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Elucidating the Mechanism of the Halide-Induced Ligand Rearrangement Reaction

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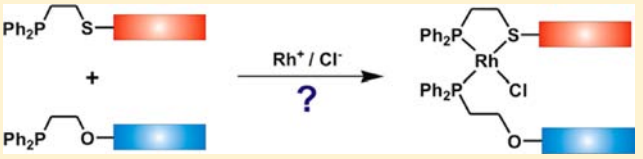
Supporting Information

ABSTRACT: The formation of heteroligated Rh^{I} complexes containing two different hemilabile phosphinoalkyl ligands, (κ^2-$Ph_2PCH_2CH_2S$-Aryl)(κ^1-$Ph_2PCH_2CH_2O$-C_6H_5)RhCl, through a halide-induced ligand rearrangement (HILR) reaction has been studied mechanistically. The half-life of this rearrangement reaction depends heavily on the Rh^{I} precursor used and the chelating ability of the phosphinoalkyl thioether (PS) ligand, while the chelating ability of the phosphinoalkyl ether (PO) ligand has less of an effect. An intermediate complex which contains two PO ligands, (nbd)(κ^1-$Ph_2PCH_2CH_2O$-C_6H_5)$_2$RhCl (nbd = norbornadiene), converts to (nbd)(κ^1-$Ph_2PCH_2CH_2O$-C_6H_5)RhCl resulting in a free PO ligand. The free PO ligand can then react with a homoligated PS complex [(κ^2-$Ph_2PCH_2CH_2S$-Aryl)$_2$Rh]$^+$Cl$^-$ producing the heteroligated product. The PS ligand generated during the reaction pathway can be trapped by the monoligated PO complex (nbd)(κ^1-$Ph_2PCH_2CH_2O$-C_6H_5)RhCl, leading to the formation of the same heteroligated product. In this study, some of the key intermediates and reaction steps underlying the HILR reaction have been identified by variable temperature $^{31}P\{^1H\}$ NMR spectroscopy and in two cases by single-crystal X-ray diffraction studies. Significantly, this work provides mechanistic insight into the HILR process, which is a key reaction used to prepare a large class of highly sophisticated three-dimensional metallosupramolecular architectures and allosteric catalysts.



INTRODUCTION

There are now a variety of methods that allow one to construct two- and three- dimensional supramolecular structures based on coordination-chemistry principles and judicious ligand design.[1] Three of the most utilized are the directional bonding (DBA),[1g,i,2] symmetry interaction (SIA),[1l,3] and weak-link approaches (WLA).[4] The DBA is based on transition metal centers with blocking ligands, leaving open coordination sites at fixed geometries that can direct the assembly of conformationally rigid multitopic ligands into multimetallic macrocycles, squares, triangles, and polyhedral cages.[1g,2a−g,5] The SIA is related to the DBA as it is also based on the templating of higher-order structures using transition metals that enforce specific coordination geometries.[1a,l,3a−f,6] This templating allows for the rational design of macrocycles, helices, polyhedral cages, and other structures in the absence of blocking ligands. Both the SIA and DBA, by design and virtue of the rigid linkers, yield structurally rigid systems.

The WLA utilizes flexible hemilabile ligands (**1**) and transition metal centers free of directing ligands to synthesize metallosupramolecular cyclophanes (**2**), triple-layer complexes, tweezers, and other structures (Scheme 1).[4] In contrast to the DBA and the SIA, the WLA yields structures with chemically addressable metal hinge sites that allow one to toggle between complexes with different coordination geometries and flexibilities (**2** and **3**) by the addition or removal of small molecules or elemental anions; importantly, these conformations often exhibit significantly different stoichiometric or catalytic reactivities.[7] Consequently, this synthetic approach has led to the discovery and development of an entire new class of allosteric enzyme mimics, with the ability to amplify chemical recognition events through subsequent catalytic reactions.[8]

For all three supramolecular coordination chemistry approaches, methodologies have been developed to synthesize heteroligated coordination structures.[9] For example, in the case of the DBA, the combination of sterically hindered and unhindered pyridines has been used to synthesize heteroligated complexes, such as rectangles and box structures.[10] Similarly, with the SIA, researchers have used the preferred 5-fold coordination mode of Cu^{II} ions with respect to bis- and tripyridines, to make heteroligated helices.[11] With the WLA and the halide-induced ligand rearrangement (HILR) reaction, heteroligated macrocyclic, tweezer, and three-tiered coordination structures can be synthesized with parallel planar alignment of two different functional groups (A, B, Scheme 2).[4d,12] The position between functional groups A and B can be regulated in situ in a reversible fashion via the addition or removal of small molecules or elemental anions.

The HILR reaction results in the formation of a semiopen Rh^{I} complex, in which a phosphinoalkyl-thioether (PS) ligand is present as a five-membered κ^2-PS chelate and a phosphinoalkyl-

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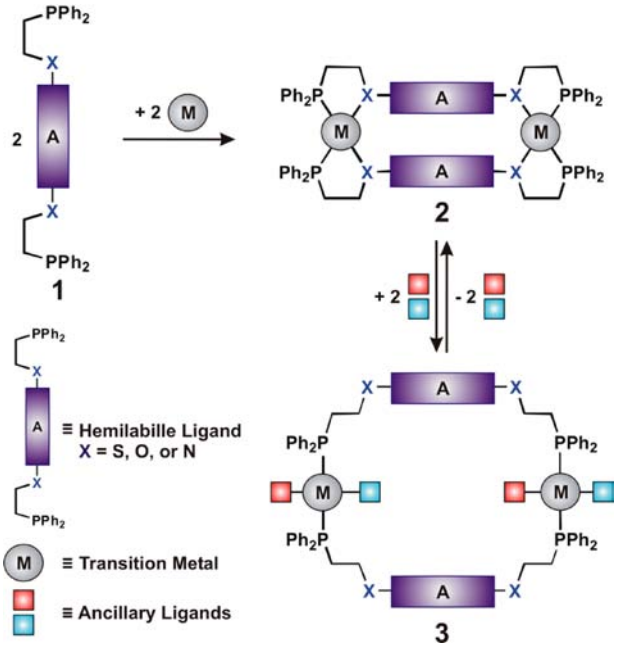
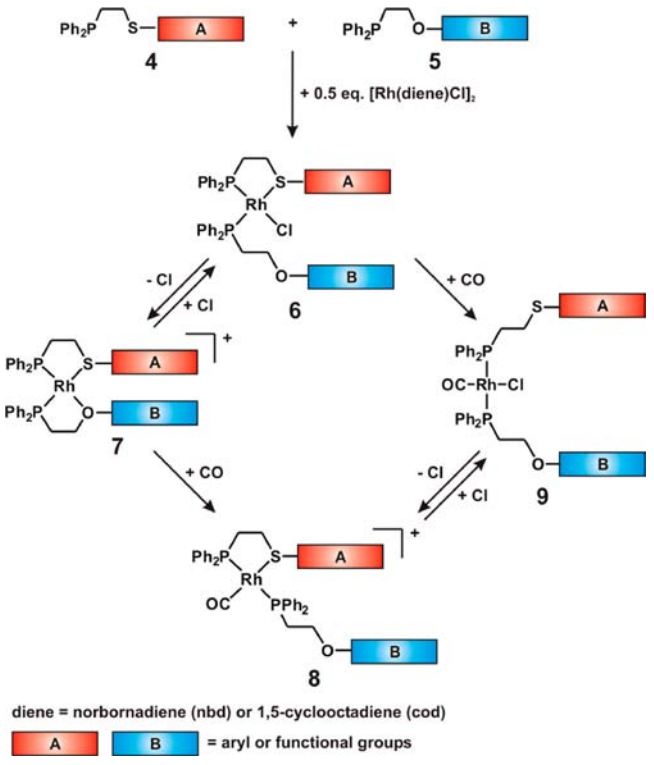
Scheme 1. Weak-Link Approach (WLA) to Supramolecular Chemistry



Scheme 2. Formation of Heteroligated Rh^{I} Tweezer Complexes



ether (PO) ligand is present in a κ^1-PO unchelated form, with the chloride ion occupying the fourth coordination site of the Rh^{I} center (**6**, Scheme 2). The initial semiopen complex **6** can be closed upon abstraction of chloride, yielding a closed structure **7** in which both ligands are chelated to the Rh^{I} center. Heteroligated structures prepared by the HILR reaction and WLA allow one to chemically address the different metal-heteroatom bonds (Rh−O or Rh−S) of the complex in a stepwise fashion with a variety of small molecules (e.g., CO, **8**, Scheme 2).[4d,12a] With the HILR reaction, researchers now have the ability to synthesize designer molecules that incorporate two different functionalities within one complex aligned in a parallel planar manner (Figure 1). Moreover, the HILR reaction is not restricted to Rh^{I} and has been shown to work with other d^8 transition metals (e.g., Pt^{II} and Pd^{II}).[12g,h,13]

Although many complexes have been made via the HILR reaction, little is still known about the mechanism of this rearrangement reaction. Herein, we identify some of the key intermediates and reaction steps underlying the HILR reaction by systematically changing the chelating ability of the hemilabile ligands, specifically the aryl substituents appended to the chalcogens on the labile portions of the ligands, and investigating the role of the chalcogen itself and the olefin in the Rh^{I} precursor. In this study, we have focused on monometallic Rh^{I} tweezer complexes; however, the lessons learned are likely extendable to many of the other Rh^{I} macrocyclic and three-tiered complexes formed via the HILR reaction (Figure 1).[12b,c,f,k]

RESULTS

Known hemilabile PS ligands (**4a−e**, Table 1)[7c,12a] and PO ligands (**5a−c**, Table 2)[7c,12c] were synthesized according to previously published procedures. These ligands were used to form heteroligated Rh^{I} tweezer complexes via the HILR reaction, and $^{31}P\{^1H\}$ NMR spectroscopy at 25 °C was used to measure the corresponding half-lives of the reactions ($t_{1/2}$). Several variables were considered in the context of this ligand rearrangement reaction; among them were (1) the Rh^{I} precursor, (2) the aryl substituents attached to the sulfur and oxygen atoms in the hemilabile ligands, and (3) the chalcogens used in the hemilabile ligands.

