Triple-Decker Complexes Formed via the Weak Link Approach

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Summary: Through the weak link approach and a halide-induced ligand rearrangement process, semi-open and condensed triple-decker complexes (TDCs) were prepared and fully characterized. These triple-decker structures with tailorable layers through choice of hemilabile ligand starting materials can be chemically opened and closed to expose the interior layer in a reversible fashion using small-molecule and elemental anion ligand substitution reactions.

Supramolecular cyclophanes and tweezer complexes have received a significant amount of attention, due to their encapsulating properties and potential applications in catalysis, sensing, mixture separation, molecular electronics, and facilitated small-molecule transport.[1,2] Recently, we have shown that one can prepare mimics of allosteric enzymes by creating multimetallic structures with distinct and chemically addressable shape-regulating and catalytic sites.[3] These systems typically rely on the use of macrocycles or tweezers with catalytic pockets that can be turned on and off through the reaction of small molecules or anions with sites that open or close the supramolecular entity. These systems all rely on catalysts that function in a bimetallic fashion. An alternative strategy to realizing allosteric enzyme mimics would be to create a reactive site that is blocked above and below with chemically inert entities in the form of a triple-decker complex with chemically displaceable top and bottom layers. At present, there are no methods for reliably synthesizing such structures. Herein, we describe an approach to such complexes that utilizes the weak link approach (WLA) for synthesizing supramolecular tweezer complexes[2−5]

Scheme 1. On/Off Regulation of the Central Functional Group via a Blocking Mechanism
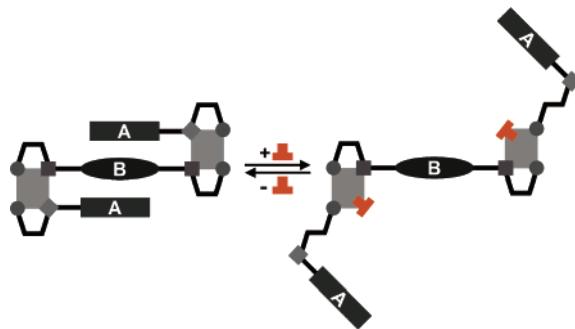
and a halide-induced ligand rearrangement process[6] that allows one to realize triple-decker structures with chemically tailorable layers through the choice of hemilabile ligand starting materials. Importantly, these structures can be chemically opened and closed to expose the interior layer in a reversible fashion using small-molecule and elemental anion ligand substitution reactions (Scheme 1). This work opens the door to synthesizing allosteric structures with single sites that can be reversibly activated and

