Molecular Tricorns: Self-Assembly of Trinuclear Palladium(II) Complexes

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Cyclometalation of the ligand 1,3-bis(1-alkylbenzimidazol-2-yl)benzene (**1**) with palladium carboxylates leads to a trimeric complex $[Pd_3(ligand)_3(carboxylate)_3]$ (**3**). Studies in solution show that the trinuclear core is stable but that the carboxylates are labile, undergoing intra- and intermolecular exchange on an NMR time scale. The structural analogue of **1**, 2,6-bis(1-alkylbenzimidazol-2-yl)pyridine (**4**), gives only the mononuclear species [Pd(**4**)-$(carboxylate)_2$], characterized by X-ray diffraction. This complex forms a trimer if one carboxylate is labilized by the addition of strong acid; the resulting trinuclear species is readily cleaved by nucleophiles but can include weakly basic anions within its cavity.

Introduction

The use of metal ions in the assembly of complex structures has become a well-established field of supramolecular chemistry.[1,2] The basis of the synthetic strategy is the linking of more or less rigid organic ligands with suitably disposed coordination sites via metal ions whose stereochemical preferences may be used to guide the self-assembly reaction. The helicates[3] are probably the best studied of these complexes, but complex cyclic structures such as the metallacrowns[4] are also well-known. Square planar palladium(II) complexes have attracted attention for the synthesis of molecular boxes by Fujita[5] and by Stang,[6] and these boxes have recently been shown to form catenanes in which one of the rings acts as a receptor for the hydrophobic part of another ring.[7] The potential use of such metallacyclic complexes as receptors has been reviewed.[8] In principle, of course, three metal ions suffice to generate a cyclic structure that may act as a receptor, and a number of trimeric complexes of the platinum metals have been reported.[9−11]

In this paper we report further on the chemistry of a trinuclear system whose structure was published some years ago,[11] the trinuclear complex $[Pd(\mathbf{1a}\text{-H})(OCCH_3)]_3$ formed in high yield by the cyclometalation of a 1,3-bis(alkylbenzimidazol-2-yl)-benzene ligand. The formation of this structure could be explained according to Scheme 1, by a cyclometalation of the ligand **1** in the 6 position followed by the trimerization of the unit **2**, which possesses a vacant coordination site on the palladium atom and a pendant noncoordinated benzimidazole moiety. The resulting product, **3**, forms a cup-shaped trimer or tricorn (Figure 1) that includes a molecule of acetonitrile in the crystal structure. Here we address three questions arising from these observations.

First, we investigate to what extent the structure observed in the crystal structure is maintained in solution. The fast kinetics associated with complexation reactions may result in rapid equilibration of a number of species in solution. Lehn[12] has reported recently on a pathological case in which a dinuclear double helicate of copper(I) dissolves to give a mixture of the dinuclear double helicate, a trinuclear circular helicate, and a tetranuclear grid, and others have reported similar phenomena with helicates.[13,14] Second, we investigate to what extent the self-assembly is affected by ligand type. While the geometry of the self-assembled product is clearly dependent on the stereochemistry of the coordinating groups and the metal ion, as has been clearly demonstrated by Raymond for tetrahedral

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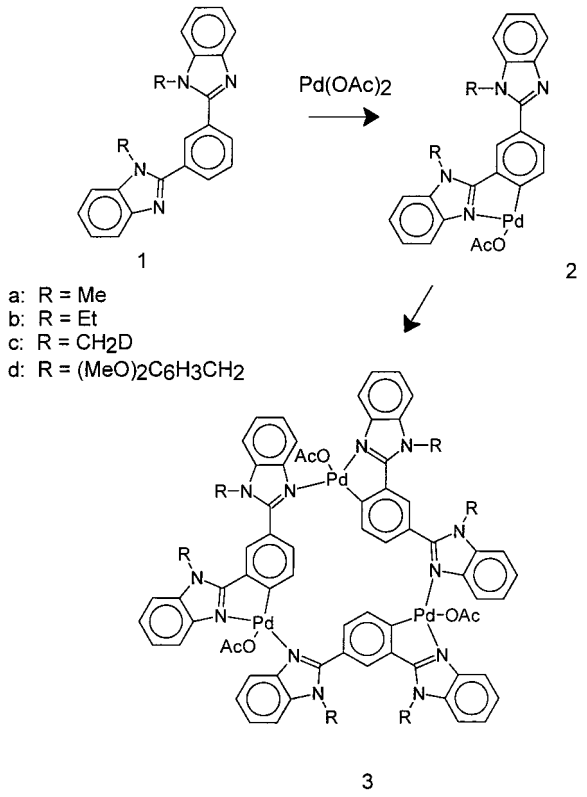
Scheme 1



clusters,[15,16] the question as to whether self-assembly will still take place if a metal binding center is modified without change of geometry has not, to our knowledge, been studied previously. More specifically, we examine the effect of replacing the Pd−C σ-bond in fragment **2** by a Pd−N(pyridine) bond. Finally, we examine the potential of these systems as hosts in solution.

Results

Stability of the Trimer in Solution. The simple ^{1}H NMR spectrum of **3a** in DMSO-d_6 does not allow one to confirm the existence of the trimer in solution. Furthermore, it has been shown[17] that treatment of **3a** with excess $Pd(O_2CCH_3)_2$ leads to the formation of a dicyclopalladated derivative of **2a**, suggesting that dissociation of the trimer is indeed possible in solution. To distinguish between **2a** and **3a** as the dominant species in solution, one may use the fact that **2a** is achiral but that **3a** is chiral (although both enantiomers are formed in equal amounts in the synthesis). If the complex could be derivatized to introduce a methylene group in a suitable position, then the methylene protons would be diastereotopic in structure **3** but not in structure **2.** We have previously used this approach in the study of helicates,[18] but the bulky 3,5-dimethoxybenzyl group used in this work (**1d**) could not be used here because its steric bulk prevented the cyclopalladation reaction. A simple alternative was to replace the acetate by propionate, which should show the expected effect.

$[Pd_3(\mathbf{1a}\text{-H})_3(O_2CEt)_3]$ was prepared from **1a** and $Pd(O_2CEt)_2$ under reflux in propionic acid, similar to the preparation of **3a**.

