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A Highly Modular and Convergent Approach for the Synthesis of Stimulant-Responsive Heteroligated Cofacial Porphyrin Tweezer Complexes

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The synthesis of new hemilabile phosphine ligands and their reaction with $[Rh(COE)_2Cl]_2$ to form dissymmetric heteroligated tweezer complexes using a halide-induced ligand rearrangement reaction are reported. These complexes can undergo reactions with small-molecule ligands and elemental anions quantitatively in situ, which serve to regulate the porphyrin−porphyrin distances and interactions within the assembly.

Introduction

Cofacial porphyrin complexes[1] are an important class of molecules that have received a significant amount of attention due to their interesting catalytic[2–10] and photophysical properties.[11–14] While many approaches have been described for the synthesis of both organic and coordination chemistry-based cofacial porphyrin complexes, most of them yield products which are structurally rigid and do not allow for the selective modification of the cavity formed by both porphyrin moieties.[9,11,15–17] Such control is necessary for tuning the photophysical properties[11,18,19] and, in certain cases, the catalytic properties[2–6] of these complexes. To address these issues, our group has developed the weak-link approach (WLA),[20–22] for preparing highly flexible supramolecular complexes capable of mimicking the properties of allosteric biological systems.[23–29] A key component of this

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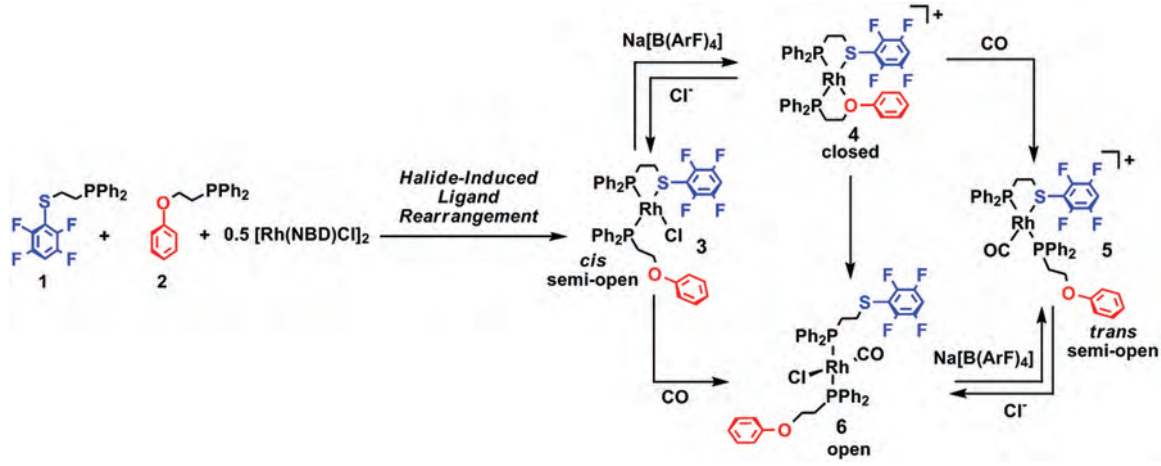
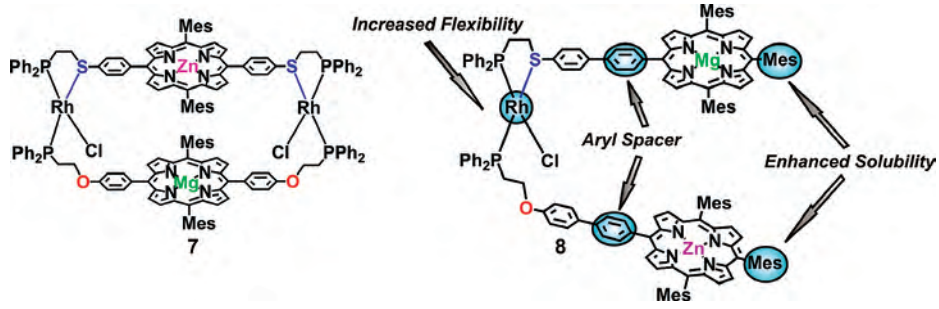
Scheme 1. Example of the Halide-Induced Ligand Rearrangement (HILR)



Scheme 2. Dissymmetric Heteroligated Cofacial Porphyrin Macrocycle and Tweezer Complexes



versatile approach is the ability to modify and regulate supramolecular structures in situ via the introduction or removal of external chemical stimuli.

Through the course of our studies, we have discovered a unique and novel halide-induced ligand rearrangement (HILR) reaction[30–32] that allows one to use two hemilabile ligands (**1** and **2**) and a Rh^I precursor to form dissymmetric heteroligated Rh^I complexes **3**−**6** (Scheme 1). This reaction is quite general and has led to a highly convergent and modular approach for the preparation of heteroligated dissymmetric cofacial porphyrin macrocycles (**7**; Scheme 2).[33] A key feature of the assemblies that are formed via this approach is their ability to react with small-molecule ligands or halide-abstracting agents that allow for the selective modification of both porphyrin−porphyrin distance and orientation. In spite of these advantages, a limitation of the heteroligated porphyrin macrocycles that we have studied thus far is their low solubility in organic solvents. One strategy for overcoming this problem is to remove one of the two Rh^I regulatory sites in the supramolecular assemblies and form tweezer complexes.[26] This result led us to hypothesize that a general approach for making tweezer-type complexes (**8**) with porphyrin arms would greatly facilitate the realization of soluble coordination chemistry-based cofacial porphyrins with structures that can be regulated in situ via the addition of small-molecule chemical effectors.

Herein, we report the synthesis of new ether− and thioether−phosphine hemilabile porphyrin ligands. Upon reaction with a suitable Rh^I precursor, these ligands form dissymmetric heteroligated porphyrin tweezer complexes in quantitative yield (Scheme 2). Significantly, since these tweezer complexes contain a single Rh^I regulatory site, they can undergo significant geometrical distortions in situ when triggered by external chemical stimuli. The extra mesityl group on the porphyrin ring in **8**, as compared with the ligands used to form **7**, greatly enhances the solubility of this complex in organic solvents such as CH_2Cl_2 and THF, enabling it to undergo reversible reactions with small-molecule ligands without undesirable precipitation.

Results and Discussion

Design and Synthesis of Ether−Phosphine Ligand 13. While the aldehyde porphyrin precursor used to prepare the thioether ligand in macrocycle **7** can be made in high yield, the corresponding precursor for the ether analogue required two additional steps and, consequently, a lower overall yield.[24] In designing the ether-containing hemilabile ligand **13**, we reasoned that direct incorporation of an aryl aldehyde into the ligand framework, which could be delivered via a Suzuki–Miyaura coupling reaction[34,35] at the beginning

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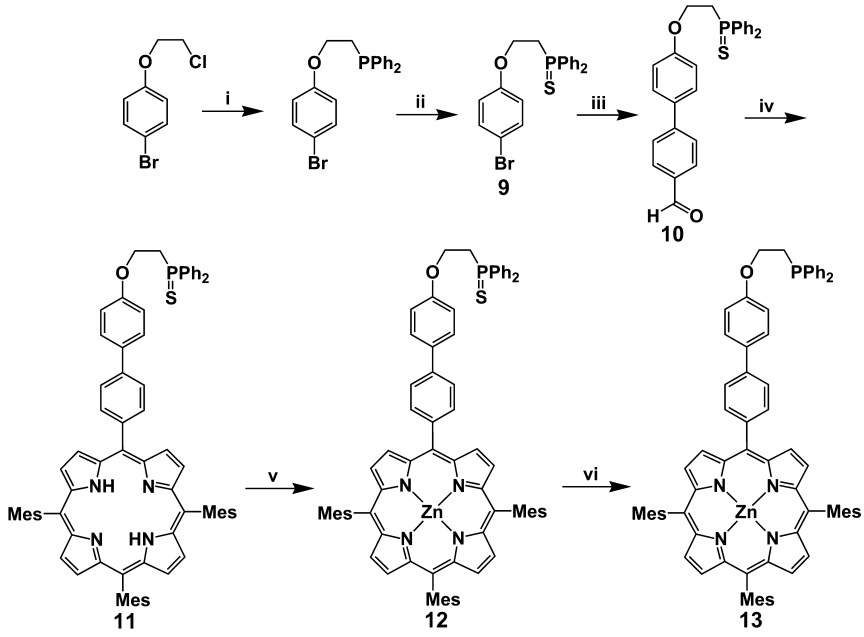
Scheme 3. Synthesis of the Ether-Based Hemilabile Phosphine Tweezer Ligand **13**[a]



