

Table 11. Selected Bond Distances (Å) and Angles (deg) for Complex **17**

Pd−N(21)	2.114(3)	Pd−P(2)	2.2589(11)
Pd−N(11)	2.124(2)	Pd−P(1)	2.2671(11)
C(17)−O(18)	1.231(7)	C(27)−O(28)	1.204(5)
C(17)−O(19)	1.297(7)	C(27)−O(29)	1.327(5)
N(21)−Pd−N(11)	92.92(11)	P(2)−Pd−P(1)	71.58(4)
N(11)−Pd−P(2)	96.74(7)	N(21)−Pd−P(1)	98.82(10)
N(11)−Pd−P(1)	168.26(7)	N(21)−Pd−P(2)	169.61(10)
O(18)−C(17)−O(19)	124.0(5)	O(28)−C(27)−O(29)	124.6(4)
O(18)−C(17)−C(13)	121.8(5)	O(28)−C(27)−C(23)	122.4(4)
O(19)−C(17)−C(13)	114.2(5)	O(29)−C(27)−C(23)	113.0(4)

Table 12. Selected Bond Distances (Å) and Angles (deg) for Complex **13**

Pd(A)−N(1A)	2.104(5)	Pd(B)−N(1B)	2.100(5)
Pd(A)−N(2A)	2.110(5)	Pd(B)−N(2B)	2.118(5)
Pd(A)−P(2A)	2.2721(19)	Pd(B)−P(2B)	2.277(2)
Pd(A)−P(1A)	2.2784(19)	Pd(B)−P(1B)	2.2803(19)
N(1A)−Pd(A)−N(2A)	87.56(18)	N(1B)−Pd(B)−N(2B)	87.44(19)
N(1A)−Pd(A)−P(2A)	176.75(15)	N(1B)−Pd(B)−P(2B)	178.52(14)
N(2A)−Pd(A)−P(2A)	90.33(14)	N(2B)−Pd(B)−P(2B)	91.51(15)
N(1A)−Pd(A)−P(1A)	92.86(14)	N(1B)−Pd(B)−P(1B)	91.01(14)
N(2A)−Pd(A)−P(1A)	178.75(15)	N(2B)−Pd(B)−P(1B)	178.35(15)
P(2A)−Pd(A)−P(1A)	89.19(7)	P(2B)−Pd(B)−P(1B)	90.05(7)

Table 13. Selected Bond Distances (Å) and Angles (deg) for Complex **14**

Pd−N(11)	2.115(6)	Pd−P(1)	2.264(2)
Pd−N(21)	2.120(6)	Pd−P(2)	2.272(2)
N(11)−Pd−N(21)	83.1(2)	P(1)−Pd−P(2)	90.13(9)
N(11)−Pd−P(2)	93.58(17)	N(21)−Pd−P(1)	93.05(18)
N(11)−Pd−P(1)	175.79(18)	N(21)−Pd−P(2)	175.25(18)

molecule lie on the same side of the *cis*-PdN_2P_2 coordination plane, and they are twisted out of the pyridyl planes. However, they are oriented differently so that one adopts the anti conformation with respect to the pyridyl nitrogen atom while the other is syn. Each of the carboxylic acid groups takes part in hydrogen bonding O−H···O(OTf) with one triflate counterion (Figure 11). Furthermore, one of the oxygen atoms of a triflate interacts with the palladium(II) center of the adjacent molecule [Pd···O(36) = 2.935 Å], finally leading to a coiled polymeric chain (Figure 11b).

There are two independent but similar molecules in the structure of **13**·0.875(acetone) (Figure 12 and Table 12). As expected, the sulfur atoms in the ligands do not coordinate to the palladium(II) center. The orientation of the CH_2COOH groups in the two independent molecules is different. Three of the four carboxylic groups take part in hydrogen bonding with triflate counterions, while one does not. All hydrogen bonding parameters can be found in Table 2. There are close interactions between an oxygen atom of a triflate anion and a palladium(II) center in both independent molecules, with Pd(A)···O(33A) = 3.06 Å and Pd(B)···O(41) = 2.89 Å, respectively. One molecule (PdB in the crystal structure) gives polymeric chains through the combination of hydrogen bonding and Pd···O interactions, as shown in Figure 12b, while the other one does not form an interesting supramolecular structure.

No noteworthy supramolecular structure was formed in the highly solvated crystal of **14**·5.35(acetone) (Table 13), but the carboxylic acids take part in hydrogen bonding to acetone molecules or triflate anion as shown in Figure 13.

