Direct and Quantitative Characterization of Dynamic Ligand Exchange between Coordination-Driven Self-Assembled Supramolecular Polygons

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Methods and Materials. 0° and 60° organoplatinum acceptor **3**[1] and **4**[2] as well as the rectangles[1] (**5a** and **5b**) and triangles[2] (**6a** and **6b**) were prepared according to literature procedures. 4,4'-dipyridyl-d_8 **2** was purchased from C/D/N Isotope Inc. Deuterated acetone and water was purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded on a Varian Unity 300 spectrometer. The ^{1}H NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system.

General Procedure for the Dynamic Ligand Exchange Experiment. Individually prepared rectangles (**5a** and **5b**) and triangles (**6a** and **6b**) were mixed in 1:1 ($[\mathbf{5a}]_0$= 2.14 mM and $[\mathbf{5b}]_0$ =2.14 mM), 1:1 ($[\mathbf{6a}]_0$ =1.43 mM and $[\mathbf{6b}]_0$ =1.43 mM), and 3:2 ($[\mathbf{5a}]_0$= 2.14 mM and $[\mathbf{6b}]_0$ =1.43 mM) ratios in the aqueous acetone solution (Acetone-d_6/D_2O 1:1) to carry out the study of ligand exchange between the same (**5a** + **5b** as well as **6a** + **6b**) and different (**5a** + **6b**) types of polygons. Upon heating at 64 ± 1 °C, the mixtures were periodically transferred for ESI-MS and NMR analysis.

Figure S1. Calculated (blue) and experimental (red) ESI-MS spectra (Acetone-d_6/D_2O 1:1) (a) individually prepared **5b**, (b) individually prepared **5a**, (c) **5c** (calculated) (d) initial mixture of **5a** and **5b**, and (e) equilibrated mixture of **5a**, **5b**, and **5c**.