[a] Where, Mes = mesityl. (i) $KPPh_2$, THF; (ii) S_8, THF, 85%; (iii) 4-formylphenylboronic acid, $Pd(PPh_3)_4$ (5 mol %), Na_2CO_3 (aq. 2 M), toluene/EtOH (6:1, v/v), reflux, 95%; (iv) mesitaldehyde (1 equiv), 5-mesityldipyrromethane (2 equiv), $BF_3 \cdot OEt_2$, DDQ, NEt_3, 22%; (v) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3$/MeOH (4:1, v/v), reflux, 98%; (vi) Cp_2ZrHCl, THF, 92%.

of the ligand synthesis, would reduce the number of steps required to synthesize **10** and increase its yield at the same time. To this end, we combined the commercially available 4-(bromophenyl)-2-chloroethyl ether with $KPPh_2$ in THF to obtain the corresponding phosphine,[32] which was then protected with elemental sulfur to yield **9** in 85% yield (Scheme 3). Compound **9** underwent Suzuki–Miyaura coupling with 4-formylphenylboronic acid to afford **10** in 95% yield. Significantly, using this approach allowed for the synthesis of the ether-based aldehyde precursor **10** to be reduced to three steps (from five for the analogous precursor used in making macrocycle complex **7**)[24,33] with an increase in yield from 31 to 77%.

To obtain porphyrin ligand **11**, the aldehyde precursor **10** (1 equiv), 5-mesityldipyrromethane[36] (2 equiv), and mesitaldehyde (1 equiv) were reacted under Lewis-acidic conditions followed by oxidation. Importantly, **11** can be isolated in gram quantities (22% yield) via simple chromatographic separation over silica gel using only CH_2Cl_2 as the eluent. The Zn^{II}−porphyrin complex **12** was prepared in quantitative yield by refluxing **11** in $CHCl_3$/MeOH (4:1 v/v) with $Zn(OAc)_2 \cdot 2H_2O$. After metalation, the sulfide protecting group was removed using Cp_2ZrHCl, affording **13** in 92% yield.

Design and Synthesis of Thioether−Phosphine Ligands 17a and 17b. For the thioether−porphyrin ligand, we employed a synthetic approach similar to the one used for the ether-based ligand **13** (Scheme 4). Commercially available 4-bromothiophenol was alkylated with 1-chloro-2-diphenylphosphinoethane followed by protection of the diphenylphosphine moiety with elemental sulfur to give 1-bromo-4-[2-(diphenylphosphinothioyl)ethylsulfanyl]benzene (Scheme 4).[24] This compound was then coupled to 4-formylphenylboronic acid to give **14** in 81% yield. Once isolated, aldehyde **14** (1 equiv) was condensed with mesitaldehyde (1 equiv) and 5-mesityldipyrromethane[36] (2 equiv) under Lewis-acidic conditions to yield porphyrin **15** in 20% yield after oxidation. Again, this compound can be isolated in gram quantities via flash chromatography over silica gel using only CH_2Cl_2 as the eluent. Compound **15** was then metallated with Zn^{II} (**16a**) or Mg^{II} (**16b**) using either $Zn(OAc)_2 \cdot 2H_2O$ in $CHCl_3$/MeOH (4:1, v/v) or $MgBr_2$ and NEt_3 in CH_2Cl_2, respectively. Upon isolation of compounds **16a** and **16b**, the sulfide protecting groups were removed by reaction with Cp_2ZrHCl in THF followed by chromatography over neutral alumina, which afforded ligands **17a** and **17b** in 90 and 89% yield, respectively.

Synthesis of Dissymmetric Heteroligated Rh^I Tweezer Complexes 18–25. The dissymmetric complexes **18** and **19** were prepared via the HILR using 2 equiv of the appropriate ligands and 1 equiv of the Rh^I precursor, $[Rh(COE)_2Cl]_2$. The reagents were dissolved in THF and the mixture was sonicated for 1 h, resulting in the quantitative formation of the desired $RhCl(\kappa^2\text{-PS})(\kappa^1\text{-PO})$ products **18** and **19**, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 5). The $^{31}P\{^1H\}$ NMR spectra for both compounds **18** and **19** show two resonances at δ 72 (dd, $J_{Rh-P} = 185$ Hz, $J_{P-P} = 41$ Hz) and δ 29 (dd, $J_{Rh-P} = 166$ Hz, $J_{P-P} = 40$ Hz), which are highly diagnostic of this heteroligated $Rh^ICl(PS)(PO)$ coordination environment.[31] The matrix-assisted laser desorption/ionization−time of flight (MALDI-TOF) mass spectrum for **18** contains a peak at 2335.88 *m/z* corresponding to the $[M - Cl]^+$ ion. A similar trend is observed in the

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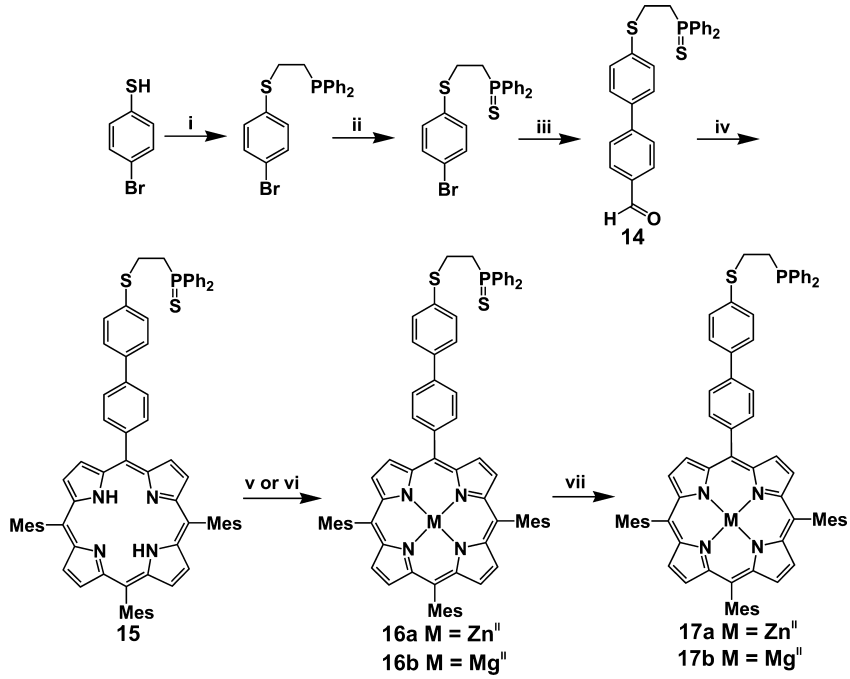
Scheme 4. Synthesis of the Thioether-Based Hemilabile Phosphine Tweezer Ligands **17a** and **17b**[a]



[a] Where, Mes = mesityl. (i) 1-chloro-2-diphenylphosphinoethane, Cs_2CO_3, CH_3CN, reflux; (ii) S_8, THF; (iii) 4-formylphenylboronic acid, $Pd(PPh_3)_4$ (5 mol %), Na_2CO_3 (aq. 2 M), toluene/EtOH (6:1, v/v), reflux, 81%; (iv) mesitaldehyde (1 equiv), 5-mesityldipyrromethane (2 equiv), $BF_3 \cdot OEt_2$, DDQ, NEt_3, 20%; (v) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3$/MeOH (4:1, v/v), reflux, 97%; (vi) $MgBr_2$, Net_3, CH_2Cl_2, 96%; (vii) Cp_2ZrHCl, THF (90% Zn^{II}, 89% Mg^{II}).

MALDI-TOF mass spectrum of **19**, with the $[M - Cl]^+$ ion at 2295.15 *m*/*z* and the $[M - Mg - Cl]^+$ ion at 2270.21 *m*/*z*, as commonly observed.[33] Together with the multinuclear NMR data obtained for these complexes (Table 1), the observations conclusively support our proposed structure for **18** and **19**.

