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Heteroligated Supramolecular Coordination Complexes Formed via the Halide-Induced Ligand Rearrangement Reaction

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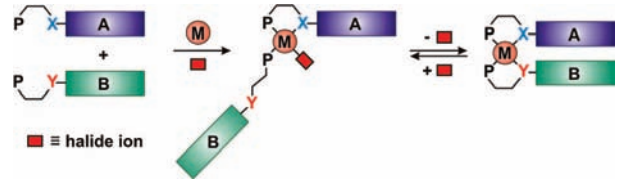

Supramolecular coordination chemistry allows researchers to synthesize higher-order structures that approach the nanoscale dimensions of small enzymes. Frequently, such structures have highly symmetric macrocyclic square or cage shapes. To build functional structures that mimic the complex recognition, catalytic, and allosteric properties of enzymes, researchers must do more than synthesize highly symmetric nanoscale structures. They must also simultaneously incorporate different functionalities into these structures and learn how to regulate their relative arrangement with respect to each other. Designing such *heteroligated* coordination complexes remains a significant challenge for supramolecular chemists.

This Account focuses on the discovery and development of a novel supramolecular reaction known as the halide-induced ligand rearrangement (HILR) reaction. Two hemilabile ligands with different binding strengths combine with d^8 transition metal precursors that contain halide ions. The reaction spontaneously results in heteroligated complexes and is highly modular and general. Indeed, it not only can be used to prepare tweezer complexes but also allows for the rapid and quantitative formation of heteroligated macrocyclic triple-decker/step and rectangular box complexes from a variety of different ligands and transition metal ions. The relative arrangement between functional groups A and B in these structures can be regulated *in situ* using small ancillary ligands such as halides, CO, and nitriles.

Based on this reaction, zinc- and magnesium-porphyrin moieties can be incorporated into heteroligated macrocyclic or tweezer scaffolds. These examples demonstrate the convergent and cofacial assembly of functional sites that are known to be involved in numerous processes in enzymes. They also show how the relative spatial and lateral distances of these sites can be varied, in many cases reversibly. Researchers can use such complexes to study a wide range of enzymatic processes, including catalysis, molecular recognition, electron transfer, and allosteric signal transfer.

Introduction

Over the past few years, coordination chemistry-based synthetic methodologies have become increasingly attractive for the design of supramolecular complexes.[1−11] Two of the most commonly used methods for preparing supramolecular coordination complexes are the directional bonding[5−10] and symmetry interaction[2,3,11] approaches. These methods rely on rigid ligands with strategically located functional groups and metal complexes with available coordination sites to form the desired structures. These approaches often provide access to highly symmetric structures with rigid, well-defined cavities that impart unique chemical reactivity, with respect to catalysis[12−18] and molecular recognition.[19−22] Our group has focused on developing a synthetic methodology known as the weak-link approach (WLA),[1,4,23] which uses flexible hemilabile ligands **1** (Scheme 1) along with simple transition metal precursors to access structurally flexible supramolecular structures. Traditionally, the WLA has pro-

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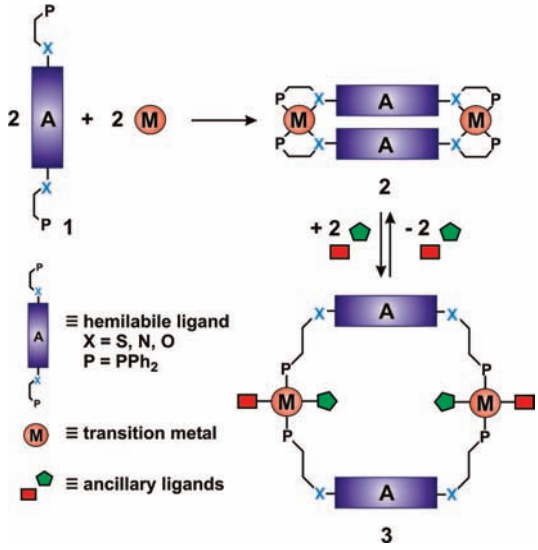
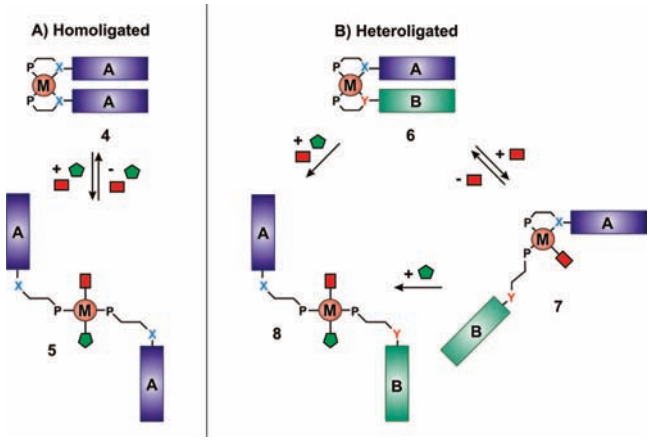
SCHEME 1. Formation of Supramolecular Macrocycles via the WLA



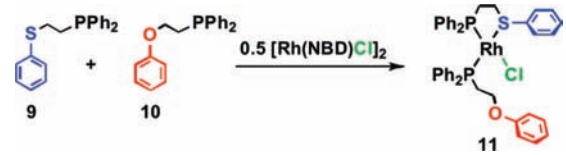
SCHEME 2. (A) Homoligated Tweezer Complexes Formed via the Conventional WLA and (B) Heteroligated Tweezer Complexes Formed via the WLA and HILR



vided access to *symmetric*, homoligated supramolecular complexes, which are capable of adopting two different conformations: closed (**2**) and open (**3**) (Scheme 1). The ability to toggle between these two different conformations *in situ* via the addition or removal of chemical stimuli has enabled our group to design the first examples of supramolecular allosteric enzyme mimics,[24–29] which when properly designed can provide a means of signal amplification in the context of chemical sensing.[30,31]

A significant advance in the field of supramolecular chemistry would be the development of methodologies that expand synthetic capabilities from homoligated structures with two accessible states (**4** and **5**, Scheme 2A) to heteroligated[32] architectures capable of undergoing multiple *in situ* transformations (**6**–**8**, Scheme 2B), providing control over the interactions of two different functionalities, **A** and **B**. The ability to

SCHEME 3. The Halide-Induced Ligand Rearrangement (HILR)



target heteroligated structures containing two unique ligands with similar coordination motifs[33–39] represents a significant challenge, with most methods involving multiple, often low yielding, steps with major product separation and isolation difficulties.

