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Metallomacrocycles That Incorporate Cofacially Aligned Diimide Units

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Abstract: Pyromellitic diimide and naphthalene diimide moieties were incorporated into hemilabile phosphanylalkyl thioether ligands. These ligands reacted with $[Cu(CH_3CN)_4]PF_6$ and $[Rh(NBD)Cl]_2$ (NBD = norbornadiene) by the weak-link approach to form condensed intermediates. Upon reaction of each diimide ligand with these transition-metal precursors, the two diimide units became cofacially aligned within a supramolecular macrocyclic architecture. The introduction of ancillary ligands to each of these condensed intermediates caused the weak thioether–metal bonds to break, thus generating a large macrocycle in which the distance between diimide units is significantly larger than for the condensed intermediates. The two Rh^I cationic condensed intermediates were characterized by single-crystal X-ray diffraction studies, and the electrochemical activity of these macrocycles was demonstrated with the naphthalene diimide–Cu^I macrocycles.

Keywords: electron-deficient compounds · hemilabile ligands · macrocycles · metallacycles · supramolecular chemistry

Introduction

Coordination-chemistry-driven assembly processes are now commonly used to prepare a wide variety of supramolecular complexes. Several general synthetic approaches have emerged that rely on metal–ligand interactions, including the directional-bonding, symmetry-interaction, and weak-link approaches (WLA).[1–5] An attractive feature of these methods is that through careful ligand design and choice of transition-metal precursor, one can rapidly put together complex architectures such as squares, rectangles, cubes, cylinders, and other two- and three-dimensional structures.[1–3,6–8] Moreover, in certain cases, one can position chiral moieties, fluorophores, and redox-active centers within such structures in a deliberate and high-yielding fashion.[6,9–15] This capability has allowed researchers to design large functional structures with tailored recognition and catalytic properties that have formed the basis for a series of new chemical sensors and several novel classes of catalysts.[9,10,16–19] Most recently, our group showed how one can use the WLA to prepare a new type of allosteric catalyst that mimics the properties of allosteric enzymes and can be used in the context of amplified chemical detection.[20]

Redox-active ligands are attractive because, once incorporated into a supramolecular architecture, they can be used either as probes to follow recognition or as modulators of chemical reactivity. Indeed, we and others have developed routes to use ferrocenyl moieties, Wurster crowns, and porphyrins to build macrocyclic structures that, in some cases, retain the reversible redox activity of the ligand from which they derive.[21–26] One class of metallomacrocyclic structures that have not been fully explored are those that derive from pyromellitic diimide and naphthalene diimide, two molecules in the rylene family of dyes. Some initial work has utilized the symmetry-interaction and directional-bonding approaches to assemble rigid macrocycles.[6,14,27–31] Of the few existing examples, most had to combat problems with instability of the resulting metallomacrocycles or the formation of mixtures of products.[14,27–29] Despite limited success with attempts to make metallomacrocycles with these ligand building blocks, organic chemists have used it as a motif in the preparation of a wide variety of donor/acceptor complexes, host/guest complexes, and electron-transfer systems.[32–43]

