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Palladium(II) Weak-Link Approach Complexes Bearing Hemilabile N-Heterocyclic Carbene−Thioether Ligands

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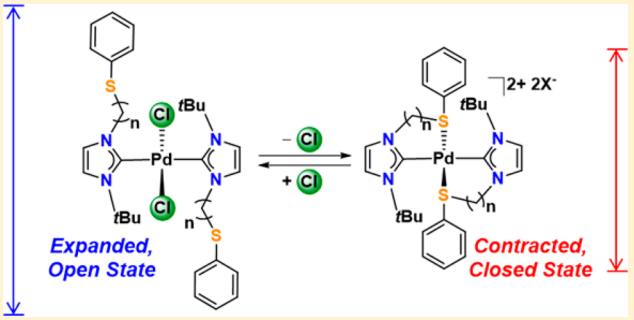
Supporting Information

ABSTRACT: A new class of homoligated palladium(II) weak-link approach (WLA) complexes bearing hemilabile N-heterocyclic carbene (NHC)−thioether ligands is reported that, unlike previous tweezer-like WLA complexes, expand and contract in a linear fashion when switching between configurational states. These complexes can be chemically switched between a trans open state and a trans closed state via the addition or subsequent extraction of Cl^-. These bis(NHC) complexes also display unusual isomerization behavior. For example, an NMR spectroscopic investigation into the solution-state configuration of the open complex reveals the presence of interconverting syn,trans and anti,trans isomers, and a kinetic study shows that the barrier is large enough to isolate, store, and study the anti,trans isomer at room temperature. Notably, the linker length between the NHC and thioether moieties can be tailored with additional $-CH_2-$ groups, which affords considerable control over the geometric changes imposed by switching. Therefore, this class of complexes may be useful in the construction of allosterically regulated supramolecular assemblies and materials.



INTRODUCTION

Advances in supramolecular chemistry have allowed chemists to synthesize biomimetic molecular assemblies for applications in catalysis,[1,2] molecular recognition,[3,4] and drug delivery.[5,6] In particular, coordination-chemistry-based approaches have been exploited as an efficient means to synthesize supramolecular constructs in a predictable and modular fashion.[7] Generally, there are three strategies[8,9] used for the assembly of such structures: the directional-bonding approach,[10] the symmetry-interaction approach,[11] and the weak-link approach (WLA).[12,13] Among these three strategies, the WLA is unique in that it incorporates addressable transition-metal nodes in conjunction with hemilabile ligands, resulting in systems that can be allosterically regulated via the reversible coordination of anions or small-molecule effectors. With the advent of the halide-induced ligand rearrangement reaction,[14,15] it is now possible to make WLA complexes with two different hemilabile ligands, providing the ability to synthesize complexes with asymmetric reaction sites, complex recognition pockets, and more sophisticated architectural parameters and reactivities.[16,17] The stimuli-responsive properties of these assemblies render the WLA an emerging and important tool for preparing allosterically addressable supramolecular constructs that mimic enzymes.[18−21]

Typically, WLA complexes are assembled from d^8 transition metals (such as Rh^I and Pt^{II}) and hemilabile bidentate phosphino−chalcoether (P,X; X = O, S, Se) ligands.[22−24] Upon assembly, the resulting complexes can be switched between a flexible open state and a rigid closed state by the addition or subsequent removal of allosteric effectors (such as CO and Cl^-) that displace the weakly coordinating X moiety in a metal−X bond while retaining the strongly coordinating metal−P bond. Through the rational design of ligands, the WLA has led to a variety of different supramolecular architectures, such as tweezer,[21,25,26] macrocycle,[13,20,25,27] and triple-decker complexes (Figure 1).[25,28,29]

The initial work focused on Rh^I-based WLA complexes, which could be toggled between a trans open state and a cis closed state (Scheme 1a).[30] Benefiting from dramatic geometry changes, Rh^I-based WLA complexes formed the basis for allosteric catalysts for applications in switchable polymerization,[29] ELISA/PCR mimicking detection and signal amplification,[31,32] and photochemical switches,[33−35] when tethered to functional ligands. The Rh^I metal center, however, is air-sensitive, thus limiting the scope of applications of those supramolecular constructs.[25]

Recently, our group reported a stepwise synthesis of air-stable heteroligated WLA complexes, utilizing Pt^{II} metal centers[24] and N-heterocyclic carbene−thioether (NHC,S) hemilabile ligands,[36−40] in combination with traditional (P,S) ligands.[41,42] In contrast to previous Rh^I-based WLA complexes, which can be switched between trans open and cis closed states, Pt^{II}-based