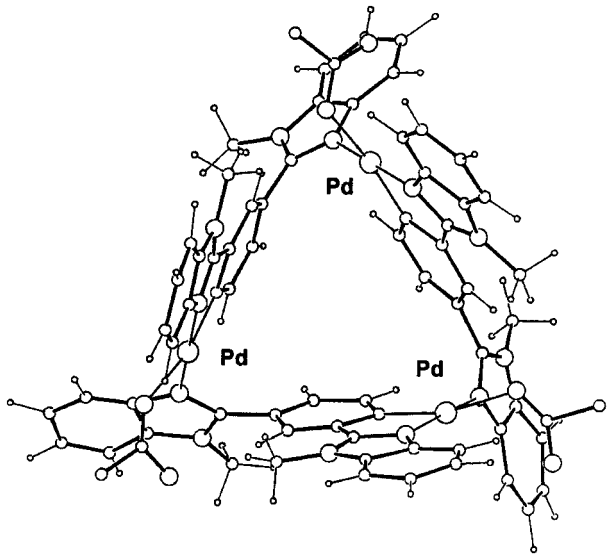


Figure 1. Crystal structure of $[Pd_3(\mathbf{1a}\text{-H})_3(O_2CCH_3)_3]$, **3a** (ref 11). The molecule of acetonitrile has been omitted for clarity.

The ^{1}H NMR spectrum of this compound showed only an A_2M_3 spectrum for the ethyl group (200 MHz, $CDCl_3$), and this was unchanged at 400 MHz at −60 °C. This suggested either a mononuclear achiral structure of type **2** or scrambling via a rapid exchange process. Addition of free carboxylate gave one broad signal for the methyl protons at 200 MHz, confirming an exchange process, which was not entirely unexpected given the long Pd−O bond distances (average 2.15 Å) trans to the σ-bonded phenyl group observed in the crystal structure of **3a**.[11] At 400 MHz and 0 °C, however, the free and bound carboxylate signals were distinct, and both gave A_2M_3 spectra. Thus, a rapid *intramolecular* mechanism for exchanging the diastereotopic protons must exist if the trimeric structure exists in solution.

The lability of the carboxylate allowed us to follow a substitution reaction: titration of a solution of $[Pd_3(\mathbf{1a}\text{-H})_3(O_2CMe)_3]$ with LiBr was followed by ^{1}H NMR in DMSO-d_6, and the signal due to the phenyl proton ortho to the palladium atom is shown in Figure 2. Four different signals are observed in the course of the titration corresponding to the four possible complexes $[Pd_3(\mathbf{1a}\text{-H})_3(O_2CMe)_{3-x}Br_x]$ ($x = 0-3$). This observation is not consistent with the predominance of a mononuclear complex of type **2** for which only two signals would be expected. Furthermore, the equivalence of the three phenyl rings of the trimer in the intermediate, partially substituted species is in agreement with the rapid intramolecular exchange proposed above.

The rapid exchange of the carboxylate ligands suggested therefore that the diastereotopic protons should be introduced onto the organic ligand. The bulky dimethoxybenzyl group mentioned above could not be used for steric reasons, and an attempt using the $-CH_2D$ group (**1c**) showed no diastereotopy. Finally the ethylated ligand **1b** was synthesized and the complex **3b** prepared. Ligand **1b** shows the expected A_2M_3 signal for the ethyl group in solution, but complex **3b** shows clearly two ABM_3 patterns in which the methylene protons are diastereotopic (Figure 3). No change in the spectrum was observed over a period of 5 days, showing that this was not merely a consequence of slow dissociation. Finally complex **3b** was examined by electrospray mass spectrometry in acetonitrile solution to which a small amount of formic acid was added to facilitate ionization. The spectrum obtained was in complete agreement with the stability of the trimer and the lability of the carboxylate sites; peaks were observed for $[Pd_3(\mathbf{1b}\text{-H})_3(CH_3-$

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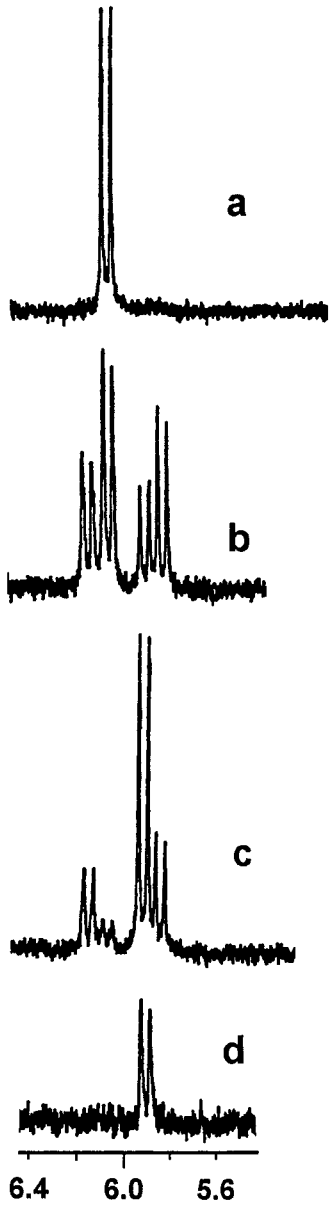
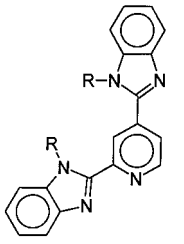


Figure 2. ^{1}H NMR signal of the hydrogen atom ortho to palladium during addition of bromide ion to a solution of $[Pd_3(\mathbf{1a}\text{-H})_3(O_2CCH_3)_3]$ in DMSO-d_6: (a) 0 equiv; (b) 0.33 equiv; (c) 0.67 equiv; (d) 1.0 equiv.

$CN)_x]^{3+}$ ($x = 0-3$) and $[Pd_3(\mathbf{1b}\text{-H})_3(O_2CH)(MeCN)_x]^{2+}$ ($x = 0-2$) (Figure S1 of Supporting Information).

Influence of Ligand Type. The ligand 2,4-bis(alkylbenzimidazol-2-yl)pyridine, **4**, can in principle give a square planar



4a R = Me
4b R = Et

complex with palladium that is very similar to **2**, possessing both a pendant benzimidazole group and an accessible coordination site at the palladium(II), and thus might be expected form a tricorn similar to **3**. There is indeed no particular reason to believe that the formation of the trinuclear species is a specific consequence of the cyclometalation, the stereochemistry of the Pd−C and Pd−(heterocyclic N) bonds differing little. The ligand was synthesized readily by the modified Phillips reaction[19] between the *N*-alkyldiaminobenzene and 2,4-pyridine dicarboxylic acid.