Conclusions

Both neutral and cationic palladium(II) complexes containing carboxylic acid groups that are capable of taking part in hydrogen bonding can be readily prepared, and the nature and scope of the subsequent self-assembly have been determined in many cases. The complexes *trans*-[$PdCl_2L_2$], where L = NC_5H_4-4-COOH, NC_5H_4-3-COOH, 2-Ph-NC_9H_5-4-COOH, can self-assemble to give 1-D polymers through formation of pairwise O−H···O hydrogen bonds giving **R^2_2(8)** rings, as shown by structure determinations of the complexes **1**, **2**, and **5** (Figures 1−3 and 5). However, crystallization from DMSO or DMF gave the solvated complexes **2**·2DMSO and **5**·4DMF, in which hydrogen bonding to solvent molecules is preferred (Figures 4 and 6). Interestingly, in complex **2**·2DMSO, the molecules take part in weak intermolecular C−H···O hydrogen bonding leading to a 1-D polymeric tape structure. Pyridine-2-carboxylic acid gave a neutral chelate complex, [$Pd(NC_5H_4C\{O\}O)_2$], in which deprotonation of the carboxylic acid group occurred, thus illustrating a limitation of this approach to forming hydrogen-bonded polymers. The complex forms stacked columns in the solid state with CO···HC hydrogen bonding cross-linking them to give a highly insoluble complex with a 3-D network structure (Figure 7).

The complexes *trans*-[$PdCl_2L_2$], **9**·2MeOH and **10**·4H_2O, containing pyridine dicarboxylic acid ligands, form similar **R^4_4(12)** rings by hydrogen bonding between carboxylic acid groups mediated by methanol or water molecules. However, in **9**·2MeOH, half of the carboxylic acid groups take part in that type of hydrogen bonding while the other half form hydrogen bonds with Cl−Pd groups, forming an interesting 2-D sheet structure (Figure 8). In **10**·4H_2O, all carboxylic acid groups form the same type of hydrogen bonding, leading to formation of 2-D sheets with large cavities (Figure 9). The 2-D sheets pack together to give a porous crystal structure with channels along the *c*-axis.

Several new cationic palladium(II) complexes containing pyridine carboxylic acid ligands were prepared, but there was no hydrogen bonding between the carboxylic groups. Instead, anions or solvate molecules take part in hydrogen bonding with the carboxylic acid groups. However, interesting supramolecular structures were obtained through the combination of hydrogen bonding between the carboxylic acid groups and triflate counteranions and secondary Pd···O bonding interactions (Figures 10 and 11). Given this competition for hydrogen bonding, it is clearly necessary to choose recrystallization solvents and counterions carefully when designing new materials. Carboxamide groups hydrogen bond more strongly than carboxylic acids and so give a wider range of supramolecular structures in palladium(II) complexes,[6k] but the carboxylic acids do give novel and interesting 1-D polymer and 2-D network structures. There is clearly scope for further developments.

Experimental Section

NMR spectra were recorded by using a Varian Gemini 300 NMR spectrometer. ^{1}H and ^{13}C{^{1}H} chemical shifts are reported relative to tetramethylsilane(TMS). ^{31}P{^{1}H} chemical shifts were referenced to 85% H_3PO_4 as an external reference. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 2000 FTIR spectrometer. All manipulation of air- or water-sensitive materials was carried out using standard Schlenk techniques under an atmosphere of nitrogen or in a drybox. $[PdCl_2(PhCN)_2]$, $[Pd(dppp)(CF_3SO_3)_2]$, and $[Pd(dppm)(CF_3SO_3)_2]$ were prepared following the literature procedures.[14]

$[PdCl_2(NC_5H_4\text{-}4\text{-}COOH)_2]$ (1). To an aqueous solution (10 mL) of $Na_2[PdCl_4]$ (0.50 mmol), prepared in situ by the reaction of $PdCl_2$ and NaCl, was added pyridine-4-carboxylic acid (123.1 mg, 1.00 mmol) in distilled water (10 mL). A pale yellow precipitate was formed immediately. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with distilled water and acetone, and dried in vacuo to afford a pale yellow powder. Yield: 93%. Anal. Calcd for $C_{12}H_{10}Cl_2N_2O_4Pd$: C, 34.03; H, 2.38; N, 6.61. Found: C, 33.51; H, 2.46; N, 6.17. IR (Nujol): $\nu_{C=O}$ 1705 cm^{-1}, $\nu_{OH} = 2568, 2677$ cm^{-1}. ^{1}H NMR (DMF-d_7): δ 9.10 (d, $^3J_{HH} = 7$ Hz, 4H, H^{2,6}); 8.07 (d, $^3J_{HH} = 7$ Hz, 4H, H^{3,5}). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 164.7 (COOH), 154.0 (C^2), 140.7 (C^3), 124.4 (C^4). Mp: >350 °C, decomposed. Yellow needle crystals of **1** were obtained by slow diffusion of $[PdCl_2(PhCN)_2]$ in acetone into a solution of pyridine-4-carboxylic acid in water in about one month.

