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A Series of Pincer-Ligated Rhodium Complexes as Catalysts for the Dimerization of Terminal Alkynes

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ABSTRACT. A series of pincer complexes of Rh has been prepared and tested as catalysts for the dimerization of terminal alkynes. The pincers included aryl/bis(phosphinite) POCOP, aryl/bis(phosphine) PCP, and diarylamido/bis(phosphine) PNP ligands. Rh^{I} complexes of the general form (pincer)Rh($S^{i}Pr_2$) or (pincer)Rh(H_2) were used as catalysts. In addition, the apparent donating ability of the pincer ligands was gauged through the carbonyl stretching frequencies in (pincer)Rh(CO) complexes by IR spectroscopy. All surveyed Rh complexes acted as catalysts for dimerization of 4-ethynyltoluene, 1-hexyne, or trimethysilylacetylene. The products were a mixture of *E*- and *gem*-enyne isomers, with small amounts of oligomers in some cases. The *Z*-enyne isomers were not observed except in two reactions. None of the catalysts showed useful selectivity for either the *E*- or the *gem*-enyne product. However, the POCOP-based catalysts bearing $P^{i}Pr_2$ donor arms performed faster and possessed apparently greater longevity (up to 20,000 TON) than the previously reported pincer Rh catalysts.

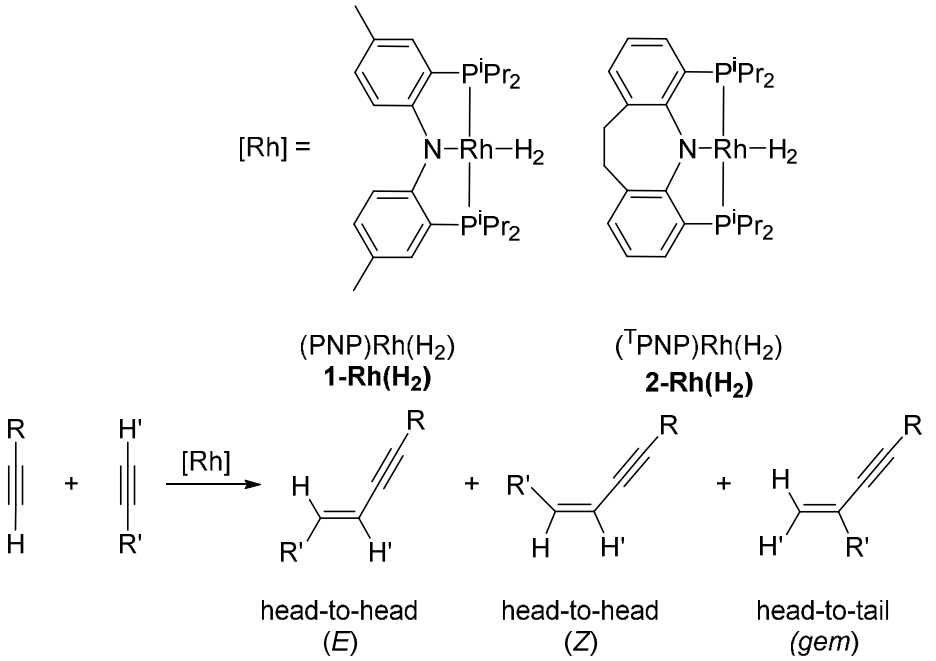
KEYWORDS. Pincer, alkyne dimerization, rhodium, catalysis, phosphine, enyne

Introduction

Alkyne dimerization is a process in which a C_{sp}-H bond in a terminal alkyne is formally added across the C≡C bond in another molecule of alkyne. The products of alkyne dimerization, conjugated enynes, are versatile building blocks for a variety of organic transformations.[1] This process is 100% atom-economical and requires a catalyst.[2] The desired role for the catalyst is not limited to enabling a faster reaction, but formation of the desired product in a selective fashion. In principle, three isomers of a conjugated enyne arising from dimerization of a terminal alkyne are possible: *E*, *Z*, and *gem* (Scheme 1). In addition, terminal alkynes may undergo dimerization to a butariene,[3] cyclotrimerization to arenes, or oligo- and polymerization to polyenes with various catalysts.[4] Catalytic alkyne dimerization has been investigated using a number of transition metals,[5-12] main group elements,[13] and lanthanides.[14] While some of these catalytic systems give mixtures of enyne and oligomeric products, several systems show excellent selectivity for a specific isomer. A recent NHC palladium (NHC = N-heterocyclic carbene) catalyst has achieved perfect regio- and stereoselectivity to form the *E*-enyne with a range of terminal alkynes possessing various functional groups.[10b] Palladium has also been used as a selective head-to-tail dimerization catalyst for a range of substituted alkynes when paired with a Brønsted acid.[10c] Selective dimerization to form the *Z*-enyne has been primarily the specialty of ruthenium catalysts,[7a,b] but lanthanide and zirconium complexes have also shown *Z*-selectivity.[12,14]

In the domain of Rh-catalyzed alkyne dimerization, the frontier of cross dimerization is experiencing advancements. Miura's group was able to take advantage of sterically different terminal alkynes and a bulky Rh catalyst to selectively produce *E*-enynes with a high tolerance for functionalities.[11a] More recently, the Xu group showed that a Rh phosphine system could effectively cross-dimerize arylacetylenes with propargylic alcohols, ethers, and amides.[11e] Head-to-tail selective homodimerization has also been achieved by an NHC Rh catalyst.[11c]

Scheme 1. (PNP)Rh complexes and alkyne dimerization.

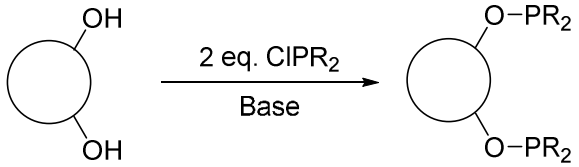


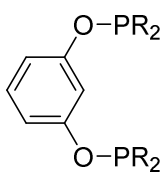
Several years ago, we reported that Rh complexes supported by diarylamido/bis(phosphine) PNP pincer ligands served as efficient catalysts for alkyne dimerization (Scheme 1).[15] The more common member of this family, **1-Rh(H$_2$)**, produced an unselective mixture of *E* and *gem* isomers, but the "tied" ^{T}PNP rhodium catalyst (**2-Rh(H$_2$)**) enabled selective production of predominantly isomer *E* for a rather broad selection of terminal alkynes.[16] The ^{T}PNP ligand requires multi-step synthesis and the reactions catalyzed by **2-Rh(H$_2$)** were not particularly fast, on the order of 10 TON/h at 100 °C. We surmised that there may be other, more easily accessible pincer ligands that could give rise to analogous Rh catalysts. To this end, we set out to prepare a series of (pincer)Rh complexes and test their prowess in alkyne dimerization.

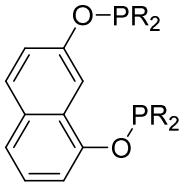
Results and discussion.

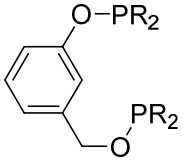
Synthesis of pincer ligands and their Rh complexes. We selected ligands **3-H** through **10-H** for our study. We primarily focused on aryl/bis(phosphine) ligands as they are most easily prepared, especially in the case of aryl/bis(phosphinite) variants (Scheme 2).

Scheme 2. Synthesis of bis(phosphinite) ligands.









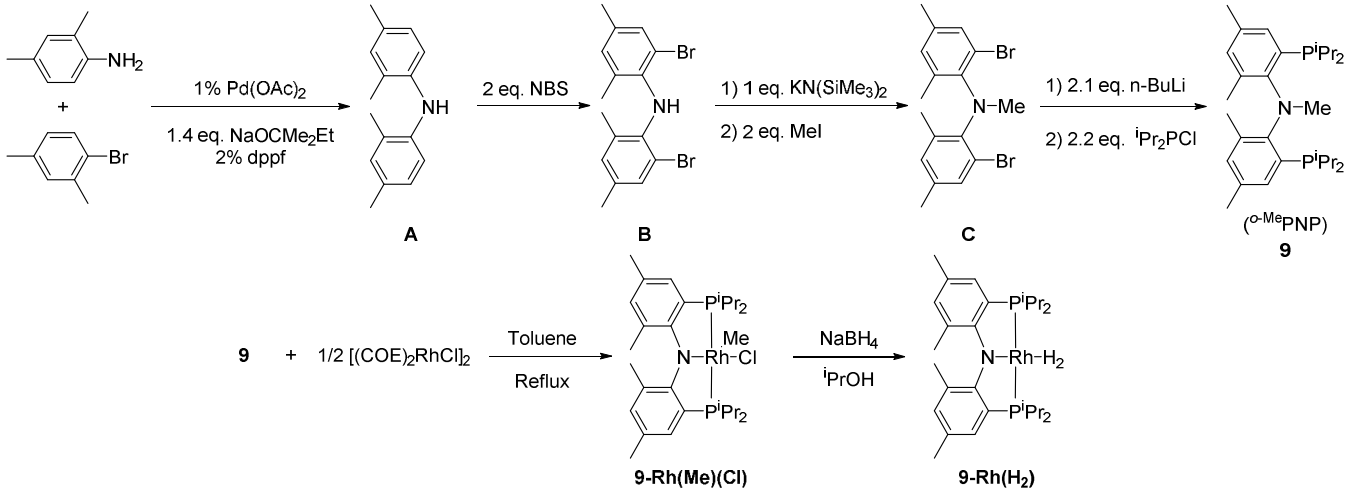
3-H: R = ^{i}Pr = (POCOP^{iPr})H **5-H**: R = ^{i}Pr = (^{Napth}POCOP^{iPr})H **7-H**: R = ^{i}Pr = (POCCH$_2$OP^{iPr})H
4-H: R = ^{t}Bu = (POCOP^{tBu})H **6-H**: R = ^{t}Bu = (^{Napth}POCOP^{tBu})H **8-H**: R = ^{t}Bu = (POCCH$_2$OP^{tBu})H

Ligands, **3-H,**[17] **4-H,**[18] and **7-H**[19] have been previously reported and were synthesized as described in the literature (with some changes in the procedure for **7-H**). Ligands **5-H**, **6-H** and **8-H** were prepared analogously from 1,7-naphthalenediol or 3-hydroxybenzyl alcohol, $ClPR_2$ (R = ^{i}Pr or ^{t}Bu), and base. Ligands **3-H**, **5-H**, **7-H**, and **8-H** were obtained as oils of 95% or better purity as judged by ^{1}H NMR spectroscopy and were used as is for the synthesis of the Rh complexes. The aryl/bis(PR_3) ligands in this study differ by the size of the substituent on phosphorus, by the size of the pincer rings fused at the central M-C bond (5,5 vs 5,6), and by the difference in the electron richness of the backbone. The {[5,6]-PCP}$^{-}$ ligands[20] (**5-H**, **6-H**, **7-H**, and **8-H**) were intended to favor selectivity for the *E*-enyne isomer by increasing the steric bulk around the active site of the metal, a strategy that has been used in several other systems.[9, 11a, 15]

We also examined a new C_2-symmetric PNP ligand **9-Me**, which offered a variation on the diarylamido backbone (Scheme 3). Diarylamine **A** was synthesized via Buchwald-Hartwig coupling[21] of 2,4-dimethylaniline and 2,4-dimethylbromobenzene. Bromination of **A** with *N*-bromosuccinimide

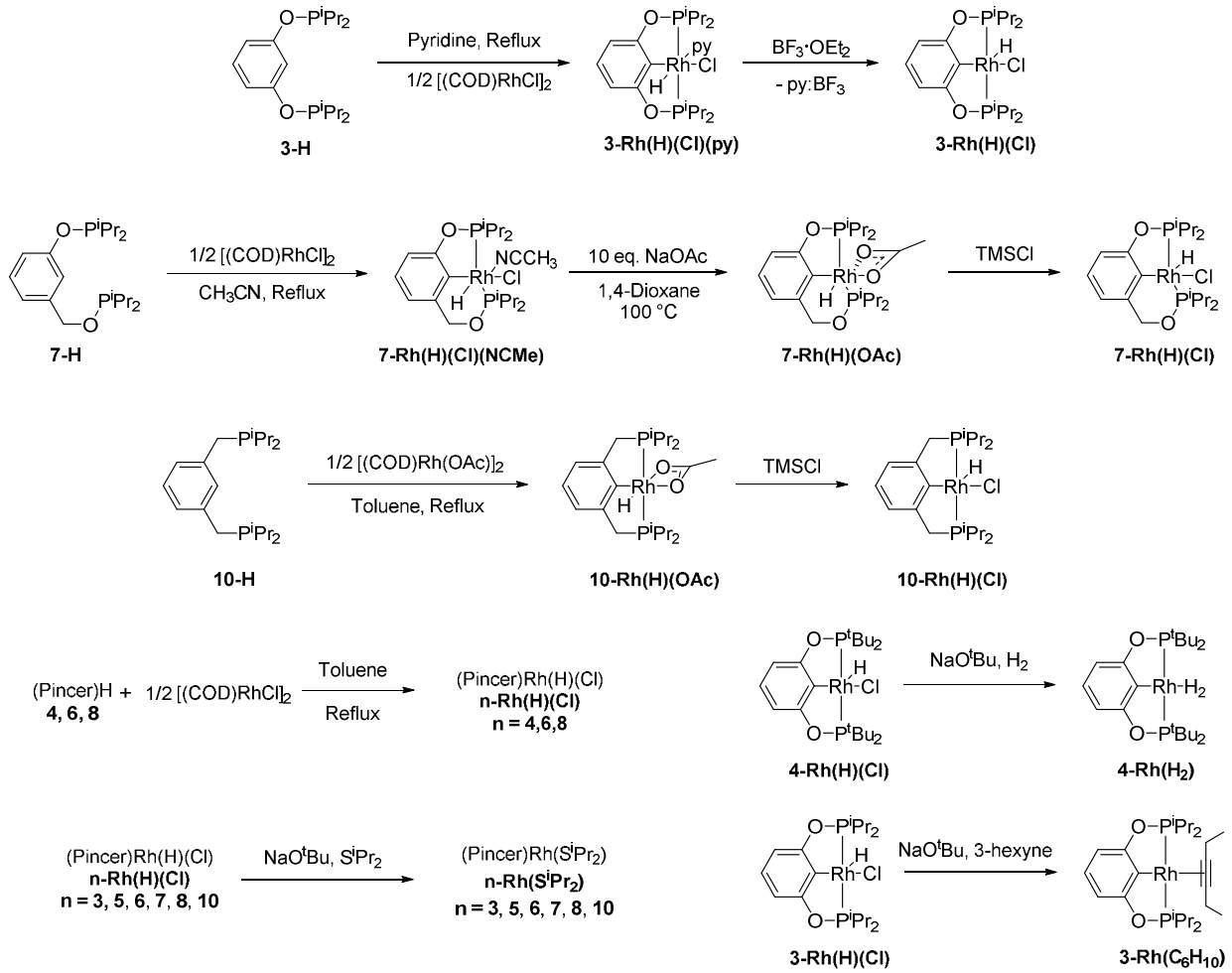
yielded compound **B**, which was *N*-methylated with $KN(SiMe_3)_2$ and iodomethane to give **C**. Treatment of **C** with *n*-butyllithium and ClP^iPr_2 yielded **9-Me** as a white solid. Ligand **9-Me** differs from **1** by possessing methyl groups *ortho* to the central nitrogen donor. This causes a high barrier to the rotation about the Ar-N bond and results in C_2-symmetry on the NMR time scale as seen by the presence of two methine signals and four doublets of doublets for the P^iPr_2 methyls.[22] The C_2-symmetry of the ligand is reduced down to C_1 once the ligand is metalated with $[(COE)_2RhCl]_2$ (COE = cyclooctene) to form ($^{o\text{-}Me}$PNP)Rh(Me)(Cl) (**9-Rh(Me)(Cl)**). This is evidenced by the appearance of eight signals for the P^iPr_2 methyls by ^1H NMR. The $^{31}P\{^1H\}$ NMR spectra showed two different doublets of doublets and large coupling between the two inequivalent phosphorus donors, $^2J_{PP} = 414$ Hz. Reduction of **9-Rh(Me)(Cl)** with $NaBH_4$ in isopropanol yielded the Rh^I species **9-Rh(H_2)**, which showed atropisomeric C_2-symmetry. Complexes of ligand **9** differ from other atropisomeric pincer complexes to date due to the chirality being generated by a twist in the backbone of the ligand and the use of five-membered metallacycles. Previous atropisomeric pincer complexes rely on long pincer "arms" to establish six- or seven-membered metallacycles that twist the structure of the molecule out of planarity.[23] The presence of five-membered metallacycles in complexes of **9-Me** is notable because smaller metallacycles in atropisomeric compounds tend to lead to faster rates of atropisomerism that averages the two conformations.[24,25]

Scheme 3. Synthesis of the $^{o\text{-}Me}$PNP ligand and its Rh complexes.



