

Chemical Origami: Formation of Flexible 52-Membered Tetranuclear Metallacycles via a Molecular Square Formed from a Hemilabile Ligand

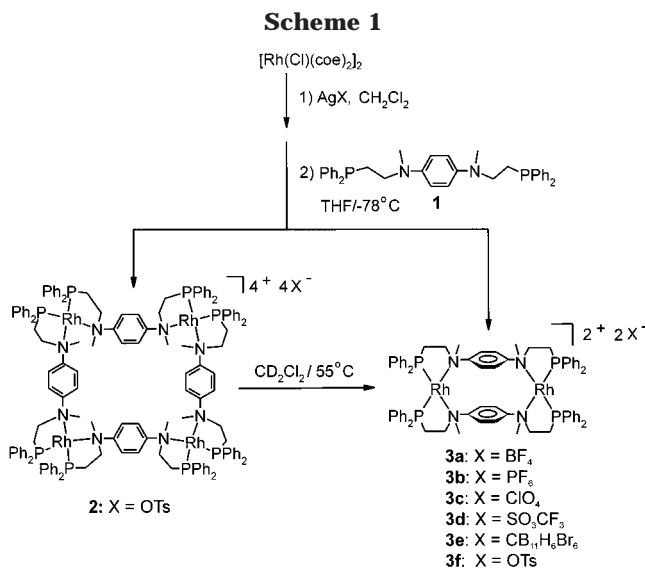
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Summary: A novel tetranuclear rhodium complex has been synthesized by reaction of *N,N*-dimethyl-*N,N*-bis[2-(diphenylphosphino)ethyl]-1,4-phenylenediamine with a “Rh(I) source” generated from the reaction between $[\text{RhCl}(\text{coe})_2]_2$ (coe = cyclooctene) and AgOTs (OTs = *p*-toluenesulfonate). Significantly, the complex can be reacted with small molecules that selectively break the *N*–Rh links to afford flexible, 52-membered tetranuclear macrocycles.

The “directional-bonding approach” to supramolecular synthesis relies on directional and typically rigid ligands to prepare supramolecular coordination complexes with predesigned geometries in high yield.¹ Molecular squares, triangles, and boxes are all examples of structures that can be assembled via this synthetic approach. Thus far, squares are the most common products, and most squares prepared to date contain Pd(II) or Pt(II) metals as corners and use rigid or semirigid aromatic bifunctional ligands as edge linkers.² Significantly, the metal centers in these complexes are coordinatively saturated and displacement of the rigid edge ligands from the metal centers with small monodentate molecules will result in destruction of the square geometry. Herein, we report the formation, characterization, and preliminary reactivity of a novel square complex (**2**) formed



from the structurally flexible hemilabile ligand³ *N,N*-dimethyl-*N,N*-bis[2-(diphenylphosphino)ethyl]-1,4-phenylenediamine (**1**) and a Rh(I) precursor (Scheme 1). This reaction effectively folds a larger flexible macrocyclic structure (52-membered ring) into a 28-membered square that is held together via the rigid diaminophenyl groups of the hemilabile ligands used to prepare it. Significantly, the square can be opened into a variety of 52-membered rings by introducing it to small molecules that break its weak amino–Rh bonds but not its strong Rh–phosphine bonds.

Previously, we reported the synthesis of binuclear metallomacrocycles and other supramolecular coordination compounds from flexible hemilabile ligands via the “weak-link synthetic approach”.⁴ The approach takes advantage of the design of intermediates with strategically located strong and weak links to create a rigid

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condensed structure that can be subsequently opened into a flexible macrocycle by introducing it to small molecules that can selectively break its weak links. Besides yielding flexible rather than rigid structures, the weak-link approach utilizes kinetic rather than thermodynamic control (as in the case of the directional bonding approach) to target macrocyclic compounds. Therefore, the reaction used to produce **2** is an interesting new hybrid of the two approaches, which takes advantage of intermediates and concepts common to the two approaches to give extraordinarily large and flexible ring structures in high yield.

