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An Allosterically Regulated, Four-State Macrocycle

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Supporting Information

ABSTRACT: Macrocycles capable of host-guest chemistry are an important class of structures that have attracted considerable attention because of their utility in chemical separations, analyte sensing, signal amplification, and drug delivery. The deliberate design and synthesis of such structures are rate-limiting steps in utilizing them for such applications, and coordination-driven supramolecular chemistry has emerged as a promising tool for rapidly making large classes of such systems with attractive molecular recognition capabilities and, in certain cases, catalytic properties. A particularly promising subset of such systems are stimuli-responsive constructs made from hemilabile ligands via the weak-link approach (WLA) to supramolecular coordination



chemistry. Such structures can be reversibly toggled between different shapes, sizes, and charges based upon small-molecule and elemental-anion chemical effectors. In doing so, one can deliberately change their recognition properties and both stoichiometric and catalytic chemistries, thereby providing mimics of allosteric enzymes. The vast majority of structures made to date involve two-state systems, with a select few being able to access three different states. Herein, we describe the synthesis of a new allosterically regulated four-state macrocycle assembled via the WLA. The target structure was made via the stepwise assembly of ditopic bidentate hemilabile N-heterocyclic carbene thioether (NHC,S) and phosphino thioether (P,S) ligands at Pt^{II} metal nodes. The relatively simple macrocycle displays complex dynamic behavior when addressed with small-molecule effectors, and structural switching can be achieved with several distinct molecular cues. Importantly, each state was fully characterized by multinuclear NMR spectroscopy and, in some cases, single-crystal X-ray diffraction studies and density functional theory computational models. This new structure opens the door to complex multicue switching reminiscent of multistate chemoswitches that could be important in controlling stoichiometric and catalytic transformations as well as generating molecular logic systems.

INTRODUCTION

The rational design of supramolecular systems, which undergo reversible structural changes, has been a long-standing goal of chemists because of the potential for developing technologically useful catalysts, switches, and sensors.^{1,2} Coordination-driven supramolecular chemistry has emerged as a powerful means to assemble large and complex macrocycles, cages, and capsules, with general methods developed by several groups,³⁻¹¹ including our own,¹²⁻¹⁴ for assembling such multicomponent structures. Among the different approaches to coordinationdriven supramolecular constructs, the weak-link approach (WLA) has emerged as a powerful means for synthesizing complexes that can undergo reversible small-molecule-induced structural changes and therefore be toggled between "closed" rigid states and "open" flexible ones (Figure 1a-c).^{10,11,15} Through the modular and convergent assembly of metal ions and hemilabile ligands, the WLA provides a platform for engineering molecular selectivity and stimuli-responsiveness

with deliberate control. WLA-based supramolecular systems are attractive because they offer (1) chemical access to multiple different states with tailorable selectivity and binding affinities, 16,17 (2) high functional group tolerance, 11,18 and (3) modularity, including access to structures with a wide variety of metal nodes and ligand types.^{9,10,18} Many stimuli-responsive systems have been developed based on this platform, through the incorporation of catalytic,^{19–23} redox-active,^{24,25} and host– guest recognition sites¹⁷ into the ligands in such a way that small-molecule-induced structural changes result in marked changes in the properties of these complexes.

The addressable nature of these structures arises from the hemilabile phosphinoalkyl chalcoether or amine (P,X; P = $Ph_2PCH_2CH_2-$ and X = O, S, Se, N) ligands typically

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Figure 1. WLA to coordination-driven supramolecular (a) macrocycles, (b) tweezers, and (c) triple-decker complexes. For the sake of this example, complexes with Pd^{II} and Pt^{II} metal centers are illustrated, but the WLA works with many other metal systems including Rh^{I} , Cu^{I} , and $Ir^{I,26-29}$.

coordinated to d⁸ transition metals (such as Rh^I, Pd^{II}, or Pt^{II}). These complexes can reversibly access three distinct states (fully open, semiopen, and fully closed) through the removal and introduction of small molecules coordinating ligands (X_c) or elemental anions, which can easily displace the metal-S bond ("weak-link", in this example), while preserving the metal-P bond ("strong-link"; Figure 1; for simplicity, the semiopen macrocycle is not shown in Figure 1a and the fully open states are omitted from Figure 1b,c). Recently, our group reported the stepwise synthesis of heteroligated Pt^{II} WLA tweezer and triple-decker complexes with monotopic bidentate hemilabile N-heterocyclic carbene thioether (NHC,S) and phosphino thioether (P,S) ligands (Scheme 1a).³⁰ This strategy allowed for the assembly of air-stable heteroligated structures without the requirement of different electron-donating abilities at the "weak-links", a requisite for previous heteroligated Pt^{II} WLA systems.³¹ This stepwise approach was demonstrated in the synthesis of heteroligated tweezer and triple-decker

complexes.³⁰ Recently, this approach was used to synthesize a switchable molecular receptor that can access two distinct structural states: flexible "open" and rigid "closed" states (Scheme 1b).¹⁶ Although this construct was the first example of a heteroligated Pt^{II} macrocyclic system, the limited structural states accessible by this complex prevented switching between multiple binding pockets, each capable of binding a different guest molecule or exhibiting a different, but complementary function. Developing allosterically regulated structures that can access multiple states with different properties is a fundamental challenge and remains an important synthetic goal. The structures reported herein are the first step toward the development of multistate, stimuli-responsive receptors, catalysts, and chemoswitches, with fundamentally interesting functions relating to their different chemically tunable structures.

