

Stepwise Formation of Heterobimetallic Macrocycles Synthesized via the Weak-Link Approach

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Architecturally sophisticated metallomacrocycles are important for their potential in a variety of molecular recognition-based chemical applications, including chemical sensing, molecular electronics, and catalysis.¹ Several groups have employed a variety of strategies, such as the “directional-bonding” or “symmetry-interaction” approaches for building such structures.² Our group has developed a methodology now known as the weak-link approach for the synthesis of homomultimetallic macrocycles from elementary metal and ligand precursors.^{3–6} This approach has further utilized flexible and *symmetric* hemilabile⁷ multidentate ligands to yield metastable intermediates that contain both strong and weak bonds. The weak bonds in these condensed intermediates are subsequently broken to create the desired supramolecular complexes in very high yields, Scheme 1. In this manner, the thermodynamic products generated when directly targeting the flexible macrocyclic products are avoided.

Using this approach, we have synthesized over 50 examples of metallomacrocycles which vary in metal, hemilabile ligand, and ancillary ligand attached to the metal that make up the macrocycle.^{4,5} Herein, we report the synthesis of the first heterobimetallic macrocycles prepared via this approach. These macrocycles incorporate a novel dissymmetric ligand that contains both ether and thioether weak links. This allows one to exploit the difference in lability between metal–ether and metal–thioether bonds to form a variety of heterobimetallic architectures, Scheme 2. Because of the relative differences in the binding strengths of these relatively weak binding moieties toward late transition metals,^{6,7} heterobimetallic macrocyclic intermediates with metals placed selectively in either coordination pocket can be synthesized through a judicious choice of reaction conditions, Scheme 2. The weak bonds of these intermediates can be sequentially broken through the appropriate ligand substitution reactions to generate open, macrocyclic architectures **8** and **9**, Scheme 2.

The moderately air-stable dissymmetric ligand, **1**, was synthesized based, in part, on a modified literature procedure⁸ (see Supporting Information for details). The ³¹P{¹H} NMR spectrum of **1** contains two singlets at –15.4 and –20.5 ppm assigned to the two inequivalent phosphine moieties, Figure 1A. These two resonances compare well with those for the related symmetric ether or thioether ligands.^{4,6} Upon addition of 2 equiv of ligand **1** to 1 equiv of a Pd(II)⁹ or Rh(I)¹⁰ starting material, monometallic intermediates **2**¹¹ and **3**¹² were synthesized in nearly quantitative yields, respectively.¹³

The metals in these two intermediates selectively coordinate to the thioether ends of **1** to yield structures that contain (1) strong phosphorus–metal bonds, (2) relatively weak sulfur–metal bonds, and (3) uncoordinated phosphine and ether moieties (**2** and **3**). The ³¹P{¹H} NMR spectra of **2** and **3**, Figure 1B and C, are consistent with their proposed structures showing preferential coordination of the thioether to the metal center. Notably, no mixed (thioether/

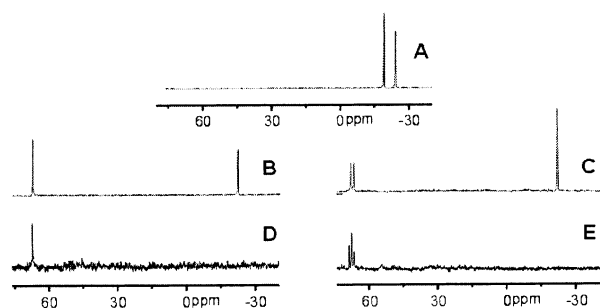
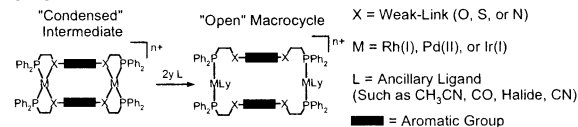
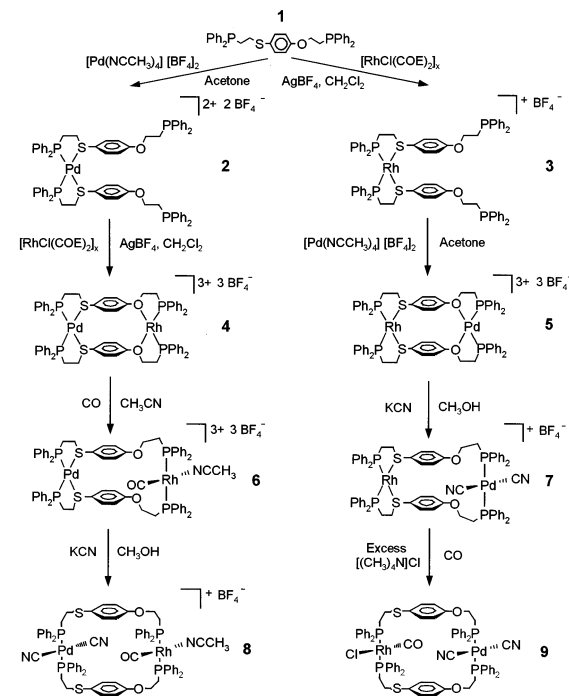


Figure 1. ³¹P{¹H} NMR spectra of compounds **1** (A), **2** (B), **3** (C), **4** (D), and **5** (E). The spectrum of **3** is shown at –50 °C.