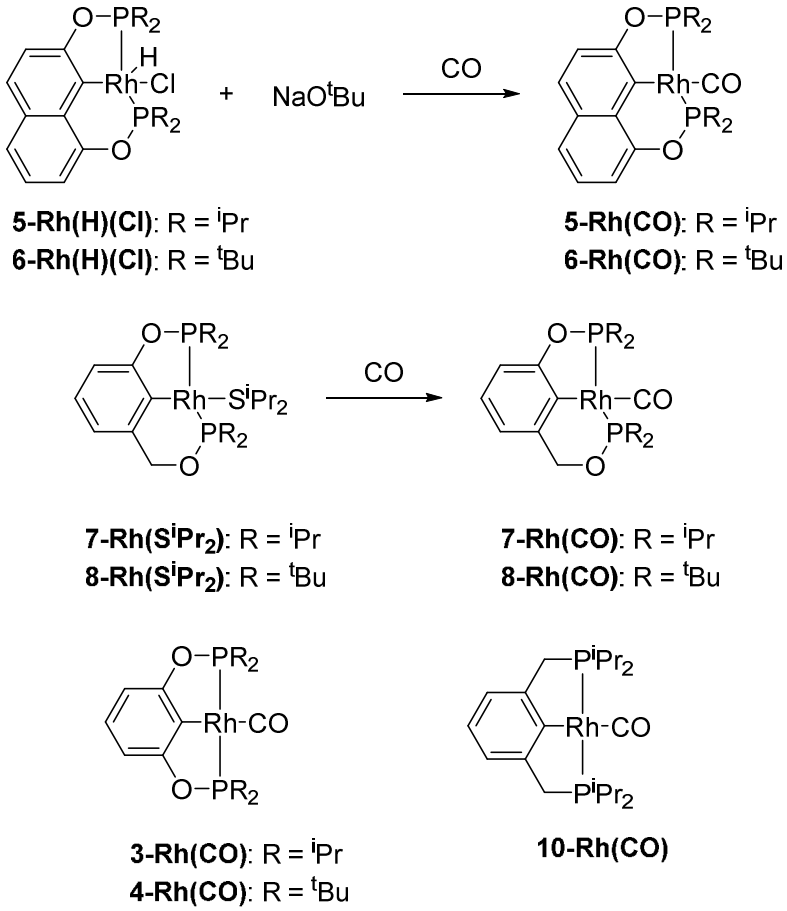
Installation of PCP/POCOP ligands into the coordination sphere of Rh is also most conveniently accomplished via reaction of the ligand precursor with $[(COD)RhCl]_2$ (Scheme 4). This reaction is ideally accompanied by loss of COD (= 1,5-cyclooctadiene) and insertion of Rh into the central C-H bond to give (pincer)Rh(H)(Cl). However, this reaction appeared to work cleanly only for the relatively sterically imposing POCOP ligands **4-H**, **5-H**, **6-H**, and **8-H**. In other cases, the reaction was not clean. We previously described these issues in the synthesis of **3-Rh(H)(Cl)** where a second equivalent of free ligand can coordinate to rhodium, resulting in mixtures of six-coordinate rhodium products.[26] For **3-Rh(H)(Cl)**, the problem was solved via a two-step procedure, first preparing a pyridine adduct **3-Rh(H)(Cl)(py)** followed by extraction of pyridine by BF_3. A similar approach was successful for the synthesis of **7-Rh(H)(Cl)** (Scheme 4). The reaction of **7-H** with $[(COD)RhCl]_2$ in acetonitrile cleanly gave the acetonitrile adduct **7-Rh(H)(Cl)(NCMe)**, which in reaction with excess NaOAc released the coordinated acetonitrile to produce **7-Rh(H)(OAc)**. Treatment of **7-Rh(H)(OAc)** with Me_3SiCl after removal of all of acetonitrile under vacuum resulted in the formation of **7-Rh(H)(Cl)**. In a yet another variation, six-coordinate **10-Rh(H)(OAc)** was prepared directly from **10-H**[27] and $[(COD)Rh(OAc)]_2$ and metathesis with Me_3SiCl gave the corresponding five-coordinate hydrido-chloride complex **10-Rh(H)(Cl)**. The five-coordinate complexes **n-Rh(H)(Cl)** (**n** = **3-8, 10**) displayed a hydride resonance in the -24 to -27 ppm range in the ^1H NMR spectra. Complexes with inequivalent phosphorus donors showed strong phosphorus-phosphorus coupling in the $^{31}P\{^1H\}$ NMR spectra, with $^2J_{PP}$ values in the 400-430 Hz range.

Scheme 4. Synthesis of Rh pincer complexes.



The desired Rh^{I} precursors were made from complexes **n-Rh(H)(Cl)** (**n = 3, 5, 6, 7, 8, 10)** by treating them with NaO^{t}Bu in the presence of diisopropyl sulfide, which led to clean formation of **n-Rh(S^{i}Pr$_2$)** (**n** = **3, 5**, **6**, **7**, **8, 10**). We also prepared the 3-hexyne adduct **3-Rh(C$_6$H$_{10}$)** in an analogous fashion. For ligands **4-H** and **9-Me**, dihydrogen complexes **4-Rh(H$_2$)**[28] and **9-Rh(H$_2$)** were synthesized. We also prepared **9-Rh(HD)** from which the J_{HD} value of 20 Hz was extracted. Using established[29] relationships between H-H distances and $J_{H\text{-}D}$ coupling, we conclude that **9-Rh(H$_2$)** is a "stretched" or "elongated" dihydrogen complex,[30] with a predicted H-H distance of 1.1 Å. This matches a previously synthesized PNP-based rhodium dihydrogen adduct.[16] We have previously used S^{i}Pr$_2$ as a useful placeholder ligand in the chemistry of (PNP)Rh complexes: it forms isolable adducts with Rh^{I}, dissociates rather easily, and has no affinity for coordinating to Rh^{III} complexes.[31] The Rh^{I} complexes possessed larger $^{1}J_{Rh\text{-}P}$ values compared to the Rh^{III} compounds described above, but lower $^{2}J_{P\text{-}P}$ values.

Scheme 5. Synthesis of Rh(I) pincer carbonyl complexes.



Treatment of **5-Rh(H)(Cl)** and **6-Rh(H)(Cl)** with NaO^{t}Bu under an atmosphere of CO gave the corresponding (pincer)Rh(CO) complex (**5-Rh(CO)** and **6-Rh(CO)**, Scheme 5). Pincer carbonyl complexes could also be obtained by treating the (pincer)Rh(S^{i}Pr$_2$) complexes (**7-Rh(S^{i}Pr$_2$)** and **8-Rh(S^{i}Pr$_2$)**) with an atmosphere of CO to form **7-Rh(CO)** and **8-Rh(CO)**. Complexes **n-Rh(CO)** (**n** = **5-8**) were analyzed using IR spectroscopy and compared to the reported CO stretching frequencies of **3-Rh(CO)**,[32] **4-Rh(CO)**,[33] **10-Rh(CO)**[32] to gauge the electron richness[34] of the ligand backbone (Table 1). Not surprisingly, the bis(phosphinite) POCOP ligands showed lower electron donation to the metal center than the bis(phosphine) PCP ligand, due to the electron withdrawing ability of the oxygen atoms.

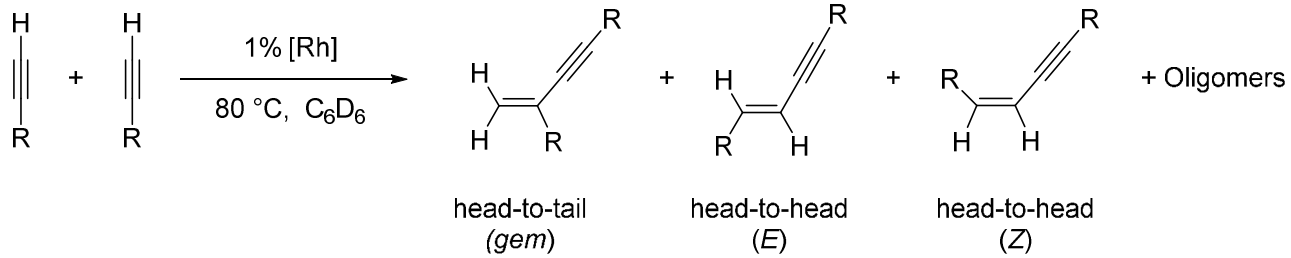
Table 1: Carbonyl stretching frequencies of PCP/POCOP rhodium carbonyl compounds .

Complex	IR ν_{CO} (cm^{-1})
($POCOP^{iPr}$)Rh(CO) (**3-Rh(CO)**)	1962
($POCOP^{tBu}$)Rh(CO) (**4-Rh(CO)**)	1961
($^{Napth}POCOP^{iPr}$)Rh(CO) (**5-Rh(CO)**)	1950
($POCCH_2OP^{iPr}$)Rh(CO) (**7-Rh(CO)**)	1948
($^{Napth}POCOP^{tBu}$)Rh(CO) (**6-Rh(CO)**)	1945
($POCCH_2OP^{tBu}$)Rh(CO) (**8-Rh(CO)**)	1943
(PCP^{iPr})Rh(CO) (**10-Rh(CO)**)	1941

Catalysis of alkyne dimerization. We selected three alkynes for the screening of catalysts: $^{n}BuC{\equiv}CH$, $Me_3SiC{\equiv}CH$, and 4-$MeC_6H_4C{\equiv}CH$. These three substrates did not allow for the evaluation of the functional group tolerance of the catalysts, but they provided a reasonable sampling of steric and electronic differences in terminal alkynes. In this study, we were primarily interested in gauging catalyst activity, longevity, and selectivity. All catalysts were introduced as either Rh^{I} diisopropyl sulfide adducts or as Rh^{I} dihydrogen adducts.

Table 2 details the results of our screening in reactions conducted at 80 °C with 1% catalyst loading. To more closely match the conditions used in our previous study,[15] we additionally conducted the dimerization of the three alkynes using 0.5% **3-Rh($S^{i}Pr_2$)** at 100 °C, and found little difference with the selectivities observed with 1% **3-Rh($S^{i}Pr_2$)** at 80 °C.[35] We also conducted a comparison of **3-Rh($S^{i}Pr_2$)** and **3-Rh(C_6H_{10})** as catalysts in a separate pair of experiments, and found them giving the same conversion and isomer distribution within errors of measurement, thus confirming the irrelevance of the placeholder ligand L in **n-Rh(L)** compounds as catalysts.

Table 2. Conversion of alkyne and the isomeric distribution of the produced enynes.



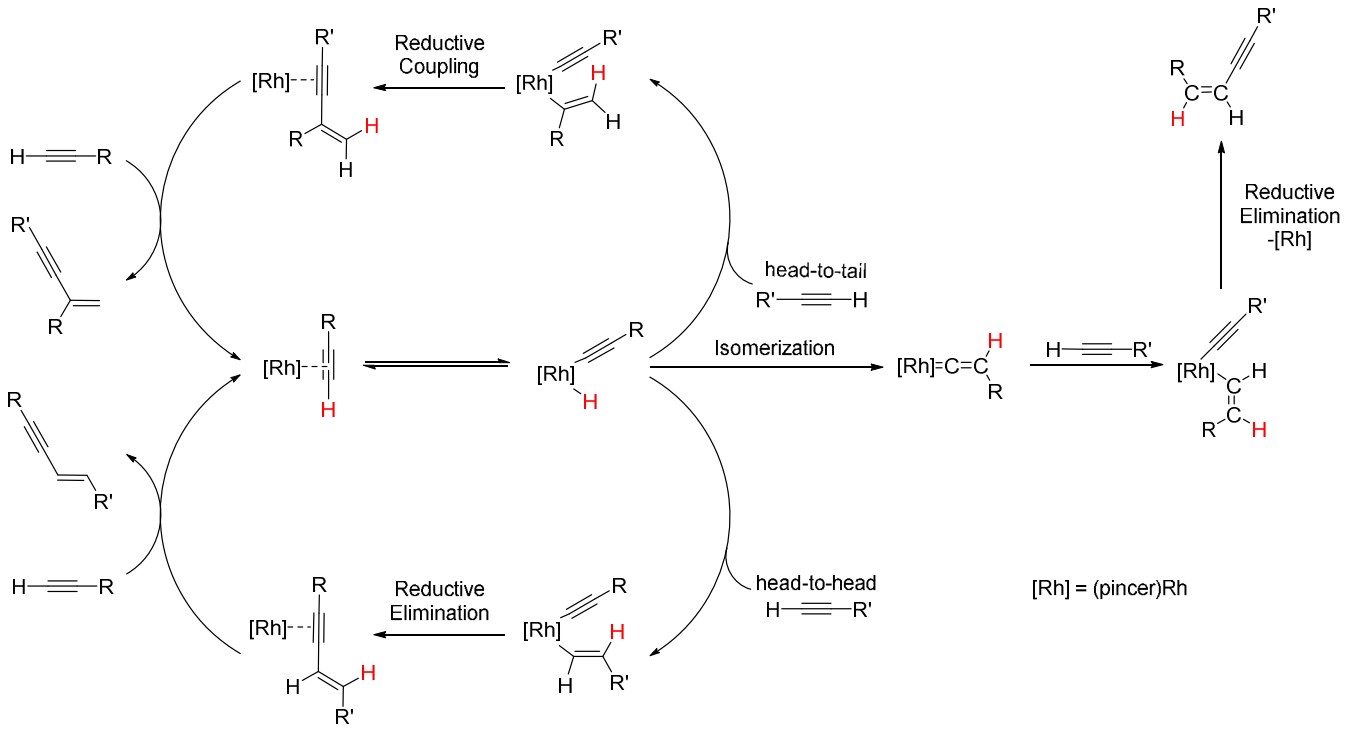
Substrate	[Rh] =	Time	Gem : E : Z : oligomers	% Conversion[a]
4-$MeC_6H_4C{\equiv}CH$	**3-Rh(S^iPr_2)**	3 h	29 : 69 : 0 : 2	>97
^{n}BuC≡CH	**3-Rh(S^iPr_2)**	3 h	73: 19 : 0 : 8	97
$Me_3SiC{\equiv}CH$	**3-Rh(S^iPr_2)**	3 h	63: 35 : 0 : 2	>97
4-$MeC_6H_4C{\equiv}CH$	**4-Rh(H_2)**	36 h	11: 73 : 0 : 16	83
^{n}BuC≡CH	**4-Rh(H_2)**	36 h	84 : 16: 0 : 0	7
$Me_3SiC{\equiv}CH$	**4-Rh(H_2)**	36 h	76: 24 : 0 : 0	80
4-$MeC_6H_4C{\equiv}CH$	**5-Rh(S^iPr_2)**	3 h	24 : 70 : 0 : 6	>97
^{n}BuC≡CH	**5-Rh(S^iPr_2)**	3 h	62 : 31: 0 : 7	95
$Me_3SiC{\equiv}CH$	**5-Rh(S^iPr_2)**	3 h	10 : 79 : 0 : 11	>97
4-$MeC_6H_4C{\equiv}CH$	**6-Rh(S^iPr_2)**	36 h	11 : 46 : 0 : 43	5
^{n}BuC≡CH	**6-Rh(S^iPr_2)**	36 h	89 : 11 : 0 : 0	1
$Me_3SiC{\equiv}CH$	**6-Rh(S^iPr_2)**	36 h	25 : 33 : 0 : 42	5
4-$MeC_6H_4C{\equiv}CH$	**7-Rh(S^iPr_2)**	36 h	13 : 62 : 0 : 25	>97
^{n}BuC≡CH	**7-Rh(S^iPr_2)**	36 h	82 : 14 : 0 : 4	47
$Me_3SiC{\equiv}CH$	**7-Rh(S^iPr_2)**	36 h	19 : 66 : 8 : 7	95
4-$MeC_6H_4C{\equiv}CH$	**8-Rh(S^iPr_2)**	36 h	16 : 11: 0 : 73	4
^{n}BuC≡CH	**8-Rh(S^iPr_2)**	36 h	74 : 26 : 0 : 0	3
$Me_3SiC{\equiv}CH$	**8-Rh(S^iPr_2)**	36 h	15 : 60 : 0 : 25	22
4-$MeC_6H_4C{\equiv}CH$	**9-Rh(H_2)**	70 h	2 : 73 : 0 : 25	74
^{n}BuC≡CH	**9-Rh(H_2)**	70 h	29 : 71 : 0 : 0	25
$Me_3SiC{\equiv}CH$	**9-Rh(H_2)**	70 h	17 : 53 : 0 : 30	45
4-$MeC_6H_4C{\equiv}CH$	**10-Rh(S^iPr_2)**	36 h	22 : 56 : 0 : 22	94

^{n}BuC≡CH	**10-Rh(S^{i}Pr$_2$)**	36 h	65 : 18 : 0 : 17	63
Me$_3$SiC≡CH	**10-Rh(S^{i}Pr$_2$)**	36 h	16 : 65 : 1 : 18	>97

[a] Fraction of consumed alkyne by ^{1}H NMR spectroscopy versus a 1,4-dioxane internal standard.