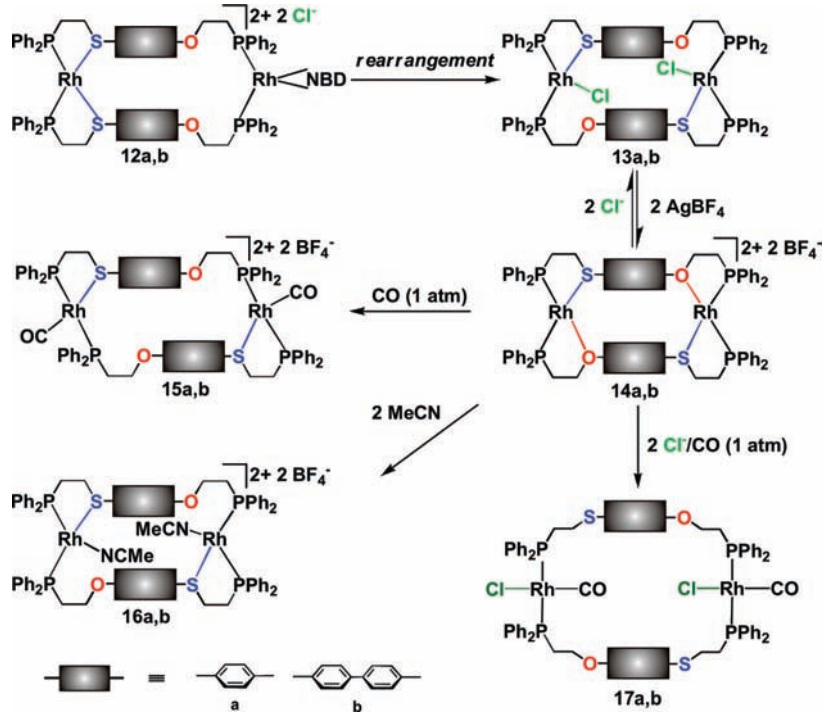
Recently, our group has discovered and developed a reaction known as the halide-induced ligand rearrangement (HILR), which allows one to access such complexes (Scheme 3).[40,41] Therefore, these complexes can be chemically modified *in situ* to form closed (**6**), semiopen (**7**), and open (**8**) forms (Scheme 2B). The reaction allows for the cofacial arrangement of two different ligands in which the interactions between these ligands can be adjusted by the addition of small molecule chemical regulators. Indeed, we have shown that this capability can be used to realize a new class of allosteric enzyme mimics where a reactive pocket can be formed and destroyed through reactions that occur at the allosteric regulatory site, which is the metal hinge in this case (Scheme 2A).[27]

Over the past several years, we have evaluated the generality of this rearrangement process by (1) using a wide variety of ligands with significantly different physical and chemical properties (i.e., size, shape, electronics, sterics, and symmetry) and (2) studying the effect of using different transition metal ions for the assembly of these complexes. Herein, we describe the development of several high-yielding ligand rearrangement processes and their ability to provide access to supramolecular assemblies that can incorporate many different functional sites, which can be used in molecular recognition, detection, catalysis, and electron transfer. The examples presented illustrate the high degree of selectivity and molecular diversity afforded by the HILR. Moreover, the supramolecular products obtained show how one can use external chemical stimuli to effectively regulate structural changes within these complexes.

The Halide-Induced Ligand Rearrangement (HILR)

Macrocyclic Complexes. Our initial discovery of this rearrangement reaction originated from studying a series of ligands that contain both thioether–phosphine (PS) and ether–phosphine (PO) hemilabile coordination domains.[40] Upon addition of the appropriate amounts of the desired

SCHEME 4. The HILR for Macrocyclic Complexes



hemilabile ligand and $[Rh(NBD)Cl]_2$ (NBD = 2,5-norbornadiene) in CH_2Cl_2, the initial homoligated complexes **12a**,**b** (Scheme 4) are formed. Interestingly, the $^{31}P\{^1H\}$ NMR spectroscopic resonances corresponding to the homoligated PS and PO moieties gradually disappear over several hours (time varies for each ligand set) with a concomitant appearance of a pair of doublet of doublets at $\sim\delta$ 73 and 32, corresponding to complexes **13a**,**b**, indicating the formation of the heteroligated macrocycles. Although the phenyl (**13a**) and biphenyl (**13b**) macrocycles were insoluble in common organic solvents (i.e., CH_2Cl_2 and THF), crystals of **13a**, isolated as a precipitate, allowed for a single-crystal X-ray diffraction study (Figure 1A), which confirms the formation of the heteroligated product and is consistent with the solution structure deduced from spectroscopic data.

A key attribute of the complexes formed using this reaction is the combination of both S and O coordination about the Rh^I metal center. Abstraction of the Cl^- ligand bound to the Rh^I centers of **13a**,**b** results in the corresponding condensed macrocyclic products **14a**,**b**. Since the Rh−O bonds are weaker than the Rh−S bonds in **14a**,**b**, they can be cleaved selectively using Cl^- to form **13a**,**b**, CO to form **15a**,**b**, or monodentate N-donors (pyridines and nitriles) to form **16a**,**b**, leaving the Rh−S bonds intact. The ability to selectively cleave the Rh−O bonds in **14a**,**b** without disrupting the Rh−S bonds not only allows one to easily regulate the aryl−aryl distance in this class of complexes (the vertical component) and therefore the size of the cavity of the resulting structure but also provides an orthogonal means to tailor the resulting structures via modification of the coordination environment at the structural site (the lateral component). For example, when Cl^- or monodentate N-donors are used, the P−Rh−P geometry adopts a *cis* configuration (**13a**,**b** or **16a**,**b**, respectively), whereas addition of CO (1 atm) converts the