Effect of the Olefin Binding Strength in the Rh^{I} Precursor. It has been previously reported that, in general, the rate of the HILR reaction increases with Rh^{I} precursors containing weaker binding olefins.[12a] Therefore, the HILR reaction was studied using three different Rh^{I} precursors $[Rh(nbd)Cl]_2$, $[Rh(cod)Cl]_2$, and $[Rh(coe)_2Cl]_2$ (nbd = norbornadiene, cod = 1,5-cyclooctadiene, and coe = cyclooctene) with PS-(2,4-$(CH_3)_2$-C_6H_3) (**4c**, Table 1) and PO-C_6H_5 (**5a**, Table 1) in CD_2Cl_2 at 25 °C. The reaction half-lives, based upon product formation, were measured by $^{31}P\{^1H\}$ NMR spectroscopy, following literature procedures.[12a] The half-lives measured with each Rh^{I} precursor were less than 5 min for $[Rh(coe)_2Cl]_2$, 3 h for $[Rh(cod)Cl]_2$, and 7 h for $[Rh(nbd)Cl]_2$, indicating that the displacement of the olefin from the Rh^{I} center has a large effect on the rate of the HILR reaction. Consequently, the nbd precursor was used for the remainder of the reactions investigated, since it allowed for easier observation of some of the reaction intermediates.

Effect of the Aryl Groups Appended to the Thioethers in the PS Ligands. Five different PS ligands were studied using $[Rh(nbd)Cl]_2$ as the Rh^{I} source and PO-C_6H_5 (**5a**) as the ether-containing ligand (Table 1). The reaction half-lives, based on product formation, were measured in CD_2Cl_2 by $^{31}P\{^1H\}$ NMR spectroscopy at 25 °C, and show that the rate of the reaction is inversely proportional to the electron donating ability of the aryl substituents tethered to the sulfur (**4e** > **4d** > **4a** > **4c** > **4b**).[12a,14] This trend is consistent with the conclusion that displacement of the PS ligand from the Rh^{I} center is a key step in the HILR reaction and, as expected, the use of more electron-donating ligands results in a longer half-life.

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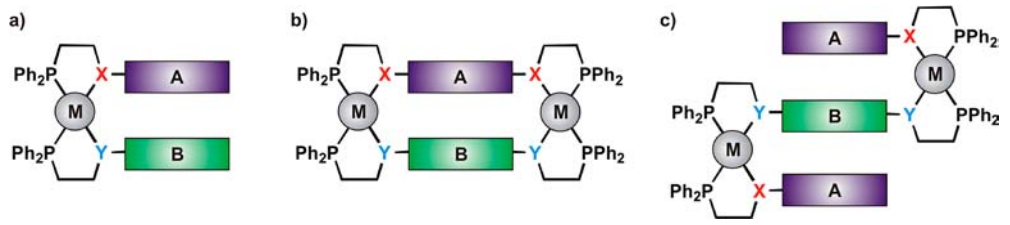
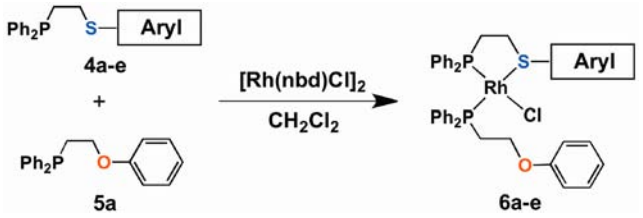


Figure 1. Wide range of supramolecular assemblies constructed via the HILR reaction including (a) tweezers,[12a,g,18] (b) macrocycles,[12b,d,f] and (c) triple-layer complexes.[12c,k] The geometries of the complexes can be modified in situ by reversible chemistry on the metal regulatory sites. Here X represents the weak-link moiety (O, S, Se, or N) and A and B are functional groups. When A = B and/or when X = Y the complex is homoligated.

Table 1. Comparison of Half-Lives ($t_{1/2}$) Using PS Hemilabile Ligands of Varying Chelating Ability



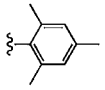
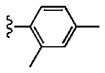
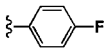
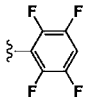
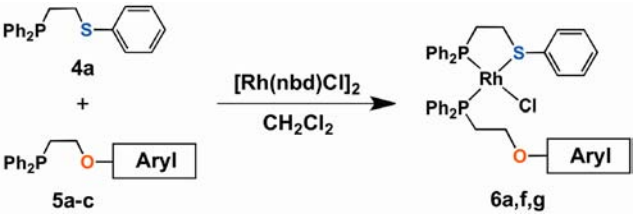
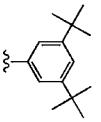
Aryl		$t_{1/2}$ (hr)
	**4b**	> 24 (**6b**)
	**4c**	7.0 (**6c**)
	**4a**	3.2 (**6a**)
	**4d**	2.4 (**6d**)
	**4e**	1.5 (**6e**)

Table 2. Comparison of the Half-Lives ($t_{1/2}$) Using Different PO Ligands



Aryl		$t_{1/2}$ (hr)
	**5a**	3.2 (**6a**)
	**5b**	4.2 (**6f**)
	**5c**	7.5 (**6g**)

Effect of the Aryl Groups Appended to the Ethers in the PO Ligands. Three phosphinoalkyl ether ligands (**5a**–**c**) were studied in the context the HILR reaction with $[Rh(nbd)Cl]_2$ as the Rh^I source and **4a** as the thioether ligand in CD_2Cl_2 (Table 2). The functional groups on the aryl groups of the ether-based hemilabile ligands have only a modest effect on the rate of the HILR reaction, with $t_{1/2}$ increasing by a factor of 2.3, from 3.2 h for PO-C_6H_5 (**5a**) to 7.5 h for PO-(2,3,5,6-$(CH_3)_4$-C_6H_1) (**5c**). Consequently, the chelating ability of the PO ligand has less of an influence on the HILR reaction rate than does the chelating ability of the PS ligand. In fact, when the ether is replaced by a methylene unit, the heteroligated product is still obtained.[12a]

Reaction of $[Rh(nbd)Cl]_2$ with One PS Ligand. In an attempt to identify some of the intermediates in the HILR reaction, the initial reaction between the PS ligands (**4a**–**e**) and $[Rh(nbd)Cl]_2$ was investigated by $^{31}P\{^1H\}$ NMR spectroscopy at 25 °C in CD_2Cl_2. In all cases a rapid reaction with 1 equiv of the PS ligand to form square planar complexes, **10** or **11**, is observed, regardless of the aryl substituents employed (Scheme 3). The main differences between these two structures are the position of the Cl^- counterion (inner or outer sphere) and the mode of PS ligand binding to the metal center (mono- or bidentate). Both steric[15] and electronic effects of the PS ligand determine which structure is favored (Scheme 3). Thioether ligands with more electron-donating aryl substituents favor the formation of the bidentate isomer (**10a**, **c**, **d**), while ligands that are more electron-withdrawing, such as **4e**, result in the formation of the monodentate isomer (**11e**). Steric factors may also influence the formation of the monodentate isomer, as with **11b** (vide infra).

For example, treatment of 1 equiv of PS-C_6H_5 (**4a**) with 0.5 equiv of $[Rh(nbd)Cl]_2$ ([PS]:[Rh] = 1:1) leads to the rapid formation of $[(nbd)(\kappa^2\text{-}Ph_2PCH_2CH_2SC_6H_5)Rh]^+Cl^-$ (**10a**) in CD_2Cl_2 at 25 °C. The $^{31}P\{^1H\}$ NMR spectrum of complex **10a** exhibits a resonance at δ 57.1 (d, J_{Rh-P} = 153 Hz, CD_2Cl_2), which is similar to the NMR resonance of the four-coordinate Rh^I complex, $[(nbd)(\kappa^2\text{-}Ph_2PCH_2CH_2SC_6H_5)Rh]^+BF_4^-$, containing a BF_4^- rather than a Cl^- counterion (δ 55.9, J_{Rh-P} = 161 Hz, CD_2Cl_2).[16] Complex **10a** contains a square planar Rh^I center where the PS ligand is present as part of a five-membered chelate ring, and the nbd ligand occupies the two remaining coordination sites. The Cl^- counterion is in the outer coordination sphere. This structural assignment is supported by the observation of a single $^{31}P\{^1H\}$ NMR resonance, which is downfield of the

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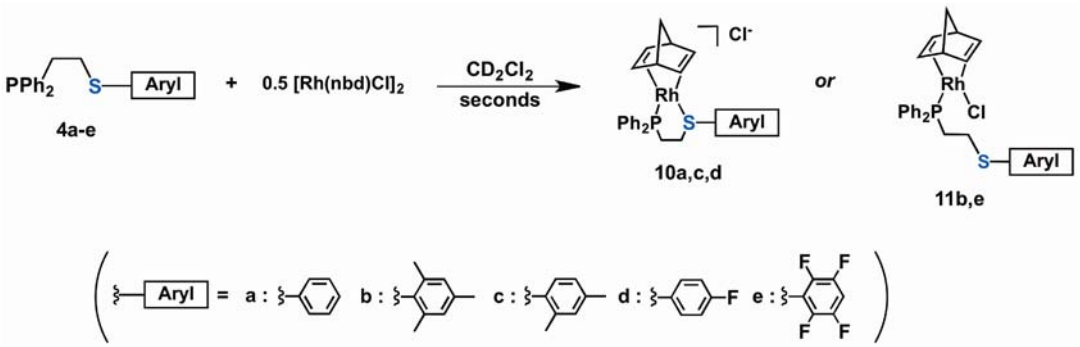
Scheme 3. Reaction of $[Rh(nbd)Cl]_2$ with One Equivalent of a PS Ligand