Scheme 1



Scheme 2



ether) products are observed. This preferred coordination environment can be attributed to the stronger binding affinity of the thioether groups to either Rh(I) or Pd(II) than that for ether functionalities.¹⁴ Complexes **2** and **3** are stable with respect to isomerization and decomposition when heated in CD₂Cl₂ solution under N₂ at 60 °C for 3 days. When an additional equivalent of a

metal precursor is added to **2** or **3**, the heterobimetallic condensed intermediates **4** and **5** are formed in nearly quantitative yields (>95%) and contain (1) two different metal atoms, (2) strong metal–phosphorus bonds, (3) weak metal–thioether bonds, (4) weaker metal–ether bonds, and (5) substitutionally labile metal centers. The spectra indicate that there is a set of equivalent phosphine moieties coordinated to each metal center. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **4** contains a singlet at 65.0 ppm, and this singlet lies on top of a buried doublet, Figure 1D.¹⁵ Complex **5** displays a singlet at 65.4 ppm and a doublet at 67.3 ppm ($J_{\text{P-Rh}} = 161$ Hz) in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, Figure 1E. The $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts and coupling constants for all four of these intermediates, **2–5**, are consistent with their structural formulations and compare well with those for the symmetric, homobimetallic model complexes.^{4–6}

The weak ether and thioether bonds can be selectively broken through simple substitution chemistry. By varying the reaction conditions and incoming ligands, we synthesized fully and partially opened macrocycles (with respect to the coordination environment around the metal center) with 0, +1, +2, or +3 charges. Two examples are shown in Scheme 2. In the first example, a charged macrocycle, **8**, is synthesized by first adding excess acetonitrile in the presence of CO (1 atm). These weak ligands selectively break the weak metal–ether bond to yield the half-opened intermediate **6**.¹⁶ The thioether bonds are then broken by adding 2 equiv of a methanol solution of KCN to yield the fully opened macrocycle **8**.¹⁷ Following a similar route to synthesize the neutral macrocycle **9**, 2 equiv of a methanol solution of KCN are added to a methanol suspension of **5**. The cyanide selectively breaks the palladium–ether bonds to yield **7** as a solid that can be dissolved in methylene chloride.¹⁸ The remaining metal–thioether bonds are then broken by adding excess $[(\text{CH}_3)_4\text{N}]\text{Cl}$ and charging the resulting solution with CO (1 atm) to yield the fully opened, neutral macrocycle **9**.¹⁹ Both sets of reactions are nearly quantitative.¹³ The $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts and coupling constants of these complexes correspond to the trans position of the phosphine ligands and compare well with the analogous symmetric, homobimetallic complexes.^{4–6}

In conclusion, by taking advantage of the stepwise synthetic control offered by the weak-link approach, we have prepared partially opened and structurally flexible, fully opened heterobimetallic macrocycles in high yields. The mechanistic distinction offered by this method not only provides a synthetic route to structures unobtainable via other, thermodynamically driven, approaches, but also substantially increases the scope of the types of structures that can be targeted via the weak-link approach.

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Supporting Information Available: Detailed experimental procedures and data for the syntheses of **1–9** and the precursors to **1**.

Detailed X-ray structural data including a summary of crystallographic parameters, select bond angles and distances, an ORTEP diagram, and CIF file for **1**. Correlation table between structural and spectroscopic properties of selected Rh(I) and Pd(II) macrocycles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) $[\text{Pd}(\text{NCCH}_3)_4][\text{BF}_4]_2$.
- (10) Generated from $[\text{RhCl}(\text{COE})_2]_x$ via reaction with AgBF_4 in CH_2Cl_2 (COE = cyclooctene); see Supporting Information.
- (11) **2**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 63.7 (s, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S}$), –21.5 (s, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{O}$).
- (12) **3**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 66.1 (d, $J_{\text{Rh-P}} = 162$ Hz, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S}$), –20.3 (s, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{O}$).
- (13) As determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.
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- (15) This doublet can be seen upon opening the Pd side of the intermediate as the prominent Pd–P resonance shifts upon addition of KCN.
- (16) **6**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 63.2 (s, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S}$), 22.0 (d, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{O}$, $J_{\text{Rh-P}} = 120$ Hz).
- (17) **8**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 17.9 (s, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S}$), 16.9 (d, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{O}$, $J_{\text{Rh-P}} = 122$ Hz).
- (18) **7**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 64.2 (d, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S}$, $J_{\text{Rh-P}} = 164$ Hz), 17.3 (s, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{O}$).
- (19) **9**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 21.4 (d, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S}$, $J_{\text{Rh-P}} = 122$ Hz), 16.6 (s, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{O}$).

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