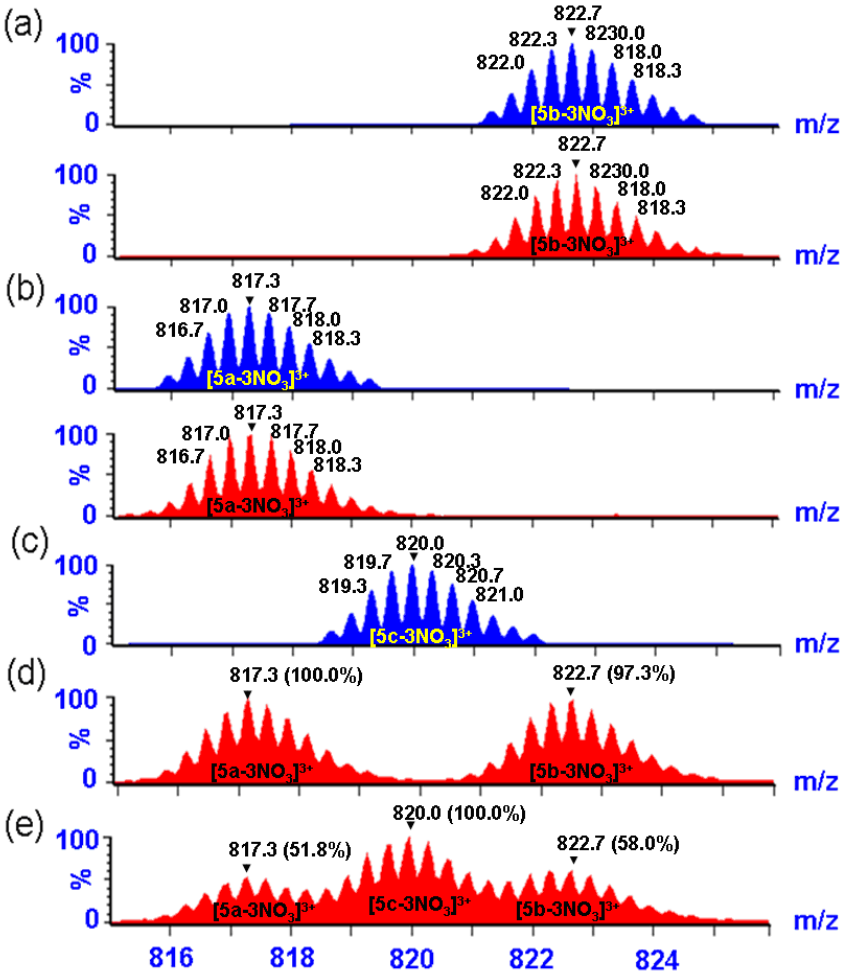


Figure S2. Calculated (blue) and experimental (red) ESI-MS spectra (Acetone-d_6/D_2O 1:1) (a) individually prepared **6b**, (b) individually prepared **6a**, (c) **6c** (calculated), (d) **6d** (calculated), (e) initial mixture of **6a** and 6**b**, and (f) equilibrated mixture of **6a**, **6b**, **6c**, and **6d**.