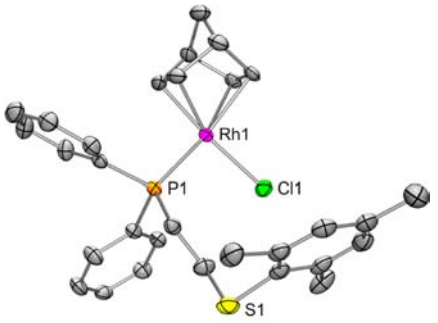
resonances associated with nonchelated structures (~ δ 10–30).[17]

Interestingly, PS-(2,4,6-$(CH_3)_3$-C_6H_2) (**4b**) reacts with $[Rh(nbd)Cl]_2$ to form the nonchelated, open complex, (nbd)(κ^1-$Ph_2PCH_2CH_2S$(2,4,6-$(CH_3)_3$-C_6H_2))RhCl (**11b**), in which the PS ligand is bound to the Rh^I center through only its phosphorus atom. Complex **11b** has been isolated and fully characterized by NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectrum of **11b** exhibits a doublet at δ 25.9 (J_{Rh-P} = 172 Hz, CD_2Cl_2), which is significantly upfield of the resonances associated with the closed chelated complexes **10a,c,d**. The $^{31}P\{^1H\}$ NMR spectrum of **11b** does not exhibit a significant temperature dependence over the −60 to 50 °C temperature range.

Formation of the open complex **11b** may be a consequence of unfavorable steric interactions between the nbd ligand and the sterically demanding methyl groups in the *ortho* position of the mesityl substituent, supported by the observation that the addition of a second equivalent of the PS-(2,4,6-$(CH_3)_3$-C_6H_2) (**4b**) ligand results in a complex with both ligands chelated to the Rh^I center.[18] This is consistent with the trend discussed above that the use of more electron-donating ligands results in a longer half-life. The open structure is also observed in the case of (nbd)(κ^1-$Ph_2PCH_2CH_2S$(2,3,5,6-F_4−C_6H))RhCl (**11e**), which is generated from the reaction of 1 equiv of PS-(2,3,5,6-F_4−C_6H) (**4e**) with 0.5 equiv of $[Rh(nbd)Cl]_2$. The $^{31}P\{^1H\}$ NMR resonance of **11e** is observed at δ 26.3 (J_{Rh-P} = 172 Hz, CD_2Cl_2) as a doublet at 25 °C and corresponds well with the resonance observed for **11b**. The relatively electron-withdrawing tetrafluorophenyl group appended to the thioether in **11e** greatly decreases the propensity for Rh−S bond formation, resulting in the nonchelated, open complex **11e**.[14]

Yellow crystals of **11b**, suitable for a single-crystal X-ray diffraction study, were grown by diffusion of pentane into a CH_2Cl_2 solution saturated with **11b**. The solid state structure of complex **11b** shows a monometallic complex with the Rh^I center coordinated by phosphine, Cl^-, and nbd ligands (Figure 2). With an interatomic distance between the Rh and S atoms of 5.735(1) Å, it is clear that the PS-(2,4,6-$(CH_3)_3$-C_6H_2) ligand in **11b** is not chelated in the solid state and is consistent with conclusions drawn about its solution-phase structure based on NMR spectroscopy.

Reaction of $[Rh(nbd)Cl]_2$ with Two Equivalents of PS Ligand. Treatment of the Rh^I precursor, $[Rh(nbd)Cl]_2$, with 2 equiv of PS-C_6H_5 (**4a**) in CD_2Cl_2 (PS:Rh = 2:1) leads to the formation of the closed homoligated structure, [(κ^2-$Ph_2PCH_2CH_2S$-C_6H_5)$_2$Rh]$^+Cl^-$ (**12**; Scheme 4). The $^{31}P\{^1H\}$ NMR resonance for **12** is observed at δ 64.2 (J_{Rh-P} = 162 Hz, CD_2Cl_2) as a doublet at 25 °C, which is diagnostic of a square planar Rh^I complex with a *cis*-thioether and *cis*-phosphine coordination geometry.[7a−c] Complexes with two chelated ligands like **12** are also initially formed during the HILR reaction in CD_2Cl_2, as evidenced by the observation of $^{31}P\{^1H\}$ NMR resonances at ~δ 65 (d, J_{Rh-P} = ~160 Hz).[12a−c] Note with bis-thioether complexes like **12**, association of the Cl^- counterion with the Rh^I center to form the semiopen complex **13** does not occur in CD_2Cl_2 at room temperature, but has been observed in more polar solvents such as THF (Scheme 4).[18]



11b

Figure 2. ORTEP drawing of complex **11b** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Rh = pink, S = yellow, P = orange, Cl = green, C = gray.

Reaction of $[Rh(nbd)Cl]_2$ with One PO Ligand. The ether analogue of **11b**, (nbd)(κ^1-$Ph_2PCH_2CH_2OC_6H_5$)RhCl (**14**), was synthesized by reacting 1 equiv of PO ligand, **5a**, with $[Rh(nbd)Cl]_2$ (PO:Rh = 1:1) in CD_2Cl_2 (Scheme 5). Complex **14** has been characterized in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, ESI-MS, and in the solid state by a single-crystal X-ray diffraction study. The $^{31}P\{^1H\}$ NMR spectrum of **14** exhibits a single resonance at δ 25.9 (d, J_{Rh-P} = 172 Hz), which is indicative of the assigned structure with a nonchelated ligand based on a comparison with model literature analogues (e.g., (diene)Rh(PPh_3)Cl).[19] Orange single crystals of **14** were grown by diffusion of pentane into a CH_2Cl_2 solution saturated with **14**. The structure of **14** in the solid-state shows the four-coordinate Rh^I complex, consistent with the solution-phase spectroscopic results (Figure 3).

Reaction of $[Rh(nbd)Cl]_2$ with Two PO Ligands. Two equivalents of **5a** react with $[Rh(nbd)Cl]_2$ (PO:Rh = 2:1) in CD_2Cl_2 to form (nbd)(κ^1-$Ph_2PCH_2CH_2OC_6H_5$)$_2$RhCl (**15**, Scheme 5), which has been characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and a comparison with similar data for literature model complexes.[20] The $^{31}P\{^1H\}$ NMR spectrum of **15**

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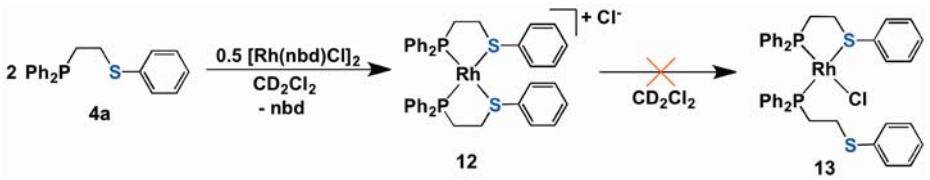
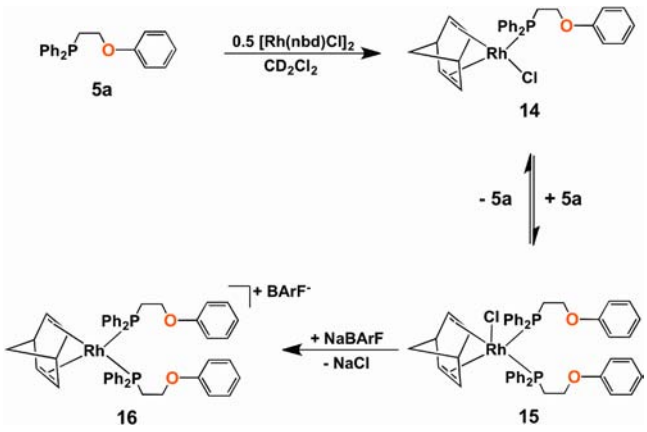
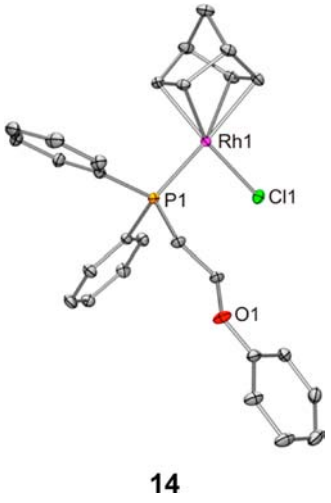
Scheme 4. Reaction of $[Rh(nbd)Cl]_2$ with Two Equivalents of PS Ligand



Scheme 5. Reaction of $[Rh(nbd)Cl]_2$ with PO Ligands





14

Figure 3. ORTEP diagram of complex **14**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Rh = pink, O = red, P = orange, Cl = green, C = gray.