$[PdCl_2(NC_5H_4\text{-}3\text{-}COOH)_2]$ (2). This was prepared by a similar procedure as for **1** except that pyridine-3-carboxylic acid was used. The product was obtained as a yellow solid. Yield: 96%. Anal. Calcd for $C_{12}H_{10}Cl_2N_2O_4Pd$: C, 34.03; H, 2.38; N, 6.61. Found: C, 34.14; H, 2.39; N, 6.44. IR (Nujol): $\nu_{C=O}$ 1706 cm^{-1}, $\nu_{OH} =$ 2667, 2776 cm^{-1}. ^{1}H NMR (DMF-d_7): δ 9.41 (d, $^4J_{HH} = 2$ Hz, 2H, H^2); 9.13 (dd, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 2$ Hz, 2H, H^6); 8.58 (ddd, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 2$ Hz, $^4J_{HH} = 2$ Hz, 2H, H^4); 7.83 (dd, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 6$ Hz, 2H, H^5). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 164.2 (COOH), 156.3 (C^2), 153.5 (C^6), 140.0 (C^3), 128.4 (C^4), 125.6 (C^5). Mp: >350 °C, decomposed. Yellow needle crystals of **2**·2DMSO were grown from a saturated solution of **2** in DMSO. TGA showed weight loss of DMSO from 165 to 180 °C. Yellow needle crystals of **2** were obtained by slow diffusion of pyridine-3-carboxylic acid in methanol into a solution of $[PdCl_2(PhCN)_2]$ in chloroform in about one month.

$[PdCl_2(NC_9H_6\text{-}4\text{-}COOH)_2]$ (3). This compound was prepared by a similar procedure as for **1** except that quinoline-4-carboxylic acid was used. The product was obtained as a pale yellow solid. Yield: 95.8%. Anal. Calcd for $C_{20}H_{14}Cl_2N_2O_4Pd$: C, 45.87; H, 2.69; N, 5.35. Found: C, 45.55; H, 2.69; N, 5.23. IR (Nujol): $\nu_{C=O}$ 1697 cm^{-1}, $\nu_{OH} = 2628$ cm^{-1}. Mp: 330 °C, decomposed. The complex was soluble only in DMSO, but it decomposed rapidly so that NMR spectra could not be recorded.

$[PdCl_2(NC_9H_6\text{-}3\text{-}COOH)_2]$ (4). To a solution of $[Pd(PhCN)_2Cl_2]$ (95.8 mg, 0.25 mmol) in a 1:1 benzene/methanol mixture (10 mL) was added a solution of quinoline-3-carboxylic acid (86.6 mg, 0.50 mmol) in a 1:1 benzene/methanol mixture (10 mL). A yellow precipitate was formed rapidly. The mixture was stirred for 2 h. The pale yellow powder was obtained by filtration, washed with acetone, and dried in vacuo. Yield: 91%. Anal. Calcd for $C_{20}H_{14}Cl_2N_2O_4Pd$: C, 45.87; H, 2.69; N, 5.35. Found: C, 45.55; H, 2.69; N, 5.23. IR (Nujol): ν(C=O) 1710 cm^{-1}, $\nu_{OH} = 2652$ cm^{-1}. Mp: 350 °C, decomposed. Because this complex can only be dissolved in DMSO and there is an exchange between the ligand and DMSO, good NMR spectra cannot be obtained.

$[PdCl_2(2\text{-}Ph\text{-}NC_9H_5\text{-}4\text{-}COOH)_2]$ (5). To a solution of $[Pd(PhCN)_2Cl_2]$ (95.9 mg, 0.25 mmol) in benzene (10 mL) was added a solution of 2-phenyl-quinoline-4-carboxylic acid (124.7 mg, 0.50 mmol) in acetone (10 mL). A yellow precipitate was formed after 2 h. The mixture was stirred for a further 2 h. The yellow powder was obtained by filtration, washed with acetone, and dried in vacuo. Yield: 80%. Anal. Calcd for $C_{32}H_{22}Cl_2N_2O_4Pd$: C, 56.87; H, 3.28; N, 4.14. Found: C, 56.20; H, 3.34; N, 4.00. IR (Nujol): $\nu_{C=O}$ 1715 cm^{-1}, $\nu_{OH} = 2610$ cm^{-1}. ^{1}H NMR (DMF-d_7): δ 9.11 (d, $^3J_{HH} = 8$ Hz, 2H, H^8); 8.71 (dd, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, 2H, H^5); ~8.21−8.30 (br, m, 4H, H^{6,7}); ~7.78−8.14 (br, m, 12H, 2H^3 + 2Ph). Mp: 294 °C, decomposed. Single crystals of **5** were obtained by a diffusion reaction of 2-phenyl-quinoline-4-carboxylic acid solution in acetone and $[Pd(PhCN)_2Cl_2]$ solution in toluene. Single crystals of **5·4DMF** were obtained from saturated DMF solution of the complex. TGA indicated solvent loss over the temperature range 70−150 °C.