Herein, we apply this stepwise approach to the synthesis of a heteroligated multistate macrocycle, possessing two different Scheme 1. (a) Stepwise Approach to the Synthesis of WLA Tweezer and Triple-Decker Complexes, (b) Stepwise Assembly of a WLA Heteroligated Pt^{II} Macrocyclic Capsule, and (c) the Scope of This Work Applying This Approach to the Synthesis of an Allosterically Regulated, Multistate, Heteroligated Macrocycle^{*a*}



ditopic bidentate ligands bridging two Pt^{II} metal nodes, which exhibits four-state switching behavior, considerably more complex than previously reported for WLA systems (Scheme 1c). Experimental and computational evidence suggest that, while the addressability of the system arises from the coordination chemistry, the resulting complexity of the macrocycle behavior is a function of multiple factors, including geometry, strain, strength of coordination bonds, and electronics. This is in contrast with previously reported WLA systems that rely on the use of weakly chelating ligands to achieve the assembly of heteroligated structures, which are too unstable to form significantly strained structures.¹¹

RESULTS AND DISCUSSION

WLA Macrocycle Synthesis and Characterization. In order to synthesize the Pt^{II} heteroligated WLA macrocycle, we utilized a previously reported stepwise approach employing a ditopic bidentate NHC,S-based ligand in conjunction with a traditional ditopic bidentate P,S-based ligand, both of which bind Pt^{II} strongly enough to result in kinetically stable structures. Benzimidazolium chloride salt 1 was treated with 2 equiv of dichloro(1,5-cyclooctadiene)platinum(II) [PtCl₂(cod)] and 1 equiv of silver(I) oxide (Ag₂O) in dichloromethane (CH₂Cl₂) to produce Pt₂Cl₄($\kappa^2:\mu:\kappa^2$ -NHC,S) (2) as an insoluble white solid (Scheme 2). In order to confirm that the metalation reaction of 1 with Ag₂O and the subsequent transmetalation reaction with $PtCl_2(cod)$ were successful, complex 2 was characterized by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), with the monoisotopic mass and isotopic distribution matching those of the molecular ion $[M - Cl]^+$ (see the Supporting Information, SI). Because of the low solubility of complex 2 in CH_2Cl_2 , single crystals suitable for X-ray diffraction were obtained by the slow diffusion of diethyl ether (Et₂O) into a solution of complex 2 in dimethyl sulfoxide (DMSO). The solid-state structure reveals a complex with DMSO ligands coordinated to the metal center, displacing the weakly bound thioether groups on the NHC,S hemilabile ligand (see the SI).

The irreversible metalation-transmetalation reaction at the NHC ligand allows for the subsequent use of strongly binding P,S ligands without the occurrence of previously observed ligand-exchange reactions.^{31,32} Because of the low solubility of **2** in CH₂Cl₂, complex **2** was dissolved in a 1:1 mixture of CH₂Cl₂ and methanol (MeOH) and reacted with 1 equiv of the P,S-aryl-S,P ligand **3** (Scheme 2). Characterization of the resulting product by ¹H and ³¹P NMR spectroscopy revealed that the fully open macrocycle was obtained as a mixture of isomers (4**a**-4**c**) when synthesized under homogeneous conditions in a 1:1 mixture of MeOH and CH₂Cl₂ (Scheme

Scheme 2. Synthesis of Fully Open Heteroligated Macrocycles 4a-4c^a



^{*a*}Reaction conditions: (i) 2 equiv of $PtCl_2(cod)$; 1 equiv of Ag_2O ; 6:1 $CH_2Cl_2/MeOH$, 24 h, 60 °C. (ii) 1:1 $MeOH/CH_2Cl_2$, 25 °C. (iii) CH_2Cl_2 , 25 °C.

2). Consistent with this observation, a high-resolution mass spectrometry (HRMS) spectrum of the sample exhibited a peak with a mass-to-charge (m/z) ratio corresponding to the molecular ion $[M - Cl]^+$ (see the SI).

