Articles

Thioether, Dinitrogen, and Olefin Complexes of (PNP)Rh: Kinetics and Thermodynamics of Exchange and Oxidative Addition Reactions

Sylvain Gatard, Chengyun Guo, Bruce M. Foxman, and Oleg V. Ozerov*

Department of Chemistry, Brandeis University, MS 015, 415 South Street, Waltham, Massachusetts 02454

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A variety of (PNP)Rh−L complexes (where L = organic sulfide or sulfoxide, dinitrogen, or *tert*-butylethylene) have been synthesized by trapping transient (PNP)Rh (**1**) in situ. Equilibrium studies established the relative affinity of the (PNP)Rh fragment (**1**) for various L in the following order (of decreasing affinity): Ph_2SO > $SBu^n{}_2$ > SPhMe > dibenzothiophene > SPh_2 > benzothiophene > $SPr^i{}_2$ > thiophene ≈ SBu^tMe > $SBu^s{}_2$ ≈ $H_2C{=}CHCMe_3$ ≫ $SBu^t{}_2$. Dinitrogen reacted with **1** to yield a mixture of terminal and bridging N_2 complexes and was found to bind more strongly than $SPr^i{}_2$. Reaction of (PNP)Rh($SPr^i{}_2$) (**10**) with PhHal led to the corresponding oxidative addition products (PNP)Rh(Ph)(Hal) (Hal = Cl, **18a**; Hal = Br, **18b**; Hal = I, **18c**). The relative rates of oxidative addition of PhHal to **10** were found to be in the order PhI > PhBr > PhCl. Kinetic studies of the reaction of **10** with PhBr were consistent with the reaction proceeding via reversible dissociation of $SPr^i{}_2$, followed by irreversible addition of PhBr. Evidence for a similar dissociative mechanism for the conversion of **10** to (PNP)Rh($S(O)Ph_2$) in a ligand exchange reaction was also discovered. Solid-state structures of $[(PNP)Rh]_2(N_2)$ (**19a**) and (PNP)Rh($H_2C{=}CHCMe_3$) (**21**) were determined using X-ray crystallography. Approximately square-planar geometry about Rh was registered.

Introduction

Oxidative addition (OA)[1] of aryl halides to complexes of zerovalent Pd and other group 10 metals has received a great deal of attention, due to the importance of the OA step in the rich catalytic coupling chemistry.[2,3] The analogous Rh-catalyzed coupling chemistry of aryl halides is only beginning to emerge,[4] and examples of well-defined OA of aryl halides to Rh are rare.[5−8] Recently, we reported that a rigid PNP pincer ligand[9,10] supports a system where reactions of oxidative addition (OA) of aryl halides to Rh^I and C−C reductive elimination from Rh^{III} can be studied in a well-defined fashion (Scheme 1).[11a] Our experiments demonstrated critical importance of the generation of unobserved[12] unsaturated (PNP)Rh (**1**), which rapidly undergoes OA reactions with aryl halides.[11a]

* Corresponding author. E-mail: ozerov@brandeis.edu.

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(11) (a) Gatard, S.; Çelenligil-Çetin, P R.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2006**, *128*, 2808. (b) We previously showed that **1** is converted to (PNP)Rh(η^2-C_2H_4) in the presence of Et_2O.[11a]

(12) A related three-coordinate (PNP*)Co species (where PNP* = [($Bu^t{}_2$-$PCH_2SiMe_2)_2$N], the Fryzuk-type PNP ligand) has been recently characterized: Ingleson, M.; Fan, H.; Pink, M.; Tomaszewski, J.; Caulton, K. G. *J. Am. Chem. Soc.* **2006**, *128*, 1804.

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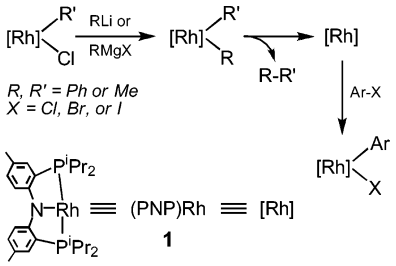
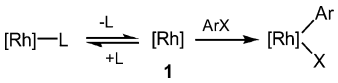
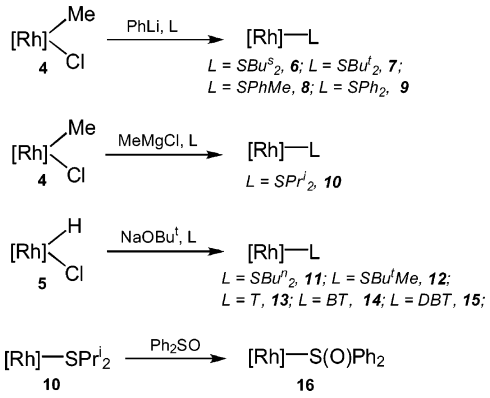
Scheme 1



Scheme 2



Scheme 3



In our previous report, we used C−C reductive elimination from (PNP)Rh(Ph)(Me) (**2**) or (PNP)RhPh$_2$ (**3**) to generate **1** in situ.[11a] This is not entirely convenient for the following reasons. Complexes **2**/**3** are not stable enough to be isolated and thus only afford the in situ approach to the generation of **1**. The in situ production of **1** by the path outlined in Scheme 1 requires the utilization of a methyl- or phenyllithium or Grignard reagent, and thus normally would take place in the presence of the solvent[11b] in which the RLi or RMgX is available, not to mention the possible excess of the reagent. We sought to access **1** in a different fashion, and the ligand dissociation path (Scheme 2) appeared sensible and straightforward. The requirements for L in Scheme 2 can be outlined as follows: (1) L must form a complex that is isolable; (2) L should not bind to Rh too strongly so that dissociation of L (and thus access to **1**) is kinetically retarded; (3) OA of the substrate (e.g., aryl halide) must be thermodynamically favorable over coordination of L; (4) L must not be reactive with the products of reactions of **1** with substrates (e.g., aryl halides); and (5) L must be easily removable upon workup. In the present work, we concentrate on thioethers and related organosulfur compounds as L, but also compare them to N_2 and the bulky olefin $H_2C{=}CHCMe_3$.

Results and Discussion

Synthesis of (PNP)Rh(SR′R″) Complexes 6−15 and of (PNP)Rh(S(O)Ph$_2$) (16). Several different routes were used to prepare (PNP)Rh(L) complexes (Scheme 3). Addition of PhLi to (PNP)Rh(Me)(Cl) (**4**) in the presence of excess of L cleanly produced compounds **6**−**9** in <24 h at 22 °C. Analogously, addition of MeMgCl to **4** in the presence of excess of L was used to synthesize **10**. Dehydrochlorination of (PNP)Rh(H)(Cl) (**5**) with NaOBu^t in the presence of L also served well and allowed synthesis of **11**−**15**. Compound **16** was prepared by reacting **10** with Ph_2SO. Compounds **6**, **8**−**12**, and **16** were isolated as air-sensitive orange solids. Compounds **7** and **13**−**15** were not isolated and were only characterized by solution NMR methods in situ. In all of these methods, the (PNP)Rh intermediate is presumably generated and then captured by L. After all, we have previously shown that C−C elimination generates **1**,[11,13] and dehydrochlorination has been used to generate (PCP)Rh and (PCP)Ir fragments in situ.[14,15] The mechanism of the ligand exchange at (PNP)Rh will be discussed later in this Article.

All of the compounds **6**−**16** displayed time-averaged C_{2v} symmetry by NMR at ambient temperature.[16] This is the highest possible symmetry for a PNP complex. A single doublet $^{31}P\{^1H\}$ resonance ($^1J_{Rh-P}$ = 133−148 Hz) was observed for each compound in the δ 36−48 ppm region. The high symmetry even for complexes of unsymmetrical sulfides implies fast rotation about the Rh−S bond and also fast inversion at S.[17] IR data are often used to distinguish between the O-bound and the S-bound modes in sulfoxide complexes.[18] In the case of **16**, the IR data were ambiguous because of overlapping bands in the region of interest. It seems most likely, however, that Ph_2SO in **16** is bound through the sulfur because of the perceived better soft−soft match with an electron-rich Rh^I center. Indeed,[19] O-bound sulfoxide complexes of Rh^I have only been encountered in cases where (a) O-binding is enforced by a chelate[20] or (b) the complex is cationic.[21]

We also propose coordination through sulfur for compounds **13**−**15**. Coordination via the π-system would lead to more upfield ^{13}C resonances of the aromatic system (as compared to free thiophene (T), benzothiophene (BT), or dibenzothiophene

(13) We have not observed the putative (PNP)RhMe$_2$ in the reactions of **4** with MeMgCl, although ethane and, ostensibly, (PNP)Rh are produced. We speculate that MeMgCl may preferentially attack the Me group of **4** via a direct S_N2 mechanism. Similarly, while PhLi reacts with **4** to produce detectable quantities of **2**, the amount of the toluene coupling product (ca. 50%) formed in the time of mixing (<10 min) is inconsistent with the known[11a] and relatively slow rate of C−C elimination from **2**. S_N2 attack of PhLi on **4** is also plausible.

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(16) Commercial SBu$^s_2$ comes as a mixture of *rac*- and *meso*-forms (in ca. 1:1 ratio). Strictly speaking, this mixture forms two diastereomeric products upon complexation with (PNP)Rh that do not interconvert. However, most of the NMR resonances of these diastereomeric Rh complexes are indistinguishable from each other, and the mixture appears to be of 1:1 ratio as well. For simplicity, here we treat this mixture of diastereomers as one compound (**6**). Furthermore, for the *rac*-diastereomer of **6**, C_{2v} symmetry is not possible. However, the deviation is not practically apparent by NMR.

