Flexible Redox-Active Binuclear Macrocycles Formed via the Weak-Link Approach and Novel Hemilabile Ligands with *N*,*N*,*N*′,*N*′-Tetramethyl-1,4-phenylenediamine Units

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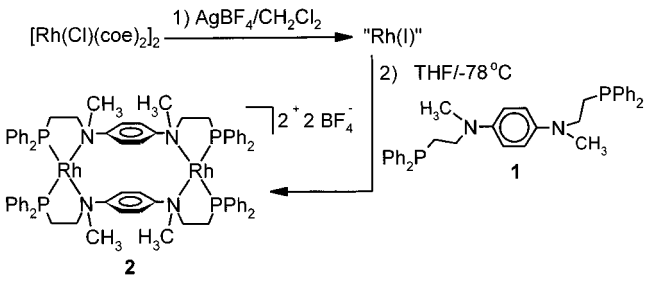
Redox-active units, derived from ferrocene, nitrobenzene, and tetrathiafulvalene, have been utilized to prepare a variety of crown ether and cryptand-based macrocycles with host−guest chemistry that can be controlled via an applied electrochemical potential.[1] These compounds, often referred to as redox switches, have been used in the development of chemical sensors and materials for facilitated small molecule and ion transport.[2] In comparison, there are relatively few strategies for preparing redox-active transition-metal-containing macrocycles where the redox-active group is part of the organic portion of the macrocycle that connects the metals that comprise the rings. The use of bipyridine-containing redox-active ligands to make rigid macrocycles, via the molecular library strategy, is one such approach,[3] but general strategies for flexible structures are not readily available. Strategies for making both rigid and flexible structures with tailorable architectural parameters are attractive because they will allow one to design supramolecular structures with preconceived small molecule binding properties and either (1) a probe to detect macrocycle−guest molecule binding events in the case of chemical sensors or (2) an electrochemical switch to adjust macrocycle-mediated stoichiometric or catalytic chemistry.

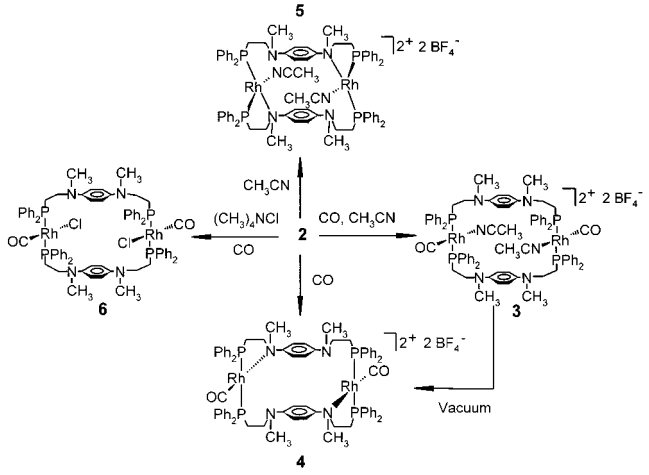
Herein, we report a method that utilizes our "weak-link synthetic approach"[4] and hemilabile ligands[5] derived from Wurster's reagent (*N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (TMPD)) to prepare a new class of flexible, redox-active binuclear macrocycles. TMPD, which can exhibit up to two sequential reversible one-electron-transfer processes,[6] can be converted into *N*,*N*′-dimethyl-*N*,*N*′-bis[2-(diphenylphospino)ethyl]-1,4-phenylenediamine (**1**) via six steps (Supporting Information). Sibert and co-workers have pioneered the use of such units in crown ether and cryptand-based structures.[7] Ligand **1** cleanly reacts with a "Rh(I) source" generated via the reaction between $[RhCl(coe)_2]_2$ (coe = cyclooctene) and $AgBF_4$ to form binuclear condensed intermediate **2**, Scheme 1. **2** has been spectroscopically characterized, and all data are consistent with its formulated structure. For example, the ^{31}P $\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2 exhibits a single resonance at δ 59.3 (d, $J_{Rh-P} = 187$ Hz), which is consistent with that for the ether and thioether analogues[4a,c,e] of **2** (δ 61.4 d, $J_{Rh-P} = 213$ Hz, and δ 64.0 d, $J_{Rh-P} = 161$ Hz, respectively).