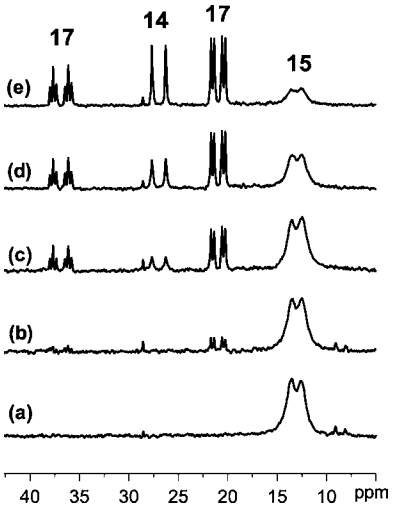


Figure 4. Time-dependent $^{31}P\{^1H\}$ NMR spectra of **15**. The reaction was performed at 25 °C and the $^{31}P\{^1H\}$ NMR spectra were recorded at −60 °C. (Reaction time: (a) 3 min; (b) 8 min; (c) 13 min; (d) 28 min; (e) 60 min at 25 °C).

reveals a broad doublet at δ 13.0 (J_{Rh-P} = 128 Hz; Figure 4a), corresponding to *cis*-phosphine/nbd coordination environments at the Rh^I centers.[12b,20] On the basis of previous literature reports regarding Rh^I phosphine complexes, Cl^- may coordinate to the Rh center resulting in a neutral five-coordinate geometry (Scheme 5).[20] When sodium tetrakis[(3,5-trifluoromethyl)-phenyl]borate is used to abstract the chloride ligand from complex **15**, the cationic four-coordinate complex, $[(nbd)(\kappa^1\text{-}Ph_2PCH_2CH_2OC_6H_5)_2Rh]^+BArF^-$ (BArF = $B[3,5\text{-}C_6H_3(CF_3)_2]_4$) (**16**) is formed (Scheme 5). The $^{31}P\{^1H\}$ NMR spectrum of **16** (δ 18.6 (d, J_{Rh-P} = 155 Hz), CD_2Cl_2, 25 °C) is similar to that of previously reported four-coordinate $[(diene)Rh(PR_3)_2]^+X^-$ complexes (PR_3 = chelating or non-chelating phosphines, diene = nbd or cod, X^- = noncoordinating counterion).[16,19b,21] The change in coordination number of the Rh^I center (from 5 in **15** to 4 in **16**) may result in the observed 27 Hz increase in the Rh−P coupling constant.[20a,21a,22] Complex **16** is indefinitely stable in CD_2Cl_2 at room temperature.

On the basis of NMR spectroscopic data (vide infra), at room temperature, complex **15** is in equilibrium with **14** and **17**, $(Ph_2PCH_2CH_2OC_6H_5)_3RhCl$, in CD_2Cl_2 (Scheme 6, Figure 4). This transformation is presumably a consequence of dissociation of a PO ligand from complex **15**, resulting in complex **14**, followed by the association of the metal-free PO ligand to a second equivalent of **15** and dissociation of the nbd ligand, resulting in complex **17**. Attempts to observe free PO ligand by VT-NMR spectroscopy (down to −80 °C) have been unsuccessful presumably because the dissociation step is also inhibited at low temperatures. Similar reversible phosphine ligand exchange reactions in $(diene)(PR_3)_2RhCl$ systems (PR_3 = nonchelating phosphines, diene = nbd or cod) have been extensively studied kinetically and thermodynamically.[19c−e]

Although complex **17** has not been characterized by a single-crystal X-ray diffraction study, the solution-state NMR spectroscopic data are consistent with a structure similar to $Rh(PR_3)_3Cl$ (PR_3 = chelating or nonchelating phosphines).[19a,21b,23] Mechanistic investigations of $Rh(PR_3)_3Cl$ complexes have shown that dissociation of PR_3 occurs in solution resulting in the catalytically active species $Rh(PR_3)_2Cl$.[23e−g] Intermediate **17** reversibly converts back to **15** via the dissociation of a PO ligand and the reassociation of a nbd ligand. Using $^{31}P\{^1H\}$ NMR spectroscopy to follow this equilibrium process, one can initially see the formation of **15** as evidenced by a broad doublet at δ 13 followed by new resonances associated with **14** and **17**, respectively (Figure 4). In the case of **17**, resonances are observed at δ 21.9 (dd, J_{Rh-P} = 137 Hz, J_{P-P} = 40 Hz) and δ 37.1 (dt, J_{Rh-P} = 187 Hz, J_{P-P} = 40 Hz), and assigned to the

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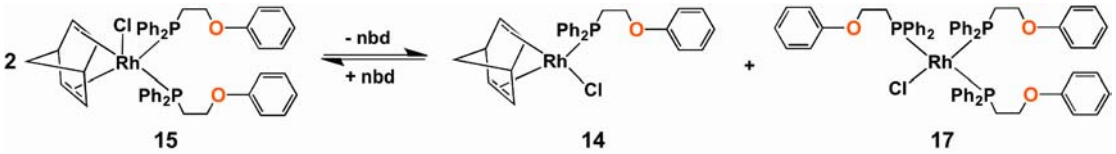
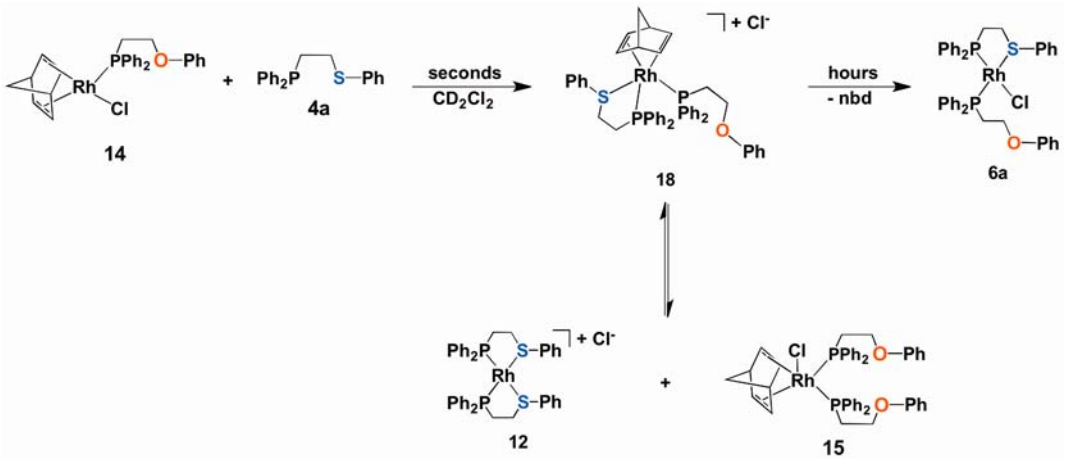
Scheme 6. Transformation of Complex 15 into Complexes 14 and 17



Scheme 7. Reaction of PO Rh^I Complex 14 and PS Ligand 4a



phosphines cis and trans to the Cl^-, respectively, based on comparisons with isostructural and isoelectronic species.[19a,21b,23e–i] Increase of the signals corresponding to **14** and **17** with a concomitant decrease in the resonance assigned to **15** can be clearly observed by VT-NMR spectroscopy (Figure 4).

Interestingly, when complex **14** is reacted with 1 equiv of PS-C_6H_5 ligand **4a** in CD_2Cl_2 at 25 °C, complex **18**, $[(nbd)(\kappa^2\text{-}Ph_2PCH_2CH_2SC_6H_5)(\kappa^1\text{-}Ph_2PCH_2CH_2OC_6H_5)Rh]^+Cl^-$, is rapidly formed (Scheme 7). Complex **18** is in equilibrium with **12** and **15**, which are also observed by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 5). The structure assigned to **18** is based on comparisons with $^{31}P\{^1H\}$ and ^1H NMR spectroscopic data for an isostructural and isoelectronic model five-coordinate macrocyclic intermediate structure, $[((nbd)_2(\kappa^2\text{-}Ph_2PCH_2CH_2S)_2\text{-}C_6H_4)\text{-}(\kappa^1\text{-}Ph_2PCH_2CH_2N(CH_3))_2\text{-}C_6H_4)Rh_2]^{2+}2BF_4^-$ previously reported by our group[12f] and similar structures reported by other groups.[24] The $^{31}P\{^1H\}$ NMR spectrum of **18** exhibits a signal at δ 60.3 (dd, J_{Rh-P} = 164 Hz, J_{P-P} = 30 Hz), corresponding to a chelated PS ligand, as it is significantly downfield from resonances typically associated with nonchelated phosphine ligands[12a,f,17] and the resonance at δ 10.1 (dd, J_{Rh-P} = 120 Hz, J_{P-P} = 30 Hz) is assigned to the nonchelated PO ligand of **18** (Scheme 7). In principle, a geometry with the Cl^- counterion instead coordinated to the Rh^I center is also possible but less likely since it requires the dissociation of one ethylene unit of the chelated nbd ligand. Over 4 h at room temperature, complexes **18**, **12**, and **15** are completely transformed into heteroligated Rh^I complex **6a** with a concomitant loss of a nbd ligand (Scheme 7; Figure 5).

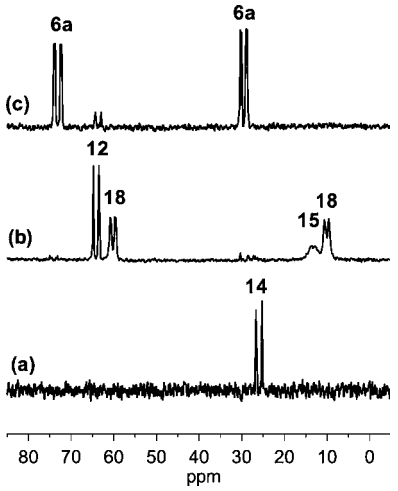


Figure 5. $^{31}P\{^1H\}$ NMR spectra depicting the reaction of **14** and **4a** (CD_2Cl_2). The reaction was performed at 25 °C, and each $^{31}P\{^1H\}$ NMR spectrum was recorded at −60 °C. (a) Complex **14** before the addition of **4a**, (b) 1 min, and (c) 14 h after addition of **4a**.