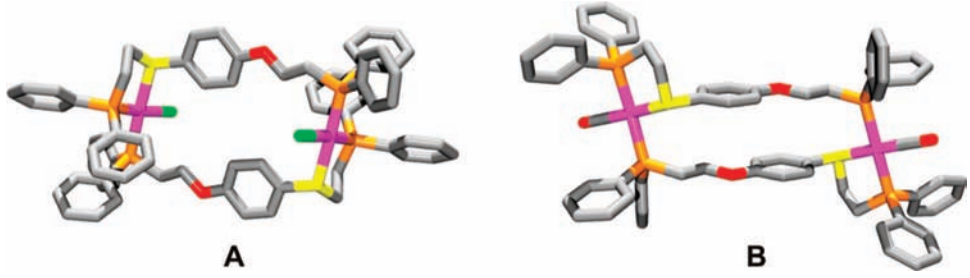
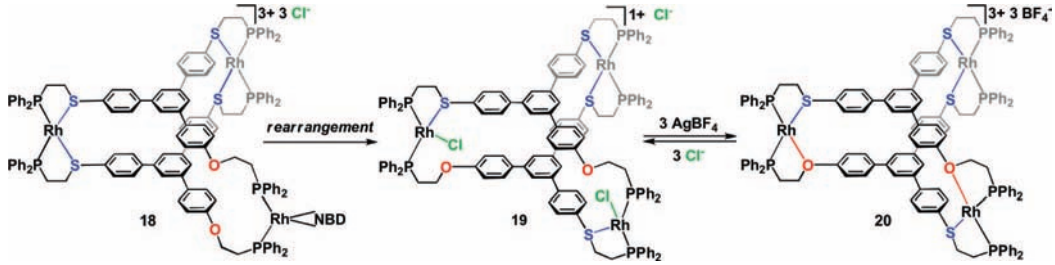


FIGURE 1. Stick representations for the crystal structures of **13a** (A) and **15a** (B). Color scheme: Rh (pink), C (gray), P (orange), S (yellow), O (red), and Cl (green).

SCHEME 5. The HILR for a Three-Dimensional Complex



P−Rh−P geometry from *cis* to *trans* (**15a**,**b**), as confirmed by X-ray crystallography (Figure 1B). While the Rh−O bonds in **14a**,**b** can be selectively cleaved to yield the semiopen complexes **15a**,**b** or **16a**,**b**, the fully open complexes **17a**,**b** can be formed via the addition of Cl^-/CO (1 atm) to the corresponding closed complexes **14a**,**b** or by the addition of CO (1 atm) to **13a**,**b**. The study also showed that the supramolecular ligand rearrangement process is induced by halide ions (Cl^-, Br^-, and I^-), but not by several weakly or noncoordinating anions (BF_4^-, PF_6^- and $B(ArF)_4^-$ ($B(ArF)_4^-$ = B[3,5-$(CF_3)_2(C_6H_3)]_4^-$)).[40]

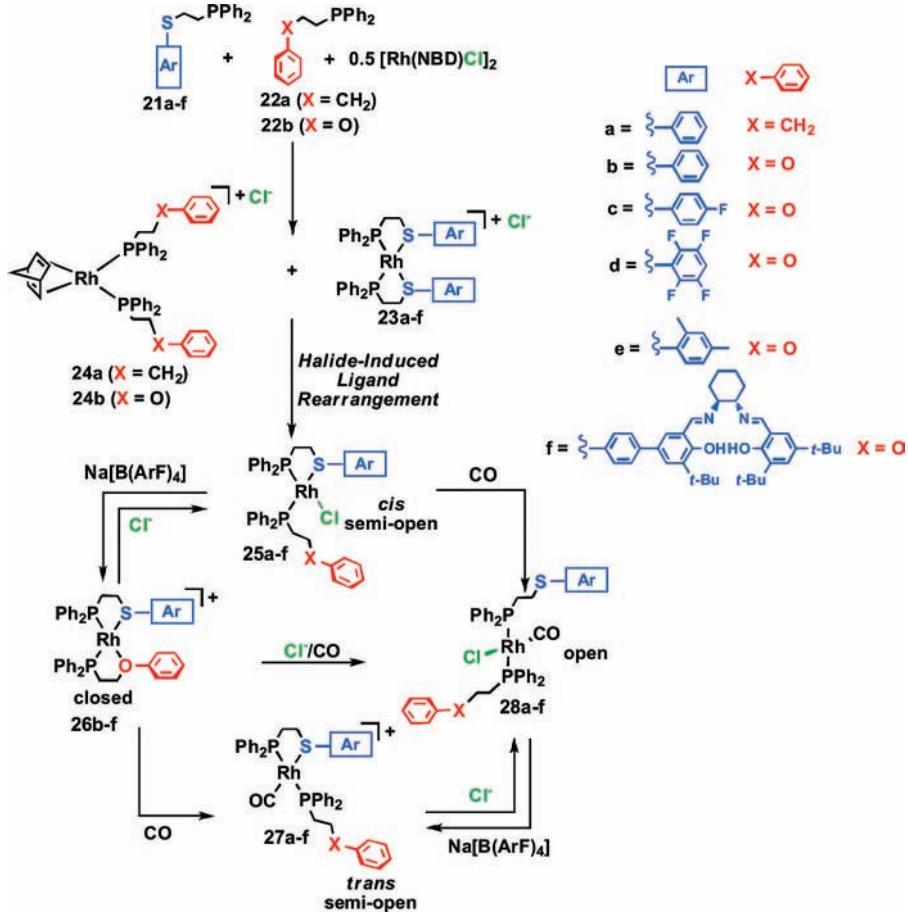
We have shown that the HILR also works with larger polydentate structures.[40] For example, a 1,3,5-triphenylbenzene ligand containing two PS coordination domains and one PO coordination domain was synthesized and used to prepare trimetallic Rh^I complex **19** (Scheme 5). $^{31}P\{^1H\}$ NMR data show this complex also forms in a stepwise manner via the initial homoligated complex **18**. Complex **19** undergoes a pattern of reactivity similar to the two-dimensional complexes **13a**,**b**, resulting in fully closed complex **20** upon abstraction of chloride with $AgBF_4$ (one homoligated Rh(κ^2-PS)$_2$ site in **18**−**20** remains unchanged). The observation of the HILR in trimetallic complexes was the first indication of the versatility of the rearrangement to generate multimetallic structures.

