Halide-Induced Supramolecular Ligand Rearrangement

Aaron M. Brown, Maxim V. Ovchinnikov, Charlotte L. Stern, and Chad A. Mirkin*

Department of Chemistry and the Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60201-3113

Received August 3, 2004; E-mail: camirkin@northwestern.edu

There are now a variety of coordination chemistry approaches that allow one to construct two- and three-dimensional supramolecular structures using appropriate ligand design and coordination chemistry principles.[1] The weak-link approach (WLA) allows one to rationally template the formation of flexible, supramolecular macrocycles in nearly quantitative yields by utilizing appropriate transition-metal precursors and hemilabile ligands.[1c,2–4] Recently, we reported the synthesis of ligand 1-($Ph_2PCH_2CH_2O$)-4-($Ph_2PCH_2CH_2S$)C_6H_4 (**1a**) and its ability to facilitate the formation of a variety of heterobimetallic macrocycles.[5] Through the course of our investigation into the WLA, we have discovered a fascinating and what appears to be unprecedented halide-induced rearrangement of macrocycles containing Rh(I) *cis*-thioether/*cis*-phosphine and Rh-(I) NBD/*cis*-phosphine (NBD is norbornadiene) coordination environments (Scheme 1). An intentionally added halide or a halide which acts as a counterion within a preformed complex (**2a–c**) will facilitate the conversion of such complexes to condensed binuclear macrocycles **4a–c**. This intramolecular process involves the formal rotation of only one hemilabile ligand along the axis that is perpendicular to the plane defined by the aryl backbone of the hemilabile ligands. The reaction is general, high yielding, and allows one to prepare structures not attainable via any other known synthetic route, providing access to a series of heteroligated macrocycles that potentially can be used as receptors in chemical sensors and as flexible allosteric catalysts.[3]

Bimetallic Rh(I) macrocycles **4a** and **4b**, as well as trimetallic macrocycle **4c**, were synthesized in two-step procedures from the corresponding hemilabile ligands, **1a**, 4′-(2-$Ph_2PCH_2CH_2O$)-4-(2-$Ph_2PCH_2CH_2S$)biphenyl (**1b**), and ($Ph_2PCH_2CH_2O$)($Ph_2PCH_2CH_2S$)$_2$TPB (TPB is 1,3,5-triphenylbenzene) (**1c**), respectively, and stoichiometric amounts of the Rh(I) precursor, [Rh(NBD)Cl]$_2$. Complexes **2a,b** were prepared by treating 1 equiv of [Rh(NBD)Cl]$_2$ with a CH_2Cl_2 solution containing 2 equiv of ligands **1a** and **1b**, respectively, at room temperature. Trimetallic complex **4c** was made in an analogous manner; however, 1.5 equiv of [Rh(NBD)Cl]$_2$ to 2 equiv of ligand **1c** were used. All three NBD-containing complexes **2a–c** exhibit highly diagnostic resonances[6] in their ^{31}P {^1H} NMR spectra in the δ 65.3–64.6 range (d, $J_{Rh-P} = 162$ Hz), corresponding to the Rh(I) centers with *cis*-thioether/*cis*-phosphine coordination environments, and δ 13.5 (br m), corresponding to the Rh(I) centers with *cis*-phosphine/NBD coordination environments. Elemental analysis, ^1H NMR, and ES-MS are in full agreement with the proposed formulations.

When Cl$^-$ is the counterion, compounds **2a–c** slowly convert to intermediate complexes **3a–c**, where 1 equiv of ligand has formally rotated and the Cl$^-$ ion has moved to the inner coordination sphere (Scheme 1). These processes, which are rare examples of molecular rotations within metallosupramolecular structures,[7] have been studied by ^{31}P NMR spectroscopy under ambient conditions in CD$_2$Cl$_2$, and corresponding half-lives have been measured ($t_{1/2}$ = 1.5 h (**2b**), 4 h (**2a**), and 6 h (**2c**), 20mM [Rh(NBD)Cl]$_2$). Further

Scheme 1. Synthesis of Rearranged Macrocycles[a]
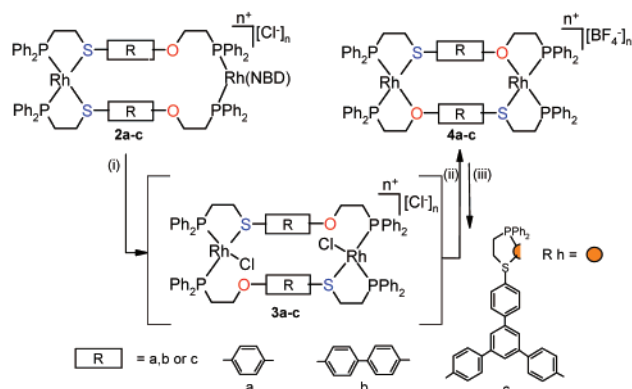
[a] Reagents and solvents: (i) CH_2Cl_2; (ii) CH_2Cl_2, 2 (**3a** and **3b**) or 3 equiv (**3c**) of $AgBF_4$; (iii) benzyltriethylammonium chloride.
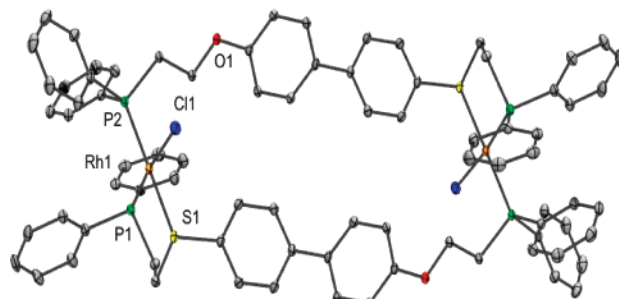

