*Organometallics* **2008,** *27,* 6257–6263

# Oxidative Addition Reactions of Silyl Halides with the (PNP)Rh Fragment

Sylvain Gatard, Chun-Hsing Chen, Bruce M. Foxman, and Oleg V. Ozerov*

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

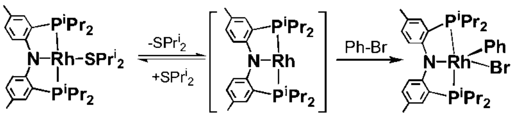
*Received March 7, 2008*

The (PNP)Rh fragment, where PNP is the bis(*o*-diisopropylphosphinophenyl)amide "pincer" ligand, has been shown to undergo a series of silicon−halogen oxidative addition reactions. (PNP)Rh(SPr$^i_2$) (**1**) reacted with certain silyl halides with formation of (PNP)Rh(Silyl)(Hal) and release of SPr$^i_2$. The reactions with 1.1 equiv of Me$_3$Si-I, Cl$_3$Si-Cl, or MeCl$_2$Si-Cl proceeded to completion, the reactions with 1.1 equiv of Me$_2$ClSi-Cl or Me$_3$Si-Br produced an equilibrium mixture of (PNP)Rh(Silyl)(Hal) and (PNP)Rh(SPr$^i_2$) (**1**), and the reaction with Me$_3$Si-Cl did not proceed at all. (PNP)Rh(SiMe$_3$)(Cl) was instead prepared via the reaction of (PNP)Rh(Me)(CH$_2$Ph) with Me$_3$Si-Cl, which proceeds with concomitant elimination of ethylbenzene. The reaction of (PNP)Rh(SPr$^i_2$) (**1**) with Me$_2$SiHCl led to the exclusive formation of (PNP)Rh(SiMe$_2$Cl)(H) (**14**), containing a borderline Si···H contact. (PNP)Rh(SPr$^i_2$) (**1**) and (PNP)Rh(SiMe$_2$Cl)(Cl) (**7**) displayed similar rates in the reaction with PhBr that results in (PNP)Rh(Ph)(Br), presumably via the rate-limiting elimination of either SPr$^i_2$ or Me$_2$SiCl$_2$.

## Introduction

Oxidative addition (OA) and its reverse (RE) are among the most fundamental reactions in organometallic chemistry.[1] OA/RE reactions involving carbon−element bonds are a customary focus because of their importance in the syntheses of organic compounds.[2] OA/RE reactions involving silicon, the heavier congener of carbon, receive less attention.[3−9] We have previously reported a series of OA and RE reactions, as well as ligand exchange reactions, occurring at a Rh(I) center[10,11] supported by the diarylamido-based PNP pincer ligand.[12,13] The (PNP)Rh fragment is especially convenient for these studies, as it is compatible with a large variety of reactions, potentially allowing for well-defined comparisons of the kinetic and thermodynamic parameters. For example,[10b] we showed that (PNP)Rh(SPr$^i_2$) (**1**) reacts with PhBr to give the Rh(III) OA product (PNP)-Rh(Ph)(Br) (**3**) via a dissociative mechanism with intermediate generation of the unsaturated (PNP)Rh fragment **2** (Scheme 1).[14] Herein, we report our studies of Si-Hal OA reactions with the (PNP)Rh fragment. Our work provides insight into the relative thermodynamic affinity of the (PNP)Rh fragment toward addition of various halosilanes and how it compares with its affinity toward addition of other species.

**Scheme 1**



(PNP)Rh(SPr$^i_2$)
**1**

[(PNP)Rh]
**2**

(PNP)Rh(Ph)(Br)
**3**

---

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

(1) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-Interscience: New York, 2001; pp 149−173. (b) van Leeuwen, P. W. N. M. *Homogeneous Catalysis: Understanding the Art*; Kluwer Academic Publishers: Dordrecht, 2004; pp 271−298 and 387−402.

(2) Negishi, E. I., Ed. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley-Interscience: New York, 2002.

(3) Yoo, H.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **2006**, *128*, 6038.

