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Dynamic NMR Study of the Hindered Pt–N(bipyridine) Rotation in Metal-Directed Self-Assembled Macrocycles

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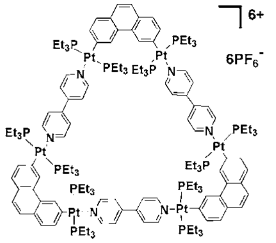
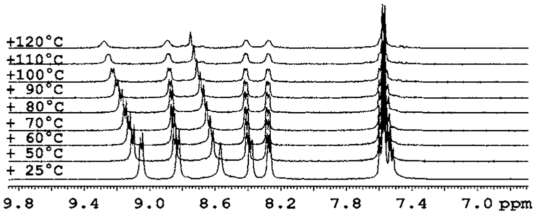
ABSTRACT





The activation parameters for the hindered Pt–N(bipyridyl) rotation observed for a self-assembled rectangle and triangle have been investigated by temperature-dependent and selective inversion recovery (SIR) NMR spectroscopy. The enthalpy of activation ($\Delta H^{\ddagger}$) and change in entropy ($\Delta S^{\ddagger}$) were determined to be +52.2 kJ/mol and –58.2 J/mol·K for the rectangle and +59.1 kJ/mol and –71.8 J/mol·K for the triangle, respectively, by SIR.

Coordination-driven self-assembly of discrete nanoscopic structures is an area of intense interest and research activity.[1] The structures of self-assembled polygons and polyhedra have been successfully characterized by single-crystal X-ray diffraction, mass spectrometry, and multinuclear NMR spectroscopy. However, only a few studies have been devoted to the solution dynamics of these systems, even though there is continuous interest in this area.[1a,2] In the ^{1}H NMR spectra of several coordination-driven self-assembled polygons and polyhedra, we observed chemically nonequivalent resonances for the α and β proton pairs of 4,4′-bipyridine, as a result of hindered rotation about the Pt−N(bipyridyl) bond.[3] In this

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paper we report the activation parameters for the hindered bipyridyl rotation of a self-assembled rectangle (**1**)[3d,e] and triangle (**2**)[3a] (Figure 1) by temperature-dependent ^{1}H NMR spectroscopy.

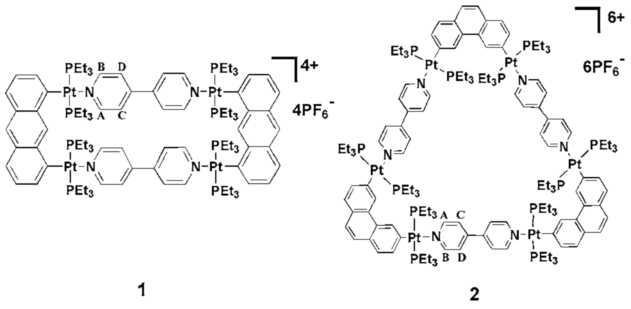

Figure 1. Molecular structure of the self-assembled supramolecular rectangle (**1**) and triangle (**2**).

For **1**, resonances A and B and resonances C and D coalesce at 110 °C (Figure 2), and the rectangle decomposes above the coalescence temperature (T_c). As long as the system is not heated above T_c, it returns to the original state upon cooling. Complex **2** appears to be more stable than **1**, and the original spectrum could be regained after heating to +120 °C (Figure 2B), the highest temperature to which the sample could safely be heated. The bipyridyl signal pairs of the triangle failed to coalesce at this temperature; in fact, resonances A and B differ more in frequencies at high temperature due to the large downfield shift of A. This shift counteracts the coalescence[4] of resonances A and B, possibly due to a deshielding effect associated with the removal of solvent and/or counterions (PF_6^-) at elevated temperatures. Additional experiments were needed to verify the cause of this unusually large shift.

