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Reversible CO-Induced Chloride Shuttling in Rh^{I} Tweezer Complexes Containing Urea-Functionalized Hemilabile Ligands

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The urea moiety, which acts as a good hydrogen-bond donor, has been incorporated into a hemilabile phosphinoalkyl thioether ligand. Upon reaction of the ligand with a Rh^{I} precursor, a tweezer complex with near-parallel planar urea moieties **2** forms. The host−guest interaction of **2** with Cl^{-} has been characterized in solution and in the solid state. Cl^{-} binding with the urea groups in **2** is retained under CO in nonpolar solvents to give a five-coordinate CO adduct **3**. In polar solvents, CO binding to Rh^{I} results in a Cl^{-} shift from the urea host site to the Rh^{I} metal center with a concomitant breaking of the Rh−S bonds. This is an unusual example of how two types of different interactions important in molecular recognition (ligand coordination to a metal and hydrogen bonding) can be regulated within one molecule through small-molecule coordination chemistry.

Two general approaches have been used to develop recognition properties in supramolecular complexes: those that involve cumulative weak interactions such as hydrogen bonding and others that involve coordination bonds.[1,2] Many novel metallosupramolecular complexes have now been prepared via the weak-link approach (WLA).[3−5] These structures are based upon hemilabile ligands and allow one to build macrocycle,[3] triple decker,[4] and tweezer-based complexes[5] with chemistry that can be regulated based upon structural changes induced by the displacement of the weak binding group of the hemilabile ligand at metal hinge sites. This approach and these structures have allowed us to design a wide variety of molecules with stoichiometric and catalytic chemistries that can be turned on and off or up and down using the concept of allosteric regulation.[3−5]

Urea is a common motif used in molecular recognition chemistry, and it has an especially high affinity for anions under the appropriate conditions.[6] We hypothesized that the WLA could be used to assemble hemilabile ligands based upon urea groups and phosphines into tweezer complexes that would position the urea moieties to cooperatively recognize anionic analytes such as Cl^{-}. Moreover, we thought the chemistry that occurs at the metal hinge in these complexes could be used to subsequently alter the pocket and perhaps the chemistry that occurs between the urea-based host and Cl^{-}. We have designed one such ligand, **1**, which when reacted with a Rh^{I} precursor forms the desired tweezer complex **2** (eq 1). This complex indeed binds Cl^{-} through hydrogen bonding with the urea moieties and undergoes a

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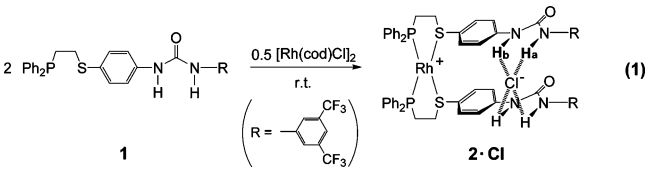
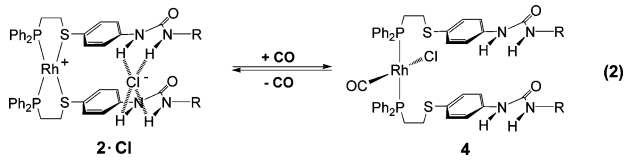
novel solvent-assisted CO-induced intramolecular shuttling of the Cl^- guest between the urea tweezer pocket and the Rh hinge in a reversible fashion (eq 2). Although the irreversible migration of Cl^- assisted by CO in a transition-metal complex with urea groups has been reported by other research groups,[1b] two of the most interesting aspects of the system that we are reporting are the reversibility and the corresponding ability to regulate the position of the two urea groups (and the pendant R groups) through small-molecule coordination chemistry within one complex.





The urea-based hemilabile ligand, **1** (PS ligand), was synthesized by the reaction of 4-aminothiophenol with 1-isocyanato-3,5-bis(trifluoromethyl)benzene to generate the urea functionality, followed by the reaction with $PPh_2(CH_2)_2Cl$ over K_2CO_3. The electron-withdrawing 3,5-bis(trifluoromethyl)benzyl group was used to enhance the acidity of the urea groups, thus generating stronger hydrogen bonds with anions, a strategy utilized by others.[6b] The tweezer Rh^I complexes with Cl^- and BF_4^- counterions, **2·Cl** and **2·BF$_4$**, respectively, were synthesized from stoichiometric amounts of the ligand **1** and the Rh^I precursors ($[Rh(cod)Cl]_2$ or $[Rh(cod)_2]BF_4$ (cod = 1,5-cyclooctadiene)) in CH_2Cl_2 at room temperature (eq 1).