We recently reported the synthesis of ligand **1** and its reactivity in forming the homobinuclear Rh(I) condensed intermediate **3a** (Scheme 1).⁵ The binuclear complex has now been prepared with a variety of other counterions **3b–e** (PF_6^- , ClO_4^- , SO_3CF_3^- , $\text{CB}_{11}\text{H}_6\text{Br}_6^-$) using the corresponding silver salt via similar procedures. All complexes exhibit the diagnostic $^{31}\text{P}\{^1\text{H}\}$ NMR resonances in CD_2Cl_2 between δ 59.5 and 60.0 (d, $J(\text{Rh},\text{P}) = 187$ Hz), which compare well with that of the BF_4^- salt **3a** (δ 60.2 d, $J(\text{Rh},\text{P}) = 187$ Hz).⁵ However, upon addition of a "Rh(I) source" generated via the reaction between $[\text{RhCl}(\text{coe})_2]_2$ (coe = cyclooctene) and AgOTs (OTs = *p*-toluenesulfonate) to ligand **1**, the tetrametallic square **2** was formed and isolated as a pure solid in 65% yield (Scheme 1).⁶ The binuclear complex **3f** was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy as the only other reaction byproduct (Scheme 1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a CD_2Cl_2 solution of **2** exhibits two resonances at δ 60.3 (dd, $J(\text{Rh},\text{P}) = 185$ Hz, $J(\text{P},\text{P}) = 51$ Hz) and δ 63.5 (dd, $J(\text{Rh},\text{P}) = 189$ Hz, $J(\text{P},\text{P}) = 52$ Hz), assigned to the two sets of magnetically inequivalent phosphorus atoms. In addition, the electrospray mass spectrum, ^1H NMR spectroscopy, and combustion analysis of **2** were consistent with its formulated structure.

The tetramer **2** slowly converts to the dimer **3f** in CD_2Cl_2 , as indicated by the formation of a $^{31}\text{P}\{^1\text{H}\}$ NMR resonance at δ 60.2 (d, $J(\text{Rh},\text{P}) = 187$ Hz). The assignment of this resonance to the binuclear complex **3f** is based on a comparison of the spectrum with that of the reported binuclear complex with BF_4^- counterions, **3a**.⁵ Further investigation shows that the tetramer **2** can be cleanly converted to the binuclear condensed intermediate **3f** in quantitative yield by heating a CD_2Cl_2 solution of **2** at 55 °C for 20 h (Scheme 1).

Recrystallization of tetramer **2** from CH_2Cl_2 by slow diffusion into pentane afforded deep red crystals suit-

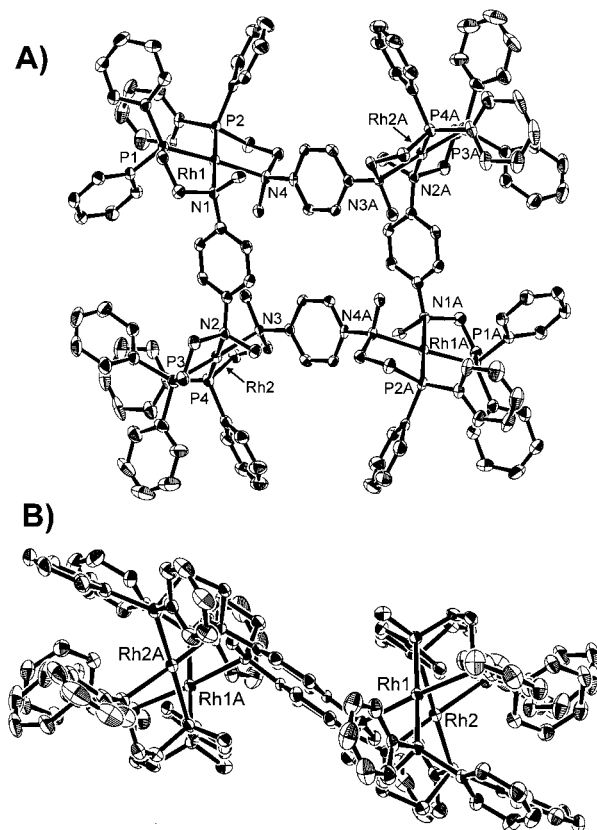


Figure 1. ORTEP diagrams showing the structure of $2 \cdot 10\text{CH}_2\text{Cl}_2 \cdot 2\text{C}_5\text{H}_{12}$ with thermal ellipsoids drawn at the 50% probability level: (A) top view; (B) side view. Hydrogen atoms, solvent molecules, and counterions have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Rh1–P1, 2.193(2); Rh1–P2, 2.189(2); Rh1–N1, 2.270(5); Rh1–N4, 2.276(5); Rh2–P3, 2.188(2); Rh2–P4, 2.195(2); Rh2–N2, 2.326(2); Rh2–N3, 2.258(5); P1–Rh1–P2, 96.22(6); P1–Rh1–N1, 83.13(13); P1–Rh1–N4, 174.96(13); P2–Rh1–N1, 177.34(13); P2–Rh1–N4, 82.47(13); N1–Rh1–N4, 98.4(2).