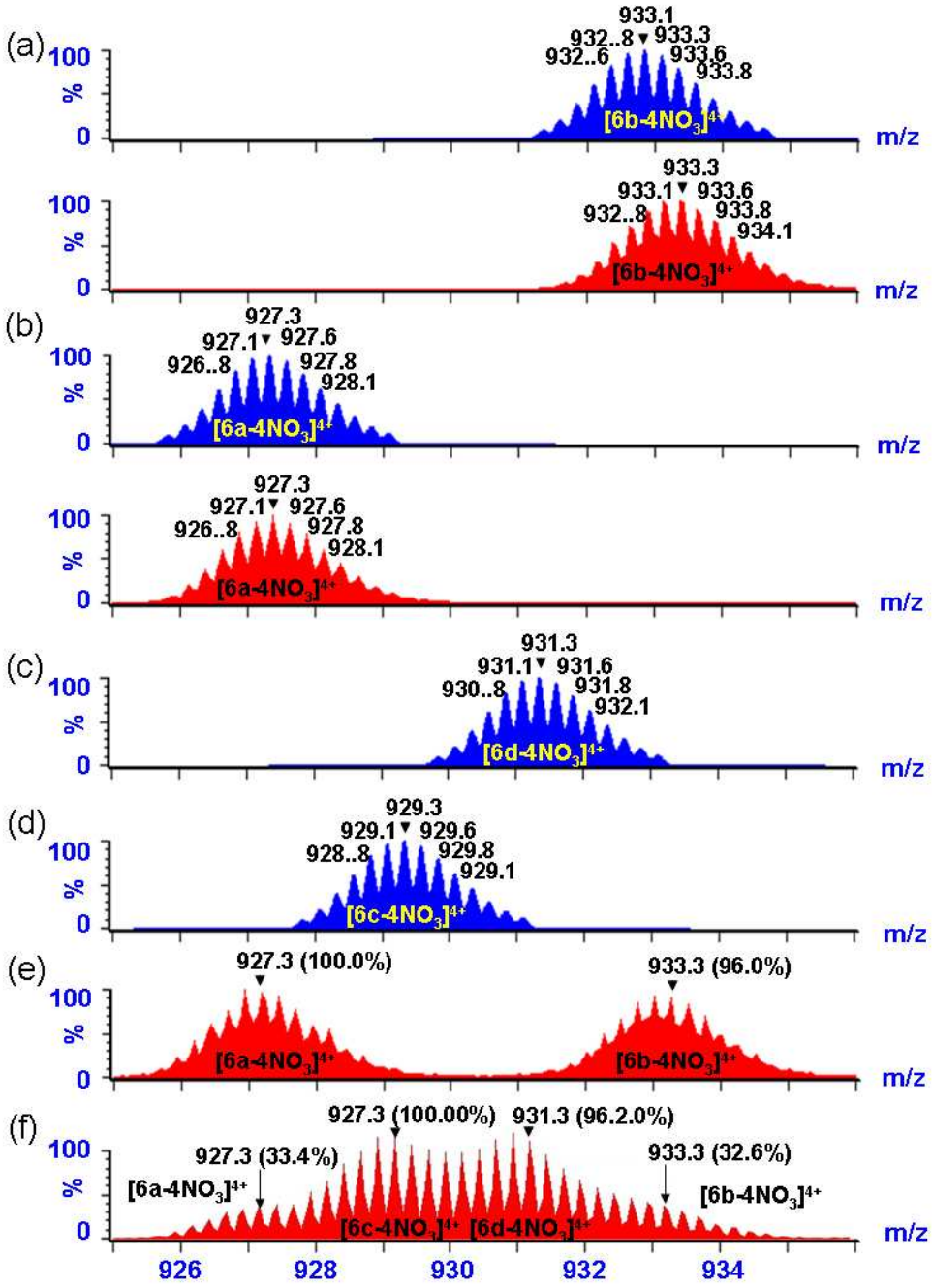


Figure S3. ESI-MS spectra (Acetone-d_6/D_2O 1:1) (a) and (c) initial mixture of **5a** and 6**b** an (b) and (d) equilibrated mixture of **5a**, **5b**, **5c**, **6a**, **6b**, **6c**, and **6d**.