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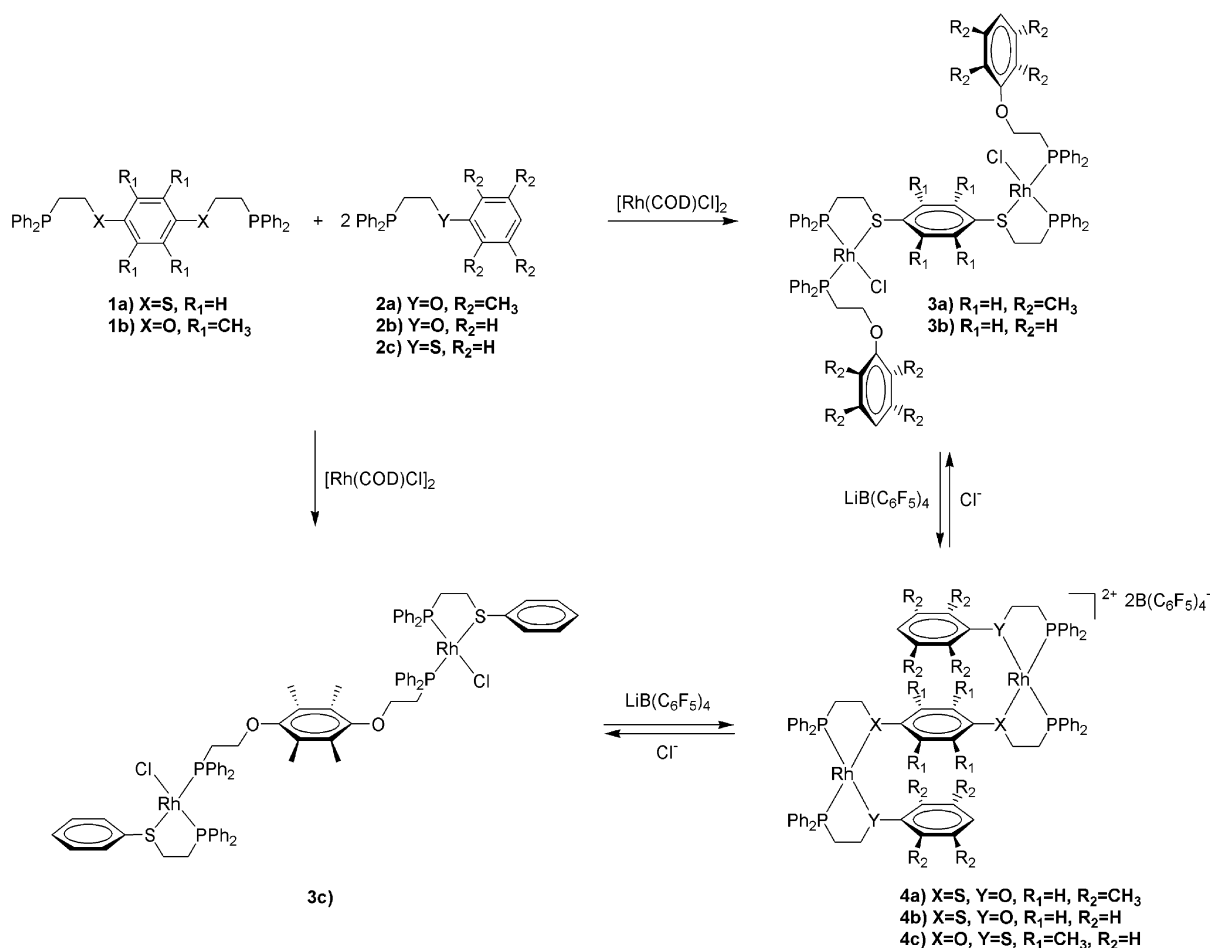
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Scheme 2.   Synthesis of Triple-Decker Complexes

deactivated through small-molecule reactions that assemble and disassemble the novel trilayer structures.

The neutral heteroligated bimetallic semi-open triple-decker complexes (TDCs) were synthesized according to the procedure for preparing heteroligated monometallic Rh(I) tweezers, from stoichiometric amounts of the corresponding bidentate and monodentate hemilabile ligands $Ph_2P(CH_2)_2X(C_6(R_1)_4)X-(CH_2)_2PPh_2$ and $Ph_2P(CH_2)_2YC_6H(R_2)_4$ and $[Rh(COD)Cl]_2$ (COD = cyclooctadiene) in CH_2Cl_2 at room temperature (Scheme 2).[6]

All spectroscopic data, including ^{1}H NMR spectroscopy, ^{31}P{^{1}H} NMR spectroscopy, and ES-MS, are in full agreement with the proposed formulations. For example, the ^{31}P{^{1}H} NMR spectrum of **3a** exhibits highly diagnostic resonances at δ 73.4 (dd, η^2-PS, J_{Rh-P} = 183 Hz, J_{P-P} = 41 Hz) and δ 25.8 (dd, η^1-PO, J_{Rh-P} = 167 Hz, J_{P-P} = 41 Hz), indicative of the two inequivalent phosphorus atoms in the semi-open Rh(I) complex.[6,7] The solid-state structure of **3a**, determined by single-crystal X-ray diffraction, is consistent with its proposed solution structure (Figure 1).[8] Each of the Rh(I) centers is coordinated by η^2-PS, η^1-PO, and Cl⁻ moieties in a distorted-square-planar geometry with Cl(1)−Rh(1)−P(2) and Cl(1)−Rh(1)−S(1) angles of 89.5 and 86.0°, respectively. This coordination geometry is very similar to that of previously reported semi-open Rh(I) macrocycles and tweezers.[6] The two Rh(I) metals

reside above and below the plane of the central aromatic bridge, most likely due to the steric limitations of having a cofacial arrangement. The Rh−Rh distance is 9.31 Å.