Tweezer Complexes. While the macrocyclic complexes described in the previous section provide a convenient approach for regulating the degree of cooperativity between two functional groups, they do not allow for the creation or total destruction of a reactive pocket, as observed in tweezer structures (Scheme 2). Such a phenomenon has been shown to have a significant effect on the rate of catalysis and enantioselectivity for a bimetallic epoxide ring-opening reaction.[27] Indeed, the design of such tweezer complexes could become a general strategy for preparing new supramolecular sensors and allosteric enzyme mimics, a topic covered in a previous Account.[23] In principle, the design of heteroligated tweezer complexes would allow for a gradual *in situ* switching among the following conformations: (1) those that possess a well-defined cavity incorporating two groups **A** and **B** in close proximity (**6**, Scheme 2B), (2) highly flexible open structures where groups **A** and **B** interact to a lesser degree or do not interact at all (**8**, Scheme 2B), and (3) intermediate structures in which only one arm is flexible (**7**, Scheme 2B). Furthermore, our group has previously demonstrated that moving from a macrocyclic- to a tweezer-based system often provides coordination complexes that are more soluble in common organic solvents.[27] Additionally, ligands containing one hemilabile coordination domain are typically easier to synthesize than those that contain two, an important consideration as the complexity of the target supramolecular systems increases.

In order to glean more information regarding the effect of electronics and sterics on this reaction, a series of thioether−phosphine tweezer ligands were prepared and studied in the context of the HILR (**21a**−**f**, Scheme 6).[41] Upon reaction of the appropriate combination of thioether−phosphine ligands **21a**−**f** with phenyl-based tweezer ligands **22a**,**b** and $[Rh(NBD)Cl]_2$, the corresponding heteroligated RhCl(κ^2-PS)(κ^1-PO) complexes **25a**−**f** formed in quantitative yield over a 4−18 h period as indicated by $^{31}P\{^1H\}$ NMR spectroscopy and X-ray crystallography (Figure 2). $^{31}P\{^1H\}$ NMR spectroscopy shows that the reaction proceeds via a process that is analogous to the one for the corresponding macrocyclic structures, in that the initial homoligated cationic tweezer products **23a**−**f** and **24a**,**b** form and react with one another over time to yield the desired heteroligated tweezer complexes **25a**−**f**. The half-lives ($t_{1/2}$) measured for each ligand combination indicate that the reaction is accelerated for ligands containing electron-deficient substituents on the aromatic groups appended to the thioether−phosphine moieties. Similar to the macrocyclic complexes, when noncoordinating, nonhalide counterions are used (e.g., BF_4^-), the rearrangement process is not observed. Interestingly, the reaction still proceeds in the absence of an ether moiety (**22a**) and in the presence of sterically demanding ligands (**21e**,**f**), illustrating the potential for incorporating a variety of different ligands and functional groups around the Rh^I metal center.

Compounds **25b**−**f** (but not **25a** where X = CH_2) can be converted to the corresponding cationic complexes **26b**−**f** via

SCHEME 6. Heteroligated Tweezer Complexes Formed via the HILR



abstraction of Cl^- using a stoichiometric amount of $Na[B(ArF)_4]$. This transformation can be accomplished reversibly via the successive addition and abstraction of Cl^-. Addition of CO (1 atm) to a solution of complexes **26b**−**f** results in the quantitative formation of the corresponding cationic products **27b**−**f** and also induces a change in geometry of the P−Rh−P coordination from *cis* to *trans*. The fully open complexes **28a**−**f** can be generated via (1) the addition of CO (1 atm) to solutions of **25a**−**f**, (2) the addition of Cl^- to solutions of **27a**−**f**, or (3) the addition of Cl^- and CO to solutions of **26b**−**f**. As these data illustrate, once the tweezer complexes **26b**−**f** have been formed, they can be converted *in situ* to different structures, allowing for the facile control of the aryl−aryl interactions via small molecule reactions at the Rh^I structural site.

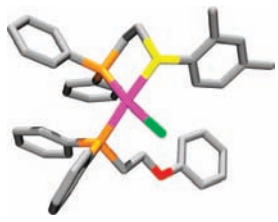
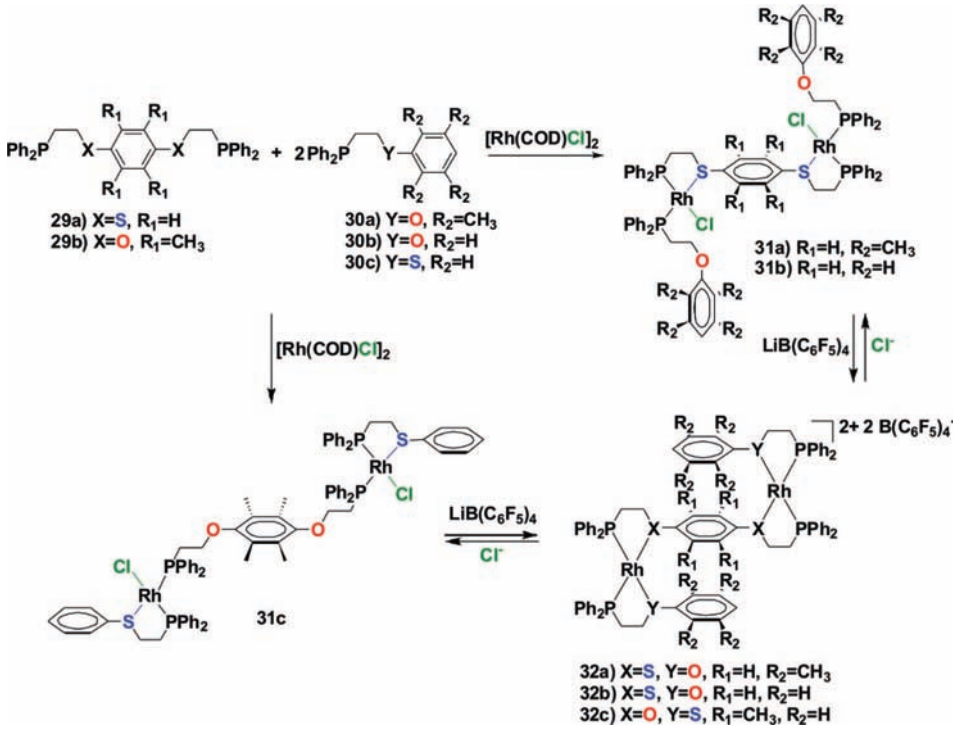


FIGURE 2. Stick representation for the crystal structure of **25e**. Color scheme: Rh (pink), C (gray), P (orange), S (yellow), O (red), and Cl (green).