³¹P NMR spectroscopy was used to further characterize the resulting compounds because it is highly diagnostic of the coordination environment. Additionally, the resonance shifts and platinum-phosphorus coupling patterns were consistent with the presence of a combination of cis-4a, trans-4b, and combined cis/trans (4c) fully open complexes (Figure 2a). $^{33-35}$ As summarized in Figure 2, the fully open trans species 4b [*trans*-Pt₂Cl₄(κ^1 : μ : κ^1 -NHC,S)(κ^1 : μ : κ^1 -P,S)] contains two platinum nodes in which the phosphine and carbene are trans to one another; this configuration is evidenced by a resonance at 9.7 ppm with a J_{P-Pt} coupling constant of 2300 Hz. The presence of the cis complex 4a [*cis*-Pt₂Cl₄(κ^1 : μ : κ^1 -NHC₂S)- $(\kappa^1:\mu:\kappa^1-P,S)$] is evidenced by a resonance at 1.8 ppm with a larger J_{P-Pt} of 3740 Hz. Downfield from each of the two major resonances are additional sets of signals at 2.5 and 10.5 ppm, which are of equal intensity relative to one another (Figure 2a). We proposed that they correspond to a species that has both cis and trans nodes in one complex, 4c [*cis*-PtCl₂(κ^1 : μ : κ^1 -NHC,S)($\kappa^1:\mu:\kappa^1-P,S$)-trans-PtCl₂($\kappa^1:\mu:\kappa^1-NHC,S$)($\kappa^1:\mu:\kappa^1-P,S$)]. This assignment is supported by the ${}^{31}P-{}^{195}Pt$ coupling constants, which are comparable to that of the purely cis and purely trans isomers (Figure 2). The relative chemical shifts along with the ³¹P-¹⁹⁵Pt coupling constants reveal important information about the trans influence inherent to these structures.³⁴⁻³⁶ In the case of strongly donating ligands, the chemical shift typically appears further downfield,³⁵ such as in the trans complex 4b. Between isostructural complexes, larger ³¹P-¹⁹⁵Pt coupling constants are indicative of a more weakly coordinating ligand trans to the phosphine ligand, while smaller coupling constants indicate the presence of a more strongly coordinating ligand. The NHC is a more strongly donating ligand than the chloride; therefore, the coupling constant of the



Figure 2. (a) ³¹P NMR spectrum of the complex mixture 4 in CD_2Cl_2 , (b) ³¹P NMR spectrum of single crystals of the fully open cis complex 4a dissolved in CD_2Cl_2 , (c) ³¹P NMR spectrum of 4a after several hours, indicating the reappearance of resonances attributable to the cis (4a), trans (4b), and cis/trans (4c) species.

trans complex 4b ($J_{P-Pt} = 2300 \text{ Hz}$) is significantly smaller than that of the cis complex 4a ($J_{P-Pt} = 3740 \text{ Hz}$). The cis/trans species (4c) follows the same trend, with one Pt^{II} node in the cis configuration and the other in the trans orientation, each having a chemical shift and coupling constant in the same region of the spectrum as the fully cis and trans counterparts, respectively. The resonance at 2.5 ppm has a larger coupling constant ($J_{P-Pt} = 2943 \text{ Hz}$), while the resonance of equal intensity further downfield at 10.5 ppm has a smaller coupling constant ($J_{P-Pt} = 2270 \text{ Hz}$).

When the solvent from the solution of 4a-4c was slowly evaporated, single crystals composed exclusively of 4a were isolated. The solid-state structure of 4a is consistent with the solution-phase spectroscopic characterization of the fully open cis isomer, with one $\kappa^1:\mu:\kappa^1$ -P,S ligand and one $\kappa^1:\mu:\kappa^1$ -NHC,S ligand coordinated to Pt^{II} through the phosphines and carbenes, respectively (Figure 3). We hypothesized that the



Figure 3. Crystal structure of **4a**, drawn with a 50% thermal ellipsoid probability. Solvent molecules and H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pt1–Cl2 2.360(2), Pt1–Cl2 2.352(2), Pt2–Cl3 2.340(2), Pt2–Cl4 2.357(2); Cl1–Pt1–Cl2 90.57(6), Cl3–Pt2–Cl4 89.42(6).

fully open cis structure would dynamically equilibrate back to the 4a-4c complexes initially observed in solution, an indication of fully open isomers that are similar in energy. To assess the kinetic stability of 4a, its crystals were dissolved in CD₂Cl₂ and the corresponding ³¹P NMR spectrum was collected (Figure 2b), confirming our assignment of the 1.8 ppm shift belonging to 4a. Over time, we observed the reappearance of resonances attributable to the trans (4b) and cis/trans (4c) species, in addition to the cis complex 4a, indicating that the complex undergoes isomerization in solution (Figure 2c). Consistent with an equilibrium that involves small energetic differences between isomers, we observed strong solvent effects in the synthesis of 4a-4c. In an alternative procedure, we reacted 2 with 3 in CH₂Cl₂ under heterogeneous conditions (Scheme 2), resulting in the selective formation of 4a, as confirmed by ¹H and ³¹P NMR spectroscopy and HRMS. These results suggest that solvent effects play a key role in lowering the kinetic barriers to establish an equilibrium between isomers 4a-4c.

Solid-State Structure of 4a. The solid-state structure of **4a** confirms that the fully open cis complex contains two innersphere Cl atoms in the cis orientation. Complex **4a** crystallized in the triclinic centrosymmetric space group $P\overline{I}$, and the asymmetric unit contains distinct Pt–Cl bond lengths and angles (Figure 3) comparable to those found in the literature.^{11,30} The Pt^{II} metal nodes adopt a square-planar geometry [Cl1–Pt1–Cl2 = 90.57(6)°], with the phosphine moieties cis to the carbene moieties [P1–Pt1–C1 = 94.6(2)°] (Figure 3). The solid-state structure supports the assignments made in the ¹H and ³¹P NMR spectra (see the SI).