$[PdCl_2(NC_5H_4\text{-}4\text{-}CH_2COOH)_2]$ (6). It was prepared by a similar procedure as for **1** except that 4-pyridylacetic acid was used. A pale yellow product was obtained. Yield: 82%. Anal. Calcd for $C_{14}H_{14}Cl_2N_2O_4Pd$: C, 37.23; H, 3.12; N, 6.20. Found: C, 37.13; H, 3.14; N, 6.04. IR (Nujol): $\nu_{C=O}$ 1735 cm^{-1}, $\nu_{OH} = 3226$ cm^{-1}. ^{1}H NMR (CD_3OD/CD_3CN): δ 8.65 (d, $^3J_{HH} = 7$ Hz, 4H, H^{2,6}); 7.37 (d, $^3J_{HH} = 7$ Hz, 4H, H^{3,5}); 3.80 (s, 4H, CH$_2$). Mp: 300 °C, decomposed.

$[PdCl_2(NC_5H_4\text{-}4\text{-}SCH_2COOH)_2]$ (7). This compound was prepared by a similar procedure as for **1** except that (4-pyridylthio)acetic acid was used. A yellow product was obtained. Yield: 84%. Anal. Calcd for $C_{14}H_{14}Cl_2N_2O_4PdS_2$: C, 32.61; H, 2.74; N, 5.43. Found: C, 31.55; H, 2.74; N, 5.09. IR (Nujol): $\nu_{C=O}$ 1719 cm^{-1}, $\nu_{OH} = 2608$ cm^{-1}. ^{1}H NMR (DMF-d_7): δ 8.56 (d, $^3J_{HH} = 7$ Hz, 4H, H^{2,6}); 7.51 (d, $^3J_{HH} = 7$ Hz, 4H, H^{3,5}); 4.22 (s, 4H, SCH$_2$); 13.62 (br s, COOH). Mp: 222 °C, decomposed.

$[Pd(NC_5H_4\text{-}2\text{-}C\{O\}O)_2]$ (8). This compound was prepared by a similar procedure as for **1** except that pyridine-2-carboxylic acid was used. The product was obtained as a white solid. Yield: 99%. The compound also can be synthesized by the reaction of $[PdCl_2(PhCN)_2]$ and pyridine-2-carboxylic acid in acetone. Anal. Calcd for $C_{12}H_8N_2O_4Pd$: C, 41.11; H, 2.30; N, 7.99. Found: C, 40.22; H, 2.28; N, 7.70. IR (Nujol): $\nu_{C=O}$ 1676 cm^{-1} (s); ν_{C-O^-} 1606 cm^{-1} (m). Mp: >330 °C, decomposed. Colorless needle crystals of **3** were obtained by slow diffusion of $[PdCl_2(PhCN)_2]$ in acetone into a solution of pyridine-2-carboxylic acid in water in about 2 months.

$[PdCl_2(NC_5H_3\text{-}3,5\text{-}(COOH)_2)_2]$ (9). To a solution of pyridine-3,5-dicarboxylic acid (66.8 mg, 0.40 mmol) in THF (30 mL) was added $[Pd(PhCN)_2Cl_2]$ (76.7 mg, 0.20 mmol), giving a yellow solution. The resulting solution was stirred for 3 h and then was concentrated to 10 mL, and pentane (50 mL) was added, giving a yellow precipitate. The yellow powder was obtained by filtration, washed with pentane, and dried in vacuo. Yield: 95%. Anal. Calcd

Table 14. Crystallographic Data for the Complexes

	1	**2**	**2**·2DMSO	**8**	**5**	**5**·4DMF
formula	$C_{12}H_{10}Cl_2N_2O_4Pd$	$C_{12}H_{10}Cl_2N_2O_4Pd$	$C_{16}H_{22}Cl_2N_2O_6PdS_2$	$C_{12}H_8N_2O_4Pd$	$C_{32}H_{22}Cl_2N_2O_4Pd$	$C_{44}H_{50}Cl_2N_6O_8Pd$
fw	423.52	423.52	579.78	350.60	675.82	968.20
temp (K)	295(2)	295(2)	294(2)	200(2)	150(2)	294(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.69150	0.71073
cryst syst, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	triclinic, $P1$
a (Å)	3.9554(2)	3.92340(10)	4.7722(10)	3.7077(2)	8.145(2)	7.9009(2)
b (Å)	7.4830(4)	13.5352(6)	10.139(2)	12.8197(5)	9.422(2)	9.3964(2)
c (Å)	12.5456(7)	13.4180(6)	12.788(3)	11.5267(6)	10.092(2)	15.9253(2)
α (deg)	75.625(3)	90	107.353(10)	90	65.601(2)	77.992(1)
β (deg)	88.898(3)	96.0520(10)	90.549(10)	91.008(3)	75.142(2)	77.342(1)
γ (deg)	80.313(3)	90	96.331(10)	90	78.015(3)	82.234(1)
V (Å^3), Z	354.47(3), 1	708.58(5), 2	586.4(2), 1	547.80(5), 2	677.2(3), 1	1123.34(3), 1
D_{calcd} (g/cm^3)	1.984	1.985	1.642	2.126	1.657	1.431
μ (mm^{-1})	1.701	1.702	1.230	1.706	0.925	0.590
F(000)	208	416	292	344	340	500
θ range (deg)	1.68−24.99	2.14−27.49	2.12−24.98	3.18−27.49	2.2−27.0	1.33−25.00
range h	−5 to 5	−4 to 5	0 to 6	−4 to 4	−10 to 9	−10 to 10
range k	−8 to 10	−13 to 19	−12 to 12	−16 to 16	−12 to 12	−12 to 12
range l	−15 to 17	−19 to 16	−17 to 17	−14 to 14	−12 to 13	−21 to 19
reflns collected	3711	6533	1933	7363	3927	7079
unique reflns	1251	1618	1933	1933	2752	7079
max and min transmn	0.3522, 0.3118	0.2790, 0.2451		0.9196, 0.7266	0.870, 0.577	0.2790, 0.2451
GOF on F^2	1.021	1.026	1.065	0.997	1.017	1.083
final R indices [$I > 2\sigma(I)$]	R1 = 0.0238	R1 = 0.0275	R1 = 0.0278	R1 = 0.0271	R1 = 0.0353	R1 = 0.0304
	wR2 = 0.0582	wR2 = 0.0690	wR2 = 0.0769	wR2 = 0.0625	wR2 = 0.0949	wR2 = 0.0835
R indices (all data)	R1 = 0.0271	R1 = 0.0387	R1 = 0.0306	R1 = 0.0447	R1 = 0.0364	R1 = 0.0418
	wR2 = 0.0607	wR2 = 0.0752	wR2 = 0.0784	wR2 = 0.0664	wR2 = 0.0954	wR2 = 0.1078