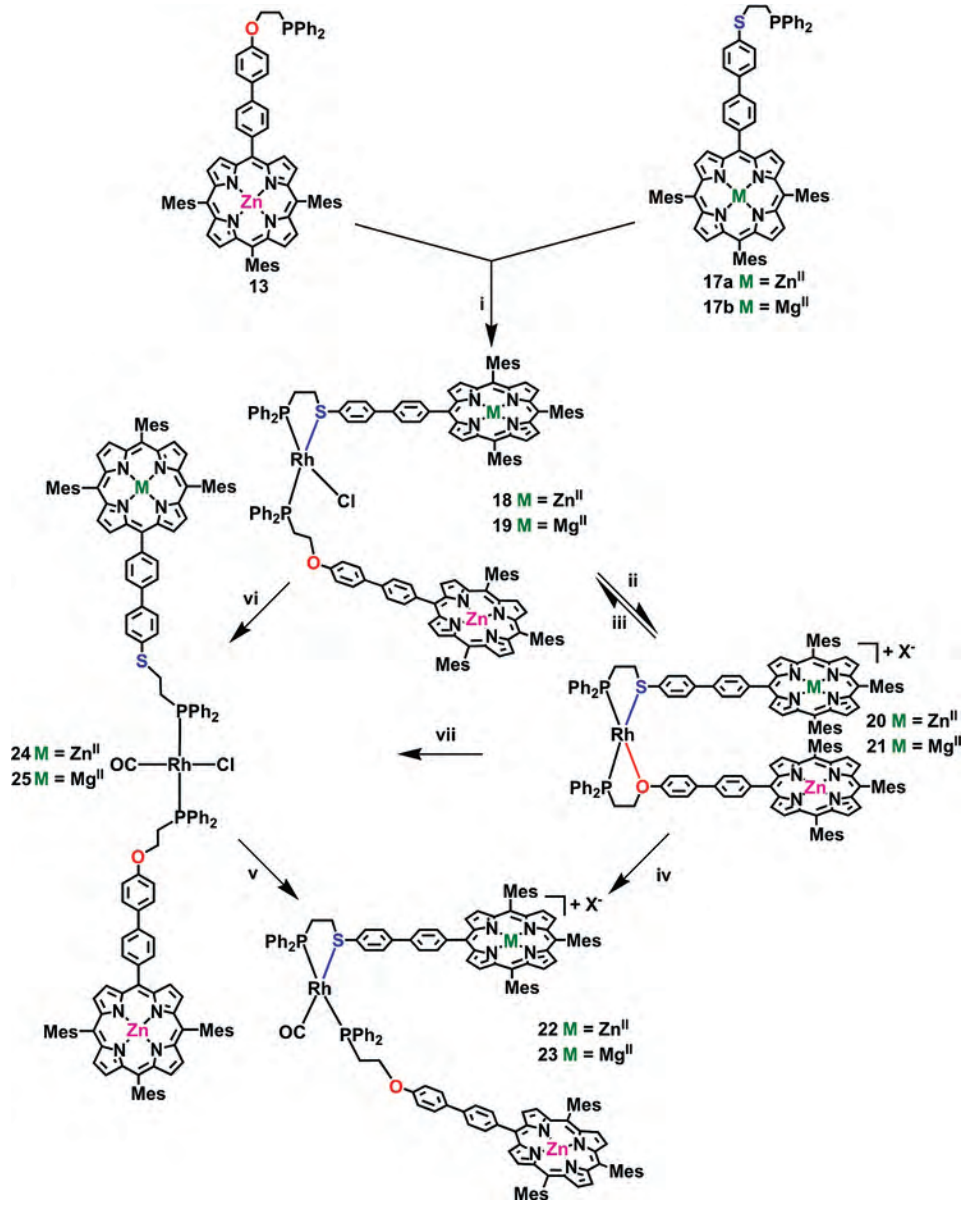
The semi-open complexes **18** and **19** can be converted into the closed complexes **20** and **21** quantitatively via abstraction of Cl^- upon sonication with $Na[B(ArF)_4]$ (1 equiv, where $B(ArF)_4$ = tetrakis[(3,5-trifluoromethyl)phenyl]borate) in CH_2Cl_2 (Scheme 5). The $^{31}P\{^1H\}$ NMR spectra for both **20** and **21** contain two resonances at δ 72 (dd, $J_{Rh-P} = 198$ Hz, $J_{P-P} = 40$ Hz) and 51 (dd, $J_{Rh-P} = 167$ Hz, $J_{P-P} = 41$ Hz), consistent with the formation of the $[Rh(\kappa^2\text{-PS})(\kappa^2\text{-PO})][B(ArF)_4]$ adducts.[31] The MALDI-TOF mass spectrum for **20** contains a peak at 2336.99 *m*/*z* corresponding to the desired M^+ ion. In the case of **21**, the MALDI-TOF mass spectrum contains an M^+ peak at 2295.22 *m*/*z* and the $[M - Mg]^+$ peak at 2270.92 *m*/*z*, as has been observed in previous studies.[33] Together, these characterization data strongly support the formation of the desired closed complexes **20** and **21** (Table 1).

Since tweezer complexes **18**−**21** are much more soluble in organic solvent compared to their macrocyclic analogues, one can reversibly address the Rh^I hinge sites in situ with selected small-molecule ligands and elemental anions. For example, the addition of $(n\text{-Bu})_4NCl$ (1 equiv) to a CH_2Cl_2 solution of complex **20** or **21** results in their quantitative conversion to complexes **18** and **19**, respectively. Importantly, this transformation is reversible and complexes **20** and **21** can be quantitatively reformed upon the addition of a stoichiometric amount of $Na[B(ArF)_4]$ as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. These transformations are near-instantaneous and can be observed visually as the color changes slightly for each transformation.

Upon introduction of CO (1 atm) to solutions of **20** and **21** in CD_2Cl_2, the semi-open $[Rh(\kappa^2\text{-PS})(\kappa^1\text{-PO})(CO)][B(ArF)_4]$ adducts **22** and **23** are formed in quantitative yield according to both ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 5). The $^{31}P\{^1H\}$ NMR spectra for compounds **22** and **23** both show two resonances at δ 61 (dd, $J_{Rh-P} = 114$ Hz, $J_{P-P} = 266$ Hz) and 18 (dd, $J_{Rh-P} = 117$ Hz, $J_{P-P} = 266$ Hz), whose coupling constants clearly indicate a *cis*-to-*trans* conversion of phosphine geometry (Table 1).[31,33] The FTIR spectra of compounds **22** and **23** in CH_2Cl_2 exhibit a $\nu_{C\equiv O}$ stretch at 1970 cm^{-1}, which is also highly diagnostic of trans-phosphine $Rh^I(CO)$ complexes.[31,33] Additionally, the methylene groups of the $XCH_2CH_2PPh_2$ moieties (where X = S or O) provide an additional handle for following the partial opening of the tweezer framework in situ. For example, the methylene protons in the ^1H NMR spectra of both **22** and **23** exhibit four well-resolved resonances (SCH_2CH_2P, SCH_2CH_2P, OCH_2CH_2P, and OCH_2CH_2P) as compared with the broad, overlapping resonances observed for the methylene protons in **20** and **21**.

Although the ether moieties in complexes **20** and **21** can be selectively displaced from the Rh centers via the introduction of CO (1 atm), displacing the thioether moieties in **20** and **21** requires the use of both halides and CO. For instance, introducing CO (1 atm) to a CD_2Cl_2 solution of half-open complexes **18** or **19** quantitatively yielded the fully open, highly flexible tweezer complexes **24** and **25** as indicated by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 5). These complexes

Scheme 5. Synthesis and In Situ Regulation of Dissymmetric Porphyrin Tweezer Complexes **18**–**25**[a]



[a] Mes = mesityl and X$^-$ = tetrakis[(3,5-trifluoromethyl)phenyl]borate. (i) [Rh(COE)$_2$Cl]$_2$ (0.5 equiv), THF (**18** = 93%; **19** = 94%); (ii) Na[B(ArF)$_4$] (1 equiv), CH_2Cl_2 (**20** = 93%; **21** = 93%); (iii) (*n*-Bu)$_4$NCl (1 equiv), CH_2Cl_2 (**18** = **19** = quant); (iv) CO (1 atm), CD_2Cl_2 (**22** = **23** = quant); (v) Na[B(ArF)$_4$] (1 equiv), CH_2Cl_2 (**22** = **23** = quant); (vi) CO (1 atm), CD_2Cl_2 (**24** = **25** = quant); (vii) (*n*-Bu)$_4$NCl (1 equiv), CO (1 atm), CD_2Cl_2 (**24** = **25** = quant).