(4) (a) Uson, R.; Oro, L. A.; Fernandez, M. J. *J. Organomet. Chem.* **1980**, *193*, 127. (b) Uson, R.; Oro, L. A.; Ciriano, M. A.; Gonzalez, R. *J. Organomet. Chem.* **1981**, *205*, 259.

(5) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1826.

(6) Yamashita, H.; Kawamoto, A. M.; Tanaka, M.; Goto, M. *Chem. Lett.* **1990**, 2107.

(7) Clark, H. C.; Hampden-Smith, M. J. *Coord. Chem. Rev.* **1987**, *79*, 229.

(8) (a) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M.; Goto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4417. (b) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1997**, *16*, 4696.

(9) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447.

(10) (a) Gatard, S.; Çelenligil-Çetin, R.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2006**, *128*, 2808. (b) Gatard, S.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2007**, *26*, 6066.

(11) For other reports on the chemistry of (PNP)Rh complexes, see the following:(a) Weng, W.; Guo, C.; Çelenligil-Çetin, R.; Foxman, B. M.; Ozerov, O. V. *Chem. Commun.* **2006**, 197. (b) Weng, W.; Guo, C.; Moura, C. P.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2005**, *24*, 3487. (c) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792. (d) Winter, A. M.; Eichele, K.; Mack, H.-G.; Potuznik, S.; Mayer, H. A.; Kaska, W. C. *J. Organomet. Chem.* **2003**, *682*, 149.

(12) For reviews on the chemistry of diarylamido-based PNP complexes, see: (a) Liang, L.-C. *Coord. Chem. Rev.* **2006**, *250*, 1152. (b) Ozerov, O. V. In *The Chemistry of Pincer Compounds*; Morales-Morales, D., Jensen, C., Eds.; Elsevier: Amsterdam, 2007; pp 287−309.

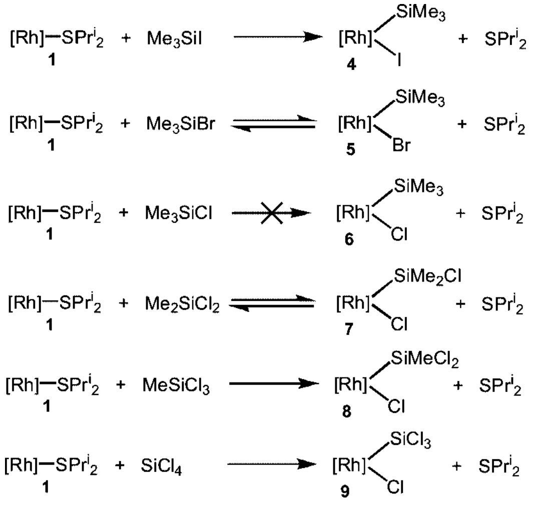
(13) The diarylamido-based PNP ligand used in this work is preceded and to some degree inspired by the Fryzuk amido/(bis)phosphine ligand[13a,b] of the [(R$_2$PCH$_2$SiMe$_2$)N] type that has more recently been employed by Caulton et al.:[13c,d]

(a) Fryzuk, M. D. *Can. J. Chem.* **1992**, *70*, 2839–2845. (b) Fryzuk, M. D.; Berg, D. J.; Haddad, T. S. *Coord. Chem. Rev.* **1990**, *99*, 137. (c) Ingleson, M. J.; Fullmer, B. C.; Buschhorn, D. T.; Fan, H.; Pink, M.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **2008**, *47*, 407. (d) Ozerov, O. V.; Watson, L. A.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2007**, *129*, 6003.

(14) The instability of the "naked" (PNP)Rh fragment precludes its characterization. While we do not know its precise structure and whether it is truly a 14-electron three-coordinate fragment, it behaves as a kinetic equivalent of such. A recent study by Caulton et al. demonstrated that a closely related (PNP*)Rh fragment (where PNP* is the Fryzuk-type ligand ($^t$Bu$_2$PCH$_2$SiMe$_2$) $_2$N) favors a Rh(III) ground state resulting from the intramolecular OA of a C−H bond. Verat, A. Y.; Pink, M.; Fan, H.; Tomaszewski, J.; Caulton, K. G. *Organometallics* **2008**, *27*, 166.