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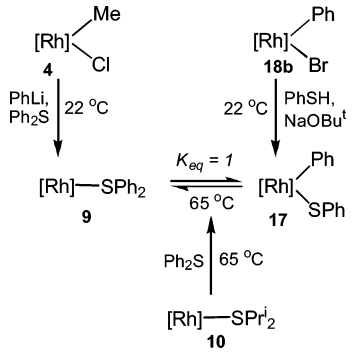
Scheme 4



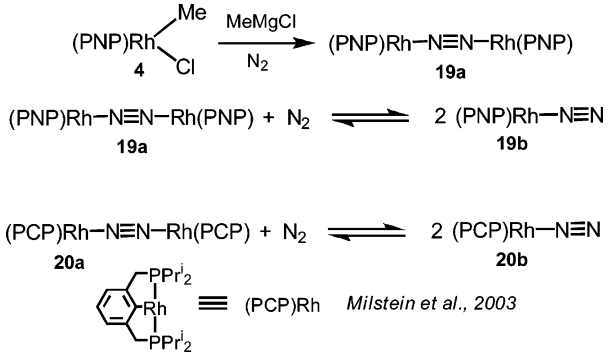
(DBT), Scheme 3).[22] This was not observed for compounds **13**−**15**; on the contrary, a downfield shift (relative to free T, BT, DBT) was observed for the α-C of the coordinated thiophene. These data are consistent with those for other S-bound thiophenes reported in the literature.[23]

Reversible C−S Oxidative Addition. Thermolysis of a pure sample of **9** (or of **10** with SPh_2) at 65 °C for 18 h generated a 1:1 mixture of Rh^I complex **9** and the Rh^{III} C−S oxidative addition product **17** (Scheme 4). **17** was prepared independently (at ambient temperature) from (PNP)Rh(Ph)(Br) (**18b**), PhSH, and $NaOBu^t$. Thermolysis of **17** (65 °C, 18 h) also led to a 1:1 mixture of **9** and **17**. In contrast, no evidence for the formation of C−S oxidative addition products was observed in any of the experiments involving thermolysis of **8**.

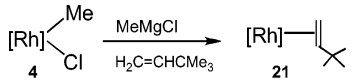
The identity of **17** was deduced on the basis of the solution NMR data. The following distinct NMR features associated with the Rh-bound Ph group in **17** are similar to the analogous features of the previously characterized (PNP)Rh(Ph)(Cl) (**18a**), (PNP)Rh(Ph)(Br) (**18b**), and (PNP)Rh(Ph)(I) (**18c**).[11a] The $^{13}C\{^1H\}$ resonance of the Rh-bound carbon of the Ph group displays telltale coupling to both Rh and the two phosphorus nuclei (δ 140.5 ppm, doublet of triplets, $J_{Rh-C} = 38$ Hz, $J_{P-C} = 9$ Hz). Because of the slow rotation about the Rh−C bond, the Rh-bound Ph group in **17** gives rise to (a) five ^1H resonances, four of them broad (slow exchange of the *ortho*- and *meta*-positions, resolved at −50 °C) and one a sharp triplet (*para*-CH) at 22 °C; and (b) five ^{13}C NMR resonances besides the Rh-bound *ipso*-C (vide supra), four of which are broad. One of the four resonances of the ^{i}Pr CH_3 groups of the PNP ligand is shifted characteristically upfield to ca. 0.4 ppm in the ^1H NMR spectrum (presumably, this is due to the selective influence of the ring current effect of the Rh−Ph group on a specific pair of Me groups). Unlike **9**, which is orange, **17** is green, similar in color to **18a/b**.

Cleavage of C−S bonds in various thiophenes by Rh^I complexes has been studied by Jones et al. in the context of homogeneous models for hydrodesulfurization.[24] We saw no evidence of C−S OA with T, BT, or DBT in the present study. On the other hand, C−S reductive elimination is a requisite step in the thiolation of aryl halides.[25] The example of **9**/**17** presented here is unusual in that the thermodynamics are perfectly balanced and the kinetic barrier is modest so that observation of both forms in equilibrium is possible.

Scheme 5



Scheme 6



Synthesis of Dinitrogen Complexes. Mixing **4** with MeMgCl under an N_2 atmosphere in PhF resulted in the formation of a single product $[(PNP)Rh]_2(\mu\text{-}N_2)$ (**19a**) after 10 min at room temperature. **19a** could be isolated in the pure form. Under N_2, **19a** slowly establishes an equilibrium with the terminal dinitrogen complex **19b**. Thus, thermolysis of a pure sample of **19a** under N_2 (3 d, 65 °C) in C_6D_6 in a J. Young NMR tube resulted in conversion to a 5:95 mixture of **19a**:**19b** (NMR evidence). Removing the overhead N_2 gas and allowing the solution to stand for 3 d under argon increased the ratio in favor of **19a** to 50:50. In contrast, thermolysis (65 °C, 1 d) of **19a** under argon did not lead to any change in the composition of the solution. These results are consistent with the assigned identity of **19a** as the bridging N_2 complex (N_2-poor) and **19b** as the terminal N_2 complex (N_2-rich). The structure of **19a** was investigated by an X-ray diffraction study in the solid state (vide infra).

Both **19a** and **19b** displayed maximal symmetry in the ambient-temperature NMR spectra (C_{2v} for each PNP fragment). The ^{31}P NMR chemical shifts for **19a** and **19b** were very similar as were the corresponding $^1J_{Rh-P}$ values (**19a**, δ 51.1, $^1J_{Rh-P} =$ 139 Hz; **19b**, δ 52.4, $^1J_{Rh-P} = 137$ Hz). The similarities in these data and the apparent small difference in free energies are reminiscent of the analogous bridging and terminal (PCP)Rh complexes described by Milstein et al. (**20a**/**20b**, Scheme 5).[26] Similar interconversion between bridging and terminal dinitrogen PCP complexes of iridium has also been studied.[27]

Synthesis of (PNP)Rh(H_2C═CHBu^t) (21). Complex **21** was prepared analogously to the synthesis of **10** by treatment of **4** with MeMgCl in the presence of H_2C═$CHCMe_3$ (Scheme 6). The product was isolated in 62% yield upon workup. **21** displays C_1 symmetry in its NMR spectra. The two inequivalent ^{31}P nuclei form an AB system with a coupling constant ($J_{PP} = 328$ Hz) characteristic of *trans*-disposed phosphines. The olefinic resonances of the coordinated H_2C═$CHCMe_3$ appear at 4.43,

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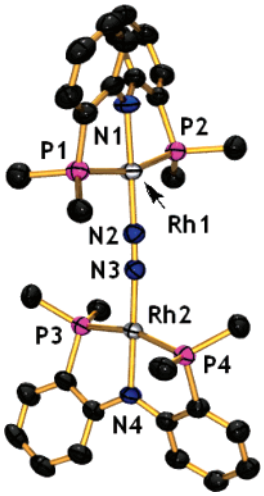


Figure 1. ORTEP drawing[29] (80% probability ellipsoids) of **19a** showing selected atom labeling. Hydrogen atoms and all methyl groups are omitted for clarity. Selected bond distances (Å) and angles (deg) follow: N2−N3, 1.1191(17); Rh1−N2, 1.9035(12); Rh1−N1, 2.0358(12); Rh1−P1, 2.2818(4); Rh1−P2, 2.2808(4); Rh1−N2−N3, 178.16(12); P1−Rh1−N2, 82.18(4); P2−Rh1−N2, 81.98(4); N1−Rh1−N2, 179.52(5); P1−Rh1−P2, 163.623(14).

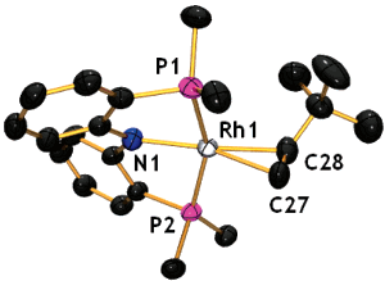


Figure 2. ORTEP drawing[29] (50% probability ellipsoids) of **21** showing selected atom labeling. Hydrogen atoms and all methyl groups are omitted for clarity. Selected bond distances (Å) and angles (deg) follow: Rh1−C27, 2.132(5); Rh1−C28, 2.189(5); Rh1−P1, 2.3220(19); Rh1−P2, 2.2964(14); Rh1−N1, 2.062(4); C27−Rh1−C28, 36.7(2); C27−Rh1−P1, 97.64(16); C28−Rh1−P1, 110.42(14); C27−Rh1−P2, 96.65(15); C28−Rh1−P2, 92.72(14); P1−Rh1−P2, 155.64(5); C27−Rh1−N1, 161.04(17); C28−Rh1−N1, 160.64(17); P1−Rh1−N1, 80.69(11); P2−Rh1−N1, 79.40(11).

2.88, and 2.78 ppm in the ^{1}H NMR spectrum, within a typical region for olefin complexes.

Structures of 19a and 21. Structures of **19a** and **21** were determined in the course of X-ray diffraction studies on appropriate single crystals (Figures 1 and 2). In both compounds, the environment about all Rh centers is approximately square planar, with deviations primarily attributable to the geometric constraints of the PNP ligands. The metrics relating to the PNP ligands in these compounds are unremarkable. The Rh−$N_{dinitrogen}$ distance in **19a** of 1.9035(12) Å is markedly shorter than the corresponding distance in the closely related **20a**,[26] presumably a reflection of a weaker *trans*-influence of the amido ligand in **19a** as compared to the aryl ligand in **20a**. Despite the greater proximity of the N_2 ligand to Rh in **19a**, the N−N distance in **19a** of 1.1191(17) Å is only slightly longer than that in **20a** (1.108(3) Å).[26] These distances are close to the N−N distance in free N_2, signifying only modest back-donation into the π*-orbitals of the dinitrogen ligand.[28]

The two Rh−C distances in **21** are different, with the distance to the carbon bearing a *tert*-butyl substituent being greater by ca. 0.05 Å (likely for steric reasons). The C−C distance of 1.360(7) Å in the coordinated olefin is indicative of modest back-donation into the π*-orbital of H_2C═$CHBu^t$. This C−C distance is at the lower end of the range for olefin complexes, similar to other Rh^I olefin complexes.[30]

Equilibrium Studies. To determine the comparative thermodynamic affinity of the (PNP)Rh fragment (**1**) for various ligands, we measured equilibrium constants (*K*) for a series of ligand exchange reactions. Equilibrium constants were measured for the reactions generically depicted in Scheme 7. To establish equilibrium, the solutions of reactants in C_6D_6 were heated in a J. Young tube by placing them into an oil bath at 65 °C until the observed ratios ceased to change. The concentrations were measured using NMR after cooling of the sample. Because the reactions do not involve a change in the number of particles, we assume that the ΔS_{rxn} values are negligible and and therefore so is ΔG_{rxn}; thus the relative order of the values of *K* should be independent of temperature. Three experiments with different starting ratios of reactants were performed for each determination of *K*. No decomposition was detected by NMR. The results are presented in Table 1.