Reaction of **4** with $Pd(O_2CR)_2$ (R = Me, Et) in chloroform or acetonitrile gave the complexes $[(\mathbf{4})Pd(O_2CR)_2]$. For ligand **4a** with $Pd(O_2CEt)_2$ the ^{1}H NMR spectra ($CDCl_3$/MeOH-d_4) differed slightly for the preparations in the two different solvents, although the elemental analysis results indicating $[(\mathbf{4a})Pd(O_2CEt)_2]\cdot 2H_2O$ and the infrared spectra were essentially identical. Analysis of the spectra suggested linkage isomerism with the product synthesized in chloroform containing one coordinated and one free propionate, whereas the product from acetonitrile contained two coordinated propionates. In agreement with this, addition of free propionate to the proposed hypothetical $[(\mathbf{4a})Pd(O_2CEt)]^+$ complex led to the observation of the ^{1}H NMR spectrum observed for $[(\mathbf{4a})Pd(O_2CEt)_2]$. Interchange between the two forms was observed by NMR as a function of solvent. For these complexes no rapid exchange of carboxylates was noted, distinct signals for free and bound carboxylates being observed even at room temperature at 200 MHz. The ^{1}H NMR spectrum of $[(\mathbf{4b})Pd(O_2CMe)_2]$ (DMSO-d_6) showed two A_2M_3 signals for the ethyl substituents of the ligand, in agreement with the expected achiral structure of a mononuclear complex.

The crystal structure of $[(\mathbf{4a})Pd(O_2CEt)_2]\cdot CH_3CN$ (Figure 4) confirms the square planar mononuclear structure deduced from the NMR studies. The Pd−N (Pd−N3, 2.027(7) Å; Pd−N1, 1.985(7) Å) and Pd−O (1.996(6) Å (O201), 1.997(7) Å (O101)) bond distances are typical for palladium(II) complexes.[20] Comparison with the structure of **3a**[11] shows no significant difference in the binding of the benzimidazole, and the Pd−N(pyridine) bond is only slightly longer than the Pd−C bond (average 1.98 Å). The Pd−O bond in **3a** is, however, significantly longer (average 2.15 Å), and this may be attributed to the strong trans influence of the σ-bonded aryl ligand; this is the only significant difference in the coordination sphere of the palladium. Comparison of the structure of the $[(\mathbf{4a})Pd]^{2+}$ fragment with that of a $[(\mathbf{1a}\text{-H})Pd]^+$ fragment isolated from the structure of **3a** shows the two units to be essentially superposable. The only difference is the orientation with respect to the chelate plane of the pendant benzimidazole group in $[(\mathbf{4a})Pd(O_2CEt)_2]$, which is rotated by roughly 180° in comparison with that in the $[(\mathbf{1a}\text{-H})Pd]^+$ fragment. This is not likely to be a significant difference. We may therefore deduce first that the formation of the trimeric structure **3** does not require any major distortion of the mononuclear fragment **2** and, second, that there is no structural barrier to prevent the formation of a trimeric species from a $[(\mathbf{4})Pd]^{2+}$ fragment.

It was therefore rather surprising that no trace of a trimeric species could be observed in solution. Reasoning that fragment **2** has a free coordination site by virtue of the loss of an acetate as acetic acid during the cyclometalation reaction, we investigated the effect of adding 1 equiv of strong acid to a solution of $[(\mathbf{4b})Pd(O_2CMe)_2]$ to favor the loss of a carboxylate. Acidification with TsOH, $HClO_4$, or MsOH in DMSO produced a change in the UV−visible spectrum that was complete within a minute. The ^{1}H NMR spectrum (DMSO-d_6) showed the expected two ABM_3 signals for the ethyl substituents of the

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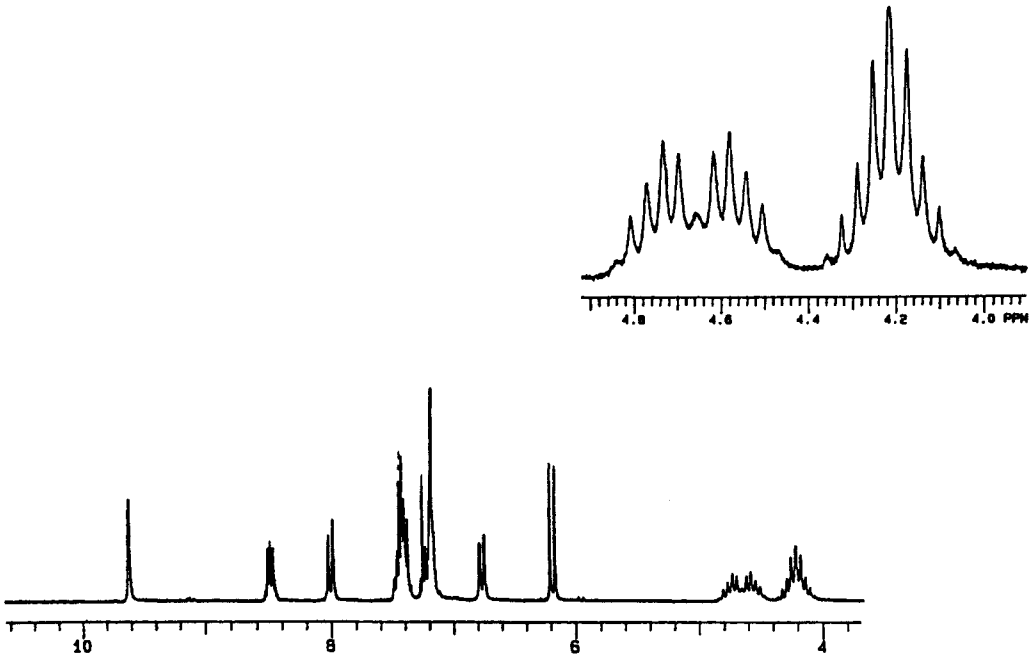

Figure 3. ^{1}H NMR spectrum of $[Pd_3(\mathbf{1b}\text{-H})_3(O_2CCH_3)_3]$ in DMSO-d_6. The enlargement shows the two ABM_3 signals of the ethyl substituents at 4 ppm.

