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Article

Molecular Triangle of Palladium(II) and Its Anion Binding Properties

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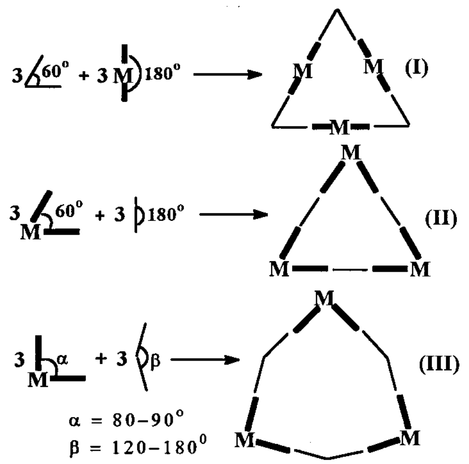
The ligand 4(3*H*)-pyrimidone (Hpm) forms the complexes *trans*-[$PdCl_2(Hpm)_2$] and [$Pd(PP)(Hpm)_2$]($(CF_3SO_3)_2$) (PP = $Ph_2PCH_2PPh_2$ or $Ph_2P(CH_2)_3PPh_2$), with the neutral ligand (Hpm), and a bowl-like molecular triangle, [{Pd(bu$_2$bipy)(μ-pm)}$_3$]$^{3+}$ (bu$_2$bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), with the deprotonated ligand (pm). This triangular complex acts as a host for binding of several anionic guests.

Introduction

Self-assembled metallomacrocycles have attracted a great amount of attention because of their shape- and size-selective encapsulating properties, with potential applications in catalysis, sensing devices, molecular electronics, and small molecule transport.[1−5] The synthesis of these compounds often proceeds in excellent yields, high selectivity, and few steps using simple metal centers and bidentate ligands as building blocks.[1−5] For example, *cis*-blocked, square planar palladium(II) and platinum(II) complexes with bidentate or tridentate pyridine-based ligands have been used to prepare molecular boxes and cages that are soluble in either water or organic solvents.[2−5] Although there has been much interest in the metal molecular triangle, as the simplest such polygon, there are still relatively few examples and fewer studies of the binding properties of these compounds.[1−5]

Molecular triangles can, in principle, be formed according to the three methods shown in Scheme 1. Method I uses three bridging ligands with 60° angles in combination with three linear metal centers.[6−8] Method II is the reverse situation but is not practical because metal units with 60° bond angles are not available. Method III is a variation in which distortion of the metal center with natural bond angles of 90° and/or introduction of a nonlinear bridging ligand can give molecular triangles.[9−22]

Scheme 1



The Lippert group has reported tetranuclear metallamacrocycles, analogous to calix[4]arenes, and molecular hexa-

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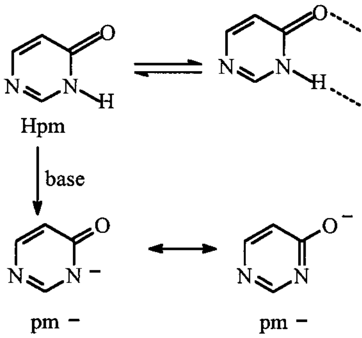
Scheme 2



gons by combining metal entities with 90° bond angles such as palladium(II) and platinum(II) with simple pyrimidine derivatives including uracil and 2-hydroxypyrimidine.[4] However, 4(3*H*)-pyrimidone (Hpm), the structural isomer of 2-hydroxypyrimidine, has rarely been used as a ligand in coordination chemistry,[23] though it has the potential to give supramolecular structures through hydrogen bonding of the NH group (Scheme 2) and could act as either a monodentate neutral ligand or as a bidentate ligand in the deprotonated form.[24] This article reports the synthesis and characterization of palladium(II) complexes with this ligand, including a cationic molecular triangle, and a study of the binding ability of this tripalladium complex with anions.

Results and Discussion

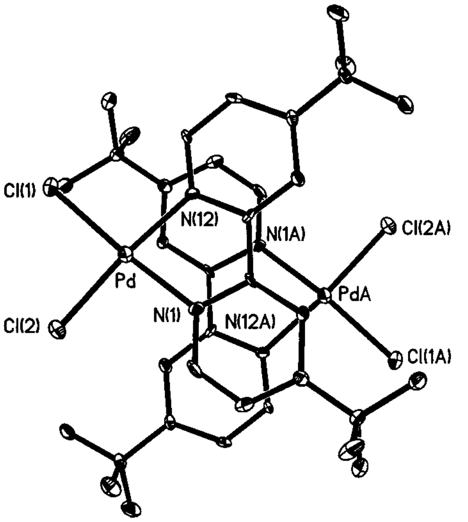
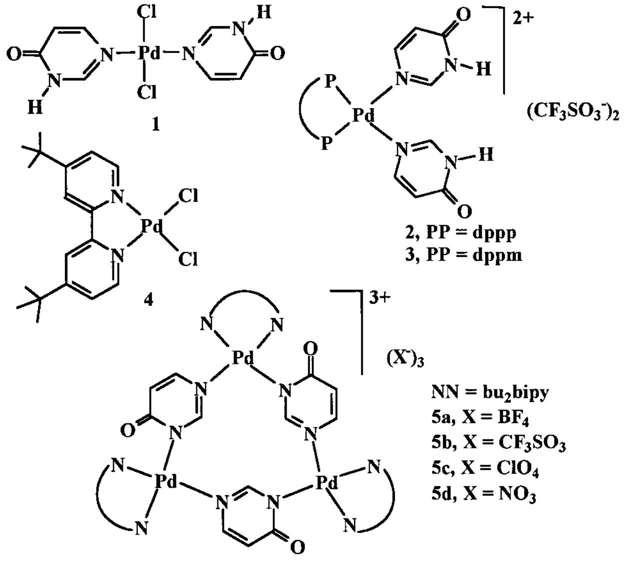


Figure 1. Molecular structure of complex **4**.

Scheme 3



Synthesis and Characterization of Complexes. The reaction of the ligand 4(3*H*)-pyrimidone (Hpm) with $[PdCl_2(PhCN)_2]$ gave the complex *trans*-$[Pd(Hpm)_2Cl_2]$, **1**, by displacement of the weakly bonded benzonitrile ligands (Scheme 3). Complex **1** was isolated as an air-stable, yellow solid that was soluble in DMF and DMSO but not in other common organic solvents. The IR spectrum of **1** showed two bands at 1733 and 1687 cm^{-1} due to $\nu(C{=}O)$ and at 3080 and 3050 cm^{-1} due to $\nu(NH)$, indicating the presence of $NH\cdots O{=}C$ hydrogen bonding in the solid state.[25] Reaction of Hpm with $[Pd(dppp)(OTf)_2]$[26] or $[Pd(dppm)(OTf)_2]$ gave the cationic complexes $[Pd(dppp)(Hpm)_2](OTf)_2$, **2**, and $[Pd(dppm)(Hpm)_2](OTf)_2$, **3**, respectively. Their ^1H NMR spectra showed peaks at $\delta = 12.0$ and 12.3, respectively, for the NH proton. Crystals of these Hpm complexes proved unsuitable for structure determinations, but they are characterized by the spectroscopic and analytical data.

