Inorg. Chem. **2000,** *39,* 3432−3433

Neutral Macrocycles via Halide-Induced Ring Opening of Binuclear Condensed Intermediates

Felicia M. Dixon, Adam H. Eisenberg, Joshua R. Farrell, and Chad A. Mirkin*

Department of Chemistry, 2145 Sheridan Road, Northwestern University, Evanston, Illinois 60208

Louise M. Liable-Sands and Arnold L. Rheingold

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received January 18, 2000

Recently, our group reported a novel, high-yield synthetic method for preparing polycationic binuclear macrocycles and three-dimensional complexes from flexible hemilabile ligands[1] and simple transition metal precursors.[2] The premise behind this approach is that the entropic costs of preparing a large ring structure from flexible ligands can be minimized by first targeting a condensed intermediate held together via both strong and weak metal−heteroatom links; the weak metal−heteroatom bonds of the condensed intermediates are subsequently broken via ligand substitution reactions affording macrocyclic structures. Using this approach, our group has synthesized a series of 26-, 30-, and 34-membered polycationic rings from Rh^I and phosphinoarylether ligands.[2]

Weak links, used thus far, have been limited to metal−ether and metal−η^6-arene bonds.[2] Herein, we report the first use of thioether-based ligands to form a condensed macrocycle (**2**), which can be opened via a novel halide-induced ring-opening reaction, whereby a halide source is used to break the Rh^I−S bonds in **2** (Scheme 1). We have found that this halide-induced ring opening can be extended to condensed intermediates held together via metal−ether and metal−η^6-arene interactions, giving entry into an entire new class of *neutral* macrocycles with highly tailorable cavity sizes and properties. The synthesis of neutral macrocycles, as opposed to cationic systems, is highly desirable for the preparation of hosts for electron-deficient guests (ions can clog the cavities of charged macrocyclic structures) and as precursors for a variety of catalytic processes.[3]

The ligand 1,4-bis[2-(diphenylphosphino)ethylthio]benzene (**1**) was synthesized in >90% yield via modified literature procedures (see Supporting Information).[4] Compound **2** was synthesized by first stirring $[RhCl(COT)_2]_2$ (COT = cyclooctene) (80 mg, 0.223 mmol) with $AgBF_4$ (44 mg, 0.226 mmol) in 3 mL of CH_2Cl_2. After 1.5 h the mixture was filtered, diluted with THF (100 mL), and cooled to −78 °C. Then, **1** (126 mg, 0.223 mmol), dissolved in 100 mL of THF, was added dropwise to the reaction mixture to form the condensed intermediate (**2**). As the solution warmed to room temperature, compound **2** formed and precipitated in pure form from the reaction mixture, allowing one to easily separate it from the COT. The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits a characteristic doublet at 64 ppm with $J_{Rh-P} = 161$ Hz, which is diagnostic of a Rh^I *cis*-phosphine complex with five-membered chelates.[1,2] ^1H NMR spectroscopy, mass spectrometry (see Supporting Information), and a single-crystal X-ray diffraction study of $\mathbf{2}[B(C_6F_5)_4]_2$ are consistent with the proposed formulation of **2**. Each Rh^I metal center is in a square-planar *cis*-phosphine, *cis*-thioether geometry, and the parallel-planar arene rings are 3.51 Å apart (Figure 1A).[5]

The 2,3,5,6-tetramethyl/ether intermediate (**3**) is analogous to **2**, but composed of ether instead of thioether linkages, and reacts with small molecules such as CO and CH_3CN to form large macrocyclic ring structures.[2] We examined the lability of the Rh^I−S bonds of **2** under similar conditions. Overall, the thioether moieties of **2** proved to be substitutionally inert under conditions that result in the displacement of the ether moieties from the Rh^I centers in **3**. Compound **2** was completely unreactive toward the σ-donating ligand CH_3CN (neat at room temperature), and although CO reacts with **2**, it results not in the displacement of the thioether moieties but rather in the reversible formation of five-coordinate CO adducts.[7] A variety of reagents were tested when attempting to break the Rh^I−S bonds such as triethylphosphine, 1,2-bis(diethylphosphino)ethane, H_2, MeI, sodium thiophenoxide, and potassium diphenylphosphide. None of the above reagents proved to be suitable for breaking the Rh^I−S interactions without concomitant decomposition of **2**.