Scheme 7

Table 1

no.	L	L′	*K*
1	SPr^i_2	S^tBu_2	$<10^{-4}$
2	SPr^i_2	CH_2═$CHCMe_3$	0.2(1)
3	SPr^i_2	S^tBuMe	0.4(1)
4	SPr^i_2	T	0.4(1)
5	SPr^i_2	BT	3(1)
6	SPr^i_2	SPh_2	10(2)
7	SPr^i_2	DBT	33(5)
8	SPr^i_2	SPhMe	48(10)
9	SPr^i_2	S^nBu_2	63(5)
10	SPr^i_2	$S(O)Ph_2$	400(100)
11	SPhMe	S^sBu_2	0.004(1)

The equilibrium constant for a reaction of **10** with N_2 was not measured because of the uncertainty in the N_2 concentration.[31] However, addition of 1 atm of N_2 (ca. 100 μmol) to a J. Young tube containing a solution of 31 mmol of **10** in 0.7 mL of C_6D_6 and subsequent thermolysis in a closed tube (65 °C, 1 d) led to the formation of predominantly **19a**/**19b**. Because the concentration of N_2 in C_6D_6 would be rather small, this is indicative of greater affinity of (PNP)Rh toward N_2 (or toward N≡N−Rh(PNP) for the case of **19a**) than for SPr^i_2.

For bis(hydrocarbyl) sulfides, the trend that emerged from our studies indicated that steric considerations played a primary role in the relative strength of binding of various L to (PNP)-Rh. Increasing the size of the substituents on S (be that alkyl or aryl) led to weaker binding.[32,33] Di-*tert*-butylsulfide was by far the most weakly binding L. Accurate equilibrium constant

(28) For reviews on the chemistry of dinitrogen complexes, see the following: (a) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385. (b) Shaver, M. P.; Fryzuk, M. D. *Adv. Synth. Catal.* **2003**, *345*, 1061. (c) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200*−*202*, 379.

(29) (a) ORTEP plots were created using Ortep-3 for Windows. Farugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565. (b) 3D-rendering was done using Persistence of Vision Ray Tracer (POV-Ray), available at http://www.povray.org/.

(30) Cohen, S. A.; Auburn, P. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

(31) For treatment of N_2 concentration for equilibrium constant calculation, see ref 27a (Goldman) and references within.

(32) For discussion of steric effects in dialkylsulfides, see: (a) Shi, T.; Elding, L. I. *Inorg. Chem.* **1996**, *35*, 5941. (b) Tracey, A. A.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1399.

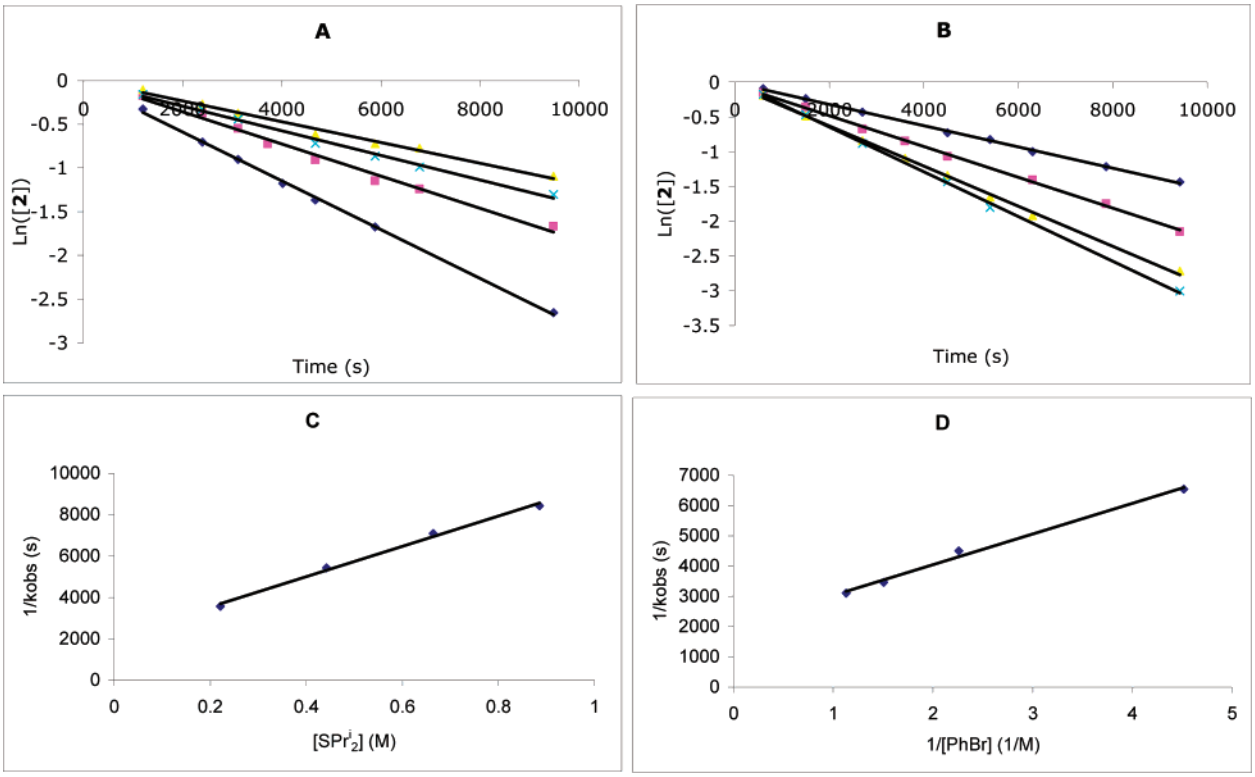


Figure 3. (A) Pseudo first-order decay of **10** in the presence of four concentrations of SPr^i_2 (0.22−0.88 M). (B) Pseudo first-order decay of **10** in the presence of four concentrations of PhBr (0.22−0.88 M). (C) Inverse dependence of k_{obs} on the concentration of SPr^i_2. (D) Positive dependence of k_{obs} on the concentration of PhBr.

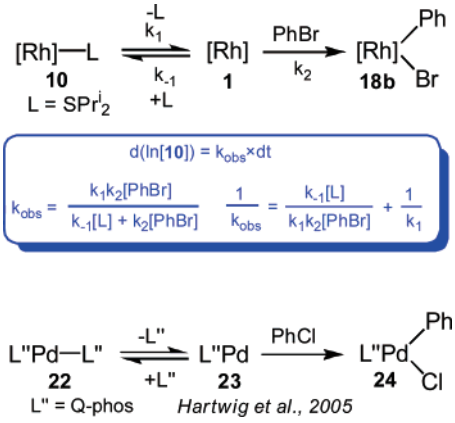
determination in a reaction involving SPr^i_2 versus SBu^s_2 was not possible due to overlap of resonances in the NMR spectra. This equilibrium constant was estimated at ca. 0.2 (favoring binding of SPr^i_2) from the data in lines 8 and 11 of Table 1.

For the thiophenic ligands T, BT, and DBT, an opposite trend was observed. DBT was found to bind more strongly than BT, which in turn was found to bind more strongly than T. A similar trend has been previously reported.[23a,c] Binding of the metal to S in a thiophene presumably disrupts the aromaticity of the five-membered cycle. This becomes less of a loss for the fused BT and DBT, and so DBT binds most strongly despite being the largest of the three.[34]

Diphenylsulfoxide was found to bind most strongly of all ligands studied. Specifically, it displayed a *K* of an order of magnitude higher than the corresponding sulfide Ph_2S. *tert*-Butylethylene was found to bind comparably to the moderately bulky dialkylsulfides.

Kinetics of Oxidative Addition of PhHal to 10. As we expected, **10** cleanly reacted with aryl halides to produce the C-Hal oxidative addition products with release of free SPr^i_2. We were interested in the mechanism of this transformation and set out to investigate it by means of kinetic studies. Particularly, the issue in question is whether addition of aryl halide occurs prior to, in concert with, or following the dissociation of SPr^i_2. Oxidative addition of alkyl halides to four-coordinate d^8 metal centers via an (associative) S_N2 mechanism is well-documented.[35] However, this mechanism is not available

Scheme 8



to aryl halides. The generic mechanistic situation in our case is fully analogous to the oxidative addition of aryl halides to (Q-phos)-Pd^0-(Q-phos) (**22**) investigated in detail by Barrios-Landeros and Hartwig in 2005 (Scheme 8).[36]

To gain insight into the mechanism, we investigated the kinetics of oxidative addition of PhBr to **10** as a function of both [PhBr] and [SPr^i_2] under pseudo first-order conditions. Kinetic data were obtained by monitoring the disappearance of **10** by ^{31}P NMR in C_6D_6 at 65 °C. In the first set of experiments (Figure 3A), the concentration of PhBr was kept approximately constant (0.22 M) while the concentration of SPr^i_2 was varied (0.22−0.88 M). In the second set of experiments (Figure 3B), the concentration of SPr^i_2 was kept constant (0.88 M) while varying the concentration of PhBr (0.22−0.88 M). The plots of ln[**10**] versus time were linear over 3 half-lives. Figure 3C

(33) For a general discussion of cone angles, see: (a) Tolman, C. A. *J. Am. Chem. Soc*. **1970**, *92*, 2956. (b) Tolman, C. A. *Chem. Rev*. **1977**, *77*, 313. (c) Bunten, K. A.; Chen, L.; Fernandez, A. L.; Poë, A. J. *Coord. Chem. Rev*. **2002**, *233*−*234*, 41.