The *Z* isomer was absent in all but two experiments with Me$_3$SiC≡CH where it was produced in small amounts, possibly indicating the similarity in mechanism between PCP/POCOP and PNP-based catalysts (Scheme 6). The appearance of the *Z* isomer might be indicative of a competing vinylidene intermediate in the catalytic cycle that is accessible when using a strongly electron-donating terminal alkyne. It has been shown experimentally that ethynyltrimethylsilane can react with a nominally 14-electron Rh^{I} compound ([Rh(Cl)(P^{i}Pr$_3$)$_2$]$_2$) to give a five-coordinate rhodium(III) hydridoalkynyl, which rearranges to the corresponding vinylidene isomer.[36] This mechanism of coupling a vinylidene with an acetylide is a common motif found in *Z*-selective ruthenium alkyne dimerization catalysts[7a,b] and was also considered by Goldman et al. in a study of alkyne dimerization by (pincer)Ir catalysts.[37]

Scheme 6. Possible alkyne dimerization mechanisms.



The ratios of *gem*- vs *E*-isomers (Table 3) varied depending on the substrate and the supporting pincer ligand, but none of the catalysts screened in this study demonstrated high selectivity for either the *gem*- or the *E*-product. With 1-hexyne, the *gem*-isomer was typically preferred; with 4-ethynyltoluene, the *E*-isomer typically formed in greater quantity. However, no clear trend can be extracted from these results as far as analyzing the influence of the nature of the pincer ligand on selectivity. For example, there is no obvious correlation between ν_{CO} stretching frequencies of **n-Rh(CO)** (Table 1) and the rates of the dimerization reactions or selectivity. **9-Rh(H$_2$)** performed more similarly to **1-Rh(H$_2$)** than **2-Rh(H$_2$)**: sluggishly and not selectively. It would seem that catalyst **9-Rh(H$_2$)** had a high selectivity for forming the *E*-isomer over the *gem*-enyne for 4-ethynyltoluene, but by monitoring the reaction by ^{1}H NMR over the course of the 70 h reaction time, it was seen that the *gem* isomer was formed and reacts further to form oligomeric products, which is a known behavior of 1,3-diarylbutenynes.[38]

Table 3. Geminal/*E* enyne isomer ratios for dimerization catalysts.

	1-hexyne *Gem*/*E*	4-ethynyltoluene *Gem*/*E*	Ethynyltrimethylsilane *Gem*/*E*
3-Rh(S^{i}Pr$_2$)	3.8	0.42	1.8
4-Rh(H$_2$)	5.3	0.15	3.2
5-Rh(S^{i}Pr$_2$)	2.0	0.34	0.13
6-Rh(S^{i}Pr$_2$)	8.1	0.24	0.75
7-Rh(S^{i}Pr$_2$)	5.9	0.21	0.25
8-Rh(S^{i}Pr$_2$)	2.9	1.5	0.28
9-Rh(H$_2$)	0.4	0.03	0.32
10-Rh(S^{i}Pr$_2$)	3.6	0.39	0.25

With respect to the rates of reaction, (POCOP)- and (^{Napt}POCOP)-supported catalysts bearing P^{i}Pr$_2$ arms appeared to work the fastest, and faster than those reported with **2-Rh(H$_2$)**. Catalysts based on P^{t}Bu$_2$-containing ligands **4**, **6**, and **8** operated much more slowly, presumably owing the prohibitive steric bulk of the four *tert*-butyl groups. In an effort to gauge the longevity of the catalyst, we have also

performed dimerization of $Me_3SiC{\equiv}CH$ using 0.005% of **3-Rh(S^{i}Pr$_2$)** at 100 °C, and observed >97% conversion to the dimerization products after 36 h, amounting to *ca.* 20,000 turnovers.

Conclusion

In summary, we have prepared a series of (pincer)Rh^I complexes for study as potential catalysts for alkyne dimerization to enynes. Some of the reported ligands and their Rh complexes are new. Our findings indicate that aryl/bis(phosphine/phosphinite) PCP or POCOP pincer ligands do result in Rh catalysts capable of alkyne dimerization. Similarly to the PNP-based catalysts reported previously, the PCP/POCOP systems produce little to no *Z*-enynes as products, possibly suggesting a common mechanism. PCP- and POCOP-based Rh compounds with P^{i}Pr$_2$ side arms are faster catalysts than the PNP-based Rh complexes. However, none of the compounds under study in this work displayed notable selectivity for either *E*- or *gem*-enyne isomer. While the isomeric ratios vary considerably as a function of the catalyst and the alkyne substrate, clear trends are not apparent.

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Experimental

General Considerations. Unless otherwise specified, all manipulations were performed under an argon atmosphere using standard Schlenk line or glove box techniques. Toluene, THF, pentane, and isooctane were dried and deoxygenated (by purging) using a solvent purification system and stored over molecular sieves in an Ar-filled glove box. C_6D_6 was dried over and distilled from NaK/Ph_2CO/18-crown-6 and stored over molecular sieves in an Ar-filled glove box. Fluorobenzene and 1,4-dioxane were dried with and then distilled or vacuum transferred from CaH_2. Synthesis of **3-H**,[17] **4-H**,[18] **10-H**,[27] **3-Rh(H)(Cl)**,[26] **4-Rh(H_2)**,[28] $[(COD)RhCl]_2$,[39] $[(COD)Rh(OAc)]_2$,[40] $[(COE)_2RhCl]_2$[41] was accomplished according to literature procedures. **7-H** was synthesized by modification of a literature procedure.[19] NMR spectra were recorded on a Varian NMRS 500 (^{1}H NMR, 499.686 MHz; ^{13}C NMR, 125.659 MHz; ^{31}P NMR, 202.298 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. Alkynes and isopropyl sulfide were freeze-pumped-thawed to remove oxygen before entering the glovebox. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ).

Synthesis of (POCOP)Rh(S^iPr_2) (3-Rh(S^iPr_2). In a Schlenk flask, **3-Rh(H)(Cl)** (298 mg, 0.624 mmol) was dissolved in toluene and was treated with NaO^tBu (148 mg, 1.54 mmol), and S^iPr_2 (82.4 μL, 0.624 mmol). The reaction was stirred for 60 min at RT, the reaction was passed through a pad of Celite and the volatiles were removed by vacuum and recrystallized from pentane to give a brown-yellow solid (294 mg, 84% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 184.8 (d, J_{Rh-P} = 174 Hz); ^{1}H NMR (C_6D_6): δ 6.99 (t, 1H, Ar-*H*, *J* = 7.5 Hz), 6.89 (d, 2H, Ar-*H*, *J* = 8.0 Hz), 2.70 (m, 2H, SC*H*Me_2), 2.20 (m, 4H, C*H*Me_2), 1.29 (apparent q (dvt), 12H, P(CHCH_3)$_2$, *J* = 7 Hz), 1.25 (apparent q (dvt), 12H, P(CHCH_3)$_2$, *J* = 7 Hz), 1.21 (d, 12H, S(CHCH_3)$_2$, *J* = 7 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 167.7 (t, J_{C-P} = 9 Hz, *Ar*-OP), 140.9 (dt, J_{Rh-C} = 35 Hz, J_{C-P} = 10 Hz, *Ar*-Rh), 124.7 (s, *Ar*), 103.8 (t, J_{C-P} = 7 Hz, *Ar*-H), 40.9 (s, S*C*HMe_2), 30.6 (dvt,

$J_{C\text{-}P}$ = 10 Hz, $J_{Rh\text{-}C}$ = 2 Hz, PCH*Me*$_2$), 24.1 (s, SCH*Me*$_2$), 18.7 (t, $J_{C\text{-}P}$ = 4 Hz, PCH*Me*$_2$), 17.6 (s, PCH*Me*$_2$). Elem. Anal. Found (Calculated) for $C_{24}H_{45}O_2P_2RhS$: C, 50.98 (51.24); H, 7.97 (8.06).

Synthesis of (POCOP)Rh(C_6H_{10}) (3-Rh(C_6H_{10})). 3-Rh(H)(Cl) (150 mg, 0.312 mmol) was dissolved in toluene and treated with NaO^{t}Bu (33 mg, 0.343 mmol) and 3-hexyne (39 μL, 0.343 mmol) and stirred for 2 h. The volatiles were removed under vacuum and the product was extracted with pentane and filtered through silica and Celite. The volatiles were removed under vacuum to yield a light orange solid judged to be >97% pure by ^{1}H NMR spectroscopy (85 mg, 52% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 182.0 (d, $J_{Rh\text{-}P}$ = 166 Hz); ^{1}H NMR (C_6D_6): δ 6.99 (t, 1H, *J* = 8 Hz, Ar-*H*), 6.93 (d, 2H, *J* = 8 Hz), 2.47 (q, 4H, *J* = 7.5 Hz, hexyne-C*H*$_2$), 2.03 (m, 4H, PC*H*Me$_2$), 1.24 (apparent q (dvt), 12H, P(CHC*H*$_3$)$_2$, *J* = 7 Hz), 1.16 (t, 6H, *J* = 7.5 Hz, hexyne-CH$_3$), 1.11(apparent q (dvt), 12H, P(CHC*H*$_3$)$_2$, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 168.7 (vt, $J_{C\text{-}P}$ = 8.7 Hz, *Ar*-OP), 143.3 (dvt, $J_{Rh\text{-}C}$ = 31.0 Hz, $J_{P\text{-}C}$ = 9.2 Hz, *Ar*-Rh), 127.3 (s, *Ar*), 104.2 (t, $J_{C\text{-}P}$ = 6.6 Hz, *Ar*-H), 77.4 (d, $J_{Rh\text{-}C}$ = 6.8 Hz, Rh-(*C*≡*C*), 29.9 (dt, $J_{C\text{-}P}$ = 9.6 Hz, $J_{Rh\text{-}C}$ = 2.1 Hz, P*C*HMe$_2$), 20.8 (s, hexyne), 17.6 (t, $J_{C\text{-}P}$ = 4.5 Hz, PCH*Me*$_2$), 17.5 (s, PCH*Me*$_2$), 16.0 (s, hexyne).

Synthesis of (^{Napt}POCOP)H (5-H). In a Teflon screw-top flask, 1,7-dihydroxynaphthalene (479 mg, 2.99mmol) was dissolved in THF and ClP^iPr_2 (956 mg, 6.26 mmol) was added slowly while stirring. The solution turned from dark to light brown with the dropwise addition of NEt_3 (994 mg, 9.82 mmol). The reaction mixture was heated at 85 °C for 1.5 h. The mixture was then passed through Celite, and the volatiles were removed under vacuum to produce a thick brown oil that was determined to be >95% pure by ^{1}H NMR spectroscopy (926 mg, 79% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 148.1 (s), 146.9 (s); ^{1}H NMR (C_6D_6): δ 8.41 (t, 1H, *J* = 2.5 Hz, Ar-*H*), 7.56 (t, 1H, *J* = 2.5 Hz, Ar-*H*), 7.53 (d, 1H, *J* = 9.5 Hz, Ar-*H*), 7.37 (m, 1H, Ar-*H*), 7.29 (d, 1H, *J* = 8 Hz, Ar-*H*), 7.15 (m, 1H, Ar-*H*), 1.83 (m, 4H, P-C*H*Me$_2$), 1.20 (m, 12H, CH(CH$_3$)$_2$), 1.01 (m, 12H, CH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6): δ 157.6 (d, $J_{C\text{-}P}$ = 8 Hz, *Ar*-OP), 154.9 (d, $J_{C\text{-}P}$ = 9 Hz, *Ar*-OP), 131.4 (*Ar*), 129.8 (*Ar*), 124.2 (*Ar*), 121.3 (*Ar*), 121.1 (d, $J_{C\text{-}P}$ = 6 Hz, *Ar*), 111.8 (*Ar*), 111.7 (*Ar*), 108.4 (d, $J_{C\text{-}P}$ = 16 Hz, *Ar*), 28.7 (d , $J_{C\text{-}P}$ = 19 Hz, 2 *C*HMe$_2$), 18.0 (d,

$J_{C\text{-}P}$ = 15 Hz, CH*Me*$_2$), 17.8 (d, $J_{C\text{-}P}$ = 15 Hz, CH*Me*$_2$), 17.3 (d, $J_{C\text{-}P}$ = 5 Hz, CH*Me*$_2$), 17.24 (d, $J_{C\text{-}P}$ = 5 Hz, CH*Me*$_2$).

Synthesis of (^{Napt}POCOP)Rh(H)(Cl) (5-Rh(H)(Cl)). In a Teflon screw-top flask, **5** (209 mg, 0.533 mmol) and [(COD)RhCl]$_2$ (131 mg, 1.066 mmol) were dissolved in toluene and stirred overnight at 90 ºC. The reaction mixture was passed through silica and Celite, and the volatiles were removed under vacuum. The resulting red solid was dissolved in a minimum amount of toluene and layered with pentane. A red solid precipitated out of solution (215 mg, 76%). ^{31}P{^{1}H} (C_6D_6): δ 183.7 (dd, $J_{P\text{-}P}$ = 424 Hz, $J_{P\text{-}Rh}$ = 111 Hz), 164.4 (dd, $J_{P\text{-}P}$ = 418 Hz, $J_{P\text{-}Rh}$ = 121 Hz); ^{1}H NMR (C_6D_6): δ 7.38 (t, 2H, *J* = 8.5 Hz, Ar-*H*), 7.20 (d, 1H, *J* = 9 Hz, Ar-*H*), 7.11 (d, 1H, *J* = 7.5 Hz, Ar-*H*), 7.05 (t, 1H, *J* = 8 Hz, Ar-*H*), 2.75 (m, 1H, PC*H*Me$_2$), 2.64 (m, 1H, PC*H*Me$_2$), 2.46 (m, 1H, PC*H*Me$_2$), 2.21 (m, 1H, PC*H*Me$_2$), 1.35 (dd, 3H, $J_{H\text{-}P}$ = 17.5 Hz, $J_{H\text{-}H}$ = 7.5 Hz, PCH(C*H*$_3$)$_2$), 1.18 (m, 21H, PCH(C*H*$_3$)$_2$), -24.10 (apparent dt, 1H, $J_{H\text{-}Rh}$ = 45 Hz, $J_{H\text{-}P}$ = 15 Hz, Rh-*H*); ^{13}C{^{1}H} NMR (C_6D_6): δ 166.1 (m, *Ar*-OP), 154.7 (m, *Ar*-OP), 133.1 (s, *Ar*), 130.1 (d, *J* = 9 Hz, *Ar*), 128.4 (*Ar*), 125.4 (*Ar*), 123.4 (*Ar*), 123.1 (m, *C*-Rh) 115.5 (d, *J* = 2.5 Hz, *Ar*), 115.3 (d, $J_{C\text{-}P}$ = 13 Hz, *Ar*), 29.8 (m, P*C*HMe$_2$), 29.5 (m, P*C*HMe$_2$) 29.0 (m, P*C*HMe$_2$), 28.17 (d, $J_{C\text{-}P}$ = 23 Hz, P*C*HMe$_2$), 18.7 (d, $J_{C\text{-}P}$ = 4 Hz, PCH*Me*$_2$), 18.3 (s, PCH*Me*$_2$), 18.0 (s, PCH*Me*$_2$), 17.7 (s, PCH*Me*$_2$), 17.6 (s, PCH*Me*$_2$), 17.1 (m, PCH*Me*$_2$), 16.4 (m, PCH*Me*$_2$), 16.1 (s, PCH*Me*$_2$). Elem. Anal. Found (Calculated) for $C_{22}H_{34}ClO_2P_2Rh$: C, 49.91 (49.78); H, 6.24 (6.46).