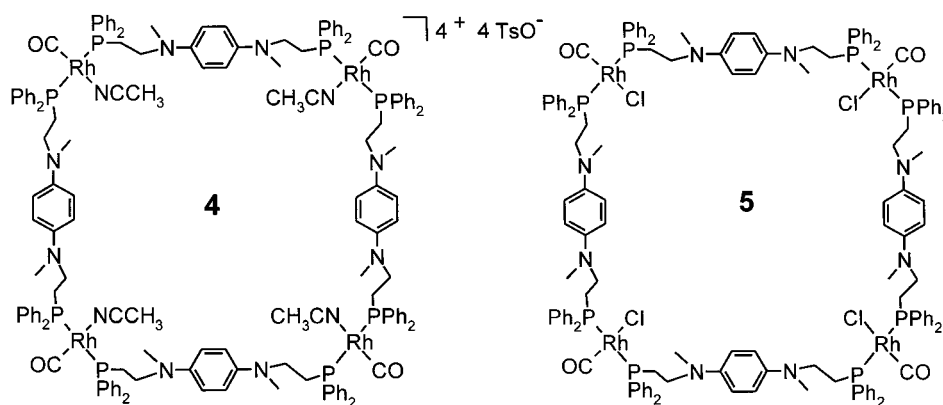
able for a single-crystal X-ray diffraction study.⁷ Consistent with the formulated structure of **2** in solution, the solid structure shows that ligand **1** bridges the four Rh centers through its diaminophenyl groups and chelates through its phosphine moieties (Figure 1A). Each Rh exhibits cis phosphine coordination. A side view of the solid-state structure of $2 \cdot 10\text{CH}_2\text{Cl}_2 \cdot 2\text{C}_5\text{H}_{12}$ shows that the methyl groups attached to the nitrogen atoms are directed to the internal core defined by the

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(6) Synthesis of **2**: in a glovebox, a mixture of solid $[\text{RhCl}(\text{coe})_2]_2$ (320 mg, 0.89 mmol) and AgOTs (248 mg, 0.89 mmol), dissolved in 5 mL of CH_2Cl_2 , was stirred for 1 h. The resulting reaction mixture was filtered through Celite to remove a light gray precipitate, and the filtrate was diluted with 50 mL of THF. A solution of **1** (500 mg, 0.89 mmol) in 50 mL of THF was added dropwise to the filtrate at -78 °C. The solution was stirred over 3.5 h, followed by removal of the solvent in vacuo to afford an orange powder. The crude product was further recrystallized by vapor diffusion of pentane into a CH_2Cl_2 solution to yield microcrystals of **2** (484 mg, 65%). ^1H NMR (300 MHz, CD_2Cl_2): δ 2.40 (m (br), 16H; CH_2N), 2.80 (s, 12H; CH_3Ar), 3.32 (s, 24H; CH_3N), 3.40 (m (br), 16H; CH_2P), 6.50 (s, 16H; $\text{NC}_6\text{H}_4\text{N}$), 6.80 (d, 8H; $\text{MeC}_6\text{H}_4\text{SO}_3$), 7.20 (d, 8H; $\text{MeC}_6\text{H}_4\text{SO}_3$), 7.35 & 7.40 (m (br), 80H; $\text{P}(\text{C}_6\text{H}_5)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2): δ 60.3 (dd, $J(\text{Rh},\text{P}) = 185$ Hz, $J(\text{P},\text{P}) = 51$ Hz), 63.5 (dd, $J(\text{Rh},\text{P}) = 189$ Hz, $J(\text{P},\text{P}) = 52$ Hz). ESMS (*m/z*): $[\text{M} - \text{TsO}]^+$ calcd 3165, found 3165; $[\text{M} - 2\text{TsO}]^{2+}$ calcd 1497.3, found 1497; $[\text{M} - 3\text{TsO}]^{3+}$ calcd 941.2, found 941; $[\text{M} - 4\text{TsO}]^{4+}$ calcd 663, found 663. Anal. Calcd for $\text{C}_{172}\text{H}_{180}\text{N}_8\text{O}_{12}\text{S}_4\text{P}_8\text{Rh}_4$: C, 61.87, H, 5.43, N, 3.36. Found: C, 61.57, H, 5.70, N, 3.30. Dec pt: 180–183 °C.