10.1021/om800216h CCC: $40.75

**Scheme 2**



## Results and Discussion

**Reactions of Si-Hal-Containing Compounds with (PNP)Rh(SPr$^i_2$) (1).** Complex **1** proved to be a viable (PNP)Rh synthon in reactions with halobenzenes,[10b] and we set out to explore its reactivity in Si-Hal OA reactions. We initially focused on the reactions of **1** with $Me_3Si$-Hal reagents (Scheme 2). No oxidative addition product was observed in the reactions of **1** with $Me_3Si$-Cl. The OA of $Me_3SiBr$ to (PNP)Rh is approximately isoergic with the binding of SPr$^i_2$ ($K_{eq} = 0.8(1)$ for the conversion from **1** to **5**). The reaction of 1.1 equiv of $Me_3Si$-I with **1** proceeded to completion, giving **4** as product. This is in contrast to the OA reactions of Ph-Hal, where Hal = Cl, Br, and I, all leading to thermodynamically favorable OA reaction with **1**. The intrinsic bond energetics must play a role here, but the conical $Me_3Si$ group must also create greater steric encumbrance compared to the flat, “wedge-like” Ph group in the OA products.

The second set of compounds we explored were compounds with a varying number of Cl and Me groups on Si (Scheme 2). As mentioned before, **1** did not react with $Me_3SiCl$. The reaction of **1** with $Me_2SiCl_2$ required 35 equiv of $Me_2SiCl_2$ to proceed to >95% conversion to **7** (<24 h, 70 °C), while the reactions of **1** with 1.1 equiv of $MeSiCl_3$ or $SiCl_4$ proceeded completely to form the OA products **8** and **9**, respectively. The incomplete conversion in the reaction with $Me_2SiCl_2$ is a thermodynamic issue ($K_{eq} = 1.0(1)$ from a set of exchange reactions), similarly to $Me_3SiBr$. We have also tested the reactivity of **1** with $Me_3SiOTf$, $Me_3SiOSiMe_3$, and $Me_3SiSiMe_3$ and found that **1** remained unchanged after extended thermolysis (48 h, 85 °C, $C_6D_6$) in the presence of these reagents.

Tanaka et al. studied the reactions of Pt(0) phosphine complexes with the same set of Si-Hal reagents as used in Scheme 2 here.[8] Interestingly, the thermodynamic trends in the Tanaka work are the same as observed in this work: higher thermodynamic preference for OA of heavier halogen−silicon bonds and for OA of Si−Cl bonds with more Cl substituents on Si.

**Synthesis of (PNP)Rh(SiMe$_3$)(Br) (5) and (PNP)-Rh(SiMe$_3$)(Cl) (6) via C−C Elimination at Rh.** We recently described complexes (PNP)Rh(Ph)(Me) (**11**) and (PNP)RhPh$_2$ (**12**).[10a] Both undergo clean C−C RE to generate the (PNP)Rh fragment (**2**) in situ (Scheme 3). However, both **11** and **12** are too short-lived to be conveniently isolable on the experimental time scale. We surmised that C(sp$^3$)−C(sp$^3$) RE should proceed more slowly than either C(sp$^2$)−C(sp$^2$) or C(sp$^3$)−C(sp$^2$) RE, as has been shown for Pd/Pt systems.[15,16] (PNP)Rh(Me)(Cl) (**10**) was found to react with $PhCH_2MgCl$ to give a 95:5 mixture of two new compounds that we have identified as (PNP)Rh(Me)(CH$_2$Ph) (**13**) and (PNPRh(CH$_2$Ph)$_2$[17] (**14**) on the basis of solution NMR data. While we have not performed rigorous kinetic measurements (as we did with **11/12**),[10a] the rates of C−C RE for **13** and especially **14** are much lower than those for **11** or **12**, insofar as the workup at 22 °C (ca. 30 min) does not result in significant degradation (<5%). When a $C_6D_6$ solution of a 95:5 mixture of **13/14** was treated with 1.1 equiv of $Me_3SiCl$ and allowed to stand for 3 days, >95% conversion to (PNP)Rh(SiMe$_3$)(Cl) (**6**) was observed in situ by NMR methods with concomitant production of ethylbenzene and bibenzyl (Scheme 3).

