The tuning of binding properties *via* the change in cavity size of unsaturated palladium trinuclear clusters

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An increase in cavity size is achieved by using dpam instead of dppm (As instead of P) in the $[Pd_3(dpam)_3(CO)]^{2+}$ cluster host, which results in an increase in binding constants with various neutral and anionic substrates.

The control of host-molecule binding properties represents an extremely important aspect of host–guest chemistry, and ultimately of molecular recognition. Such a control can only be achieved *via* structural modification of the host molecule which could be synthetically demanding on most occasions. Over the past 2–3 years our group has investigated the host–guest properties of rare kinds of host systems. These systems are the unsaturated trinuclear clusters of the type $[M_3(dppm)_3(CO)]^{2+}$ (M = Pd, Pt; dppm = $Ph_2PCH_2PPh_2$).[1–4] X-Ray structures reveal that the M_3 metals are located at the bottom of a cavity described by six dppm phenyl groups forming a picket fence array of *ca.* 2–3 Å opening.[5] These systems exhibit a bifunctional binding cavity with the M_3^{2+} centre acting as a soft Lewis-acid centre, and the phenyl groups acting as a hydrophobic pocket. This work demonstrates that the cavity structural features and binding properties can, in fact, easily be modified where a larger cavity leads to greater binding constants, *via* a simple substitution of the P atoms of the dppm assembling ligands by As. We also report an unprecedented oxidation reaction of the adduct product $[Pd_3(dpam)_3(CO)(I)]^+$ **2** in the presence of O_2 in solution which leads to the oxidative fragmentation of the complex down to $[Pd_2(dpam)_2I_4]$ **3** and to an uncharacterized dark solid. In the absence of O_2, compound **2** is stable.

1 can be obtained in good yields as both $CF_3CO_2^-$ (**1a**) and PF_6^- (**1b**) salts.† The X-ray structure of **1b** (Fig. 1)† demonstrates the isomorphicity with the dppm analogue,[2] but also exhibits an important difference; one of the PF_6^- counter anions is now located well inside the cavity (Pd···F = 3.10, 3.01 Å). In the $[Pd_3(dppm)_3(CO)]^{2+}$ unit the cavity H···H distances are of the order of 5.5–6.5 Å (distance between opposite H atoms).[2] In **1b**, these distances are 5.9–7.3 Å. This phenomenon is due to a gain in degrees of freedom of the phenyl groups (*i.e.* longer Pd–L bonds). This gain has allowed two of the dpam

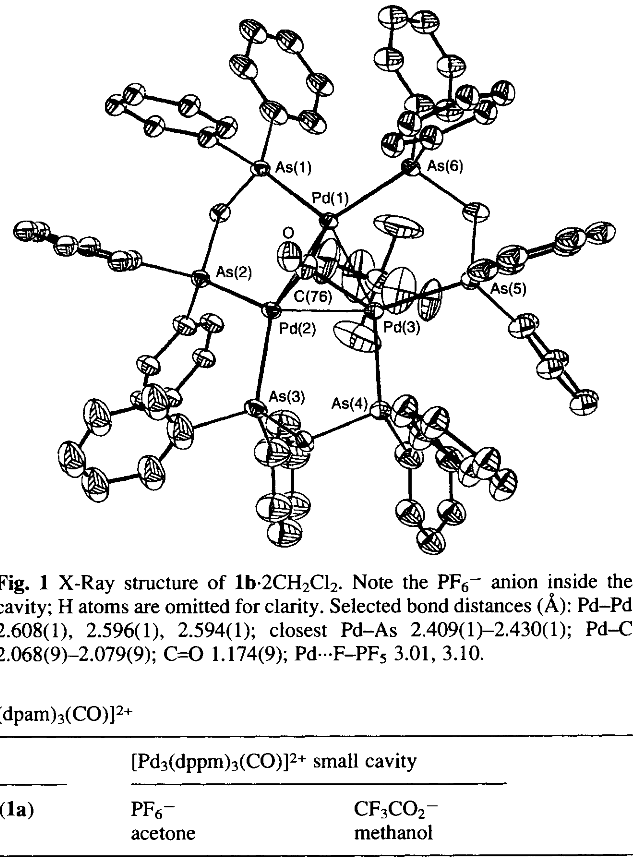

Fig. 1 X-Ray structure of **1b**·$2CH_2Cl_2$. Note the PF_6^- anion inside the cavity; H atoms are omitted for clarity. Selected bond distances (Å): Pd–Pd 2.608(1), 2.596(1), 2.594(1); closest Pd–As 2.409(1)–2.430(1); Pd–C 2.068(9)–2.079(9); C=O 1.174(9); Pd···F–PF$_5$ 3.01, 3.10.