2 can be opened into a variety of macrocycles via ligand substitution reactions with small molecules, which result in the breakage of the N−Rh weak links, Scheme 2. For example, when CO (1 atm) is introduced to an acetonitrile solution of **2**, the CO/acetonitrile adduct **3** is formed in quantitative yield. The assignment of trans phosphine stereochemistry for **3** is based upon a comparison of its ^{31}P $\{^1H\}$ NMR data (δ 21.0 d, $J_{Rh-P} = 126$ Hz) with that of the ether analogue, which has been crystallo-

Scheme 1



Scheme 2



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graphically determined to exhibit trans phosphine stereochemistry.[4c] Significantly, when the reaction between **2** and CO is carried out in CH_2Cl_2, the half-open macrocycle **4** is formed. Similarly, the reaction between **2** and acetonitrile (neat) results in the formation of half-opened macrocycle **5**. Both of these compounds have been fully characterized in solution and by solid-state single-crystal X-ray diffraction studies (Supporting Information). The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits two resonances at δ 15.6 (dd, $J_{P-P} = 130$ Hz, $J_{Rh-P} = 278$ Hz) and δ 53.6 (dd, $J_{P-P} = 126$ Hz, $J_{Rh-P} = 280$ Hz) assigned to its inequivalent phosphines. Similarly, **5** exhibits a pair of resonances at δ 32.9 (dd, $J_{P-P} = 50$ Hz, $J_{Rh-P} = 165$ Hz) and δ 64.8 (dd, $J_{P-P} = 50$ Hz, $J_{Rh-P} = 190$ Hz). The difference in P−P coupling constants for **4** and **5** can be attributed to the difference in phosphine stereochemistry around the metal centers (trans vs cis).

Significantly, the ether and thioether analogues of **2** do not exhibit its reactivity pattern, which results in the formation of half-open complexes. This is a result of the relative ligating properties of the three functional groups; the N-donor atoms in **2**, in terms of ligating ability to Rh(I), lie between that for O and S. In the case of the ether analogue of **2**, CO (1 atm) and acetonitrile (neat), respectively, completely open the condensed macrocycle,[4c] and, in the case of the thioether analogue, neither small molecule, alone, can open the condensed intermediate.[4e] While **3** is stable in acetonitrile solution, upon vacuum removal of solvent, **3** quantitatively converts back to **4**. Interestingly, in CH_2Cl_2 **2** can be opened into **6** by reacting it with tetramethylammonium chloride (10 equiv) and CO (1 atm), Scheme 2. Neutral macrocycle **6** was obtained as a yellow solid and shows a characteristic doublet at δ 21.0 (d, $J_{Rh-P} = 121$ Hz), which is consistent with the NMR data for its oxygen- and sulfur-based analogues[4e] (δ 19.4, d, $J_{Rh-P} = 132$ Hz and δ 24, d, $J_{Rh-P} = 124$ Hz). Single crystals of doubly protonated **6**, compound **7**,[8] were obtained by slow cooling of a saturated acetic acid solution of **6** with 10 equiv of CH_3CN to 0 °C. The crystal structure of **7** consists of two discrete molecules in a triclinic unit cell. The geometrical data of the two molecules, which have virtually identical coordination spheres around Rh, are very similar, and therefore, only one molecule will be described. The structure of **7** exhibits square planar Rh(I) centers with a Rh−Rh distance of 9.427 Å, Figure 1. The parallel planar arenes are 6.872 Å apart, and the CO and the Cl ligands are in an anti conformation. The structure of **7** clearly shows that protonated N(2) and N(2A) have adopted a distorted trans stereochemistry about the macrocyclic ring. Consistent with the N atom protonation, the bond angles around N(2) and N(2A) are in the 110.0−112.9° range, which significantly differs from the 117.9−122.2° range observed for its nonprotonated N(1) and N(1A) atoms or the nonprotonated or metalated nitrogen atoms in **4** and **5**.

Cyclic voltammetry was employed to probe the electrochemical response of the redox center in ligand **1** to metal ions. Ligand **1**, like its dichloride precursor and the parent redox-active TMPD unit,[6] exhibits an initial reversible one-electron oxidation at −150 mV (vs Fc/Fc^+H) in CH_2Cl_2/0.1 M $^nBu_4NPF_6$. However, unlike its dichloride precursor and the parent redox-active TMPD unit, which exhibit second reversible one-electron oxidations at 462 and 310 mV, respectively, **1** exhibits an irreversible oxidation at 450 mV. When **1** is coordinated to Rh(I) as in **2**, only irreversible oxidation is observed ($E_{pa} = 320$ mV). Macrocycles **4** and **5** also exhibit irreversible cyclic voltammetry ($E_{pa} = 170$ and 205 mV, respectively). Interestingly, macrocycle **6**, where the TMPD redox center is no longer coordinated to the Rh centers, exhibits a reversible, two-electron oxidation/reduction with an $E_{1/2} = -120$ mV, Figure 1 (inset).[9] Taken together these observations demonstrate our ability to generate macrocycles from this new ligand with reversible redox couples, but only when the redox-active group does not bond to the metal centers that comprise the macrocycle rings.

