Electronic Supplementary Information

Assembly of new discrete metallocycles incorporating palladium(II) and platinum(II) termini and dipyridyldibenzotetraaza[14]annulene side units

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Additional ³¹P{¹H} NMR data

Spectra illustrating the temperature dependence of the 1-containing systems are shown in Figures S1 and S2. Figure S3 emphasises the influence of solvent on product distribution; it shows the presence of three species for the $[2b + 1]_n$ system in dichloromethane, compared to two in nitrobenzene as discussed in the main text. Although the identity of the third species is unclear, it may correspond to the next smallest cyclic species, that is, the 'square'.



Figure S1. Temperature dependence of the ${}^{31}P{}^{1}H$ -NMR spectrum of a 1:1 mixture of **2a** and **1** in nitrobenzene (5 mM with respect to **2a**); (top to bottom): 280, 290, 300, 320, 355 K; after 30 minutes equilibration in each case.



Figure S2. ³¹P{¹H} NMR study in nitrobenzene of a 1:1 mixture of **1** and **2b** as equilibrium is re-established showing the variation in the relative abundance of the minor and major metallocyclic species with time. Concentration 5.8 mM with respect to **2b**. The solution was heated to 350 K then cooled to 300 K and then allowed to stand at this temperature. The spectrum was then monitored over time. Top to bottom: initial spectrum at 300 K, immediately after cooling to 300K, after 1 hour, 13.5 hours, 23 hours and 72 hours.



Figure S3 ${}^{31}P{}^{1}H$ NMR spectra of a 1 : 1 mixture of 1 and 2a in dichloromethane at different concentrations (top to bottom) at 4.0, 2.0, 1.0, 0.2 mM.

PGSE studies

The diffusion co-efficient (D) can be related to the 'hydrodynamic radius' (r_H) via the *Stokes-Einstein* equation,¹

$$D = \frac{kT}{6\pi\eta r_H}$$
 Equation 1

where k is the *Boltzmann* constant, T is the absolute temperature, η is the viscosity of the solution and r_H is the hydrodynamic radius. The hydrodynamic radius can then, in turn, be related to molecular size by assuming molecules to be spheres with the hydrodynamic radius as the

radius.^{1,2} No clear consensus exists in the literature for the most accurate method of correlating D values with a molecular 'size'. A direct relationship between D values and molecular size is often difficult to determine for non-spherical molecules.¹ The most common method^{2,3} is to use an approximation for a 'sphere' with a radius equal to the longest 'axis' in the molecule; this has resulted in a more or less satisfactory relationship between D and the molecular radius in a range of cases. In some instances an 'average radius' of the molecule has been used⁴ and in others a radius found using a 'solvent excluded volume' has been employed.⁵ Several reviews have appeared that cover most of the theoretical¹ and experimental^{2,6,7} aspects of PGSE in detail.

The magnetic field gradient was calibrated such that measuring the diffusion coefficient of pure water at 25 °C yielded a value of 2.3 x 10⁻⁹ m²s^{-1.8} The experimental parameters employed were as follows: field-gradient pulse duration, $\delta = 2$ ms; time interval separating gradient pulses, $\Delta = 20$ ms. The magnitude of the field gradient, *g*, was incremented from 0.01 T m⁻¹ to between 0.65 T m⁻¹ (dichloromethane) and 4 T m⁻¹ (nitrobenzene) in 16 equal steps. A spoiler gradient of G intensity 0.5 Tm⁻¹ and duration 2 ms was used in all experiments. The D1 delay was set to approximately 5T1. Between 256 and 1024 transients were collected per spectrum, depending on the concentration employed. Typical experiment times were 12-18 hours. The signal intensity was measured as the integral of the ³¹P{¹H} NMR peak after automatic phase and baseline correction. Signal intensities were normalized with respect to that of the first spectrum. Diffusion coefficients were calculated by plotting the logarithm of the normalized signal intensities as a function of the Stejskal–Tanner parameter [b = $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$, where γ is the phosphorus magnetogyric ratio] and calculating the slope of the regression line.⁹

Convection compensated sequence: experiments employing a double spin-echo sequence in order to compensate for convection used the same settings as above with $\Delta = 0$ ms.

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Results for dichloromethane: Both the palladium and platinum 4,4'-bipyridine-containing systems (**5a** and **5b**) were analysed at a concentration of 4 mM (with respect to their 'corners' **2a** or **2b**) in dichloromethane. However, due to poorer solubility of the macrocycle-containing systems $[2a + 1]_n$ and $[2b + 1]_n$ lower concentrations (saturated solutions) were employed.

Although diffusion measurements are more precise when conducted in higher viscosity solvents such as DMSO (which will minimise convection), initial experiments were performed using dichloromethane with its lower viscosity. Despite its low viscosity, the latter solvent has the advantage that it has frequently been used for characterisation (including for ³¹P{¹H} NMR assignments) of analogous species; the use of dichloromethane for diffusion studies of organometallic systems has also been reported previously.² The results for the present diffusion experiments in dichloromethane are summarised in Table S1. The data are internally consistent, with the calculated radii for both 'corners' close to each other and, as expected, the determined radii for both 4,4'-bipyridine-containing squares are similar. Additionally, the calculated hydrodynamic radii for both the palladium-containing and platinum-containing macrocycle products (**4a** and **4b**) are again in reasonable agreement with each other.