Table 1. Comparison of $^{31}P\{^1H\}$ Chemical Shifts and Coupling Constants for Porphyrin Complexes **18**–**25** vs Analogous Model Complexes (**3**–**6**, Scheme 4)

	δ(PS)[a]	J_{Rh-P} (PS)[b]	J_{P-P} (PS)[b]	δ(PO)[a]	J_{Rh-P} (PO)[b]	J_{P-P} (PO)[b]
3	73	185	41	30	168	41
4	73	200	41	51	168	41
5	63	116	268	19	121	268
6			broad multiplet at approx δ 24			
18 and **19**	72	185	41	29	166	40
20 and **21**	72	198	40	51	167	41
22 and **23**	61	114	266	18	117	266
24 and **25**			broad multiplet at approx δ 23			

[a] Data is reported in part per million. All chemical shifts have been rounded to the nearest whole number. [b] Data is reported in Hertz.

can be generated in situ from the closed complexes **20** and **21** upon the addition of a stoichiometric amount of (*n*-Bu)$_4$NCl and CO (1 atm). In both cases, the $^{31}P\{^1H\}$ NMR spectra of **24** and **25** yield broad multiplets at δ 23, which arise due to the overlap of two doublets of doublets (Table 1). The presence of a CO-bound Rh^I species in **24** and **25** has also been confirmed by FTIR spectroscopy ($\nu_{C\equiv O}$ = 1967 and 1971 cm^{-1}, respectively).

Attempts to isolate diffraction-quality single crystals of the complexes presented herein have thus far proven unsuccessful. In the instances where small crystals formed, they quickly lose solvent upon being removed from the mother liquor. Nevertheless, their solution structures can be readily

established based upon the large spectroscopic database that we have obtained for fully characterized Rh^I model tweezer complexes without porphyrins. As illustrated in Table 1, $^{31}P\{^1H\}$ NMR spectroscopic data provide a powerful means for unequivocally identifying the product that results from each in situ reaction. For example, the chemical shifts and coupling constants for both complexes **18** and **19** only vary by ~2 ppm and 2 Hz, respectively, when compared to model complex **3** (Scheme 1), definitively indicating formation of the desired *cis*-phosphine, thioether-bound Rh^I complex.

Conclusions

In conclusion, we have demonstrated how the HILR can be used to quantitatively assemble porphyrin-based hemilabile ligands and simple transition metal precursors into dissymmetric, heteroligated tweezer complexes. In contrast with their macrocyclic analogues, which contain two regulatory sites, these tweezer complexes have a single site that can be used to modulate the porphyrin−porphyrin interactions. The addition or removal of small-molecule ligands and elemental anions can be used to interconvert the open and closed conformations of the tweezer complexes in situ. The enhanced solubility of these tweezer complexes allows for such transformations to proceed in a completely reversible manner, in contrast to the macrocyclic analogues, which often precipitate during analogous transformations. Therefore, the tweezer complexes and their corresponding reactivity with small molecules and ions provide a convenient means for manipulating the interactions between both porphyrins. Efforts to utilize these transformations in the regulation of both catalytic and photophysical properties are currently underway.

General Methods and Instrument Details

All reactions were carried out under an inert atmosphere of dinitrogen using standard Schlenk techniques or an inert-atmosphere glovebox unless otherwise noted. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and hexanes were purified according to published methods.[37] All solvents were deoxygenated with nitrogen prior to use. Deuterated solvents (Cambridge Isotope Laboratories Inc.) were obtained from commercial sources and used as received. 5-Mesityldipyrromethane,[36] 2-(4-bromophenoxy)ethyl)-diphenylphosphine,[32] 2-(4-bromophenylthio)ethyl)diphenylphosphine,[32] and 1-bromo-4-[2-diphenylphosphinothioyl)ethylsulfanyl]benzene[24] were prepared according to literature procedures. All other chemicals were used as received from Aldrich Chemical Co. ^1H NMR (300.22 or 400.18 MHz) spectra were recorded on either a Varian Mercury 300 MHz FTNMR spectrometer or a Varian Mercury 400 MHz FTNMR spectrometer and referenced relative to residual proton resonances. $^{31}P\{^1H\}$ NMR (121.53 or 161.95 MHz) spectra were recorded on either a Varian Mercury 300 MHz or a Varian Mercury 400 MHz NMR spectrometer and referenced relative to an external 85% H_3PO_4 standard. $^{13}C\{^1H\}$ (100.16 MHz) spectra were recorded on a Varian Mercury 400 MHz FTNMR spectrometer. All chemical shifts are reported in part per million. Electrospray ionization mass spectra (ESIMS) were recorded on a Micromass Quatro II triple quadrupole mass spectrometer or a Micromass Q-TOF Ultima mass spectrometer. Electron-impact mass spectra (EIMS) were recorded on a Fisions VG 70-250 SE mass spectrometer. Matrix-assisted laser desorption/ionization−time of flight (MALDI-TOF) mass spectra were recorded on a PE Voyager DE-Pro MALDI-TOF mass spectrometer. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

1-Bromo-4-[2-(diphenylphosphinothioyl)ethoxy]benzene (Compound 9). In a 100-mL Schlenk round-bottom flask, [2-(4-bromophenoxy)ethyl]diphenylphosphane (7.00 g, 18.2 mmol) and elemental sulfur (583 mg, 18.2 mmol) were stirred in THF (70 mL) under N_2 at rt for 3 h. The remaining steps were then performed under ambient conditions. The reaction mixture was concentrated in vacuo and the resulting oil was dissolved in a minimal amount of CH_2Cl_2 and precipitated from solution with pentane to afford **9** as a white solid (6.48 g, 85% yield). ^1H NMR (CD_2Cl_2): δ 2.93 (m, 2H, CH_2P═S), 4.33 (m, 2H, OCH_2), 6.57 (d, 2H, J_{H-H} = 8.7 Hz, Ar*H*), 7.70 (d, 2H, J_{H-H} = 9.3 Hz, Ar*H*), 7.47–7.57 (br m, 8H, Ar*H*), 7.83–7.90 (br m, 6H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.2 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 32.2 (d, *C*H_2P = S, J_{C-P} = 56.4 Hz), 62.8 (O*C*H_2), 116.4, 128.7, 128.8, 131.0, 131.1, 131.8, 132.5. HREIMS (*m*/*z*): Calcd. 415.9999. Found 416.0005. Elemental analysis for $C_{20}H_{18}BrOPS$: Calcd. C, 57.56; H, 4.35. Found C, 58.31; H, 4.20.

4′-[2-(Diphenylphosphinothioyl)ethoxy]biphenyl-4-carbaldehyde (Compound 10). In a 500-mL Schlenk round-bottom flask, **9** (10.0 g, 23.9 mmol), 4-formylphenylboronic acid (3.63 g, 26.3 mmol), and $Pd(PPh_3)_4$ (5 mol %, 1.38 g) were stirred in a degassed 6:1 toluene/ethanol (400 mL) solution under N_2. To this flask, a degassed solution of Na_2CO_3 in H_2O (2 M, 60 mmol, 30 mL) was added and the contents were refluxed under N_2 for 20 h. All purification was then carried out under ambient conditions. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (300 mL) and washed with H_2O (2 × 100 mL). The organic solvent was separated and evaporated to yield a crude brown oil that was purified via column chromatography (2:1 hexanes/ethyl acetate as eluent) to yield **10** as beige solid which was further purified by precipitation from a CH_2Cl_2 solution with pentane (10.1 g, 95% yield). ^1H NMR (CD_2Cl_2): δ 2.98 (m, 2H, CH_2P═S), 4.42 (m, 2H, OCH_2), 6.80 (d, 2H, J_{H-H} = 6.6 Hz, Ar*H*), 7.50–7.57 (br m, 8H, Ar*H*), 7.70 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 7.85–7.93 (br m, 6H, Ar*H*), 10.0 (1H, C*H*O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.1 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 32.2 (d, *C*H_2P = S, J_{C-P} = 56.7 Hz), 62.7 (O*C*H_2), 115.1, 127.1, 128.6, 128.8, 128.9, 130.3, 131.1, 131.2, 131.8, 131.8, 132.4, 132.6, 133.7, 135.0, 146.6, 158.8, 191.9. HREIMS (*m*/*z*): Calcd. 442.1156. Found 442.1139. Elemental analysis for $C_{27}H_{23}O_2PS$: Calcd. C, 73.28; H, 5.24. Found C, 72.73; H, 4.96.