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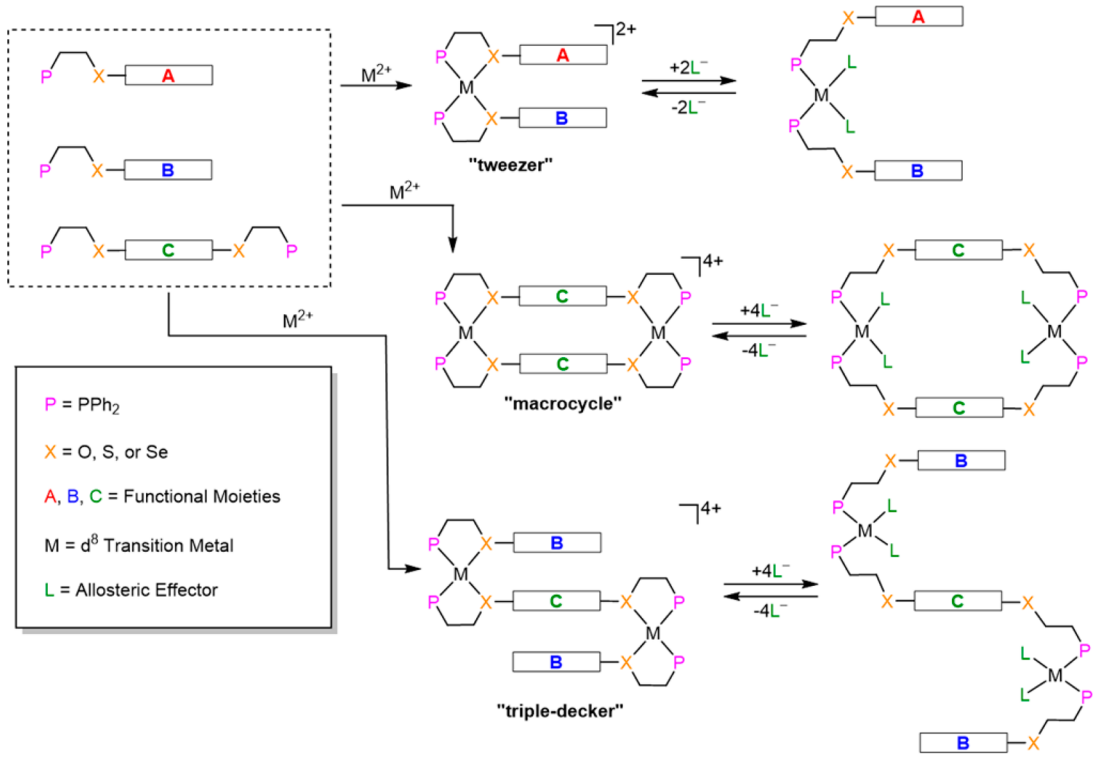
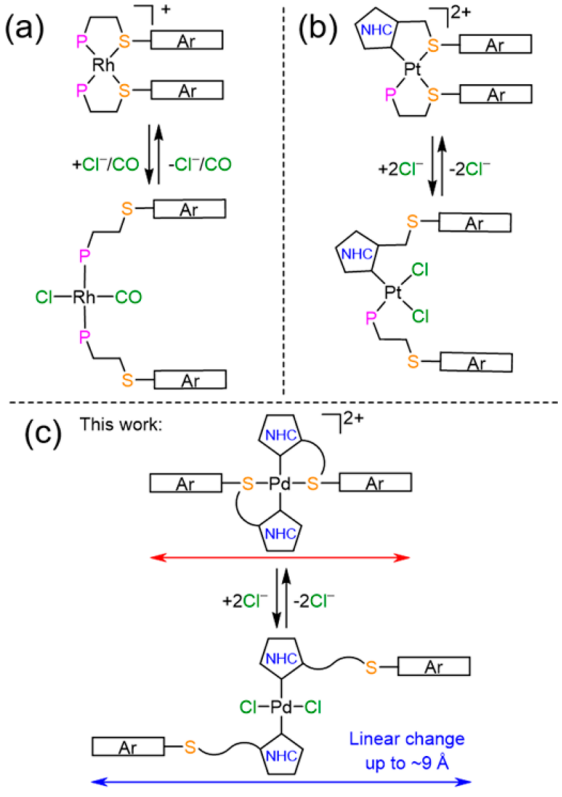


Figure 1. Supramolecular tweezer, macrocycle, and triple-decker complexes via the WLA. Charges and anions have been omitted for clarity.

Scheme 1. Allosteric Regulation of (a) Classical Rh^{I}-Based WLA Systems, (b) Pt^{II}-Based Heteroligated Systems, and (c) Pd^{II}-Based Systems Reported Herein[a]



[a]P = PPh_2, Ar = aryl group, and NHC = N-heterocyclic carbene.

complexes undergo interconversion between cis open and cis closed states (Scheme 1b).[43] The resulting constructs display smaller changes in shape and interligand spacing than their Rh^{I}-based counterparts, thereby restricting the possible structures and applications of Pt^{II}-based WLA complexes.

To address the aforementioned limitations, we decided to explore the chemistry of Pd^{II}-based WLA complexes bearing bis(NHC,S) hemilabile ligands.[44,45] In contrast to previously reported (NHC,S)(P,S)PtX_2 systems,[42] bis(NHC)PdX_2 (X = Cl, Br) complexes typically adopt a trans geometry around the Pd^{II} metal center because of steric interactions, an effect that is amplified when bulky groups are installed on the NHC ligands.[46−49] We hypothesized that halide extraction could result in the reversible conversion of the trans open state to the trans closed state, allowing for a large and linear change in the overall shape of the complex (Scheme 1c). Furthermore, we believe that by replacing the phosphine ligands with the NHCs, the resulting complexes would be kinetically more stable because of a stronger binding affinity of the NHCs to the metal center.[50,51] In addition to their stronger σ-donating nature, NHC ligands are also synthetically tailorable by altering the substituents of the imidazolium salt precursors. This feature allows one to study how the structural elements, such as the linker length between the NHC and thioether moieties, influence the geometry and properties of the resulting complexes.

Herein, we report the first example of homoligated bis-(NHC,S)-Pd^{II} WLA complexes with different linker lengths between the NHC and thioether moieties. Unlike the classical WLA complexes, this family of compounds adopts a trans geometry in both the open and closed states, which allows for a linear change in geometry upon the addition or subsequent removal of an allosteric effector (Cl^{-}), thus enabling the exploration of a new class of allosteric complexes, flexible coordination polymers, or molecular muscles.[52−54] We observe dramatically different changes in the structure upon switching between fully open and fully closed states, when the linker length between the NHC and thioether moieties is altered. Additionally, as a result of

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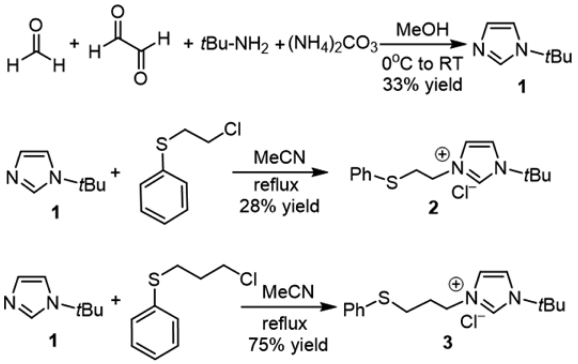
our investigations into the switching behavior, we have discovered, for the first time, a method for the selective preparation of syn,trans-bis(NHC)Pd^{II} (**5a**) and anti,trans-bis(NHC)Pd^{II} (**5b**) complexes. Not only does this work expand the scope of the WLA chemistry, but it also adds to the fundamental understanding of the isomerization behavior of bis(NHC)Pd^{II} complexes.