DISCUSSION

The reaction of different PS and PO ligands with $[Rh(nbd)Cl]_2$ in CD_2Cl_2 initially leads to the formation of $[(\kappa^2\text{-}Ph_2PCH_2CH_2S\text{-}Aryl)_2Rh]^+Cl^-$ (**12**) and $(nbd)(\kappa^1\text{-}Ph_2PCH_2CH_2O\text{-}Aryl)_2RhCl$ (**15**) and ultimately results in the generation of heteroligated complexes, $(\kappa^2\text{-}Ph_2PCH_2CH_2S\text{-}Aryl)(\kappa^1\text{-}Ph_2PCH_2CH_2O\text{-}Aryl)\text{-}RhCl$ (**6**), via the HILR reaction. The Cl^-, or other coordinating counteranion, is essential in this process; quantitative formation of heteroligated complexes has never been observed in the presence of noncoordinating counteranions.[12a] In general, hemilabile PO chelating ligands bind weakly to Rh^I centers compared to PS ligands.[7c] In addition, the Rh−O interactions are easily replaced by a Rh-halide bond in the presence of Cl^- or other halides, whereas the Rh−S bonds are relatively robust in polar solvents.[4d,8a,12a,18,19b] Importantly, the intermediate complex **15** converts to $(nbd)(\kappa^1\text{-}Ph_2PCH_2CH_2O\text{-}C_6H_5)RhCl$ (**14**) and a free PO ligand, **5a** (Scheme 5). One of the key steps in the HILR reaction involves the reaction of **5a**, generated from **15**, with complex **12** to generate complex **6** and a free PS ligand, **4** (Scheme 8).

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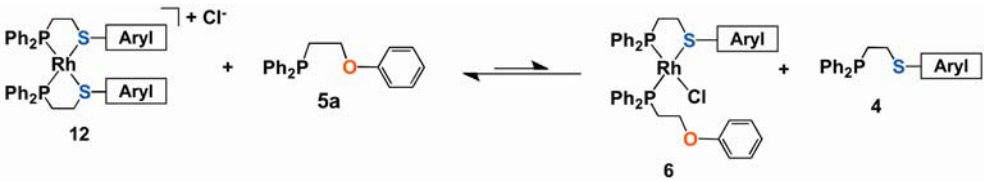
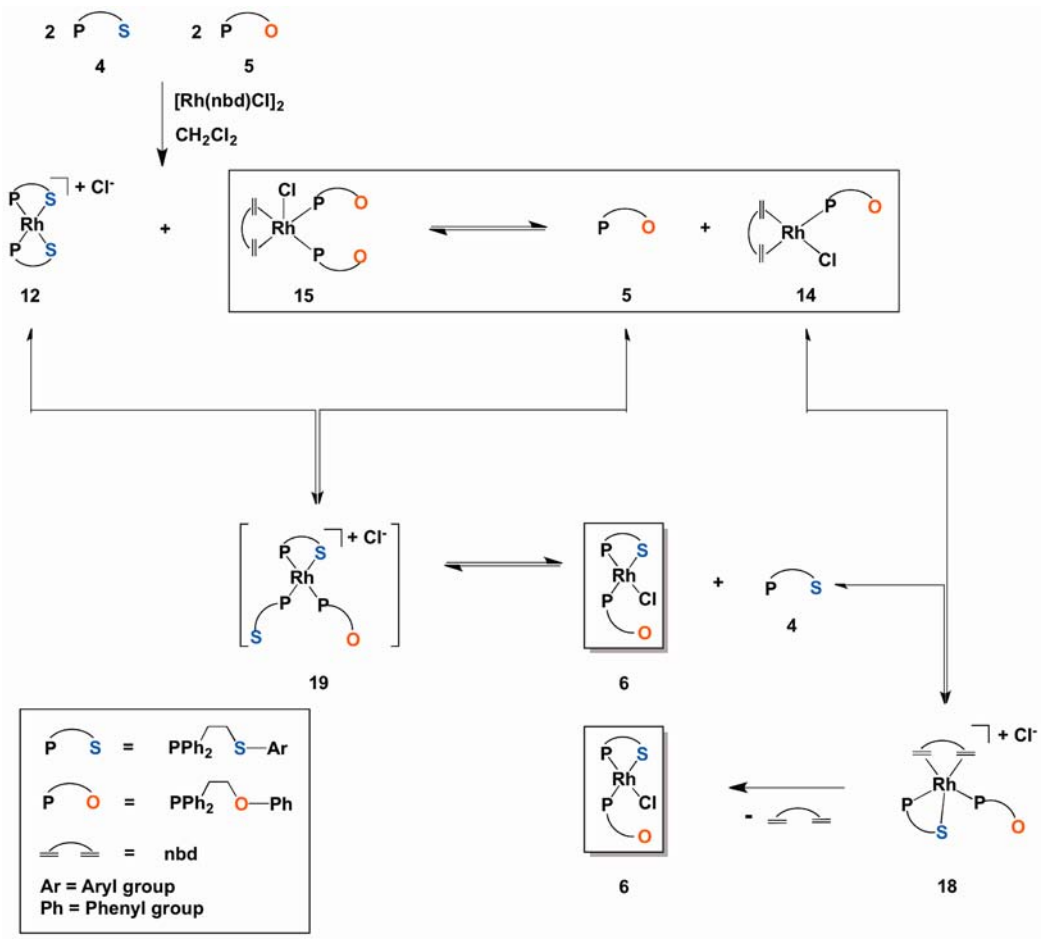
Scheme 8. Reaction of 12 with 5a



Scheme 9. Proposed Reaction Mechanism of the HILR Reaction in CD_2Cl_2



Because of the Rh^I center's stronger affinity for the PS ligand compared to the PO ligand, the formation of **6** and **4** is not favored at room temperature. In an experiment in which **5a** was added to a solution of **12** at 25 °C in CH_2Cl_2, only about 25% of **12** is reversibly converted to **6**, with concomitant formation of **4**. The equilibrium is shifted to favor the formation of **6** and **4a** in the presence of complex **14**, to which the freed PS ligand can coordinate, also forming **6**, leading to the quantitative formation of heteroligated complex **6** via the HILR reaction (Scheme 9).

Taking all of the experimental results together, we propose a reaction mechanism for the HILR reaction in CD_2Cl_2 (Scheme 9). In this mechanism, 2 equiv of a PS ligand, **4**, react with the Rh^I precursor to form a square planar complex, **12**, in which the two PS ligands are chelated to the Rh^I center. In the same reaction vessel, 2 equiv of a PO ligand, **5**, react with the same Rh^I precursor to form complex **15**, which has been spectroscopically characterized and shown to be in equilibrium with free PO ligand, **5**, and the square planar complex **14**. The square planar complex with chelated PS ligands, **12**, can then react with the free PO ligand, **5**, to form the HILR product, **6**. This likely occurs through intermediate **19**, which, if formed, must be transient as it has not been observed spectroscopically, even at low temperature. The movement of the Cl^- ion from outer to inner sphere is essential for this reaction, as the HILR reaction does not proceed without coordinating counterions (i.e., complexes with BF_4^- counterions do not yield the same products).

Consistent with the proposed mechanism, the rates of formation of complex **6** are inversely proportional to the electron density of the aryl groups tethered to the S atom (Table 1). Note that the reaction rate reflects the increase in the strength of the Rh−S bond as a function of the increase in electron density of the aromatic group appended to the S atom (**4e** > **4d** > **4a** > **4c** > **4b**, Table 1).[14] This explains the different rates for the formation of intermediate structure **19**, which involves the dissociation of the thioether from the Rh^I center in complex **12** (Schemes 8, 9). Regardless of whether or not the reaction between **12** and the PO ligand, **5**, is an associative or dissociative

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process, the strength of the Rh−S bond clearly influences the rate of the transformation to form **6**.

Displacement of the olefin ligand is important for the conversion from **18** to **6**, and is consistent with the observation that the rate of the HILR reaction increases with Rh^I precursors with weaker binding olefins (vide supra). When $[Rh(nbd)Cl]_2$ is used as a Rh^I precursor, the HILR reaction rate decreases in comparison to the reaction rates with the relatively weaker 1,5-cyclooctadiene (cod) and cyclooctene (coe) ligands, which are relatively fast.

CONCLUSIONS

In summary, we report the first mechanistic investigation of the HILR reaction. The proposed mechanism is based on the identification of several key intermediates by $^{31}P\{^1H\}$ NMR spectroscopy and single-crystal X-ray diffraction studies as well as by analyzing trends in reactivity for the olefinic, phosphinoalkyl-thioether (P,S), and phosphinoalkyl-ether (P,O) ligands involved in this reaction. Importantly, this mechanism accounts for the quantitative yield of heteroligated complexes (such as **6**, Scheme 9) synthesized via the HILR reaction. Indeed, while we observe intermediates in which two of the same phosphinoalkyl-chalcoether ligands are coordinated to one Rh^I center (**12** and **15**, Scheme 9), the ability of the chloride to move between the inner and the outer coordination spheres allows the system to converge to the desired heteroligated product. The remarkable efficiency and generality of the HILR reaction for other d^8 metal centers like Pd^{II} [12h] and Pt^{II}[12g,j,l] make it a powerful tool for assembling a wide variety of supramolecular architectures. Consequently, the tweezer, macrocyclic, and triple-layer complexes that have been assembled from libraries of phosphino-chalcoether ligands via the HILR reaction have formed the basis for novel allosteric catalysts and chemical detection systems.[4d,7,8,12]

EXPERIMENTAL SECTION

General Methods and Instrument Details. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques or an inert atmosphere glovebox unless otherwise noted.[25] ^1H NMR (300.22 MHz) spectra were recorded on a Varian Mercury 300 MHz FTNMR spectrometer and referenced relative to residual solvent proton resonances in deuterated solvents. $^{31}P\{^1H\}$ NMR (121.53 MHz) spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer and referenced relative to an external 85% H_3PO_4 standard. All chemical shifts are reported in ppm. All reactions were carried out at 25 °C and 20 mM, unless otherwise stated. The temperature of the NMR probe was calibrated against methanol and ethylene glycol. Electrospray ionization mass spectra (ESI) were recorded on a Micromass Q-TOF ultima mass spectrometer.