The complex $[PdCl_2(bu_2bipy)]$, **4**, was readily prepared, and its structure was determined for comparison with later compounds (Figure 1, Table 1). The molecular structure is similar to that of $[PdCl_2(bipy)]$,[27] but the complexes stack

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Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex **4**

Pd−N(1)	2.028(6)	Pd−Cl(1)	2.288(2)
Pd−N(12)	2.029(6)	Pd−Cl(2)	2.280(2)
N(1)−Pd−N(12)	79.6(3)	Cl(2)−Pd−Cl(1)	89.89(8)
N(1)−Pd−Cl(2)	95.3(2)	N(12)−Pd−Cl(1)	95.4(2)
N(12)−Pd−Cl(2)	174.4(2)	N(1)−Pd−Cl(1)	174.1(2)

in columns. Nearest neighbors are staggered, presumably so as to allow π-stacking of the bipyridyl groups while minimizing steric repulsions between *tert*-butyl substituents (Figure 1). The separation between closest bipyridyl rings is about 3.4 Å. Complex **4** is more soluble than [PdCl$_2$(bipy)], and so, it can be treated with AgBF$_4$ or AgO$_3$SCF$_3$ in tetrahydrofuran to generate the corresponding salts of the cation [Pd(bu$_2$bipy)(thf)$_2$](X$^-$)$_2$ (X$^-$ = BF$_4^-$, CF$_3$SO$_3^-$).

The reaction of Hpm with [Pd(bu$_2$bipy)(thf)$_2$](X$^-$)$_2$ (X$^-$ = BF$_4^-$, CF$_3$SO$_3^-$) gave mixtures of products, whose ^{1}H NMR spectra showed only a weak, broad peak at δ = 12 for the NH group, suggesting that partial deprotonation had occurred spontaneously. When the similar reaction was carried out under basic conditions, the pure product [{Pd(bu$_2$bipy)}$_3$(μ-pm)$_3$](BF$_4$)$_3$ (**5a**) or [{Pd(bu$_2$bipy)}$_3$(μ-pm)$_3$](CF$_3$SO$_3$)$_3$ (**5b**) was formed (Scheme 3). There were no bands corresponding to ν(NH) in the IR spectra and no NH resonance in the ^{1}H NMR spectra of these compounds. The ^{1}H NMR spectrum for **5a** contained six resonances in the aryl region and two in the *tert*-butyl region for the bu$_2$bipy ligand, showing inequivalence of the two pyridyl rings, and three resonances for the 4-pyrimidonate ligand, consistent with structure **5**. ^{1}H NMR spectra of **5a** were recorded at low temperature, but there was no major change at −90 °C. The spectra suggest that the product has C_n symmetry, with a single axis of symmetry, but the value of n is not defined by the spectra. The product is expected to be formed as a racemate, but it cannot have a random orientation of the pyridonate ligands because the NMR spectrum would then be more complex. The cyclic trimer structure, with effective C_3 symmetry, was finally confirmed by a crystal structure determination.

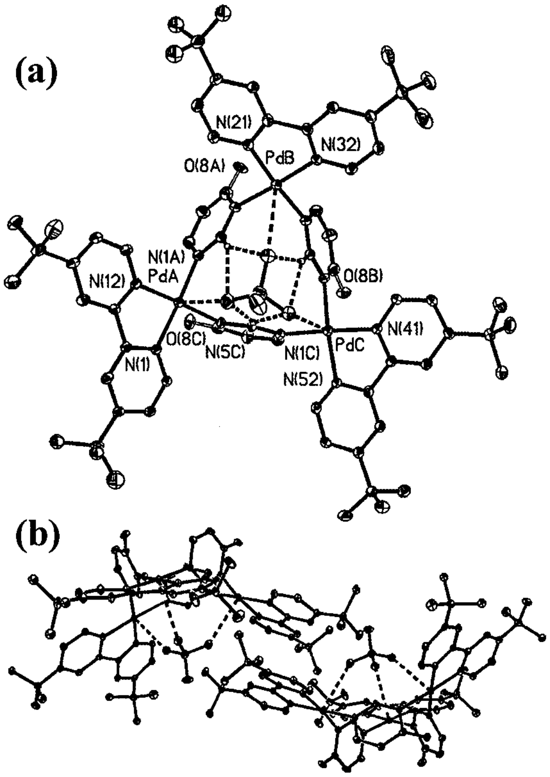

Figure 2. (a) View of the structure of **5a** showing one BF$_4^-$ bound at the base of the cationic bowl through Pd···F and C−H···F interactions. (b) View of the dimer formed via π-stacking.

Structures of Complexes [{Pd(bu$_2$bipy)}$_3$(μ-pm)$_3$]$^{3+}$(X$^-$)$_3$ (X = BF$_4$, 5a; CF$_3$SO$_3$, 5b; ClO$_4$, 5c; NO$_3$, 5d). A view of the molecular structure of the compound **5a** is shown in Figure 2, while selected bond distances and angles are given in Table 2. The structure establishes the presence of the trinuclear complex cation [{Pd(bu$_2$bipy)}$_3$(μ-pm)$_3$]$^{3+}$ with tetrafluoroborate anions. The tripalladium cation consists of alternating [(bu$_2$bipy)Pd]$^{2+}$ vertices and 4-pyrimidonate anion edges. There was disorder of all pyrimidonate ligands with the oxygen atom at 50% occupancy on either side (only one component is shown in Figure 2). The X-ray data do not fully define this disorder, but the NMR data discussed here, in conjunction with the X-ray data, show that the disorder is between two trimers with C_3 symmetry and not a random disorder of individual pyrimidonate ligands that would give lower symmetry molecules. This selectivity is clearly a result of steric effects that keep the carbonyl groups well apart. The geometry of the Pd$_3$(pm)$_3$ units leads to secondary Pd···O distances to the carbonyl oxygen atoms, with Pd···O in the range 2.95−2.99 Å. This feature is present in all examples of complexes **5**, but it is not clear if it represents a bonding interaction. Each of the three palladium(II) centers adopts a slightly distorted square-planar coordination geometry, and each palladium atom is bonded to four nitrogen atoms, two from the neutral bu$_2$bipy ligand and the other two from bridging 4-pyrimidonate ligands. The individual CN distances within the N−C−N fragments of the 4-py-