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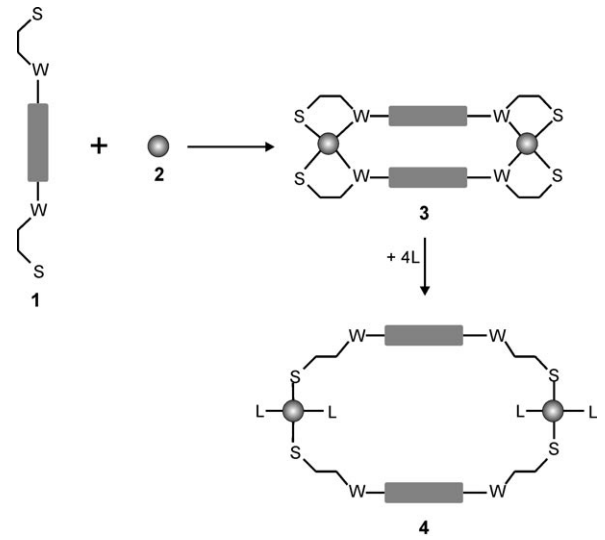
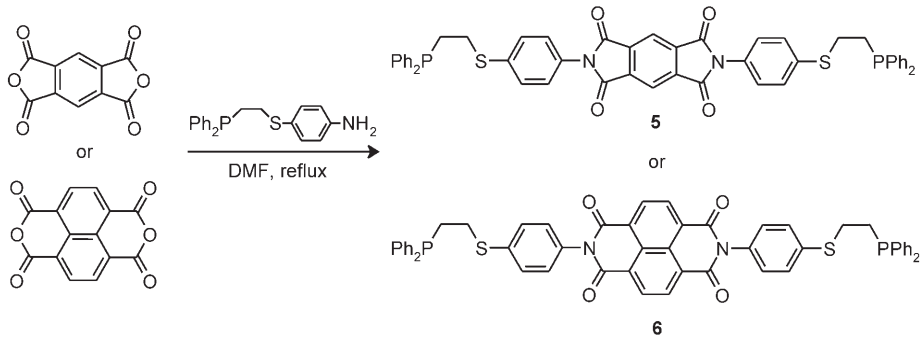
The WLA is a highly generalized synthetic methodology for the formation of metallomacrocycles.[1,44] In this approach, a hemilabile ligand **1** containing a strongly binding phosphine group and a more weakly binding moiety, such as oxygen or sulfur, is combined in a one-to-one ratio with a monomeric metal source **2** (Scheme 1). These reagents react to form a condensed intermediate or closed macrocycle **3**. Upon introduction of an ancillary ligand, the weak atom–metal bond is selectively cleaved to yield a large open macrocycle **4**. This approach was shown to be highly general with respect to choice of transition metals, hemilabile ligands, and ancillary ligands, but has not been explored in the context of the rylene family of ligands.[10,12,13,45–50] Herein, we report how the WLA can be used to synthesize a series of bimetallic Rh^I and Cu^I macrocycles that contain redox-active pyromellitic diimide and naphthalene diimide groups.



Scheme 1. The weak-link approach. ● = Transition-metal center, W = weakly binding atom, S = strongly binding atom, L = ancillary ligand.

dianhydride in a condensation reaction to form **5** and **6**, respectively (Scheme 2). Both ligands have poor solubility in most solvents; consequently, purification was difficult. Therefore, they were characterized primarily by mass spectrometry, elemental analysis, and their reactivity in forming the targeted macrocyclic structures.



Scheme 2. Synthesis of ligands **5** and **6**. DMF = *N*,*N*-dimethylformamide.