Compound	Diffusion Coefficient ^a	Hydrodynamic Radius ^b	\pm^{c}
	$(x \ 10^{-10} \ m^2 s^{-1})$	(Å)	
2a	12.3	4.3	0.8
5a	8.7	6.1	0.5
$4a^d$	6.8	7.8	1.6
2b	12.5	4.2	0.3
5b	8.9	5.9	0.6
$\mathbf{4b}^{d}$	6.5	8.2	1.1
PPh ₃ ^e	21.4	2.5	0.1
PPh ₃ ^f	14.4	3.7	0.1

Table S1 Diffusion Coefficients in dichloromethane (no convection correction applied).

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^b Using the viscosity of CH₂Cl₂ of 0.413 x 10^{-3} kg.s⁻¹.m⁻¹ 10^{-1}

 c Errors calculated from a \pm 5% difference between the r_{H} quoted values

^d The lowest frequency peak was assigned to 4, as was also done for the studies in nitrobenzene. The lower solubility in dichloromethane (resulting in a poorer signal-to-noise ratio) combined with the poor separation of the individual peaks prevented accurate determination of the diffusion coefficient for 3.

 e^{25} mM, D1 = 60s = 5T1

^f The convection correction sequence¹¹ was applied. $1.44 \times 10^{-9} \text{ m}^2 \text{s}^{-1.12}$

Nevertheless, the calculated values for all the hydrodynamic radii (r_H) are too small to correspond to the actual radii of the respective species. Comparison of the diffusion coefficient determined for a 'standard' compound, triphenylphosphine (PPh₃), in dichloromethane with its literature value¹² strongly suggested significant convection occurred under the conditions employed. The effect of convection cannot be separated from diffusion simply by fitting experimental data points to an equation containing a fixed convection term.¹³ The simplest remedy is to use pulse sequences that suppress signal attenuation due to convection.¹³ In the present study it was found that use of a compensating pulse sequence¹¹ gave a diffusion coefficient that was in excellent agreement with the literature value¹² for PPh₃ in dichloromethane. Consequently, this pulse sequence was then applied to the remaining systems; the results (Table S2) show much better agreement with the expected values.

Table S2 Diffusion coefficients in dichloromethane for the species shown

 obtained using a convection-compensated pulse sequence.

	Diffusion Coefficient ^a	±	Hydrodynamic Radius ^b	
Compound	$(x \ 10^{-10} \ m^2 s^{-1})$	$(x \ 10^{-10} \ m^2 s^{-1})$	(Å)	±
2a	8.3	2.8 °	6.3	2.2 °
5a	4.1	0.4	13.0	1.1
4 a	4.3	0.8	12.3	2.2
2b	12.6	6.1 ^c	4.2	2.2 °

^a 4 mM in CH₂Cl₂, 298 K

5b	4.7	0.5	11.3	1.2
4b	_d		_d	

^a In CH₂Cl₂, 298K

^b Using the literature¹² viscosity for CH₂Cl₂ of 0.413 x 10⁻³ kg.s⁻¹.m⁻¹

^c Errors for **2a** and **2b** are larger as fewer scans per data point were used for their determination to economise on NMR machine time.

^d Due to poor solubility, the resulting poor signal-to-noise ratio resulted in no value being obtained in this case.

The incorporation of a double stimulated echo in the convection-compensated pulse sequence resulted in a halving of the signal-to noise ratio relative to that obtained when a standard stimulated echo pulse sequence was employed. It needs to be noted that the combination of low solubility together with this lower signal-to-noise ratio prevented the determination of the diffusion coefficient for the **4a** system while the value for the **4b** system has a substantial uncertainty.

Additional X-ray Structural Details

The crystal structure of $[Pt_2(dppp)_2(1)_2]$ (OTf)₄·5CH₂Cl₂·4H₂O comprises two structurally distinct but conformationally similar metallocyclic, di-platinum(II) metal complexes both of which exhibit crystallographic inversion symmetry. ORTEP representations of the two asymmetric components are provided in Figure S4.



Figure S4. ORTEP plot of $[Pt_2(dppp)_2(1)_2]$ (OTf)₄·5CH₂Cl₂·4H₂O with 30% probability displacement ellipsoids. Only one orientation of the disordered triflate anion comprising C(2T), F(4)-(6), O(4)-(6) and S(2) is shown. Disordered solvent molecules, the extensively disordered triflate anion and dibenzoannulene NH hydrogens have been omitted for clarity.

The dinuclear complexes are arranged in columns parallel to the *b* axis in the crystal lattice (Figure S5) with π - π stacking interactions present between the macrocycles of adjacent complexes (Figure S6). Adjacent columns interact via edge-to-face phenyl-phenyl interactions between diphenyl phosphine groups to form 2D sheets parallel to the *ab* plane as shown in Figure S7.

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Figure S5. The crystal lattice viewed along the *b* axis. The red arrow indicates the π - π stacking between macrocycles. The orange dotted oval indicates the anion/solvent region between adjacent cation sheets and the red dotted oval indicates the anion/solvent region within cation sheets. The black dotted ovals highlight the phenyl-phenyl interactions between diphenylphosphine groups that connect adjacent columns into sheets (parallel to the *ab* plane).



Figure S6. Section of π -stacked $[Pt_2(dppp)_2(1)_2]^{4+}$ complex cations.





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