Complexes **2·Cl** and **2·BF$_4$** were characterized by multinuclear NMR and FT-IR spectroscopies, ESI-MS, and elemental analysis. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **2·Cl** are almost identical with analogous spectra for **2·BF$_4$**, except N−H resonances assigned to the urea moiety in **2·Cl** [δ 9.85 (H_a) and 9.36 (H_b)], which are significantly downfield from those observed for **2·BF$_4$** [δ 8.04 (H_a) and 7.83 (H_b)]. This observation is consistent with the conclusion that Cl^- is bound to the urea groups in solution. The sequestration of Cl^- by **2·BF$_4$** can be monitored by ^1H NMR spectroscopy, by titrating a CD_2Cl_2 solution of **2·BF$_4$** with tetrabutylammonium chloride ($^nBu_4NCl$), which results in a gradual downfield shift of the urea N−H resonances as a function of the Cl^- concentration (Figure 1). The $^{31}P\{^1H\}$ NMR spectra of these solutions did not significantly change (δ 65, d, J_{Rh-P} = 163 Hz in CD_2Cl_2) during the titration. A Job plot was also used to characterize the host−guest interactions and confirms a 1:1 stoichiometery between the coordination complex host and the Cl^- guest anion (Figure 2). Finally, gel-permeation chromatography (GPC) of **2·Cl** is consistent with the molecular weight of a monomer rather than an oligomer (Supporting Information). This is important because the structure forms a dimer in the solid state (vide infra).

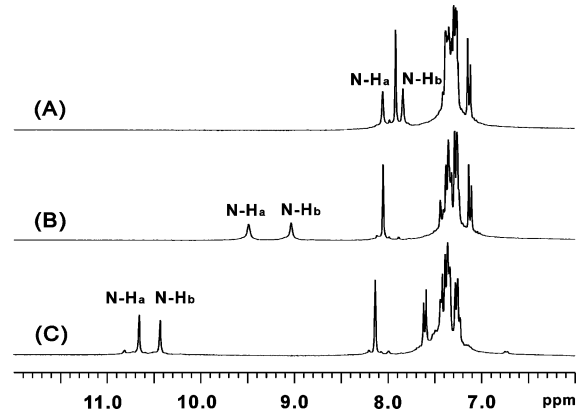


Figure 1. Binding of Cl^- in complex **2·BF$_4$** monitored by ^1H NMR spectroscopy (CD_2Cl_2): (A) a solution of **2·BF$_4$**; (B) a solution of **2·BF$_4$** with 0.5 equiv of $^nBu_4NCl$; (C) a solution of **2·BF$_4$** with 5.0 equiv of $^nBu_4NCl$.

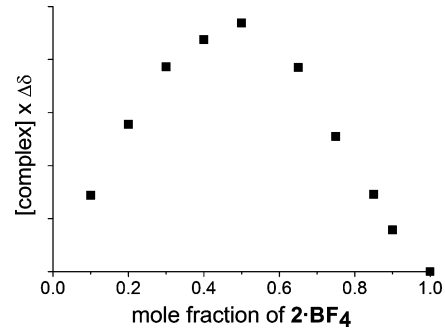


Figure 2. Job plot from the addition of $^nBu_4NCl$ to the complex **2·BF$_4$**.