Successful clean displacement of the Rh^I−S bonds in **2** was achieved via the addition of $[Me_4N]Cl$ in the presence of CO (1 atm), which resulted in the *quantitative* formation of the neutral macrocycle (**5**) (Scheme 1). Compound **5** has been characterized

---

(1) (a) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27−110. (b) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. In *Progress in Inorganic Chemistry*; Karlin, K., Ed.; Wiley & Sons: New York, 1999; Vol. 48, pp 233−350.

(2) (a) Farrell, J. R.; Mirkin, C. A.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 465−467. (b) Holliday, B. J.; Farrell, J. R.; Mirkin, C. A.; Lam, K.-C.; Rheingold, A. L. *J. Am. Chem. Soc*. **1999**, *121*, 6316−6317. (c) Farrell, J. R.; Mirkin, C. A.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1998**, *120*, 11834−11835. (d) Farrell, J. R.; Eisenberg, A. H.; Mirkin, C. A.; Guzei, I. A.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L.; Stern, C. L. *Organometallics* **1999**, *18*, 4856−4868.

(3) (a) Bélanger, S.; Hupp, J. T.; Stern, C. L.; Slone, R. V.; Watson, D. F.; Carrell, T. G. *J. Am. Chem. Soc.* **1999**, *121*, 557−563. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; John Wiley & Sons: New York, 1992.

(4) DuBois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1011−1015.

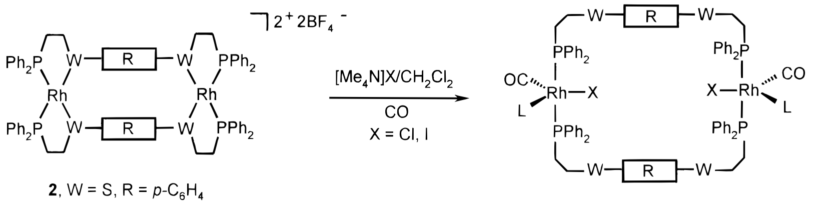
(5) (a) Single crystals for X-ray diffraction study were grown by slow diffusion of pentane into a solution of $\mathbf{2}[B(C_6F_5)_4]_2$ in CH_2Cl_2 to form $\mathbf{2}[B(C_6F_5)_4]_2 \cdot 2C_5H_{12}$. Crystal data for $\mathbf{2}[B(C_6F_5)_4]_2$: triclinic, $P\bar{1}$, $a = 12.1280(2)$ Å, $b = 15.7693(2)$ Å, $c = 16.0488(2)$ Å, $\alpha = 91.9086(9)°$, $\beta = 102.4122(7)°$, $\gamma = 96.2327(5)°$, $V = 2974.80(6)$ Å^3, $Z = 1$, $T = 173(2)$ K, $D_{calc} = 1.586$ g cm^{-3}, $R(F) = 6.96\%$ for 10051 observed independent reflections ($4° \le 2\theta \le 57°$). Two severely disordered pentane solvent molecules were analyzed by and accounted for using PLATON/SQUEEZE.[6] (b) Crystallographic data (excluding structure factors) for structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135115($\mathbf{2}[B(C_6F_5)_4]_2$), CCDC-133333(**6**), and CCDC-135116-(**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

(6) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

(7) This is a complex mixture of interconverting compounds where CO binds to the Rh^I centers. For examples of analogous *mononuclear* compounds and their reactivity with CO, see: (a) Sanger, A. R. *Can. J. Chem.* **1983**, *61*, 2214−2219. (b) Kourkine, I. V.; Slone, C. S.; Singewald, E. T.; Mirkin, C. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 2758−2759.