Computational Studies of Complexes 4a–4c. In order to further investigate and understand the intramolecular interactions and relative energies of each fully open isomer in solution, we explored the electronic structures of 4a-4c and their possible diastereomers with density functional theory (DFT) calculations in the gas phase. DFT calculations were carried out on the solid-state structure of **4a** with the *Gaussian* 09 suite of programs at the B97D/LANL2DZ level of theory. The selected functional B97D empirically includes dispersion effects, which allows for a better description of the electronic structure. The geometry-optimized model of **4a** provided the basis for developing the energy-minimized models of **4b** and **4c** and their respective isomers. The bond lengths and angles of model **4a** are nearly identical with those measured in the solid-state crystal structure. All structures correspond to local minima on the potential energy surfaces and, therefore, are chemically accessible states. Population analysis was performed within the natural bond orbital formalism to provide a localized, pairwise description of the electron density.

We hypothesized that complexes 4a-4c would be relatively close in their free energies because of the observation of rapid and dynamic conversion from the purely cis state to the mixture of cis, trans, and cis/trans states. Energy-minimized models (Figure 4) were obtained for each complex (4a-4c), and their



Figure 4. Energy-minimized models of complexes 4a-4c, obtained from DFT calculations.

respective frontier orbitals were identified because they point to the identity of the orbitals involved in WLA bonding. The relative highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies were calculated, and free energies were compared across different structures. Table 1 summarizes the free energies calculated from the DFT results.

Computational modeling of the fully open states suggests that the overall free energies of the three states are close enough that there is no strong preference to form one isomer over the others. This is consistent with a system that has very small energy differences between isomers, suggesting that 4a-4c are nearly isoenergetic.

Table 1. Free Energies (kcal/mol) of 4a-4c Obtained from DFT Calculations

compound	free energy (kcal/mol)	relative free energy (kcal/mol)
4a	-2811.3087	0.0
4b	-2811.3029	0.006
4c	-2811.3018	0.007

Formation of the Semiopen WLA Macrocycle. Upon exposure of the neutral, fully open state 4a (or the mixture of 4a-4c) to MeOH, the dicationic, semiopen complex [*cis*-Pt₂Cl₂($\kappa^1:\mu:\kappa^1$ -NHC,S)($\kappa^2:\mu:\kappa^2$ -P,S)][Cl]₂ (5) was formed via the transfer of a chloride anion from the inner coordination sphere of each Pt^{II} center to the outer coordination sphere (Scheme 3). In polar protic solvents such as MeOH, outersphere chloride counterions are stabilized by hydrogen bonding, and the overall charge of the complex is stabilized by the polar solvent, thus favoring the semiopen state. This transformation is enthalpically driven and has been observed in similar systems.^{11,37,38}

The driving force of the switching from the fully open to the semiopen state is 2-fold: (i) the two outer-sphere Cl ions and the charged complex are stabilized by the polar solvent and (ii) the structure is able to relieve ring strain by adopting the semiopen configuration, as evidenced by DFT calculations (see the SI). Complex 5 was thoroughly characterized via ¹H and ³¹P NMR spectroscopy, diffusion ordered spectroscopy (DOSY), two-dimensional correlation spectroscopy, and HRMS (see the SI). The chemical shift observed in the ³¹P NMR spectrum of complex 5 (δ 36 ppm) is shifted dramatically downfield from that of the fully open Pt^{II} complexes with a concurrent decrease in the coupling constant ($J_{P-Pt} = 3421$ Hz; Figure 5a). The downfield chemical shift and the decrease in J_{P-Pt} are consistent with increased back-donation from the Pt atoms in the semiopen state in which the P,S ligand is fully chelated with the phosphine moiety trans to the chloride. Additionally, this downfield shift is diagnostic of phosphinecontaining ligands forming a five-membered ring.

A small shoulder at 37 ppm, hypothesized to be due to the presence of diastereomers, is present just downfield of the major resonance at 36 ppm in the ³¹P NMR spectrum. Previous reports have shown that stereoisomers in WLA tweezer complexes with two phosphinoalkyl thioether ligands, as well as in WLA complexes bearing NHC,S and P,S ligands, can be observed via ¹H and ³¹P NMR spectroscopy.^{11,30} This is attributed to the intramolecular inversion of the thioether moiety trans to a ligand with a strong trans effect (such as

phosphines).^{40,41} A variable-temperature (VT) ³¹P NMR study revealed that the two signals (36 and 37 ppm) present at room temperature coalesce at high temperature (330 K) in methanol d_4 , indicating rapid interconversion of the diastereomers in solution (Figure 6). These results were further supported by energy-minimized DFT calculations of the two diastereomers (see the SI).