Synthesis of (^{Napt}POCOP^{iPr})Rh(S^{i}Pr$_2$) (5-Rh(S^{i}Pr$_2$)). In a Schlenk flask, **5-Rh(H)(Cl)** (180 mg, 0.339 mmol), NaO^{t}Bu (56 mg, 0.509 mmol), and diisopropyl sulfide (100 µL, 0.688 mmol) were dissolved in toluene. The reaction mixture was stirred for 1 h at RT, and the volatiles were removed under vacuum. The resulting solid was washed with pentane and dissolved in benzene to be filtered over a pad of Celite. The volatiles were removed to yield a dark orange solid (73 mg, 35%). ^{31}P{^{1}H} NMR (C_6D_6): δ 181.6 (dd, $J_{P\text{-}P}$ = 362 Hz, $J_{P\text{-}Rh}$ = 162 Hz), 156.2 (dd, $J_{P\text{-}P}$ = 362 Hz, $J_{P\text{-}Rh}$ = 172 Hz); ^{1}H NMR (C_6D_6): δ 7.49 (m, 3H, Ar-*H*), 7.20 (d, *J* = 10 Hz, 1H, Ar-*H*), 7.15 (t, obscured by benzene peak, 1H, Ar-*H*), 2.71 (m, 2H, S(C*H*Me$_2$)$_2$), 2.40 (m, 2H, P(C*H*Me$_2$)$_2$), 2.22 (m, 2H, P(C*H*Me$_2$)$_2$), 1.30 (dd, 6H, *J*

= 7 Hz, J = 5 Hz, PCH(CH_3)$_2$), 1.28 (dd, 6H, J = 8 Hz, J = 4 Hz, PCH(CH_3)$_2$), 1.27 (dd, 6H, J = 7 Hz, J = 5 Hz, PCH(CH_3)$_2$), 1.25 (dd, 6H, J = 9 Hz, J = 5 Hz, PCH(CH_3)$_2$), 1.21 (d, 12H, J = 10 Hz, S(CH*Me*$_2$)); ^{13}C{^{1}H} NMR (C_6D_6): δ 166.2 (d, $J_{C\text{-}P}$ = 16 Hz, *Ar*-OP), 156.1 (d, $J_{C\text{-}P}$ = 3 Hz, , *Ar*-OP), 135.0 (br d, $J_{C\text{-}Rh}$ = 41 Hz, *Ar*-Rh), 132.6 (*Ar*), 131.5 (d, J = 12 Hz, *Ar*), 126.6 (*Ar*), 123.7 (*Ar*), 122.2 (*Ar*), 114.3 (d, J = 15 Hz, *Ar*), 113.2 (d, J = 5 Hz, *Ar*), 37.6 (dd, J = 13 Hz, S(*C*HMe$_2$)$_2$), 31.0 (ddd, $J_{C\text{-}P}$ = 13 Hz, J = 5 Hz, J = 3 Hz, P(*C*HMe$_2$)$_2$), 30.5 (ddd, $J_{C\text{-}P}$ = 19 Hz, J = 5 Hz, J = 3 Hz, P(*C*HMe$_2$)$_2$), 24.9 (s, (S(CH*Me*$_2$)$_2$), 19.2 (d$J_{C\text{-}P}$ = 9 Hz, P(CH*Me*$_2$)$_2$), 18.8 (d, $J_{C\text{-}P}$ = 6 Hz, P(CH*Me*$_2$)$_2$), 17.8 (s, P(CH*Me*$_2$)$_2$), 17.6 (s, P(CH*Me*$_2$)$_2$). Elem. Anal. Found (Calculated) for $C_{28}H_{47}O_2P_2RhS$: C, 54.90 (54.81); H, 7.73 (7.69).

Synthesis of (^{Napt}POCOP^{iPr})Rh(CO) (5-Rh(CO)). In a Teflon screw-top flask, **5-Rh(H)(Cl)** (106 mg, 0.200 mmol) was dissolved in toluene and treated with NaO^{t}Bu (30 mg, 0.312 mmol). The flask was then degassed, filled with CO, and stirred at RT for 2 h. The volatiles were removed and product was extracted with pentane and filtered through silica and Celite. The volatiles were removed and the product was recrystallized from hexamethyldisiloxane as yellow crystals in >98% purity as judged by ^{1}H NMR (64 mg, 62% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 199.3 (dd, $J_{P\text{-}P}$ = 318 Hz, $J_{P\text{-}Rh}$ = 140 Hz), 170.0 (dd, $J_{P\text{-}P}$ = 317 Hz, $J_{P\text{-}Rh}$ = 147 Hz); ^{1}H NMR (C_6D_6): δ 7.52 (dd, 1H, J = 9 Hz, J = 2 Hz), 8.5 (d, 2H, J = 9 Hz), 7.44 (dd, 1H, J = 8 Hz, 2 Hz), 7.20 (dd, 1H, J = 8 Hz, 2 Hz), 7.11 (dd, 1H, apparent t, 8 Hz), 2.13 (m, 4H, C*H*Me$_2$), 0.87 (dd, 6H, $J_{H\text{-}P}$ = 17.5 Hz, J = 7 Hz, PCH(*Me*)$_2$), 0.86 (dd, 6H, $J_{H\text{-}P}$ = 18 Hz, J = 7 Hz, PCH(*Me*)$_2$), 0.86 (dd, 6H, $J_{H\text{-}P}$ = 14.5 Hz, 7 Hz, PCH(*Me*)$_2$), 0.85 (dd, 6H, $J_{H\text{-}P}$ = 14 Hz, 7 Hz, PCH(*Me*)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 196.8 (ddd (apparent dt), $J_{Rh\text{-}C}$ = 56 Hz, $J_{C\text{-}P}$ = 14 Hz, $J_{C\text{-}P}$ = 14 Hz, Rh-*C*O), 168.0 (dd, $J_{C\text{-}P}$ = 16 Hz, $J_{C\text{-}Rh}$ = 3 Hz, *Ar*-OP), 155.5 (dd (apparent t), $J_{C\text{-}P}$ = 2 Hz, $J_{C\text{-}Rh}$ = 2 Hz, *Ar*-OP), 137.8 (ddd, $J_{C\text{-}Rh}$ = 31 Hz, $J_{C\text{-}P}$ = 13 Hz, $J_{C\text{-}P}$ = 6 Hz, *Ar*-Rh), 132.0 (m, *Ar*), 130.3 (s, *Ar*-H), 129.9 (d, J = 12 Hz, *Ar*), 124.9 (s, *Ar*-H), 122.7 (s, *Ar*-H), 114.9 (d, J = 5 Hz, *Ar*-H), 114.8 (d, J = 5 Hz, *Ar*-H), 114.8 (d, J = 15 Hz, *Ar*-H), 32.3 (ddd, $J_{C\text{-}P}$ = 24 Hz, J = 4 Hz, J = 2 Hz, P(*C*HMe$_2$)$_2$), 30.4

(apparent dt (ddd), $J_{C\text{-}P}$ = 22 Hz, J = 3 Hz, P(*C*HMe$_2$)$_2$), 18.6 (d, $J_{C\text{-}P}$ = 8 Hz, P(CH*Me*$_2$)$_2$), 17.9 (d, $J_{C\text{-}P}$ = 7 Hz, P(CH*Me*$_2$)$_2$), 17.6 (s, P(CH*Me*$_2$)$_2$), 17.5 (s, P(CH*Me*$_2$)$_2$). IR: 1950 cm^{-1}, ν_{CO}.

Synthesis of 1,7-bis(ditertbutylphosphinyl)naphthalenediol (6-H). In a culture tube, 1,7-dihydroxynaphthalene (78 mg, 0.487mmol) was dissolved in THF and NaH (36 mg, 1.5 mmol) was added slowly. The reaction mixture was refluxed for 4 h and passed through a pad of Celite with diethyl ether. The volatiles were removed under vacuum to give a brown solid determined by ^{1}H NMR spectroscopy to be >95% pure (156 mg, 71%). ^{31}P{^{1}H} NMR (C_6D_6): δ 154.8 (s), 150.5 (s); ^{1}H NMR (C_6D_6): 8.51 (s, 1H, Ar-*H*), 7.62 (m, 1H, Ar-*H*), 7.55 (d, 1H, J = 9 Hz, Ar-*H*), 7.35 (m, 1H, Ar-*H*), 7.29 (d, 1H, J = 8 Hz, Ar-*H*), 7.18 (d, 1H, J = 8 Hz, Ar-*H*), 1.19 (d, 36H, C(C*H*$_3$)$_3$, $J_{H\text{-}P}$ = 11 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 158.1 (d, $J_{C\text{-}P}$ = 10 Hz, *Ar*-OP), 155.2 (d, $J_{C\text{-}P}$ = 9 Hz, *Ar*-OP), 131.4 (Ar), 129.7 (Ar), 124.2 (Ar), 121.1 (d, $J_{C\text{-}P}$ = 6 Hz, Ar), 120.9 (Ar), 111.3 (Ar), 111.2 (Ar), 108.4 (Ar, $J_{C\text{-}P}$ = 16 Hz), 36.0 ($J_{C\text{-}P}$ = 16 Hz, P*C*Me$_3$), 35.8 ($J_{C\text{-}P}$ = 15 Hz, P*C*Me$_3$), 27.7 (d, $J_{C\text{-}P}$ = 2 Hz, PC(*C*H$_3$)$_3$), 27.6 (d, $J_{C\text{-}P}$ = 2 Hz, PC(*C*H$_3$)$_3$). HRMS (ESI+TOF) m/z: [M + H]$^+$ Calcd. for $C_{26}H_{44}O_2P_2$ 449.2733; found 449.2728

Synthesis of (^{Napth}POCOP^{tBu})Rh(H)(Cl) (6-Rh(H)(Cl)). In a Teflon screw-top flask, **6-H** (64.4 mg, 0.144 mmol) and [(COD)Rh(Cl)]$_2$ (35.4 mg, 0.717 mmol) were dissolved in toluene and stirred overnight at 80 °C. The reaction mixture was filtered through Celite and the volatiles were removed under vacuum. The resulting solid recrystallized from diethyl ether at -35 °C to yield brown crystals judged to be >97% pure by ^{1}H NMR (78 mg, 92%). ^{31}P{^{1}H} NMR (C_6D_6): δ 184.8 (dd, $J_{P\text{-}P}$ = 408 Hz, $J_{P\text{-}Rh}$ = 115 Hz), 166.5 (dd, $J_{P\text{-}P}$ = 406 Hz, $J_{P\text{-}Rh}$ = 121 Hz); ^{1}H NMR (C_6D_6): δ 7.40 (m, 2H, Ar-*H*), 7.21 (d, 2H, J = 9 Hz, Ar-*H*), 7.07 (m, 2H, Ar-*H*), 1.47 (d, 9H, $J_{H\text{-}P}$ = 14 Hz, PC(C*H*$_3$)$_3$), 1.42 (d, 9H, $J_{H\text{-}P}$ = 14 Hz, PC(C*H*$_3$)$_3$), 1.38 (d, 9H, $J_{H\text{-}P}$ = 15 Hz, PC(C*H*$_3$)$_3$), 1.35 (d, 9H, $J_{H\text{-}P}$ = 15 Hz, PC(C*H*$_3$)$_3$), -25.21 (ddd, 1H, $J_{H\text{-}Rh}$ = 46 Hz, $J_{H\text{-}P}$ = 12 Hz, $J_{H\text{-}P}$ = 12 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 167.2 (dd, $J_{C\text{-}P}$ = 11 Hz, $J_{C\text{-}Rh}$ = 4 Hz, *Ar*-OP), 154.7 (dd, J = 4 Hz, J = 3 Hz, *Ar*-OP), 133.06 (*Ar*), 130.1 (d, J = 8 Hz, *Ar*), 125.2 (*Ar*), 123.3 (*Ar*), 115.47 (*Ar*), 115.43 (*Ar*), 115.37 (*Ar*), 115.27 (*Ar*), 43.0 (dd, $J_{C\text{-}P}$ = 8 Hz, $J_{C\text{-}Rh}$ = 6 Hz, P(*C*Me$_3$)$_2$), 41.4 (dd, $J_{C\text{-}P}$ = 9 Hz, $J_{C\text{-}Rh}$ = 6 Hz, P(*C*Me$_3$)$_2$), 40.4 (ddd, $J_{C\text{-}P}$ = 20 Hz, J = 5 Hz, J = 1 Hz,

P(*C*Me$_3$)$_2$), 38.6 (ddd, $J_{C\text{-}P}$ = 14 Hz, J = 5 Hz, J = 3 Hz, P(*C*Me$_3$)$_2$), 28.9 (d, $J_{C\text{-}P}$ = 6 Hz, P(C*Me*$_3$)$_2$), 28.8 (d, $J_{C\text{-}P}$ = 5 Hz, P(C*Me*$_3$)$_2$), 28.7 (d, $J_{C\text{-}P}$ = 5 Hz, P(C*Me*$_3$)$_2$), 28.1 (d, $J_{C\text{-}P}$ = 5 Hz, P(C*Me*$_3$)$_2$).

Synthesis of (^{Napt}POCOP^{tBu})Rh(S^{i}Pr$_2$) (6-Rh(S^{i}Pr$_2$)). In a Schlenk flask, **6-Rh(H)(Cl)** (110 mg, 0.187 mmol), NaO^{t}Bu (30 mg, 0.281 mmol), diisopropyl sulfide (55 μL, 0.374 mmol) were mixed in toluene and stirred for 3 h at RT. The volatiles were removed under vacuum, and the resulting solid was dissolved in pentane and passed through Celite. The resulting brown solid was dissolved in a minimum of pentane and placed in a -35 °C freezer overnight to produce brown crystals (59 mg, 47% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 185.4 (dd, $J_{P\text{-}P}$ = 327 Hz, $J_{P\text{-}Rh}$ = 168 Hz), 163.2 (dd, $J_{P\text{-}P}$ = 323 Hz, $J_{P\text{-}Rh}$ = 175 Hz); ^{1}H NMR (C_6D_6): δ 7.41 (br s, 2H, Ar-*H*), 7.27 (br s, 1H, Ar-*H*), 7.15 (br s, 2H, Ar-*H*), 2.82 (m, 2H, S(C*H*Me$_2$)$_2$), 1.40 (d, 36H, $J_{H\text{-}P}$ = 6 Hz, P(C*Me*$_3$)$_2$), 1.21 (d, 12H, $J_{H\text{-}H}$ = 4 Hz, S(CH*Me*$_2$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6): δ 166.8 (d, $J_{C\text{-}P}$ = 19 Hz, *Ar*-OP), 156.1 (d, $J_{C\text{-}P}$ = 3 Hz, *Ar*-OP), 132.8 (*Ar*), 131.6 (m, *Ar*-Rh), 126.3 (*Ar*), 124.1 (*Ar*), 122.2 (*Ar*), 114.4 (d, $J_{C\text{-}P}$ =14 Hz, *Ar*), 113.32 (*Ar*), 113.29 (*Ar*), 41.0 (m, S(*C*HMe$_2$)$_2$), 39.7 (m, P(*C*Me$_3$)$_2$), 38.2 (s, P(*C*Me$_3$)$_2$) 29.5 (d, $J_{C\text{-}P}$ = 9 Hz, P(C*Me*$_3$)$_2$), 29.4 (d, J = 8 Hz, P(C*Me*$_3$)$_2$), 24.9 (s, S(CH*Me*$_2$)). Elem. Anal. Found (calculated) for $C_{32}H_{55}O_2P_2RhS$: C, 57.29 (57.48); H, 8.16 (8.29).