Results and Discussion

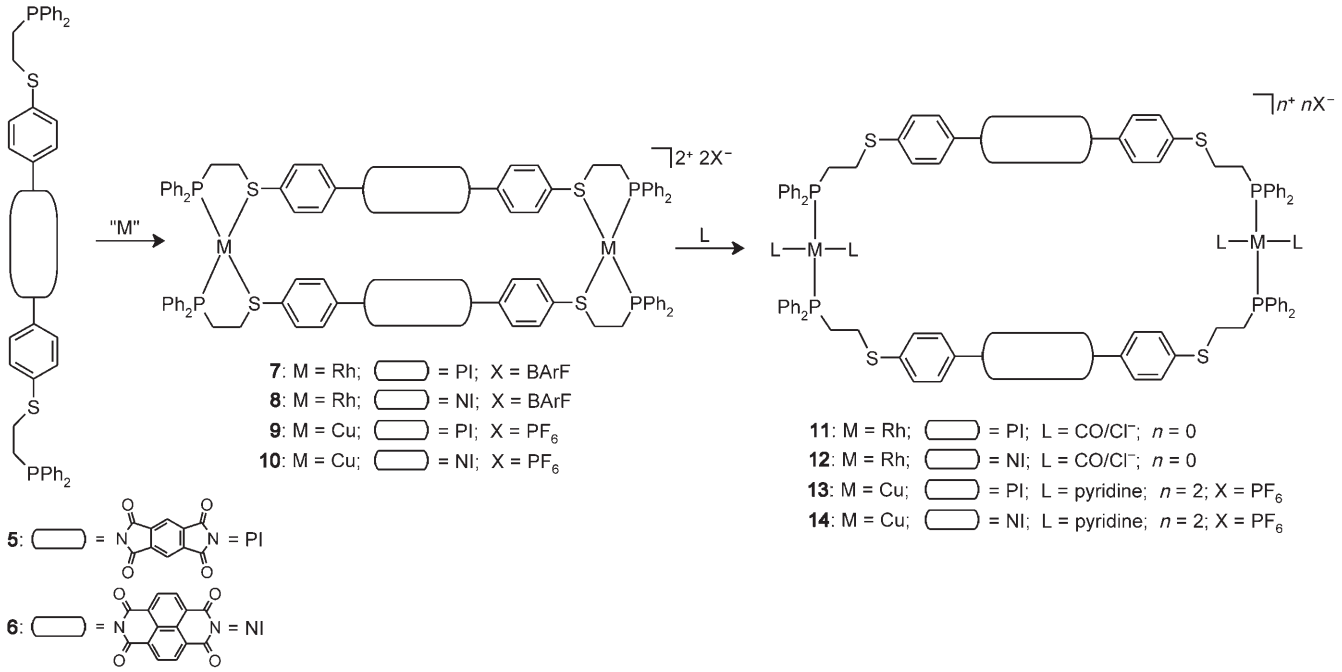
Synthesis of Ligands 5 and 6

Ligands **5** and **6** were each synthesized in two steps from commercially available starting materials. 4-(2-Diphenylphosphanylethylthio)phenylamine was synthesized according to literature procedures and then combined with either pyromellitic dianhydride or 1,4,5,8-naphthalenetetracarboxylic

Synthesis of Condensed Intermediates 7–10

The Rh^I condensed intermediates **7** and **8** were synthesized by a route similar to published methods for analogous compounds formed from different hemilabile ligands (Scheme 3).[45] $[Rh(NBD)Cl]_2$ and NaBArF (NBD = norbornadiene, BArF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) were allowed to stir in CH_2Cl_2 to abstract the chloride ligands from the Rh^I center. This solution was then added to a suspension of ligand **5** or **6**. The thioether and phosphine moieties of **5** and **6** displaced the NBD moieties on the Rh^I center to yield cationic condensed intermediates **7** and **8**, respectively. Although the ligands are not soluble in CH_2Cl_2, once complexed to the Rh^I metal centers, the condensed intermediates **7** and **8** are quite soluble, with all precipitates dissolving under the conditions studied. Owing to this lack of ligand solubility, reaction times were significantly longer than those used in published methods for previously studied analogous complexes (overnight versus immediate reaction). Macrocycles **7** and **8** were fully characterized in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, and elemental analysis, and in the solid state by single-crystal X-ray diffraction studies (Figures 1 and 2).

Condensed intermediates **9** and **10** were synthesized by methods analogous to published procedures, but with longer reaction times owing to the limited solubility of ligands **5** and **6** in CH_2Cl_2 (Scheme 3).[48] A solution of $[Cu(CH_3CN)_4]PF_6$ in CH_2Cl_2 was added to a suspension of ligand **5** or **6** in CH_2Cl_2. The thioether and phosphine moieties of the ligands chelated to the Cu^I metal center, displacing the CH_3CN ligands and generating macrocycles **9** and **10**. Again, unlike the precursor ligands, **9** and **10** are soluble in CH_2Cl_2 and were characterized in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, and elemen-



Scheme 3. Synthesis of condensed intermediates **7**–**10** and open macrocycles **11**–**14**.

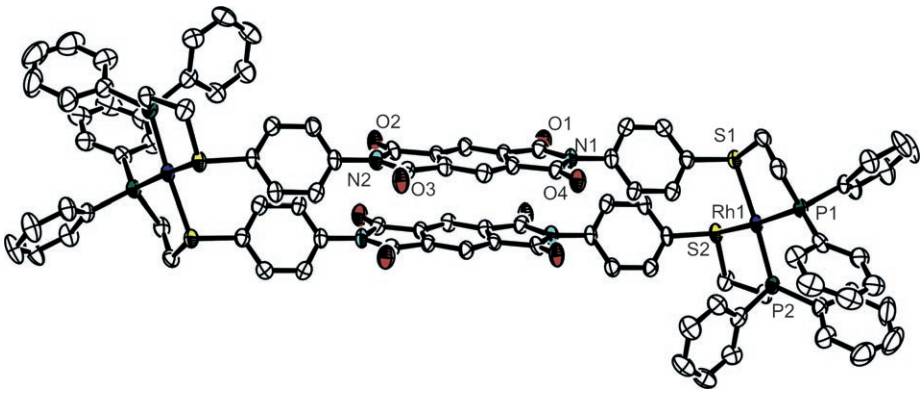


Figure 1. ORTEP diagram of **7**·4CH_2Cl_2 showing the labeling scheme of selected atoms. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

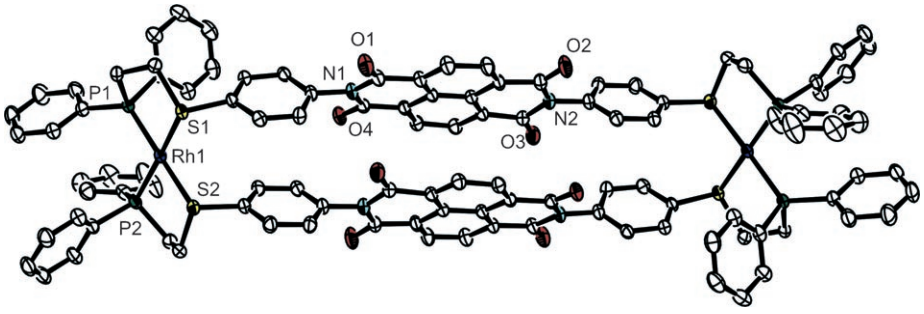


Figure 2. ORTEP diagram of **8**·3CH_2Cl_2·2H_2O showing the labeling scheme of selected atoms. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

tal analysis. All data are consistent with the assigned structures.