(34) Harris, S. *Organometallics* **1994**, *13*, 2628.

(35) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 306.

(36) Barrios-Landeros, F.; Hartwig, J. F. *J. Am. Chem. Soc*. **2005**, *127*, 6944.

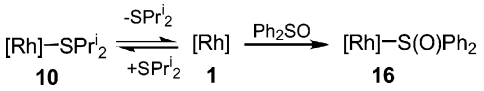
clearly shows that the observed pseudo first-order rate constant (k_{obs}) is inversely proportional to the concentration of SPr^i_2. On the other hand, Figure 3D clearly shows the linear dependence of $1/k_{obs}$ on the concentration of 1/[PhBr], indicating positive dependence of the reaction rate on [PhBr].

The combination of positive dependence on [PhBr] and inverse dependence on [SPr^i_2] is only consistent with a mechanism that involves reversible dissociation of SPr^i_2 followed by irreversible addition of PhBr (Scheme 8).[36] In other words, dissociation of SPr^i_2 produces (PNP)Rh (**1**), which subsequently can either re-coordinate SPr^i_2 or undergo addition of PhBr. Importantly, addition of PhBr occurs only after loss of SPr^i_2. This reaction follows (qualitatively) the same rate law as the addition of PhCl to **22**.[36] However, in the latter study, addition of PhBr was faster, and the reaction did not display inverse dependence on [Q-phos] and thus followed an apparently different rate law. However, that still can be construed as the same mechanism as the difference amounts simply to the much greater k_2 for PhBr. The addition of PhI to **22** was reported to proceed even faster and by an associative mechanism.[36] We have not performed scrupulous kinetic studies for aryl halides other than PhBr, but we have determined that, qualitatively, the rate of oxidative addition increases in the series PhCl < PhBr < PhI. For instance, in reactions of **10** with 3 equiv of PhI, PhBr, or PhCl at 65 °C in C_6D_6, the conversions to the corresponding OA products after 1 h, as measured by $^{31}P\{^1H\}$ NMR, were as follows: (**18c**, 95%) > (**18b**, 85%) > (**18a**, 45%).

Oxidative Addition of PhBr to 10, 19a/b, and 21. The activation energy for dissociation of L from (PNP)Rh(L) can be roughly equated to the Rh−L bond dissociation energy.[37] In essence, we have measured the differences among the latter in our equilibrium studies (vide supra). If we assume the same mechanism for OA reactions of various (PNP)Rh(L) with, for instance, PhBr, then the rate of the reaction should increase with decreasing strength of binding of L. Toward this end, we used ^{31}P NMR to monitor the reactions of PhBr with **10**, **19a/b**, and **21** at 65 °C in C_6D_6. The relative rates for the OA reaction were as follows, based on the observed conversions after 40 min: **21** (95%) > **10** (85%) > **19a/b** (4%). These results are consistent with the relative affinities of (PNP)Rh for the three ligands (vide supra) in the order $H_2C{=}CHBu^t$ < SPr^i_2 < N_2.

Kinetics of the Conversion of 10 to 16. To investigate whether ligand exchange in (PNP)Rh(L) systems occurs by a mechanism similar to that of OA of PhBr, we set out to probe the dependence of the rate of conversion of **10** to **16** as a function of [SPr^i_2] and [Ph_2SO]. We selected this pair of ligands primarily because the reaction can be practically considered irreversible for the purposes of this investigation ($K = 400$, vide supra). We observed faster conversion to **16** in the presence of higher concentration of [Ph_2SO] when [SPr^i_2] was kept constant and, conversely, slower conversion to **16** in the presence of higher concentration of [SPr^i_2] when [Ph_2SO] was kept constant. These experiments qualitatively demonstrate that the rate of the forward reaction depends positively on [Ph_2SO] and inversely on [SPr^i_2]. No evidence of five-coordinate Rh^I compounds (putative intermediates in an associative exchange pathway) was detected, including in a separate experiment where **10** was treated with 50 equiv of SPr^i_2. Although our qualitative findings do not allow one to paint a definitive mechanistic picture, they are consistent with the displacement of SPr^i_2 in **10** by Ph_2SO to give **16** proceeding similarly to OA of PhBr (Scheme 8), that is, reversible dissociation of SPr^i_2, followed by effectively irreversible coordination of Ph_2SO (Scheme 9). It seems likely that these findings might apply to other ligands in this study.

Scheme 9



Summary

We have prepared a series of complexes (PNP)Rh(L) where L is an organic sulfide, dinitrogen, or an olefin. The relative affinity of (PNP)Rh (**1**) for various organic sulfides is guided primarily by steric factors. On the other hand, the affinity for (PNP)Rh (**1**) increases in the following series thiophene < benzothiophene < dibenzothiophene, which is ascribed to electronic effects. (PNP)Rh(SPh_2) (**9**) exists in observable equilibrium with its C−S oxidative addition form (PNP)Rh(Ph)(SPh) (**17**) at 65 °C. The (PNP)Rh(L) complexes generate the fleeting (PNP)Rh species **1** in situ via dissociation of L and serve well as synthons for **1** in oxidative addition reactions with aryl halides. The reaction of (PNP)Rh(SPr^i_2) (**10**) with PhBr was determined to proceed via reversible dissociation of SPr^i_2 followed by irreversible addition of PhBr. Displacement of SPr^i_2 in **10** with Ph_2SO to give (PNP)Rh(Ph_2SO) (**16**) proceeds by an analogous mechanism.

Experimental Section

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, ethyl ether, THF, pentane, and isooctane were dried and deoxygenated (by purging) using a solvent purification system[38] by MBraun and stored over molecular sieves in an Ar-filled glovebox. C_6D_6 was dried over and distilled from NaK/Ph_2CO/18-crown-6 and stored over molecular sieves in an Ar-filled glovebox. Fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, and CD_2Cl_2 were dried, then distilled or vacuum transferred from CaH_2 and stored over molecular sieves in an Ar-filled glovebox. Liquid dialkyl sulfides were degassed prior to use and stored over molecular sieves in an Ar-filled glovebox. (PNP)Rh(Me)(Cl) (**4**),[39] (PNP)Rh(H)(Cl) (**5**),[39] and (PNP)Rh(Ph)(Br) (**18b**)[11a] were prepared according to modified published procedures. All other chemicals were used as received from commercial vendors. PhLi was used as a 2 M solution in Bu_2O; MeMgCl was used as a 3.1 M solution in THF. NMR spectra were recorded on a Varian iNova 400 (^1H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz; ^{19}F NMR, 376.104 MHz) spectrometer. For ^1H 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 0 ppm.

Synthesis of (PNP)Rh(SBu^s_2) (6). 4 (40.0 mg, 0.068 mmol) was treated with S^sBu_2 (13 μL, 0.074 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube followed by addition of PhLi (36.0 μL, 0.074 mmol). After 24 h at ambient temperature, the solution was evaporated to dryness, and the residue was passed through a plug of silica gel with Et_2O as eluent. The resultant ether solution was

(37) There is some debate in the literature pertaining to this approximation: (a) Zhang, S.; Dobson, G. R. *Inorg. Chim. Acta* **1991**, *181*, 103. (b) Asali, K. J.; Awad, H. H.; Kimbrough, J. F.; Lang, B. C.; Watts, J. M.; Dobson, G. R. *Organometallics* **1991**, *10*, 1822. (c) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379. (d) Klassen, J. K.; Selke, M.; Sorensen, A. A.; Yang, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 1267.

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(39) (a) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792. (b) Weng, W.; Guo, C.; Moura, C. P.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2005**, *24*, 3487.

evaporated to dryness to yield an orange solid residue. This residue was dissolved in Et_2O and placed in the freezer at −35 °C to afford **6** by precipitation. Yield: 18 mg (39%). NMR data for **6** follow.[16] ^{1}H NMR (C_6D_6): δ 7.72 (d, 2H, 8 Hz, Ar−*H* of PNP), 6.99 (s, 2H, Ar−*H* of PNP), 6.78 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.65 (m, 2H, SC*H*), 2.48 (m, 4H, SCHCH_2), 2.25 (s, 6H, Ar−CH_3 of PNP), 2.25 (m, 4H, C*H*Me$_2$), 1.40 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.34 (d, 6H, 8 Hz, SCHCH_3), 1.16 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 0.85 (m, 6H, SCHCH$_2$CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.3 (vt, 10 Hz, *C*−N of PNP), 131.2 (s, C_{Ar} of PNP), 131.0 (s, C_{Ar} of PNP), 123.2 (vt, 18 Hz, C_{Ar} of PNP), 122.6 (vt, 3 Hz, C_{Ar} of PNP), 115.6 (vt, 5 Hz, C_{Ar} of PNP), 50.2 (s, S*C*H), 31.5, 31.4 (two s, SCH*C*H$_2$), 24.3 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 21.1 (s, SCH*C*H$_3$), 20.7 (s, Ar−*C*H$_3$), 19.7, 17.4 (two s, CH(*C*H$_3$)$_2$), 11.6 (two s, SCHCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 41.0 (d, 146 Hz, *P*(Pr^i)$_2$).

N.B.: Commercial S^{s}Bu$_2$ is a 1:1 mixture of *rac*- and *meso*-isomers. Some, but not all, of their ^{1}H and ^{13}C NMR resonances are distinguishable. Data for this mixture follow. ^{1}H NMR (C_6D_6): δ 2.54 (sextet, 2H, 7 Hz, SC*H*), 1.50 (m, 2H, SCHCH_aH$_b$), 1.40 (m, 2H, SCHCH$_a$$H_b$), 1.15 (2 d are overlapping, 6H, 7 Hz, SCHCH_3), 0.91 (t, 3H, 8 Hz, SCHCH$_2$CH_3), 0.90 (t, 3H, 8 Hz, SCHCH$_2$CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ. 40.4 (s, S*C*H), 30.4, 30.3 (two singlets, SCH*C*H$_2$), 21.5 (two singlets, SCH*C*H$_3$), 11.7, 11.3 (two singlets, SCHCH$_2$*C*H$_3$).