Table 1 Comparison of the binding constants for $[Pd_3(dppm)_3(CO)]^{2+}$ and $[Pd_3(dpam)_3(CO)]^{2+}$

	$[Pd_3(dpam)_3(CO)]^{2+}$ large cavity		$[Pd_3(dppm)_3(CO)]^{2+}$ small cavity	
	PF_6^- (**1b**) acetone	$CF_3CO_2^-$ (**1a**) methanol	PF_6^- acetone	$CF_3CO_2^-$ methanol
KI	(> 10 000)[a]	(> 10 000)[a]	[a]	[a]
Acetate	[b]	3100 ± 100	[b]	730 ± 30
Benzonitrile	0.95 ± 0.01	1.65 ± 0.02	0.28 ± 0.01	1.35 ± 0.20
thf	0.27 ± 0.03	[b]	0.19 ± 0.01	[b]
Pyridine	0.80 ± 0.01	0.56 ± 0.01	0.14 ± 0.01	0.30 ± 0.01
dmf	0.33 ± 0.01	0.13 ± 0.01	< 0.01	0.090 ± 0.005
Methanol	0.21 ± 0.01		0.024 ± 0.001	
Acetonitrile	0.047 ± 0.001	0.085 ± 0.002	< 0.01	0.042 ± 0.005
Water	0.065 ± 0.001	0.15 ± 0.01	0.019 ± 0.001	[c]
NH_4PF_6	< 0.01	< 0.01	[c]	[c]

[a] The K_{11} values are highly irreproducible for $[Pd_3(dppm)_3(CO)]^{2+}$ even with 10–15 different measurements. For **1**, the situation is better and an approximated K_{11} value can be provided. This is due to the presence of a quasi-irreversible process in these cases leading to the formation of $[Pd_3(dppm)_3(CO)(X)]^+$ (X = Cl, Br, I), and $[Pd_3(dpam)_3(CO)(X)]^+$. Nonetheless, based upon the amount of X^- necessary to induce a fixed ΔA in the UV–VIS spectra, we find that $[Br^-] > [I^-]$, and that $[X^-]$ is greater for $[Pd_3(dppm)_3(CO)]^{2+}$ than for **1**. We come to the conclusion that K_{11} (Br^-) < K_{11} (I^-) and that K_{11} (**1**) > K_{11} ($[Pd_3(dppm)_3(CO)]^{2+}$). The value reported is the lowest measured value obtained in a large series of measurements. [b] Not measured. [c] No binding.

phenyl groups to adopt an axial configuration. This difference urged us to examine the binding ability of PF_2^- (and other substrates) with **1**. For $[Pd_3(dppm)_3(CO)]^{2+}$, substrates such as PF_6^- and water showed no or very weak binding. The binding constants for **1a**, **b** (K_{11}), measured by UV–VIS spectroscopy,[2,6] are compared to those of $[Pd_3(dppm)_3(CO)]^{2+}$ (Table 1). Due to a difference in solubility, two salt–solvent systems are investigated ($CF_3CO_2^-$–MeOH, PF_6^-–acetone). For a same salt–solvent system, K_{11} is always larger for **1**, and is clearly a direct consequence of the increase in cavity size. Interestingly both PF_6^- and water bind weakly to **1** and clear isosbestic points are observed in the UV–VIS spectra. The data analysis (from the Scott, Scatchard and Benesi Hildebrand's plots)[6] are consistent with a 1 : 1 stoichiometric complexation. All bindings are reversible except for the halide salts (KBr and KI) for which K_{11} cannot be accurately measured. For the halides, Puddephatt *et al.*[5,7] reported the X-ray structures for the Cl^- and I^- adducts to $[Pd_3(dppm)_3(CO)]^{2+}$.[2] **1** also reacts in solutions with I^- to form the expected $[Pd_3(dpam)_3(CO)(I)]^+$ saturated cluster†‡ **2** as a $CF_3CO_2^-$ salt. In the presence of O_2, the product is unexpectedly oxidized in solution to form $[Pd_2(dpam)_2I_4]$ **3** as identified from X-ray crystallography (Fig. 2)‡ and an uncharacterized dark solid. **2** is stable in the solid state and in solution in the absence of O_2. This reaction is unprecedented for two reasons. First, the oxidation–fragmentation of these clusters have never been observed for halide substrates before. Secondly, the palladium(II) product reveals a dinuclear structure with dpam, not a mononuclear geometry as typically found for the $[Pd(dppm)X_2]$ species (X = Cl, Br, I). The larger As atom may be responsible for the lack of chelating ability of the dpam ligand.[8] There is no evidence for weak Pd···Pd interactions [(Pd···Pd) 3.3896(9) Å].