RESULTS AND DISCUSSION

Our design of the (NHC,S) hemilabile ligands was motivated by the hypothesis that if the substituent attached to the imidazole is of sufficient steric bulk, the trans isomer will be favored in the resulting coordination complex. Thus, we synthesized imidazolium salts substituted with a *tert*-butyl group (*t*Bu) and a tethered thioaryl group (Scheme 2), where the linker between the NHC

Scheme 2. Synthesis of (NHC,S) Hemilabile Ligands 2 and 3

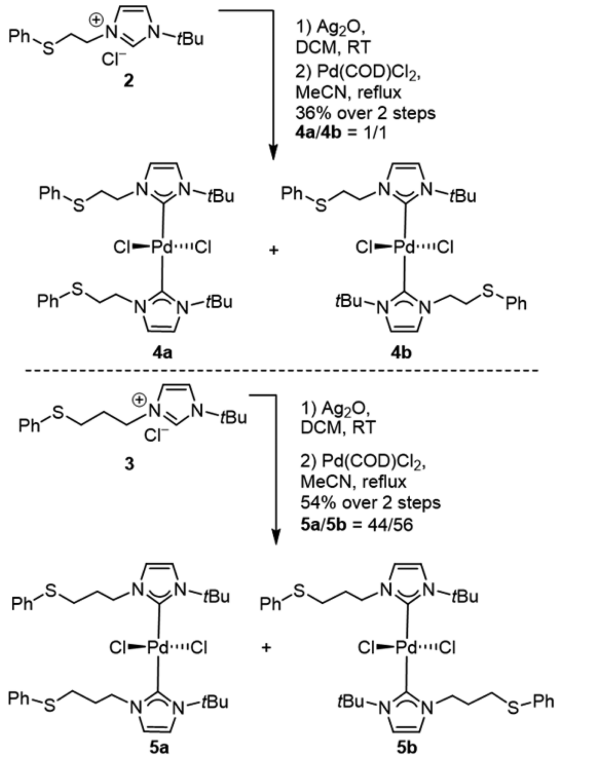


and thioether moieties was either an ethylene (**2**) or a propylene (**3**) chain. The synthesis of asymmetrically substituted imidazolium salt precursors (**2** and **3**) began with the preparation of 1-*tert*-butylimidazole (**1**), which was prepared via the condensation reaction of *tert*-butylamine, paraformaldehyde, ammonium carbonate, and glyoxal, according to a modified procedure.[55] We synthesized two ligands with two different linker lengths in order to understand how the structure of the chelating ligand affects the geometry of the rigid, fully closed WLA complexes. Therefore, **1** was subsequently reacted with either 2-chloroethylphenyl sulfide or 3-chloropropyl phenyl sulfide in refluxing acetonitrile (MeCN) to yield imidazolium chlorides **2** and **3**, respectively (Scheme 2).

The homoligated fully open complexes were synthesized using a silver transmetalation procedure,[47,56] in which the imidazolium salt **2** was first reacted with silver oxide (Ag_2O) to afford a silver carbene intermediate, as evidenced by the disappearance of the diagnostic ^{NHC}C−H resonance in the downfield region of the ^{1}H NMR spectrum ($\delta \sim 11$ ppm, $CDCl_3$). This carbene intermediate, in turn, was transmetalated with dichloro(1,5-cyclooctadiene)palladium(II) [Pd(COD)Cl_2, where COD = 1,5-cyclooctadiene] in refluxing MeCN to afford the fully open complex **4** with an isolated yield of 36% over two steps. In an analogous fashion, fully open complex **5** was synthesized with an overall yield of 54% (Scheme 3).

Notably, we observed two sets of resonances in the ^{1}H and ^{13}C NMR spectra for both **4** and **5**, suggesting the formation of two isomers during the reaction: syn (**4a** or **5a**) and anti (**4b** or **5b**) isomers. The formation of syn and anti isomers has been studied for bis(NHC)NiX_2 complexes;[57] however, this observation differs from other reported bis(NHC)PdX_2 complexes that adopt a single anti,trans conformation,[47−49,58] a geometry that minimizes

Scheme 3. Synthesis of the Homoligated Fully Open Complexes 4 and 5 via a Silver Transmetalation Procedure



the steric interaction between the two bulky substituents on the ligands. We hypothesize that the mixture of syn (**4a** or **5a**) and anti (**4b** or **5b**) isomers was obtained as a result of the decreased steric demand of the flexible ethylene or propylene chains in our system relative to the previously reported aryl substituents. Furthermore, we observed the ratio of **4a** to **4b** to be approximately 1:1 based upon ^{1}H NMR spectroscopy (see the Supporting Information, SI). To verify the chemical structure of the two isomers, we investigated the solution-state conformations, using one-dimensional nuclear Overhauser effect (1D NOE) experiments. For the fully opened complex **4**, we utilized two diagnostic resonances at 5.05 ppm (H^a) and 5.01 ppm (H^b) in the ^{1}H NMR spectrum of **4** in dichloromethane-d_2 (CD_2Cl_2; Figure 2a). Upon irradiation of H^a, we observed no correlation resonance from the *t*Bu^a at 2.00 ppm in the 1D NOE spectrum. This observation is consistent with a syn isomer of **4a**, where H^a and *t*Bu^a are pointing away from each other. In contrast, when H^b was irradiated, a resonance from *t*Bu^b at 2.03 ppm was observed in the 1D NOE spectrum, indicating that H^b and *t*Bu^b are within a distance of 5 Å from each other, thus supporting **4b** as the anti isomer (Figure S1). The stereochemistry of **5a** and **5b** was also determined by 1D NOE experiments (Figures 2b and S2), which similarly confirmed that the downfield and upfield resonances of the *t*Bu groups were attributable to the anti (**5b**) and syn (**5a**) isomers, respectively.