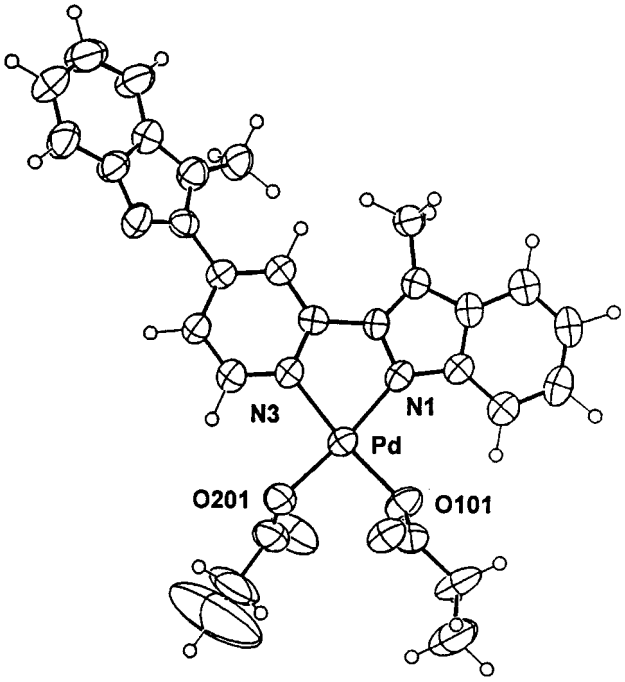

Figure 4. ORTEP[27] plot of the structure of $[Pd(\mathbf{4a}\text{-H})(O_2CC_2H_5)_2]$.

ligand, suggesting the formation of the chiral trimer. In support of this, only one coordinated acetate was observed in the NMR spectrum, and the proton bound to C3 of the pyridine group (i.e., that between the two benzimidazole groups) showed a downfield shift of 1.8 ppm similar to that observed for the analogous proton in **3b**. No exchange was observed between free acetic acid and coordinated acetate. The elemental analysis of the isolated product agrees with the formulation $[(\mathbf{4b})_3Pd_3(O_2CMe)_3](ClO_4)_3\cdot 6DMSO$. Acidification in acetonitrile or chloroform solution led to a mixture of products, but the NMR spectrum showed that the isolated product, dissolved in these solvents, was stable. Finally the electrospray mass spectrum (Figure 5) is dominated by the ions $[(\mathbf{4b})_3Pd_3(O_2CMe)_3(ClO_4)_x]^{(3-x)+}$ $(x = 0-2)$.

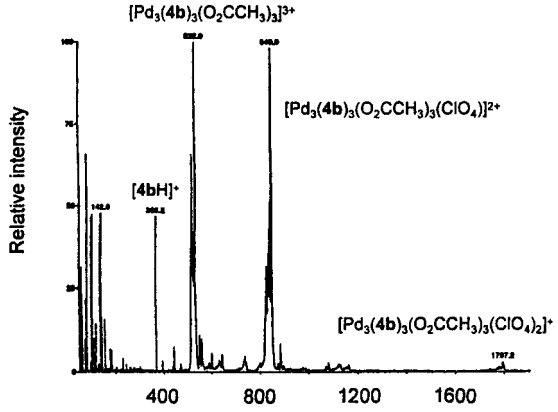

Figure 5. ES-MS spectrum in acetonitrile of $[Pd_3(\mathbf{4b})_3(O_2CCH_3)_3]^{3+}$.

Formation of the trimer is reversible. Addition of an equivalent of acetate leads to formation of $[(\mathbf{4b})Pd(O_2CMe)_2]$ as shown by NMR, and addition of bromide ion leads to the formation of a species whose NMR spectrum shows it to be achiral and compatible with the planar mononuclear complex $[(\mathbf{4b})Pd(O_2CMe)Br]$. This is significantly different from **3a** where bromide ion could be substituted for coordinated acetate but does not cleave the trimer. The trinuclear fragment $[(\mathbf{4b})_3Pd_3(O_2CMe)_3]^{3+}$ is thus much less robust than **3a**.

Inclusion in Tricorns. The crystal structure of **3a** showed a molecule of acetonitrile to be included in the cavity.[11] Examination of interatomic distances suggested that this molecule might be held in the cavity by interactions between the aromatic ring and the weakly acidic protons of acetonitrile, and consequently, an effort was made to observe this inclusion in solution. However, neither NMR nor infrared measurements showed any sign of inclusion of acetonitrile in solution, and we conclude that the phenomenon observed in the crystal results from space-filling requirements. Similar results were obtained with nitromethane.

The cationic trimer $[(\mathbf{4b})_3Pd_3(O_2CMe)_3]^{3+}$ showed different behavior. Figure 5 shows that the peak in the ES-MS spectrum corresponding to $[(\mathbf{4b})_3Pd_3(O_2CMe)_3(ClO_4)]^{2+}$ is surprisingly

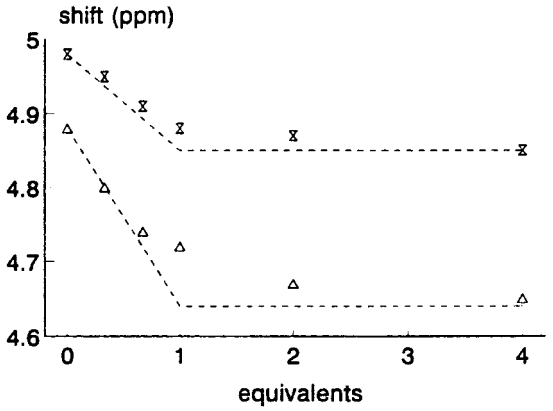

Figure 6. Variation of chemical shifts of two methylene protons of $[Pd_3(\mathbf{4b})_3(O_2CCH_3)_3](MsO)_3$ on titration with perchlorate ion in DMSO-d_6. The dashed lines show the variation expected for 100% complexation of one perchlorate.