Table 2. Bond Distances (Å) and Angles (deg) for Complex **5a**

Pd(A)−N(1A)	2.016(5)	Pd(B)−N(1B)	2.028(5)	Pd(C)−N(1C)	2.036(5)
Pd(A)−N(5C)	2.047(5)	Pd(B)−N(5A)	2.028(5)	Pd(C)−N(5B)	2.038(5)
Pd(A)−N(1)	2.012(5)	Pd(B)−N(21)	2.000(5)	Pd(C)−N(41)	2.017(5)
Pd(A)−N(12)	2.011(5)	Pd(B)−N(32)	2.019(5)	Pd(C)−N(52)	2.010(5)
N(1A)−C(6A)	1.334(8)	N(1B)−C(6B)	1.332(8)	N(1C)−C(6C)	1.333(7)
N(5A)−C(6A)	1.327(8)	N(5B)−C(6B)	1.321(8)	N(5C)−C(6C)	1.328(7)
N(1A)−Pd(A)−N(5C)	86.9(2)	N(1B)−Pd(B)−N(5A)	86.6(2)	N(1C)−Pd(C)−N(5B)	86.7(2)
N(12)−Pd(A)−N(1)	80.7(2)	N(21)−Pd(B)−N(32)	80.7(2)	N(52)−Pd(C)−N(41)	80.3(2)
N(1)−Pd(A)−N(5C)	96.8(2)	N(21)−Pd(B)−N(5A)	96.1(2)	N(41)−Pd(C)−N(5B)	95.5(2)
N(12)−Pd(A)−N(1A)	95.8(2)	N(32)−Pd(B)−N(1B)	96.6(2)	N(52)−Pd(C)−N(1C)	97.5(2)
N(1)−Pd(A)−N(1A)	176.2(2)	N(21)−Pd(B)−N(1B)	175.3(2)	N(41)−Pd(C)−N(1C)	177.7(2)
N(12)−Pd(A)−N(5C)	176.8(2)	N(32)−Pd(B)−N(5A)	176.9(2)	N(52)−Pd(C)−N(5B)	173.9(2)

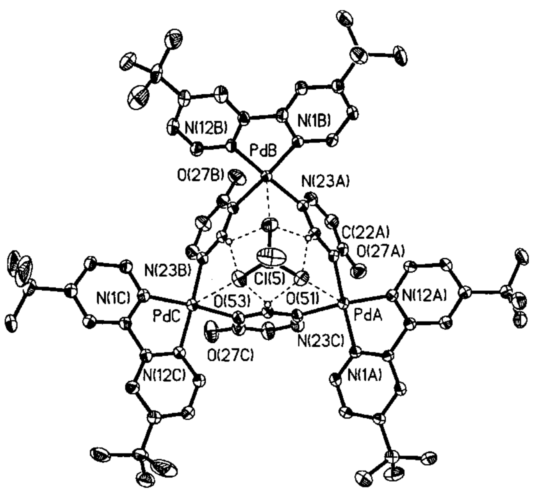

Figure 3. View of the structure of **5c** showing one ClO_4^- bound through Pd···O and C−H···O interactions.

rimidonate residues are effectively equal at 1.33(1) Å (Table 2), suggesting electron delocalization in the pyridonate anion.

The three palladium(II) centers in **5a** form an almost perfect equilateral triangle with 5.88 Å edges. The pyrimidone rings are not coplanar with the Pd_3 plane, with similar deviations of 68.7°, 69.8°, and 68.7° for the three rings, and the PdN_4 coordination planes are similarly angled out of the Pd_3 plane by 35.6°, 31.3°, and 31.1°, for Pd(A), Pd(B), and Pd(C), respectively. This arrangement evidently minimizes ring strain and gives a bowl-like molecule. Interestingly, all 4-pyrimidonate groups are oriented in the same direction (*syn, syn, syn)* with respect to the Pd_3 plane to give a structure similar to the cone conformation of the metallacalix[4]arenes[4] but different from the *syn, anti, anti* conformation adopted by related trimers with bridging imidazolate or benzimidazolate ligands.[10,11] Bowl-shaped molecules can often act as hosts, but the bowl formed by the three 4-pyrimidonate groups of **5a** is too small to accommodate guest molecules. However, on the other side of the molecule, the open cavity defined by the [(bu_2bipy)Pd] units can accommodate a suitable anion along the C_3 axis where it can interact with the three palladium(II) centers and the three C^2−H groups of the 4-pyrimidonate residues. One of three tetrafluoroborate anions is indeed located at the base of the bowl, with three of the fluorine atoms directed toward the Lewis acidic, cationic palladium(II) centers, showing weak Pd···F interactions with distances of 3.127, 3.234, and 3.501 Å (Figure 2a). The plane defined by F(32)−F(33)−F(34) is roughly parallel to the Pd_3 plane as indicated by the dihedral angle of 5.2° between them. In addition, the three fluorine atoms are also involved in weak C−H···F hydrogen bonding with C···F distances range from 3.21 to 3.42 Å in which all F···H distances are shorter than the sum of van de Waals radii of 2.67 Å. The other two tetrafluoroborate ions are located in the spaces between adjacent bu_2bipy groups. In addition, there is evidence for intermolecular π-stacking interactions involving two bu_2bipy groups between neighboring molecules with interplanar centroid separation of around 4.13 Å, resulting in a dimer of the cation complex (Figure 2b). The orientation of the stacked bipyridyl rings is similar to that in the parent complex **4** (Figure 1), but steric effects prevent such close contact as found for **4**.

The crystals of $[\{Pd(bu_2bipy)\}_3(\mu\text{-pm})_3](ClO_4)_3\cdot 2.75$(acetone) (**5c**·2.75(acetone)) were grown from an acetone solution of a mixture of **5a** and tetrabutylammonium perchlorate in a 1:6 molar ratio. The compound crystallized in the same space group as that of **5a**·2(acetone), and the two structures are very similar (Figure 3, Table 3). One perchlorate anion was bound below the bowl of the cation in **5c** through Pd···O (distances 3.33, 3.11, 3.51 Å) interactions and weak C−H···O hydrogen bonding with C···O distances in the range 3.28 to 3.42 Å and the distances O···H at 2.5−2.6 Å (Figure 3). Similar dimers of cationic complexes as shown in Figure 3b were also formed with slightly shorter (and hence stronger) π-stacking interactions (4.10 vs 4.13 Å).

The structure of the triflate complex $[\{Pd(bu_2bipy)\}_3(\mu\text{-pm})_3](CF_3SO_3)_3$, **5b**, is shown in Figure 4, and selected bond distances and angles are listed in Table 4. The overall bowl shape, as indicated by the dihedral angles of 40.9°, 32.4°, and 40.1° between the Pd_3 plane and PdN_4 coordination planes and 77.2°, 59.9°, and 66.2° between the Pd_3 plane and 4-pyrimidonate rings, is similar to those in **5a** and **5c**. In complex **5b**, the triflate ions were disordered, and some were refined only isotropically. The guest triflate (only one of the disordered forms is shown in Figure 4) tilts to one side of the bowl, and thus, only two of its oxygen atoms [O(111) and O(112)] are involved in close interactions with two of the three palladium(II) centers (Pd···O = 3.07−3.29 Å) and in weak hydrogen bonding with the C^2−H groups of the three 4-pyrimidonate units (O···H = 2.3−2.6 Å) (Figure 4a). The shortest distance O···Pd for the remaining palladium atom, Pd(2), and triflate oxygen is 5.3 Å, which is much too long for a bonding interaction. Thus, the symmetry is different from that in compounds **5a** and **5c**,