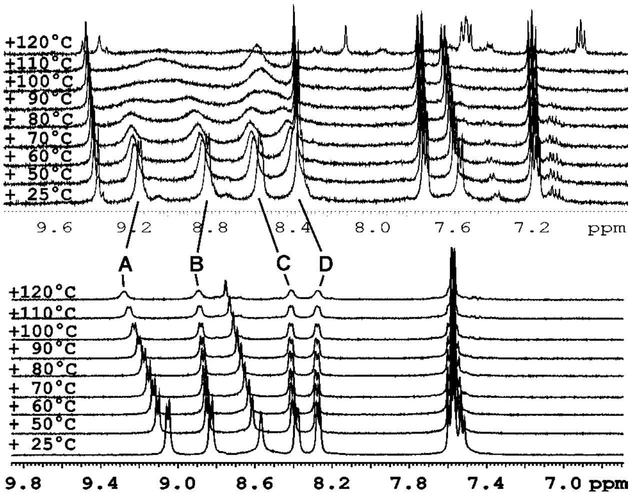

Figure 2. Temperature-dependent ^{1}H NMR spectra of **1** (top) and **2** (bottom) recorded at 400 MHz in $CDCl_2-CDCl_2$.

The exchange rates[4] (k) for **1** and **2** were determined from proton lineshape analysis[5] (Figure S1), and the Eyring plots[6] (Figure S2) were constructed to estimate the thermodynamic parameters (Table 1). The enthalpy of activation ($\Delta H^\ddagger$) was found to be higher for the rectangle (+37.9 kJ/mol) than for the triangle (+29.7 kJ/mol). These values do not agree with the higher thermal stability of the triangle nor with the lower T_c of **1**. The accuracy of these results may be influenced by the following: (1) At high temperatures the exchange process associated with the intramolecular rotational motion of the bipyridyl groups is perturbed by intermolecular ligand exchange. This process incorporates the mutual interchange of bipyridyl groups between polygons that is inherent in the nature of self-assembled systems formed under thermodynamic control. This behavior, which is absent in classical exchange processes (e.g., *N*,*N*-dimethylformamide) causes extra line broadening, affecting the results of the lineshape analysis, most likely by lowering $\Delta H^\ddagger$. (2) The exchange broadening does not exclusively dominate the lineshapes of **2**, and deviation of the Eyring plot from linearity has been observed.

Table 1. Thermodynamic Parameters for 4,4′-Bipyridyl Rotation of **1** and **2** in 1,1,2,2-Tetrachloroethane-d_2

	1		**2**	
activation parameters	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol·K)	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol·K)
line shape	+37.9	−93.1	+29.7[a]	−137.3[a]
SIR	+52.2	−58.1	+59.1	−71.8

[a] Using temperature data only between +110 and +120 °C.

To verify the results of the lineshape analysis, selective inversion recovery (SIR) NMR experiments have been employed.[7] SIR experiments have the advantage that the proton exchange rates can be measured in a lower temperature range where intermolecular bipyridyl exchange processes are relatively more suppressed. The variation of the z-magnetization intensities of the A and B exchanging resonances in a SIR experiment is described by the Bloch−McConnell[8] differential equations (see Supporting Information). The efficiency of the magnetization transfer depends on the rate constant (k), which can be extracted from the

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experimental data set using a Bayesian analysis[9] to solve the Bloch−McConnell equations in agreement with the experimental dataset.