Materials. Diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), acetonitrile (CH_3CN), pentane, and hexanes were purified by published methods.[26] All solvents were deoxygenated with nitrogen prior to use. Deuterated solvents (Cambridge Isotope Laboratories Inc.) were obtained from commercial sources and used as received. All other chemicals were used as received from Aldrich Chemical Co. PS-Aryl ligands (**4a-e**), PO-Aryl ligands (**5a-c**), (κ^2-$Ph_2PCH_2CH_2S$-Aryl)(κ^1-$Ph_2PCH_2CH_2O$-Aryl)RhCl (**6a-h**), and $[(\kappa^2$-$Ph_2PCH_2CH_2S$-Aryl$)_2Rh]^+Cl^-$ (**12**) were synthesized according to the literature procedures.[7c,12a]

Reaction of $[Rh(nbd)Cl]_2$ with One Equivalent of PS Ligand. Complexes **10a,c,d** and **11b,e** were all prepared by the same method; the general procedure for their preparation is given below.

*Formation of [(nbd)(κ^2-$Ph_2PCH_2CH_2SC_6H_5$)Rh]$^+Cl^-$ (**10a**).* An NMR tube was loaded with a CD_2Cl_2 solution of $[Rh(nbd)Cl]_2$ (9.3 mg, 0.0202 mmol) and PS-C_6H_5 (**4a**) (13.0 mg, 0.0404 mmol) and sealed under nitrogen. The reaction was monitored via ^1H and $^{31}P\{^1H\}$ NMR spectroscopy for 1 day. All $[Rh(nbd)Cl]_2$ was consumed within 1 min, and formation of **10a** was observed. ^1H NMR of **10a** (CD_2Cl_2): δ 2.53 (m, -CH_2P-), 3.29 (m, -CH_2S-), 1.26, 3.64, and 3.73 (*norbornadiene*), 7.3−7.5 and 7.8 (m, S-C_6H_5 and PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 47.3 (d, J_{Rh-P} = 159 Hz).

*Formation of [(nbd)(κ^2-$Ph_2PCH_2CH_2S$(2,4-$(CH_3)_2$-C_6H_3))Rh]$^+Cl^-$ (**10c**).* ^1H NMR (CD_2Cl_2): δ 2.36 and 2.52 (s, 2,4-$(CH_3)_2$-C_6H_3), 2.51 (m, -CH_2P-), 3.08 (m, -CH_2S-), 1.26, 3.61, and 3.77 (*norbornadiene*), 7.09 and 7.85 (d, J_{H-H} = 8.0 Hz, S-(2,4-$(CH_3)_2$-C_6H_3)), 7.14 (s, S-(2,4-$(CH_3)_2$-C_6H_3)), 7.35−7.55 (m, PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.6 (d, J_{Rh-P} = 162 Hz).

*Formation of [(nbd)(κ^2-$Ph_2PCH_2CH_2S$(p-F-C_6H_4))Rh]$^+Cl^-$ (**10d**).* ^1H NMR (CD_2Cl_2): δ 2.51 (m, -CH_2P-), 3.24 (m, -CH_2S-), 1.27, 3.62, and 3.73 (*norbornadiene*), 7.17 (t, J_{H-H} = 8.7 Hz, S-(*p*-F-C_6H_4)), 7.84 (m, S-(*p*-F-C_6H_4)), 7.33−7.5 (m, PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 45.7 (d, J_{Rh-P} = 160 Hz).

*Synthesis of (nbd)($Ph_2PCH_2CH_2S$(2,4,6-$(CH_3)_3$-C_6H_2))RhCl (**11b**).* A mixture of $[Rh(nbd)Cl]_2$ (61 mg, 0.132 mmol) and PS-(2,4,6-$(CH_3)_3$-C_6H_2) (**4b**) (97 mg, 0.266 mmol) was stirred in CH_2Cl_2 (20 mL) for 30 min. The reaction mixture was then reduced in volume to approximately 3 mL in vacuo. The resulting material was purified by recrystallization from CH_2Cl_2/hexanes at room temperature, yielding 101 mg of yellow crystals (64% yield). ^1H NMR (CD_2Cl_2): δ 2.27 (s, CH_3), 2.44 (s, CH_3), 2.42 (m, -CH_2P-), 2.85 (m, -CH_2S-), 1.35, 3.69, and 4.05 (*norbornadiene*), 6.95 (s, S-(2,4,6-$(CH_3)_3$-C_6H_2)), 7.3−7.5 (m, PPh_2, 10H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 25.9 (d, J_{Rh-P} = 172 Hz). HRMS (ESI, *m*/*z*): $[M\text{-}Cl^-]^+$ = 559.1115 (calcd for $[C_{30}H_{33}SPRh]^+$ = 559.1096).

*Formation of (nbd)($Ph_2PCH_2CH_2S$(2,3,5,6-F_4−C_6H)RhCl (**11e**).* ^1H NMR (CD_2Cl_2): δ 2.56 (m, -CH_2P-), 3.24 (m, -CH_2S-), 1.36, 3.71, and 4.08 (*norbornadiene*), 7.35−7.51 (m, S-2,3,5,6-F_4−C_6H and PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 26.3 (d, J_{Rh-P} = 172 Hz).

*Synthesis of (nbd)($Ph_2PCH_2CH_2OC_6H_5$)RhCl (**14**).* A mixture of $[Rh(nbd)Cl]_2$ (100 mg, 0.217 mmol) and PO-C_6H_5 (**5a**) (132 mg, 0.431 mmol) was stirred in CH_2Cl_2 (20 mL) for 3 h at room temperature. The reaction mixture was then reduced in volume to approximately 3 mL in vacuo. The product was recrystallized from CH_2Cl_2/hexanes at room temperature, yielding 207 mg of a yellow solid (90% yield). ^1H NMR (CD_2Cl_2): δ 2.80 (m, -CH_2P-), 4.55 (m, -CH_2O−), 1.30, 2.99, 3.56, and 5.15 (*norbornadiene*), 6.93, 7.28, 7.42, and 7.62 (m, O-C_6H_5 and PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 25.9 (d, J_{Rh-P} = 172 Hz). HRMS (ESI, *m*/*z*): $[M\text{-}Cl^-]^+$ = 501.0860 (calcd for $[C_{27}H_{27}OPRh]^+$ = 501.0855).

*Formation of $[(\kappa^2$-$Ph_2PCH_2CH_2SC_6H_5)_2Rh]^+Cl^-$ (**12**).* An NMR tube was loaded with a CD_2Cl_2 solution of $[Rh(nbd)Cl]_2$ (9.3 mg, 0.0202 mmol) and PS-C_6H_5 (**4a**) (25.5 mg, 0.0833 mmol) and sealed under nitrogen. The reaction was monitored via ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 1 day, the complete formation of $[(\kappa^2$-$Ph_2PCH_2CH_2SC_6H_5)_2Rh]^+Cl^-$ (**12**) was observed. ^1H NMR (CD_2Cl_2): δ 2.51 (m, -CH_2P-), 2.77 (m, -CH_2S-), 7.25 and 7.45 (m, S-C_6H_5 and PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 64.2 (d, J_{Rh-P} = 162 Hz).

*Reaction of $[Rh(nbd)Cl]_2$ with 2 Equivalents of PO-C_6H_5 (**5a**).* An NMR tube was loaded with a CD_2Cl_2 solution of $[Rh(nbd)Cl]_2$ (9.3 mg, 0.0202 mmol) and PO-C_6H_5 (**5a**) (25.5 mg, 0.0833 mmol) and sealed under nitrogen. The reaction was monitored via ^1H and $^{31}P\{^1H\}$ NMR spectroscopy for 1 day. The reaction was carried out at 25 °C, and ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at −60 °C. Time resolved $^{31}P\{^1H\}$ NMR spectra are shown in Figure 4. All reactants were consumed within 3 min, and the formation of $[(nbd)(\kappa^1$-$Ph_2PCH_2CH_2OC_6H_5)_2]RhCl$ (**15**) was initially observed. After 3 min, an increase of (nbd)($Ph_2PCH_2CH_2OC_6H_5$)RhCl (**14**) and ($Ph_2PCH_2CH_2OC_6H_5$)$_3$RhCl (**17**) was observed along with a concomitant decrease in **15**. After 60 min, the product ratio was estimated by $^{31}P\{^1H\}$ NMR spectrum to be about 1:1:1 (**14**:**15**:**17**). ^1H NMR of **15** (CD_2Cl_2): δ 2.61 (m, -CH_2P-), 4.09 (m, -CH_2S-), 1.19, 3.49, and 3.67 (*norbornadiene*), 6.73 (d, J_{H-H} = 7.8 Hz, S-C_6H_5), 6.90 (t, J_{H-H} = 7.8 Hz, S-C_6H_5), 7.35 and 7.54 (m, S-C_6H_5 and PPh_2). $^{31}P\{^1H\}$ NMR of **15** (CD_2Cl_2, −55 °C): δ 13.0 (d, J_{Rh-P} = 128 Hz). ^1H NMR of **17** (CD_2Cl_2): 1.46 (m, -CH_2P-), 2.62 (m, -CH_2P-), 4.13 (m, -CH_2S-), 4.50

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(m, -CH_2S-), 6.6−7.6 (m, S-C$_6H_5$ and PPh_2). ^{31}P{^{1}H} NMR of **17** (CD_2Cl_2): δ 21.9 (dd, J_{Rh-P} = 137 Hz, J_{P-P} = 40 Hz), 37.1. (dt, J_{Rh-P} = 187 Hz, J_{P-P} = 40 Hz).