The condensed cationic Rh(I) TDCs **4a**−**c** were synthesized by the abstraction of Cl⁻ ions from the corresponding complexes **3a**−**c** with a small excess of $LiB(C_6F_5)_4$ in CH_2Cl_2 (Scheme 2).[6] The remaining $LiB(C_6F_5)_4$ was removed by washing with dry benzene. All data for these compounds are consistent with the proposed formulations as well. ^{1}H NMR spectroscopy is diagnostic of Cl⁻ abstraction and the trilayer structure formation. For example, the resonance due to the aryl protons of the central arene and the resonance for the *p*-H atoms of the upper and lower aromatic rings of the trilayer were shifted upfield by 1.29 and 0.24 ppm, respectively. These upfield shifts are diagnostic of aromatic π−π stacking.[9] Furthermore, a 2D NOESY experiment of **4a** in CD_2Cl_2 clearly shows NOE cross-peaks between H_a and H_b (H_a = protons of the central aromatic ring, H_b = methyl protons of the upper/lower methylated aromatic rings)

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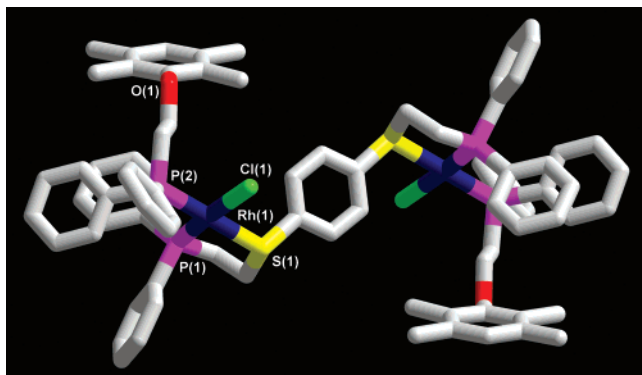
(8) (a) Crystal data for **3a** (CCDC-287009): $C_{90}H_{106}Cl_2O_4P_4Rh_2S_2$, monoclinic, space group $P2_1/c$, a = 17.497(5) Å, b = 14.530(4) Å, c = 16.851(5) Å, β = 104.004(5)°, V = 4157(2) Å³, Z = 2, T = 153(2) K, $2\theta_{max}$ = 57.7°, Mo Kα (λ = 0.710 73 Å). R1 = 0.0443 (for 6715 reflections with $I > 4\sigma(I)$), wR2 = 0.1018, and S = 1.012 for 475 parameters and 9840 unique reflections. (b) Crystal data for **4a** (CCDC-287010): $C_{130}H_{86}B_2$-$F_{40}O_2P_4Rh_2S_2$, triclinic, space group $P\bar{1}$, a = 12.6015(10) Å, b = 16.0906(13) Å, c =17.2636(14) Å, α = 110.401(1)°, β = 105.726(1)°, γ = 102.030(1)°, V = 2974.8(4) Å³, Z = 1, T = 153 K, $2\theta_{max}$ = 57.84°, Mo Kα (λ = 0.710 73 Å). R1 = 0.0501 (for 9401 reflections with $I > 2\sigma(I)$), wR2 = 0.1106, and S = 0.964 for 820 parameters and 14 003 unique reflections.