Triple-Decker/Step Complexes. When the WLA is used to synthesize tweezer and macrocycle complexes that behave as abiotic allosteric enzyme mimics, the design of complexes capable of facilitating a bimetallic reaction has become a necessity. Indeed, we have shown that one can construct reactive pockets in molecules that facilitate catalytic acyl transfer[25,30,31] and epoxide ring opening reactions.[27,28] Small molecules that change the conformation or destroy these pockets significantly affect the rate and in certain cases enantioselectivities of the reactions.[25,27−31] Since there are a relatively few documented bimetallic/multimetallic[42−44] catalytic processes compared with reactions catalyzed by a monometallic species, it would be advantageous to design complexes whereby a catalyst or functional group can be activated or deactivated via steric blocking. In principle, a triple-decker type structure would allow for regulation of the interactions around an active catalytic site via the addition or removal of the appropriate chemical effector molecules.

SCHEME 7. Triple-Decker/Step Complexes Prepared via the HILR



In this regard, we have discovered that upon addition of both a suitable symmetric thioether−phosphine (or ether−phosphine) hemilabile ligand (i.e., **29a**,**b**, Scheme 7) typically used to prepare macrocycles and an ether−phosphine (or thioether−phosphine) hemilabile ligand (i.e., **30a**−**c**) typically used to form tweezer complexes to a solution containing $[Rh(COD)Cl]_2$, the corresponding heteroligated complexes **31a**−**c** form in quantitative yield as indicated by $^{31}P\{^1H\}$ NMR spectroscopy.[45] These structures form via a process analogous to that presented for the macrocycle- and tweezer-based complexes.[40,41] Similar to the analogous Rh^I tweezer complexes, the Cl^- ligands can be abstracted from **31a**−**c** to form the condensed complexes **32a**−**c**. Significantly, this transformation can be effected reversibly, thereby providing a convenient way to regulate the sterics around the central aromatic group.

The solid state and solution data for complex **31a** (Scheme 7, Figure 3A) both illustrate the lack of close interaction between the aromatic groups of the tweezer ligands and the aromatic group of the central bifunctional hemilabile ligand. For complex **32a**, the crystallographic data illustrate that the three aromatic groups are not aligned cofacially and form a step-like complex (Figure 3B). Although the complex adopts this orientation in the solid state, 2D NOESY NMR data indicate that the complexes are quite fluxional in solution and the outer aromatic groups can move back and forth freely, with the average structure best described as a triple-decker structure.

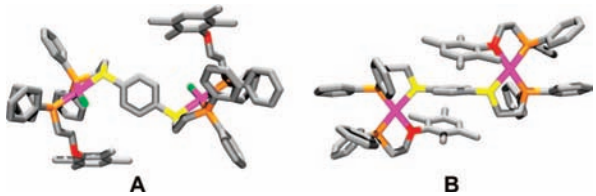
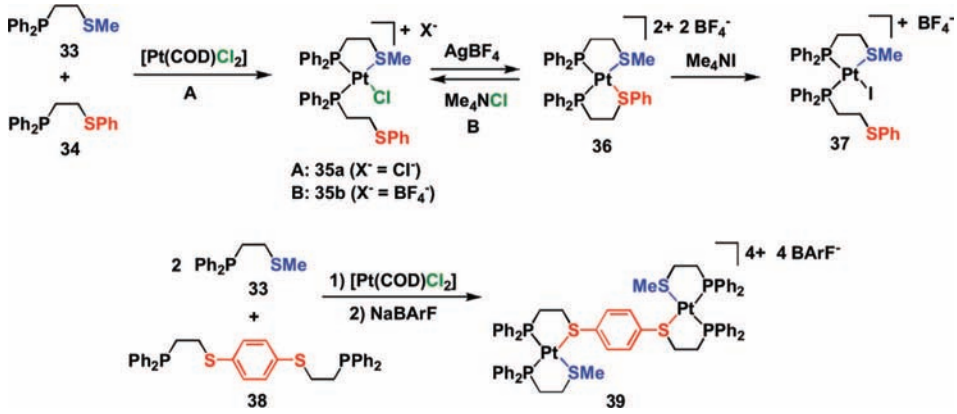


FIGURE 3. Stick representation for the crystal structure of **31a** (A) and **32a** (B). Color scheme: Rh (pink), C (gray), P (orange), S (yellow), O (red), and Cl (green).

Heteroligated Pt^{II} Complexes

While Rh^I has proven useful for targeting otherwise inaccessible heteroligated supramolecular coordination complexes, the resulting compounds often must be handled and manipulated under an inert atmosphere. This requirement precludes using these complexes under conditions that would closely resemble those found in Nature. We hypothesized that Pt^{II}, which is also a d^8 metal known to support phosphorus−sulfur hemilabile ligands,[46] may also exhibit similar reactivity as the Rh^I system in the context of supramolecular ligand rearrangements. Furthermore, it is well established that isoelectronic and structurally related Pt^{II} complexes are not as susceptible to degradation under ambient conditions,[47] which makes this transition metal an attractive candidate for the synthesis of new heteroligated coordination complexes.

SCHEME 8. Heteroligated Pt^{II} Complexes



While the heteroligated Rh^{I} analogues were formed using a combination of thioether− and ether−phosphine hemilabile ligands, the Pt^{II} analogues form via the participation of both alkyl- and arylthioether ligands (Scheme 8).[48] Although the cationic complexes **36** and **39** can be isolated via a one-pot procedure, analysis of this process via $^{31}P\{^{1}H\}$ NMR spectroscopy illustrates that semiopen complexes (e.g., **35a**) form initially, and Cl^{-} can be abstracted using Na^{+} and Ag^{+} salts to give closed complexes **36** and **39**. Furthermore, X-ray crystallographic analyses of single crystals of **35a** and **36** confirm the presence of the heteroligated environment around the Pt^{II} metal center (Figure 4).

Since halides (either Cl^{-} or I^{-}) can be used to cleave the relatively weak $Pt-S_{aryl}$ bonds in **36** to form **35b** and **37**, one can easily regulate the interactions between the groups appended to both S atoms. These heteroligated, thioether-based Pt^{II} complexes show a reactivity pattern different from the Rh^{I} complexes mentioned above. For example, acetonitrile is not a strong enough binder to cleave either Pt−S bond in complex **36**, while it does break the Rh−O bond in **14a**,**b** (Scheme 4). Thus, by choosing the appropriate metal and hemilabile ligands for the heteroligated rearrangement, one can tailor the small molecule reactivity with respect to the metal center, and systems can be designed that exhibit reactivities at regulatory and functional (catalytic) sites in the allosteric enzyme mimics that are orthogonal.