Table 3. Bond Distances (Å) and Angles (deg) for Complex **5c**

Pd(A)−N(21A)	2.038(6)	Pd(B)−N(21B)	2.030(6)	Pd(C)−N(21C)	2.036(6)
Pd(A)−N(23C)	2.037(6)	Pd(B)−N(23A)	2.036(6)	Pd(C)−N(23B)	2.033(6)
Pd(A)−N(1A)	2.015(6)	Pd(B)−N(1B)	1.997(6)	Pd(C)−N(1C)	1.998(6)
Pd(A)−N(12A)	2.007(6)	Pd(B)−N(12B)	2.000(6)	Pd(C)−N(12C)	2.011(6)
N(21A)−C(22A)	1.314(9)	N(21B)−C(22B)	1.336(9)	N(21C)−C(22C)	1.325(9)
N(23A)−C(22A)	1.305(9)	N(23B)−C(22B)	1.320(9)	N(23C)−C(22C)	1.327(9)
N(23C)−Pd(A)−N(21A)	86.3(2)	N(21B)−Pd(B)−N(23A)	87.0(2)	N(23B)−Pd(C)−N(21C)	86.1(2)
N(12A)−Pd(A)−N(1A)	79.9(2)	N(1B)−Pd(B)−N(12B)	80.5(2)	N(1C)−Pd(C)−N(12C)	80.7(3)
N(1A)−Pd(A)−N(23C)	96.1(2)	N(1B)−Pd(B)−N(23A)	97.0(2)	N(1C)−Pd(C)−N(23B)	96.6(3)
N(12A)−Pd(A)−N(21A)	97.6(2)	N(12B)−Pd(B)−N(21B)	95.6(2)	N(12C)−Pd(C)−N(21C)	96.5(2)
N(1A)−Pd(A)−N(21A)	177.5(2)	N(1B)−Pd(B)−N(21B)	175.9(3)	N(1C)−Pd(C)−N(21C)	174.6(3)
N(12A)−Pd(A)−N(23C)	174.3(3)	N(12B)−Pd(B)−N(23A)	177.0(3)	N(12C)−Pd(C)−N(23B)	177.4(3)

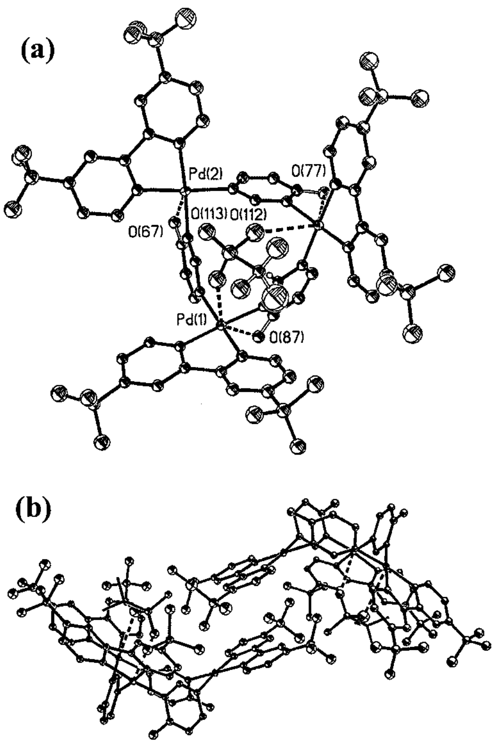

Figure 4. (a) View of the structure of **5b** showing one $CF_3SO_3^-$ ion bound through Pd···O and C–H···O interactions. (b) View of the dimer formed through π-stacking interactions, showing why the triflate ion is displaced from the center (thermal ellipsoids of the CF_3 group are not shown for clarity).

with the triflate deviating greatly from the 3-fold axis of the tripalladium unit. In addition, there is intermolecular π-stacking between pairs of bu$_2$bipy ligands (centroid distance 4.13 Å), similar to that in **5a** and **5c**. It is this effect that appears responsible for the unsymmetrical binding of the triflate anion, because there would be severe steric effects between the CF_3 group of the bound triflate and the bipyridine of the neighboring molecule if bound symmetrically, so the triflate bends away from the bipy group (Figure 4b). There is structural evidence for further supramolecular association through weak, head-to-head C=O···H–C hydrogen bonding (O···C = 3.26–3.34 Å, O···H = 2.42–2.62 Å) between 4-pyrimidonate units of adjacent molecules, and this leads to loosely bound polymeric chains in the crystal lattice.

The complex $[\{Pd(bu_2bipy)\}_3(\mu\text{-pm})_3](NO_3)_3$, **5d**, was prepared by the reaction of complex **5a** with tetrabutylammonium nitrate in acetone. The structure is shown in Figure 5, with bond parameters in Table 5. The lattice contained many disordered solvent molecules that could not be modeled, but the structure of the complex was well-defined. The bowl structure is similar to those in **5a**–**c**, with one nitrate ion at the bowl base. Two structures can be envisaged, with the nitrate lying flat and, so, weakly bonded to all three palladium atoms as in **5a** or **5b**, or upright and loosely bonded to two palladium atoms as in **5c**. The vertical alignment of nitrate was found, two Pd···O distances of 3.27 and 3.37 Å. The binding is also enhanced by weak C–H···O hydrogen bonding with C···O = 3.11–3.47 Å, as shown in Figure 5.

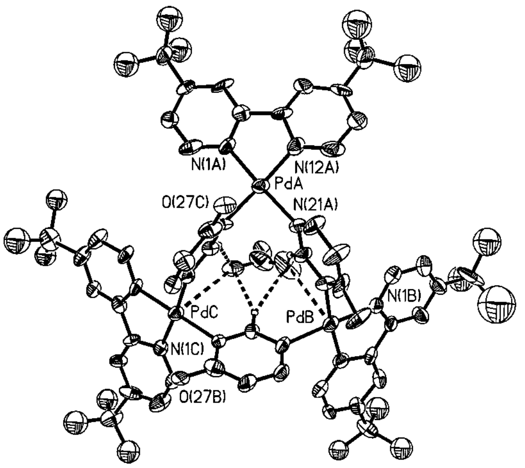

Figure 5. View of the structure of **5d** showing one NO_3^- ion bound through Pd···O and C–H···O interactions.

Anion Binding in Solution as Studied by ^{1}H NMR Titration. Given the convincing evidence for anion inclusion by the cationic tripalladium(II) complex in the solid state, ^{1}H NMR titration studies in CD_2Cl_2 at 293 K were carried out to assess the anion recognition ability of the complex in solution. The tetrafluoroborate salt $[\{Pd(bu_2bipy)\}_3(\mu\text{-pm})_3](BF_4)_3$, **5a**, was selected as host. The ^{1}H NMR spectrum was not affected by addition of $[n\text{-}Bu_4N]BF_4$ (2.5–10 mM) to the 2.5 mM solution of **5a**, and it is therefore deduced that one tetrafluoroborate ion remains bound to the cation in solution giving the ion $[\{Pd(bu_2bipy)\}_3(\mu\text{-pm})_3(BF_4)]^{2+}$. A solution obtained by redissolving single crystals of **5a** gave an identical ^{1}H NMR spectrum. Only a single tetrafluoroborate resonance was observed in the ^{19}F NMR spectrum, indicating easy exchange between free and guest anions. Changes in the spectra upon addition of other anions, X$^-$, are considered to be due to different host–guest interactions caused by displacement of tetrafluoroborate (eq 1).