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Figure 1. Stick representation for the crystal structure of **3a**. Hydrogen atoms and a solvent molecule (diethyl ether) have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−P(1) = 2.1964(10), Rh(1)−P(2) = 2.2527(9), Rh(1)−S(1) = 2.3419(10), Rh(1)−Cl(1) = 2.3945(9), Rh···Rh = 9.313(6); P(1)−Rh(1)−P(2) = 98.50(4), P(1)−Rh(1)−S(1) = 86.46(4), P(2)−Rh(1)−Cl(1) = 89.49(4), S(1)−Rh(1)−Cl(1) = 85.99(4), P(2)−Rh(1)−S(1) = 173.65(3), P(1)−Rh(1)−Cl(1) = 170.26(3).
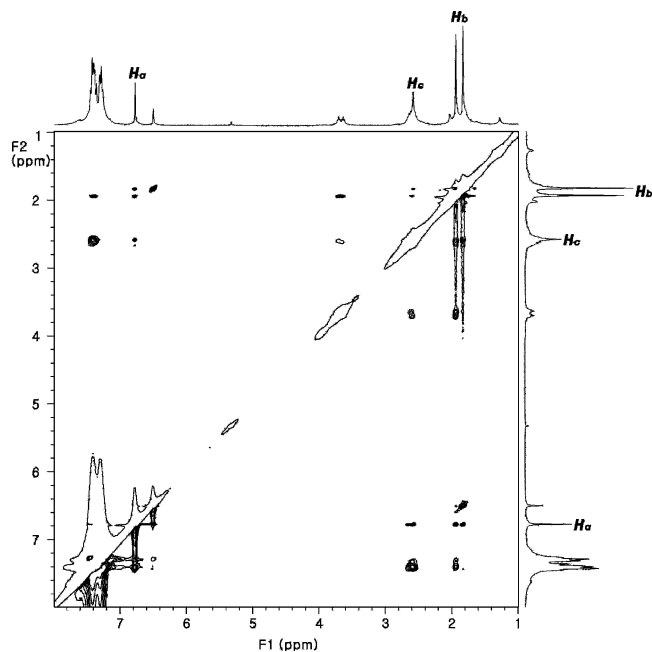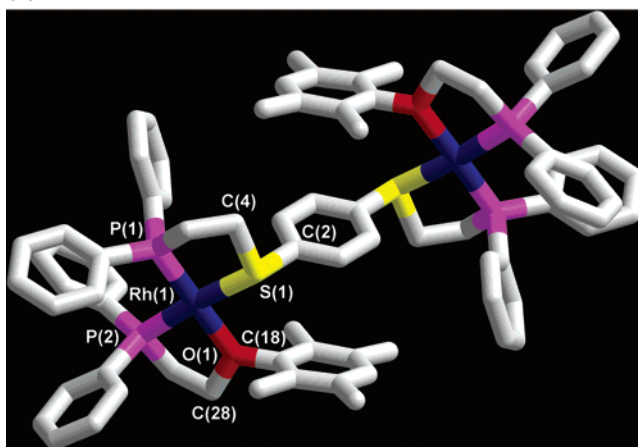

Figure 2. NOESY spectrum of **4a** in CD$_2$Cl$_2$ (H$_a$ = the protons of the central aromatic ring, H$_b$ = methyl protons of the upper/lower methylated aromatic rings, H$_c$ = methylene protons α to sulfur).

and between H$_b$ and H$_c$ (H$_c$ = methylene protons α to sulfur), showing that the three aromatic rings are stacked on top of one another (Figure 2).[10] Consistent with this conclusion, the corresponding semi-open complex **3a**, which does not have closely spaced aromatic rings, does not show a similar NOE correlation. The ^{31}P{^{1}H} NMR spectrum of complex **4a** exhibits two resonances at δ 72.7 (dd, $J_{Rh−P}$ = 197 Hz, $J_{P−P}$ = 42 Hz) and δ 53.0 (dd, $J_{Rh−P}$ = 170 Hz, $J_{P−P}$ = 42 Hz), corresponding to the P atom of the η^2-PS ligand and the P atom of the η^2-PO chelating ligand, respectively.[6,7]

The reactions to form the trilayer structures are completely reversible. Indeed, when **4a**−**c** were treated with stoichiometric

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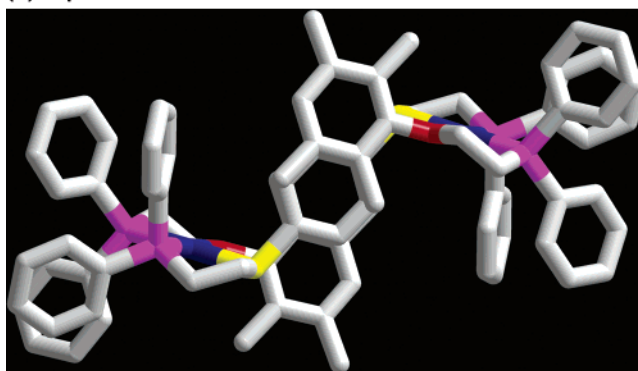
(a) Side View