	9·2CH$_3$OH	**10**·4H$_2$O	**11**·ClCH$_2$CH$_2$Cl·H$_2$O	**13**	**14**	**17**
formula	$C_{16}H_{18}Cl_2N_2O_{10}Pd$	$C_{18}H_{26}Cl_2N_2O_{12}Pd$	$C_{43}H_{40}Cl_2F_6N_2O_{11}P_2PdS_2$	$C_{45.63}H_{45.25}F_6N_2O_{10.88}P_2PdS_4$	$C_{59.05}H_{68.10}F_6N_2O_{19.35}P_2PdS_2$	$C_{39.50}H_{32}ClF_6N_2O_{10}P_2PdS_2$
fw	575.62	639.71	1178.13	1206.17	1461.92	1076.58
temp (K)	215(2)	150(2)	200(2)	150(2)	150(2)	200(2)
λ (Å)	0.71073	0.69150	0.71073	0.71073	0.71073	0.71073
cryst syst, space group	triclinic, $P\bar{1}$	monoclinic, $C2/m$	orthorhombic, $Pbca$	triclinic, $P\bar{1}$	monoclinic, $P2(1)/c$	orthorhombic, $Pbcn$
a (Å)	4.9006(4)	11.625(2)	19.8192(2)	12.24(3)	12.6459(8)	14.2300(2)
b (Å)	7.9416(9)	20.765(4)	17.1480(2)	19.737(4)	39.284(3)	24.6236(3)
c (Å)	14.2851(15)	6.5940(10)	29.6791(2)	23.865(5)	14.8286(9)	25.7343(3)
α (deg)	97.815(6)	90	90	75.76(3)	90	90
β (deg)	99.871(6)	116.12(3)	90	84.96(3)	107.204(3)	90
γ (deg)	100.030(6)	90	90	72.70(3)	90	90
V (Å^3), Z	531.42(9), 1	1429.2(4), 2	10086.73(17), 8	5340.9(19), 4	7036.9(8), 4	9017.1(2), 8
D_{calcd} (g/cm^3)	1.799	1.487	1.552	1.500	1.380	1.586
μ (mm^{-1})	1.181	0.891	0.700	0.641	0.451	0.716
F(000)	288	648	4768	2456	3013	4336
θ range (deg)	3.60−30.05	2.12−27.07	2.59−27.53	4.08−25.36	4.08−20.63	2.70−27.48
range h	0 to 6	−14 to 15	−25 to 25	0 to 14	−12 to 12	−18 to 18
range k	−11 to 11	−26 to 20	−22 to 22	−22 to 23	−30 to 38	−31 to 31
range l	−20 to 19	−8 to 8	−38 to 38	−28 to 28	−14 to 14	−33 to 33
reflns collected	6582	4263	3927	51930	18113	132331
unique reflns	3043	1594	161575	19353	6768	10342
max and min transmn	0.8245, 0.7729		0.8308, 0.7101	0.9535, 0.8309	0.9520, 0.9313	0.9651, 0.8139
GOF on F^2	1.038	1.051	1.054	0.916	1.094	1.018
final R indices [$I > 2\sigma(I)$]	R1 = 0.0516	R1 = 0.0438	R1 = 0.0555	R1 = 0.0590	R1 = 0.0677	R1 = 0.0560
	wR2 = 0.0985	wR2 = 0.1087	wR2 = 0.1570	wR2 = 0.1364	wR2 = 0.1682	wR2 = 0.1772
R indices (all data)	R1 = 0.0744	R1 = 0.0473	R1 = 0.0862	R1 = 0.1371	R1 = 0.0836	R1 = 0.0870
	wR2 = 0.1085	wR2 = 0.1107	wR2 = 0.1794	wR2 = 0.1593	wR2 = 0.1778	wR2 = 0.1945