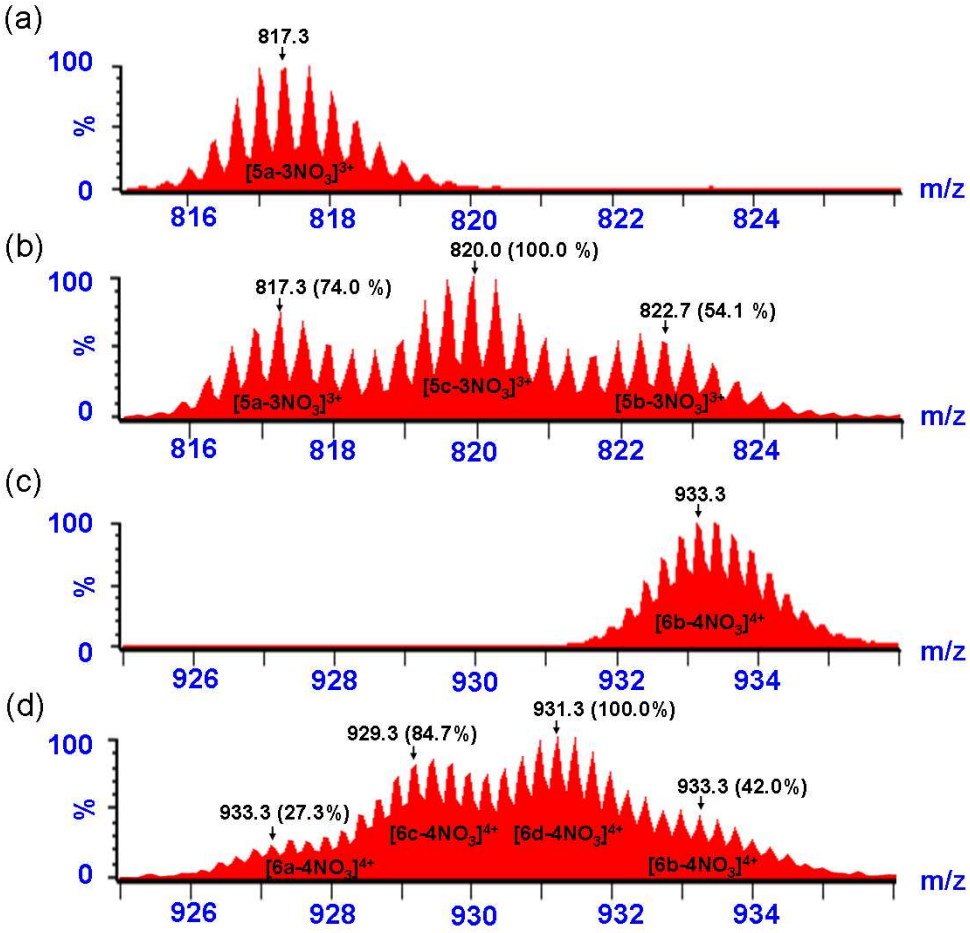


Figure S4. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of (a) individually prepared **5b**, (b) individually prepared **5a**, (c) initial mixture of **5a** and **5b**, and (d) equilibrated mixture of **5a**, **5b**, and **5c**.