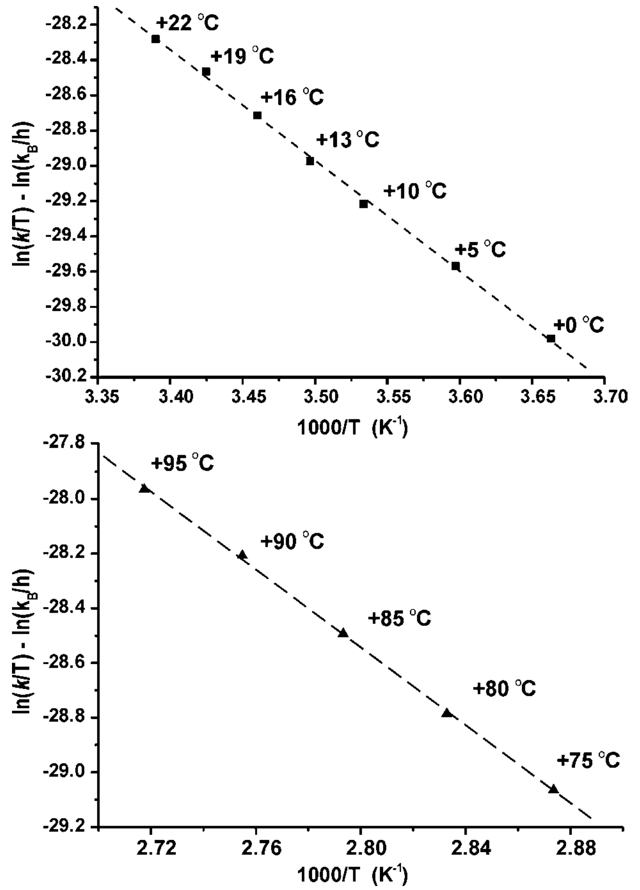

Figure 3. Eyring plots for **1** (top), and **2** (bottom) obtained from SIR experiments in $CDCl_2-CDCl_2$ at 400 MHz.

The Eyring plots for **1** and **2** obtained from SIR experiments are shown in Figure 3. Excellent linear fits ($r = 0.98$) were obtained for the rates $k = 1-5$ s^{-1}. These rate constants fell into the 0.1−10 s^{-1} range where accurate results from SIR measurements are expected.[10] The activation enthalpies determined by SIR were found to be noticeably higher than those based on lineshape analysis. Moreover, SIR provided a higher $\Delta H^{\ddagger}$ for the triangle (Table 1), whereas the lineshape analysis estimated a higher value for the rectangle. The free energy of activation $\Delta G^{\ddagger}$ for rotation of the bipyridine unit in the rectangle was calculated to be 73.5 and 74.4 kJ/mol from the lineshape and SIR experiments, respectively, at the coalescence temperature (383 K). However, since coalescence could not be achieved for the triangle, we can only conclude that $\Delta G^{\ddagger}$ for rotation of the bipyridine unit must be greater than 85 kJ/mol, determined by averaging the values obtained from $T = 393$ K. The higher rotational barrier for the triangle compared to the rectangle is likely due to the greater number of Pt−N bonds (6 vs 4) in the triangle that have to undergo a correlated rotation for coalescence to occur. The large negative entropy associated with these inversions is likely due to the concomitant solvent reorganization involved in the rotations.

In conclusion, we have determined the activation parameters for the hindered Pt−N(bipyridyl) rotation in two supramolecular platinum self-assemblies, a rectangle and a triangle. To our knowledge, this is the first report of these parameters for a platinum assembly. Park et al.[1a] determined the energy of activation for a restricted pyridyl rotation in an interclipped supramolecular Pd(dppp) resorcin[4]arene bowl to be 62.3 kJ/mol. This $\Delta G^{\ddagger}$ is lower than what we observed in the present study, consistent with the more labile Pd(II)−N(pyridyl) bonds and the less sterically hindered dppp groups. Stang et al.[11] used ^{31}P NMR to study rotation about a Pt−N(quinoline or isoquinoline) bond in a series of monomer complexes and found the rotational energy barrier to be >70 kJ/mol. Similarly, Rotondo et al.[12] determined the Pt−N(pyridine) rotations for three Pt(2,2′-bipyridine)-$(L_2)^{2+}$ complexes where L = 3-CN-py, 3-Ph-py, and 3-Me-py to be 71.9, 71.6, and 68.5 ± 1 kJ/mol, respectively. Even though these compounds involve a single metal center and are not as complex as the assemblies **1** and **2**, the energy of activation for the restricted pyridyl rotations is similar to what we observed for the self-assembled rectangle.

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Supporting Information Available: Experimental conditions, description of the SIR experiments, Bloch−McConnell and Eyring equations, measured exchange rate constants and fitting parameters. Figures showing ^{1}H NMR lineshape analysis, Eyring plots from the lineshape analysis, and SIR experiment for the rectangle. This material is available free of charge via the Internet at http://pubs.acs.org.

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