for $C_{14}H_{10}Cl_2O_8N_2Pd \cdot H_2O$: C, 31.75; H, 2.28; N, 5.29. Found: C, 31.45; H, 2.60; N, 5.00. IR (Nujol): $\nu_{C=O}$ 1721, 1745 cm^{-1}; ν_{OH} 2521 cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 9.54 (d, $^4J_{HH} = 2$ Hz, 4H, H^{2,6}); 8.94 (t, $^4J_{HH} = 2$ Hz, 2H, H^4). ^{13}C{^{1}H} NMR (CD$_3$OD): 164.96 (COOH), 158.28 (C^2), 141.57 (C^3), 129.97 (C^4). Mp: 316 °C, decomposed. Single crystals of **9**·2MeOH suitable for X-ray structure determination were obtained from the solution of the complex in methanol by very slow evaporation in several months.

[PdCl$_2$(2,6-Me$_2$−NC$_5$H-3,5-(COOH)$_2$)$_2$] (10). It was prepared by a similar procedure as for **9** except that 2,6-dimethyl-pyridine-3,5-dicarboxylic acid was used and the reaction was carried out for 24 h, because of the insolubility of the ligand in THF. A yellow product was obtained. Yield: 96%. Anal. Calcd for $C_{18}H_{18}Cl_2N_2O_8$-Pd·2H$_2$O·2THF: C, 41.75; H, 5.12; N, 3.75. Found: C, 41.38; H, 5.03; N, 3.88. IR (Nujol): $\nu_{C=O}$ 1698, 1724 cm^{-1}; ν_{OH} 2626 cm^{-1}. ^{1}H NMR (acetone): δ 8.84 (s, 2H, H^4); 4.13 (s, 12H, CH$_3$); 3.62 (m, 8H, O−CH$_2$/THF), 1.78 (m, 8H, CH$_2$/THF). ^{13}C{^{1}H} NMR (acetone): 165.82 (COOH), 165.40 (C^2), 143.38 (C^3), 127.20 (C^4), 26.84 (CH$_3$). THF: 67.99, 26.10. Mp: 245 °C, decomposed. Single crystals of **10**·4H$_2$O were grown from an acetone solution of the complex.

[Pd(dppp)(NC$_5$H$_4$-4-COOH)$_2$] (CF$_3$SO$_3$)$_2$ (11). To a mixture of [Pd(dppp)$_2$(SO$_3$CF$_3$)$_2$] (81.7 mg, 0.10 mmol) and pyridine-4-carboxylic acid (24.6 mg, 0.20 mmol) was added THF (15.0 mL). The resulting solution changed in color from yellow to colorless. The solution was stirred for a total of 4 h and then was concentrated to about 5 mL. After pentane (50 mL) was added to the described solution, a white precipitate was formed. The white solid product was obtained by filtration, washed with pentane, and dried in vacuo. Yield: 90%. Anal. Calcd for $C_{41}H_{36}F_6N_2O_{10}P_2PdS_2$: C, 46.32; H, 3.41; N, 2.63. Found: C, 46.02; H, 3.65; N, 2.50. IR (Nujol): $\nu_{C=O}$ 1732 cm^{-1}; ν_{OH} 3455 cm^{-1}. ^{1}H NMR (acetone): δ 9.22 (br s, 4H, H^{2,6}); ∼7.20−7.80 (br m, 24H, H^{3,5}−Py + 4Ph); 3.40 (br, 4H, PCH$_2$); 2.40 (br, 2H, PCH$_2$CH$_2$); 12.00 (br, COOH). ^{31}P{^{1}H} NMR (acetone): δ 9.15 (s). Mp: 176 °C. Colorless single crystals of **11** were grown from a solution of the complex in 1,2-dichloroethane/hexane.

[Pd(dppp)(NC$_5$H$_4$-3-COOH)$_2$] (CF$_3$SO$_3$)$_2$ (12). This compound was prepared in a similar way as for **11** except that pyridine-3-carboxylic acid was used. A white solid product was obtained. Yield: 90%. Anal. Calcd for $C_{41}H_{36}F_6N_2O_{10}P_2PdS_2$: C, 46.32; H, 3.41; N, 2.63. Found: C, 46.56; H, 3.31; N, 2.50. IR (Nujol): $\nu_{C=O}$ 1746 cm^{-1}; ν_{OH} 3189 cm^{-1}. ^{1}H NMR (acetone): δ 9.43 (br, s, 2H, H^2); 9.27 (br, s, 2H, H^6); 8.18 (br, s, 2H, H^4); ∼7.30−7.80 (br m, 22H, H^5−Py + 4Ph); 3.40 (br, 4H, PCH$_2$); 2.40 (br, 2H, PCH$_2$-CH$_2$); 12.00 (br s, 2H, COOH). ^{31}P{^{1}H} NMR (acetone): δ 9.38 (s). Mp: 192 °C. Colorless single crystals of **12** were obtained from a solution of the complex in THF/pentane.