We next investigated the complex geometries in the solid state via single-crystal X-ray diffraction. A solution of **4** (mixture of **4a** and **4b** isomers) was subjected to crystallization by slow vapor diffusion, resulting in the formation of crystals composed exclusively of **4b**. The solid-state structure of **4b** confirms that the two NHC ligands are anti and trans to one another [C1−Pd1−C16 = 179.9(3)°], and the Pd−^{NHC}C bond length [Pd1−C1 = 2.045(4) Å; Pd1−C16 = 2.042(4) Å] values are comparable to those found in the literature (Figure 3a).[48,49,58]

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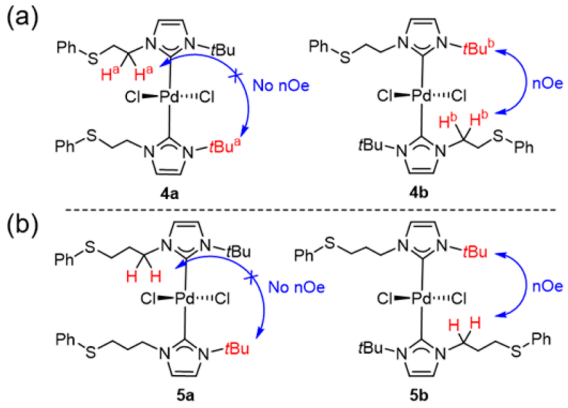


Figure 2. 1D NOE experiments on the fully opened complexes (a) **4** and (b) **5**. All experiments were conducted in CD_2Cl_2 at room temperature.

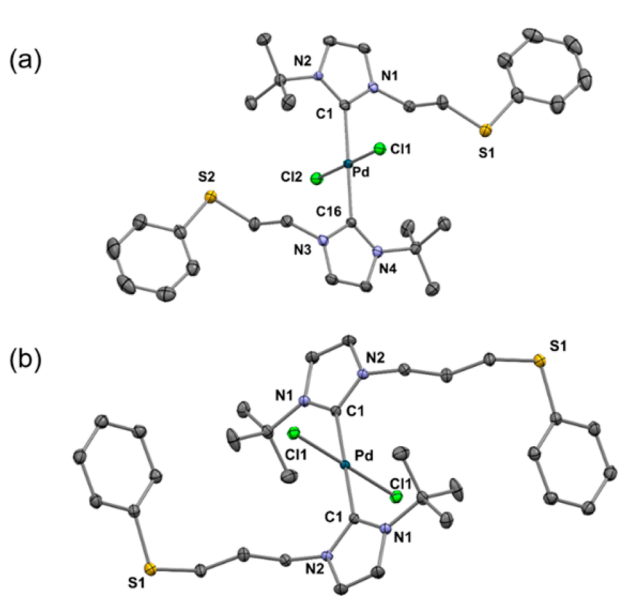


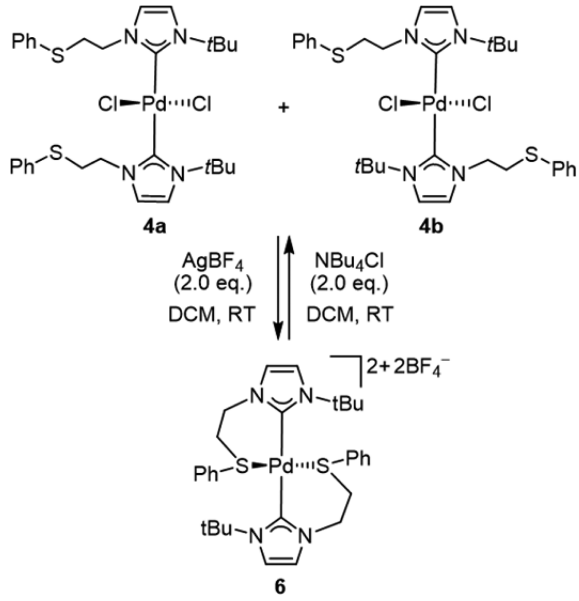
Figure 3. Crystal structures of (a) the fully open complex **4b** and (b) the fully open complex **5b** drawn with 50% thermal ellipsoid probability. Hydrogen atoms, solvent molecules, and anions have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: (a) **4b**, Pd1−Cl1 2.315(1), Pd1−Cl2 2.313(1), Pd1−C1 2.045(4), Pd1−C16 2.042(4), Cl1−Pd1−Cl2 179.71(7), C1−Pd1−C16 179.9(3); (b) **5b**, Pd1−Cl1 2.3259(2), Pd1−C1 2.0416(7).

When a crystal of **4b** was redissolved in CD_2Cl_2, only one set of resonances was observed, corresponding to the anti isomer (see the SI). No isomerization was observed for either **4b** or **4a** at ambient temperature, which suggested that the activation barrier for the isomerization of **4b** into **4a** is relatively high with respect to the thermal energy at room temperature. We believe that the barrier to rotation is the result of steric interaction between the *t*Bu groups and chloride atoms, which must be overcome in order for isomerization to occur.

Slowly diffusing diethyl ether into a solution of **5** in 1,2-dichloroethane (DCE) resulted in the formation of crystals exclusively composed of **5b** (see the SI), while the mother liquor contained no remaining **5a**, as determined by ^{1}H NMR spectroscopy. This indicates that either the crystallization process mediates conversion of **5a** into **5b** or the isomerization is fast enough such that the crystallization of **5b** drives the consumption of **5a** in solution at equilibrium. Similar to **4b**, a single-crystal X-ray diffraction study indicates that **5b** adopts the anti,trans conformation, with bond lengths of Pd−Cl [2.3259(2) Å] and Pd−^{NHC}C [2.0416(7) Å] (Figure 3b). We then sought to determine the activation barrier to isomerization ($\Delta G^{\ddagger}$) by calculating the isomerization rate constant (k) using ^{1}H NMR spectroscopy. Complex **5b** was dissolved in MeCN-d_3 (CD_3CN) and subsequently heated to 65 °C, which resulted in the conversion of **5b** to an equilibrium concentration of **5a** over approximately 4 h (Figure S3). The value of $\Delta G^{\ddagger}$(338 K) is 108.54 kJ mol^{-1}, as calculated using the Eyring equation and the rate constant observed at the early stages of the reaction. This large $\Delta G^{\ddagger}$ value is consistent with the slow syn-to-anti isomerization of **5** observed at room temperature. Furthermore, this elevated-temperature study underscores the thermal stability of the NHC−Pd^{II} bond in bis(NHC,S)Pd^{II} WLA complexes, which are comparable to their Pt^{II}-based WLA counterparts.[42]