Recently Puddephatt and coworkers[9] reported a series of related clusters where the dppm ligands were modified in order to reduce the cavity size. They observed a trend in equilibrium constants for phosphine addition on the basis of steric hindrance induced by the substituents on the dppm ligands.

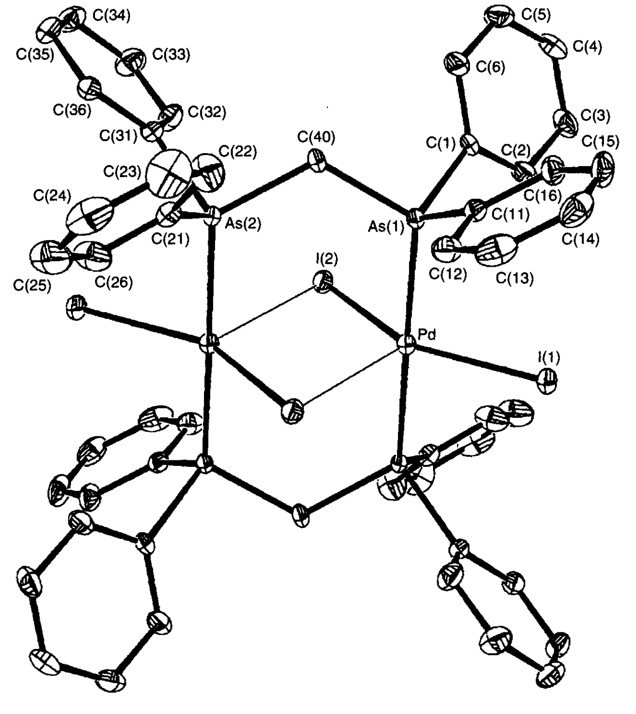

Fig. 2 X-Ray structure of $3{\cdot}CH_2Cl_2$; H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd···Pd 3.3896(9), $Pd–I_b$ 2.6395(10), 3.1562(11) [for shorter $Pd–I_b$ (dark) and longer $Pd–I_b$ bonds (narrow), respectively]; $Pd–I_t$ 2.6217(10), av Pd–As 2.392(8); $Pd–I_b–Pd$ 70.95(2), $I_b–P–I_b$ 109.05(2), $I_t–Pd–I_b$ 150.41(2), As–Pd–As 179.02(3).