intense, approximately equal to that of $[(\mathbf{4b})_3Pd_3(O_2CMe)_3]^{3+}$ and an order of magnitude greater than $[(\mathbf{4b})_3Pd_3(O_2CMe)_3(ClO_4)_2]^+$. While association of counterions is frequently observed in electrospray mass spectrometry, the difference in intensity between the two ion adducts was very great and suggested that a more specific association might be taking place with the first perchlorate. This hypothesis was confirmed by NMR studies, which showed the spectrum of the trimer to depend on the counterion. In DMSO-d_6, the shifts of one pair of methylene protons of **4b** were strongly dependent on the counterion, being almost identical for the mesylate salt and quite distinct for the perchlorate. The change in chemical shift observed upon adding perchlorate to a solution of $[(\mathbf{4b})_3Pd_3(O_2CMe)_3](MsO)_3$ is shown in Figure 6 and shows an end point for 1 equiv of perchlorate per trimer, in agreement with the ES-MS spectrum. The end point is not sharp because the mesylate is itself associated with the trimer; the signal of the mesylate methyl group in $[(\mathbf{4b})_3Pd_3(O_2CMe)_3](MsO)_3$ is observed at 2.17 ppm compared to 2.30 ppm for free mesylate. If free mesylate is added to a solution of $[(\mathbf{4b})_3Pd_3(O_2CMe)_3](ClO_4)_3$, the observed shift is 2.24 ppm, showing that partial displacement of the perchlorate is occurring. Tosylate, on the other hand, does not displace perchlorate ion, showing the same chemical shift as the free anion.

Discussion

The stability of the trinuclear structure **3** in solution has been clearly established by NMR spectroscopy and ES-MS. Although the carboxylates of **3** show rapid exchange with free ligands in solution and also appear to undergo a rapid intramolecular exchange between the three palladium atoms, the structure itself is not cleaved by nucleophiles. The contrast with the complexes of ligand **4** is quite remarkable; although the analogous trinuclear structure may be generated, giving similar ^{1}H NMR spectra, the cationic structure $[(\mathbf{4})_3Pd_3(O_2CR)_3]^{3+}$ does not form spontaneously and is readily cleaved by nucleophiles. The stability of **3** is thermodynamic because we have shown elsewhere[11] that **3** is in equilibrium with **2**, which may be trapped by a second cyclopalladation reaction. There is no obvious structural reason for this difference. In both cases Pd−N(benzimidazole) bonds are used to generate the trimer, and the crystal structure shows that no structural distortion of the Pd(ligand) unit is necessary to form the trimer. The bonds forming the trimer are cis to the Pd−C bond in **3** and show no unusual features. The only plausible explanation remaining is thus the different electrostatic charge of $[(\mathbf{4})_3Pd_3(O_2CR)_3]^{3+}$ and $[(\mathbf{1}\text{-H})_3Pd_3(O_2CR)_3]$; the formation of the triply charged ion from three $[(\mathbf{4})Pd(O_2CR)]^+$ units will be electrostatically unfavorable, and this effect may be aggravated by the fact that in the tricorn the palladium atoms cannot be effectively solvated on the inside of the cavity. The different behavior of **1** and **4** shows the dangers of planning self-assembly routes based solely on the coordination geometry of metals and ligands.

The formation of the trimer by protonation of $[(\mathbf{4})Pd(O_2CR)_2]$ may be understood in terms of labilization of the carboxylate, but because the pK values of benzimidazole and acetate are close, protonation and deactivation of the pendant benzimidazole are also possible. We suspect that the trimer may be stabilized by a certain kinetic inertness: whereas a monodentate carboxylate may always be protonated on the nonbonded oxygen and activated for dissociation, the coordinated benzimidazole has no lone pair available for protonation. Furthermore, dissociation of a Pd−N bond in the trimer requires perturbation of the cycle as a whole and will therefore be disfavored. We would thus expect a certain stability for the trimer in acid solution but not in the presence of nucleophiles that may attack the palladium and favor Pd−N bond breakage, as is indeed observed.

Tricorn **3** shows no signs of acting as a receptor in solution, but $[(\mathbf{4})_3Pd_3(O_2CR)_3]^{3+}$ is clearly a reasonable acceptor for nonnucleophilic anions such as mesylate and perchlorate, and it seems reasonable to associate this with the electrostatic charge. A cyclic complex containing three palladium and three platinum atoms with a charge of +12 has recently been shown to act as a receptor for similar ions in water.[21] There is clearly a potential for the development of cationic metallacycles for anion complexation.

Experimental Section

Starting Materials. Solvents and starting materials were purchased from Fluka AG (Buchs, Switzerland) and used without further purification unless otherwise stated. Palladium carboxylates were synthesized according to the method of Wilkinson[22] using finely divided palladium obtained by hydrazine reduction of an aqueous solution of K_2PdCl_4; purity was checked by elemental analysis.

Physical Measurements. ^{1}H NMR spectra were recorded on Varian Gemini 300 XL 200 and Bruker AMX 400 spectrometers. Chemical shifts are given in ppm with respect to TMS. ^{1}H NMR titrations were performed at a controlled temperature. In a typical experiment 0.7 mL of complex solution was used and a spectrum recorded after the addition of each aliquot of 0.3 equiv. ES-MS spectra were recorded from acetonitrile solution (10^{-4} M) with a trace of formic acid on API III and API 300 tandem mass spectrometers (PE Sciex). EI-MS spectra (70 eV) were recorded with VG-7000^E and Finnigan-4000 instruments. Infrared spectra were obtained from KBr pellets with a Perkin-Elmer 883 spectrometer. Elemental analyses were performed by Dr. H. Eder of the Microchemical Laboratory of the University of Geneva. Pd content was determined by atomic absorption (Pye Unicam SP9) after acidic oxidative mineralization of the complex.

Preparation of the Ligands. 1. Ligand 1a. Ligand **1a** was obtained according to the literature.[18]

2. Preparation of *N*-Ethyl-1,2-phenylenediamine Dihydrochloride. 2-Nitro-*N*-ethylaniline[23] (1.8 g, 10.8 mmol) was dissolved in ethanol and heated to reflux. A total of 0.3 g of Raney nickel was added, and concentrated hydrazine (24% in water) was added in portions of 0.5 mL at intervals of 10 min until complete decoloration of the solution had occurred. The solution was filtered on Celite and

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evaporated to dryness, and 2 mL of concentrated hydrochloric acid was added slowly. THF was added slowly until the solution became cloudy. Cooling gave 2.0 g (9.7 mmol, 90%) of the product as pale-pink crystals. ^{1}H NMR (200 MHz, DMSO-d_6, ppm): 9.2 (5H, s), 6.98 (4H, m), 3.18 (2H, q, $J^3 = 7$ Hz), 1.25 (3H, t, $J^3 = 7$ Hz).