(b) Top View

Figure 3. Stick representations for the crystal structure of **4a**: (a) side view; (b) top view. Hydrogen atoms and counteranions (B(C$_6$F$_5$)$_4$$^-$) have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−P(1) = 2.1814(9), Rh(1)−P(2) = 2.2356(8), Rh(1)−S(1) = 2.3488(8), Rh(1)−O(1) = 2.161(2), Rh···Rh = 9.154(8); P(1)−Rh(1)−P(2) = 98.66(3), P(1)−Rh(1)−S(1) = 86.46(3), P(2)−Rh(1)−O(1) = 82.49(6), O(1)−Rh(1)−S(1) = 92.40(6), P(1)−Rh(1)−O(1) = 178.84(6), P(2)−Rh(1)−S(1) = 174.56(3).

amounts of tetrabutylammonium chloride in CD$_2$Cl$_2$, the corresponding semi-open complexes **3a**−**c** were formed in quantitative yields, as evidenced by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.[6,7]

For **4a**, the trilayer structure was confirmed by a single-crystal X-ray diffraction study (Figure 3).[8] As indicated by the solution NMR data, each of the Rh(I) metal centers is coordinated by η^2-PS and η^2-PO ligands in a distorted-square-planar geometry with P(1)−Rh(1)−S(1) and P(2)−Rh(1)−O(1) angles of 86.5 and 82.5°, respectively. In addition, the intermetallic distance, 9.15 Å, is slightly shorter than that of the corresponding semi-open Rh(I) TDC **3a**, 9.31 Å. While the oxygen center has a distorted-trigonal-planar geometry, the sum of the bond angles around the coordinating oxygen is 358.7°, indicating that Rh(1), O(1), C(18), and C(28) constitute a common plane. The coordinating sulfur atom has a trigonal-pyramidal geometry with C(2)−S(1)−Rh(1), C(2)−S(1)−C(4), and C(4)−S(1)−Rh(1) angles of 110.5, 100.3, and 100.5° respectively. Therefore, in the solid state, the three aromatic rings that make up the trilayer are in a three-step configuration with a torsion angle of 60.9°. This is clearly shown in a top view of **4a** (Figure 3b). This is in contrast with the solution structure of **4a**, which indicates fast rehybridization and coordination to the Rh centers resulting in an average structure characterized by three symmetrical stacking aromatic rings (e.g., the two methyl groups in the outer

aromatic rings are in an equivalent chemical environment, as determined by NMR spectroscopy). This is a fast process where the interconverting structure could not be observed by low-temperature ^{1}H NMR spectroscopy. Indeed, the signals for the two methyl groups at −60 °C only broaden, with no definitive identification of the two exchanging isomers. In the solid-state structure of **4a**, the two outer oxy-aromatic rings are parallel to each other and are separated by ∼7.73 Å. The central aromatic ring is equidistant to the other two rings and 16.7° from being parallel planar with them. The average interplane distance in **4a** is ∼3.86 Å, which is ∼0.34 Å shorter than that of the coordination-mediated triple-decker Rh(I) metallacyclophanes, ∼4.20 Å,[4] but slightly longer than those of the corresponding condensed Rh(I) macrocycles, 3.51 and 3.59 Å, respectively.[11]

This work is important for the following reasons. First, it demonstrates that one can construct triple-decker complexes via the WLA in a few steps and in high yield in a chemically reversible fashion. Second, the ability to systematically and convergently introduce different functional groups into an A−B−A triple-layered structure via coordination chemistry provides an advantage over serial organic chemistry approaches to analogous structures. Third, the metal centers and hemilabile ligands in such structures allow one to chemically address the metal sites in a way that allows one to controllably protect and expose the central aromatic ring of the trilayer structure. Therefore, this approach provides a blueprint for synthesizing and evaluating a new class of trilayered structures with chemical and physical (electron transfer and optical) properties that can be selectively turned on and off through the reversible formation of the trilayer unit. Note that it has been shown that one can build hemilabile ligands with catalytic salen complexes in place of the bridging aromatic ring used in these studies.

Supporting Information Available: Text giving details of the synthesis and characterization of the compounds prepared in this paper and a CIF file giving crystallographic data for **3a** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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