Footnotes

† Both $[Pd_3(dpam)_3(CO)]^{2+}$ salts ($CF_3CO_2^-$ and PF_6^-) have been prepared according to published procedures outlined for $[Pd_3(dppm)_3(CO)]^{2+}$ (see L. Manojlovic-Muir, K. W. Muir, B. R. Lloyd and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1983, 1336) with the exception that dpam was used instead of dppm. $[Pd_3(dpam)_3(CO)][CF_3CO_2]_2$ **1a**: IR[ν(CO)] 1837 cm^{-1}; ^1H NMR $[(CD_3)_2CO]$, $\delta(CH^aH^bP_2)$ 4.56, 4.62, $^2J(H^aH^b)$ 12 Hz; UV–VIS(MeOH), λ_{max} 498 nm (ε = 19.5 × 10^3 dm^3 mol^{-1} cm^{-1}); (Me_2CO), λ_{max} 502 (20.2 × 10^3). $[Pd_3(dpam)_3(CO)][PF_6]_2$ **1b**: IR[ν(CO)] 1837 cm^{-1}; ^1H NMR $[(CD_3)_2CO]$, $\delta(CH_2)$ 5.03(s), FWHM 15 Hz; UV–VIS (Me_2CO), λ_{max} 510 nm (ε 20.8 × 10^3 dm^3 mol^{-1} cm^{-1}). $[Pd_3(dpam)_3(CO)(I)][CF_3CO_2]$ **3**: IR[ν(CO)] 1845, 1680 cm^{-1} for $CF_3CO_2^-$, μ^3-CO, respectively; ^1H NMR $[(CD_3)_2CO]$, $\delta(CH_2)$ 4.61(s), FWHM = 5 Hz; UV–VIS (MeOH), λ_{max} 482, 420 nm.

‡ *Crystal data* for **1**. $C_{76}H_{66}As_6F_{12}OP_2Pd_3{\cdot}2CH_2Cl_2$, M = 2223.85, monoclinic, space group $P2_1$, a = 10.835(2), b = 26.808(4), c = 14.413(1) Å, β = 102.16(2)°, U = 4092.6(10) $Å^3$, Z = 2, D_c = 1.805 g cm^{-3}. Intensity data were collected at 180 K on an Enraf-Nonius CAD-4 automatic diffractometer using graphite-monochromated Mo-Kα radiation. The NRCCAD programs were used for centring, indexing, and data collection. The unit-cell dimensions were obtained by least-squares fit of 24 centred reflections in the range $20 \leqslant 2\theta \leqslant 35°$. During data collection, the intensities of two standard reflections were monitored every 60 min. No significant decay of direct methods was found using the SOLVER program and refined by least-squares using LSTSQ program, both from NRCVAX. The atomic scattering factors in stored NRCVAX are from Cromer and Waber (International Tables for X-ray Crystallography, vol. 4); R = 0.045, wR = 0.052, S = 1.27; ρ_{max}, ρ_{min} = 0.05, 0.75 e $Å^{-3}$ and were located in the vicinity of the PF_6 anions. Two solvent CH_2Cl_2 molecules were located in the asymmetric unit by a difference Fourier map. All non-H atoms were refined anisotropically. The H atoms were geometrically placed but not refined. Restrain refinement was used on U_{ij} to be identical for all carbons in each phenyl groups.

For **2**. $C_{76}H_{66}As_6IOPd_3{\cdot}CF_3CO_2{\cdot}C_2H_6O$, M = 2062.08, monoclinic, space group = $P2_1/c$, a = 10.902(2), b = 18.559(4), c = 37.243(3) Å, β = 96.21(1)°, U = 7491(2) $Å^3$, z = 4, D_c = 1.828 g cm^{-3}. The experimental procedure is identical to that of compound **1**; R = 0.052, wR = 0.055, S = 1.32; ρ_{max}, ρ_{min} = 0.95, −0.92 e $Å^{-3}$ and were located in the vicinity of the Pd atoms. One solvent acetone molecule was located in the asymmetric unit by a difference Fourier map. Refinement as above. The μ-CO and μ-I atoms were placed but not refined. The μ-CO and μ-I atoms were disordered. The occupancy refinement shows a 55 : 45 ratio for the two orientations.

For **3**. $C_{50}H_{46}As_4I_4Pd_2{\cdot}CH_2Cl_2$, M = 1749.98, monoclinic, space group $C2/n$, a = 21.3996(3), b = 10.132(3), c = 24.553(3) Å, β = 94.403(7)°, U = 5307.8(17) $Å^3$, Z = 4, D_c = 2.190 g cm^{-3}. The experimental procedure is identical to that of compound **1**; R = 0.027, wR = 0.030 S = 1.17; ρ_{max}, ρ_{min} 0.59, −0.72 e $Å^{-3}$ and were located in the vicinity of the I atoms. Half of a solvent CH_2Cl_2 molecule was located in the asymmetric unit by a difference Fourier map. All non-H atoms were refined anisotropically. The H atoms were geometrically placed but not refined.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/8.

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