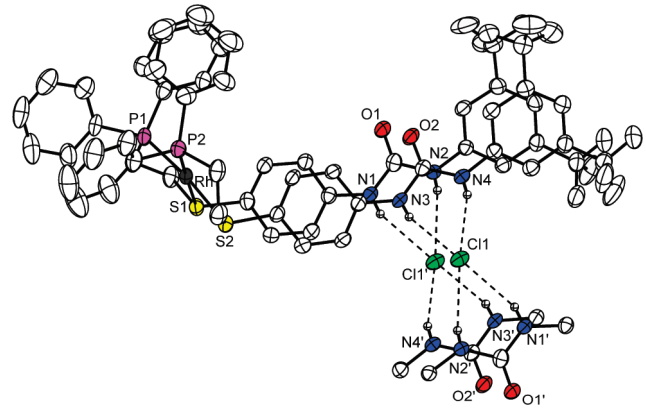


Figure 3. X-ray crystal structure of complex **2·Cl** with thermal ellipsoids set at 50% probability. For clarity, all H atoms except those on the urea N atoms are omitted. Dotted lines indicate the intermolecular hydrogen-bonding interactions between the Cl atoms and the urea H atoms. Symmetry code: $' = 1 - x, 1 - y, -z$.

Single crystals of **2** were grown in two different ways: by slow evaporation of a CH_2Cl_2 solution saturated with **2** and by slow diffusion of hexane into such a solution. The two methods yielded two different crystals, **2·Cl** and **2·BF$_4$**, respectively. Both structures were determined by single-crystal X-ray diffraction studies, which show dimers held together by either Cl^- (**2·Cl**) or BF_4^- (**2·BF$_4$**) (Supporting Information). The Rh^I centers in both complexes are coordinated by two κ^2-PS ligands, and each shows a Rh center with a four-coordinate, distorted square-planar geometry with a trans arrangement of phosphines and thioether ligands. This geometry and ligand coordination

Table 1. $^{31}P\{^1H\}$ NMR Resonances for **3·BF$_4$**[a] as a Function of Added Cl^-

Cl^-(equiv)	0	0.5	1	2	3	4	5	10
δ (ppm)[b]	42.7	42.6	42.3	38.6	36.8	30.8	28.9	26.7

[a] $^{31}P\{^1H\}$ NMR spectra were taken at 20 °C in CD_2Cl_2 (external ref 85% H_3PO_4). [b] Doublets (J_{Rh-P} = 106−120 Hz).

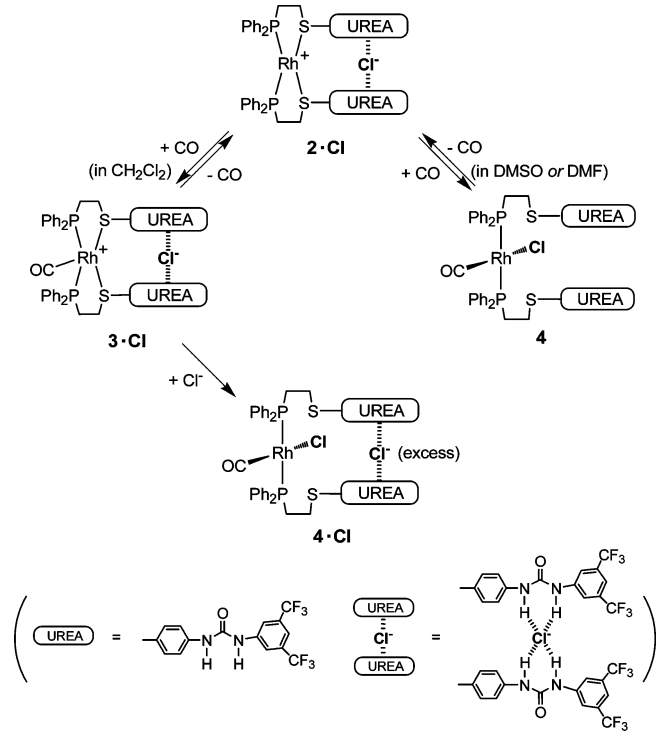
mode are very similar to those observed for previously reported Rh^I macrocycles and tweezers.[3,5]

In **2·Cl**, the urea moieties are approximately parallel to each other and form hydrogen bonds to the Cl^- counterions. In the solid state, Cl^- does not reside within an intramolecular bis-urea pocket. Instead, the complex forms a 2:2 structure with two pairs of ureas from two different Rh^I complexes creating intermolecular pockets, each with one Cl^-. The average distance between the Cl^- and H atoms of urea is 2.55 Å. It is interesting to note that intermolecular hydrogen bonding with Cl^- is more favorable in the solid state than the intramolecular hydrogen bonding observed in solution. The solid-state structure of **2·BF$_4$** also shows intermolecular hydrogen bonding between urea groups and BF_4^- (Supporting Information).