We next studied the switching of the fully open complex **4** with the fully closed form **6** via halide extraction. Upon the addition of 2 equiv of silver tetrafluoroborate ($AgBF_4$) to a solution of **4** in CH_2Cl_2, the chloride atoms were extracted, generating the fully closed complex **6** upon coordination of the pendant thioether moieties to the metal center (Scheme 4). ^{1}H NMR spectroscopy

Scheme 4. Reversible Conversion of the Fully Open Complex 4 to the Fully Closed Complex 6



(CD_2Cl_2 at room temperature) evidence for the reaction included the disappearance of the sharp resonances attributed to the open complex **4** and the concomitant appearance of broad resonances assigned to complex **6**, along with a downfield shift of the aromatic proton resonances.

The solid-state structure of **6** was verified by a single-crystal X-ray diffraction study, showing that the two NHC ligands maintain their trans geometry [C9−Pd1−C24 = 171.25(5)°] with Pd−^{NHC}C bond lengths [Pd1−C9 = 2.061(2) Å; Pd1−C24 = 2.038(2) Å] similar to those of the fully open complex **4**, while the two thioether moieties are now bound to the metal center with a small amount of torsion [S1−Pd1−S2 = 169.52(1)°] (Figure 4a). This distortion from ideal square-planar geometry is likely due to the short length of the ethylene chain, which imparts significant ring strain in the square-planar complex. To explore the ability to toggle between states, we reopened the fully closed

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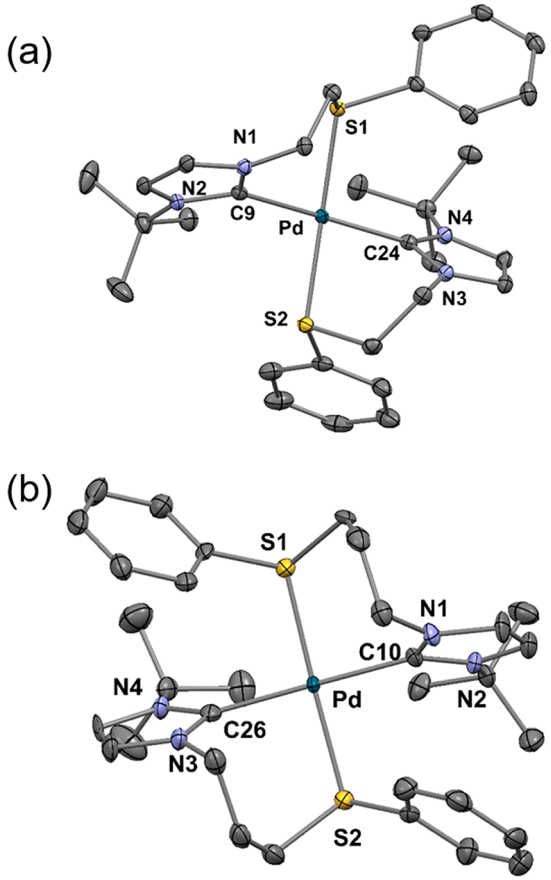
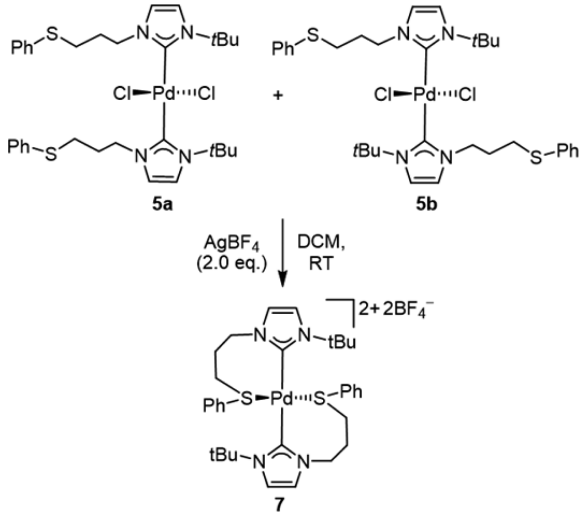


Figure 4. Crystal structures of the (a) fully closed complex **6** and (b) the fully closed complex **7**, drawn with a 50% thermal ellipsoid probability. Hydrogen atoms, solvent molecules, and anions have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: (a) **6**, Pd1−S1 2.328(1), Pd1−S2 2.357(1), Pd1−C9 2.061(2), Pd1−C24 2.038(2), S1−Pd1−S2 169.52(1), C9−Pd1−C24 171.25(5); (b) **7**, Pd1−S1 2.324(1), Pd1−S2 2.326(1), Pd1−C10 2.058(6), Pd1−C26 2.067(6), S1−Pd1−S2 178.37(6), C10−Pd1−C26 174.7(3).

complex **6** to complex **4** by the addition of 2 equiv of tetrabutylammonium chloride (nBu$_4$NCl). As indicated by ^{1}H NMR spectroscopy in CD_2Cl_2, a mixture of syn (**4a**) and anti (**4b**) isomers is observed when the open complex **4** is obtained via this route (Figure S4).