To solutions of **5a** were added increasing amounts of a variety of anions, $n\text{-}Bu_4N^+A^-$ ($A^- = HSO_4^-, NO_3^-, ClO_4^-,$

Table 4. Bond Distances (Å) and Angles (deg) for the Complex **5b**

Pd(1)–N(61)	2.046(8)	Pd(2)–N(71)	2.039(8)	Pd(3)–N(81)	2.009(9)
Pd(1)–N(83)	2.038(8)	Pd(2)–N(63)	2.033(9)	Pd(3)–N(73)	2.008(8)
Pd(1)–N(1)	1.978(8)	Pd(2)–N(21)	2.004(8)	Pd(3)–N(41)	1.996(9)
Pd(1)–N(12)	2.031(8)	Pd(2)–N(32)	1.997(9)	Pd(3)–N(52)	1.995(8)
N(61)–C(62)	1.336(12)	N(71)–C(72)	1.344(12)	N(81)–C(82)	1.301(12)
N(63)–C(62)	1.313(12)	N(73)–C(72)	1.337(12)	N(83)–C(82)	1.336(12)
N(61)–Pd(1)–N(83)	85.7(3)	N(71)–Pd(2)–N(63)	87.8(3)	N(81)–Pd(3)–N(73)	86.3(3)
N(12)–Pd(1)–N(1)	80.1(3)	N(21)–Pd(2)–N(32)	79.8(4)	N(52)–Pd(3)–N(41)	80.5(4)
N(1)–Pd(1)–N(83)	96.0(3)	N(21)–Pd(2)–N(63)	96.3(3)	N(41)–Pd(3)–N(73)	96.7(3)
N(12)–Pd(1)–N(61)	98.1(3)	N(32)–Pd(2)–N(71)	96.1(3)	N(52)–Pd(3)–N(81)	96.5(3)
N(1)–Pd(1)–N(61)	173.6(3)	N(21)–Pd(2)–N(71)	175.8(3)	N(41)–Pd(3)–N(81)	176.8(3)
N(12)–Pd(1)–N(83)	176.1(3)	N(32)–Pd(2)–N(63)	174.6(3)	N(52)–Pd(3)–N(73)	173.9(3)

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

Pd(A)−N(21A)	2.019(14)	Pd(B)−N(21B)	2.018(14)	Pd(C)−N(21C)	2.028(14)	2.022
Pd(A)−N(23C)	1.976(15)	Pd(B)−N(23A)	2.014(14)	Pd(C)−N(23B)	2.030(13)	2.007
Pd(A)−N(1A)	1.984(14)	Pd(B)−N(1B)	1.990(15)	Pd(C)−N(1C)	1.991(14)	1.988
Pd(A)−N(12A)	1.983(16)	Pd(B)−N(12B)	1.978(15)	Pd(C)−N(12C)	2.003(13)	1.998
N(21A)−C(22A)	1.331(16)	N(21B)−C(22B)	1.334(15)	N(21C)−C(22C)	1.338(16)	1.334
C(22A)−N(23A)	1.346(16)	C(22B)−N(23B)	1.320(16)	C(22C)−N(23C)	1.308(15)	1.325
N(23C)−Pd(A)−N(21A)	86.0(6)	N(23A)−Pd(B)−N(21B)	90.4(6)	N(23B)−Pd(C)−N(21C)	85.7(6)	87.4
N(1A)−Pd(A)−N(12A)	79.0(7)	N(12B)−Pd(B)−N(1B)	79.6(7)	N(1C)−Pd(C)−N(12C)	79.2(6)	79.3
N(23C)−Pd(A)−N(1A)	97.6(7)	N(1B)−Pd(B)−N(23A)	94.4(7)	N(1C)−Pd(C)−N(23B)	97.8(6)	96.6
N(12A)−Pd(A)−N(21A)	97.5(6)	N(12B)−Pd(B)−N(21B)	95.7(7)	N(12C)−Pd(C)−N(21C)	97.4(6)	96.9
N(23C)−Pd(A)−N(12A)	176.6(6)	N(12B)−Pd(B)−N(23A)	173.8(8)	N(12C)−Pd(C)−N(23B)	175.9(6)	175.4
N(1A)−Pd(A)−N(21A)	176.4(7)	N(1B)−Pd(B)−N(21B)	174.6(7)	N(1C)−Pd(C)−N(21C)	174.7(7)	175.2

$$[\{Pd(bu_2bipy)\}_3(\mu\text{-pm})_3(BF_4)]^{2+} + X^- \leftrightarrows [\{Pd(bu_2bipy)\}_3(\mu\text{-pm})_3(X)]^{2+} + [BF_4]^- \quad (1)$$

$CF_3SO_3^-$, PF_6^-, $H_2PO_4^-$, $CH_3CO_2^-$, Cl^-, Br^-), and the changes of chemical shifts of the aromatic C^2−H proton of the 4-pyrimidonate ligands were monitored. In all cases, averaged signals were always observed under the titration conditions, implying that the anion binding is a rapid and reversible process in solution. Upon addition of the anions, significant downfield shifts were observed for H^2 up to limiting values of $\Delta\delta = 0.49$ and 0.41 ppm with HSO_4^- and NO_3^-, respectively (Table 6, Figures 6 and 7), with smaller downfield shifts of H^2 on addition of ClO_4^- or $CF_3SO_3^-$. There was no change upon titration with PF_6^-, indicating the absence of binding. The addition of more strongly binding anions $H_2PO_4^-$, $CH_3CO_2^-$, Cl^-, and Br^- caused cleavage of the trimer, with significant changes of the ^{1}H NMR spectra, so these data could not be analyzed for binding constants. In addition, to assess solvent effects on the binding, the titrations were carried out in acetone-d_6 for HSO_4^-, NO_3^-, ClO_4^-, and $CF_3SO_3^-$. The addition of NO_3^- or HSO_4^- in acetone resulted in precipitation, and thus, the binding constants for these anions could not be determined, but data were obtained for ClO_4^- and $CF_3SO_3^-$. The binding constants were determined by using a nonlinear least-squares calculation, using the stoichiometry of eq 1, and the results are listed in Table 6.[28] On the basis of the crystal structures of **5a**−**d**, all the data were expected to fit with a 1:1 binding model. The data for ClO_4^- and $CF_3SO_3^-$ fit this model well. However, the data for both NO_3^- and HSO_4^- failed to give reasonable binding constants by using the 1:1 binding model, but a 2:1 binding ratio of anion/**5a** was indicated. The results indicate the existence of multiple binding processes, as has been observed in the binding of NO_3^-, Cl^-, and Br^- anions by some π-metalated calixarene hosts.[29a] The binding ability was clearly affected by solvent, probably because of different anion solvation energies.[29]