Synthesis of (PNP)Rh(SBu$^t_2$) (7). 4 (20.0 mg, 0.034 mmol) was treated with *tert*-butyl sulfide (18.5 μL, 0.103 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube followed by addition of PhLi (19.0 μL, 0.038 mmol). After 24 h at ambient temperature, **7** was observed by ^{1}H and ^{31}P{^{1}H} NMR and characterized in solution in situ. ^{1}H NMR (C_6D_6): δ 7.56 (d, 2H, 8 Hz, Ar−*H* of PNP), 6.99 (s, 2H, Ar−*H* of PNP), 6.73 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.33 (m, 4H, C*H*Me$_2$), 2.23 (s, 6H, Ar−CH_3 of PNP), 1.51 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.43 (s, 18H, SC(CH_3)$_3$), 1.21 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 36.6 (d, 148 Hz).

Synthesis of (PNP)Rh(SPhMe) (8). This was synthesized analogously to the preparation of **6** from **4** (40.0 mg, 0.068 mmol), PhLi (38 μL, 0.076 mmol), and thioanisole (9 μL, 0.076 mmol). Yield: 0.025 g (58%). ^{1}H NMR (C_6D_6): δ 7.83 (d, 2H, 9 Hz, Ar−*H* of PNP), 7.76 (d, 2H, 8 Hz, SC$_6H_5$), 7.02 (t, 2H, 8 Hz, SC$_6H_5$), 7.01 (s, 2H, Ar−*H* of PNP), 6.88 (t, 1H, 8 Hz, *p*-SC$_6H_5$), 6.80 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.39 (s, 3H, SCH_3), 2.23 (s, 6H, Ar−CH_3 of PNP), 2.16 (m, 4H, C*H*Me$_2$), 1.22 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.15 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$). ^{13}C-{^{1}H} NMR (C_6D_6): δ 163.6 (vt, 10 Hz, *C*−N of PNP), 142.9 (s, S−*i*-C$_6$H$_5$), 131.6 (s, C_{Ar} of PNP), 131.1 (s, C_{Ar} of PNP), 129.1 (s, SC$_6$H$_5$), 127.3 (s, SC$_6$H$_5$), 126.5 (s, S−*p*-C$_6$H$_5$), 123.1 (vt, 3 Hz, C_{Ar} of PNP), 122.8 (vt, 18 Hz, C_{Ar} of PNP), 115.7 (vt, 5 Hz, C_{Ar} of PNP), 26.8 (t, 4 Hz, S*C*H$_3$), 25.1 (vt, 15 Hz, *C*H(CH$_3$)$_2$), 20.6 (s, Ar−*C*H$_3$), 19.3, 18.0 (two singlets, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.6 (d, 142 Hz). Anal. Calcd for $C_{33}H_{48}NRhP_2S$: C, 59.97; H, 7.26. Found: C, 60.45; H, 7.37.

Synthesis of (PNP)Rh(SPh$_2$) (9). This was synthesized analogously to the preparation of **6** from **4** (40.0 mg, 0.068 mmol), PhLi (38.0 μL, 0.076 mmol), and diphenyl sulfide (12.8 μL, 0.076 mmol). Yield: 25 mg (51%). ^{1}H NMR (C_6D_6): δ 7.84 (d, 2H, 9 Hz, Ar−*H* of PNP), 7.78 (d, 4H, 8 Hz, SC$_6$H$_5$), 7.01 (s, 2H, Ar−*H* of PNP), 6.96 (t, 4H, 8 Hz, SC$_6$H$_5$), 6.88 (t, 2H, 8 Hz, *p*-SC$_6$H$_5$), 6.80 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.22 (s, 6H, Ar−CH_3 of PNP), 1.88 (m, 4H, C*H*Me$_2$), 1.17 (2 app. quartets (dvt) are overlapping, 24H, 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.6 (vt, 10 Hz, *C*−N of PNP), 139.6 (s, S−*i*-C$_6$H$_5$), 131.6 (s, C_{Ar} of PNP), 131.5 (s, SC$_6$H$_5$), 131.1 (s, C_{Ar} of PNP), 129.3 (s, SC$_6$H$_5$), 127.3 (s, S−*p*-C$_6$H$_5$), 123.3 (vt, 18 Hz, C_{Ar} of PNP), 123.3 (vt, 18 Hz, C_{Ar} of PNP), 115.8 (vt, 5 Hz, C_{Ar} of PNP), 24.9 (vt, 12 Hz, *C*H(CH$_3$)$_2$), 20.6 (s, Ar−*C*H$_3$), 19.4, 17.9 (two singlets, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.6 (d, 142 Hz, *P*(Pr^i)$_2$).

Synthesis of (PNP)Rh(SPr$^i_2$) (10). 4 (809.0 mg, 1.40 mmol) was treated with SPr$^i_2$ (222 μL, 1.53 mmol) in fluorobenzene (10 mL) in a Teflon stoppered gastight round-bottom flask. The reaction mixture was stirred for 10 min at ambient temperature, and MeMgCl (493 μL, 1.53 mmol) was added. After being stirred for 10 min, the solution was filtered through Celite, then passed through a short column of silica, and then filtered through Celite again. The resultant solution was evaporated to dryness to yield an orange solid residue. This residue was dissolved in Et_2O and placed in the freezer at −35 °C to afford **10** by precipitation. Yield: 478 mg (53%). ^{1}H NMR (C_6D_6): δ 7.70 (d, 2H, 9 Hz, Ar−*H* of PNP), 6.98 (s, 2H, Ar−*H* of PNP), 6.77 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.64 (septet, 2H, 6 Hz, SC*H*Me$_2$), 2.25 (s, 6H, Ar−CH_3 of PNP), 2.25 (m, 4H, C*H*Me$_2$), 1.37 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.37 (d, 12H, 6 Hz, SCH*Me*$_2$), 1.17 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.3 (vt, 10 Hz, *C*−N of PNP), 131.2 (s, C_{Ar} of PNP), 130.9 (s, C_{Ar} of PNP), 123.2 (vt, 18 Hz, C_{Ar} of PNP), 122.5 (vt, 3 Hz, C_{Ar} of PNP), 115.6 (vt, 5 Hz, C_{Ar} of PNP), 44.0 (s, S*C*HMe$_2$), 25.1 (s, SCH(*C*H$_3$)$_2$), 24.4 (vt, 15 Hz, *C*H-(CH$_3$)$_2$), 20.7 (s, Ar−*C*H$_3$), 19.7, 17.5 (two s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 40.9 (d, 105 Hz). Anal. Calcd for $C_{32}H_{54}$-$NRhP_2S$: C, 58.94; H, 8.21. Found: C, 59.15; H, 8.37.

Synthesis of (PNP)Rh(SBu$^n_2$) (11). 5 (30.0 mg, 0.053 mmol) was treated with SBu$^n_2$ (9.3 μL, 0.053 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube followed by NaO^{t}Bu (7.6 mg, 0.079 mmol). After 10 min, the solution was treated with water (1.5 mL) and then evaporated to dryness, and the residue was extracted with ether and filtered through Celite. The filtrate was evaporated to dryness to yield an orange solid residue. This residue was triturated three times with toluene (3 × 1 mL) and dried to give **11** that was >95% pure by NMR. Yield: 27 mg (90%). ^{1}H NMR (C_6D_6): δ 7.78 (d, 2H, 9 Hz, Ar−*H* of PNP), 7.04 (s, 2H, Ar−*H* of PNP), 6.79 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.47 (t, 4H, 8 Hz, SCH_2), 2.26 (s, 6H, Ar−CH_3 of PNP), 2.26 (m, 4H, C*H*Me$_2$), 1.70 (q, 4H, 8 Hz, SCH$_2$CH_2), 1.42 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.30 (sextet, 4H, 8 Hz, SCH$_2$CH$_2$CH_2), 1.22 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 0.85 (t, 6H, 8 Hz, SCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.5 (vt, 10 Hz, *C*−N of PNP), 131.4 (s, C_{Ar} of PNP), 131.0 (s, C_{Ar} of PNP), 123.1 (vt, 18 Hz, C_{Ar} of PNP), 122.8 (vt, 3 Hz, C_{Ar} of PNP), 115.6 (vt, 5 Hz, C_{Ar} of PNP), 42.9 (s, S*C*H$_2$), 31.4 (s, SCH$_2$*C*H$_2$), 25.1 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 22.5 (s, SCH$_2$-CH$_2$*C*H$_2$), 20.6 (s, Ar−*C*H$_3$), 19.9, 17.9 (two singlets, CH(*C*H$_3$)$_2$), 13.9 (s, SCH$_2$CH$_2$CH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.2 (d, 145 Hz).

Synthesis of (PNP)Rh(S^{t}BuMe) (12). This was synthesized analogously to the preparation of **11** from **5** (23.0 mg, 0.040 mmol), NaO^{t}Bu (4.27 mg, 0.044 mmol), and S^{t}BuMe (6 μL, 0.044 mmol). Yield: 0.011 g (43%). ^{1}H NMR (C_6D_6): δ 7.73 (d, 2H, 8 Hz, Ar−*H* of PNP), 7.07 (s, 2H, Ar−*H* of PNP), 6.77 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.24 (s, 6H, Ar−CH_3 of PNP), 2.24 (m, 4H, C*H*Me$_2$), 1.93 (s, 3H, S−CH$_3$), 1.41 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.17 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.16 (s, 9H, SC(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.7 (vt, 10 Hz, *C*−N of PNP), 131.4 (s, C_{Ar} of PNP), 131.1 (s, C_{Ar} of PNP), 123.1 (vt, 18 Hz, C_{Ar} of PNP), 122.8 (vt, 3 Hz, C_{Ar} of PNP), 115.9 (vt, 6 Hz, C_{Ar} of PNP), 44.5 (s, S*C*(CH$_3$)$_3$), 29.7 (s, SC(*C*H$_3$)$_3$), 25.2 (m, S*C*H$_3$), 22.7 (vt, 6 Hz, *C*H(CH$_3$)$_2$), 20.6 (s, Ar−*C*H$_3$), 19.9, 18.1 (two singlets, CH-(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 41.0 (d, 146 Hz).