Ideally, we would like to develop complexes capable of large-amplitude coparallel linear changes, and although toggling between the fully open complex **4** and fully closed complex **6** has been demonstrated, the distorted geometry of the closed complex was less than ideal. We therefore wanted to study the solid-state geometry of the closed complex **7** to determine whether it would adopt a more favorable structure. To obtain **7**, the remaining chlorides in **5** were abstracted by the addition of 2 equiv of $AgBF_4$ (Scheme 5). Unlike **6**, no broad resonances are observed in the ^{1}H NMR spectrum of **7**; however, the appearance of diastereotopic resonances assigned to the methylene protons is indicative of the formation of a rigid fully closed complex (Figure 5d). The X-ray crystal structure of **7** further confirms the coordination of both thioether moieties to the Pd^{II} center in the solid state; however, in comparison to **6**, less deviation from an ideal square-planar geometry is observed, and the two phenyl groups are oriented in a nearly antiparallel manner [S1−Pd1−S2 178.37(6)°; C10−Pd1−C26 174.7(3)°] (Figure 4b). These observations contrast with those for **6**, suggesting that the

Scheme 5. Conversion of the Fully Open Complex 5 to the Fully Closed Complex 7



increased linker length between the NHC and thioether motifs in **7** results in reduced ring strain, a relatively undistorted square-planar geometry around the Pd^{II} metal center, and an antiparallel orientation of the terminal phenyl moieties.

We then examined the reversibility of this complex closing process by reacting the closed complex **7** with Cl^- ions. Intriguingly, we obtained the syn isomer **5a** as the sole reaction product (Figure 5e). Although the mechanism of the selective formation of the syn isomer **5a** is unclear, we believe it is the result of a kinetically controlled process because it differs from the observed ratio of the isomers obtained via direct synthesis at the elevated temperature. Because the activation barrier for syn-to-anti isomerization is relatively high, the syn isomer **5a** can be isolated, analyzed, and stored. As a result, we can selectively prepare isomers **5a** and **5b** through chloride addition to the fully closed complex **7** or by crystallization from the thermodynamic mixture, respectively (Figure 5a).

CONCLUSION

In summary, we have reported a new class of WLA complexes bearing trans-bis(NHC,S) hemilabile ligands. These complexes are air-stable and exhibit dramatic changes in the shape (up to ∼9 Å) and flexibility between the fully closed and fully open forms, thus enabling the design and synthesis of stimuli-responsive supramolecular systems possessing a new linear change in geometry. In addition, by adjusting the linker length between the NHC and thioether moieties, we probed the influence of the linker length on the geometry of the fully closed complex and the closed-to-open transformation and discovered an unusual isomerization behavior and the conditions that allow the selection of one isomer over another. This isomerization has not been explored for bis(NHC)Pd^{II} complexes, yet it could be critical in the design of new palladium(II) catalysts, where the isomeric state is important with regard to the stereoselectivity of the catalysts.[59−61]

EXPERIMENTAL SECTION

General Methods/Instrument Details. 3-Chloropropyl phenyl sulfide was prepared according to a modified literature procedure.[62] All other chemicals and anhydrous solvents were purchased from Sigma-Aldrich and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. All NMR

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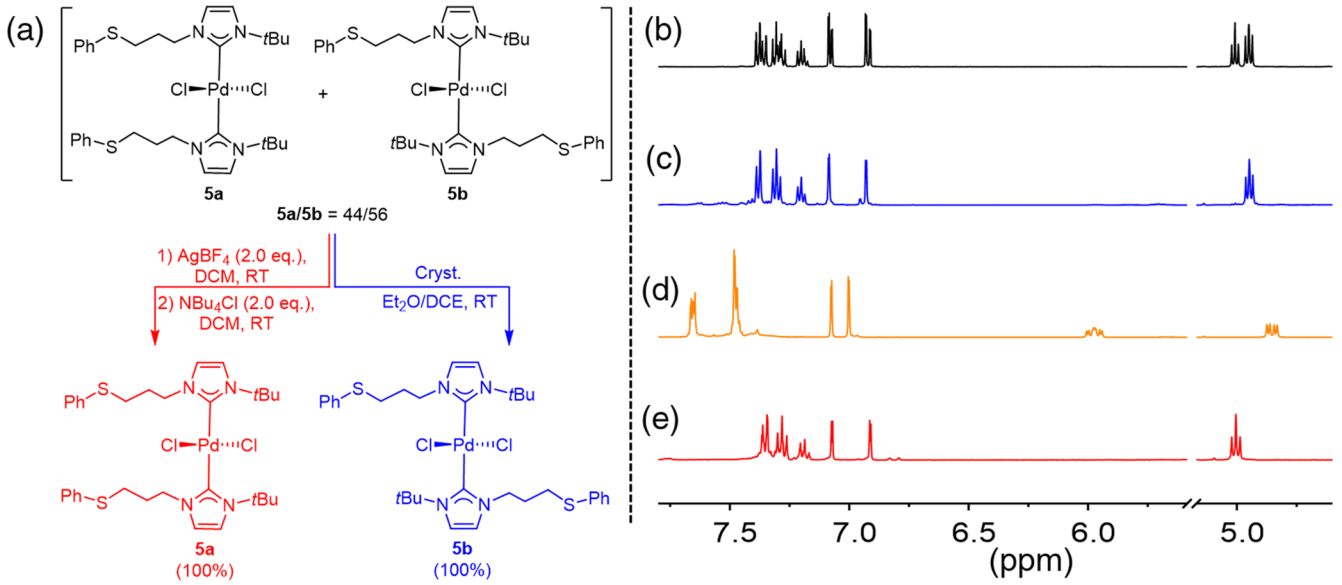

Figure 5. (a) Selective formation of **5a** and **5b** from the isomeric mixture via a chloride extraction/addition sequence and crystallization, respectively. ^{1}H NMR spectra of the complex in the (b) fully open form **5**, (c) crystallized fully open form **5b**, (d) fully closed form **7**, and (e) regenerated fully open form **5a**. All of the spectra were taken in CD_2Cl_2. Regions of the spectra between 1.0−4.6 and 5.2−5.6 ppm have been omitted for clarity.

spectra were recorded on a Bruker Advance 400 MHz spectrometer, a Bruker Advance III 500 MHz spectrometer, an Agilent DD 400 MHz spectrometer, and an Agilent DD2 500 MHz spectrometer. ^{1}H NMR spectra were referenced to residual protons in the deuterated solvents (chloroform-*d*, δ 7.26; dichloromethane-d_2, δ 5.32) internally. ^{13}C NMR spectra were referenced to residual carbons in the deuterated solvents (chloroform-*d*, δ 77.16; dichloromethane-d_2, δ 54.00) internally. Electrospray ionization (ESI) mass spectrometry (MS) spectra were recorded on an Agilent 6210 LC-TOF instrument in positive-ion mode.