The calculated binding constants from the ^{1}H NMR titration data demonstrate that the palladium(II) cyclic trimer is capable of acting as an effective host for both planar nitrate and tetrahedral oxoanions. This binding ability can be attributed to a shape specific match between the open cavity and the anions. The attractions Pd···O or Pd···F are probably mostly electrostatic and enhanced by hydrogen bonding between slightly acidic C^2−H protons of the 4-pyrimidonate ligands and the anion. In contrast, the related Pd(II) and Pt(II) tetranuclear macrocycles $[M(en)(pymo)]_4^{4+}$ (en = $H_2NCH_2CH_2NH_2$, pymo = 2-hydroxypyrimidine) are not suitable for anion inclusion because of the small cavity present for both the 1,3-alternate and cone conformations of the cations.[4b] Furthermore, the similar macrocylic tetramers capped by metal ions, which give a much more open cavity, can only include sulfonate anions (via apolar−apolar interaction with the hydrophobic groups within the cavity) or nitrate anions via hydrogen bonding between nitrate and an included water molecule.[30]

Table 6. Binding Constants at 293 K in CD_2Cl_2 and in Acetone-d_6

anion X	solvent	Δd_{max}(obsd)^a	K_a
NO_3^-	CD_2Cl_2	0.49	*b*
HSO_4^-	CD_2Cl_2	0.41	*b*
ClO_4^-	CD_2Cl_2	0.08	2.4
	acetone-d_6	0.05	5.0
$CF_3SO_3^-$	CD_2Cl_2	0.05	1.2
	acetone-d_6	0.07	2.5

^{a} $\Delta d_{max} = d(X) - d(BF_4)$. ^{b} Poor fit to 1:1 binding model.

Conclusions

It is established that 4(3*H*)-pyrimidone is a versatile ligand, either in the neutral or deprotonated form. Neutral palladium(II) complex **1** and cationic complexes with diphosphine ligands **2** and **3** (Scheme 3) contain the neutral ligand while the cationic tripalladium complexes **5** contain the deprotonated ligand acting as a bridging group. Complex **5** can act as a host to bind anions, and the nature of the binding has been determined by structure determinations and by NMR studies in solution. The oxoanions, including perchlorate, nitrate, bisulfate, and triflate, are bound more strongly than tetrafluoroborate while hexafluorophosphate is bound more weakly.

Experimental Section

All reactions were conducted under a dry nitrogen atmosphere using Schlenk techniques, but products were handled in air. NMR spectra were recorded using a Varian Mercury-400 spectrometer.

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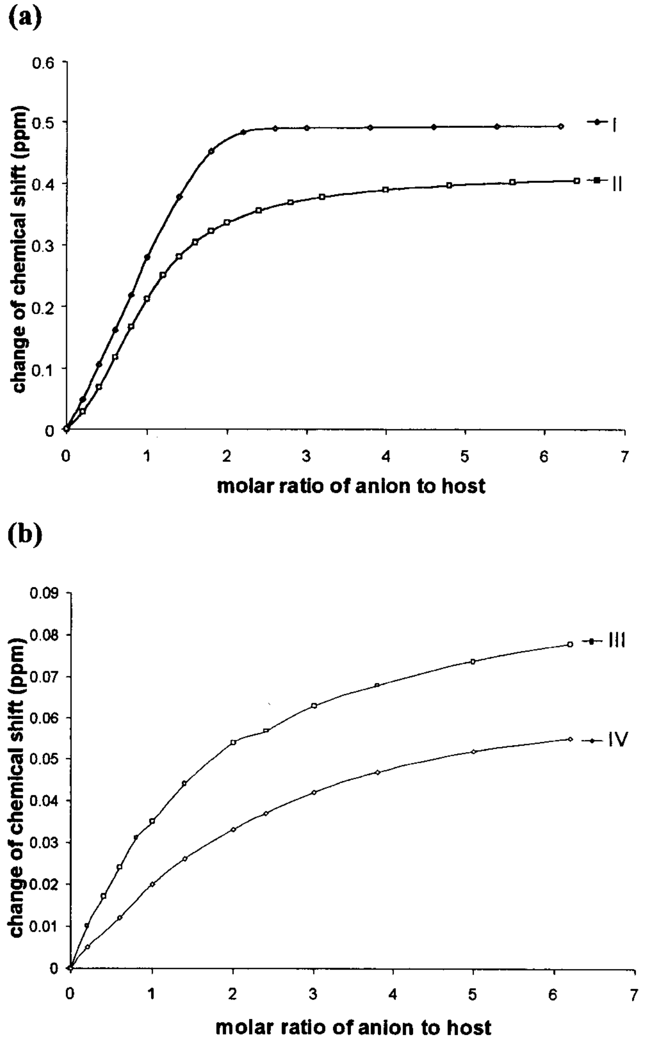

Figure 6. Titration curves between the host **5a** and guest anions HSO_4^- (I, a), NO_3^- (II, a), ClO_4^- (III, b), and $CF_3SO_3^-$ (IV, b) in CD_2Cl_2, plotting the chemical shift change of the H^2 proton of the 4-pyrimidonate ligand vs molar equivalents of the added anion.

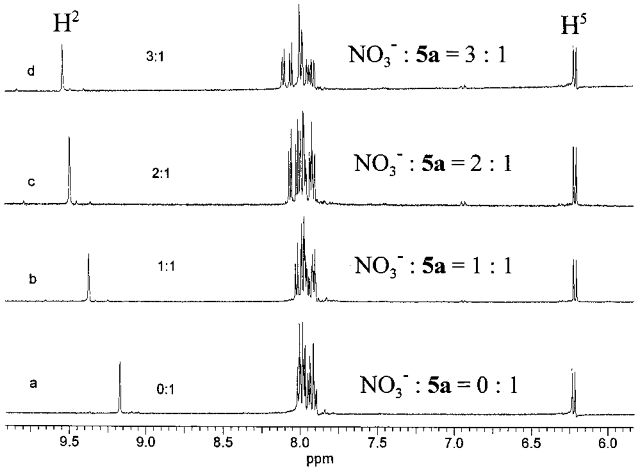

Figure 7. Changes in the ^1H NMR spectrum of complex **5a** on addition of nitrate to give **5d**. Spectra a−d are obtained after addition of 0−3 molar equiv of nitrate.

^1H chemical shifts are reported relative to TMS. ^{31}P and ^{19}F chemical shifts are reported relative to external reference 85% H_3PO_4 and to external $CFCl_3$, respectively. The gCosy spectrum was recorded for each compound, and all peak assignments were confirmed by this method. IR spectra were recorded as Nujol mulls using a Perkin-Elmer 2000 FTIR spectrometer.