5-{4′-[2-(Diphenylphosphinothioyl)ethoxy]biphenyl-4-yl}−10,15,20-mesitylporphyrin (Compound 11). In an aluminum foil-wrapped 1000-mL Schlenk round-bottom flask, **10** (2.21 g, 5.00 mmol), 5-mesityldipyrromethane (2.64 g, 10.0 mmol), and mesitaldehyde (0.725 mL, 5.00 mmol) were dissolved in degassed $CHCl_3$ (800 mL) and stirred under N_2 over activated 4Å molecular sieves. To this solution, $BF_3 \cdot OEt_2$ (2 mL) was added at once and the solution stirred in the absence of light for 3 h at room temperature. The flask was opened to ambient conditions at which point DDQ (2.64 mg, 12 mmol) and NEt_3 were added and allowed to stir for an additional 30 min. The solvent was removed and the crude product was purified via column chromatography (CH_2Cl_2 as eluent) to yield **11** as a purple solid (1.21 g, 22%). ^1H NMR (CD_2Cl_2): δ −2.58 (s, 2H, N*H*), 1.86 (s, 18H, mesityl CH_3), 2.62 (s, 9H, mesityl CH_3), 3.05 (m, 2H, CH_2P═S), 4.50 (m, 2H, OCH_2), 6.92 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 7.31 (s, 4H, Ar*H*), 7.54 (m, 6H, Ar*H*), 7.80

(37) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

(d, 2H, J_{H-H} = 8.7 Hz, Ar*H*), 7.91 (m, 10H, Ar*H*), 8.26 (d, 2H, J_{H-H} = 8.1 Hz, Ar*H*), 8.65 (s, 4H, Ar*H*), 8.69 (d, 2H, J_{H-H} = 4.5 Hz, Ar*H*), 8.89 (d, 2H, J_{H-H} = 4.5 Hz, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.4 (s). ESIMS (*m*/*z*): Calcd. 1077.4. Found 1077.7. Elemental analysis for $C_{73}H_{65}OPS$: Calcd. C, 81.38; H, 6.08; N, 5.20. Found C, 80.26; H, 5.97; N, 5.45.

[5-{4′-[2-(Diphenylphosphinothioyl)ethoxy]biphenyl-4-yl}-10,15,20-mesitylporphyrinato]zinc^{II} (Compound 12). In a 250-mL round-bottom flask, **11** (500 mg, 0.464 mmol), and $Zn(OAc)_2\cdot 2H_2O$ (1.02 g, 4.64 mmol) were refluxed in 4:1 $CHCl_3$/MeOH (200 mL) for 3 h. Upon completion, the solution was washed with H_2O (2 × 100 mL) and dried over Na_2SO_4. The contents were filtered and the solvent was removed in vacuo yielding **12** as a purple solid (518 mg, 98% yield). ^1H NMR (CD_2Cl_2): δ 1.84 (s, 18H, mesityl C*H*$_3$), 2.62 (s, 9H, mesityl C*H*$_3$), 3.07 (m, 2H, C*H*$_2$P═S), 4.49 (m, 2H, OC*H*$_2$), 6.92 (d, 2H, J_{H-H} = 8.7 Hz, Ar*H*), 7.31 (s, 6H, Ar*H*), 7.57 (m, 6H, Ar*H*), 7.80 (d, 2H, J_{H-H} = 8.7 Hz, Ar*H*), 7.90 (m, 6H, Ar*H*), 8.26 (d, 2H, J_{H-H} = 8.1 Hz, Ar*H*), 8.70 (m, 6H, Ar*H*), 8.94 (d, 2H, J_{H-H} = 4.5 Hz, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.4 (s). ESIMS(*m*/*z*): Calcd. 1140.7. Found 1141.3. Elemental analysis for $C_{73}H_{63}OPSZn$: Calcd. C, 76.86; H, 5.57; N, 4.91. Found C, 76.90; H, 6.02; N, 4.42.

[5-[4′-(2-Diphenylphosphanylethoxy)biphenyl-4-yl]-10,15,20-mesitylporphyrinato]zinc^{II} (Compound 13). In a 50-mL Schlenk round-bottom flask, **12** (405 mg, 0.355 mmol) and Cp_2ZrHCl (293 mg, 1.14 mmol) were stirred under N_2 in THF (30 mL) at 60 °C for 4 h. Upon completion, the solvent was removed and the contents were purified via column chromatography on neutral alumina (THF as eluent) under an atmosphere of N_2 to yield **13** as a purple solid (361 mg, 92% yield). ^1H NMR (CD_2Cl_2): δ 1.85 (s, 18H, mesityl C*H*$_3$), 2.60 (s, 9H, mesityl C*H*$_3$), 2.65 (m, 2H, C*H*$_2$P), 4.20 (m, 2H, OC*H*$_2$), 7.02 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 7.28 (s, 6H, Ar*H*), 7.36 (d, 2H, J_{H-H} = 6.9 Hz, Ar*H*), 7.51 (m, 6H, Ar*H*), 7.83 (d, 2H, J_{H-H} = 9.3 Hz, Ar*H*), 7.94 (d, 2H, J_{H-H} = 7.8 Hz, Ar*H*), 8.20 (d, 2H, J_{H-H} = 7.8 Hz, Ar*H*), 8.61 (s, 4H, Ar*H*), 8.63 (d, 2H, J_{H-H} = 4.8 Hz, Ar*H*), 8.83 (d, 2H, J_{H-H} = 4.2 Hz, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −23.8 (s). ESIMS (*m*/*z*): Calcd. 1106.4. Found 1106.4. Elemental analysis for $C_{73}H_{63}OPZn$: Calcd. C, 79.08; H, 5.73; N, 5.05. Found C, 78.09; H, 5.55; N, 4.77.

4′-[2-(Diphenylphosphinothioyl)ethylsulfanyl]biphenyl-4-carbaldehyde (Compound 14). In a 500-mL Schlenk round-bottom flask, 1-bromo-4-[2-(diphenylphosphinothioyl)ethylsulfanyl] benzene (10.0 g, 23.1 mmol), 4-formylphenylboronic acid (3.51 g, 25.3 mmol), and $Pd(PPh_3)_4$ (5 mol %, 1.34 g) were stirred in a degassed 6:1 toluene/ethanol (400 mL) solution under N_2. To this solution, a degassed solution of Na_2CO_3 in H_2O (2 M, 58 mmol, 29 mL) was added and the contents were refluxed under N_2 for 20 h. All purification was then carried out under ambient conditions. The solvent was removed in vacuo and the residue was washed with H_2O (2 × 100 mL), extracted with CH_2Cl_2 (300 mL), and the solvent was evaporated to yield a crude brown oil. The oil was purified via column chromatography (2:1 hexanes/ethyl acetate as eluent) to yield **14** as a beige solid, which was further purified by precipitation from a CH_2Cl_2 solution with pentane (8.63 g, 81% yield). ^1H NMR (CD_2Cl_2): δ 2.75 (m, 2H, C*H*$_2$P═S), 3.17 (m, 2H, SC*H*$_2$), 7.34 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 7.45–7.60 (br m, 8H, Ar*H*), 7.76–7.85 (br m, 6H, Ar*H*), 7.94 (d, 2H, J_{H-H} = 8.7 Hz, Ar*H*), 10.0 (s, 1H, C*H*O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.5 (s). $^{13}C\{^1H\}$ NMR: δ 26.4 (S*C*H$_2$), 32.3 (*C*H$_2$P═S, J_{C-P} = 51.8 Hz), 127.1, 128.0, 128.9, 129.0, 129.3, 130.4, 131.1, 131.2, 131.9, 132.0, 132.4, 133.0, 135.5, 136.3, 137.5, 146.2, 191.8. HREIMS (*m*/*z*): Calcd. 458.0927. Found 458.0929. Elemental analysis for $C_{27}H_{23}OPS_2$: Calcd. C, 70.72; H, 5.06. Found C, 70.81; H, 4.75.

5-{4′-[2-(Diphenylphosphinothioyl)ethylsulfanyl]biphenyl-4-yl}-10,15,20-mesitylporphyrin (Compound 15). In an aluminum foil-wrapped 1000-mL Schlenk round-bottom flask, **14** (2.29 g, 5.00 mmol), 5-mesityldipyrromethane (2.64 g, 10.0 mmol), and mesitaldehyde (0.725 mL, 5.00 mmol) were dissolved in degassed $CHCl_3$ (800 mL) and stirred under N_2 over activated 4Å molecular sieves. To this solution, $BF_3\cdot OEt_2$ (2 mL) was added at once and the solution stirred in the absence of light for 3 h at room temperature. The flask was opened to ambient conditions at which point DDQ (2.64 g, 12 mmol) and NEt_3 were added and allowed to stir for an additional 30 min. The solvent was removed and the crude product was purified via column chromatography (CH_2Cl_2 as eluent) to yield **15** as a purple microcrystalline solid (1.11 g, 20%). ^1H NMR (CD_2Cl_2): δ −2.59 (s, 2H, N*H*), 1.84 (s, 18H, mesityl C*H*$_3$), 2.60 (s, 9H, mesityl C*H*$_3$), 2.84 (m, 2H, C*H*$_2$P═S), 3.24 (m, 2H, SC*H*$_2$), 7.29 (s, 4H, Ar*H*), 7.47 (m, 10H, Ar*H*), 7.84 (m, 6H, Ar*H*), 7.98 (d, 2H, J_{H-H} = 8.7 Hz, Ar*H*), 8.28 (d, 2H, J_{H-H} = 8.1 Hz, Ar*H*), 8.62 (s, 4H, Ar*H*), 8.67 (d, 2H, J_{H-H} = 4.8 Hz, Ar*H*), 8.86 (d, 2H, J_{H-H} = 4.5 Hz, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.5 (s). ESIMS (*m*/*z*): Calcd. 1093.4. Found 1093.7. Elemental analysis for $C_{73}H_{65}N_4PS_2$: Calcd. C, 80.19; H, 5.99; N, 5.12. Found C, 79.52; H, 5.86; N, 4.91.