Synthesis of (PNP)Rh(T) (13). 5 (40.0 mg, 0.070 mmol) was treated with thiophene (6.20 μL, 0.078 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube followed by NaO^{t}Bu (7.5 mg, 0.078 mmol). **13** was characterized in situ by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 7.80 (d, 2H, 9 Hz, Ar−*H* of PNP), 7.10 (br s, 2H, SC*H*), 6.98 (s, 2H, Ar−*H* of PNP), 6.79 (br s, 2H, SCHC*H*), 6.79 (d, 2H, 6 Hz, Ar−*H* of PNP), 2.19 (s, 6H, Ar−CH_3 of PNP), 1.94 (m, 4H, C*H*Me$_2$), 1.13 (app. quartet (dvt), 24H, 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.7 (vt, 10 Hz, *C*−N of PNP), 133.3 (s, S*C*H),

131.8 (s, C_{Ar} of PNP), 131.4 (s, C_{Ar} of PNP), 126.4 (s, SCH*C*H), 123.8 (vt, 3 Hz, C_{Ar} of PNP), 122.5 (vt, 18 Hz, C_{Ar} of PNP), 115.6 (vt, 5 Hz, C_{Ar} of PNP), 25.2 (vt, 11 Hz, *C*H(CH_3)$_2$), 20.5 (s, Ar−*C*H_3), 19.0, 18.3 (two s, CH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 47.9 (d, 133 Hz).

Synthesis of (PNP)Rh(BT) (14). 5 (40.0 mg, 0.070 mmol) was treated with benzothiophene (10.4 mg, 0.078 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube followed by NaO^{t}Bu (7.5 mg, 0.078 mmol). **14** was characterized in situ by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 8.03 (br d, 1H, SC$_8$*H*$_6$), 7.81 (d, 2H, 8 Hz, Ar−*H* of PNP), 7.44 (br d, 1H, SC$_8$*H*$_6$), 7.15−6.89 (other SC$_8$*H*$_6$ resonances overlapped with C_6D_5H and free benzothiophene resonances, 4H), 6.96 (s, 2H, Ar−*H* of PNP), 6.80 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.21 (s, 6H, Ar−C*H*$_3$ of PNP), 2.07 (m, 4H, C*H*Me$_2$), 1.10 (app. quartet (dvt), 24H, 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.6 (vt, 10 Hz, *C*−N of PNP), 147.5 (s, S*C*$_8$H$_6$), 140.0 (s, S*C*$_8$H$_6$), 134.8 (s, S*C*$_8$H$_6$), 131.7 (s, C_{Ar} of PNP), 131.4 (s, C_{Ar} of PNP), 125.2 (s, S*C*$_8$H$_6$), 124.8 (s, S*C*$_8$H$_6$), 124.6 (s, S*C*$_8$H$_6$), 124.3 (s, S*C*$_8$H$_6$), 123.7 (vt, 3 Hz, C_{Ar} of PNP), 123.5 (s, S*C*$_8$H$_6$), 122.5 (vt, 18 Hz, C_{Ar} of PNP), 115.5 (vt, 5 Hz, C_{Ar} of PNP), 25.1 (vt, 10 Hz, *C*H(CH_3)$_2$), 20.5 (s, Ar−*C*H_3), 19.0, 18.2 (two s, CH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 46.1 (d, 135 Hz).

Synthesis of (PNP)Rh(DBT) (15). 5 (40.0 mg, 0.070 mmol) was treated with dibenzothiophene (14.3 mg, 0.078 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube followed by NaO^{t}Bu (7.5 mg, 0.078 mmol). **15** was characterized in situ by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 8.11 (d, 2H, 8 Hz, SC$_{12}$*H*$_8$), 7.82 (d, 2H, 8 Hz, Ar−*H* of PNP), 7.72 (d, 2H, 8 Hz, SC$_{12}$*H*$_8$), 7.21−7.15 (other SC$_{12}$*H*$_8$ resonances overlapped with C_6H_6 and free dibenzothiophene resonances, 4H), 6.94 (s, 2H, Ar−*H* of PNP), 6.81 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.21 (s, 6H, Ar−C*H*$_3$ of PNP), 2.03 (m, 4H, C*H*Me$_2$), 1.07 (app. quartet (dvt), 24H, 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.5 (vt, 10 Hz, *C*−N of PNP), 145.7 (s, S*C*$_{12}$H$_8$), 136.4 (s, S*C*$_{12}$H$_8$), 131.7 (s, C_{Ar} of PNP), 131.4 (s, C_{Ar} of PNP), 126.8 (s, S*C*$_{12}$H$_8$), 125.8 (s, S*C*$_{12}$H$_8$), 124.6 (s, S*C*$_{12}$H$_8$), 123.7 (vt, 3 Hz, C_{Ar} of PNP), 123.5 (s, S*C*$_{12}$H$_8$), 122.6 (vt, 18 Hz, C_{Ar} of PNP), 121.7 (s, S*C*$_{12}$H$_8$), 115.5 (vt, 5 Hz, C_{Ar} of PNP), 24.8 (vt, 10 Hz, *C*H(CH_3)$_2$), 20.5 (s, Ar−*C*H_3), 18.9, 18.0 (two s, CH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 46.0 (d, 136 Hz).

Synthesis of (PNP)Rh(S(O)Ph$_2$) (16). 10 (40.0 mg, 0.062 mmol) was treated with phenyl sulfoxide (13.7 mg, 0.068 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube and heated at 65 °C for 18 h. The resultant solution was evaporated to dryness to yield an orange solid residue. Next, this residue was dissolved in Et_2O and placed in the freezer at −35 °C to afford **16** by precipitation. Yield: 0.025 g (55%). ^{1}H NMR (C_6D_6): δ 8.07 (d, 4H, 7 Hz, SC$_6$*H*$_5$), 7.77 (d, 2H, 8 Hz, Ar−*H* of PNP), 7.07 (s, 2H, Ar−*H* of PNP), 6.90 (2 triplets overlapped, 6H, 8 Hz, SC$_6$*H*$_5$), 6.79 (d, 2H, 8 Hz, Ar−*H* of PNP), 2.19 (s, 6H, Ar−C*H*$_3$ of PNP), 1.94 (m, 4H, C*H*Me$_2$), 1.20 (app. quartet (dvt), 24H, 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 162.9 (vt, 10 Hz, *C*−N of PNP), 153.3 (s, S−*i*-*C*$_6$H$_5$), 131.6 (s, C_{Ar} of PNP), 131.3 (s, C_{Ar} of PNP), 130.4 (s, S*C*$_6$H$_5$), 129.1 (s, S*C*$_6$H$_5$), 124.5 (s, S*C*$_6$H$_5$), 123.8 (vt, 3 Hz, C_{Ar} of PNP), 122.8 (vt, 18 Hz, C_{Ar} of PNP), 116.1 (vt, 6 Hz, C_{Ar} of PNP), 24.8 (vt, 6 Hz, *C*H(CH_3)$_2$), 20.6 (s, Ar−*C*H_3), 19.8, 18.1 (two singlets, CH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 41.0 (d, 146 Hz). Anal. Calcd for $C_{38}H_{50}NORhP_2S$: C, 61.98; H, 6.68. Found: C, 62.20; H, 6.86.

Synthesis of (PNP)Rh(SPh)(Ph) (17). 18b (63.0 mg, 0.091 mmol) was treated with thiophenol (10.3 μL, 0.100 mmol) in fluorobenzene (2 mL) in a Teflon stoppered gastight round-bottom flask. The reaction mixture was stirred for 10 min at ambient temperature, and NaO^{t}Bu (9.6 mg, 0.100 mmol) was added. After another 10 min, the solution was treated with water (1.8 mL) and then evaporated to dryness. The residue was extracted with Et_2O and filtered through Celite. The filtrate was evaporated to dryness to yield a green solid residue. This residue was triturated three times with toluene (3 × 5 mL) to give **17** that was >95% pure by NMR. Yield: 60 mg (92%). ^{1}H NMR (CD_2Cl_2, −50 °C): δ 8.20 (br d, 8 Hz, 1H, C$_6$*H*$_5$), 7.76 (d, 2H, 8 Hz, Ar−*H* of PNP), 7.50 (d, 2H, 8 Hz, SC$_6$*H*$_5$), 7.06−6.98 (three triplets are overlapping, 3H, SC$_6$*H*$_5$), 6.97 (d, 2H, 8 Hz, Ar−*H* of PNP), 6.91 (s, 2H, Ar−*H* of PNP), 6.68 (t, 1H, 8 Hz, C$_6$*H*$_5$), 6.61 (t, 1H, 8 Hz, C$_6$*H*$_5$), 6.41 (br d, 8 Hz, 1H, C$_6$*H*$_5$), 6.29 (t, 1H, 8 Hz, C$_6$*H*$_5$), 2.48 (br m, 2H, C*H*Me$_2$), 2.39 (br m, 2H, C*H*Me$_2$), 2.22 (s, 6H, Ar(PNP) −C*H*$_3$), 1.08 (br app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.01 (br app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 0.80 (br app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 0.12 (br app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, −50 °C): δ 160.0 (vt, 10 Hz, *C*−N of PNP), 148.2 (t, J_{C-Rh} = 6 Hz, S−*i*-*C*$_6$H$_5$), 141.3 (s, Ar−*C*), 140.5 (dt, J_{C-P} = 9 Hz, J_{C-Rh} = 38 Hz, *i*-*C*$_6$H$_5$), 134.6, 134.1 (two s, 2C, Ar−*C*), 132.9, 131.4 (s, 2C, C_{Ar} of PNP), 127.7 (s, Ar−*C*), 126.6 (s, Ar−*C*), 126.1 (s, Ar−*C*), 125.8 (vt, 3 Hz, C_{Ar} of PNP), 123.9 (s, Ar−*C*), 122.6 (s, Ar−*C*), 118.3 (vt, 18 Hz, C_{Ar} of PNP), 117.5 (vt, 6 Hz, C_{Ar} of PNP), 25.9 (vt, 11 Hz, *C*H(CH_3)$_2$), 23.9 (vt, 13 Hz, *C*H(CH_3)$_2$), 20.26, 20.16 (two s, 2C, Ar−*C*H_3), 19.4 (br s, CH(*C*H_3)$_2$), 17.2−16.5 (seven br s, 7C, CH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 37.7 (d, 108 Hz).