[Pd(dppp)(NC$_5$H$_4$-4-SCH$_2$COOH)$_2$] (CF$_3$SO$_3$)$_2$ (13). This compound was prepared in a similar way as for **11** except that (4-pyridylthio)acetic acid was used. A white product was obtained. Yield: 81%. Anal. Calcd for $C_{43}H_{40}F_6N_2O_{10}P_2PdS_4$: C, 44.70; H, 3.49; N, 2.42. Found: C, 44.67; H, 3.24; N, 2.31. IR (Nujol): $\nu_{C=O}$ 1727 cm^{-1}; ν_{OH} 3450 cm^{-1}. ^{1}H NMR (acetone): δ 8.62 (br s, 4H, H^{2,6}); 7.02 (br s, 4H, H^{3,5}); ∼7.24−7.90 (br m, 20H, 4Ph); 3.34 (br, 4H, PCH$_2$); 2.40 (br, 2H, PCH$_2$CH$_2$); 3.92 (s, 4H, SCH$_2$). ^{31}P{^{1}H} NMR (acetone): δ 9.19 (s). Mp: 179 °C. Colorless single crystals of **13** were obtained from a solution of the complex in acetone/pentane.

[Pd(dppp)(NC$_5$H$_3$-3,5-(COOH)$_2$)$_2$] (CF$_3$SO$_3$)$_2$ (14). This compound was prepared in a similar way as for **11** except that pyridine-3,5-dicarboxylic acid was used. A white product was obtained. Yield: 83%. Anal. Calcd for $C_{43}H_{36}F_6N_2O_{14}P_2PdS_2$: C, 44.68; H, 3.15; N, 2.43. Found: C, 44.74; H, 3.59; N, 2.18. IR (Nujol): $\nu_{C=O}$ 1734, 1641 cm^{-1}; ν_{OH} 3447 cm^{-1}. ^{1}H NMR (acetone): δ 9.68 (br s, 4H, H^{2,6}); 8.55 (br s, 2H, H^4); ∼7.20−7.90 (br m, 20H, 4 Ph); 3.40 (br, 4H, PCH$_2$); 2.40 (br, 2H, PCH$_2$CH$_2$). ^{31}P{^{1}H} NMR (acetone): δ 10.14 (s). Mp: 210 °C. Single crystals of **14**·5.35-(acetone) were grown by slow evaporation of an acetone solution. The complex easily lost acetone of solvation at room temperature.

[Pd(dppp)(2,6-Me$_2$−NC$_5$H-3,5-(COOH)$_2$)$_2$] (CF$_3$SO$_3$)$_2$ (15). This compound was prepared in a similar way as for **11** except that 2,6-dimethyl-pyridine-3,5-dicarboxylic acid was used. A white product was obtained. Yield: 77%. Anal. Calcd for $C_{47}H_{44}F_6N_2O_{14}P_2$-PdS$_2$: C, 46.76; H, 3.67; N, 2.32. Found: C, 47.21; H, 3.93; N, 2.08. IR (Nujol): $\nu_{C=O}$ 1730, 1648 cm^{-1}; ν_{OH} 3462 cm^{-1} (s). ^{1}H NMR (acetone): δ 8.03 (s, 2H, H^4); ∼7.10−7.95 (br m, 20H, 4 Ph); 3.15 (br, 4H, PCH$_2$); 2.30 (br, 2H, PCH$_2$CH$_2$); 2.97 (br s, 12H, CH$_3$). ^{31}P{^{1}H} NMR (acetone): δ 16.26 (s). Mp: 195 °C.

[Pd(dppm)(NC$_5$H$_4$-4-COOH)$_2$] (CF$_3$SO$_3$)$_2$ (16). This compound was prepared in a similar way as for **11** except that [Pd(dppm)-(CF$_3$SO$_3$)$_2$] was used. White product was obtained. Yield: 88%. Anal. Calcd for $C_{39}H_{32}F_6N_2O_{10}P_2PdS_2$: C, 45.25; H, 3.12; N, 2.71. Found: C, 44.80; H, 3.17; N, 2.59. IR (Nujol): $\nu_{(C=O)}$ 1733 cm^{-1}; ν_{OH} 2655, 3462. ^{1}H NMR (acetone): δ 9.23 (br s, 4H, H^{2,6} −Py); 7.96 (br m, 12H, H^{3,5}−Py + H^{2,6}−Ph); 7.66 (br m, 4H, H^4−Ph); 7.53 (br m, 8H, H^{3,5}−Ph); 5.23 (t, $^2J_{PH}$ = 12.0 Hz, 2H, PCH$_2$); 12.50 (br s, 2H, COOH). ^{31}P{^{1}H} NMR (acetone): $\delta = -36.99$ (s). Mp: 146 °C.