[5-{4′-[2-(Diphenylphosphinothioyl)ethylsulfanyl]biphenyl-4-yl}-10,15,20-mesityl-porphyrinato]zinc^{II} (Compound 16a). In a 250-mL round-bottom flask, **15** (500 mg, 0.457 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (1.00 g, 4.57 mmol) were refluxed in $CHCl_3$/MeOH (200 mL, 4:1 v/v) for 3 h. Upon completion, the solution was washed with H_2O (2 × 100 mL) and dried over Na_2SO_4. The contents were filtered and the solvent was removed in vacuo yielding **16a** as a purple microcrystalline solid (513 mg, 97% yield). ^1H NMR (CD_2Cl_2): δ 1.84 (s, 18H, mesityl C*H*$_3$), 2.62 (s, 9H, mesityl C*H*$_3$), 2.82 (m, 2H, C*H*$_2$P═S), 3.22 (m, 2H, SC*H*$_2$), 7.30 (s, 4H, Ar*H*), 7.46 (m, 10H, Ar*H*), 7.81 (m, 6H, Ar*H*), 7.98 (d, 2H, J_{H-H} = 8.1 Hz, Ar*H*), 8.29 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 8.71 (s, 4H, Ar*H*), 8.75 (d, 2H, J_{H-H} = 4.5 Hz, Ar*H*), 8.94 (d, 2H, J_{H-H} = 4.8 Hz, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.3 (s). ESIMS (*m*/*z*): Calcd. 1154.3. Found 1154.5 Elemental analysis for $C_{73}H_{63}PS_2Zn$: Calcd. C, 75.79; H, 5.49; N, 4.84. Found C, 75.09; H, 5.13; N, 4.51.

[5-{4′-[2-(Diphenylphosphinothioyl)ethylsulfanyl]biphenyl-4-yl}-10,15,20-mesityl-porphyrinato]magnesium^{II} (Compound 16b). Under ambient conditions, **15** (602 mg, 0.550 mmol), $MgBr_2$ (4.03 g, 21.9 mmol), and NEt_3 (12.2 mL, 88.0 mmol) were combined in a 500-mL round-bottom flask and stirred for 6 h at rt in CH_2Cl_2 (350 mL). The solution was then washed with H_2O (2 × 100 mL) and extracted with CH_2Cl_2 (200 mL). The organic layer was further washed with H_2O (100 mL), dried over $MgSO_4$, and concentrated to give **16b** as a crude purple microcrystalline solid which was further purified via column chromatography on neutral alumina (CH_2Cl_2 as eluent to yield a small amount of unreacted freebase porphyrin then THF to elute product) which provided **16b** (608 mg, 96% yield). ^1H NMR (CD_2Cl_2): δ 1.84 (s, 18H, mesityl C*H*$_3$), 2.62 (m, 9H, mesityl C*H*$_3$), 2.87 (m, 4H, C*H*$_2$P═S), 3.25 (m, 4H, SC*H*$_2$), 7.29 (s, 6H, Ar*H*), 7.47 (br m, 10H, Ar*H*), 7.82 (br m, 6H, Ar*H*), 7.97 (d, 2H, J_{H-H} = 7.5 Hz, Ar*H*), 8.30 (d, 2H, J_{H-H} = 7.8 Hz, Ar*H*), 8.60 (s, 4H, Ar*H*) 8.66 (d, 2H, J_{H-H} = 4.2 Hz, Ar*H*), 8.85 (d, 2H, J_{H-H} = 4.2 Hz, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.5 (s). EIMS (*m*/*z*): Calcd. 1114.4. Found 1114.4. Elemental analysis for $C_{73}H_{63}MgPS_2$: Calcd. C, 77.95; H, 5.65; N, 4.98. Found C, 77.14; H, 5.72; N, 4.53.

5-[4′-(2-Diphenylphosphanylethylsulfanyl)biphenyl-4-yl]-10,15,20-mesitylporphyrinato]zinc(II) (Compound 17a). In a 50-mL Schlenk round-bottom flask, **16a** (431 mg, 0.372 mmol) and

Cp_2ZrHCl (307 mg, 1.19 mmol) were stirred under N_2 in THF (30 mL) at 60 °C for 4 h. Upon completion, the solvent was removed and the contents were purified via column chromatography on neutral alumina (THF as eluent) under an atmosphere of N_2. The product was isolated and the solvent was removed to yield **17a** as a purple microcrystalline solid (373 mg, 90% yield). ^{1}H NMR (CD_2Cl_2): δ 1.85 (s, 18H, mesityl CH_3), 2.45 (m, 2H, CH_2P), 2.60 (s, 9H, mesityl CH_3), 3.04 (m, 2H, SCH_2), 7.29 (s, 4H, Ar*H*), 7.39–7.48 (br m, 14H, Ar*H*), 7.88 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 8.00 (d, 2H, J_{H-H} = 7.8 Hz, Ar*H*), 8.24 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 8.61 (s, 4H, Ar*H*), 8.64 (d, 2H, J_{H-H} = 4.8 Hz, Ar*H*), 8.82 (d, 2H, J_{H-H} = 4.8 Hz, Ar*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −15.8 (s). ESIMS (*m*/*z*): Calcd. 1124.7. Found 1125.6. Elemental analysis for $C_{73}H_{63}PSZn$: Calcd. C, 77.95; H, 5.65; N, 4.98. Found C, 77.14; H, 5.72; N, 4.53.

5-[4′-(2-Diphenylphosphanylethylsulfanyl)biphenyl-4-yl]-10,15,20-mesitylporphyrinato] magnesium^{II} (17b). In a 50-mL Schlenk round-bottom flask, **16b** (438 mg, 0.393 mmol) and Cp_2ZrHCl (406 mg, 1.26 mmol) were stirred in THF under N_2 (30 mL) at 60 °C for 4 h. The solvent was removed and the reaction was purified via column chromatography on neutral alumina (THF as eluent) in a glovebox under an atmosphere of N_2. The solvent was removed in vacuo to yield **17b** as a purple microcrystalline solid (378 mg, 89% yield). ^{1}H NMR (THF-d_8): δ 1.86 (s, 18H, mesityl CH_3), 2.64 (m, 2H, CH_2P), 2.60 (s, 9H, mesityl CH_3), 3.07 (m, 2H, SCH_2), 7.28 (s, 6H, Ar*H*), 7.36 (d, 6H, J_{H-H} = 4.5 Hz, Ar*H*), 7.45 (br d, 6H, J_{H-H} = 6.6 Hz, Ar*H*), 7.88 (d, 2H, J_{H-H} = 7.8 Hz, Ar*H*), 7.99 (d, 2H, J_{H-H} = 7.2 Hz, Ar*H*), 8.25 (d, 2H, J_{H-H} = 7.8 Hz, Ar*H*), 8.53–8.57 (br m, 6H, Ar*H*), 8.74 (d, 2H, J_{H-H} = 3.6 Hz, Ar*H*). ^{31}P{^{1}H} NMR (THF-d_8): δ −15.8 (s). EIMS (*m*/*z*): Calcd. 1082.4 [M^+]. Found 1082.6. Elemental analysis for $C_{73}H_{63}MgPS$ (2 THF): Calcd. C, 79.36; H, 6.33; N, 4.57. Found C, 78.19; H, 6.15; N, 4.58.