X-ray Crystallographic Analysis of 7 and 8

Single crystals of **7**·4CH_2Cl_2 were grown by layering pentane over a dilute solution of **7** in CH_2Cl_2 at room temperature. Crystallographic parameters are summarized in Table 1. All samples studied diffracted diffusely. No symmetry higher than triclinic was observed, and the centrosymmetric alternative was determined by the results of refinement. The structure was solved by direct methods in *P*1 and then translated to an inversion center for refinement in *P*(−1). All non-hydrogen atoms of the ion pair were refined anisotropically, and hydrogen atoms were treated as idealized contributions. The highly diffuse contributions of the four molecules of methylene chloride were treated by using the void-volume-analysis program SQUEEZE (A. Spek; calcd:

Table 1. Crystallographic parameters for **7** and **8**.

Complex	**7**	**8**
Formula	$C_{164}H_{100}B_2F_{48}N_4O_8P_4Rh_2S_4{\cdot}4CH_2Cl_2$	$C_{172}H_{104}B_2F_{48}N_4O_8P_4Rh_2S_4{\cdot}3CH_2Cl_2{\cdot}2H_2O$
M_r	3985.74	4038.98
space group	$P\bar{1}$	$P\bar{1}$
crystal system	triclinic	triclinic
A [Å]	10.2666(17)	13.974(2)
B [Å]	18.847(3)	18.004(3)
C [Å]	24.640(4)	20.234(3)
A [°]	92.618(3)	101.974(2)
B [°]	94.269(3)	104.710(2)
Γ [°]	92.968(3)	111.444(2)
V [Å^3]	4242.2(14)	4320.5(11)
Z	1	1
crystal size [mm^3]	$0.25\times0.20\times0.10$	$0.350\times0.280\times0.154$
D_{calcd} [Mg cm^{-3}]	1.396	1.552
$2\theta_{max}$	47.00	56.88
radiation, wavelength	$Mo_{K\alpha}$, 0.71073 Å	$Mo_{K\alpha}$, 0.71073 Å
T [K]	100(2)	293(2)
R, Rw	0.0793, 0.2116	0.0641, 0.1834

168 electrons per unit cell; found: 163 electrons per unit cell). The solvent molecules were included in the computed intensive properties. The solution was refined against $F2$, and the final $R1$ and $wR2$ values were computed as 7.93 and 21.16, respectively.

Single yellow plate crystals of **8**·$3CH_2Cl_2{\cdot}2H_2O$ were grown by slow liquid diffusion of pentane into a solution of **8** in CH_2Cl_2 at room temperature. Crystallographic parameters are given in Table 1. A crystal suitable for study was mounted on a glass fiber. All measurements were made on a charge-coupled detector (CCD) with graphite monochromated $Mo_{K\alpha}$ radiation. Data were collected at 293(2) K with a Bruker SMART detector and processed with SAINT-NT from Bruker. The structure was solved by direct methods[51] and expanded by using Fourier techniques.[52] The disordered fluorine and chlorine atoms were refined with group anisotropic displacement parameters. The chlorine atoms from the disordered solvent were fixed in places found from the difference map. The remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement on $F2$ was based on 19459 reflections and 1158 variable parameters and converged with $R1$ and $wR2$ values of 6.41 and 18.34, respectively.

Both crystal structures illustrate the cofacial alignment of the diimide moieties, with distances between the arene rings of 3.64 Å for **7** and 4.05 Å for **8**. These distances compare well with analogous condensed intermediates formed through the WLA with π–π interactions.[45–47,49,53] The rhodium–rhodium distance is 20.42 Å for **7** and 20.61 Å for **8**. These are among the longest metal–metal distances for bimetallic macrocycles formed by the WLA.