Formation of a New WLA Intermediate State. The semiopen complex 5 was then reacted with 4 equiv of silver tetrafluoroborate $(AgBF_4)$ in MeOH to abstract the four Cl ions (two inner sphere and two outer sphere) and form the fully closed complex with fully chelated ditopic bidentate P,S and NHC,S ligands (Scheme 4a). Despite being a widely reported method for closing WLA complexes, the reaction did not result in a fully closed complex, as evidenced by ³¹P NMR and MALDI-TOF MS. Instead, the signals in the $^{31}\mathrm{P}$ NMR spectrum indicate a seemingly nonsymmetric product, displaying two distinct ³¹P resonances of equal intensity: one at 37 ppm and the other at 47 ppm (Figures 5a, 6). The signal at 37 ppm is consistent with previously reported Pt^{II} semiopen complexes bearing NHC,S ligands,³⁰ while the resonance downfield at 47 ppm is characteristic of a fully closed complex.³⁰ Given that the peaks were of approximately equal intensity, we hypothesized that a new WLA structural state was obtained, namely, a macrocycle with one Pt^{II} metal center in a fully closed state and the other in a semiopen state with methanol- d_4 bound to the Pt center rather than the expected thioether moiety ([cis-Pt₂(κ^1 : μ : κ^2 -NHC,S)(κ^2 : μ : κ^2 -P,S)- $CD_3OD][BF_4]_4$ (6); Scheme 4a). This hypothesis was supported by the observation that the relative intensities of the two peaks did not change when additional AgBF4 was added, indicating that the reaction had gone to completion and that the signal at 37 ppm does not belong to the residual starting material. Although single crystals suitable for X-ray diffraction were not obtained, ¹H and ³¹P NMR spectroscopy, MALDI-TOF MS, and DFT calculations support the formation of complex 6. MALDI-TOF MS analysis of complex 6 revealed a peak at m/z 1767.308, which matches the simulated mass of the molecular ion $[M + H]^+$ (see the SI). Additionally, DFT calculations were used to calculate the strength of the Pt^{II}-OHCH₃ bond, for comparison to the traditional Pt^{II}-S bond. The Pt^{II}–OHCH₃ interaction was calculated to be 30.70 kcal/ mol, which is comparable to that of the Pt^{II}-S bond energy in the same compound (42.25, 57.10, and 63.77 kcal/mol), further supporting the formation of 6 (see the SI).





^aReaction conditions: (i) MeOH, 25 °C. (ii) CH₂Cl₂, 25 °C.



Figure 5. (a) ³¹P NMR spectra of each distinct state accessible by the WLA macrocycle, namely, fully open (4), semiopen (5), and new intermediate (6) states with one Pt^{II} node in the closed state and the other in a semiopen state and a fully closed state (7). (b) MALDI-TOF spectrum compared with the ISOPRO simulation of the molecular ion $[M - BF_4]^+$ of complex 7.



Figure 6. ³¹P NMR spectra of complex **5** in methanol- d_4 from 213 to 330 K. Coalescence of the major resonance (36 ppm) and the corresponding diastereomer's resonance (37 ppm) is observed at high temperature, consistent with the presence of rapidly interconverting diastereomers at elevated temperature.

Formation of the Fully Closed State. In order to fully close the macrocycle, complex **6** was subjected to high vacuum for 2 h to liberate what was hypothesized to be a methanol- d_4 molecule bound to the Pt^{II} metal center and form the $\kappa^2:\mu:\kappa^2$ -NHC,S and $\kappa^2:\mu:\kappa^2$ -P,S coordinated complex (Scheme 4b). Characterization by ¹H and ³¹P NMR spectroscopy (Figure 5a, 7), MALDI-TOF MS, and DFT calculations confirmed the formation of a fully closed state. Specifically, when the fully dried product was dissolved in a noncoordinating deuterated

solvent (nitromethane- d_3) and analyzed by ³¹P NMR spectroscopy (Figure 5a, 7), two major resonances at 49 ppm (J_{P-Pt} = 3450 Hz) and 51 ppm (J_{P-Pt} = 3450 Hz) were observed with an integral ratio of 2:1 (see the SI). This result is consistent with the formation of the fully closed complex 7 with a 2:1 mixture of diastereomers, as was the case in the semiopen complex. Complex 7 was further investigated by a VT ³¹P NMR study from room temperature to 338 K, a temperature range in which thioether inversion was previously observed (see the SI).^{30,37} The coalescence of the two signals at high temperature confirmed that the two peaks stem from the two diastereomers of the fully closed complex 7.

To further investigate the structures and energies of the two diastereomers, energy-minimized models were calculated by DFT, and their relative energies were obtained (see the SI). The energy-minimized models suggest that both diastereomers are structurally accessible states and are comparable in their free energies, consistent with the nearly equal proportion observed in the ³¹P NMR spectrum (see the SI). The presence of complex 7 was further confirmed by MALDI-TOF MS with a peak at m/z 1647.070, which matches the simulated isotopic distribution of the molecular ion $[M - BF_4]^+$ (Figure 5b). Additionally, complex 7 can also be obtained directly from the semiopen complex 5 via a reaction with 4 equiv of AgBF₄ in the noncoordinating solvent nitromethane (Scheme 4b).