3. Preparation of (1,3-Bis-(1-ethylbenzimidazol-2-yl)benzene), 2a. Isophthalic acid (1 g, 6 mmol) and *N*-ethyl-1,2-phenylenediamine dihydrochloride (2.7 g, 13 mmol) were mixed in concentrated H_3PO_4 (25 mL) and stirred for 15 h at 100 °C and then at 200 °C for 4 h. After cooling, the solution was poured into water (100 mL) and neutralized with NaOH (5 M). The white solid was filtered, washed with 10% K_2CO_3 (50 mL) and then with water, and recrystallized from MeOH to give 1 g of **2a** (2.7 mmol, 45%). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 8.05 (1H, t, $J^4 = 1$ Hz, H_1), 7.9−7.8 (4H, m., $H_2 + 2H_{benz}$), 7.7 (1H, dd, $J^3 = 6$ Hz, $J^3 = 7.5$ Hz, H_3), 7.45 (2H, m, H_{benz}), 7.35 (4H, m, H_{benz}), 4.32 (4H,q, $J^3 = 7$ Hz, H_{Et}), 1.54 (6H,t, $J^3 = 7$ Hz, H_{Et}). MS (70 eV, EI), *m*/*z* (%): 366 (100) [M^+], 351 (50) [$M - CH_3^+$], 337 (30) [$M - Et^+$].

4. Preparation of (2,4-Bis-(1-ethylbenzimidazol-2-yl)pyridine), 4b. Pyridine-2,4-dicarboxylic acid monohydrate (3.32 g, 20 mmol) and *N*-ethyl-1,2-phenylenediamine dihydrochloride (9 g, 43 mmol) were mixed in concentrated H_3PO_4 (25 mL) and stirred at 200 °C for 4 h. After the mxiture was cooled, the solution was poured into water (300 mL) and neutralized with NaOH (5 M). The white solid was filtered, washed with 10% K_2CO_3 (300 mL) and then with water, and recrystallized from MeOH to give 3.22 g of **4b** (8.8 mmol, 44%). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 8.87 (1H, dd, $J^5 = 0.9$ Hz, $J^3 = 5$ Hz, H_3), 8.76 (1H, dd, $J^5 = 0.9$ Hz, $J^4 = 1.7$ Hz, H_1), 7.9−7.8 (3H, m, $H_2 + 2H_{benz}$), 7.5 (2H, m, H_{benz}), 7.4−7.3 (4H, m, H_{benz}), 4.9 (2H,q, $J^3 = 7$ Hz, H_{Et}), 4.42 (2H,q, $J^3 = 7$ Hz, H_{Et}), 1.55 (3H,t, $J^3 = 7$ Hz, H_{Et}), 1.53 (3H,t, $J^3 = 7$ Hz, H_{Et}),

5. Preparation of (2,4-Bis(1-methylbenzimidazole-2-yl)pyridine), 4a. **4a** was obtained similarly to **4b**, with a yield of 54%.^{1}H NMR (200 MHz, $CDCl_3$, ppm): 9.6 (1H, dd, $J^5 = 0.9$ Hz, $J^3 = 5$ Hz, H_3), 8.76 (1H, dd, $J^5 = 0.9$ Hz, $J^4 = 1.7$ Hz, H_1), 8.88 (1H, dd, $J^4 = 1.7$ Hz, $J^3 = 5.5$ Hz, H_2), 7.85−7.8 (2H, m, H_3+$2H_{benz}$), 7.5 (2H, m, H_{benz}), 7.4−7.3 (4H, m, H_{benz}), 4.38 (3H,s, H_{Me}), 4.03 (3H,s, H_{Me})

Preparation of Complexes. 1. Cyclopalladated Trimers (3). These complexes were prepared as described previously[12] by refluxing ligand **1** with $Pd(O_2CR)_2$ in the corresponding carboxylic acid. Yields were typically 85% with the remainder of the palladium forming the dicyclometalated complex,[17] which was removed by filtration.

1.1. [Pd(1b-H)(O$_2$CMe)]$_3$. Yield = 88%. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 9.6 (3H, d, $J^4 = 1$ Hz, H_1), 8.5 (3H, m, H_{benz}), 8.00 (3H, dd, $J^4 = 1.7$ Hz, $J^3 = 6.5$ Hz, H_{benz}), 7.40 (9H, m, H_{benz}), 7.20 (9H, m, H_{benz}), 6.78 (6H, dd, $J^4 = 1$ Hz, $J^3 = 6.4$ Hz, H_2), 6.18 (3H, d, $J^3 = 6.4$ Hz, H_3), 4.63 (6H, ABX_3 system, $J^2_{AB} = 15$ Hz, $J^3_{(AB)X3} = 7$ Hz, H_{Et}), 4.2 (3H, ABX_3 system, $J^2_{AB} = 10$ Hz, $J^3_{(AB)X3} = 7$ Hz, H_{Et}), 1.80 (9H,s, H_{AcO}), 1.50 (9H, t, $J^3 = 7$ Hz, H_{Et}), 1.38 (9H, t, $J^3 = 7$ Hz, H_{Et}). IR (KBr pellet, cm^{-1}): 3060(m), 2980(m), 2940(m), 1610-(vs), 1452(vs), 1420(vs), 1375(vs), 1322(s), 1010(m), 748(s). Anal. Calcd for $C_{78}H_{72}N_{12}O_6Pd_3 \cdot H_2O$: C, 57.73; H, 5.3; N, 10.36. Found: C, 57.74; H, 4.9; N, 10.23. ES-MS (in MeCN + trace of HCOOH): *m*/*z* 771.2 (20%, [Pd(**1b**-H)]$_3$(HCOO)(MeCN)$_2^{2+}$), 750.7 (15%, [Pd-(**1b**-H)]$_3$(HCOO)(MeCN)$^{2+}$), 730.5 (5%, [Pd(**1b**-H)]$_3$(HCOO)$^{2+}$), 512 (100%, [Pd(**1b**-H)]$_3$(MeCN)$_3^{3+}$), 499.15 (75%, [Pd(**1b**-H)]$_3$(MeCN)$_2^{3+}$), 485.2 (50%, [Pd(**1b**-H)]$_3$(MeCN)$^{3+}$), 471.55 (25%, [Pd(**1b**-H)]$_3^{3+}$).