Synthesis of Open Macrocycles 11–14

Open rhodium macrocycles **11** and **12** were synthesized by adding benzyltriethylammonium chloride to solutions of **7** and **8**, respectively, in CD_2Cl_2 (Scheme 3).[45] Upon charging the solutions with CO, the weak thioether–rhodium bonds were selectively broken to yield open macrocycles **11** and **12**; the phosphine groups on the rhodium atoms are situated with *trans* geometry, and the CO and Cl^- ligands occupy the remaining coordination sites. These macrocycles were fully characterized in solution by ^1H and $^{31}P\{^1H\}$ NMR and FTIR spectroscopy. Owing to the lability of the CO moieties, characterization by elemental analysis and mass spectrometry was not possible. All spectroscopic data are consistent with the assigned structure, and the assignments are unambiguous based on comparison of NMR and FTIR data with those in the literature for isoelectronic species made from different hemilabile ligands.[45]

Open copper macrocycles **13** and **14** were prepared by addition of four equivalents of pyridine to condensed intermediates **9** and **10**, respectively (Scheme 3).[48] Two pyridine groups displaced the thioether moieties bound to each copper center. The open copper macrocycles were fully characterized in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, and elemental analysis, and all data are consistent with the proposed structural assignments.

Electrochemical Studies of Copper Macrocycles 10 and 14

Both pyromellitic diimide and naphthalene diimide are frequently used as electron acceptors and, as such, are easily reduced. The electrochemical activity of the series of synthesized macrocycles was probed by using closed and open Cu^I macrocycles with naphthalene diimide backbones, **10** and **14**, owing to the greater degree of stability of Cu^I macrocycles to air relative to their Rh^I counterparts[48] and the greater ease of reduction of the naphthalene diimide unit ($E_{1/2}=-790$ mV vs. Fc/Fc^+; Fc = ferrocene) compared to the pyromellitic diimide moiety ($E_{1/2}=-1020$ mV vs. Fc/Fc^+).[54] Cyclic voltammagrams (CV) of both closed complex **10** and open complex **14** each displayed two reversible redox waves (**10**: $E^{0/-1}{}_{1/2}=-771$ mV, $E^{-1/-2}{}_{1/2}=-1032$ mV; **14**: $E^{0/-1}{}_{1/2}=-828$ mV, $E^{-1/-2}{}_{1/2}=-1086$ mV vs. Fc/Fc^+) (Figure 3). There is an approximately −60-mV shift in both $E^{0/-1}{}_{1/2}$ and $E^{-1/-2}{}_{1/2}$ for **14** compared to **10**, which is likely a reflection of the charge induction due to the proximity of the redox-active diimide unit to the positively charged metal center in **10**. In the closed complex, the metal centers, by virtue of their through-bond proximity to the redox-active naphthalene diimides, pull electron density away from the diimide back-

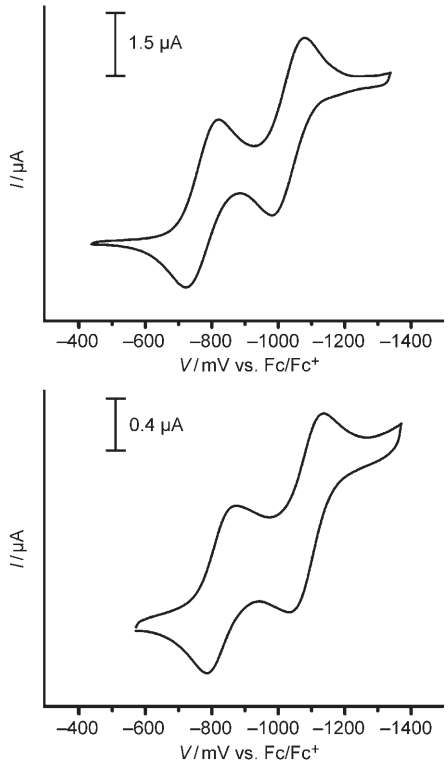


Figure 3. Cyclic voltammograms of **10** (top; $E^{0/-1}{}_{1/2} = -771$ mV, $E^{-1/-2}{}_{1/2} = -1032$ mV) and **14** (bottom; $E^{0/-1}{}_{1/2} = -828$ mV, $E^{-1/-2}{}_{1/2} = -1086$ mV) in CH_2Cl_2 with $TBAPF_6$ (0.1 M) as the supporting electrolyte.

bone, thus easing the reduction process. In the open complex, the hemilabile ligand is no longer chelated to the metal center, and the through-bond distance from Cu^I to the diimide is significantly greater, thus making the complex more difficult to reduce. The two reversible waves are indicative of a stepwise reduction of each identical diimide ligand within the macrocycle. This stepwise reduction is in part due to the electrostatic cost of creating a negatively charged ligand in the presence of another negatively charged ligand.[6,55] In the cases of **10** and **14**, the splittings (**10**: $\Delta E = 261$ mV; **14**: $\Delta E = 258$ mV) are comparable, which suggests that, under these conditions, the change in distance between diimide ligands when going from the closed to the open state is not great enough to effect the degree of electronic communication between the redox-active centers.