[Pd(dppm)(NC$_5$H$_4$-3-COOH)$_2$] (CF$_3$SO$_3$)$_2$ (17). This compound was prepared in a similar way as for **16** except that pyridine-3-carboxylic acid was used. A white solid product was obtained. Yield: 97%. Anal. Calcd for $C_{39}H_{32}F_6N_2O_{10}P_2PdS_2$: C, 45.25; H, 3.12; N, 2.71. Found: C, 45.46; H, 3.21; N, 2.57. IR (Nujol): $\nu_{C=O}$ 1730 cm^{-1}; ν_{OH} 2665, 3437 cm^{-1}. ^{1}H NMR (acetone): δ 9.39 (br s, 2H, H^6 −Py); 9.34 (s, 2H, H^2 −Py); 8.53 (br, 2H, H^4 −Py); 7.78 (br, 2H, H^5−Py); 7.96 (br m, 8H, H^{2,6}−Ph); 7.66 (br m, 4H, H^4−Ph); 7.53 (br m, 8H, H^{3,5}−Ph); 5.27 (t, $^2J_{PH}$ = 12 Hz, 2H, PCH$_2$). ^{31}P{^{1}H} NMR (acetone): $\delta = -37.93$ (s). Mp: 198 °C, decomposed. Colorless single crystals of **17** were obtained from a solution of the complex in 1,2-dichloroethane/acetone/hexane.

[Pd(dppm)(NC$_5$H$_4$-4-SCH$_2$COOH)$_2$] (CF$_3$SO$_3$)$_2$ (18). This compound was prepared in a similar way as for **16** except that pyridine-3-carboxylic acid was used. The product was obtained as a white solid. Yield: 88%. Anal. Calcd for $C_{41}H_{36}F_6N_2O_{10}P_2PdS_4$: C, 43.68; H, 3.22; N, 2.48. Found: C, 43.10; H, 3.32; N, 2.37. IR (Nujol): $\nu_{C=O}$ 1727, 1628 cm^{-1}; ν_{OH} 2665, 3457 cm^{-1}. ^{1}H NMR (acetone): δ 8.72 (br s, 4H, H^{2,6} −Py); 8.10 (br s, 4H, H^{3,5}−Py); 7.40−7.90 (br m, 20H, H of Ph); 5.15 (br, 2H, PCH$_2$); 4.08 (br s, 4H, SCH$_2$). ^{31}P{^{1}H} NMR (acetone): $\delta = -37.62$ (s). Mp: 152 °C, decomposed.

Pd(dppm)(NC$_5$H$_3$-3,5-(COOH)$_2$)$_2$] (CF$_3$SO$_3$)$_2$ (19). This compound was prepared in a similar way as for **16** except that pyridine-3,5-dicarboxylic acid was used. The product was obtained as a white solid. Yield: 90%. Anal. Calcd for $C_{41}H_{32}F_6N_2O_{14}P_2PdS_2$: C, 43.81; H, 2.87; N, 2.49. Found: C, 43.59; H, 2.93; N, 247. IR (Nujol): $\nu_{C=O}$ 1734 cm^{-1}; ν_{OH} 2655, 3457 cm^{-1}. ^{1}H NMR (acetone): δ 9.67 (br s, 4H, H^{2,6}); 8.82 (s, 2H, H^4−Py); 7.42−8.06 (m, 20H, 4Ph); 5.35 (br, 2H, PCH$_2$). ^{31}P NMR (acetone): δ −38.97 (s). Mp: 178 °C, decomposed.

X-ray Structure Determinations. Crystals were mounted on glass fibers. Data were collected using a Nonius Kappa-CCD diffractometer and Mo X-rays except for the poorly diffracting crystals **5** and **10**·4H$_2$O for which it was necessary to use synchrotron radiation in conjunction with a Bruker SMART

---

(15) Programs used. For structure solution and refinement: Sheldrick, G. M. *SHELXTL 5.1*; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998. For data collection and processing: (a) Otwinowski, Z.; Minor, W. COLLECT (Nonius) and DENZO-SCALEPACK. *Processing of X-ray Diffraction Data Collected in Oscillation Mode*; Methods in Enzymology, Volume 276, Macromolecular Crystallography, part A; Carter, C. W.; Sweet, R. M., Eds.; Academic Press: New York, 1997; p 307−326. (b) *SAINT & SADABS*; Bruker: Madison, WI, 1995.

diffractometer. In all cases, cell dimensions were derived from the complete data set. The structures were solved by direct methods and refined by least squares on F^2. Anisotropic thermal parameters were applied to all non-hydrogen atoms. A summary of crystallographic data can be found in Table 14.[15]

Acknowledgment. We thank the NSERC (Canada) for financial support, and R.J.P. thanks the Government of Canada for a Canada Research Chair. We are also grateful to EPSRC for synchrotron beam time at the C.L.R.C. Daresbury Laboratory, Warrington, U.K.

Supporting Information Available: Crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020239B