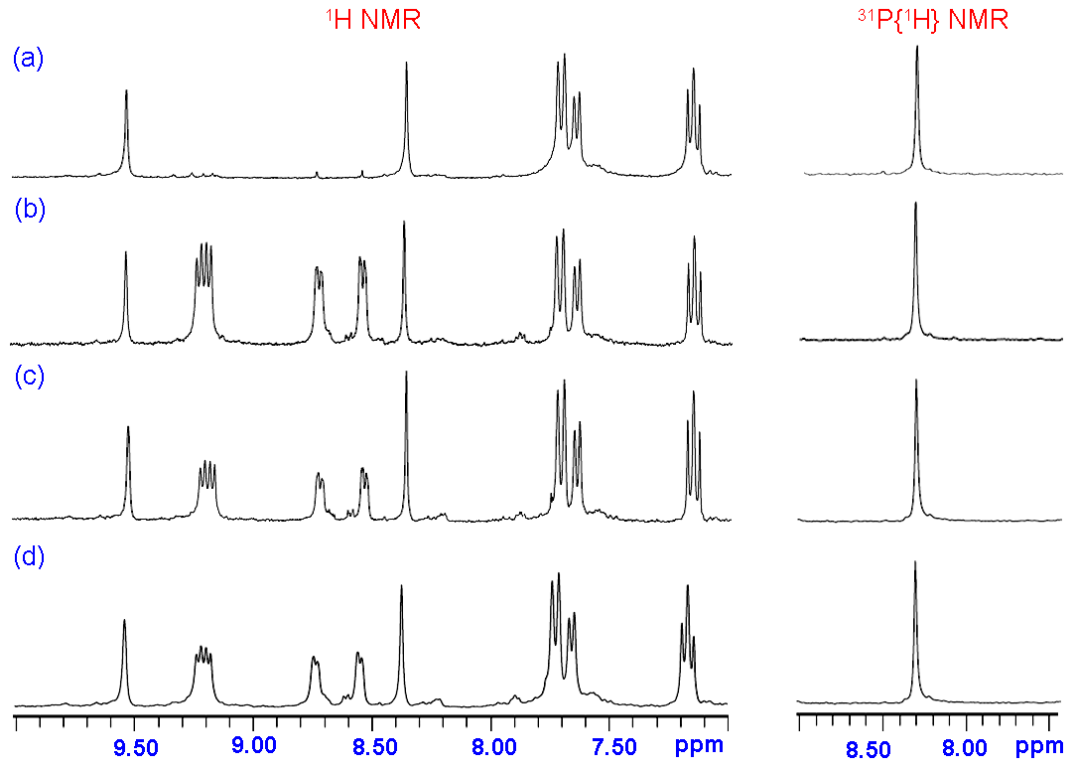


Figure S5. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of (a) individually prepared **6b**, (b) individually prepared **6a**, (c) initial mixture of **6a** and 6**b**, and (d) equilibrated mixture of **6a**, **6b**, **6c**, and **6d**.