Conclusions

The reactions of hemilabile ligands that contain pyromellitic diimide and naphthalene diimide groups with both Rh^I and Cu^I result in condensed intermediates that can be cleanly opened into metallomacrocycles in high yield. The Cu^I–naphthalene diimide complexes exhibit reversible ligand-induced redox behavior. The ligands, regardless of whether the structures are in the condensed intermediate or open macrocyclic state, communicate with one another. Ultimately, these redox centers could be useful for probing the chemistry that occurs within such structures. Indeed, incorporation of these electron-deficient moieties within the backbone of such macrocycles opens the door to future studies focused on host/guest chemistry and electron transfer.

Experimental Section

General Procedures

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere with reagent-grade solvents by using standard Schlenk techniques or an inert-atmosphere glovebox at room temperature.[56] All other solvents were purified by published methods.[57] Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. 4-(2-Diphenylphosphanylethylthio)phenylamine was synthesized according to literature methods.[58] All other chemicals were obtained from commercial sources and used as received unless otherwise noted.

CCDC-612314 (**7**) and -612106 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Physical Measurements

^1H NMR spectra were recorded on a Varian Mercury 300-MHz FTNMR spectrometer and referenced to residual proton resonances in CD_2Cl_2. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300-MHz FTNMR spectrometer at 121.4 MHz and referenced to an external H_3PO_4 (85%) standard. All chemical shifts are reported in ppm. FTIR spectra were obtained in solution with a Thermo Nicolet Nexus 670 FTIR spectrometer with NaCl cells with 0.1-mm spacers. ESI mass spectra were recorded on a Micromass Quatro II triple quadrupole mass spectrometer or a Micromass Q-Tof Ultima mass spectrometer. EI mass spectra were recorded on a Fisions VG 70-250 SE mass spectrometer. Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse, NJ). Cyclic voltammagrams were collected on a BAS 100B potentiostat using a 2-mm diameter Au disk as a working electrode, a freshly flamed Pt wire as a counterelectrode, and a polished Ag wire as a pseudoreference electrode. Fc was added as an internal reference at the end of each experiment to calibrate measured potentials, and all potentials are reported versus the Fc/Fc^+ couple. Electrolyte solutions were composed of tetrabutylammonium hexafluorophosphate ($TBAPF_6$; 0.1 M) in CH_2Cl_2, which was prepared under dry nitrogen in a glove box, purged with nitrogen, and kept under a nitrogen blanket during experiments.

Syntheses

5: Pyromellitic dianhydride (0.500 g, 2.29 mmol) and 4-(2-diphenylphosphanylethylthio)phenylamine (1.547 g, 4.58 mmol) was added to a Schlenk flask (100 mL). Degassed DMF (70 mL) was added to the reaction mixture, and the mixture was brought to reflux. After refluxing overnight, the reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The yellow solid obtained was then heated in toluene (50 mL) and filtered at 100 °C. The solid was then washed with CH_2Cl_2 (20 mL), Et_2O (20 mL), EtOH (20 mL), and hexanes (20 mL). The product was dried under vacuum and isolated as a yellow powder (863.4 mg, 44%). MS (EI): *m/z* calcd: 856.2 [*M*]; found: 856.0; elemental analysis: calcd (%) for $C_{50}H_{38}O_4N_2P_2S_2$: C 70.08, H 4.47, N 3.27; found: C 69.37, H 4.37, N 3.31.

6: 1,4,5,8-Naphthalenetetracarboxylic dianhydride (0.500 g, 1.86 mmol) and 4-(2-diphenylphosphanylethylthio)phenylamine (1.258 g, 3.73 mmol) were added to a Schlenk flask (100 mL). Degassed DMF (70 mL) was added to the reaction mixture, and the mixture was brought to reflux. After refluxing overnight, the suspension was cooled to room temperature, and the solvent was removed in vacuo. The solid was then washed with CH_2Cl_2 (20 mL), Et_2O (20 mL), EtOH (20 mL), and hexanes (20 mL). The product was dried under vacuum and isolated as a dark-

yellow powder (995.3 mg, 59%). MS (ESI): *m/z* calcd: 906.9 [*M*]; found: 907.3; elemental analysis: calcd (%) for $C_{54}H_{40}O_4N_2P_2S_2 \cdot {}^1/_2$DMF: C 70.65, H 4.64, N 3.71; found: C 70.43, H 4.33, N 3.17.