*Formation of [(nbd)(κ^1-$Ph_2PCH_2CH_2OC_6H_5$)$_2$Rh]$^+$BArF$^-$ (**16**).* An NMR tube was loaded with a CD_2Cl_2 solution of [Rh(nbd)Cl]$_2$ (7 mg, 0.0152 mmol) and PO-C$_6H_5$ (**5a**) (18.6 mg, 0.0608 mmol) and left under nitrogen. After 1 min, excess NaBArF (135 mg, 0.153 mmol) was added into the NMR tube, and sealed under nitrogen. The NMR tube was shaken vigorously for 10 min. The reaction was monitored via ^{1}H and ^{31}P{^{1}H} NMR spectroscopy for 1 day. Formation of [(nbd)(κ^1-$Ph_2PCH_2CH_2OC_6H_5$)$_2$Rh]$^+$BArF$^-$ (**16**) was observed. ^{1}H NMR (CD_2Cl_2): δ 2.27 (m, -CH_2P-), 4.08 (m, -CH_2S-), 1.56, 3.79, and 4.77 (*norbornadiene*), 6.77 (d, $^3J_{H-H}$ = 7.5 Hz, S-C$_6H_5$), 7.06 (t, J_{H-H} = 7.2 Hz, S-C$_6H_5$), 7.3−7.5, 7.58, and 7.75 (m, S-C$_6H_5$ and PPh_2). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 18.6 (d, J_{Rh-P} = 155 Hz).

*Reaction of (nbd)($Ph_2PCH_2CH_2OC_6H_5$)RhCl (14) with PS-C$_6H_5$ (**4a**).* An NMR tube was loaded with CD_2Cl_2 solution of **14** (20 mg, 0.0373 mmol) and PS-C$_6H_5$ (**4a**) (12 mg, 0.0372 mmol) and sealed under nitrogen. The reaction was performed at 25 °C and monitored via ^{1}H and ^{31}P{^{1}H} NMR spectroscopy for 1 day at −60 °C. Time resolved ^{31}P{^{1}H} NMR spectra are shown in Figure 5. All reactants were consumed within 1 min. After 1 min, the product ratio was estimated by the ^{31}P{^{1}H} NMR spectrum to be about 60% [(nbd)(κ^2-$Ph_2PCH_2CH_2SC_6H_5$)(κ^1-$Ph_2PCH_2CH_2OC_6H_5$)Rh]$^+$Cl$^-$, (**18**), 20% **12**, and 20% **15**. The mixture of Complexes **12**, **15**, and **18** completely converted to the heteroligated Rh^I complex, **6a**, within 4 h. ^{1}H NMR of **18** (CD_2Cl_2, 20 °C): δ 2.20 (m, -CH_2P-), 2.56 (m, -CH_2P-), 3.17 (m, -CH_2S-), 4.07 (m, -CH_2O−), 1.20, 3.41, and 3.49 (*norbornadiene*), 6.73 (d, J_{H-H} = 7.8 Hz), 6.90 (t, J_{H-H} = 7.5 Hz) 7.18−7.51 (m, S-C$_6H_5$, O-C$_6H_5$ and PPh_2). ^{31}P{^{1}H} NMR of **18** (CD_2Cl_2, −60 °C): δ 60.3 (dd, J_{P-Rh} = 164 Hz, J_{P-P} = 30 Hz), 10.1 (dd, J_{P-Rh} = 120 Hz, J_{P-P} = 30 Hz).

*Reaction of [(κ^2-$Ph_2PCH_2CH_2SC_6H_5$)$_2$Rh]$^+$Cl$^-$ (12) with PO-C$_6H_5$ (**5a**).* An NMR tube was loaded with a CD_2Cl_2 solution of **12** (12 mg, 0.0153 mmol) and **5a** (4.7 mg, 0.0154 mmol) and sealed under nitrogen. The reaction was monitored via ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 1 day at 25 °C, the ratio of Rh^I complexes was estimated by the ^{31}P{^{1}H} NMR spectrum to be 25% **6a** to 75% **12**. Free ligands PS-C$_6H_5$ (**4a**) and PO-C$_6H_5$ (**5a**) were also observed (the ratio of **4a**:**5a** = 1:3).

Measurements of Reaction Rates. The general method for the measurement of reaction rates was as follows: an NMR tube was loaded with a CD_2Cl_2 solution (or other deuterated solvent) of the reactants and sealed under nitrogen. The reaction was monitored via ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The reaction rates of each conversion were studied via ^{31}P{^{1}H} NMR spectroscopy at different temperatures, and the corresponding half-lives of the reactions ($t_{1/2}$) were measured.

X-ray Crystallography. X-ray quality crystals of **11b** and **14** were grown by slow diffusion of pentane into a saturated CH_2Cl_2 solution. A yellow columnar crystal of **11b** and an orange tabular crystal of **14** were mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated MoK \α radiation. Data were collected using a Bruker SMART detector (for **11b**) or a Bruker APEX II detector (for **14**), and processed using SAINTPLUS (for **11b**) or APEX2 (for **14**) from Bruker. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques.[27a] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in idealized positions, but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[27d] Anomalous dispersion effects were included in Fcalc;[27e] the values for Df′ and Df″ were those of Creagh and McAuley.[27f] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[27g] All calculations were performed using the Bruker SHELXTL3 crystallographic software package.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data and crystal data and structure refinements for **11b** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org..

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*. VCH: Weinheim, Germany, 1995; p 271; (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−908. (c) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483−3538. (d) Kovbasyuk, L.; Kramer, R. *Chem. Rev.* **2004**, *104*, 3161−3188. (e) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972−983. (f) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53−61. (g) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369−378. (h) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759−771. (i) Thanasekaran, P.; Liao, R. T.; Liu, Y. H.; Rajendran, T.; Rajagopal, S.; Lu, K. L. *Coord. Chem. Rev.* **2005**, *249*, 1085−1110. (j) Lee, S. J.; Lin, W. *Acc. Chem. Res.* **2008**, *41*, 521−537. (k) Caulder, D. L.; Raymond, R. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185−1200. (l) Caulder, D. L.; Raymond, R. N. *Acc. Chem. Res.* **1999**, *32*, 975−982. (m) Albrecht, M. *Chem. Rev.* **2001**, *101*, 3457−3497. (n) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022−2043.

(2) (a) Stricklen, P. M.; Volcko, E. J.; Verkade, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 2494−2495. (b) Fujita, M.; Ogura, K. *Coord. Chem. Rev.* **1996**, *148*, 249−264. (c) Slone, R. V.; Benkstein, K. D.; Bélanger, S.; Hupp, J. T.; Guzei, I. A.; Rheingold, A. L. *Coord. Chem. Rev.* **1998**, *171*, 221−243. (d) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−907. (e) Northrop, B. H.; Yang, H.-B.; Stang, P. J. *Chem. Commun.* **2008**, 5896−5908. (f) Zangrando, E.; Casanova, M.; Alessio, E. *Chem. Rev.* **2008**, *108*, 4979−5013. (g) Stang, P. J. *J. Org. Chem.* **2009**, *74*, 2−20. (h) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759−771. (i) Würthner, F.; You, C. C.; Saha-Möller, C. R. *Chem. Soc. Rev.* **2004**, *33*, 133−146.

(3) (a) Ruben, M.; Rojo, J.; Romero-Salguero, F. J.; Uppadine, L. H.; Lehn, J.-M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3644−3662. (b) Beissel, T.; Powers, R. E.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1996**, *35*, 1084−1086. (c) Saalfrank, R. W.; Bernt, I. *Curr. Op. Solid State Mater. Sci.* **1998**, *3*, 407−413. (d) Baxter, P. N. W.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.—Eur. J.* **1999**, *5*, 102−112. (e) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349−358. (f) Saalfrank, R. W.; Maid, H.; Scheurer, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8794−8824. (g) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246−253.

(4) (a) Farrell, J. R.; Mirkin, C. A.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 465−467. (b) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022−2043. (c) Gianneschi, N. C.; Masar, M. S., III; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825−837. (d) Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618−1629. (e) Wiester, M. J.; Ulmann, P. A.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 114−137.

(5) (a) Northrop, B. H.; Zheng, Y. R.; Chi, K. W.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 1554−1563. (b) Li, S. S.; Northrop, B. H.; Yuan, Q. H.; Wan, L. J.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 249−259. (c) Northrop,

B. H.; Yang, H.-B.; Stang, P. J. *Chem. Commun.* **2008**, 5896−5908. (d) Kumar, A.; Sun, S. S.; Lees, A. J. *Coord. Chem. Rev.* **2008**, *252*, 922−939.

(6) (a) Lehn, J. M. *Science* **2002**, *295*, 2400−2403. (b) Lehn, J. M. *Chem.—Eur. J.* **1999**, *5*, 2455−2463.