1.2. [Pd(1a-H)(EtCOO)]$_3$. Yield = 80%. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 10.15 (3H, d, $J^4 = 1.1$ Hz, H_1), 8.45 (3H, m, H_{benz}), 8.05 (3H, dd, $J^4 = 1.7$ Hz, $J^3 = 7$ Hz, H_{benz}), 7.40 (9H, m, H_{benz}), 7.20 (9H, m, H_{benz}), 6.73 (3H, dd, $J^4 = 1.1$ Hz, $J^3 = 3.8$ Hz, H_2), 6.18 (3H, d, $J^3 = 3.7$ Hz, H_3), 4.2 (9H, s, H_{Me}), 3.80 (9H,s, H_{Me}), 2.1 (6H, q, $J^3 = 7.6$ Hz, H_{Et}), 0.9 (9H, t, $J^3 = 7.6$ Hz, H_{Et}). IR (KBr pellet, cm^{-1}): 3062(m), 2965(m), 1600(vs), 1460(vs), 1404(vs), 1381(vs), 1331(s), 1103(m), 1008 (m), 745(s). Anal. Calcd for $C_{75}H_{66}N_{12}O_6Pd_3 \cdot H_2O$: C, 54.35; H, 4.7; N, 10.9; Pd, 20.0. Found: C, 54.29; H, 4.26; N, 9.91; Pd, 19.8.

1.3. Preparation of [Pd(4b)(O$_2$CMe)$_2$]. **4b** (36.7 mg, 0.1 mmol) and $Pd(O_2CMe)_2$ (22.5 mg, 0.1 mmol) were dissolved in 10 mL of MeCN, and the mixture was left to stand at room temperature without stirring for 72 h. The solution was evaporated to dryness, and the complex was dissolved in a minimum of MeCN. Slow diffusion of diethyl ether gave 47 mg of product (0.08 mmol, 80%). ^{1}H NMR (200 MHz, DMSO-d,[6] ppm): 8.58 (1H, d, $J^4 = 1.7$ Hz, H_1), 8.41 (1H, d, $J^3 = 6.5$ Hz, H_2), 8.20 (1H, dd, $J^4 = 1.7$ Hz, $J^3 = 6.5$ Hz, H_3), 7.99 (1H, d, $J^3 = 8$ Hz, H_{benz}), 7.80 (2H, m, H_{benz}), 7.65 (1H, m, H_{benz}), 7.54 (2H, m, H_{benz}), 7.38 (2H, m, H_{benz}), 4.88 (2H, q, $J^3 = 7.5$ Hz, H_{Et}), 4.51 (2H, q, $J^3 = 7.5$ Hz, H_{Et}), 1.97 (3H, s, H_{AcO}), 1.92 (3H, s, H_{AcO}), 1.55 (3H, t, $J^3 = 7.5$ Hz, H_{Et}), 1.42 (3H, t, $J^3 = 7.5$ Hz, H_{Et}). IR (KBr pellet, cm^{-1}): 3060(w), 2985(m), 2940(m), 1630(s), 1518(m), 1480-(m), 1420(m), 1354(m), 1330(m), 827(w), 750(s). Anal. Calcd for $C_{27}H_{27}N_5O_4Pd \cdot H_2O$: C, 53.2; H, 4.7; N, 11.5; Pd, 18.1. Found: C, 53.95; H, 4.44; N, 11.7; Pd, 18.0.

1.4. Preparation of [Pd(4a)(O$_2$CEt)$_2$]. **4a** (33.9 mg, 0.1 mmol) and $Pd(O_2CEt)_2$ (25.2 mg, 0.1 mmol) were dissolved in 10 mL of MeCN and then left to stand at room temperature and without stirring for 24 h. The crystals formed were filtered and dried to obtain 38.4 mg of product (0.065 mmol, 65%). ^{1}H NMR (200 MHz, DMSO-d_6, ppm): 8.8 (1H, s, H_1), 8.3(2H, m, $H_{2,3}$), 7.98 (1H, d, $J^3 = 8$ Hz, H_{benz}), 7.82 (1H, d, $J^3 = 8$ Hz, H_{benz}), 7.76 (1H, d, $J^3 = 8$ Hz, H_{benz}), 7.6−7.3 (5H, m, H_{benz}), 4.41 (3H, s, H_{Me}), 4.1 (3H, s, H_{Me}), 2.26 (2H, q, $J^3 = 7$ Hz, H_{Et}), 2.20 (2H, q, $J^3 = 7$ Hz, H_{Et}), 1.01 (6H, t, $J^3 = 7$ Hz, H_{Et}). IR (KBr pellet, cm^{-1}): 3060(w), 2985(m), 2940(m), 1630(s), 1518(m), 1480(m), 1420(m), 1354(m), 1330(m), 827(w), 750(s). Anal. Calcd for $C_{27}H_{27}N_5O_4Pd \cdot H_2O$: C, 53.2; H, 4.7; N, 11.5; Pd, 18.1. Found: C, 53.0; H, 4.32; N, 11.4; Pd, 18.2.