(7) Crystallographic data for $2 \cdot 10\text{CH}_2\text{Cl}_2 \cdot 2\text{C}_5\text{H}_{12}$: crystal dimensions $0.22 \times 0.23 \times 0.13$ mm; triclinic; space group $P1$ (No. 2); $a = 12.682(2)$ Å, $b = 20.722(3)$ Å, $c = 21.236(3)$ Å, $\alpha = 112.892(3)^\circ$, $\beta = 102.500(3)^\circ$, $\gamma = 95.127(3)^\circ$, $V = 4925.0(13)$ Å³; $Z = 1$; $\rho_{\text{calcd}} = 1.444$ g cm⁻³; $2\theta_{\text{max}} = 56.6^\circ$; Mo K α radiation, $\lambda = 0.71069$ Å; scan mode ω ; $T = 153$ K; 45 567 reflections, of which 22 823 are unique, and of which 15 035 were included in the refinement; data corrected for Lorentz polarization effects; solution by direct methods (Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. SIR92. *J. Appl. Crystallogr.* **1993**, *26*, 343) and refinement on $|F^2|$ by full-matrix least-squares procedures (TeXsan for Windows v1.03, Molecular Structure Corp., The Woodlands, TX); 1099 parameters; non-hydrogen atoms (except the disordered O and solvent Cl) were refined anisotropically; H atoms were included in idealized positions except those on the disordered dimethyl chloride and pentane solvent, but not refined; final values $R[F] = 0.058$, $R_w[F^2] = 0.129$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-170371. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Chart 1



tetrametallic square and are in a cis geometry with respect to the 1,4-phenylenediamine framework (Figure 1B). Moreover, Figure 1B shows the interesting way this molecule is folded through the multidentate bonding interaction between the hemilabile ligands and the metal centers. One ligand (defined by P1–N1–N2–P3), Rh1, and Rh2 sit on top of the plane defined by the ligands P2–N4–N3A–P4A and P4–N3–N4A–P2A, while Rh1A, Rh2A, and one ligand (defined by P3A–N2A–N1A–P1A) reside below that plane. This conformational geometry alleviates steric repulsions between the diphenylphosphino groups and the methyl groups while maintaining the square-planar coordination geometry at the Rh centers. The dimensions of the square are 7.738×6.691 Å, and the Rh1...Rh2 distance is 7.892 Å. Neither solvent molecules nor counterions were found in the cavity of $2 \cdot 10\text{CH}_2\text{Cl}_2 \cdot 2\text{C}_5\text{H}_{12}$.

Significantly, the condensed tetranuclear complex **2** can be opened into a variety of 52-membered macrocycles via ligand substitution reactions with small molecules such as CO and acetonitrile, which result in the selective cleavage of the N–Rh weak links. For example, when CO (1 atm) is introduced to an acetonitrile solution of **2** in a dry ice/acetone bath, the CO/acetonitrile adduct **4** is formed in quantitative yield (Chart 1). Additionally, neutral macrocycle **5** can be formed by reacting a CD_2Cl_2 solution of **2** with tetramethylammonium chloride (10 equiv) and CO (1 atm) in a dry ice/acetone bath (Chart 1). A space-filling representation of **4** shows that the expanded inner cavity (~ 11 Å in diameter) is large enough to accommodate a molecule approximately the size of C_{60} . Note that once **2** is converted into macrocycle **4** or **5**, there is no evidence for the formation of binuclear compound **3**. Therefore, the kinetic intermediate **2** serves as a route to the slightly larger macrocycles, provided it is used immediately after its formation.

In conclusion, we have discovered an interesting and novel anion-dependent route to a novel molecular square

assembled via hemilabile ligands. This reaction and complex are important not only because they provide a route to large, flexible metallomacrocycles in high yield but also because they provide insight into the basis behind the weak-link approach to macrocycle synthesis. The premise behind the approach is that a condensed intermediate such as **3** can be formed in high yield by offering a route that is energetically more favorable than oligomerization and polymerization reactions but with a high energetic barrier to monomer formation.^{1e,4c} The isolation of tetramer **2** (the first of its kind)⁸ and the observation that it can be cleanly converted to dimer **3** suggests that many possible structures could be formed en route to the local minimum **3**, such as **2**, and the approach is exhibiting the kinetic control designed into it, but in an unanticipated way.

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Supporting Information Available: Text giving experimental procedures and characterization data for new compounds and complete data for the X-ray crystallographic structure of **2**, including tables of crystal data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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