[PdCl$_2$(bu$_2$bipy)], 4. To a mixture of [PdCl$_2$(PhCN)$_2$] (382.5 mg, 1.000 mmol) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (268.4 mg, 1.000 mmol) was added CH_2Cl_2 to give an orange-yellow solution. The solution was stirred for 2 h and became pale yellow in color during that period. The solution was concentrated to about 5 mL, and pentane (20 mL) was then added to give a pale yellow precipitate. The product was collected by filtration, washed with ether and pentane, and dried under vacuum. Yield: 90%. NMR in $CDCl_3$: $\delta(H) = 9.05$ [d, $^3J(HH) = 6$ Hz, 2H, $H^{6,6'}$]; 7.95 [d, $^4J(HH) = 2$ Hz, 2H, $H^{3,3'}$]; 7.45 [dd, $^3J(HH) = 6$ Hz, $^4J(HH) = 2$ Hz, 2H, $H^{5,5'}$]; 1.45 [s, 18H, CH_3]. Single crystals were obtained from a solution of CH_2Cl_2/pentane.

***trans*-[PdCl$_2$(Hpm)$_2$], 1.** To a solution of [PdCl$_2$(PhCN)$_2$] (0.0383 g, 0.100 mmol) in dry THF (10 mL) was added 4(3*H*)-pyrimidone (0.0192 g, 0.200 mmol). A pale yellow precipitate was formed immediately. The mixture was stirred for 2 h. The product was collected by filtration, washed with THF and ether, and dried under vacuum to afford a yellow powder. Yield: 97%. Anal. Calcd for $C_8H_8Cl_2N_4O_2Pd$: C, 26.00; H, 2.18; N, 15.16. Found: C, 25.85; H, 2.28; N, 14.64. IR (Nujol): $\nu(C{=}O)$ 1733(s), 1687(s) cm^{-1}; $\nu(NH)$ 3080, 3050 cm^{-1}. NMR in DMF-d_7: $\delta(H) = 8.71$ [s, 2H, H^2]; 8.10 [d, $^3J(HH) = 7$ Hz, 2H, H^6]; 6.51 [d, $^3J(HH) = 7$ Hz, 2H, H^5]. Mp: 255 °C, decomposed.

[Pd(dppp)(Hpm)$_2$] (CF$_3$SO$_3$)$_2$, 2. To a mixture of [Pd(dppp)(OTf)$_2$] (81.7 mg, 0.100 mmol) and 4(3*H*)-pyrimidone (19.2 mg, 0.200 mmol) was added CH_2Cl_2 (20 mL), giving a pale yellow solution. The solution was stirred for 3 h and, then, was concentrated to 10 mL, followed by the addition of pentane (40 mL) to give a very pale yellow precipitate. The product was collected by filtration, washed with pentane, and dried under vacuum to afford a pale yellow powder. Yield: 87%. Anal. Calcd for $C_{39}H_{34}F_6N_4O_8P_2PdS_2$: C, 44.04; H, 3.40; N, 5.55. Found: C, 43.58; H, 3.45; N, 5.59. IR (Nujol): $\nu(C{=}O)$ 1714, 1663 cm^{-1}; $\nu(NH)$ 3082, 3196 cm^{-1}. NMR in CD_2Cl_2: $\delta(H) = 12.00$ [br, s, 2H, H^3]; 8.31 [s, 2H, H^2]; 7.21 [d, $^3J(HH) = 8$ Hz, 2H, H^6]; 5.83 [d, $^3J(HH) = 8$ Hz, 2H, H^5]; 7.30−7.78 [m, 20H, H−Ph]; 3.12/2.97 [br, 4H, PCH_2]; 2.28 [br, 2H, PCH_2CH_2]. $\delta(P) = 6.58$ [s]. $\delta(F) = -79.17$ [s]. Mp: 225 °C, decomposed.

[Pd(dppm)(Hpm)$_2$] (CF$_3$SO$_3$)$_2$, 3. This was synthesized similarly except that [Pd(dppm)(OTf)$_2$] (78.9 mg, 0.100 mol) was used. Yield: 84%. Anal. Calcd for $C_{35}H_{30}F_6N_4O_8P_2PdS_2$: C, 42.85; H, 3.08; N, 5.71. Found: C, 42.71; H, 2.91; N, 5.68. IR (Nujol): $\nu(C{=}O)$ 1715, 1663 cm^{-1}; $\nu(NH)$ 3073, 3188 cm^{-1}. ^1H NMR (CD_2Cl_2): $\delta(H) = 12.28$ [br, s, 2H, H^3−Hpm]; 8.31 [s, 2H, H^2−Hpm]; 6.20 [br s, 2H, H^5−Hpm]; 7.40−7.90 [m, 22H, H^6−Hpm + H−Ph]; 4.38 [br, PCH_2]. ^{31}P NMR (CD_2Cl_2): $\delta(P) = -39.50$ [s]. ^{19}F NMR (CD_2Cl_2): $\delta(F) = -79.29$ [s]. Mp: 138 °C.

[Pd(bu$_2$bipy)(μ-pm)]$_3$(BF$_4$)$_3$, 5a. To a solution of complex **1** (89.1 mg, 0.200 mmol) in a mixture of dry dichloromethane (10 mL) and dry THF (10 mL) was added $AgBF_4$ (77.8 mg, 0.400 mmol). Immediately, a white precipitate formed. The mixture was stirred for 2 h, then AgCl was removed by filtration through Celite, and the filtrate was added to a solution of 4(3*H*)-pyrimidone (19.2 mg, 0.200 mmol) in THF (10 mL). Then, 0.1 mL of Et_3N was added. A white precipitate was formed quickly. The mixture was stirred for 3 h. The precipitate was collected by filtration, washed with diethyl ether, and dried under vacuum, to afford an off-white product. Yield: 85%. Anal. Calcd for $C_{66}H_{81}B_3F_{12}N_{12}O_3Pd_3$: C, 47.47; H, 4.89; N, 10.06. Found: C, 46.88; H, 4.71; N, 9.50. IR (Nujol): $\nu(C{=}O)$ 1652 cm^{-1}; $\nu(BF_4)$ 1066 cm^{-1}. ^1H NMR (acetone-

Table 7. Crystallographic Data, Data Collection, and Refinement Parameters for Complexes **4**, **5a**, **5b**, **5c**, **5d**