Observation of Interconversion of 9 and 17. Experiment A. 9 (20.0 mg) was dissolved in 0.7 mL of C_6D_6 in a J. Young NMR tube, and the solution was heated at 65 °C for 18 h. **Experiment B. 17** (20.0 mg) was dissolved in 0.7 mL of C_6D_6 in a J. Young NMR tube, and the solution was heated at 65 °C for 18 h. **Experiment C. 10** (0.020 g, 0.031 mmol) was treated with diphenyl sulfide (15.6 μL, 0.092 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube. The solution was heated at 65 °C for 24 h. In all three experiments, a 1:1 mixture of **9**:**17** was observed following the thermolyses.

Synthesis of (PNP)Rh(μ-N$_2$)Rh(PNP) (19a) and (PNP)Rh(η^1-N$_2$) (19b). A solution of **4** (30 mg, 0.051 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube was degassed by freeze−pump−thaw techniques, and the tube was back-filled with N_2. Next, the tube was taken into an argon glovebox, opened, and MeMgCl (18 μL, 0.057 mmol) was added. After 10 min at ambient temperature, **19a** was the only compound observed by ^{31}P{^{1}H} NMR (>95%). The solution was degassed again by freeze−pump−thaw techniques, and the tube was back-filled with N_2. After 18 h at ambient temperature, a 7:3 mixture of **19a**:**19b** was observed by ^{31}P{^{1}H} NMR. The resulting solution was filtered through a plug of silica. The filtrate was evaporated to dryness to yield an orange solid residue. The residue contained **19a**:**19b** in a 7:3 ratio and was >95% pure (NMR evidence). A small sample of pure **19a** was obtained by recrystallization from an ether solution of **19a**/**b** at −35 °C. **19a.** ^{1}H NMR (C_6D_6): δ 7.67 (d, 2H, 9 Hz, Ar−*H* of PNP), 6.96 (s, 2H, Ar−*H* of PNP), 6.75 (d, 2H, 9 Hz, Ar−*H* of PNP), 2.29 (m, 4H, C*H*Me$_2$), 2.20 (s, 6H, Ar−C*H*$_3$ of PNP), 1.45 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.21 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.5 (vt, 10 Hz, *C*−N of PNP), 131.9 (s, C_{Ar} of PNP), 131.6 (s, C_{Ar} of PNP), 124.3 (vt, 3 Hz, C_{Ar} of PNP), 121.0 (vt, 18 Hz, C_{Ar} of PNP), 115.9 (vt, 5 Hz, C_{Ar} of PNP), 25.5 (vt, 10 Hz, *C*H(CH_3)$_2$), 20.5 (s, Ar−*C*H_3), 19.7 (s, CH-(*C*H_3)$_2$), 18.4 (s, CH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 51.1 (d, 139 Hz). Data for **19b** follow (identified in a **19a**/**19b** mixture): 7.64 (d, 2H, 9 Hz, Ar−*H* of PNP), 6.90 (s, 2H, Ar−*H* of PNP), 6.75 (d, 2H, 9 Hz, Ar−*H* of PNP), 2.29 (m, 4H, C*H*Me$_2$), 2.20 (s, 6H, Ar−C*H*$_3$ of PNP), 1.28 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.11 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.2 (vt, 10 Hz, *C*−N of PNP), 131.7 (s, C_{Ar} of PNP), 131.5 (s, C_{Ar} of PNP), 123.9 (vt, 3 Hz, C_{Ar} of PNP), 121.0 (vt, 18 Hz, C_{Ar} of PNP), 115.9 (vt, 5 Hz, C_{Ar} of PNP), 25.1 (vt, 10 Hz, *C*H(CH_3)$_2$), 20.4 (s, Ar−*C*H_3), 19.4 (s, CH(*C*H_3)$_2$), 18.2 (s, CH(*C*H_3)$_2$). ^{31}P-{^{1}H} NMR (C_6D_6): δ 52.4 (d, 137 Hz). IR (C_6D_6): $\nu_{N\equiv N}$ 2115 cm^{-1}.

Interconversion between 19a and 19b. A solution of **4** (80 mg, 0.14 mmol) in C_6D_6 (3 mL) in a Teflon stoppered gastight round-

bottom flask was degassed by freeze−pump−thaw techniques, and the flask was back-filled with N_2. The reaction mixture was stirred for 10 min at ambient temperature, and the flask was taken into an argon glovebox, opened, and MeMgCl (49 μL, 0.15 mmol) was added. After 10 min at room temperature, **19a** was the only compound observed by $^{31}P\{^1H\}$ NMR. The solution was then degassed by freeze−pump−thaw techniques, and the flask was back-filled with N_2. Thermolysis of this solution during 3 d at 65 °C resulted in a conversion to a 5:95 mixture of **19a**:**19b** (NMR evidence). Removal of the overhead N_2 gas and continued thermolysis (65 °C) changed the ratio to 50:50.

Reaction of (PNP)Rh(SPr$^i_2$) (10) with N_2 To Yield 19a and 19b. A solution of **10** (20.0 mg, 0.031 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube was degassed by freeze−pump−thaw techniques, and the NMR tube was back-filled with N_2. The sample was placed in an oil bath, which was preheated at 65 °C. The disappearance of **10** was monitored by $^{31}P\{^1H\}$ NMR. After 24 h at 65 °C, a mixture of **19a** (66%), **19b** (17%), and **10** (17%) was observed by $^{31}P\{^1H\}$ NMR.

Synthesis of (PNP)Rh(η^2-CH$_2$=CHCMe$_3$) (21). 4 (50 mg, 0.086 mmol) was treated with 3,3-dimethyl-1-butene (14 μL, 0.094 mmol) in C_6D_6 (1 mL) in a J. Young NMR tube followed by MeMgCl (31 μL, 0.094 mmol). After 10 min, the solution was treated with water (1.7 mL) and then evaporated to dryness, and the residue was extracted with Et_2O and filtered through Celite. The ether solution was evaporated to dryness to yield a green solid residue. $^{31}P\{^1H\}$ NMR analysis of this green residue revealed the presence of (PNP)Rh(H)(Cl) **5** (δ 50.4 ppm, d, J_{P-Rh} = 104 Hz), in addition to **21**. This solution in C_6D_6 (0.7 mL) was treated with 3,3-dimethyl-1-butene (13.6 μL, 0.094 mmol) followed by NaO^t-Bu (8.2 mg, 0.086 mmol). After 10 min, the solution was treated with water (1.6 mL) and then evaporated to dryness, and the residue was extracted with Et_2O and filtered through Celite. The ether solution was evaporated to dryness to yield a green solid residue. The $^{31}P\{^1H\}$ NMR spectrum of this green residue in C_6D_6 shows only the resonance of **21**. This residue was dissolved in Et_2O and placed in the freezer at −35 °C to afford **21** by precipitation. Yield: 33 mg (62%). ^1H NMR (C_6D_6): δ 7.53 (d, 2H, 9 Hz, Ar−*H* of PNP), 6.95 (s, 2H, Ar−*H* of PNP), 6.85 (s, 2H, Ar−*H* of PNP), 6.76 (d, 2H, 8 Hz, Ar−*H* of PNP), 4.43 (br m, 1H, CH$_a$H$_b$=C*H*C(CH$_3$)$_3$), 2.88 (t, 1H, 8 Hz, C*H$_a$*H$_b$=CHC(CH$_3$)$_3$), 2.78 (d, 1H, 8 Hz, CH$_a$*H$_b$*=CHC(CH$_3$)$_3$), 2.34 (m, 1H, C*H*Me$_2$), 2.18 (two multiplets overlapping, 2H, C*H*Me$_2$), 2.18 (s, 6H, Ar−C*H*$_3$ of PNP), 2.02 (m, 1H, C*H*Me$_2$), 1.31−0.90 (eight app. quartets (dvt) overlapping, 24H, CH*Me*$_2$), 1.21 (s, 9H, CH$_a$H$_b$=CHC(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 162.2 (vt, 10 Hz, *C*−N of PNP), 131.9 (s, *C$_{Ar}$* of PNP), 130.7 (s, *C$_{Ar}$* of PNP), 124.6 (vt, 18 Hz, *C$_{Ar}$* of PNP), 122.0 (br vt, *C$_{Ar}$* of PNP), 115.4 (br vt, *C$_{Ar}$* of PNP), 72.3 (d, J_{C-Rh} = 11 Hz, CH$_a$H$_b$=*C*HC(CH$_3$)$_3$), 36.8 (d, J_{C-Rh} = 11 Hz, *C*H$_a$H$_b$=CHC(CH$_3$)$_3$), 30.5 (s, CH$_a$H$_b$=CHC(*C*H$_3$)$_3$), 33.9 (s, *C*(CH$_3$)$_3$), 26.3 (br, *C*H(CH$_3$)$_2$), 25.8 (br, *C*H(CH$_3$)$_2$), 23.9 (br, *C*H(CH$_3$)$_2$), 23.0 (br, *C*H(CH$_3$)$_2$), 20.6 (s, Ar−*C*H$_3$), 20.0−17.2 (eight s, 8C, CH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 43.5 (dd, J_{P-P} = 328 Hz, J_{P-Rh} = 145 Hz), 37.9 (dd, J_{P-P} = 328 Hz, J_{P-Rh} = 135 Hz).