(7) (a) Oliveri, C. G.; Gianneschi, N. C.; Nguyen, S. T.; Mirkin, C. A.; Stern, C. L.; Wawrzak, Z.; Pink, M. *J. Am. Chem. Soc.* **2006**, *128*, 16286−16296. (b) Masar, M. S., III; Gianneschi, N. C.; Oliveri, C. G.; Nguyen, S. T.; Mirkin, C. A.; Stern, C. L. *J. Am. Chem. Soc.* **2007**, *129*, 10149−10158. (c) Gianneschi, N. C.; Masar, M. S., III; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825−837. (d) Yoon, H. J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 11590−11591. (e) Yoon, H. J.; Heo, J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 14182−14183.

(8) (a) Kuwabara, J.; Stern, C. L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 10074−10075. (b) Heo, J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 941−944. (c) Yoo, H.; Mirkin, C. A.; DiPasquale, A. G.; Rheingold, A. L.; Stern, C. L. *Inorg. Chem.* **2008**, *47*, 9727−9729.

(9) (a) Galindo, M. A.; Houlton, A.; Clegg, W.; Harrington, R. W.; Dobado, J.; Santoyo-Gonzalez, F.; Linarez, F.; Romero, M. A.; Navarro, J. A. R. *Chem. Commun.* **2008**, 3735−3737. (b) Toma, H. E.; Araki, K. *Coord. Chem. Rev.* **2000**, *196*, 307−329. (c) Imamura, T.; Fukushima, K. *Coord. Chem. Rev.* **2000**, *198*, 133−156. (d) Schmittel, M.; He, B.; Mal, P. *Org. Lett.* **2008**, *10*, 2513−2516. (e) Schmittel, M.; Kalsani, V.; Mal, P.; Bats, J. W. *Inorg. Chem.* **2006**, *45*, 6370−6377. (f) Kalsani, V.; Bodenstedt, H.; Fenske, D.; Schmittel, M. *Eur. J. Inorg. Chem.* **2005**, 1841−1849. (g) Kishore, R. S. K.; Paululat, T.; Schmittel, M. *Chem.—Eur. J.* **2006**, *12*, 8136−8149. (h) Sleiman, H.; Baxter, P. N. W.; Lehn, J.-M.; Airola, K.; Rissanen, K. *Inorg. Chem.* **1997**, *36*, 4734−4742. (i) Galindo, M. A.; Galli, S.; Navarro, J. A. R.; Romero, M. A. *Dalton Trans.* **2004**, 2780−2785. (j) Jeffery, J. C.; Rice, C. R.; Harding, L. P.; Baylies, C. J.; Riis-Johannessen, T. *Chem.—Eur. J.* **2007**, *13*, 5256−5271. (k) Hamacek, J.; Borkovec, M.; Piguet, C. *Chem.—Eur. J.* **2005**, *11*, 5217−5226.

(10) Yoshizawa, M.; Nagao, M.; Kumazawa, K.; Fujita, M. *J. Organomet. Chem.* **2005**, *690*, 5383−5388.

(11) Hasenknopf, B.; Lehn, J. M.; Baum, G.; Fenske, D. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 1397−1400.

(12) (a) Brown, A. M.; Ovchinnikov, M. V.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4207−4209. (b) Brown, A. M.; Ovchinnikov, M. V.; Stern, C. L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2004**, *126*, 14316−14317. (c) Jeon, Y. M.; Heo, J.; Brown, A. M.; Mirkin, C. A. *Organometallics* **2006**, *25*, 2729−2732. (d) Oliveri, C. G.; Heo, J.; Nguyen, S. T.; Mirkin, C. A.; Wawrzak, Z. *Inorg. Chem.* **2007**, *46*, 7716−7718. (e) Oliveri, C. G.; Nguyen, S. T.; Mirkin, C. A. *Inorg. Chem.* **2008**, *47*, 2755−2763. (f) Ovchinnikov, M. V.; Brown, A. M.; Liu, X.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *Inorg. Chem.* **2004**, *43*, 8233−8235. (g) Ulmann, P. A.; Brown, A. M.; Ovchinnikov, M. V.; Mirkin, C. A.; Di Pasquale, A. G.; Rheingold, A. L. *Chem.—Eur. J.* **2007**, *13*, 4529−4534. (h) Ulmann, P. A.; Mirkin, C. A.; DiPasquale, A. G.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2009**, *28*, 1068−1074. (i) Spokoyny, A. M.; Rosen, M. S.; Ulmann, P. A.; Stern, C.; Mirkin, C. A. *Inorg. Chem.* **2010**, *49*, 1577−1586. (j) Brown, A. M.; Ovchinnikov, M. V.; Stern, C. L.; Mirkin, C. A. *Chem., Commun.* **2006**, 4386−4388. (k) Yoon, H. J.; Kuwabara, J.; Kim, J.-H.; Mirkin, C. A. *Science* **2010**, *330*, 66−69. (l) Rosen, M. S.; Spokoyny, A. M; Machan, C. W.; Stern, C.; Sarjeant, A; Mirkin, C. A. *Inorg. Chem.* **2011**, *50*, 1411−1419.

(13) Ulmann, P. A.; Braunschweig, A. B.; Lee, O.-S.; Wiester, M. J.; Schatz, G. C.; Mirkin, C. A. *Chem. Commun.* **2009**, 5121−5123.

(14) (a) Singewald, E. T.; Mirkin, C. A.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1624−1627. (b) Sassano, C. A.; Mirkin, C. A. *J. Am. Chem. Soc.* **1995**, *117*, 11379−11380. (c) Allgeier, A. M.; Slone, C. S.; Mirkin, C. A.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 550−559.

(15) (a) Trogler, W. C.; Marzilli, L. *J. Am. Chem. Soc.* **1974**, *96*, 7589−7591. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348. (c) Ferguson, G.; Roberts, P. J.; Alyea, E. C.; Khan, M. *Inorg. Chem.* **1978**, *17*, 2965−2967.

(16) Bonuzzi, C.; Bressan, M.; Morandini, F.; Morvillo, A. *Inorg. Chim. Acta* **1988**, *154*, 41−43.

(17) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229−266.

(18) Wiester, M. J.; Braunschweig, A. B.; Yoo, H.; Mirkin, C. A. *Inorg. Chem.* **2010**, *49*, 7188−7196.

(19) (a) Naaktgeboren, A. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1980**, *102*, 3350−3354. (b) Lindner, E.; Wang, Q.; Mayer, H. A.; Bader, A. *J. Organomet. Chem.* **1993**, *458*, 229−232. (c) Vrieze, K.; Volger, H. C.; Praat, A. P. *J. Organomet. Chem.* **1968**, *15*, 195−208. (d) Denise, B.; Pannetier, G. *J. Organomet. Chem.* **1975**, *99*, 455−464. (e) Denise, B.; Pannetier, G. *J. Organomet. Chem.* **1978**, *148*, 155−164.

(20) (a) Slack, D. A.; Greveling, I.; Baird, M. C. *Inorg. Chem.* **1979**, *18*, 3125−3132. (b) Szalontai, G.; Bakos, J.; Aime, S.; Gobetto, R. *J. Organomet. Chem.* **1993**, *463*, 223−226. (c) Hsin-Ell, W.; Ming-Chu, C.; Gene-Hsiang, L.; Shie-Ming, P.; Shiuh-Tzung, L. *J. Organomet. Chem.* **1993**, *445*, 171−179. (d) Szalontai, G.; Sándor, P.; Bakos, J. *Magn. Reson. Chem.* **1991**, *29*, 449−458.

(21) (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397−2407. (b) Sen Reddy, V. V.; Varshney, A.; Gray, G. M. *J. Organomet. Chem.* **1990**, *391*, 259−266.

(22) Nixon, J. F.; Pidcock, A. *Annu. Rep. NMR Spectrosc.* **1969**, *2*, 345−422.

(23) (a) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711. (b) Jardine, F. H.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 1574. (c) James, B. R. *Homogeneous Hydrogenation*; John Wiley & Sons: New York, 1973; (d) Hitchcock, P. B.; McPartlin, M.; Mason, R. *J. Chem. Soc. D* **1969**, 1367. (e) Tolman, C. A.; Meakin, P. Z.; Lindner, D. I.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 2762−2774. (f) Eaton, D. R.; Suart, S. R. *J. Am. Chem. Soc.* **1968**, *90*, 4170−4172. (g) Arai, H.; Halpern, J. *J. Chem. Soc. D* **1971**, 1571. (h) Brown, T. H.; Green, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 2359−2362. (i) Anderson, G. K.; Kumar, R. *Inorg. Chim. Acta* **1988**, *146*, 89−92.

(24) (a) Anderson, M. P.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1983**, *22*, 2644−2647. (b) Kyba, E. P.; Liu, S. T. *Inorg. Chem.* **1985**, *24*, 1613−1616.

(25) Errington, R. J. *Advanced Practical Inorganic and Metalorganic Chemistry*; Chapman & Hall: New York, 1997.

(26) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, U.K., 1996.

(27) (a) Sheldrick, G. M. *SHELXTL*, Version 6.14; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2003. (b) Full-Matrix Least-Squares refinement on F^2: $wR^2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$ (c) GoF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ n = number of reflections; p = total number of reflections refined (d) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallograph*; The Kynoch Press: Birmingham, England, 1974; Vol. *IV*, Table 2.2 A. (e) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781. (f) Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol *C*, Table 4.2.6.8, pp 219−222. (g) Creagh, D. C.; Hubbell, J. H. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol *C*, Table 4.2.4.3, pp 200−206.