Accessing Each of the Reversible States. As previously mentioned, WLA complexes are unique in their ability to be allosterically regulated in a reversible manner. As such, we sought to reopen complex 7 and reform each of the previously accessed states (Scheme 5). Complex 6 was readily regenerated from complex 7 by dissolution in MeOH. Upon the addition of 4 equiv of a soluble chloride source, namely, bis-(triphenylphosphoranylidene)ammonium chloride (PPNCl), complex 6 was converted to the semiopen complex 5. The

Scheme 4. Formation of (a) the New Intermediate WLA Macrocycle State (6) and (b) the Fully Closed Macrocycle^a



^{*a*}Reaction conditions: (i) 4 equiv of AgBF₄, methanol- d_4 . (ii) (1) High vacuum to remove methanol- d_4 (MeOD), 2 h; (2) CH₃NO₂- d_3 . (iii) 4 equiv of AgBF₄, CH₃NO₂- d_3 .

Scheme 5. Reversible Closing and Reopening of the WLA Multistate $Macrocycle^a$



^{*a*}MeOD = methanol- d_4 .

opening was evidenced by the disappearance of the signal at 47 ppm and the concomitant appearance of signals at 36 and 37 ppm, corresponding to the two diastereomers of complex 5 (see the SI). Upon dissolution of the fully dried complex 5 in CD_2Cl_2 , the fully open complex 4a was regenerated, completing the closing and reopening cycle. The ³¹P NMR spectrum of the resulting product shows the disappearance of the resonances at 36 and 37 ppm and the reappearance of the signal at 1.8 ppm ($J_{P-Pt} = 3740$ Hz), consistent with the formation of the cis complex 4a (see the SI).

CONCLUSIONS

Of the various supramolecular architectures that have been synthesized through coordination-driven supramolecular assembly, the macrocycle continues to be an important architecture because of its defined cavity, making it useful for host-guest chemistry, designed molecular recognition, and catalysis.² Additionally, macrocyclic architectures have paved the way for the synthesis of larger, more sophisticated structures with three-dimensional cavities. The addressable construct described here is a potentially useful building block for the construction of higher order, chemically addressable complexes with multistate switching capabilities. Key to the success of the stepwise formation of heteroligated WLA macrocycles is the kinetic stability of the complexes where the "weak-link" thioether is a relatively strong donor. The consequence of this strong bonding is illustrated by the formation of the semiopen/fully closed complex 6, in which a MeOH molecule occupies one of the empty coordination sites. The MeOH molecule displaces a single thioether and alleviates some of the fully closed structure's strain energy, which has been investigated by DFT calculations. The ring strain present in this system suggests that the WLA may allow us to design systems in which strain can be exploited to enable the use of allosteric effectors that are not anionic. The result is a macrocyclic structure that can adopt new intermediate states previously not observed in traditional WLA systems, making it the first platinum-based system to require multiple cues or stimuli to be switched between states and the only known fourstate WLA system.

EXPERIMENTAL SECTION

General Methods/Instrument Details. Commercially available chemicals were purchased as reagent grade from Sigma-Aldrich, Acros, and Alfa Aesar, unless otherwise noted, and used as received. Unless otherwise stated, all solvents were purchased anhydrous and degassed under a stream of argon prior to use. All glassware and magnetic stirring bars were thoroughly dried in an oven (180 °C). Reactions were monitored using thin-layer chromatography (TLC), commercial TLC plates (silica gel 254, Merck Co.) were developed, and the spots were visualized under UV light at 254 or 365 nm. Flash chromatography was performed using SiO2-60 (230-400 mesh ASTM, 0.040-0.063 mm; Fluka). Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. ¹H, ³¹P, ${}^{31}P{}^{1}H$, and ${}^{19}F{}^{1}H$ NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, and chemical shifts (δ) are given in parts per million. ¹H NMR spectra were referenced internally to residual proton resonances in the deuterated solvents (dichloromethane- $d_2 = \delta$ 5.32; nitromethane- $d_3 = \delta$ 4.33; methanol- $d_4 = \delta$ 3.31). ^{31}P and $^{31}\overline{P}\{^{1}H\}$ NMR spectra were referenced to an external 85% H_3PO_4 standard (δ 0). High-resolution mass spectrometry (HRMS) measurements were recorded on an Agilent 6120 LC-TOF instrument in positive-ion mode. Electrospray ionization mass spectrometry (ESI-MS) was recorded on a Micromas Quatro II triple-quadrapole mass spectrometer. Matrix-assisted laser desorption/ionization time-of-flight

mass spectrometry (MALDI-TOF MS) was recorded on a Bruker Autoflex III smartbeam in reflectron and positive-ion mode.

Synthesis. *Benzimidazolium Salt* (1). În a modified procedure,³⁰ a solution of 1,4-bis[(chloromethyl)thio]benzene (50 mg, 0.209 mmol) and 1-methylbenzimidazole (74.09 mg, 0.627 mmol) was dissolved in 5 mL of anhydrous dimethylformamide. The reaction mixture was stirred and heated at 100 °C for 24 h in a Schlenk flask under N₂ gas. The solvent was reduced to ca. 1 mL in vacuo with heptane. The product was then washed with diethyl ether (Et₂O) and dichloromethane (CH₂Cl₂) and dried in vacuo to obtain a white solid (66.3 mg, 0.132 mmol, 63% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.85 (s, 2H), 7.68 (dtd, *J* = 15.7, 7.4, and 6.3 Hz, 4H), 7.72–7.64 (m, 4H), 7.37 (s, 4H), 6.17 (s, 4H), 4.05 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆): δ 142.32, 132.31, 131.98, 131.67, 130.12, 126.79, 126.67, 114.06, 113.91, 49.83, 33.42.