(13)(17a)RhCl (Compound 18). Ligand **13** (147 mg, 0.133 mmol), ligand **17a** (150 mg, 0.133 mmol), and $[Rh(COE)_2Cl]_2$ (47.8 mg, 0.0667 mmol) were added to a 20-mL vial and dissolved in THF (15 mL). This solution was transferred to a 50-mL Schlenk flask and sonicated for 1 h. Upon completion, the solvent was removed under vacuum to yield a purple solid which was sonicated in hexanes (20 mL) for 1 h, filtered, washed with fresh hexanes (2 × 10 mL) and dried under vacuum to yield **18** as an air-sensitive solid (146 mg, 93% yield). ^{1}H NMR (CD_2Cl_2): δ 1.78–1.83 (m, 36H, mesityl CH_3), 2.45 (br m, 2H, SCH_2CH_2P), 2.57–2.61 (m, 18H, mesityl CH_3), 2.71 (m, 2H, SCH_2CH_2P), 2.80 (m, 2H, OCH_2CH_2P), 4.64 (m, 2H, OCH_2CH_2P), 7.09 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 7.20–7.35 (br m, 20H, Ar*H*), 7.41 (br m, 4H), 7.53 (t, 4H, Ar*H*), 7.70 (t, 4H, Ar*H*), 7.88 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 7.97–8.08 (br m, 6H, Ar*H*), 8.21 (d, 2H, J_{H-H} = 8.1 Hz, Ar*H*), 8.32 (d, 2H, J_{H-H} = 7.8 Hz, Ar*H*), 8.41 (d, 2H, J_{H-H} = 8.1 Hz, Ar*H*), 8.67−8.70 (m, 10H, Ar*H*), 8.73 (d, 2H, J_{H-H} = 4.2 Hz, Ar*H*), 8.92 (d, 2H, J_{H-H} = 4.8 Hz, Ar*H*), 8.95 (d, 2H, J_{H-H} = 4.2 Hz, Ar*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 72.6 (dd, J_{Rh-P} = 185 Hz, J_{P-P} = 41 Hz), 28.8 (dd, J_{Rh-P} = 166 Hz, J_{P-P} = 40 Hz). MALDI-TOF MS (*m*/*z*): Calcd. 2336.31 [M − Cl^-]. Found 2335.88.

(13)(17b)RhCl (Compound 19). Ligand **13** (147 mg, 0.133 mmol), ligand **17b** (144 mg, 0.133 mmol), and $[Rh(COE)_2Cl]_2$ (47.8 mg, 0.0667 mmol) were added to a 20-mL vial and dissolved in THF (15 mL). This solution was transferred to a 50-mL Schlenk flask and sonicated for 1 h. Upon completion, the solvent was removed under vacuum to yield a purple solid which was sonicated in a hexanes (20 mL) for 1 h, filtered, washed with fresh hexanes (2 × 10 mL), and dried under vacuum to yield **19** as an air-sensitive solid (146 mg, 94% yield). ^{1}H NMR (CD_2Cl_2): δ 1.78–1.86 (m, 36H, mesityl CH_3), 2.46 (br m, 2H, SCH_2CH_2P), 2.57–2.62 (m, 18H, mesityl CH_3), 2.72 (m, 2H, SCH_2CH_2P), 2.81 (m, 2H, OCH_2CH_2P), 4.62 (m, 2H, OCH_2CH_2P), 7.09 (d, 2H, J_{H-H} = 8.4 Hz Ar*H*), 7.21–7.35 (br m, 20H, Ar*H*), 7.42 (br t, 4H), 7.53 (t, 4H, Ar*H*), 7.70 (t, 4H, Ar*H*), 7.87 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 7.97–8.08 (br m, 6H, Ar*H*), 8.22 (d, 2H, J_{H-H} = 8.7 Hz, Ar*H*), 8.33 (d, 2H, J_{H-H} = 8.1 Hz, Ar*H*), 8.40 (d, 2H, J_{H-H} = 8.1 Hz, Ar*H*), 8.56–8.70 (m, 12H, Ar*H*), 8.87 (d, 2H, J_{H-H} = 4.2 Hz, Ar*H*), 8.92 (d, 2H, J_{H-H} = 4.2 Hz, Ar*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 72.6 (dd, J_{Rh-P} = 184 Hz, J_{P-P} = 38 Hz), 28.6 (dd, J_{Rh-P} = 167 Hz, J_{P-P} = 41 Hz). MALDI-TOF MS (*m*/*z*): Calcd. 2295.23 [M - Cl^-]. Found 2295.15; Calcd. 2270.93 [M − Mg − Cl^-)]. Found 2270.21.

[(13)(17a)Rh][B(ArF)$_4$] (Compound 20). Compound **18** (200.0 mg, 0.0843 mmol) and Na[B(ArF)$_4$] (74.7 mg, 0.0843 mmol) were added to a 20-mL vial and sonicated in CH_2Cl_2 (15 mL) for 1 h. The solution was placed in a freezer at −30 °C for 1 h to ensure complete precipitation of NaCl. The solution was passed through a plug of Celite (to remove NaCl) into a 25-mL Schlenk flask, and the solvent was removed under vacuum to yield **20** as an air-sensitive purple solid (251 mg, 93% yield). ^{1}H NMR (CD_2Cl_2): δ 1.67–1.85 (m, 36H, mesityl CH_3), 2.51–2.84 (br m, 24H, mesityl CH_3, SCH_2CH_2P, SCH_2CH_2P and OCH_2CH_2P), 4.17 (m, 2H, OCH_2CH_2P), 7.34–8.03 (br m, 56H, Ar*H*), 7.74 (br s, 12H, Ar*H*), 8.37 (br s, 4H, Ar*H*), 8.65–8.96 (br m, 16H, Ar*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 72.7 (dd, J_{Rh-P} = 198 Hz, J_{P-P} = 40 Hz), 51.0 (dd, J_{Rh-P} = 167 Hz, J_{P-P} = 41 Hz). MALDI-TOF MS (*m*/*z*): Calcd. 2336.31 [M − B(ArF)$_4^-$]. Found 2336.99.

[(13)(17b)Rh][B(ArF)$_4$] (Compound 21). Compound **19** (200.0 mg, 0.0858 mmol) and Na[B(ArF)$_4$] (75.6 mg, 0.0858 mmol) were added to a 20-mL vial and sonicated in CH_2Cl_2 (15 mL) for 1 h. The solution was placed in a freezer at −30 °C for 1 h to ensure complete precipitation of NaCl. The solution was passed through a plug of Celite (to remove NaCl) into a 25-mL Schlenk flask, and the solvent was removed under vacuum to yield **21** as an air-sensitive purple solid (253 mg, 93% yield). ^{1}H NMR (CD_2Cl_2): δ 1.71–1.84 (m, 36H, mesityl CH_3), 2.55–2.84 (br m, 24H, mesityl CH_3, SCH_2CH_2P, SCH_2CH_2P and OCH_2CH_2P), 4.17 (m, 2H, OCH_2CH_2P), 7.21–7.98 (br m, 56H, Ar*H*), 8.38 (d, 4H, J_{H-H} = 6.6 Hz, Ar*H*), 8.64–8.97 (br m, 16H, Ar*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 72.4 (dd, J_{Rh-P} = 198 Hz, J_{P-P} = 40 Hz), 51.0 (dd, J_{Rh-P} = 167 Hz, J_{P-P} = 41 Hz). MALDI-TOF MS (*m*/*z*): Calcd. 2295.22 [M − B(ArF)$_4^-$]. Found 2295.2. Calcd. 2270.92 [M − Mg − Cl^-)]. Found 2270.92.

[(13)(17a)Rh(CO)][B(ArF)$_4$] (Compound 22). Compound **22** can be prepared according to two separate methods.

Method A. Compound **20** (15.0 mg, 0.00468 mmol) was added to a 5-mL vial, dissolved in CD_2Cl_2 (2 mL), and transferred to a 10-mL Schlenk flask. The flask was attached to a Schlenk line where the N_2 atmosphere was evacuated and replaced with CO (1 atm). The contents were sonicated for 30 s at which point the flask was brought into a glovebox and transferred to a J-Young air-free NMR tube. The yield of **22** was determined to be quantitative as indicated by ^{31}P{^{1}H} NMR spectroscopy.

Method B. In a glovebox, compound **18** (20.0 mg, 0.00843 mmol) was added to a 5-mL vial, dissolved in CD_2Cl_2 (1 mL) and transferred to a 10-mL Schlenk flask. The Schlenk flask was placed on a Schlenk line where the N_2 atmosphere in the flask was evacuated and replaced with an atmosphere of CO (1 atm), resulting in the in situ generation of compound **24**. The flask was brought back into the glovebox where Na[B(ArF)$_4$] (7.47 mg, 0.00843 mmol) was added to the solution, at which point the solution was transferred to a J-Young air-free NMR tube. The resulting mixture was sonicated for 30 min which provided compound **22** in

quantitative yield as was indicated by $^{31}P\{^{1}H\}$ NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): δ 1.83 (br s, 36H, mesityl CH_3), 2.62 (br s, 18H, mesityl CH_3), 2.88 (m, 2H, SCH$_2$CH_2P), 3.03 (m, 2H, SCH_2CH$_2$P), 3.17 (m, 2H, OCH$_2$CH_2P), 4.52 (m, 2H, OCH_2CH$_2$P), 6.98–7.97 (br m, 52H, Ar*H*), 8.29 (m, 4H, Ar*H*), 8.39 (m, 4H, Ar*H*), 8.71 (br s, 12H, Ar*H*), 8.94 (br s, 4H, Ar*H*). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 61.0 (dd, J_{Rh-P} = 114 Hz, J_{P-P} = 266 Hz), 18.5 (dd, J_{Rh-P} = 117 Hz, J_{P-P} = 266 Hz). FTIR (CH_2Cl_2): ν_{CO} = 1970 cm^{-1}.