	4	**5a**	**5b**	**5c**	**5d**
formula	$C_{18}H_{24}Cl_2N_2Pd$	$C_{72}H_{90}B_3F_{12}N_{12}O_5Pd_3$	$C_{79}H_{99}F_9N_{12}O_{13.25}Pd_3S_3$	$C_{74.25}H_{94.50}Cl_3N_{12}O_{17.75}Pd_3$	$C_{75.8}H_{99}Cl_{8.1}N_{15}O_{14}Pd_3$
fw	445.69	1783.19	2015.08	1864.67	2050.65
temp (K)	200(2)	200(2)	200(2)	200(2)	200(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
space group	$P2(1)/c$	$R\bar{3}$	$P2(1)/n$	$R\bar{3}$	$C2/c$
a (Å)	7.4164(7)	57.9820(12)	15.9790(10)	58.3769(8)	39.448(2)
b (Å)	19.215(2)	57.9820(12)	38.708(3)	58.3769(8)	29.2839(17)
c (Å)	13.0162(14)	16.5311(4)	17.9372(12)	16.4532(2)	23.9856(18)
α (deg)	90	90	90	90	90
β (deg)	96.632(6)	90	111.933(4)	90	121.287(2)
γ (deg)	90	120	90	120	90
V (Å^3), Z	1842.5(3), 4	48130.3(18), 18	10291.3(12), 4	48558.2(11), 18	23679(3), 8
D_{calcd} (g/cm^3)	1.607	1.107	1.301	1.148	1.150
μ (mm^{-1})	1.298	0.561	0.652	0.624	0.684
$F(000)$	904	16326	1172	17190	8372
θ range (deg)	2.64−24.72	2.57−30.5	3.40−24.11	1.85−24.09	1.71−25.03
range h	−8 to 8	0 to 81	−18 to 16	−67 to 67	−46 to 44
range k	−22 to 16	−70 to 0	−44 to 43	−57 to 57	−34 to 29
range l	−15 to 15	−22 to 23	−18 to 20	−18 to 16	−28 to 28
reflns collected	12565	130007	31147	108674	52691
unique reflns	3098	29037	13391	17098	18524
max and min transmn	0.9427, 0.7915	0.9618, 0.7985	0.9377, 0.7238	0.9695, 0.8397	0.9506, 0.8640
R indices $[I > 2\sigma(I)]^a$					
R1	0.0475	0.0863	0.0873	0.0714	0.1602
wR2	0.0556	0.2029	0.2462	0.2088	0.3830

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

d_6): δ(H) = 9.42 [s, 1H, H^2−pm]; 8.02 [dd, ^3J(HH) = 7 Hz, ^4J(HH) = 2 Hz, 1H, H^6−pm]; 6.27 [d, ^3J(HH) = 7 Hz, 1H, H^5−pm]; 8.74/8.73 [2 × d, overlap, ^4J(HH) = 2, 2 Hz, 2H, $H^{3,3'}$−bu$_2$bipy]; 8.34/8.31 [2 × d, overlap, ^3J(HH) = 6, 6 Hz, 2H, $H^{6,6'}$−bu$_2$bipy]; 7.91 [dd, ^3J(HH) = 6 Hz, ^4J(HH) = 2 Hz, 1H, H^5−bu$_2$bipy]; 7.85 [dd, ^3J(HH) = 6 Hz, ^4J(HH) = 2 Hz, 1H, $H^{5'}$−bu$_2$bipy]; 1.44/1.43 [2 × s, overlap, 18H, CH_3−a,b]. ^{19}F NMR (acetone-d_6): δ(F) = −150.56. Mp: 291 °C, decomposed. Single crystals were grown from an acetone solution of the complex by slow diffusion of pentane.

[Pd(bu$_2$bipy)(μ-pm)]$_3$(CF$_3$SO$_3$)$_3$, 5b. This was prepared by the same procedure as that for **5a** with the exception that AgO_3SCF_3 [102.4 mg 0.400 mmol) was used instead of $AgBF_4$. Yield: 82%. Anal. Calcd for $C_{69}H_{81}F_9N_{12}O_{12}Pd_3S_3$: C, 44.63; H, 4.40; N, 9.05. Found: C, 44.48; H, 3.94; N, 9.04. IR (Nujol): ν(C═O) 1653 cm^{-1}; ν(SO_3CF_3) 1031, 1160 cm^{-1}. ^{1}H NMR (acetone-d_6): δ(H) = 9.52 [s, 1H, H^2−pm]; 7.99 [dd, ^3J(HH) = 7 Hz, ^4J(HH) = 2 Hz, 1H, H^6−pm]; 6.27 [d, ^3J(HH) = 7 Hz, 1H, H^5−pm]; 8.71/8.70 [2 d, ^4J(HH) = 2, 2 Hz, 2H, $H^{3,3'}$−bu$_2$bipy]; 8.36/8.33 [2 d, ^3J(HH) = 6, 6 Hz, 2H, $H^{6,6'}$−bu$_2$bipy]; 7.94 [dd, ^3J(HH) = 6 Hz, ^4J(HH) = 2 Hz, 1H, H^5−bu$_2$bipy]; 7.88 [dd, ^3J(HH) = 6 Hz, ^4J(HH) = 2 Hz, 1H, $H^{5'}$−bu$_2$bipy]; 1.42, 1.43 [2s, 18H, CH_3−a,b). ^{19}F NMR (acetone-d_6): δ(F) = −79.30 [s]. Mp: 230 °C, decomposed. Single crystals were grown by diffusing pentane into an acetone solution of the complex.

[Pd(bu$_2$bipy)(μ-pm)]$_3$(ClO$_4$)$_3$, 5c. The crystals of **5c** were grown from a deuterated acetone solution of **5a** and $Bu_4N^+ClO_4^-$ (molar ratio = 1:6). CAUTION: Perchlorate salts may be explosive if subjected to heat or shock. Suitable safety precautions must be taken when handling **5c**.

[Pd(bu$_2$bipy)(μ-pm)]$_3$(NO$_3$)$_3$, 5d. To an acetone solution of **5a** was added 4 equiv of tetrabutylammonium nitrate in acetone solution, leading to a colorless precipitate. After the solvent was removed and the precipitate was washed with acetone, the solid was dissolved in $CH_2Cl_2/ClCH_2CH_2Cl$ and then was layered by hexane. Colorless crystals were obtained in one week.

^{1}H NMR Titration. The ^{1}H NMR spectra were measured at constant temperature (293 K). A 2.5 mM solution of the host complex [Pd(bu$_2$bipy)(μ-pm)]$_3$(BF$_4$)$_3$, **5a**, in CD_2Cl_2 or in deuterated acetone, and 100.0 mM solutions of the anions NO_3^-, HSO_4^-, CF_3SO^-, ClO_4^-, PF_6^-, $H_2PO_4^-$, CH_3COO^-, Cl^-, and Br^- as their tetrabutylammonium salts were prepared separately. Exactly 500 μL of the host solution was transferred to a 5-mm NMR tube sealed with a septum, and an initial ^{1}H NMR spectrum was recorded to determine the initial chemical shift (δ_{free}) of free host. Small aliquots of the anion solution (2.5−12.5 μL) were added to the host solution, and the spectrum was recorded after each addition. The association constants (K_a) were determined following the method of Sigel et al. by using a nonlinear least-squares calculation.[28]

X-ray Structure Determinations. Crystals were mounted on glass fibers. Data were collected using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set, and crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied. The SHELXTL 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 7. The structure of [Pd(bu$_2$bipy)(μ-pm)]$_3$(NO$_3$)$_3$ (**5d**) was of low quality, because several disordered solvent molecules were present and a good model for them was not obtained. However, the cationic complex and nitrate counterions were well defined. The other crystals were of higher quality, but high angle data (>25°) were too weak to be useful for **5b** and **5c**.

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

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