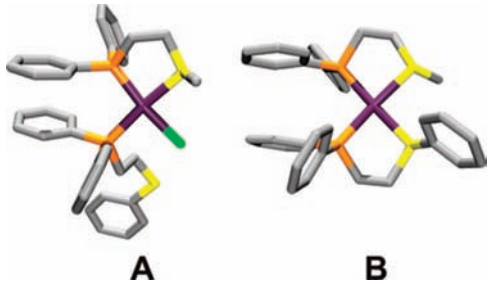


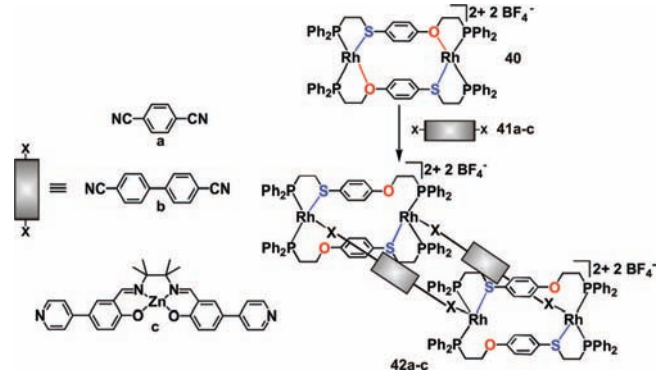
FIGURE 4. Stick representation for the crystal structures of **35a** (A) and **36** (B). Color scheme: Pt (purple), C (gray), P (orange), S (yellow), and Cl (green).

Structures Prepared via the HILR with Greater Complexity and Function

Assembly of Salen-Based Multimetallic Box Structures. Our preliminary experiments during the development of the HILR indicated that the addition of pyridyl and nitrile ligands act to selectively break the Rh−O moieties in the macrocycles while leaving the Rh−S bonds intact (Scheme 4). The ability to target macrocyclic structures containing heteroligated coordination environments has led us to investigate the potential for using these macrocycles as building blocks for the preparation of large, supramolecular architectures. In principle, if a macrocyclic complex and a suitable bifunctional ligand are reacted in a 1:1 ratio, it is possible to quantitatively and rapidly assemble multimetallic box-type structures where the bifunctional ligands are aligned cofacially.

Upon the addition of bifunctional bridging ligands **41a**−**c** to a solution of the closed heteroligated macrocycle **40** in a 1:1 ratio, the desired multimetallic structures **42a**−**c** form after 10 min as indicated by $^{31}P\{^{1}H\}$ NMR spectroscopy (Scheme 9).[49] The chemical shifts and coupling constants indi-

SCHEME 9. Multimetallic Box Complexes Formed via the HILR



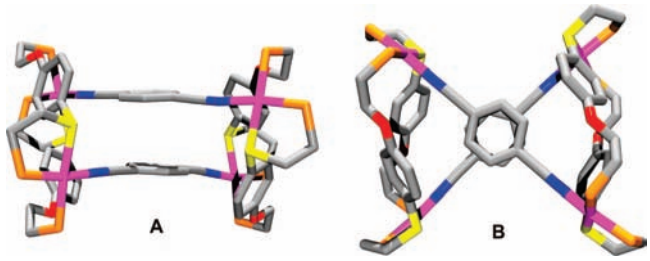


FIGURE 5. Stick representation for the crystal structure of **42a**: (A) side view; (B) top view. The phenyl groups on the phosphines in the crystal structure have been omitted for clarity. Color scheme: Rh (pink), C (gray), P (orange), S (yellow), O (red), and N (blue).

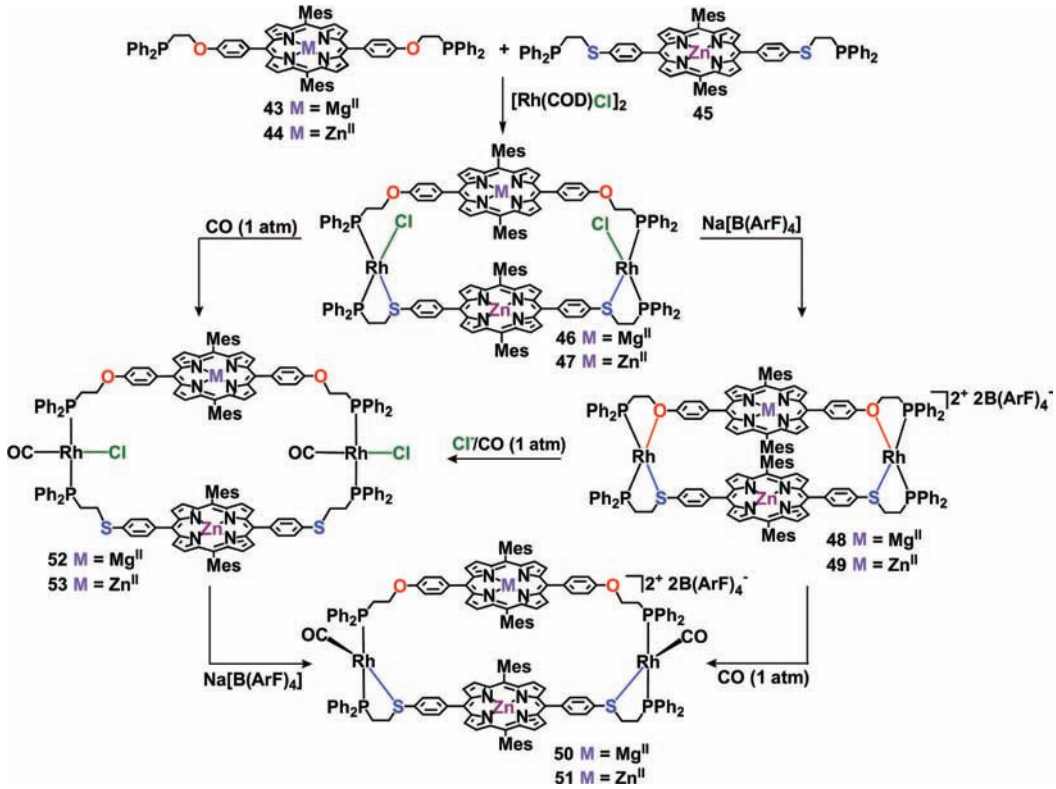
cate that the Rh−O bonds are quantitatively cleaved and the P−Rh−P coordination environment retains the original *cis* configuration. A single-crystal X-ray diffraction study of **42a** confirmed the local coordination environment about each Rh^{I} metal center and also illustrated that each 1,4-dicyanobenzene ligand is held in a cofacial orientation by the two heteroligated macrocycles (Figure 5). Importantly, while the area of the rectangle formed by the four Rh^{I} metal centers is 110 $Å^2$ for **42a**, the inherent ability to tailor complexes formed via the HILR and the WLA, in principle, will allow one to systematically vary the cavity size of the resulting structures via modification of the building blocks used for assembly.