[(13)(17b)Rh(CO)][B(ArF)$_4$] (Compound 23). Compound **23** can be prepared according to two separate methods.

Method A. Compound **21** (15.0 mg, 0.00475 mmol) was added to a 5-mL vial, dissolved in CD_2Cl_2 (2 mL), and transferred to a 10-mL Schlenk flask. The flask was attached to a Schlenk line where the N_2 atmosphere was evacuated and replaced with CO (1 atm). The contents were sonicated for 30 s at which point the flask was brought into a glovebox and transferred to a J-Young air-free NMR tube. The yield of **23** was determined to be quantitative as indicated by $^{31}P\{^{1}H\}$ NMR spectroscopy.

Method B. In a glovebox, compound **19** (20.0 mg, 0.00858 mmol) was added to a 5-mL vial, dissolved in CD_2Cl_2 (1 mL), and transferred to a 10-mL Schlenk flask. The Schlenk flask was placed on a Schlenk line where the N_2 atmosphere in the flask was evacuated and replaced with an atmosphere of CO (1 atm), resulting in the in situ generation of compound **25**. The flask was brought back into the glovebox where Na[B(ArF)$_4$] (7.60 mg, 0.00858 mmol) was added to the solution, at which point the solution was transferred to a J-Young air-free NMR tube. The resulting mixture was sonicated for 30 min which provided compound **23** in quantitative yield as was indicated by $^{31}P\{^{1}H\}$ NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): δ 1.83−1.85 (br s, 36H, mesityl CH_3), 2.61 (br s, 18H, mesityl CH_3), 2.89 (m, 2H, SCH$_2$CH_2P), 3.04 (m, 2H, SCH_2CH$_2$P), 3.17 (m, 2H, OCH$_2$CH_2P), 4.52 (m, 2H, OCH_2CH$_2$P), 7.02 (d, 4H, J_{H-H} = 8.4 Hz, Ar*H*), 7.29 (br s, 12H, Ar*H*), 7.50–7.98 (br m, 40H, Ar*H*), 8.27 (d, 4H, J_{H-H} = 8.4 Hz, Ar*H*), 8.61–8.85 (br m, 12H, Ar*H*), 8.92 (d, 4H, J_{H-H} = 8.4 Hz, Ar*H*). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 61.0 (dd, J_{Rh-P} = 113 Hz, J_{P-P} = 266 Hz), 18.6 (dd, J_{Rh-P} = 118 Hz, J_{P-P} = 266 Hz). FTIR (CH_2Cl_2): ν_{CO} = 1970 cm^{-1}.

(13)(17a)RhCl(CO) (Compound 24). Compound **24** can be prepared according to two separate methods. Since method A relies only on the addition of CO (1 atm) to the sample, the product from this reaction was used for all of the necessary characterization.

Method A. Compound **18** (20.0 mg, 0.00843 mmol) was weighed out into a 5-mL vial, dissolved in CD_2Cl_2 (1 mL), and transferred to a 10-mL Schlenk flask. The flask was placed on a Schlenk line where the N_2 atmosphere was removed and replaced with CO (1 atm). The flask was sonicated for 30 s, and the solution was transferred to a J-Young air-free NMR tube. Analysis of this solution by ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy indicated the quantitative conversion of **18** to **24**.

Method B. Compound **20** (20.0 mg, 0.00625 mmol) and (n-Bu)$_4$NCl (1.74 mg, 0.00625 mmol) were weighed out into a 5-mL vial, dissolved in CD_2Cl_2 (1 mL), and transferred to a 10-mL Schlenk flask. The flask was placed on a Schlenk line where the N_2 atmosphere was removed and replaced with CO (1 atm). The flask was sonicated for 30 s and the solution was transferred to a J-Young air-free NMR tube. Analysis of this solution by ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy indicated the quantitative conversion of **20** to **24**. ^{1}H NMR (CD_2Cl_2): δ 1.80–1.84 (m, 36H, mesityl CH_3), 2.57–2.61 (m, 18H, mesityl CH_3), 3.02 (br m, 2H, SCH$_2$CH_2P), 3.24 (m, 2H, SCH_2CH$_2$P), 3.39 (m, 2H, OCH$_2$CH_2P), 4.69 (m, 2H, OCH_2CH$_2$P), 7.06 (d, 2H, J_{H-H} = 8.4 Hz, Ar*H*), 7.24–7.28 (br m, 12H, Ar*H*), 7.43 (d, 2H, J_{H-H} = 8.1 Hz, Ar*H*), 7.52 (br s, 12H, Ar*H*), 7.80–7.87 (br m, 12H, Ar*H*), 7.93 (d, 4H, J_{H-H} = 8.4 Hz, Ar*H*), 8.24 (br t, 4H, Ar*H*), 8.68–8.74 (br m, 12H, Ar*H*), 8.92 (m, 4H, Ar*H*). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 21.6 (eight peaks which arise from overlap of two dd's: δ 21.6, 22.4, 22.6, 23.3, 23.7, 24.5, 24.8, 25.6). FTIR (CH_2Cl_2): ν_{CO} = 1967 cm^{-1}.

(13)(17b)RhCl(CO) (Compound 25). Compound **25** can be prepared according to two separate methods. Since method A relies only on the addition of CO (1 atm) to the sample, the product from this reaction was used for all of the necessary characterization.

Method A. Compound **19** (20.0 mg, 0.00858 mmol) was weighed out into a 5-mL vial, dissolved in CD_2Cl_2 (1 mL) and transferred to a 10-mL Schlenk flask. The flask was placed on a Schlenk line where the N_2 atmosphere was removed and replaced with CO (1 atm). The flask was sonicated for 30 s and the solution was transferred to a J-Young air-free NMR tube. Analysis of this solution by ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy indicated the quantitative conversion of **19** to **25**.

Method B. Compound **21** (20.0 mg, 0.00633 mmol) and (n-Bu)$_4$NCl (1.76 mg, 0.00633 mmol) were weighed out into a 5-mL vial, dissolved in CD_2Cl_2 (1 mL), and transferred to a 10-mL Schlenk flask. The flask was placed on a Schlenk line where the N_2 atmosphere was removed and replaced with CO (1 atm). The flask was sonicated for 30 s and the solution was transferred to a J-Young air-free NMR tube. Analysis of this solution by ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy indicated the quantitative conversion of **21** to **25**. ^{1}H NMR (CD_2Cl_2): δ 1.79–1.84 (m, 36H, mesityl CH_3), 2.58–2.62 (m, 18H, mesityl CH_3), 3.02 (br m, 2H, SCH$_2$CH_2P), 3.24 (m, 2H, SCH_2CH$_2$P), 3.39 (m, 2H, OCH$_2$CH_2P), 4.68 (m, 2H, OCH_2CH$_2$P), 7.06 (d, 2H, J_{H-H} = 9.1 Hz, Ar*H*), 7.24–7.28 (br m, 12H, Ar*H*), 7.43–7.52 (br s, 14H, Ar*H*), 7.79–7.86 (br m, 12H, Ar*H*), 7.94 (d, 4H, J_{H-H} = 7.8 Hz, Ar*H*), 8.25 (d, 4H, J_{H-H} = 7.2 Hz, Ar*H*), 8.60–8.75 (br m, 12H, Ar*H*), 8.85 (m, 2H, Ar*H*), 8.94 (m, 2H, Ar*H*). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 21.4 (seven peaks which arise from overlap of two dd's: δ 21.4, 22.4, 23.5, 23.6, 24.4, 24.6, 25.4). FTIR (CH_2Cl_2): ν_{CO} = 1971 cm^{-1}.

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Supporting Information Available: ^{1}H and $^{31}P\{1H\}$ NMR spectra for compounds **19**, **21**, **23**, and **25** and MALDI-TOF spectra for compounds **19** and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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