The addition of CO (1 atm) to a CD_2Cl_2 solution of **2·Cl** and **2·BF$_4$** at room temperature leads to the formation of five-coordinate CO adducts, **3·Cl** and **3·BF$_4$**, which have been characterized by ^1H NMR, $^{31}P\{^1H\}$ NMR, and FT-IR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra show doublets at δ 42.3 (**3·Cl**, J_{Rh-P} = 107 Hz) and δ 42.7 (**3·BF$_4$**, J_{Rh-P} = 107 Hz) in CD_2Cl_2, which allow us to assign these complexes as five-coordinate CO adducts, based upon a comparison to literature values.[7] Upon the addition of successively increasing amounts of $^nBu_4NCl$ to a CD_2Cl_2 solution of **3·BF$_4$** (or **3·Cl**), the $^{31}P\{^1H\}$ NMR resonances gradually shift upfield (Table 1). This shift is consistent with a change in the coordination environment, due to the cleavage of the Rh−S bonds by coordination of Cl^- and generation of the four-coordinate fully open complex **4·Cl** (Scheme 1).

In more polar solvents such as dimethyl sulfoxide (DMSO) or *N*,*N*-dimethylformamide (DMF), a slightly different reaction occurs. CO and Cl^- coordinate to the Rh center in **2**, forming a four-coordinate adduct, **4**, but a Cl^- anion does not reside in the urea pocket as in **4·Cl** (Scheme 1). This Cl^--free urea pocket is evidenced by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Indeed, significant upfield ^1H NMR shifts of the N−H resonances in the urea moiety are observed (δ 9.83 and 9.48 for **2·Cl** in DMSO-d_6; δ 9.57 and 9.19 for **4** in DMSO-d_6), indicating a Cl^--free urea pocket. The $^{31}P\{^1H\}$ NMR spectra of **4** in DMSO-d_6 and DMF-d_7 at room temperature show broad resonances at δ 32.5 and 30.0, respectively, which are far upfield compared to the analogous resonances for **2·Cl** and **3·BF$_4$**.[8] When CO is removed under vacuum, the open complex **4** reforms the closed complex **2·Cl**

Scheme 1. Systematic Structural Changes of **2·Cl** That Accompany the Addition and Removal of CO/Cl^-[a]



[a] Hydrogen bonding between the urea functionality and Cl^- is denoted with a dotted line.

in quantitative yield. The solvent dependence of the Cl^- shuttling reaction is a result of the competition of the polar solvent with Cl^- for the urea pocket because DMSO and DMF, compared to CH_2Cl_2, are good hydrogen-bond acceptors.

In conclusion, we have synthesized new coordination Rh^I tweezer complexes with near-parallel urea moieties, **2·Cl** and **2·BF$_4$**. These compounds complex anions (Cl^- and BF_4^-) in the pockets formed by the urea moieties. CO binding to the Rh atom can be used as a switch to effect the intramolecular shuttling of the Cl moiety from the urea pocket to the Rh center in a somewhat solvent-dependent manner. These types of processes may be useful in regulating the reactivity of supramolecular complexes where small molecules can be used to induce structural rearrangements that lead to the conversion of the complexes from inactive to active states in the context of both stoichiometric and catalytic reactions.

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Supporting Information Available: Details of experimental procedures, synthesis and characterization of each compound, additional key NMR spectra, Job plot, binding constant measurements, GPC traces, and CIF files giving crystallographic data for **2·Cl** and **2·BF$_4$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Kourkine, I. V.; Slone, C. S.; Mirkin, C. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 2758. Unlike model complexes studied previously, the isomers with a square-pyramidal coordination geometry for **3** are favored based upon variable-temperature NMR assignments. See the Supporting Information.

(8) The $^{31}P\{^1H\}$ NMR resonances for **3·BF$_4$** in CD_2Cl_2, DMSO-d_6, and DMF-d_7 [under a CO atmosphere (1 atm)] are δ 42.7 (d, J_{Rh-P} = 108 Hz), 49.9 (d, J_{Rh-P} = 105 Hz), and 49.1 (d, J_{Rh-P} = 108 Hz), respectively.