 $[Pt_2Cl_4(\kappa^1:\mu:\kappa^1-NHC,S)(C_2H_6OS)_2]$ (2-DMSO). A solution of benzimidazolium salt (1) (100 mg, 0.199 mmol) in a solvent mixture of $CH_2Cl_2/MeOH$ at a ratio of 6:1 (4 mL) was combined with Ag_2O (46 mg, 0.199 mmol), and the mixture was stirred at 60 °C until the solution became murky and the black Ag₂O powder disappeared. After 10 min, a solution of $PtCl_2(cod)$ (149 mg, 0.397 mmol) in the solvent mixture of CH₂Cl₂/MeOH at a ratio of 6:1 (6 mL) was added to the mixture, which was then stirred at 60 °C over 24 h. The suspension was centrifuged, washed with Et_2O (10 mL \times 3), and dried in vacuo. The product was obtained as an off-white powder (115 mg, 0.120 mmol, 60% yield). ¹H NMR (400 MHz, DMSO- d_6): δ 7.74 (dd, J =8.2 and 3.7 Hz, 2H), 7.41 (d, J = 1.7 Hz, 4H), 7.35 (t, J = 7.7 Hz, 2H), 7.29–7.16 (m, 4H), 6.20–6.02 (m, 4H), 4.19 (d, J = 3.6 Hz, 6H). ¹³C NMR (126 MHz, DMSO- d_6): δ 155.68 (d, ${}^{1}J_{C-Pt}$ = 4.2 Hz), 133.17 (s), 133.05 (s), 132.73 (s), 132.66 (s), 124.02 (s), 123.89 (s), 111.69 (s), 111.36 (s), 111.31 (s), 51.37 (s), 34.83 (s). MALDI-TOF MS (matrix: dithranol). Calcd for $[M - Cl]^+$: m/z 926.961. Found: m/z926.803.

1,4-Bis(diphenylphosphino)ethylthiobenzene (3). In a modified procedure, 42,43 benzene-1,4-dithiol (0.340 mg, 2.36 mmol) was combined with azobis(isobutyronitrile) (catalytic amount) in a Schlenk flask in THF (15 mL) under N₂ gas. Diphenylvinylphosphine (KPPh₂; 1.0 g, 4.71 mmol) was added dropwise to the reaction mixture, via a syringe, under N₂ gas over the course of 30 min. The solution turned from yellow to red. The reaction was refluxed for 18 h under N₂ gas. After stirring for 18 h, the reaction solution was concentrated in vacuo to give a yellow oil. The crude product was washed with hexanes (10 mL × 3) followed by MeOH (10 mL × 3), filtered, and dried under high vacuum. The pure product appeared as an off-white solid powder (1.18 g, 90% yield). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.41–7.35 (m, 8H), 7.34–7.31 (m, 12H), 7.10 (s, 4H), 2.96–2.90 (m, 4H), 2.36–2.32 (m, 4H). ³¹P NMR (162 MHz, CD₂Cl₂): δ –17.36.

CD₂Cl₂. *b* = 17.30. [*cis*-Pt₂Cl₄(κ^1 : μ : κ^1 -*NHC*,*S*)(κ^1 : μ : κ^1 -*P*,*S*)], [*trans*-Pt₂Cl₄(κ^1 : μ : κ^1 -*NHC*,*S*)(κ^1 : μ : κ^1 -*P*,*S*)], and [*cis*-PtCl₂(κ^1 : μ : κ^1 -*NHC*,*S*)(κ^1 : μ : κ^1 -*P*,*S*)-*trans*-*PtCl*₂(κ' : μ : κ' -*NHC*,*S*)(κ' : μ : κ' -*P*,*S*)-*trans*-*PtCl*₂(κ' : μ : κ' -*NHC*,*S*)(κ' : μ : κ' -*P*,*S*)-*trans*-*PtCl*₂(κ' : μ : κ' -*NHC*,*S*)(κ' : μ : κ' -*P*,*S*)], **(4a-4c**). A solution of 3 (81.3 mg, 0.143 mmol) in CD₂Cl₂/CD₃OD (1:1, 2.5 mL) was added to a suspension of complex 2 (115 mg, 0.120 mmol) in CD₂Cl₂/CD₃OD (1:1, 0.7 mL) in a glass vial in the glovebox. The mixture was then stirred at room temperature for 48 h, during which the yellow murky solution became clear and a dark precipitate formed (AgCl). The supernatant was then dried in vacuo to obtain a pale-yellow solid powder as the product (114 mg, 0.0745 mmol, 62% yield). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.06–6.95 (m, 38H), 4.27–3.82 (m, 4H), 3.35–3.10 (br, 8H), 1.26 (s, 6H). ³¹P NMR (162 MHz, CD₂Cl₂): δ 10.45 (d, ¹J_{P-Pt} = 2270 Hz); 9.73 (d, ¹J_{P-Pt} = 2300 Hz); 2.53 (d, ¹J_{P-Pt} = 2943 Hz); 1.81 (d, ¹J_{P-Pt} = 3740 Hz). HRMS (ESI⁺). Calcd for [M – Cl]⁺: *m/z* 1493.1039. Found: *m/z* 1493.1051.