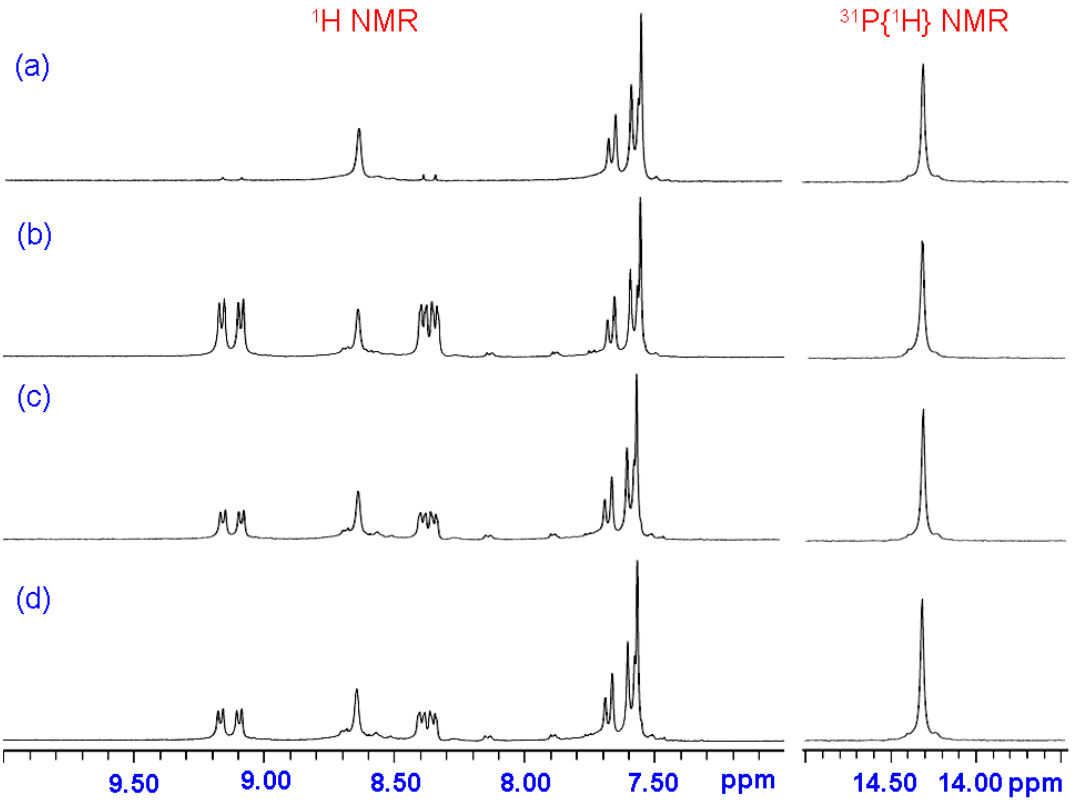
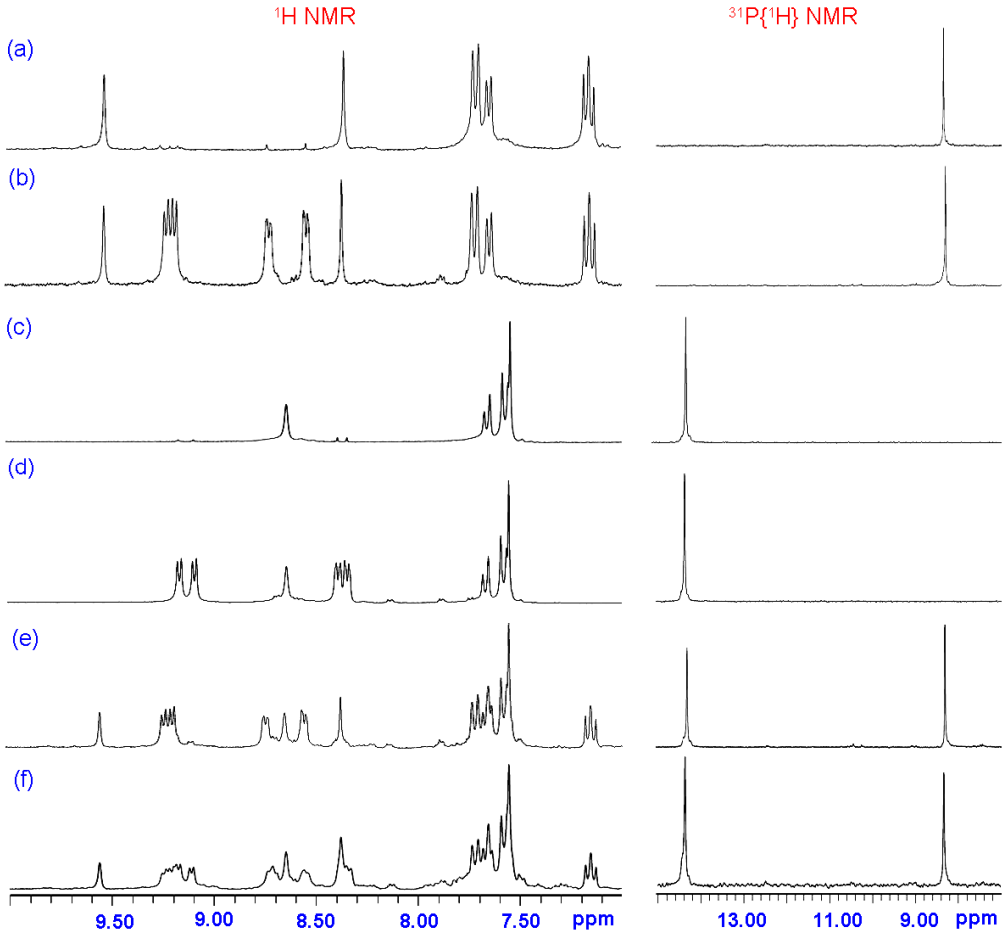