Figure 1. ORTEP diagram of **3b** ($C_{40}H_{36}ClOP_2RhS)_2$ with thermal ellipsoids drawn to 30% probability. Hydrogen atoms and solvent molecules have been omitted for clarity. Labeling and coloring scheme is as follows: Rh (orange), P (green), O (red), S (yellow), and Cl (blue).

evidence for the formation of these intermediate complexes was obtained from a single-crystal X-ray analysis of complex **3b** (Figure 1). The Rh(I) centers in **3b** exhibit square planar geometries, with Cl1–Rh1–P2 and Cl1–Rh1–S1 angles of 88.15(3) and 87.16(3)°, respectively. The cavity distance between the centroids defined by the phenyl rings of each ligand is 6.225 Å, while the distance between Rh1 and Rh2 is 13.659 Å. X-ray quality crystals of complex **3a** were grown in a similar fashion; however, refinement efforts yielded a disordered structure ($R_1 = 13\%$), which supports chemical connectivity similar to that observed for **3b** (Supporting Information). Neutral intermediate complexes **3a** and **3b** are sparingly soluble in common organic solvents (CH_2Cl_2, THF, and 1,2-dichlorobenzene) and could be in equilibrium with oligomeric species via a (μ-Cl)$_2$Rh$_2$ motif. This makes monitoring the conversion from **2a,b** to intermediates **3a,b** by NMR spectroscopy difficult as the products precipitate during the reaction. On the other hand, trimetallic complex **3c** is soluble in common organic solvents; therefore, it was possible to follow the rearrangement from **2c** to **3c** by ^{31}P NMR spectroscopy in CD$_2$Cl$_2$. Phosphorus atoms in the
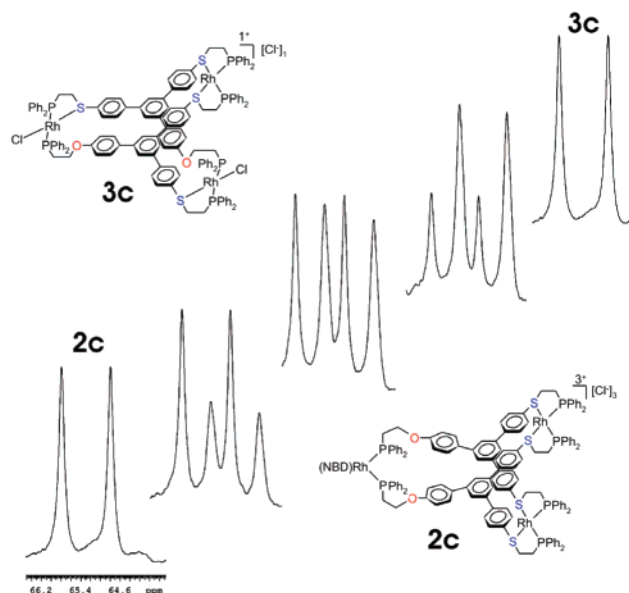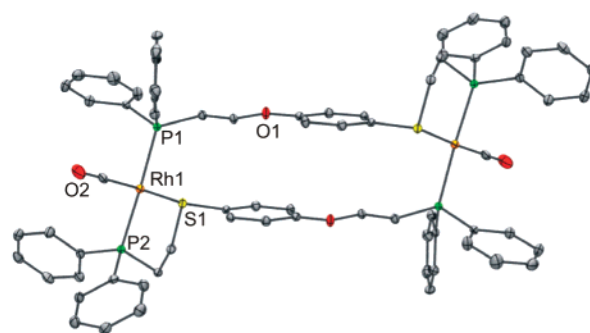
Figure 2. Rearrangement from complex **2c** to **3c** monitoring the ^{31}P {^{1}H} NMR resonances of the Rh(I) *cis*-thioether/*cis*-phosphine coordination site. The intensity of each spectrum has been normalized.