(^{Napt}POCOP^{tBu})Rh(CO) (6-Rh(CO)). In a 10 mL Teflon screw-top flask, **6-Rh(H)(Cl)** (50 mg, 0.085 mmol) was dissolved in toluene and treated with NaO^{t}Bu (10 mg, 0.10 mmol). The flask was degassed and filled with CO and stirred overnight at RT. The volatiles were removed under vacuum and the product was extracted with pentane and filtered through silica and Celite. The volatiles were removed to produce a yellow powder judged to be >97% pure by ^{1}H NMR (30 mg, 61%). ^{31}P{^{1}H} NMR (C_6D_6): δ 207.1 (dd, $J_{P\text{-}P}$ = 306 Hz, $J_{P\text{-}Rh}$ = 140 Hz), 179.7 (dd, $J_{P\text{-}P}$ = 306 Hz, $J_{P\text{-}Rh}$ = 147 Hz); ^{1}H NMR (C_6D_6): δ 7.53 (dd, 1H, J = 2 Hz, J = 9 Hz), 7.44 (t, 2H, J = 8 Hz, Ar-*H*), 7.19 (dd, 1H, J = 8 Hz, J = 2 Hz, Ar-*H*), 7.13 (t, 2H, J = 8 Hz, Ar-*H*), 1.35 (d, 18H, $J_{H\text{-}P}$ = 7 Hz, P(C*Me*$_3$)$_2$), 1.32 (d, 18H, $J_{C\text{-}P}$ = 7 Hz, P(CMe$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6): δ 198.7 (ddd (apparent dt), $J_{C\text{-}Rh}$ = 57 Hz, $J_{C\text{-}P}$ = 14 Hz, Rh-*C*O), 168.9 (dd, $J_{C\text{-}P}$ = 15 Hz, $J_{C\text{-}Rh}$ = 3 Hz, *Ar*-OP), 156.4 (m, *Ar*-OP), 138.4 (ddd, $J_{C\text{-}Rh}$ = 33 Hz, $J_{C\text{-}P}$ = 13

Hz, $J_{C\text{-}P}$ = 6 Hz, *Ar*-Rh), 132.0 (s, *Ar*), 130.2 (s, *Ar*-H), 129.3 (d, *J* = 11 Hz, *Ar*), 124.7 (s, *Ar*-H), 122.6 (s, *Ar*-H), 114.8 (d, *J* = 15 Hz, *Ar*-H), 114.5 (d, *J* = 5 Hz, *Ar*-H), 41.3 (ddd, $J_{C\text{-}P}$ = 17 Hz, *J* = 4 Hz, *J* = 2 Hz, P(*C*Me$_3$)$_2$), 39.9 (apparent dt, $J_{C\text{-}P}$ = 15 Hz, *J* = 3 Hz, P(*C*Me$_3$)$_2$), 28.6 (d, $J_{C\text{-}P}$ = 7 Hz, P(C*Me*$_3$)$_2$), 28.3 (d, $J_{C\text{-}P}$ = 7 Hz, P(C*Me*$_3$)$_2$). IR: 1945 cm^{-1}, ν_{CO}.

Synthesis of 1-(^{i}Pr$_2$PO)-3-(^{i}Pr$_2$POCH$_2$)(C$_6$H$_4$) (7-H).[42] To a solution of 3-hydroxybenzyl alcohol (0.508 g, 4.09 mmol) in THF, triethylamine (1.241 g, 12.3 mmol) was added dropwise while stirring. A solution of ClP^iPr$_2$ (1.290 g, 8.18 mmol) in THF was added slowly while stirring. A precipitate formed immediately and the reaction was stirred overnight at RT. The reaction mixture was passed through a pad of Celite, and the solvent was removed under vacuum to produce a colorless oil determined to be >95% pure by ^{1}H NMR spectroscopy (1.236 g, 85%). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 155.2 (s), 147.6 (s); ^{1}H NMR (C$_6$D$_6$): δ 6.88 (d, 1H, *J* = 8 Hz, Ar-*H*); 6.79 (t, 1H, *J* = 8 Hz, Ar-*H*), 6.62 (d, 1H, Ar-*H, J* = 8 Hz, Ar-*H*), 4.43 (d, 2H, $J_{H\text{-}P}$ = 10 Hz, C*H*$_2$OP), 1.47 (m, 2H, P(C*H*Me$_2$)$_2$), 1.37 (m, 2H, P(C*H*Me$_2$)$_2$), 0.85 (dd, 6H, $J_{H\text{-}P}$ = 10 Hz, $J_{H\text{-}H}$ = 9 Hz, PCH(C*H*$_3$)$_2$), 0.83 (dd, 6H, $J_{H\text{-}P}$ = 10 Hz, $J_{H\text{-}H}$ = 9 Hz, PCH(C*H*$_3$)$_2$) , 0.69 (dd, 12H, $J_{H\text{-}P}$ = 15 Hz, $J_{H\text{-}H}$ = 7 Hz, PCH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 160.0 (d, $J_{C\text{-}P}$ = 9 Hz, *Ar*-OP), 141.9 (d, $J_{C\text{-}P}$ = 8 Hz, *Ar*-CH$_2$OP), 129.6 (*Ar*-H), 120.9 (*Ar*-H), 118.0 (d, $J_{C\text{-}P}$ = 11 Hz, *Ar*-H), 117.8 (d, $J_{C\text{-}P}$ = 11 Hz, *Ar*-H), 74.4 (d, $J_{C\text{-}P}$ = 22 Hz, *C*H$_2$OP), 28.7 (d, $J_{C\text{-}P}$ = 14 Hz, P(*C*HMe$_2$)$_2$), 28.5 (d, $J_{C\text{-}P}$ = 14 Hz, P(*C*HMe$_2$)$_2$), 18.2 (d, $J_{C\text{-}P}$ = 20 Hz, P(CH*Me*$_2$)$_2$), 17.8 (d, $J_{C\text{-}P}$ = 20 Hz, P(CH*Me*$_2$)$_2$), 17.3 (d, $J_{C\text{-}P}$ = 9 Hz, P(CH*Me*$_2$)$_2$), 17.2 (d, $J_{C\text{-}P}$ = 9 Hz, P(CH*Me*$_2$)$_2$).

Synthesis of (POCCH$_2$OP^{iPr})Rh(H)(Cl)(NCCH$_3$) (7-Rh(H)(Cl)(NCMe)). In a Teflon screw-top flask, **7-H** (419 mg, 1.18 mmol) and [(COD)RhCl]$_2$ (299 mg, 0.59 mmol) were dissolved in acetonitrile and stirred overnight at 80 °C. The reaction mixture was passed through a pad of silica and Celite. The volatiles were removed under vacuum and the resulting solid was recrystallized from pentane to produce square yellow crystals judged to be >95% pure by ^{1}H NMR spectroscopy (520 mg, 97%) ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 186.4 (dd, $J_{P\text{-}P}$ = 428 Hz, $J_{P\text{-}Rh}$ = 119 Hz), 153.9 (dd, $J_{P\text{-}P}$ = 416 Hz, $J_{P\text{-}Rh}$ = 113 Hz); ^{1}H NMR (C$_6$D$_6$): δ 6.96 (d, 1H, *J* = 8 Hz, Ar-*H*), 6.82 (t, 1H, *J* = 8 Hz, Ar-*H*), 6.62 (d, 1H, *J* = 8 Hz, Ar-*H*), 4.82

(m, 2H, CH_2OP), 3.09 (m, 1H, CHMe$_2$), 2.55 (m, 1H, CHMe$_2$), 2.49 (m, 1H, CHMe$_2$), 2.19 (m, 1H, CHMe$_2$), 1.62 (dd, 3H, CH(CH_3)$_2$, J_{H-P} = 16 Hz, J_{H-H} = 7 Hz), 1.57 (br m, 3H, CH(CH_3)$_2$), 1.39 (dd, 3H, CH(CH_3)$_2$, J_{H-P} = 15 Hz, J_{H-H} = 7 Hz), 1.31 (m, 6H, CH(CH_3)$_2$), 1.20 (m, 6H, CH(CH_3)$_2$), 0.82 (dd, 3H, CH(CH_3)$_2$, J_{H-P} = 15 Hz, J_{H-H} = 7 Hz), 0.52 (s, 3H, NCCH_3), -17.95 (br s, 1H, Rh-H); ^{13}C{^{1}H} NMR (C_6D_6): δ 166.4 (d, J_{C-P} = 13 Hz, *Ar*-OP), 142.8 (d, J_{C-P} = 9 Hz , *Ar*-CH$_2$OP), 137.0 (m, *Ar*-Rh), 124.2 (*Ar*-H), 121.5 (*Ar*-H), 121.2 (N*C*CH$_3$), 111.5 (d, J_{C-P} = 13 Hz, *Ar*-H), 76.6 (s, *C*H$_2$OP), 31.6 (m, *C*HMe$_2$), 29.4 (s, *C*HMe$_2$), 29.1 (s, *C*HMe$_2$), 27.7 (s, *C*HMe$_2$), 18.6 (d, J = 5 Hz, CH*Me*$_2$), 18.5 (s, CH*Me*$_2$), 18.2 (s, CH*Me*$_2$), 18.0 (s, CH*Me*$_2$), 17.3 (d, J = 3 Hz, CH*Me*$_2$), 16.7 (d, J = 6 Hz, CH*Me*$_2$), 16.5 (d, J = 9 Hz, CH*Me*$_2$), 16.2 (s, CH*Me*$_2$), 1.2 (s, NC*C*H$_3$). Elem. Anal. Found (calculated) for $C_{21}H_{37}ClNO_2P_2Rh$: C, 47.07 (47.07); H, 6.98 (6.96).

Synthesis of (POCCH$_2$OP^{iPr})Rh(H)(Cl) (7-Rh(H)(Cl)). In a Teflon screw-top flask, **7-Rh(H)(Cl)(NCMe)** (261 mg, 0.483 mmol) was combined with sodium acetate (356 mg, 4.34 mmol) and dissolved in 1,4-dioxane. The reaction stirred overnight at 90 °C. The resulting orange solution was passed through a pad of Celite and the volatiles were removed under vacuum to produce **7-Rh(H)(OAc)** as an oily brown solid, which was characterized *in situ*. The brown solid was dissolved in toluene and trimethylsilyl chloride (100 μL, 0.788 mmol) was added. The reaction mixture was stirred for 1 h at RT and the volatiles were removed under vacuum. The oily orange solid produced was washed with hexamethyldisiloxane and redissolved in toluene to be passed through a plug of Celite. The volatiles were removed and the orange solid was dissolved in a minimum amount of toluene, layered with pentane, and then placed in a -35 ^{0}C freezer to produce an orange solid (118 mg, 49%). ^{31}P{^{1}H} NMR (C_6D_6): δ 186.7 (dd, J_{P-P} = 416 Hz, J_{P-Rh} = 118 Hz), 157.7 (dd, J_{P-P} = 416 Hz, J_{P-Rh} = 121 Hz); ^{1}H NMR (C_6D_6): δ 6.96 (d, 1H, J = 7 Hz, Ar-H), 6.86 (t, 1H, , J = 8 Hz, Ar-H), 6.47 (d, 1H, J = 7 Hz, Ar-H), 4.73 (dd, 1H, J = 17 Hz, J = 13 Hz, CH_2OP), 4.55 (dd, 1H, J = 17 Hz, J = 13 Hz, CH_2OP), 2.74 (m, 1H, PCHMe$_2$), 2.58 (m, 1H, PCHMe$_2$), 2.27 (m, 1H, PCHMe$_2$), 2.18 (m, 1H, PCHMe$_2$), 1.32 (dd, 3H, J_{H-P} = 17 Hz, J_{H-H} = 8 Hz, PCH(CH_3)$_2$), 1.28 (dd, 3H, J_{H-P} = 18 Hz, J_{H-H} = 8 Hz, PCH(CH_3)$_2$), 1.26 (dd, 3H,

$J_{H\text{-}P}$ = 17 Hz, $J_{H\text{-}H}$ = 8 Hz, PCH(CH_3)$_2$), 1.20 (dd, 3H, $J_{H\text{-}P}$ = 18 Hz, $J_{H\text{-}H}$ = 7 Hz, PCH(CH_3)$_2$), 1.09 (dd, 3H, $J_{H\text{-}P}$ = 17 Hz, $J_{H\text{-}H}$ = 8 Hz, PCH(CH_3)$_2$), 1.07 (m, 6H, PCH(CH_3)$_2$), 1.05 (dd, 3H, $J_{H\text{-}P}$ = 16 Hz, $J_{H\text{-}H}$ = 7 Hz, PCH(CH_3)$_2$), -25.48 (br d, 1H, $J_{H\text{-}Rh}$ = 45 Hz, Rh-*H*); ^{13}C{^{1}H} NMR (C_6D_6): δ 168.7 (dd, $J_{C\text{-}P}$ = 13 Hz, $J_{C\text{-}Rh}$ = 3.0 Hz, *Ar*-OP), 142.3 (d, *J* = 8 Hz, *Ar*-CH_2OP), 133.9 (ddd, $J_{C\text{-}Rh}$ = 29 Hz, $J_{C\text{-}P}$ = 7 Hz, $J_{C\text{-}P}$ = 5 Hz, *Ar*-Rh), 125.6 (*Ar*-H), 121.8 (*Ar*-H), 112.4 (d, $J_{C\text{-}P}$ = 12 Hz, *Ar*-H), 76.4 (d, $J_{C\text{-}P}$ = 2 Hz, *C*H_2OP), 29.3 (m, P*C*HMe_2), 29.0 (m, P*C*HMe_2), 28.6 (m, P*C*HMe_2), 28.3 (m, P*C*HMe_2), 19.3 (d, $J_{C\text{-}P}$ = 4 Hz, PCH(*C*H_3)$_2$), 18.3 (s, PCH(*C*H_3)$_2$), 18.2 (d, $J_{C\text{-}P}$ = 7 Hz, PCH(*C*H_3)$_2$), 18.0 (d, $J_{C\text{-}P}$ = 5 Hz, PCH(*C*H_3)$_2$), 17.9 (s, PCH(*C*H_3)$_2$), 17.1 (d, $J_{C\text{-}P}$ = 8 Hz, PCH(*C*H_3)$_2$), 16.4 (apparent t (dd), *J* = 2 Hz, PCH(*C*H_3)$_2$), 16.1 (dd, *J* = 4 Hz, *J* = 2 Hz, PCH(*C*H_3)$_2$). Elem. Anal. Found (calculated) for $C_{19}H_{34}ClO_2P_2Rh$: C, 46.03 (46.12); H, 6.94 (6.93).