7: $[Rh(NBD)_2Cl]_2$ (23 mg, 0.050 mmol) and NaBArF (88.6 mg, 0.100 mmol) were added to CH_2Cl_2 (10 mL), and the mixture was allowed to stir for 5 min. This solution was then added dropwise to a suspension of **5** (85.6 mg, 0.100 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was left to stir overnight at room temperature. The solvent was then removed in vacuo, and the resulting orange solid was dissolved in Et_2O. The solution was then passed through a short pad of celite. The solvent was removed under reduced pressure. The solid was then recrystallized from CH_2Cl_2 (1 mL) and hexanes (20 mL), filtered, and dried to give **7** (151.3 mg, 83%). Crystals of **7**·$4CH_2Cl_2$ were grown by layering pentane over a dilute solution of **7** in CH_2Cl_2 at room temperature. ^{1}H NMR (CD_2Cl_2): $\delta = 2.67$ (m, 8H, CH_2P), 2.88 (m, 8H, CH_2S), 7.36–7.95 ppm (complex m, 84H, Ph-H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta =$ 67.55 ppm (d, $J = 161.2$ Hz); MS (ESI): *m/z* calcd: 959.8 $[M-2BArF]^{2+}$; found: 959.1; elemental analysis: calcd (%) for $C_{164}H_{100}O_8N_4P_4S_4B_2F_{48}Rh_2$: C 54.02, H 2.76, N 1.54; found: C 53.74, H 2.65, N 1.56.

8: $[Rh(NBD)_2Cl]_2$ (23 mg, 0.050 mmol) and NaBArF (88.6 mg, 0.100 mmol) were added to CH_2Cl_2 (10 mL), and the mixture was allowed to stir for 5 min. This solution was then added dropwise to a suspension of **6** (90.6 mg, 0.100 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was left to stir overnight at room temperature. The solvent was removed in vacuo, and the resulting orange solid was dissolved in Et_2O. The solution was then passed through a short pad of celite, and the solvent was removed under reduced pressure. The solid was then recrystallized from CH_2Cl_2 (1 mL) and hexanes (20 mL), filtered, and dried to give **8** (161.1 mg, 86%). Crystals of **8**·$3CH_2Cl_2 \cdot 2H_2O$ were grown by layering pentane over a dilute solution of **8** in CH_2Cl_2 at room temperature. ^{1}H NMR (CD_2Cl_2): $\delta = 2.74$ (m, 8H, CH_2P), 2.98 (m, 8H, CH_2S), 7.29–7.81 ppm (complex m, 88H, Ph-H; includes BArF); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta =$ 65.43 ppm (d, $J = 161.0$ Hz); MS (ESI): *m/z* calcd: 1009.9 $[M-2BArF]^{2+}$; found: 1009.9; elemental analysis: calcd (%) for $C_{172}H_{104}N_4P_4O_8S_4B_2F_{48}Rh_2 \cdot CH_2Cl_2$: C 54.24, H 2.79, N 1.46; found: C 54.57, H 2.65, N 1.48.

9: A solution of $[Cu(CH_3CN)_4]PF_6$ (20 mg, 0.053 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of **5** (45 mg, 0.053 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was allowed to stir overnight under N_2. As **9** slowly started to form, the solution became increasingly yellow. After the mixture was stirred overnight, all solid material dissolved. The solvent was then removed under reduced pressure to yield a yellow solid. This solid was recrystallized from CH_2Cl_2 (1 mL) and Et_2O (10 mL), filtered, and dried to give analytically pure **9** (51.9 mg, 92%). ^{1}H NMR (CD_2Cl_2): $\delta = 2.87$ (m, 8H, CH_2P), 3.41 (m, 8H, CH_2S), 7.12–7.87 ppm (complex m, 60H, Ph-H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -0.80$ (s), -143.1 ppm (sept, PF_6); MS (ESI): *m/z* calcd: 1985.9 $[M-PF_6]^+$, 920.4 $[M-2PF_6]^{2+}$; found: 1985.6, 920.4; elemental analysis: calcd (%) for $C_{100}H_{76}O_8N_4F_{12}P_6S_4Cu_2 \cdot 2CH_2Cl_2$: C 53.25, H 3.50, N 2.44; found: C 53.50, H 3.44, N 2.72.