Heteroligated Cofacial Porphyrin Complexes

Macrocyclic Complexes. Since Collman et al. presented their initial work on the synthesis of cofacial porphyrin complexes,[50] chemists have studied the properties of variants of such complexes for over 25 years and have generated many sophisticated and potentially useful species.[17,51−53] Typically, these complexes are prepared via tedious multistep procedures, using rigid scaffolds that restrict the overall structural flexibility of the targeted complex. As a result, it is difficult to carry out comprehensive studies that address the consequences of changing the porphyrin−porphyrin distance, their orientation with respect to each other, and the metal centers that reside within them.[54,55] We hypothesized that the HILR could provide access to cofacial porphyrin structures that not only enabled the systematic placement of different metals within the cofacial assembly but also would allow for significant control over the porphyrin orientations and interporphyrin distances.

Our initial attempts to synthesize these complexes were performed in CH_2Cl_2 at room temperature. Unfortunately, these conditions were not suitable for preparing the desired heteroligated complexes. By systematically varying the reac-

SCHEME 10. Heteroligated Cofacial Porphyrin Macrocyclic Complexes Formed by the HILR



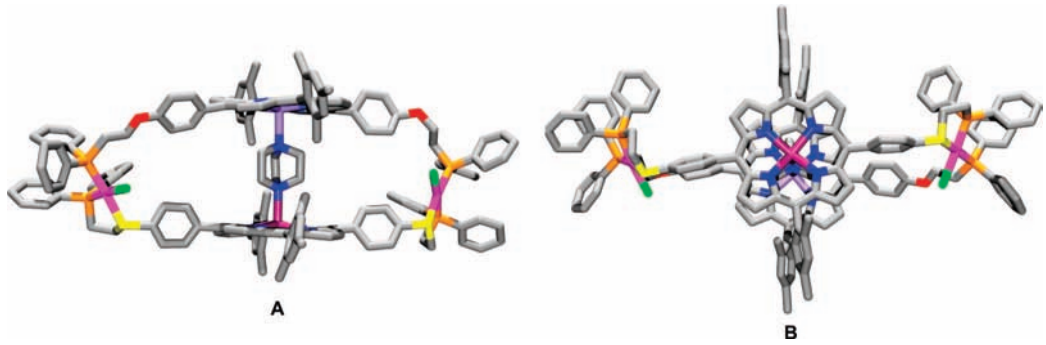


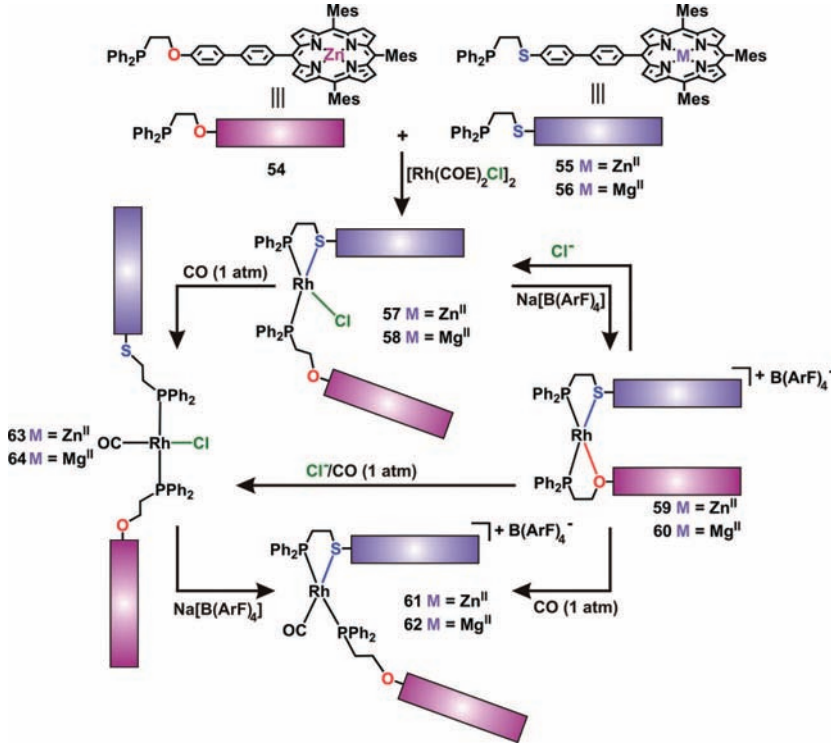
FIGURE 6. Stick representation for the crystal structure of **46**⊂DABCO: (A) side view; (B) top view. Color scheme: Rh (pink), Zn (purple), Mg (light violet), C (gray), P (orange), S (yellow), O (red), N (blue), and Cl (green).

tion conditions, we discovered that complexes **46** and **47** can be prepared in near quantitative yield by sonicating a THF solution containing ligands **43** (or **44**), **45**, and $[Rh(COD)Cl]_2$ for 1 h (Scheme 10).[56] Analysis of X-ray quality single crystals of **46** grown in the presence of DABCO show a solid state structure consistent with the one we assigned based upon solution spectroscopic data (Figure 6).