Figure 3. ORTEP diagram of the product obtained from the reaction of CO with **4a**. Thermal ellipsoids are drawn to 30% probability. Hydrogen atoms, solvent molecules, and counterions have been omitted for clarity. Labeling and coloring scheme is as follows: Rh (orange), P (green), O (red), and S (yellow).

additional Rh(I) *cis*-thioether/*cis*-phosphine coordination environment that are present in both **2c** and **3c** are useful tags for monitoring the rearrangement by ^{31}P NMR spectroscopy (Figure 2). For example, complex **2c** exhibits a ^{31}P {^{1}H} NMR signal at δ 65.3 (d, J_{Rh-P} = 162 Hz), corresponding to the magnetically equivalent P atoms that make up the two Rh(I) *cis*-thioether/*cis*-phosphine coordination environments. As the complex is transformed into **3c**, this signal decreases in intensity with a concomitant increase in intensity for the resonance associated with **3c** (δ 64.7, d, J_{Rh-P} = 162 Hz).

Abstraction of the Cl$^-$ ions from **3a**−**c** (**3a,b** suspensions in CH$_2$Cl$_2$, **3c** soluble) with stoichiometric quantities of AgBF$_4$ results in the clean formation of cationic macrocycles **4a**−**c**. Each of these complexes exhibits similar characteristic ^{31}P {^{1}H} NMR resonances at δ 74.1 (dd, J_{P-P} = 41 Hz, J_{Rh-P} = 201 Hz), corresponding to the Rh(I) phosphine/ether environment, and δ 51.0 (dd, J_{P-P} = 41 Hz, J_{Rh-P} = 170 Hz), corresponding to the Rh(I) phosphine/thioether environment. The additional coupling observed in the ^{31}P {^{1}H} NMR resonance in **4a**−**c**, as compared to that in **2a**−**c** is due to the two adjacent nonequivalent phosphorus atoms. Trimetallic complex **4c** exhibits an additional resonance at δ 65.5 (d, J_{Rh-P} = 161 Hz) due to the remaining Rh(I) *cis*-thioether/*cis*-phosphine coordination site.

A variety of anions were investigated with regard to their ability to induce ligand rearrangement reactions. These include BF$_4^-$, PF$_6^-$, BArF$^-$ (BArF$^-$ is B[3,5-(CF$_3$)$_2$(C$_6$H$_3$)]$_4^-$), Cl$^-$, Br$^-$, and I$^-$. A typical experiment involved the addition of 2 equiv of the appropriate salt (Supporting Information) to the bi- or trinuclear complex with BF$_4^-$ counterions in place of chlorides in complexes analogous to **2a**−**c** at room temperature. With the exception of the halides, no ligand rearrangement was observed.

The result of this rearrangement of the hemilabile ligand and abstraction of the chloride anions is the formation of supramolecular species **4a**−**c**, in which metal centers with mixed ether/thioether coordination environments are generated. This provides one with the ability to selectively cleave the Rh(I)−O bonds while leaving the stronger Rh(I)−S bonds intact. This control is due to the lower affinity of Rh(I) for the O donor as compared to that of the S donor. For example, reactivity studies were conducted with the condensed complex **4a**. The weaker Rh−O bonds can be selectively cleaved upon the addition of carbon monoxide (Figure 3) and nitriles, leaving the stronger Rh−S links intact.

In conclusion, we have discovered an unusual, but general, halide-induced ligand rearrangement in multimetallic Rh(I) macrocycles containing hemilabile ligands. This approach provides condensed macrocycles containing individually addressable metal centers which will be useful as building blocks for more sophisticated, heteroligated, three-dimensional architectures.

Supporting Information Available: Detailed synthetic procedures, characterization, ORTEP diagram of **3b**, and CIF files for complexes **3a**, **3b**, and the product obtained from the reaction of CO with **4a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−908. (b) Lindner, E.; Pautz, S.; Haustein, M. *Coord. Chem. Rev.* **1996**, *155*, 145−162. (c) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022−2043. (d) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53−61. (e) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975−982. (f) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759−771. (g) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483−3538. (h) Jiang, H.; Lin, W. *J. Am. Chem. Soc.* **2003**, *125*, 8084−8085. (i) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H. J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621−630.
(2) Farrell, J. R.; Mirkin, C. A.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1998**, *120*, 11834−11835.
(3) (a) Gianneschi, N. C.; Bertin, P. A.; Nguyen, S. T.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 10508−10509. (b) Gianneschi, N. C.; Cho, S.-H.; Nguyen, S. T.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2004**, in press.
(4) Ovchinnikov, M. V.; Holliday, B. J.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4927−4931.
(5) Eisenberg, A. H.; Ovchinnikov, M. V.; Mirkin, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 2836−2837.
(6) Bonuzzi, C.; Bressan, M.; Morandini, F.; Morvillo, A. *Inorg. Chim. Acta* **1988**, *154*, 41−43.
(7) (a) Special issue on molecular machines: *Acc. Chem. Res.* **2001**, *34*, 409−522. (b) Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174−179. (c) Tashiro, K.; Konishi, K.; Aida, T. *J. Am. Chem. Soc.* **2000**, *122*, 7921−7926. (d) Hiraoka, S.; Hirata, K.; Shionoya, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3814−3818.

JA045316B