Synthesis. *1-tert-Butylimidazole (1).* In a modified procedure, a solution of *tert*-butylamine (31.5 mL, 0.300 mol) in 40 mL of anhydrous ethanol (EtOH) was added dropwise to an ice-bath-cooled 250 mL flask containing a solution of paraformaldehyde (9.30 g, 0.310 mol) in anhydrous EtOH (40 mL). After the addition and once the solution reached 0 °C, ammonium carbonate (14.4 g, 0.150 mol) and a 40% glyoxal solution (34.4 mL, 0.300 mol) in 80 mL of anhydrous EtOH were added slowly. The reaction mixture was stirred overnight at room temperature, the solvent was removed in vacuo, and the crude oil was distilled under high vacuum (200 mTorr, 60 °C) to yield **1** as a yellow oil in 33% yield (12.5 g, 0.101 mol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.03 (dd, J = 1.1 and 1.1 Hz, 1H), 7.01 (dd, J = 1.3 and 1.2 Hz, 1H), 1.53 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 134.41, 129.14, 116.37, 54.79, 30.71.

Imidazolium Salt 2. 2-Chloroethyl phenyl sulfide (1.30 mL, 8.86 mmol) was added to a 25 mL flask containing a solution of **1** (1.00 g, 8.05 mmol) in anhydrous MeCN (8 mL). The resulting mixture was refluxed for 2 days, at which time the solvent was removed under reduced pressure to yield a dark-brown oil. The resulting residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 10/1) to afford the desired ligand **2** as a brown oil in 28% yield (0.661 g, 2.23 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.09 (s, 1H), 7.34−7.27 (m, 5H), 7.22−7.18 (m, 1H), 7.16 (s, 1H), 4.72 (t, J = 6.1 Hz, 2H), 3.63 (t, J = 6.1 Hz, 2H), 1.67 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.45, 133.99, 129.75, 129.54, 127.12, 123.23, 117.93, 60.62, 49.50, 34.44, 30.22. HRMS (ESI$^+$). Calcd for $C_{15}H_{21}N_2S$ ([M − Cl$^-$]$^+$): m/z 261.1420. Found: m/z 261.1416.

Imidazolium Salt 3. **1** (1.00 g, 8.05 mmol) and 3-chloropropyl phenyl sulfide (2.26 g, 12.1 mmol) were dissolved in anhydrous MeCN (8 mL). The resulting mixture was heated at reflux for 2 days. The solvent was removed under reduced pressure to yield a dark-brown oil. The resulting residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 10/1) to afford the desired ligand **3** as a brown oil in 75% yield (1.88 g, 6.06 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.74 (s, 1H), 7.32−7.21 (m, 6H), 7.15−7.12 (m, 1H), 4.56 (t, 2H, J = 7.1 Hz), 2.96 (t, 2H, J = 6.8 Hz), 2.23 (tt, 2H, J = 6.9 and 6.9 Hz), 1.64 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.01, 135.01, 129.79, 129.28, 126.70, 122.08, 119.11, 60.60, 50.69, 48.55, 30.18, 29.57. HRMS (ESI$^+$). Calcd for $C_{16}H_{23}N_2S$ ([M − Cl$^-$]$^+$): m/z 275.1576. Found: m/z 275.1578.

Fully Open Complex 4. Silver(I) oxide (39 mg, 0.165 mmol) was added to a 5 mL flask containing a solution of imidazolium salt **2** (89 mg, 0.300 mmol) in anhydrous DCM (3 mL), and the resulting mixture was stirred at room temperature for 6 h in the absence of light. The mixture was then filtered, and the filtrate was dried under reduced pressure to afford a silver carbene intermediate as a brown oil. In a 50 mL flask, silver carbene was dissolved in anhydrous MeCN (25 mL), and Pd(COD)Cl_2 (29 mg, 0.100 mmol) was added. The resulting mixture was heated at reflux for 2 days. The solvent was removed under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 10/1) to afford the desired product **4** as a yellow solid in 37% yield (26 mg, 0.0370 mmol). The product contained a mixture of two isomers (syn and anti). The assignment of these isomers was performed with the aid of NOE experiments (Figure S1). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.41−7.38 (m, 4H^{syn}, 4H^{anti}), 7.32−7.27 (m, 4H^{syn}, 4H^{anti}), 7.21−7.18 (m, 2H^{syn}, 2H^{anti}), 7.02 (d, 2H^{anti}, J = 2.0 Hz), 7.01 (d, 2H^{syn}, J = 2.0 Hz), 6.95 (d, 2H^{syn}, 2H^{anti}, J = 2.0 Hz), 5.04 (t, 4H^{syn}, J = 6.8 Hz), 5.01 (t, 4H^{anti}, J = 6.8 Hz), 3.85 (t, 4H^{syn}, J = 6.8 Hz), 3.72 (t, 4H^{anti}, J = 6.8 Hz), 2.03 (s, 18H^{anti}), 2.03 (s, 18H^{syn}). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 167.57 (syn), 167.55 (anti), 135.96 (anti), 135.80 (syn), 129.67 (syn and anti), 129.65 (anti), 129.55 (syn), 126.77 (anti), 126.75 (syn), 121.47 (anti), 121.07 (syn), 119.54 (anti), 119.24 (syn), 59.30 (anti), 59.14 (syn), 51.52 (anti), 51.45 (syn), 34.54 (anti), 34.34 (syn), 32.53 (anti), 32.32 (syn). HRMS (ESI$^+$). Calcd for $C_{30}H_{40}ClN_4PdS_2$ ([M − Cl$^-$]$^+$): m/z 663.1410. Found: m/z 663.1410. Single crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of diisopropyl ether into a solution of the fully open complex **4** in DCE.