10.1021/ic000062q CCC: $19.00

Scheme 1. Synthetic Scheme for Compounds **5**−**8**



2, W = S, R = p-C_6H_4
3, W = O, R = p-$C_6(CH_3)_4$

5, W = S, X = Cl, L = none, R = p-C_6H_4
6, W = S, X = I, L = CO, R = p-C_6H_4
7, W = O, X = Cl, L = none, R = p-$C_6(CH_3)_4$
8, W = O, X = Cl, L = none, R = p-C_6H_4

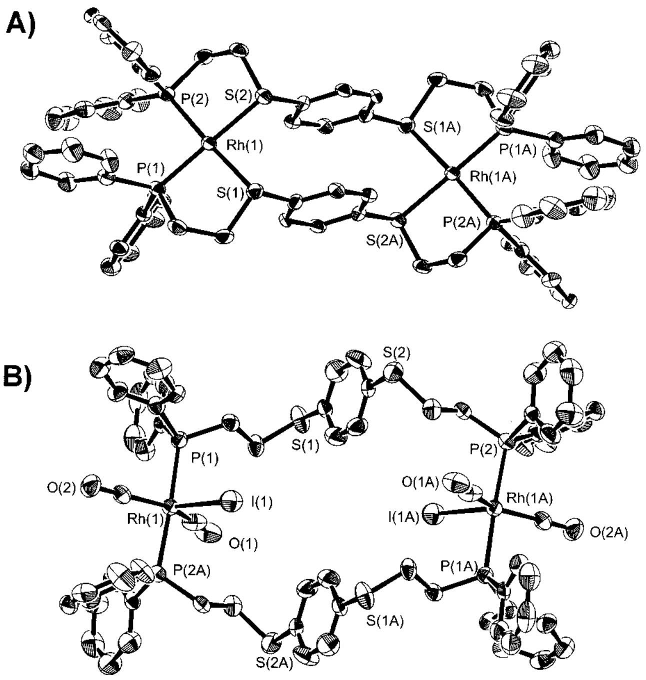


Figure 1. Atom-labeling schemes showing thermal ellipsoids at 50% probability. Hydrogen atoms, counterions, and solvent molecules have been omitted for clarity. (A) ORTEP diagram of $(\mathbf{2}[B(C_6F_5)_4]_2)\cdot 2C_5H_{12}$. Selected bond distances (Å) and angles (deg): Rh(1)−Rh(1A) = 8.381(1); Rh(1)−P(1) = 2.2456(14); Rh(1)−P(2) = 2.2606(12); Rh(1)−S(1) = 2.3502(13); Rh(1)−S(2) = 2.3493(13); P(1)−Rh(1)−S(1) = 85.63(5); P(1)−Rh(1)−P(2) = 97.36(5); P(2)−Rh(1)−S(2) = 85.80(5); S(2)−Rh(1)−S(1) = 90.89(5). **(**B) ORTEP diagram of **6**. Selected bond distances (Å) and angles (deg): Rh(1)−Rh(1A) = 11.197(12); Rh(1)−P(1) = 2.329(3); Rh(1)−P(2) = 2.329(3); Rh(1)−I(1) = 2.8167(11); P(1)−Rh(1)−P(2A) = 177.01(11); P(1)−Rh(1)−C(12) = 89.8(4); P(1)−Rh(1)−I(1) = 89.78(7); I(1)−Rh(1)−C(11) = 107.3(4); C(11)−Rh(1)−C(12) = 144.4(5); C(12)−Rh(1)−I(1) = 108.3(4).