(POCCH_2OP^{iPr})Rh(H)(OAc) (7-Rh(H)(OAc)): ^{31}P{^{1}H} NMR (C_6D_6): δ 187.1 (dd, $J_{P\text{-}P}$ = 416 Hz, $J_{P\text{-}Rh}$ = 123 Hz), 150.5 (dd, $J_{P\text{-}P}$ = 416 Hz, $J_{P\text{-}Rh}$ = 119 Hz); ^{1}H NMR (C_6D_6): δ 6.92 (d, 1H, *J* = 8 Hz, Ar-*H*), 6.80 (t, 1H, *J* = 7 Hz, Ar-*H*), 6.51 (d, 1H, *J* = 8 Hz, Ar-*H*), 5.01 (dd, 1H, $J_{H\text{-}P}$ = 8 Hz, $J_{H\text{-}H}$ = 12, CH_2OP), 4.65 (dd, 1H, $J_{H\text{-}P}$ = 29 Hz, $J_{H\text{-}H}$ = 12 Hz, CH_2OP), 2.38 (m, 1H, C*H*Me_2), 2.29 (m, 1H, C*H*Me_2), 2.21 (m, 1H, C*H*Me_2), 2.06 (m, 1H, C*H*Me_2), 1.93 (s, 3H, O_2CCH_3), 1.49 (dd, 3H, $J_{H\text{-}P}$ = 14 Hz, $J_{H\text{-}H}$ = 8 Hz, CH(CH_3)$_2$), 1.31 (dd, 3H, $J_{H\text{-}P}$ = 15 Hz, $J_{H\text{-}H}$ = 8 Hz, CH(CH_3)$_2$), 1.23 (dd, 3H, $J_{H\text{-}P}$ = 18 Hz, $J_{H\text{-}H}$ = 7 Hz, CH(CH_3)$_2$), 1.17 (dd, 3H, $J_{H\text{-}P}$ = 18 Hz, $J_{H\text{-}H}$ = 7 Hz, CH(CH_3)$_2$), 1.16 (dd, 3H, $J_{H\text{-}P}$ = 15 Hz, $J_{H\text{-}H}$ = 8 Hz, CH(CH_3)$_2$), 1.15 (dd, 3H, $J_{H\text{-}P}$ = 15 Hz, $J_{H\text{-}H}$ = 8 Hz, CH(CH_3)$_2$), 0.97 (dd, 3H, $J_{H\text{-}P}$ = 18 Hz, $J_{H\text{-}H}$ = 7 Hz, CH(CH_3)$_2$), 0.89 (dd, 3H, $J_{H\text{-}P}$ = 16 Hz, $J_{H\text{-}H}$ = 8 Hz, CH(CH_3)$_2$), -21.05 (ddd, $J_{H\text{-}Rh}$ = 27 Hz, $J_{H\text{-}P}$ = 15 Hz, $J_{H\text{-}P}$ = 12 Hz, Rh-*H*); ^{13}C{^{1}H} NMR (C_6D_6): δ 183.2 (s, O_2*C*CH_3), 167.6 (dd, $J_{C\text{-}P}$ = 13 Hz, $J_{C\text{-}Rh}$ = 3 Hz, *Ar*-OP), 142.2 (d, $J_{C\text{-}P}$ = 7 Hz, *Ar*CH_2OP), 133.5 (br d, $J_{C\text{-}Rh}$ = 31 Hz, *Ar*-Rh), 124.2 (*Ar*-H), 121.8 (*Ar*-H), 111.5 (d, *J* = 11 Hz, *Ar*-H), 76.6 (s, *C*H_2OP), 31.0 (apparent t (dd), *J* = 10 Hz, *C*HMe_2), 28.6 (ddd, $J_{C\text{-}P}$ = 26 Hz, *J* = 2 Hz, *J* = 2 Hz, *C*HMe_2); 28.4 (apparent t (dd), *J* = 10 Hz, *C*HMe_2), 28.19 (apparent t (dd), *J* = 3 Hz, *C*HMe_2), 24.4 (s, O_2C*C*H_3), 18.2 (s, CH*Me*$_2$), 18.0 (d, $J_{C\text{-}P}$ = 3

Hz, CH*Me*$_2$), 17.8 (s, CH*Me*$_2$), 17.4 (d, $J_{C\text{-}P}$ = 9 Hz, CH*Me*$_2$), 16.9 (d, $J_{C\text{-}P}$ = 6 Hz, CH*Me*$_2$), 16.5 (s, CH*Me*$_2$), 16.4 (dd, $J_{C\text{-}P}$ = 4 Hz, $J_{C\text{-}Rh}$ = 1 Hz, CH*Me*$_2$), 16.2 (d, $J_{C\text{-}P}$ = 10 Hz, CH*Me*$_2$).

Synthesis of (POCCH$_2$OP^{iPr})Rh(S^{i}Pr$_2$) (7-Rh(S^{i}Pr$_2$)). In a Teflon screw-cap culture tube, **7-Rh(H)(Cl)** (118 mg, 0.238 mmol) was dissolved in toluene with NaO^{t}Bu (40 mg, 0.363 mmol). Diisopropyl sulfide (50 μL, 0.344 mmol) was added and the mixture was stirred overnight at RT. The volatiles were removed under vacuum and the brown solid was dissolved in pentane and filtered through silica and Celite. The volatiles were removed under vacuum and the reaction mixture was dissolved in a minimum amount of diethyl ether and placed in a -35 ^{0}C freezer to precipitate the product as a reddish-brown solid. (16.3 mg, 46%). Although this material appears to be pure by NMR spectroscopy, we have been unable to obtain satisfactory elemental analysis data. ^{31}P{^{1}H} NMR (C_6D_6): δ 186.7 (dd, $J_{P\text{-}P}$ = 345 Hz, $J_{P\text{-}Rh}$ = 174 Hz), 151.7 (dd, $J_{P\text{-}P}$ = 347 Hz, $J_{P\text{-}Rh}$ = 176 Hz); ^{1}H NMR (C_6D_6): δ 7.17 (d, 1H, J = 8 Hz, Ar-*H*), 6.96 (t, 1H, J = 7 Hz, Ar-*H*), 6.70 (d, 1H, J = 8 Hz, Ar-*H*), 4.92 (d, 2H, $J_{H\text{-}P}$ = 19 Hz, C*H*$_2$OP), 2.77 (m, 2H, S(C*H*Me$_2$)$_2$), 2.23 (overlapping m, 4H, P(C*H*Me$_2$)$_2$), 1.30 (dd, 6H, $J_{H\text{-}P}$ = 16 Hz, $J_{H\text{-}H}$ = 7 Hz, P(CH(C*H*$_3$)$_2$)$_2$), 1.26 (d, 12H, $J_{H\text{-}H}$ = 7 H, S(CH(C*H*$_3$)$_2$)$_2$), 1.25 (dd, 6H, $J_{H\text{-}P}$ = 12 Hz, $J_{H\text{-}H}$ = 7 Hz, P(CH(C*H*$_3$)$_2$)$_2$), 1.22 (dd, 6H, $J_{H\text{-}P}$ = 16 Hz, $J_{H\text{-}H}$ = 7 Hz, P(CH(C*H*$_3$)$_2$)$_2$), 1.08 (dd, 6H, $J_{H\text{-}P}$ = 12 Hz, $J_{H\text{-}H}$ = 7 Hz, P(CH(C*H*$_3$)$_2$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6): δ 168.33 (d, $J_{C\text{-}P}$ = 18 Hz, *Ar*-OP), 146.38 (m, *Ar*-Rh), 144.38 (d, $J_{C\text{-}P}$ = 13 Hz, *Ar*-OP), 123.68 (*Ar*-H), 120.04 (*Ar*-H), 110.32 (d, $J_{C\text{-}P}$ = 14 Hz, *Ar*-H), 78.50 (d, $J_{C\text{-}P}$ = 6 Hz, *C*H$_2$OP), 41.95 (s, S(*C*HMe$_2$)$_2$), 37.60 (m (overlapping signals), P(*C*HMe$_2$)$_2$), 30.95 (m, P(*C*HMe$_2$)$_2$), 28.96 (dd, $J_{C\text{-}P}$ = 20 Hz, $J_{C\text{-}Rh}$ = 3 Hz, P(*C*HMe$_2$), 24.49 (s, S(CH*Me*$_2$)$_2$), 19.05 (dd, $J_{C\text{-}P}$ = 9 Hz, $J_{C\text{-}Rh}$ = 1 Hz, P(CH(*C*H$_3$)$_2$), 18.19 (dd, $J_{C\text{-}P}$ = 8 Hz, $J_{C\text{-}Rh}$ = 3 Hz, P(CH(*C*H$_3$)$_2$), 17.81 (s, P(CH(*C*H$_3$)$_2$), 17.42 (s, P(CH(*C*H$_3$)$_2$).

Synthesis of (POCCH$_2$OP^{iPr})Rh(CO) (7-Rh(CO)). In a Teflon capped 10 mL flask, **7-Rh(S^{i}Pr$_2$)** (200 mg, 0.35 mmol) was dissolved in toluene and degassed. The flask was then filled with CO and stirred for 2 h at RT. The reaction mixture was then filtered through Celite and silica and the volatiles were removed under vacuum. The resulting yellow solid was then dissolved in pentane and placed in a -

35 °C freezer to produce yellow crystals judged to be >97% pure by ^{1}H NMR (97 mg, 57% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 202.0 (dd, $J_{P\text{-}P}$ = 310 Hz, $J_{Rh\text{-}P}$ = 145 Hz, Ar-O*P*), 166.3 (dd, $J_{P\text{-}P}$ = 310 Hz, $J_{Rh\text{-}P}$ = 150 Hz, Ar-CH_2O*P*); ^{1}H NMR (C_6D_6): δ 7.16 (d, 1H, Ar-*H*, *J* = 7.5 Hz), 6.98 (t, 1H, Ar-*H*, *J* = 7 Hz), 6.62 (d, 1H, *J* = 7 Hz), 4.75 (d, 2H, CH_2OP, $J_{H\text{-}P}$ = 18 Hz), 2.11 (m, 2H, PC*H*Me_2), 2.00 (m, 2H, PC*H*Me_2), 1.20 (dd, 6H, PCH(*Me*)$_2$, $J_{H\text{-}P}$ = 17.5 Hz, $J_{H\text{-}H}$ = 7.5 Hz), 1.15 (dd, 6H, PCH(*Me*)$_2$, $J_{H\text{-}P}$ = 14.5 Hz, $J_{H\text{-}H}$ = 7 Hz), 1.15 (dd, 6H, PCH(*Me*)$_2$, $J_{H\text{-}P}$ = 17.5 Hz, $J_{H\text{-}H}$ = 7 Hz), 1.07 (dd, 6H, PCH(*Me*)$_2$, $J_{H\text{-}P}$ = 13.5 Hz, $J_{H\text{-}H}$ = 7 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 197.35 (ddd, $J_{Rh\text{-}C}$ = 56 Hz, $J_{P\text{-}C}$ = 14 Hz, $J_{P\text{-}C}$ = 13 Hz, Rh-*C*O), 169.88 (dd, $J_{C\text{-}P}$ = 16 Hz, $J_{C\text{-}Rh}$ = 3 Hz, *Ar*-OP), 148.04 (ddd, $J_{Rh\text{-}C}$ = 29 Hz, $J_{C\text{-}P}$ = 10 Hz, $J_{C\text{-}P}$ = 9 Hz, *C*-Rh), 143.02 (d, $J_{C\text{-}P}$ = 11 Hz, *Ar*-CH_2OP), 127.51 (s, *Ar*-H), 120.35 (s, *Ar*-H), 111.37 (d, $J_{C\text{-}P}$ = 14 Hz, *Ar*-H), 77.75 (t, $J_{C\text{-}P}$ = 3 Hz, *C*H_2OP), 31.6 (ddd, $J_{C\text{-}P}$ = 26 Hz, *J* = 3 Hz, *J* = 2 Hz, P*C*HMe_2), 30.69 (ddd, $J_{C\text{-}P}$ = 22 Hz, *J* = 4 Hz, *J* = 3 Hz, P*C*HMe_2), 18.55 (d, $J_{C\text{-}P}$ = 4 Hz, P(CH*Me*$_2$)$_2$), 18.48 (s, $J_{C\text{-}P}$ = 5 Hz, P(CH*Me*$_2$)$_2$) 17.75 (s, P(CH*Me*$_2$), 17.50 (s, P(CH*Me*$_2$). IR: 1948 cm^{-1}, ν_{CO}.

Synthesis of 1-(^{t}Bu$_2$PO)-3-(^{t}Bu$_2$POCH$_2$)(C$_6$H$_4$) (8-H). To a solution of 3-hydroxybenzyl alcohol (0.320 g, 2.64 mmol) in THF, sodium hydride (0.189 g, 7.71 mmol) was added slowly while stirring. The mixture was refluxed for 1 h, and a solution of Cl$P^{t}Bu_2$ (0.949 g, 5.25 mmol) in THF was added dropwise. The reaction was refluxed overnight. The volatiles were removed under vacuum and the residue was extracted with toluene and filtered through Celite. The solvent was removed under vacuum to give a colorless oil determined to be >95% pure by ^{1}H NMR spectroscopy (0.907 g, 2.20 mmol, 83%). ^{31}P{^{1}H} NMR (C_6D_6): δ 164.6 (s), 153.2 (s); ^{1}H NMR (C_6D_6): δ 6.83 (d, 1H, *J* = 8 Hz, Ar-*H*) 6.80 (s, 1H, Ar-*H*), 6.74 (t, 1H, *J* = 8 Hz, Ar-*H*), 6.58 (d, 1H, *J* = 7 Hz, Ar-*H*), 4.42 (d, 2H, *J* = 8 Hz, CH_2OP), 0.78 (d, 18H, $J_{H\text{-}P}$ = 12 Hz, PC(*Me*$_3$)$_2$), 0.76 (d, 18H, $J_{H\text{-}P}$ = 12 Hz, PC(*Me*$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6): δ 160.48 (d, $J_{C\text{-}P}$ = 9 Hz, *Ar*-OP), 141.80 (d, $J_{C\text{-}P}$ = 9 Hz, *Ar*-CH_2OP), 120.53 (s, *Ar*-H), 117.77 (d, $J_{C\text{-}P}$ = 10 Hz, *Ar*-H), 117.54 (d, $J_{C\text{-}P}$ = 11 Hz, *Ar*-H), 75.68 (d, $J_{C\text{-}P}$ = 23 Hz, *C*H_2OP), 35.73 (d, $J_{C\text{-}P}$ = 27 Hz, P(*C*Me$_3$)$_2$), 35.41 (d, $J_{C\text{-}P}$ = 26 Hz, P(*C*Me$_3$)$_2$), 27.69 (d, $J_{C\text{-}P}$ = 16 Hz, P(C*Me*$_3$)$_2$), 27.57 (d, $J_{C\text{-}P}$ = 17 Hz, P(C*Me*$_3$)$_2$). HRMS (ESI+TOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{44}O_2P_2$ 413.2733; found 413.2750.

Synthesis of ($POCCH_2OP^{tBu}$)Rh(H)(Cl) (8-Rh(H)(Cl)). In a Teflon screw-top flask, **8-H** (244 mg, 0.591 mmol) and $[(COD)RhCl]_2$ (146 mg, 0.296 mmol) were dissolved in toluene and heated at 90 °C for 18 h. The reaction mixture was passed through silica and Celite and recrystallized from toluene and pentane to produce greenish-yellow crystals judged to be >97% pure by ^{1}H NMR spectroscopy (198 mg, 61%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 188.6 (dd, $J_{P\text{-}P}$ = 398 Hz, $J_{P\text{-}Rh}$ = 117 Hz), 161.7 (dd, $J_{P\text{-}P}$ = 398 Hz, $J_{P\text{-}Rh}$ = 117 Hz); ^{1}H NMR (C_6D_6): δ 6.97 (d, 1H, J = 8 Hz, Ar-*H*), 6.89 (t, 1H, J = 7 Hz, , Ar-*H*), 6.49 (d, 1H, J = 7 Hz, Ar-*H*), 4.73 (dd, 1H, $J_{H\text{-}P}$ = 16 Hz, $J_{H\text{-}H}$ = 13 Hz, CH_2OP), 4.57 (dd, 1H, $J_{H\text{-}P}$ = 17 Hz, $J_{H\text{-}H}$ = 13 Hz, CH_2OP), 1.41 (d, 9H, $J_{H\text{-}P}$ = 14 Hz, PC(Me_3)$_2$), 1.40 (d, 9H, $J_{H\text{-}P}$ = 13 Hz, PC(Me_3)$_2$), 1.39 (d, 9H, $J_{H\text{-}P}$ = 14 Hz, PC(Me_3)$_2$), -26.84 (apparent dt, 1H, $J_{H\text{-}Rh}$ = 50 Hz, $J_{H\text{-}P}$ = 12 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 169.7 (dd, $J_{C\text{-}P}$ = 12 Hz, $J_{C\text{-}Rh}$= 3 Hz, *Ar*-OP), 142.1 (d, $J_{C\text{-}P}$ = 6 Hz , *Ar*-CH_2OP), 134.2 (m, *Ar*-Rh), 125.7 (*Ar*-H), 121.5 (*Ar*-H), 112.2 (d, $J_{C\text{-}P}$ = 12 Hz, *Ar*-H), 75.9 (d, $J_{C\text{-}P}$ = 3 Hz, *C*H_2OP,), 41.3 (dd, $J_{C\text{-}P}$ = 10 Hz, $J_{C\text{-}Rh}$ = 6 Hz, P*C*Me$_3$), 40.6 (dd, $J_{C\text{-}P}$ = 10 Hz, $J_{C\text{-}Rh}$ = 7 Hz, P*C*Me$_3$), 39.7 (ddd, $J_{C\text{-}P}$ = 18 Hz, $J_{C\text{-}Rh}$ = 6 Hz, $J_{C\text{-}P}$ = 2 Hz, P*C*Me$_3$), 38.9 (ddd, $J_{C\text{-}P}$ = 13 Hz, $J_{C\text{-}Rh}$ = 6 Hz, $J_{C\text{-}P}$ = 3Hz, P*C*Me$_3$), 29.4 (d, $J_{C\text{-}P}$ = 5 Hz, PC*Me*$_3$), 29.2 (d, $J_{C\text{-}P}$ = 5 Hz, PC*Me*$_3$), 28.15 (d, $J_{C\text{-}P}$ = 5 Hz, PC*Me*$_3$), 28.08 (d, $J_{C\text{-}P}$ = 5 Hz, PC*Me*$_3$).