Figure S6. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of (a) individually prepared **5b**, (b) individually prepared **5a**, (c) individually prepared **6b**, (d) individually prepared **6a**, (e) initial mixture of **5a** and 6**b**, and (f) equilibrated mixture of **5a**, **5b**, **5c**, **6a**, **6b**, **6c**, and **6d**.



Kinetic analysis of ESI-MS data of the dynamic exchange between rectangles 5a and 5b.

Figure S7. ESI-MS spectra (Acetone-d_6/D_2O 1:1) for dynamic ligand exchange between **5a** and **5b** recorded at different time intervals: (a) 20 h, (b) 43 h, (c) 66 h, (d) 89 h, (e) 161 h, and (f) 206 h.

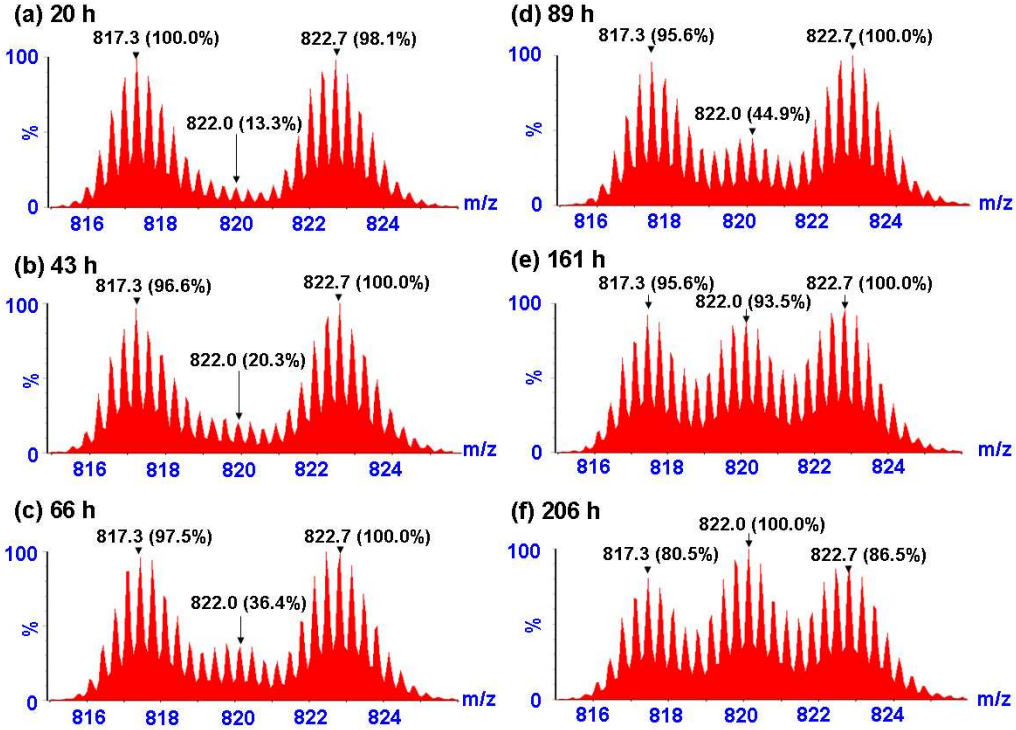


Table S1. Kinetic data extracted from ESI-MS spectra (Figure S7) of the dynamic exchange between rectangles **5a** and **5b**.

t (h)	$[\mathbf{5c}]_t$ / $[\mathbf{5a}]_t$	$[\mathbf{5a}]_0$ / $[\mathbf{5a}]_t$	Ln($[\mathbf{5a}]_0$ / $[\mathbf{5a}]_t$)
0	0. 000	1.00	0. 000
20	0. 133	1.07	0. 064
43	0. 210	1.11	0. 100
66	0. 373	1.19	0. 171
89	0. 470	1.24	0. 211
161	0. 978	1.49	0. 398
206	1. 24	1.62	0. 482

$[\mathbf{5c}]_t$ / $[\mathbf{5a}]_t$ is determined by the ratio of the intensity of peaks for **5c** (820.0) and **5a** (817.3) in the ESI-MS spectra recorded at specific time (**t**) (Figure S7).

∵ Rectangle (**5a**) + Rectangle (**5b**) ⇆ 2 Rectangle (**5c**)

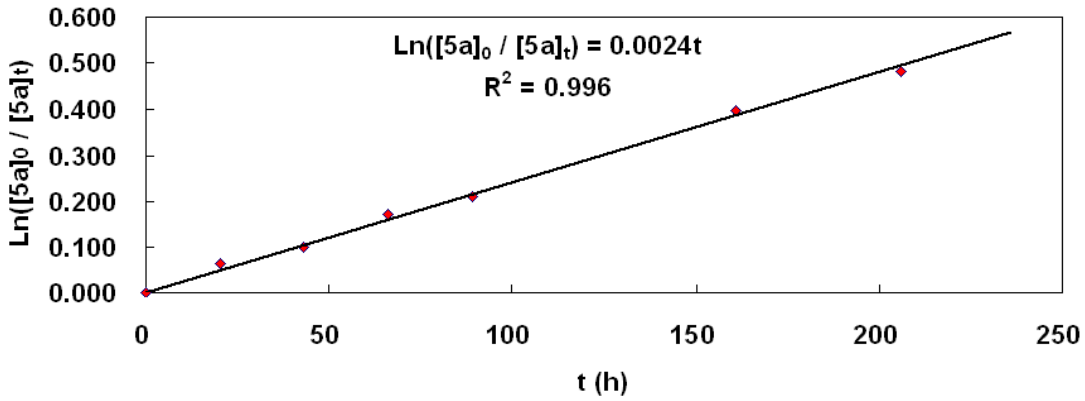
∴ $[\mathbf{5a}]_0 = [\mathbf{5a}]_t + [\mathbf{5c}]_t /2$

∴ $[\mathbf{5a}]_0 / [\mathbf{5a}]_t = 1 + ([\mathbf{5c}]_t / [\mathbf{5a}]_t) /2$

The apparent rate constant k for the dynamic exchange between rectangles **5a** and **5b** was determined by fitting the data (Table S1) to the first-order kinetic equation:

$$\mathrm{Ln}([\mathbf{5a}]_0 / [\mathbf{5a}]_t) = k\mathbf{t}$$

Figure S8. The first-order kinetic treatment of the data obtained at varied time intervals (0–240 h) for ligand exchange between **5a** and **5b**.



Reference:

(1) Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634.

(2) Kryschenko, Y. K.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 5193.