Fully Open Complex 5. Silver(I) oxide (127 mg, 0.550 mmol) was added to a 10 mL flask containing a solution of imidazolium salt **3** (311 mg, 1.00 mmol) in anhydrous DCM (5 mL), and the resulting mixture was stirred at room temperature for 6 h in the absence of light. The mixture was then filtered, and the filtrate was dried under reduced pressure to afford a silver carbene intermediate as a brown oil. In a 50 mL flask, silver carbene was dissolved in anhydrous MeCN (20 mL), and Pd(COD)Cl_2 (82 mg, 0.286 mmol) was added. The resulting mixture was refluxed for 2 days. The solvent was removed under reduced

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pressure, and the resulting residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 10/1) to afford the desired product **5** as a yellow solid in 63% yield (130 mg, 0.180 mmol). The product contained a mixture of two isomers (syn and anti). The assignment of these isomers was performed with the aid of NOE experiments (Figure S3). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.39−7.35 (m, 4H^{syn}, 4H^{anti}), 7.32−7.27 (m, 4H^{syn}, 4H^{anti}), 7.22−7.17 (m, 2H^{syn}, 2H^{anti}), 7.09 (d, 2H^{anti}, J = 2.0 Hz), 7.07 (d, 2H^{syn}, J = 2.1 Hz), 6.93 (d, 2H^{anti}, J = 2.1 Hz), 6.91 (d, 2H^{syn}, J = 2.0 Hz), 5.01 (t, 4H^{syn}, J = 7.0 Hz), 4.95 (t, 4H^{anti}, J = 7.3 Hz), 3.05 (t, 4H^{anti}, J = 7.1 Hz), 3.00 (t, 4H^{syn}, J = 7.0 Hz), 2.50−2.40 (m, 4H^{syn}, 4H^{anti}), 2.01 (s, 18H^{anti}), 2.00 (s, 18H^{syn}). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 167.70 (syn and anti), 136.57 (anti), 136.47 (syn), 129.93 (syn), 129.88 (anti), 129.56 (syn), 129.55 (anti), 126.68 (syn), 126.65 (anti), 120.57 (anti), 120.10 (syn), 119.83 (anti), 119.55 (syn), 59.14 (anti), 59.07 (syn), 50.57 (anti), 50.45 (syn), 32.50 (anti), 32.34 (syn), 31.30 (syn), 31.19 (anti), 30.45 (anti), 30.10 (syn). HRMS (ESI$^+$). Calcd for $C_{32}H_{44}ClN_4PdS_2$ ([M − Cl^-]$^+$): m/z 691.1727. Found: m/z 691.1728. Single crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of diethyl ether into a solution of the fully open complex **5** in DCE.

Fully Closed Complex ***6***. Fully open complex **4** (18 mg, 0.026 mmol) and silver tetrafluoroborate (10 mg, 0.052 mmol) were mixed in anhydrous DCM (1 mL). The resulting mixture was stirred at room temperature for 10 min in the absence of light. The mixture was then filtered, and the filtrate was dried under reduced pressure to afford the desired product **6** as a light-yellow solid in 96% yield (20 mg, 0.026 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.73−7.09 (m, 14H), 5.50−4.47 (m, 4H), 3.80−3.19 (m, 4H), 1.61−1.21 (m, 18H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 132.50, 131.48, 131.28, 131.22, 130.88, 129.15, 125.04, 124.26, 123.11, 122.44, 60.75, 59.99, 31.89, 31.20, 30.25, 29.99. HRMS (ESI$^+$). Calcd for $C_{30}H_{40}FN_4PdS_2$ ([M − 2BF_4^- + F^-]$^+$): m/z 645.1713. Found: m/z 645.1719. Single crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of diethyl ether into a solution of the fully closed complex **6** in MeCN.

Fully Closed Complex ***7***. The fully open complex **5** (20 mg, 0.028 mmol) and silver tetrafluoroborate (11 mg, 0.056 mmol) were mixed in anhydrous DCM (3 mL). The resulting mixture was stirred at room temperature for 1 h in the absence of light. The mixture was then filtered, and the filtrate was dried under reduced pressure to afford the desired product **7** as a light-yellow solid in 98% yield (23 mg, 0.027 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.73−7.60 (m, 4H), 7.54−7.36 (m, 6H), 7.08 (d, J = 2.0 Hz, 2H), 7.03 (d, J = 2.0 Hz, 2H), 5.96 (ddd, J = 14.9, 12.2, and 5.0 Hz, 2H), 4.85 (dd, J = 15.0 and 6.2 Hz, 2H), 3.22 (ddd, J = 14.5, 4.4, and 2.7 Hz, 2H), 2.51−2.42 (m, 2H), 2.34−2.17 (m, 2H), 1.94 (ddd, J = 14.5, 12.3, and 4.4 Hz, 2H), 1.79 (s, 18H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 155.33, 133.49, 132.94, 130.98, 127.17, 124.35, 123.15, 60.27, 48.96, 41.00, 32.30, 23.99. HRMS (ESI$^+$). Calcd for $C_{32}H_{44}BF_4N_4PdS_2$ ([M − BF_4^-]$^+$): m/z 741.2087. Found: m/z 741.2082. Single crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of diethyl ether layered over a solution of the fully closed complex **7** in DCM.

X-ray Crystallography. Single crystals **4b** and **6** were mounted on a glass fiber in Parabar oil on a Kappa Apex 2 diffractometer, while single crystals **5b** and **7** were mounted on a MITIGEN holder in Parabar oil on a Kappa Apex 2 diffractometer. All of the measurements were made with graphite-monochromated Mo Kα (for **4b**, **5b**, and **6**) or Cu Kα (for **7**) radiation. All of the 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

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00543.

Experimental details, including 1D NOE spectra, kinetic experiments, reversibility of the structural changes, and NMR and mass spectra (PDF)

Crystallographic data for complex **4b** in CIF format (CIF)

Crystallographic data for complex **5b** in CIF format (CIF)

Crystallographic data for complex **6** in CIF format (CIF)

Crystallographic data for complex **7** in CIF format (CIF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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