Synthesis of ($POCCH_2OP^{tBu}$)Rh(S^iPr_2) (8-Rh(S^iPr_2)). In a Teflon screw-cap vial, **8-Rh(H)(Cl)** (150 mg, 0.273 mmol), NaO^tBu (45 mg, 0.41 mmol), and diisopropylsulfide (80 μL, 0.546 mmol) were dissolved in toluene and stirred overnight at RT. The reaction mixture was passed through Celite, and then the volatiles were removed under vacuum yielding a brown solid, which was recrystallized from pentane (138 mg, 80%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 189.3 (dd, $J_{P\text{-}P}$ = 335 Hz, $J_{P\text{-}Rh}$ = 184 Hz), 160.9 (dd, $J_{P\text{-}P}$ = 331 Hz, $J_{P\text{-}Rh}$ = 176 Hz); ^{1}H NMR (C_6D_6): δ 6.96 (d, 1H, J = 8 Hz, Ar-*H*), 6.86 (t, 1H, J = 8 Hz, Ar-*H*), 6.63 (d, 1H, J = 7 Hz, Ar-*H*), 4.87 (d, 2H, $J_{H\text{-}P}$ = 19 Hz, CH_2OP), 2.85 (m, 2H, S(C*H*Me$_2$)$_2$), 1.44 (d, 18H, $J_{H\text{-}P}$ = 12 Hz, P(C*Me*$_3$)$_2$), 1.28 (d, 18H, $J_{H\text{-}P}$ = 12 Hz, P(C*Me*$_3$)$_2$), 1.29 (d, 12 H, J = 7 Hz, S(C(*Me*$_2$)$_2$)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 168.4 (d, $J_{C\text{-}P}$ = 15 Hz, *Ar*-OP), 145.2 (m, *Ar*-Rh), 143.9 (d, $J_{C\text{-}P}$ = 9 Hz, *Ar*-CH_2OP), 123.1 (*Ar*-H), 120.0 (*Ar*-H), 110.2 (d, $J_{C\text{-}P}$ = 12 Hz, *Ar*-H), 78.3 (d, $J_{C\text{-}P}$ = 5 Hz,

CH_2OP), 40.9 (s, S(*C*HMe_2)$_2$), 40.2 (m, P*C*$(CH_3)_3$), 39.8 (dd, $J_{C\text{-}P}$ = 10 Hz, $J_{C\text{-}Rh}$ = 4 Hz, P*C*$(CH_3)_3$), 37.6 (s, P*C*$(CH_3)_3$), 29.8 (d, $J_{C\text{-}P}$ = 8 Hz, P(C*Me*$_3$)$_2$), 29.7 (d, $J_{C\text{-}P}$ = 8 Hz, P(C*Me*$_3$)$_2$), 25.5 (s, S(CH*Me*)$_2$). Elem. Anal. Found (Calculated) for $C_{29}H_{55}O_2P_2RhS$: C, 55.09 (55.06); H, 8.57 (8.76); S, 4.93 (5.07).

Synthesis of (POCCH$_2$OP^{tBu})Rh(CO) (8-Rh(CO)). In a Teflon capped 10 mL flask, **8-Rh(S^{i}Pr$_2$)** (65 mg, 0.104 mmol) was dissolved in toluene and degassed. The flask was then filled with CO and stirred for 2 h at RT. The reaction mixture was filtered through silica and Celite and the volatiles were removed under vacuum, resulting in a yellow solid judged to be >98% pure by ^{1}H NMR (34 mg, 61% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 210.6 (dd, $J_{P\text{-}P}$ = 300 Hz, $J_{P\text{-}Rh}$ = 144 Hz), 177.2 (dd, $J_{P\text{-}P}$ = 300 Hz, $J_{P\text{-}Rh}$ = 150 Hz); ^{1}H NMR (C_6D_6): δ 7.14 (d, 1H, *J* = 8 Hz, Ar-*H*), 6.99 (dt, 1H, *J* = 8 Hz, $J_{H\text{-}P}$ = 1 Hz, 1H, Ar-*H*), 6.61 (d, 1H, *J* = 8 Hz, Ar-*H*), 4.78 (d, 2H, $J_{C\text{-}P}$ = 17 Hz, C*H*$_2$OP), 1.33 (d, 18H, $J_{C\text{-}P}$ = 14 Hz, P(C*Me*$_3$)$_2$), 1.30 (d, 18H, $J_{C\text{-}P}$ = 14 Hz, P(C*Me*$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6): 199.2 (apparent dt (ddd), $J_{C\text{-}Rh}$ = 57 Hz, $J_{C\text{-}P}$ = 14 Hz, Rh-*C*O), 170.8 (dd, $J_{C\text{-}P}$ = 15 Hz, $J_{C\text{-}Rh}$ = 3 Hz, *Ar*-OP), 148.6 (apparent dt (ddd), $J_{C\text{-}Rh}$ = 29 Hz, $J_{C\text{-}P}$ = 10 Hz, *Ar*-Rh) 142.5 (d, $J_{C\text{-}P}$ = 10 Hz, *Ar*-CH$_2$OP), 127.3 (s, *Ar*-H), 120.0 (s, *Ar*-H), 111.2 (d, *J* = 14 Hz), 77.4 (dd, $J_{C\text{-}P}$ = 3 Hz, $J_{C\text{-}Rh}$ = 1 Hz, *C*H$_2$OP), 39.9 (m, contains both P(*C*Me$_3$)$_2$ signals), 28.9 (d, $J_{C\text{-}P}$ = 7 Hz, P(C*Me*$_3$)$_2$), 28.7 (d, $J_{C\text{-}P}$ = 7 Hz, P(C*Me*$_3$)$_2$). IR: 1943 cm^{-1}, ν_{CO}.

Synthesis of 2,2'4,4'-tetramethyldiphenylamine (A). In a 250 mL Schlenk flask, 2,4-dimethylaniline (5.84 mL, 48 mmol), 2,4-dimethylbromobenzene (6.08 mL, 45 mmol), bis(diphenylphosphino)ferrocene (DPPF, 0.498 g, 0.90 mmol), $Pd(OAc)_2$ (0.100 g, 0.45 mmol Pd), and NaOCMe$_2$Et (7.06 g, 63 mmol) were refluxed in ca. 100 mL of toluene under argon. After 16 h, the mixture was filtered through silica and Celite and the filtrate was collected. All of the volatiles were removed under vacuum and a product judged to be >98% pure by ^{1}H NMR recrystallized from pentane. Yield: 7.51 g (74%). ^{1}H NMR ($CDCl_3$): δ 7.08 (s, 2H, Ar-*H*), 6.98 (d, 2H, *J* = 8 Hz, Ar-*H*), 6.90 (d, 2H, *J* = 8 Hz, Ar-*H*), 5.11 (br s, 1H, N-*H*), 2.36 (s, 6H, Ar-C*H*3), 2.30 (s, 6H, Ar-C*H*3); ^{13}C{^{1}H} NMR

($CDCl_3$): δ 139.9 (s, N-*Ar*), 131.6 (s, *Ar*-H), 130.8 (s, *Ar*-Me), 127.76 (s, *Ar*-Me), 127.75 (s, *Ar*-H), 118.7 (s, *Ar*-H), 20.8 (s, Ar-*Me*), 17.9 (s, Ar-*Me*).

Synthesis of 2,2'-dibromo-4,4',6,6'-tetramethyldiphenylamine (B). In a Schlenk flask under ambient atmosphere, **A** (7.44 g, 33 mmol) was dissolved in dichloromethane. *N*-bromosuccinimide (11.75 g, 66 mmol) was added slowly and the reaction mixture was left to stir overnight at RT. The reaction mixture was then passed through Celite and the volatiles were removed by vacuum. The resulting brown solid was dissolved in pentane and filtered through silica and Celite. The volatiles were removed, and a white solid was obtained by recrystallizing the product from ethanol. The purity of product judged to be >97% by ^{1}H NMR spectroscopy. Yield: 8.91 g (70%). ^{1}H NMR ($CDCl_3$): δ 7.24 (s, 2H, Ar-*H*), 6.81 (s, 2H, Ar-*H*), 5.49 (br s, 1H, N-*H*), 2.42 (s, Ar-*Me*), 1.80 (s, Ar-*Me*); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.9 (s, *Ar*-N), 133.1, 132.1, 131.4, 131.0, 118.4 (s, *Ar*-Br), 20.5 (s, Ar-*Me*), 19.7 (s, Ar-*Me*).

Synthesis of *N*-methyl-2,2'-dibromo-4,4',6,6'-tetramethyldiphenylamine (C). In a Schlenk flask, **B** (1.26 g, 3.3 mmol) was dissolved in THF and treated with $KN(SiMe_3)_2$ (5 mL, 3.3 mmol, 0.66 M in toluene). The solution was stirred at RT for 2 h and iodomethane (410 μL, 6.6 mmol) was added. The solution was stirred overnight at RT and filtered through Celite and silica gel. The product was isolated as a yellow solid after recrystallizing from pentane. The purity of the product was judged to be >97% pure by ^{1}H NMR. Yield: 767 mg (58%). ^{1}H NMR (C_6D_6): δ 7.25 (s, 2H, Ar-*H*), 6.56 (s, 2H, Ar-*H*), 3.49 (s, 3H, N-*Me*), 1.98 (s, 6H, Ar-*Me*), 1.90 (s, 6H, Ar-*Me*). ^{13}C{^{1}H} NMR (C_6D_6): δ 143.6 (s, *Ar*-N), 137.0 (s, *Ar*), 134.3 (s, *Ar*), 133.9 (s, *Ar*), 132.6 (s, *Ar*), 121.2 (s, *Ar*-Br), 43.5 (s, N*Me*), 20.9 (s, Ar-*Me*), 20.1 (s, Ar-*Me*).

Synthesis of ($^{o\text{-}Me}$PNP)Me (9-Me). In a Schlenk flask, **C** (752 mg, 1.89 mmol) was dissolved in Et_2O and *n*-BuLi (1.6 mL of 2.5M solution in hexanes, 4.0 mmol) was added slowly. The mixture was stirred for 2 h at RT and ClP^iPr_2 (635 mg, 4.16 mmol) was added slowly. The reaction was allowed to stir overnight and the volatiles were removed under vacuum. The dry solid was dissolved in toluene and

passed through a pad of Celite. Pure product was recrystallized from Et_2O to form a white solid (418 mg, 45%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -2.28; ^1H NMR (C_6D_6): δ 7.10 (s, 2H, Ar-*H*), 6.85 (s, 2H, Ar-*H*), 3.58 (s, 3H, N-*Me*), 2.40 (s, 6H, Ar-*Me*), 2.18 (s, 6H, Ar-*Me*), 1.93 (m, 2H, P(C*H*Me$_2$)$_2$), 1.59 (m, 2H, P(C*H*Me$_2$)$_2$), 1.12 (dd, 6H, J_{H-P} = 11 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$), 1.11 (dd, 6H, J_{H-P} = 13 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$), 0.93 (dd, 6H, J_{H-P} = 14 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$), 0.87 (dd, 6H, J_{H-P} = 12 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 154.5 (m, *Ar*-N), 134.8 (m, *Ar*), 134.76 (s, *Ar*), 133.8 (m, *Ar*-P), 132.5 (s, *Ar*), 131.7 (s, *Ar*), 46.7 (m, N-*Me*), 25.6 (m, P*C*HMe$_2$), 25.4 (m, P*C*HMe$_2$), 23.8 (t, J_{C-P} = 9 Hz, PCH*Me*$_2$), 22.3 (t, J_{C-P} = 10 Hz, PCH*Me*$_2$), 21.2 (t, J_{C-P} = 8 Hz, PCH*Me*$_2$), 21.0 (t, J_{C-P} = 8 Hz, PCH*Me*$_2$), 20.7 (s, Ar-*Me*), 19.4 (t, J_{C-P} = 7 Hz, Ar-*Me*). Elem. Anal. Found (Calculated) for $C_{29}H_{47}NP_2$: C, 73.75 (73.85); H, 10.15 (10.04).

Synthesis of ($^{o\text{-Me}}$PNP)Rh(Me)(Cl) (9-Rh(Me)(Cl)). In a J. Young tube, **9-Me** (104 mg, 0.22 mmol) and [Rh(COE)$_2$Cl] (79 mg, 0.11 mmol) were dissolved in C_6D_6 and the solution was heated at 70 °C for 18 h. The reaction mixture was filtered through Celite and silica and recrystallized from THF to produce a green solid judged to be >95% pure by ^1H NMR spectroscopy (44 mg, 33% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.9 (dd, J_{P-P} = 414 Hz, J_{P-Rh} = 111 Hz), 29.3 (dd, J_{P-P} = 415 Hz, J = 109 Hz); ^1H NMR (C_6D_6): δ 6.84 (d, 1H, J_{H-P} = 8 Hz, Ar-*H*), 6.73 (d, 1H, J_{H-P} = 6 Hz, Ar-*H*), 6.66 (s, 1H, Ar-*H*), 2.89 (m, 1H, P(C*H*Me$_2$)$_2$), 2.46 (m, 3H, Rh-*Me*), 2.50-2.36 (m, 2H, overlapping P(C*H*Me$_2$)$_2$), 2.26 (m, 1H, P(C*H*Me$_2$)$_2$), 2.19 (s, 3H, Ar-*Me*), 2.16 (s, 3H, Ar-*Me*), 1.72 (s, 3H, Ar-*Me*), 1.62 (dd, 3H, J_{H-P} = 15 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$), 1.61 (s, 3H, Ar-*Me*), 1.38 (dd, 3H, J_{H-P} = 15 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$), 1.25 (dd, 3H, J_{H-P} = 16 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$), 1.20 (dd, 3H, J_{H-P} = 16 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$), 1.16 (dd, 3H, J_{H-P} = 15 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$), 1.11 (dd, 3H, J_{H-P} = 14 Hz, J_{H-H} = 8 Hz, P(CH*Me*$_2$)$_2$), 1.06 (dd, 3H, J_{H-P} = 13 Hz, J_{H-H} = 7 Hz, P(CH*Me*$_2$)$_2$), 1.57 (dd, 3H, J_{H-P} = 13 Hz, J_{H-H} = 6 Hz, P(CH*Me*$_2$)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 162.5 (d, J = 19 Hz, *Ar*-N), 162.1 (d, J = 19 Hz, *Ar*-N), 135.3, 134.0, 129.8, 129.5, 129.3 (d, J = 11 Hz), 126.4 (d, J = 7 Hz), 126.3 (d, J = 10 Hz), 125.2 (d, J = 7 Hz), 123.4 (d, J = 39 Hz, *Ar*-P), 119.0 (d, J = 39 Hz, *Ar*-P), 27.3(m, P*C*HMe$_2$), 26.6 (m, P*C*HMe$_2$),

25.2 (m, P*C*HMe$_2$), 23.6 (m, P*C*HMe$_2$), 21.7, 21.1, 20.94, 20.91, 20.7, 20.6, 19.3, 19.0 (d, J = 4 Hz), 18.8, 18.7 (d, J = 4 Hz), 18.3, 17.8, 2.8 (br d, $J_{C\text{-}Rh}$ = 29 Hz, Rh-*Me*).