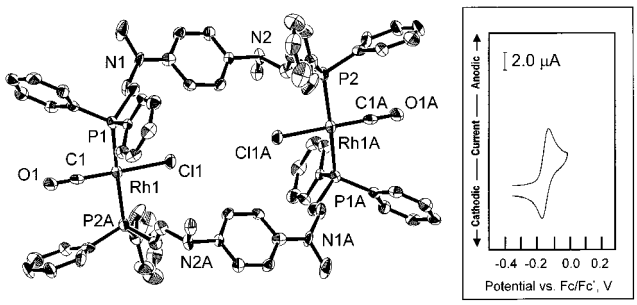

Figure 1. ORTEP diagram showing the structure of **7** with 50% probability displacement ellipsoids. Hydrogen atoms and counterions have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Rh1−Cl1 361(3); Rh1−P1 2.318(3); Rh1−P2 2.311(4); Rh1−C1 1.756(13); Rh1−Cl2 2.359(3); Cl1−Rh1−P1 90.11(11); Cl1−Rh1−C1 179.1(4); P1−Rh1−C1 89.5(4); Cl1−Rh1−P2 90.40(12); P1−Rh1−P2 167.60(13); P2−Rh1−C1 90.2(4). (Inset: cyclic voltammogram of **6**. Experimental conditions: CH_2Cl_2, 0.1 M $^nBu_4NPF_6$, scan rate = 200 mV/s, Au working electrode, Pt mesh counter electrode, and Ag wire quasi-reference electrode.)

In conclusion, we have developed an efficient synthetic method for the preparation of a new class of redox-active binuclear macrocycles that incorporate TMPD units. The work is important for the following reasons. (1) **6** is the first example of a flexible *redox-active* macrocycle formed via the weak-link approach. (2) When one considers the myriad of two- and three-dimensional cage structures (e.g., anionic, neutral, and cationic molecular cylinders) that can be generated from **2** via relatively simple coordination chemistry,[4b] this system provides a platform for preparing a diverse collection of redox-active supramolecular structures with tailorable architectural parameters and host−guest chemistries. (3) The incorporation of redox-active units within these macrocycles confers upon them a variety of novel physical properties that may allow them to sense, record, and even facilitate chemical reactions within their macrocyclic cavities.

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Supporting Information Available: Synthetic procedures for **1**−**7**, ORTEP diagrams of **4** and **5**, and crystallographic data for **4**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) X-ray structure analysis of **7** ($C_{80}H_{76}O_6N_5P_4Cl_4Rh_2$): $M = 1675.03$; colorless plate (0.27 × 0.08 × 0.02 mm); triclinic, space group $P\bar{1}$ (No. 2) with $a = 11.344(2)$ Å, $b = 14.959(3)$ Å, $c = 24.429(5)$ Å, $\alpha = 83.467(3)°$, $\beta = 87.275(3)°$, $\gamma = 74.495(3)°$, $V = 3968.1(12)$ Å^3, $Z = 2$, $D_{calc} = 1.402$ g cm^{-3}, $F(000) = 1714.00$, $\mu = 6.84$ cm^{-1}, R1 = 0.058, wR2 = 0.093. A suitable colorless plate of **7** was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a SMART-1000 CCD area detector with graphite-monochromated Mo Kα radiation $\lambda = 0.71069$ Å (ω scan, $2\theta \leq 56.6°$) at −120 °C. The structure was solved by and expanded using Fourier techniques. Owing to the paucity of the data the acetic acid and the acetyl nitrile molecules were refined isotropically without the hydrogen atoms, and the protons on nitrogen atoms were not located. The remaining non-hydrogen atoms were refined anisotropically including the chlorine ions.

(9) This is assigned as a two-electron oxidation/reduction based on a comparison with free ligand (a reversible, one-electron oxidation/reduction) and the fact that a second reversible oxidation is not observed. It should be noted that **6** also displays an irreversible oxidation at $E_{pa} = 537$ mV outside of the potential window for TMPD oxidation. Similarly, compound **3** exhibits a reversible, two-electron oxidation/reduction at $E_{1/2} = -143$ mV and an irreversible oxidation at $E_{pa} = 497$ mV.