2. Preparation of Trinuclear Complexes of Ligands 4. Warning! Perchlorate salts of organic ligands, and perchloric acid in contact with organic solvents are potentially explosive. Only small amounts should be used, and suitable protective measures should be taken.[24]

2.1. [Pd(4b)(O$_2$CMe)]$_3$(ClO$_4$)$_3$. The complex [Pd(**4b**)$(O_2CMe)_2$] (30 mg, 0.0507 mmol) was dissolved in a minimum of 3:1 $CHCl_3$/THF, and 90 μL of 0.563 M $HClO_4$ (0.0507 mmol) in 2:1 $CHCl_3$/THF was slowly added. The concentrated perchloric acid should be added in small portions to the organic solvent mixture when preparing the solution. After 10 min, 0.5 mL of DMSO was added and the volatile material evaporated. Slow diffusion of diethyl ether into the DMSO solution gave 27.3 mg of yellow crystals (0.0145 mmol, 86%). ^{1}H NMR (200 MHz, DMSO-d_6, ppm): 10.05 (3H, d, $J^4 = 0.5$ Hz, H_1), 8.52 (3H, m, H_{benz}), 8.08 (3H, d, $J^3 = 6$ Hz, H_3), 8.00 (3H, m, H_{benz}), 7.88 (3H, dd, $J^4 = 0.5$ Hz, $J^3 = 6$ Hz, H_2), 7.80 (9H, m, H_{benz}), 7.62 (6H, m, H_{benz}), 7.46 (6H, m, H_{benz}), 4.85 (3H, ABX_3 system, m, H_{Et}), 4.6 (3H, ABX_3 system, m, H_{Et}), 4.3 (6H, q, $J^3_{(AB)X3} = 7$ Hz, H_{Et}), 1.730 (9H,s, H_{AcO}), 1.38 (18H, m, H_{Et}). IR (KBr pellet, cm^{-1}): 3440(w), 3100(w), 2980-(m), 2990(w), 1630(s), 1555(w), 1433(s), 1360(m), 1307(s), 1090(vs), 750(s), 622(m). Anal. Calcd for $C_{75}H_{72}N_{15}Cl_3O_{18}Pd_3 \cdot 6DMSO$: C, 44.2; H, 4.6; N, 8.8. Found: C, 43.6; H, 4.6; N, 9.1. ES-MS (in MeCN): *m*/*z* 1797.2 (2%, [Pd(**4b**)$(O_2CMe)]_3(ClO_4)_2^+$), 849.0 (100%, [Pd(**4b**)-$(O_2CMe)]_3(ClO_4)^{2+}$), 532.5 (100%, [Pd(**4b**)$(O_2CMe)]_3^{3+}$), 368 (50%, [**4b** + H]$^+$). The presence of six DMSO molecules was confirmed by NMR spectroscopy.

2.2. [Pd(4b)(O$_2$CMe)]$_3$(OMs)$_3$. [Pd(**4b**)$(O_2CMe)_2$] (30 mg, 0.0507 mmol) was dissolved in 0.3 mL of DMSO, and 68 μL of methylsulfonic acid 0.77 M (0.0507 mmol) in DMSO was slowly added. After evaporation of half the DMSO, addition of 0.1−0.2 mL of THF and diffusion of ether gave 32.6 mg of yellow crystals (0.0165 mmol, 98%). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 10.12 (3H, s, H_1), 8.52 (3H, m, H_{benz}), 8.18 (6H, s, H_{2-3}), 8.08 (3H, m, H_{benz}), 7.93 (3H, m, H_{benz}), 7.80 (3H, m, H_{benz}), 7.65 (6H, m, H_{benz}), 7.56 (6H, m, H_{benz}), 4.95 (6H, ABX_3 system, m, H_{Et}), 4.34 (6H, ABX_3 system, m, H_{Et}), 2.17 (9H, s, H_{OMs}), 1.78 (9H, s, H_{AcO}), 1.39 (9H, t, $J^3 = 7$ Hz, H_{Et}), 1.31 (18H, t, $J^3 = 7$ Hz, H_{Et}).

2.3. [Pd(4b)(O$_2$CMe)]$_3$(OTs)$_3$. [Pd(**4b**)$(O_2CMe)_2$] (25.2 mg, 0.0426 mmol) was dissolved in 0.3 mL of DMSO, and TsOH·H_2O (8.1 mg, 0.0426 mmol) was dded. Addition of 0.1−0.2 mL of THF and diffusion of ether allowed recovery of 26 mg of yellow crystals (0.0124 mmol, 87%). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 10.11 (3H, s, H_1), 8.52 (3H, m, H_{benz}), 8.18 (6H, d, $J^3 = 6$ Hz, H_3), 8.08 (6H, d, $J^3 = 6$ Hz, H_2), 8.00 (3H, m, H_{benz}), 7.80 (6H, m, H_{benz}), 7.6 (6H, m, H_{benz}), 7.5

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(6H, m, H_{benz}), 7.34 (6H, large s, H_{OTs}), 7.02 (6H, large s, H_{OTs}), 4.95 (3H, ABX_3 system, m, H_{Et}), 4.72 (3H, ABX_3 system, m, H_{Et}), 4.32 (6H, ABX_3 system, m, H_{Et}), 2.21 (9H, s, H_{OTs}), 1.78 (9H, s, H_{AcO}), 1.35 (9H, t, $J^3 = 7$ Hz, H_{Et}), 1.28 (18H, t, $J^3 = 7$ Hz, H_{Et}).

X-ray Crystal Structure of [Pd(4a)(O_2CEt)$_2$]·MeCN. Crystals of X-ray quality were obtained directly from the synthesis of the complex. A yellow crystal (0.16 mm × 0.18 mm × 0.28 mm) was mounted on a quartz fiber. $M_r = 633.0$, monoclinic, $P2_1/c$, $a = 7.483(1)$ Å, $b = 23.615(4)$ Å, $c = 16.413(5)$ Å, $\beta = 95.903(8)°$ based on 28 reflections ($21° < 2\theta < 28°$), $V = 2885(1)$ Å^3, $Z = 4$. Intensity data were collected at room temperature on a Philips PW1100 diffractometer with Mo Kα radiation ($\lambda = 0.710\,69$ Å), $6° < 2\theta < 46°$, 4011 unique reflections measured. The structure was solved by direct methods,[25] and other calculations were made with Xtal3.2[27] and ORTEP[27] programs. Full matrix refinement with anisotropic thermal displacement parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions gave a final R factor: $R_w = 0.056$ for 2717 observed reflections ($|F_0| > 4\sigma(F_0)$), 361 variables with unit weights.

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Supporting Information Available: ES-MS spectrum of [Pd_3(**1b**-H)$_3$(O_2CCH_3)$_3$] in acetonitrile (Figure S1), ^{1}H NMR spectrum of [Pd_3(**4b**)$_3$(O_2CCH_3)$_3$]$^{3+}$ in acetonitrile-d_3 (Figure S2), and details of the crystal structure determination of [Pd_3(**4a**)$_3$($O_2CC_2H_5$)$_2$] in the form of a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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