by ^1H NMR spectroscopy (see Supporting Information), $^{31}P\{^1H\}$ NMR spectroscopy, which shows a characteristic doublet at 24 ppm (J_{Rh-P} = 124 Hz) for the two magnetically equivalent phosphine ligands, and FTIR spectroscopy, which exhibits a characteristic ν_{co} band at 1976 cm^{-1}.[8] While **5** is stable in solution, upon exposure to vacuum or nitrogen purge, **5** is converted back to **2**, which precludes characterization of it by mass spectrometry or combustion analysis. In an attempt to prepare the iodo analogue of **5**, we reacted precursor **2** with $[Me_4N]I$ in the presence of CO (1 atm). Rather than observing the mono-CO adduct, we observed a bis-CO trigonal-bipyramidal adduct (**6**) (Figure 1B). Compound **6** was characterized in the solid state by a single-crystal X-ray analysis, and in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and FTIR spectroscopy, all of which are consistent with our structural formulation (see Supporting Information).[9] In particular, the FTIR spectrum of **6** in CH_2Cl_2 exhibits two broad ν_{CO} bands at 1978 and 2017 cm^{-1}. It is interesting to note that, under identical conditions, the iodo version of these macrocycles supports an additional CO ligand at each Rh^I center. This is likely because the chloride is more electron withdrawing than the iodide ligand, and therefore, the metal centers with the Cl ligands cannot accommodate another π-accepting CO ligand.

Condensed macrocycles with ether and η^6-arene weak links also can be expanded into larger structures via this halide-induced ring-opening strategy, demonstrating its generality. For example, the addition of an excess of $[Me_4N]Cl$ in a solution of CH_2Cl_2 saturated with CO to 1 equiv of either **3** or the benzene analogue leads to quantitative formation of the corresponding neutral macrocycles **7** and **8**, respectively. Compounds **7** and **8** have been characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, FTIR spectroscopy, and mass spectrometry (see Supporting Information). Complexes **7** and **8** exhibit characteristic doublets in the $^{31}P\{^1H\}$ NMR spectrum at 19.4 ppm (J_{Rh-P} = 132 Hz) and 24 ppm (J_{Rh-P} = 124 Hz), respectively. Each has one diagnostic ν_{CO} band in the FTIR spectrum at 1973 and 1978 cm^{-1}, respectively. Complex **8** was further characterized by single-crystal X-ray diffraction, and the solid-state structure is consistent with its solution formulation.[5b]

In conclusion, we have synthesized the first example of a condensed macrocycle containing phosphinothioether ligands via the “weak-link” approach and have developed a general way of opening this type of structure as well as other condensed intermediates via novel halide-induced ring openings. Perhaps, more important is the observation that these systems provide entry into a new class of neutral macrocycles with structures and properties that can be tailored in a general way via our weak-link approach to macrocycle synthesis.

Acknowledgment. C.A.M. acknowledges the NSF (CHE-9625391) and The Georgia Institute of Technology Molecular Design Institute under ONR Contract No. G-29-X03-G6/N000 14-95-1-11 for support of this research. F.M.D. acknowledges the Committee on Institutional Cooperation/GE Fund for a predoctoral fellowship. C.A.M. and F.M.D. gratefully acknowledge Charlotte Stern for the X-ray analysis of **6**. A.L.R. acknowledges the NSF (CHE-9628768) for support.

Supporting Information Available: Experimental procedures and spectral data for all new compounds. X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000062Q

---

(8) (a) Dol, G. C.; Gaemers, S.; Hietikko, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Nolte, R. J. M. *Eur. J. Inorg. Chem.* **1998**, 1975−1985. (b) Ezhova, N. N.; Korneeva, G. A.; Kurkin, V. I.; Filatova, M. P.; Slivinsky, E. V. *Russ. Chem. Bull.* **1995**, *44*, 836−839. (c) Sanger, A. R. *J. Chem. Soc., Chem. Commun.* **1975**, 893−894.

(9) Single crystals suitable for X-ray diffraction analysis were grown by slow diffusion of a solution of pentane saturated with CO into a saturated CH_2Cl_2 solution of compound **6** under an atmosphere of CO. Crystal data for **6**: monoclinic, $P2_1/n$, a = 11.3890(8) Å, b = 15.1604(11) Å, c = 20.340(2) Å, β = 94.6132(13)°, V = 3500.5(4) Å^3, Z = 2, T = 153(1) K, D_{calc} = 1.618 g cm^{-3}, $R(F)$ = 3.9% for 2576 observed independent reflections (3.3° ≤ 2θ ≤ 56.6°).