Synthesis of ($^{o\text{-}Me}$PNP)Rh(H$_2$) (9-Rh(H$_2$)). In a Schlenk flask **(9-Rh(Me)(Cl))** (180 mg, 0.30 mmol) and $NaBH_4$ (30 mg, 0.79 mmol) was dissolved in degassed isopropanol and the reaction was stirred for 3 h at RT. The volatiles were removed and the resulting solid was dissolved in diethyl ether and passed through a pad of Celite and the volatiles were removed under vacuum. Orange crystals were formed (60 mg, 33%) by slow diffusion of pentane into a saturated toluene solution. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 58.4 (d, $J_{P\text{-}Rh}$ = 130 Hz); ^1H NMR (C_6D_6): δ 6.79-6.77 (m, 4H, overlapping Ar-*H*), 2.23 (s, 6H, Ar-*Me*), 2.04 (m, 2H, P(C*H*Me$_2$)$_2$), 1.96 (m, 2H, P(C*H*Me$_2$)$_2$), 1.81 (s, 6H, Ar-*Me*), 1.41 (apparent q (dvt), 6H, J = 8 Hz, P(CH*Me*$_2$)$_2$), 1.11 (apparent q (dvt), 6H, J = 7 Hz, P(C*H*Me$_2$)$_2$), 0.99 (apparent q (dvt), 6H, J = 8 Hz, P(C*H*Me$_2$)$_2$), 0.93 (apparent q (dvt), 6H, J = 8 Hz, P(C*H*Me$_2$)$_2$), -13.4 (dvt, 2H, $J_{Rh\text{-}H}$ = 20 Hz, $J_{P\text{-}H}$ = 9 Hz, Rh-*H*$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 163.8 (dvt, $J_{C\text{-}P}$ = 12 Hz, $J_{C\text{-}Rh}$ = 2 Hz, *Ar*-N), 134.8 (s, *Ar*-H), 129.4 (s, *Ar*-H), 125.1 (dvt, $J_{C\text{-}P}$ = 5 Hz, $J_{C\text{-}Rh}$ = 1 Hz, *Ar*-Me), 124.9 (vt, J = 4 Hz, *Ar*-Me), 122.5 (vt, J = 18 Hz, *Ar*-P), 28.0 (dvt, $J_{C\text{-}Rh}$ = 2 Hz, $J_{C\text{-}P}$ = 10 Hz, P(*C*HMe$_2$)$_2$, 22.2 (vt, $J_{C\text{-}P}$ = 13 Hz, P(*C*HMe$_2$)$_2$), 21.74 (vt, $J_{C\text{-}P}$ = 4 Hz, P(CH*Me*$_2$)), 21.68 (s, Ar-*Me*), 20. 7 (s, Ar-*Me*), 19.4 (vt, $J_{C\text{-}P}$ = 3 Hz, , P(CH*Me*$_2$)), 18.9 (vt, $J_{C\text{-}P}$ = 5 Hz, P(CH*Me*$_2$)), 18.1 (s, P(CH*Me*$_2$)). Elem. Anal. Found (Calculated) for $C_{28}H_{46}NP_2Rh$: C, 59.71(59.89); H, 8.07 (8.26).

Observation of ($^{o\text{-}Me}$PNP)Rh(HD) (9-Rh(HD)). (9-Rh(Me)(Cl)) (64 mg, 0.11 mmol) and $NaBH_4$ (22 mg, 0.57 mmol) was combined in a mixture of C_6D_6 and *d$_4$*-methanol and stirred at room temperature for 4 h. The volatiles were removed under vacuum and the product was extracted with diethyl ether and filtered through a pad of Celite. The volatiles were removed under vacuum, and the solid was washed with pentane. A mixture containing >85% of **(9-Rh(HD))** and **(9-Rh(H$_2$))** by $^{31}P\{^1H\}$ NMR was produced. Data for the ^1H signal of the H in HD in **9-Rh(HD)** follow. ^1H NMR (C_6D_6): δ -13.33 (dtvt, $J_{Rh\text{-}H}$ = 20 Hz, $J_{H\text{-}D}$ = 20 Hz, $J_{H\text{-}P}$ = 9 Hz).

Synthesis of (PCP^{iPr})Rh(H)(Cl) (10-Rh(H)(Cl)). In a Teflon screw-top flask, **10-H** (270 mg, 0.800 mmol) and $[(COD)Rh(OAc)]_2$ (216 mg, 0.400 mmol) were dissolved in toluene and heated at 80 °C for 5 h. The reaction mixture was filtered through a pad of Celite, and the volatiles were removed under vacuum to produce **10-Rh(H)(OAc)** as a light reddish-brown solid, which was characterized *in situ*. The solid was dissolved in toluene and Me_3SiCl (150 μL, 1.18 mmol) was added to the solution. After 3 h the volatiles were removed from solution under vacuum, and the resulting solid was dissolved in toluene and filtered through a pad of Celite and silica. **10-Rh(H)(Cl)** (223 mg, 58.5 %) was recrystallized as red square crystals judged to be >97% pure from a minimum amount of toluene layered with pentane in a -35 °C freezer. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 63.0 (d, $J_{P\text{-}Rh}$ = 114 Hz); ^1H NMR (C_6D_6): δ 6.98 (apparent q (heavy second order effects), 1H, J = 9 Hz, J = 6 Hz, Ar-*H*), 6.94 (d, 2H, J = 8 Hz, Ar-*H*), 2.82 (dvt, 2H, $J_{H\text{-}H}$ = 17 Hz, $J_{H\text{-}P}$ = 4 Hz, C*H*$_2$P), 2.72 (dvt, 2H, $J_{H\text{-}H}$ = 18 Hz, $J_{H\text{-}P}$ = 4 Hz, C*H*$_2$P), 2.52 (m, 2H, P(C*H*Me$_2$)$_2$), 1.85 (m, 2H, P(C*H*Me$_2$)$_2$), 1.25 (apparent q (dvt), 6H, J = 8 Hz, P(CH(C*H*$_3$)$_2$), 1.24 (apparent q (dvt), 6H, J = 7 Hz, P(CH(C*H*$_3$)$_2$), 0.91 (apparent q (dvt), 6H, J = 8 Hz, P(CH(C*H*$_3$)$_2$), 0.88 (apparent q (dvt), 6H, J = 8 Hz, P(CH(C*H*$_3$)$_2$), -24.85 (dvt, 1H, $J_{H\text{-}Rh}$ = 44 Hz, $J_{H\text{-}P}$ = 13 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 159.2 (d, $J_{C\text{-}Rh}$ = 31 Hz, *C*-Rh), 150.6 (vt, $J_{C\text{-}P}$ = 10 Hz, *C*CH$_2$P), 123.4 (s), 123.1 (vt, $J_{C\text{-}P}$ = 9 Hz, *Ar*-C-CH$_2$P) 32.2 (dvt, $J_{C\text{-}P}$ = 12 Hz, $J_{C\text{-}Rh}$ = 2 Hz, Ar-*C*P^{i}Pr$_2$), 24.33 (vt, $J_{C\text{-}P}$ = 11 Hz, P*C*Me$_2$), 24.26 (vt, $J_{C\text{-}P}$ = 11 Hz, P*C*Me$_2$,), 19.0 (s, PCH(*C*H$_3$)$_2$), 18.9 (s, PCH(*C*H$_3$)$_2$), 18.7 (s, PCH(*C*H$_3$)$_2$), 17.6 (s, PCH(*C*H$_3$)$_2$).

(PCP^{iPr})Rh(H)(OAc) (10-Rh(H)(OAc)). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 66.6 (d, $J_{P\text{-}Rh}$ = 115 Hz); ^1H NMR (C_6D_6): δ 6.89 (t, 1H, J = 7 Hz, Ar-*H*), 6.85 (d, 2H, J = 7 Hz, Ar-*H*), 2.94 (d, 2H, $J_{H\text{-}P}$ = 16 Hz, C*H*$_2$P), 2.80 (d, 2H, 16Hz, C*H*$_2$P), 2.34 (m, 2H, PC*H*Me$_2$), 1.97 (s, 3H, O$_2$CC*H*$_3$), 1.85 (m, 2H, PC*H*Me$_2$), 1.15 (apparent q (dvt), 6H, J = 8 Hz, PCH(C*H*$_3$)$_2$), 1.08 (m, 12H, PCH(C*H*$_3$)$_2$), 0.96 (apparent q (dvt), 6H, J = 7 Hz, PCH(C*H*$_3$)$_2$), -21.23 (dvt, 1H, $J_{H\text{-}Rh}$ = 30 Hz, $J_{H\text{-}P}$ = 14 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 181.8 (s, O$_2$*C*Me), 157.5 (d, $J_{C\text{-}Rh}$ = 31 Hz, *C*-Rh), 148.1 (vt, $J_{C\text{-}P}$ = 8 Hz, *C*CH$_2$P), 122.7 (s, *Ar*-H), 122.2 (vt, $J_{C\text{-}P}$ = 8 Hz, *Ar*-H), 34.1 (vtd, $J_{C\text{-}P}$ = 14 Hz, $J_{C\text{-}Rh}$ = 3 Hz, Ar-*C*H$_2$P^{i}Pr$_2$), 25.11 (vt, P*C*Me$_2$, $J_{C\text{-}P}$ = 10 Hz),

24.6 (s, O_2CCH_3), 24.4 (vt, P*C*Me$_2$, $J_{C\text{-}P}$ = 11 Hz), 19.6 (s, PCH(*C*H$_3$)$_2$), 19.0 (s, PCH(*C*H$_3$)$_2$), 18.4 (s, PCH(*C*H$_3$)$_2$), 18.2 (s, PCH(*C*H$_3$)$_2$).

Synthesis of (PCP^{iPr})Rh(S^{i}Pr$_2$) (10-Rh(S^{i}Pr$_2$)). In a Schlenk flask, **10-Rh(H)(Cl)** (125.0 mg, 0.262 mmol), NaO^{t}Bu (37.8 mg, 0.393 mmol), and diisopropyl sulfide (75 μL, 0.524 mmol) were dissolved in toluene and stirred at RT for 1 h. The volatiles were removed under vacuum, and the solid was dissolved in pentane and filtered through silica and Celite. **10-Rh(S^{i}Pr$_2$)** was recrystallized from a minimum amount of pentane in a -35 °C freezer to produce orange brown crystals (63 mg, 43% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 56.4 (d, $J_{P\text{-}Rh}$ = 164 Hz); ^1H NMR (C_6D_6): δ 7.21 (d, 2H, *J* = 8 Hz, Ar-*H*), 7.14 (t, 1H, *J* = 8 Hz, Ar-*H*), 3.05 (br s, 4H, C*H*$_2$P^{i}Pr$_2$), 2.80 (m, 2H, S(C*H*Me$_2$)$_2$), 1.99 (m, 4H, PC*H*Me$_2$), 1.36 (d, 12H, *J* = 7 Hz, S(CH(C*H*$_3$)$_2$), 1.24 (apparent q (dvt), 12H, *J* = 7 Hz, P(CHC*H*$_3$)$_2$), 1.06 (apparent q (dvt), 12H, *J* = 7 Hz, P(CHC*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 173.8 (br d, $J_{C\text{-}Rh}$ = 41 Hz, *C*-Rh), 150.6 (dvt, *Ar*-CH$_2$P, $J_{C\text{-}P}$ = 11 Hz, $J_{C\text{-}Rh}$ = 3 Hz), 122.2 (s, *Ar*-H), 120.5 (vt, $J_{C\text{-}P}$ = 9 Hz, *Ar*-H), 40.9 (s, S(*C*Me$_2$)$_2$), 37.2 (dvt, $J_{C\text{-}P}$ = 11 Hz, $J_{C\text{-}Rh}$ = 5 Hz, Ar-*C*H$_2$-P), 26.2 (vt, $J_{C\text{-}P}$ = 8 Hz, P*C*HMe$_2$), 24.8 (s, S(CH(*C*H$_3$)$_2$)$_2$), 20.3 (vt, $J_{C\text{-}P}$ = 3 Hz, P(CH(*C*H$_3$)$_2$)$_2$), 18.9 (s, P(CH(*C*H$_3$)$_2$)$_2$). Elem. Anal. Found (Calculated) for $C_{26}H_{49}O_2P_2RhS$: C, 55.75 (55.91); H, 8.96 (8.84).

Catalytic Dimerization of Terminal Alkynes. In a typical run, catalyst (0.0053 mmol), alkyne (0.530 mmol) were mixed in C_6D_6 to make an 800 μL solution in a J. Young tube. The reactions were run at 1% catalyst loading at 80 °C. Upon completion of the reaction, 5 μL 1,4-dioxane was added as an internal standard. Products were identified by ^1H NMR and comparison to literature data.[43] The product yield was determined by ^1H NMR integration versus the 1,4-dioxane standard.

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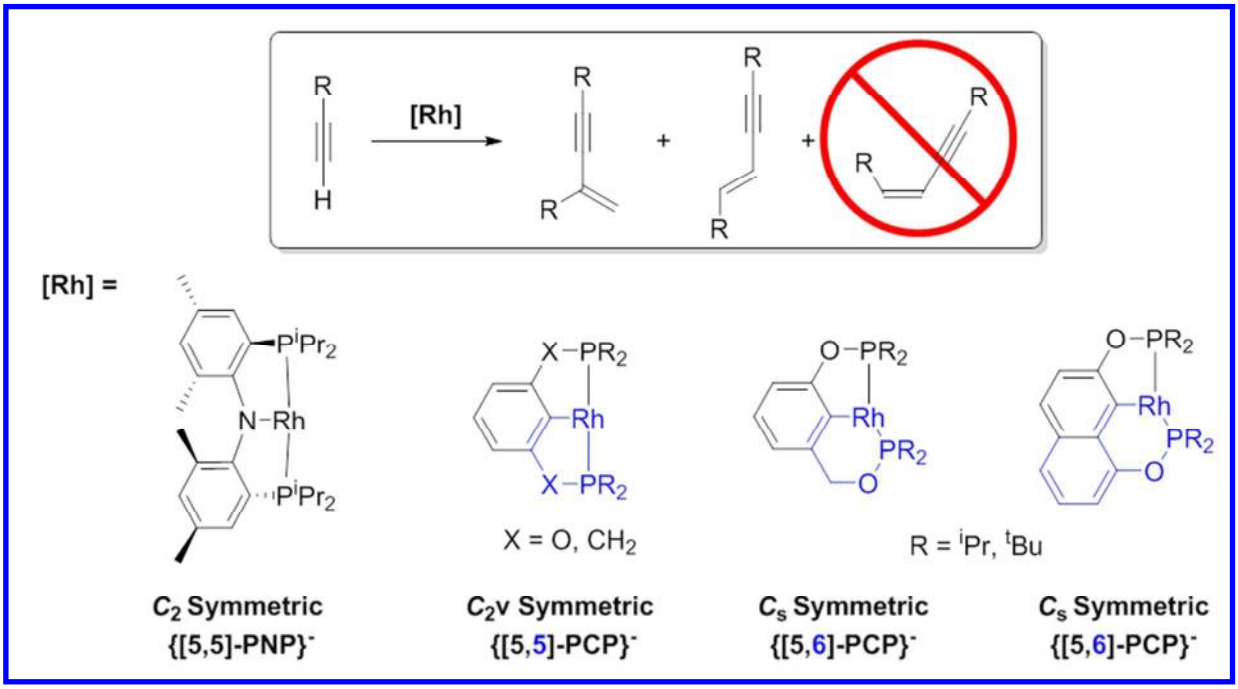
Supporting Information Available. Graphical representations of NMR spectra and select experimental details. This material is available via the Internet free of charge at http://pubs.acs.org.

Table of Contents artwork



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