[*cis-Pt₂Cl₄*(κ^1 : μ : κ^1 -*NHC*,*S*)(κ^1 : μ : κ^1 -*P*,*S*)] (*4a*). Crystals of complex 4a were obtained by the slow diffusion of Et₂O into a CH₂Cl₂ solution of 4a–4c. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.06–8.00 (m, 4H), 7.75 (s, 4H), 7.60–7.48 (m, 10H), 7.35 (s, 4H), 7.30–7.11 (m, 11H), 7.01–6.98 (m, 9H), 6.03–5.84 (d, 13.54 Hz, 2H), 5.78–5.57 (d, 13.51 Hz, 2H), 3.82 (s, 6H), 3.45–3.22 (dt, 6.16, 6.16, 11.32 Hz, 4H), 3.19–2.92 (m, 4H). ³¹P NMR (162 MHz, CD₂Cl₂): δ 1.84 (¹J_{P-Pt} = 3740 Hz).

[*cis*-*Pt*₂*Cl*₂(κ^1 : μ : κ^1 -*NHC*,*S*)(κ^2 : μ : κ^2 -*P*,*S*)][*Cl*]₂ (*5*). A complex mixture of **4a**-**4c** (or single crystals of **4a**) was fully dried and then dissolved in CD₃OD. ¹H NMR (400 MHz, methanol-*d*₄): δ 8.25 (s, 4H), 7.78–7.60 (m, 12H), 7.57–7.43 (m, 12H), 7.35–7.30 (m, 4H), 7.28 (s, 4H), 7.27–7.24 (m, 2H), 5.51 (d, *J* = 14.0 Hz, 2H), 4.40 (d, *J* = 14.0 Hz, 2H), 4.10 (s, 6H), 3.63–3.52 (m, 4H), 3.28–3.11 (m, 4H). ³¹P NMR (162 MHz, methanol-*d*₄): δ 36.83(d, ¹*J*_{*P*-Pt} = 3421 Hz), 36.29. HRMS (ESI⁺). Calcd for [M – 2Cl]²⁺: *m*/*z* 729.0677. Found: *m*/*z* 729.0680.

[cis-Pt₂(κ¹:μ:κ²-NHC,S)(κ²:μ:κ²-P,S)CD₃OD][BF₄]₄ (6). A total of 4 equiv of AgBF₄ was added to a solution of 5 in MeOH. The solution was allowed to stir for 30 min. ¹H NMR (400 MHz, methanol-d₄): δ 8.54–7.17 (m, 36H), 6.19–5.94 (br, 2H), 4.08–4.02 (s, 2H), 3.68–3.57 (m, 4H), 3.20–2.94 (br, 4H). ³¹P NMR (162 MHz, methanol-d₄): δ 37.16 (semiopen), 46.95 (fully closed). MALDI-TOF MS (matrix: α-cyano-4-hydroxycinnamic acid). Calcd for $[M + H]^+$: m/z 1767.249. Found: m/z 1767.308.

[*cis*-*Pt*₂(κ^2 : μ : κ^2 -*NHC*,*S*)(κ^2 : μ : κ^2 -*P*,*S*)][*BF*₄]₄ (7). Complex **6** was subjected to high vacuum for 2 h to remove the MeOH molecule hypothesized to be bound to the Pt^{II} metal node. The fully dried powder was then dissolved in deuterated nitromethane (CD₃NO₂). ¹H NMR (400 MHz, CD₃NO₂): δ 8.51 (s, 4H), 8.16–7.92 (m, 10H), 7.69 (s, 6H), 7.65–7.43 (m, 16H), 6.32–5.84 (m, 4H), 4.02–3.77 (m, 2H), 3.62 (d, *J* = 19.7 Hz, 6H), 3.34–3.14 (m, 2H), 2.98–2.70 (m, 4H). ³¹P NMR (162 MHz, CD₃NO₂): δ 50.93 (d, ¹*J*_{*P*-Pt} = 3450 Hz, diastereomer), δ 49.21 (d, ¹*J*_{*P*-Pt} = 3450 Hz). MALDI-TOF MS (matrix: 2,5-dihydroxybenzoic acid). Calcd for [M – BF₄]⁺: *m*/*z* 1647.070.

X-ray Crystallography. Single crystals of 2 and 4a were mounted on a MITIGEN holder in Paratone oil on a Kappa Apex 2 diffractometer. All measurements were made with graphite-monochromated Cu K α radiation, and all structures were solved with the *ShelXT* structure solution program using direct methods and refined with the *ShelXL* refinement package using least-squares minimization.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02745.

Experimental details, including VT NMR spectra, reversibility of the structural changes, and NMR and mass spectra (PDF)

Accession Codes

CCDC 1583493–1583494 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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