The neutral complexes **46** and **47** can be converted into the closed cationic macrocycles **48** and **49** upon sonication with 2 equiv of $Na[B(ArF)_4]$ in CH_2Cl_2. Since the Rh−O bonds in macrocycles **48** and **49** are weaker than the Rh−S bonds, they can be quantitatively cleaved using CO (1 atm), resulting in the formation of the semiopen assemblies **50** and **51**. Importantly, this transformation is accompanied by a change in the P−Rh−P geometry from *cis* to *trans*, which serves to modify the alignment of each porphyrin. The fully open complexes **52** and **53** can be generated via two different routes. First, adding 2 equiv of $(n\text{-Bu})_4NCl$ followed by the introduction of CO (1 atm) to solutions of **48** or **49** results in the quantitative formation of the fully open assemblies **52** or **53**, respectively. Alternatively, **52** or **53** can be directly prepared via introduction of CO (1 atm) to solutions of the semiopen assemblies **46** or **47**, respectively. These transformations illustrate how one can (1) selectively access four different cofacial assemblies from a single macrocycle and (2) rapidly access heteroligated cofacial porphyrin systems in which each porphyrin ligand contains a different metal.

Tweezer Complexes. While the macrocyclic cofacial porphyrin complexes synthesized to date have illustrated the ability for the HILR to provide access to porphyrin structures

SCHEME 11. Heteroligated Porphyrin Tweezer Complexes Prepared via the HILR



capable of *in situ* modification, a potential limitation of complexes **46** and **47** is their low solubility in common organic solvents, which, in turn, makes reversible *in situ* reactions difficult. As we mentioned earlier, one possible route to overcome limitations with respect to solubility is to design tweezer complexes, which have been shown to be significantly more soluble in many organic solvents.[27] Our group has designed the analogous cofacial porphyrin tweezer complexes, which contain a single Rh^{I} regulatory site and can undergo significant geometrical distortions *in situ* when triggered by external chemical stimuli. Compared with the macrocyclic analogues, the tweezer complexes are all highly soluble in organic solvents (i.e., CH_2Cl_2, THF) owing, in part, to the incorporation of an extra mesityl group on the porphyrin ring and the decrease in overall charge and molecular weight. Furthermore, the increased solubility of these complexes allows them to undergo reversible reactions with small-molecule ligands without undesired precipitation.

Using protocols analogous to the ones developed for the macrocyclic complexes **46** and **47**, the heteroligated complexes **57** and **58** were prepared in quantitative yield via the HILR using 2 equiv of **54** and **55** (or **56**) and 1 equiv of the Rh^{I} precursor, $[Rh(COE)_2Cl]_2$ (Scheme 11).[57] The closed cationic complexes **59** and **60** can be prepared quantitatively via abstraction of Cl^- with $Na[B(ArF)_4]$. Importantly, since tweezer complexes **57**−**60** are much more soluble in organic solvent compared with their macrocyclic analogues, the Rh^{I} hinge site can be addressed reversibly *in situ* with selected small-molecule ligands and elemental anions. For example, the addition of $(n\text{-Bu})_4NCl$ (1 equiv) to a CH_2Cl_2 solution of complex **59** or **60** results in their quantitative conversion to complexes **57** or **58**, respectively.

Upon addition of CO (1 atm) to separate solutions of **59** and **60** in CD_2Cl_2, respectively, complexes **61** and **62** are formed in quantitative yield. The fully open complexes **63** and **64** can be generated via two different routes, which both involve displacement of the thioether moieties bound to the Rh^{I} metal centers. For instance, introducing CO (1 atm) to a CD_2Cl_2 solution of complexes **57** or **58** yields the fully open, highly flexible tweezer complexes **63** or **64** quantitatively. These complexes also can be generated *in situ* from the closed complexes **59** or **60** upon the addition of a stoichiometric amount of $(n\text{-Bu})_4NCl$ and CO (1 atm).

Conclusions and Outlook

Our efforts thus far demonstrate the power of using coordination chemistry, namely, the WLA and the HILR, for the preparation of unique and otherwise inaccessible supramolecular complexes. These heteroligated complexes can be readily accessed in quantitative yield using a wide variety of hemilabile ligands with varying electronic and steric properties when reacted with simple d^8 transition metal precursors. It is anticipated that this new reaction will allow for the preparation of novel supramolecular complexes that can act in the context of allosteric catalysis/sensing and for the design of new architectures capable of mimicking the properties of enzyme active sites. For example, one can target tweezer complexes that contain both a catalyst and cocatalyst (i.e., porphyrin and imidazole/cysteine, respectively) that can be aligned cofacially, whereby the cocatalyst can activate a metal center for catalysis and potentially allow for the regulation of the catalytic rate by controlling the distance and relative alignment between the cocatalyst and the catalytic center. Additionally, it is now possible to target triple-decker complexes that contain two sterically demanding blocking ligands, which can crowd a catalytically active metal center and regulate a catalytic reaction via the addition or removal of small molecule effectors.

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Christopher G. Oliveri was born and raised in Long Island, New York. He earned a B.S. degree in chemistry (2002) and a M.S. degree in bioinorganic chemistry (2003) working under the supervision of Professor Stephen Koch at Stony Brook University. In 2003, he joined the graduate program at Northwestern University where he worked towards developing novel coordination chemistry-based cofacial porphyrin complexes under the auspices of Professors Chad A. Mirkin and SonBinh T. Nguyen. In 2007, he completed the Ph.D. program and is currently a Senior Chemist at ExxonMobil in the Process Research Laboratory in Annandale, New Jersey.

Pirmin A. Ulmann was born in Schaffhausen, Switzerland. He received his diploma in chemistry from ETH Zurich in 2004 under the guidance of Professor Erick M. Carreira. After a stint in process upscaling for a drug candidate at Merck Eprova AG, Schaffhausen, he joined the graduate program at Northwestern University, where he is currently pursuing his Ph.D. under the direction of Professor Chad A. Mirkin in the field of supramolecular coordination chemistry.

Michael J. Wiester attended the University of Texas at Austin (UT). While at UT, he did undergraduate research with Professor Richard Jones in the area of organometallic chemistry and earned his B.S. in chemistry in 2003. He joined the graduate program at

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Chad A. Mirkin received a B.S. degree from Dickinson College in 1986 and a Ph.D. degree in chemistry from the Pennsylvania State University in 1989. He was an NSF Postdoctoral Fellow at the Massachusetts Institute of Technology prior to becoming a chemistry professor at Northwestern University in 1991. He is currently the Director of the International Institute for Nanotechnology, the George B. Rathmann Professor of Chemistry, Professor of Medicine, and Professor of Materials Science and Engineering. He is author of over 335 manuscripts and over 350 patent applications (71 issued). He is the founder of two companies, Nanosphere and NanoInk, which are commercializing nanotechnology applications in the life science and semiconductor industries.

FOOTNOTES

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