10: A solution of $[Cu(CH_3CN)_4]PF_6$ (20 mg, 0.053 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of **6** (48 mg, 0.053 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was allowed to stir overnight under N_2. As **10** slowly started to form, the solution became increasingly yellow. After the mixture was stirred overnight, all solid material dissolved. The solvent was then removed under reduced pressure to yield a yellow solid. This solid was recrystallized from CH_2Cl_2 (1 mL) and Et_2O (10 mL), filtered, and dried to give pure **10** (53.8 mg, 91%). ^{1}H NMR (CD_2Cl_2): $\delta =$ 2.85 (m, 8H, CH_2P), 3.48 (m, 8H, CH_2S), 7.32–7.61 ppm (complex m, 64H, Ph-H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -0.98$ (s), -143.2 ppm (sept, PF_6); MS (ESI): *m/z* calcd: 970.5 $[M-2PF_6]^{2+}$; found: 970.4; elemental analysis: calcd (%) for $C_{108}H_{80}O_8N_4F_{12}P_6S_4Cu_2 \cdot CH_2Cl_2$: C 56.53, H 3.57, N 2.42; found: C 56.85, H 3.42, N 2.66.

11: An air-free NMR tube containing a solution of **7** (30 mg, 8.2 μmol) and benzyltriethylammonium chloride (3.7 mg, 16.4 μmol) in CD_2Cl_2 (1 mL) was charged with CO (1 atm) at room temperature. The deep-orange solution turned orange-yellow in color and gave **11** in quantitative yield. IR: $\tilde{\nu}(CO) = 1976$ cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 3.04$ (m, 8H, CH_2P), 3.56 (m, 8H, CH_2S), 7.33–7.74 ppm (complex m, 60H, Ph-H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta =$ 25.49 ppm (d, $J = 122.0$ Hz).

12: An air-free NMR tube containing a solution of **8** (30 mg, 8.0 μmol) and benzyltriethylammonium chloride (3.6 mg, 16.0 μmol) in CD_2Cl_2 (1 mL) was charged with CO (1 atm) at room temperature. The deep-orange solution turned pale and gave **12** in quantitative yield. IR: $\tilde{\nu}(CO) = 1974$ cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 3.03$ (m, 8H, CH_2P), 3.51 (m, 8H, CH_2S), 7.19–7.82 ppm (complex m, 64H, Ph-H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta =$ 25.56 (d, $J = 123.2$ Hz).

13: Pyridine (4.4 μL, 54.3 μmol, 4 equiv) was added by syringe with stirring to a solution of **9** (28.9 mg, 13.6 μmol) in CH_2Cl_2 (3 mL). The solution was allowed to stir for 1 h at room temperature. The solvent was removed in vacuo to yield a yellow solid. The solid was recrystallized with CH_2Cl_2 (1 mL) and Et_2O (10 mL), filtered, and dried to yield **13** (31.3 mg, 94%). ^{1}H NMR (CD_2Cl_2): $\delta = 2.78$ (m, 8H, CH_2P), 3.35 (m, 8H, CH_2S), 7.29–8.30 ppm (complex m, 80H, Ph-H, pyridine); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -3.01$ (s), -143.2 ppm (sept, PF_6); MS (ESI): *m/z* calcd: 1985.9 $[M-PF_6-4$ pyridine$]^+$, 920.5 $[M-2PF_6-4$ pyridine$]^{2+}$; found: 1985.6, 920.9; elemental analysis: calcd (%) for $C_{120}H_{96}O_8N_8F_{12}P_6S_4Cu_2 \cdot 3CH_2Cl_2$: C 54.67, H 3.80, N 4.15; found: C 54.33, H 3.38, N 3.66.

14: Pyridine (4.3 μL, 53.7 μmol, 4 equiv) was added by syringe with stirring to a solution of **10** (30.0 mg, 13.4 μmol) in CH_2Cl_2 (3 mL). The solution was allowed to stir for 1 h at room temperature. The solvent was removed in vacuo to yield a yellow solid. The solid was recrystallized with CH_2Cl_2 (1 mL) and Et_2O (10 mL), filtered, and dried to yield **14** (31.4 g, 92%). ^{1}H NMR (CD_2Cl_2): $\delta = 2.82$ (m, 8H, CH_2P), 3.44 (m, 8H, CH_2S), 7.28–8.24 ppm (complex m, 84H, Ph-H, pyridine); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -1.97$ (s), -143.0 (sept, PF_6); MS (ESI): *m/z* calcd: 970.5 $[M-2PF_6-4$ pyridine$]^{2+}$; found: 970.7; elemental analysis: calcd (%) for $C_{128}H_{100}O_8N_8F_{12}P_6S_4Cu_2 \cdot CH_2Cl_2$: C 58.86, H 3.91, N 4.26; found: C 58.38, H 3.71, N 3.71.

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