Equilibrium Constant Determination. C_6D_6 solutions containing (PNP)Rh−L and L′ (see Scheme 7 and Table 1) in three different ratios were prepared and subjected to thermolysis by placing the J. Young tubes containing the solutions into an oil bath preheated to 65 °C. The ratios were determined by integration of the $^{31}P\{^1H\}$ NMR spectra. Equilibrium constants were calculated as averages of three experiments. For details about each reaction, see the Supporting Information.

Oxidative Addition of PhI, PhBr, and PhCl to 10. 10 (20 mg, 0.031 mmol) and PhI (10.3 μL, 0.092 mmol) or PhBr (9.3 μL, 0.092 mmol) or PhCl (9.4 μL, 0.092 mmol) were co-dissolved in 0.8 mL of C_6D_6 in a J. Young NMR tube. The samples were placed in the same oil bath, which was preheated at 65 °C. The disappearance of **10** was monitored by $^{31}P\{^1H\}$ NMR. In the course of the reaction, **10** was converted into **18c**, **18b**, or **18a**, respectively. After 40 min at 65 °C, the conversions measured by $^{31}P\{^1H\}$ NMR were as follows: (**18c**, 95%), (**18b**, 85%), and (**18a**, 45%). Compound **18a** formed quantitatively after 16 h at 65 °C in C_6D_6.

Oxidative Addition of PhBr to 19a/b, 10, and 21. Experiment A. A mixture of complexes **19a/b** in a 7:3 ratio (27 mg, 0.049 mmol Rh) was obtained as described above from complex **4** (30.0 mg, 0.051 mmol) and MeMgCl (18.0 μL, 0.057 mmol). The mixture was dissolved in C_6D_6 (0.8 mL) in a J. Young NMR tube followed by addition of PhBr (15.6 μL, 0.154 mmol). **Experiment B. 10** (22.0 mg, 0.034 mmol) was dissolved in 0.8 mL of C_6D_6 in a J. Young NMR tube followed by addition of PhBr (10.3 μL, 0.102 mmol). **Experiment C. 21** (21.0 mg, 0.034 mmol) was dissolved in 0.8 mL of C_6D_6 in a J. Young NMR tube followed by addition of PhBr (10.3 μL, 0.102 mmol). **Thermolysis.** The three NMR tubes from experiments A, B, and C were placed into the same oil bath that was preheated to 65 °C. In the course of the reaction, **10**, **19**, and **21** were being converted into **18b**; the reaction progress was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 40 min, the conversions measured by $^{31}P\{^1H\}$ NMR were as follows: exp. C (**21**), 95%; exp. B (**10**), 85%; and exp. A (**19a/b**), 4%.

Kinetic Study of the Reaction of (PNP)Rh(SPr$^i_2$) (10) with PhBr. Experiments with Varying Concentrations of PhBr. 10 (0.020 g, 0.031 mmol) was dissolved in C_6D_6 in a J. Young NMR tube and treated with PhBr (four different experiments for four different concentrations of PhBr: 15.6 μL, 0.155 mmol, 0.22 M; 31.2 μL, 0.310 mmol, 0.44 M; 46.8 μL, 0.465 mmol, 0.66 M; 62.4 μL, 0.620 mmol, 0.88 M) and SPr$^i_2$ (90 μL, 0.620 mmol). The total volume of each solution was 0.700 mL (by using the appropriate amount of C_6D_6). All four NMR tubes were placed in the same oil bath, which was preheated to 65 °C. The disappearance of **10** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at regular intervals for at least 3 half-lives and followed pseudo first-order kinetics. **Experiments with Varying Concentrations of SPr$^i_2$. 10** (0.020 g, 0.031 mmol) was dissolved in C_6D_6 in a J. Young NMR tube and was treated with SPr$^i_2$ (four different experiments for four different concentrations of isopropyl sulfide: 22.5 μL, 0.155 mmol, 0.22 M; 45 μL, 0.310 mmol, 0.44 M; 67.5 μL, 0.465 mmol, 0.66 M; 90 μL, 0.620 mmol, 0.88 M) and PhBr (15.6 μL, 0.155 mmol). The total volume of each solution was 0.700 mL (by using the appropriate amount of C_6D_6). The samples were placed in an oil bath, which was preheated to 65 °C. The disappearance of **10** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at regular intervals for at least 3 half-lives and followed pseudo first-order kinetics. See the Supporting Information for further details.

Influence of [Ph$_2$SO] on the Rate of Conversion of 10 to 16. 10 (0.020 g, 0.031 mmol) was dissolved in C_6D_6 in a J. Young NMR tube and was treated with Ph_2SO (two different experiments for two different concentrations of Ph_2SO: 31.3 mg, 0.155 mmol, 0.22 M; 125.4 mg, 0.620 mmol, 0.88 M) and SPr$^i_2$ (22.5 μL, 0.155 mmol to each experiment). The samples were placed in an oil bath, which was preheated to 65 °C. The disappearance of **10** was monitored by $^{31}P\{^1H\}$ NMR after 19 and 39 min. At 19 min, the **16**:**10** ratio for the experiment with [Ph_2SO] = 0.88 M was 75:25, whereas for the experiment with [Ph_2SO] = 0.22 M this ratio was 50:50. At 39 min, **10** was fully converted into **16** for the experiment with [Ph_2SO] = 0.88 M, whereas for the experiment with [Ph_2SO] = 0.22 M the **16**:**10** ratio was 60:40.

Reaction of 10 with Ph$_2$SO at Ambient Temperature. 10 (17.0 mg, 0.026 mmol) was treated with Ph_2SO (5.9 mg, 0.029 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube. After 40 min at ambient temperature, **10** (>97%) and **16** (<3%) were observed by $^{31}P\{^1H\}$ NMR. After 2 h at ambient temperature, **10** (92%) and **17** (8%) were observed by $^{31}P\{^1H\}$ NMR.

Attempt at Observation of a Putative Five-Coordinate Rh^I Complex. (PNP)Rh(SPr$^i_2$) (17.0 mg, 0.026 mmol) was treated with

isopropyl sulfide (189 μL, 1.30 mmol) in C_6D_6 (0.7 mL) in a J. Young NMR tube. After 3 days at room temperature, (PNP)Rh(SPr^i_2) was the only compound observed by $^{31}P\{^1H\}$ NMR. After 7 h at 65 °C, (PNP)Rh(SPr^i_2) was still the only compound observed by $^{31}P\{^1H\}$ NMR.

Influence of [SPr^i_2] on the Rate of Conversion of 10 to 16. **10** (0.020 g, 0.031 mmol) was dissolved in C_6D_6 in a J. Young NMR tube and was treated with SPr^i_2 (two different experiments for two different concentrations of isopropyl sulfide: 31.3 mg, 0.155 mmol, 0.22 M; 125.4 mg, 0.620 mmol, 0.88 M), and Ph_2SO (31.3 mg, 0.155 mmol to each experiment) was added. The samples were placed in an oil bath, which was preheated to 65 °C. The disappearance of **10** was monitored by $^{31}P\{^1H\}$ NMR at 34 and 69 min. At 34 min, the **10**:**16** ratio for the experiment with [SPr^i_2] = 0.88 M was 60:40, whereas for the experiment with [SPr^i_2] = 0.22 M it was 50:50. At 69 min, the **10**:**16** ratio for the experiment with [SPr^i_2] = 0.88 M was 50:50, whereas for the experiment with [SPr^i_2] = 0.22 M it was 80:20.

X-ray Data Collection, Solution, and Refinement for 19a. Single crystals of **19a** suitable for X-ray diffraction measurements were obtained by recrystallization from ether and were mounted on a MiteGen mount using Paratone oil. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo Kα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections, were carried out using the Bruker Apex2 software.[40] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120 K, using a frame time of 10 s and a detector distance of 60 mm. The optimized strategy used for data collection consisted of ϕ and ω scan sets, with 0.5° steps in ω; completeness was 99.6%. A total of 4149 frames were collected. Final cell constants were obtained from the *xyz* centroids of 9054 reflections after integration.

From the lack of systematic absences, the observed metric constants, and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structures were solved using SIR-92[41] and refined (full-matrix least-squares) using the Oxford University "Crystals for Windows" program.[42] All non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were fixed at calculated geometric positions and allowed to ride on the corresponding carbon atoms. The asymmetric unit contains one dirhodium complex and one ether solvate molecule. The ether molecule contains disordered ethyl groups. The sum of the two disordered components was constrained to sum to 1.0; the major component had an occupancy of 0.817(16). The final least-squares refinement converged to $R_1 = 0.0242$ ($I > 2\sigma(I)$, 14 881 data) and w$R_2 = 0.0624$ (F^2, 17 360 data, 613 parameters).

X-ray Data Collection, Solution, and Refinement for 21. Single crystals of **21** suitable for X-ray diffraction measurements were obtained by recrystallization from ether/pentane and were mounted in a glass capillary. Data collection was carried out at room temperature (low temperature apparatus was not available) on a CAD-4 Turbo diffractometer equipped with Mo Kα radiation;[43] completeness was 100%. The structure was solved by direct methods (SIR92).[41] From the lack of systematic absences, the observed metric constants, and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. Full-matrix least-squares refinement was carried out using the Oxford University "Crystals for Windows" system.[42] All nonhydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were fixed at calculated geometric positions and updated after each least-squares cycle. The final least-squares refinement converged to $R_1 = 0.0563$ ($I > 2\sigma(I)$, 5180 data) and w$R_2 = 0.0624$ (F, 6500 data, 325 parameters).

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Supporting Information Available: Crystallographic information for **19a** and **21** in the form of CIF files, experimental details on the equilibrium and kinetics experiments, and pictorial NMR spectra for select compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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