Interestingly, the isolation of a (PNP)Rh(R)(R′) precursor apparently is not always necessary. When (PNP)Rh(Me)(Cl) (**10**) was treated *first* with 1.1 equiv of $Me_3SiBr$ and *then* with 1.1 equiv of PhLi and allowed to stand for 24 h at ambient temperature, **5** was the major product of the reaction (NMR evidence) and was isolated in 40% yield (unoptimized yield of 14 mg) upon workup as an analytically pure solid. This is rather surprising, as it appears to indicate that PhLi reacted with **10** *faster* than with $Me_3SiBr$.

**Solution NMR Characterization of the Si-Hal OA Products.** All of the Si-X OA products (**4**−**9**) demonstrated time-averaged $C_s$ symmetry at 22 °C in the NMR experiments. These compounds are rich in NMR information and were fully characterized by $^1$H, $^{13}$C, $^{31}$P, and $^{29}$Si NMR in solution (Table 1 and the Experimental Section). The $^{31}$P chemical shift ($\delta$ 36−42 ppm) and the $J_{P-Rh}$ (100−112 Hz) data for the silicon−halogen oxidative addition products **4**−**9** are similar to those previously observed for (PNP)Rh(H)(Cl),[11c] (PNP)-Rh(Me)(Cl) (**10**),[11c] and (PNP)Rh(Ar)(X).[10a] In the series of (PNP)Rh(SiMe$_3$)(Hal) complexes (**4**−**6**), the nature of the halide has very little effect on the chemical $^{29}$Si chemical shift or the $J_{Si-Rh}$ or $J_{Si-P}$ values. On the other hand, in the series of (PNP)Rh(SiMe$_{3-n}$Cl$_n$)(Cl) complexes (**6**−**9**), the $J_{Si-Rh}$ and $J_{Si-P}$ values steadily increase with increasing $n$. This is indicative of a stronger interaction of the silyl group with Rh as the number of electron-withdrawing substituents on Si increases. A similar trend in the corresponding coupling constants was reported by Tanaka et al. for (Me$_{3-n}$Cl$_n$Si)(Cl)Pt(PEt$_3$)$_2$ complexes.[8]

**Structural Characterization of 7.** The solid-state structure of **7** was established in the course of a single-crystal X-ray diffraction study (Figure 1). The environment about Rh is best described as approximately square pyramidal with the silyl ligand occupying the apical position. Silyl is a ligand of strong trans-influence, and square pyramid with a strong trans-influence ligand trans to an empty site is a common motif for five-coordinate d$^6$ complexes.[18] Among the PNP-supported Rh complexes in our work, analogous structures have been determined in the solid state for (PNP)Rh(Ph)(Br) (**3**, apical Ph) and

---

(15) (a) Hartwig, J. F. *Inorg. Chem.* **2007**, *46*, 1936. (b) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892.

(16) (a) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *Organometallics* **2005**, *24*, 715. (b) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *Eur. J. Inorg. Chem.* **2007**, 5390.

(17) **13** is presumably formed via benzyl/methyl exchange between **13** and $PhCH_2MgCl$.

(18) (a) For analysis of the structural preferences of five-coordinate d$^6$ complexes see the following: Lam, W. H.; Shimada, S.; Batsanov, A. S.; Lin, Z.; Marder, T. B.; Cowan, J. A.; Howard, J. A. K.; Mason, S. A.; McIntyre, G. J. *Organometallics* **2003**, *22*, 4557. (b) Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671. (c) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pelissier, M. *Organometallics* **1992**, *11*, 729. (d) Olivan, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1997**, *16*, 2227.

**Scheme 3**

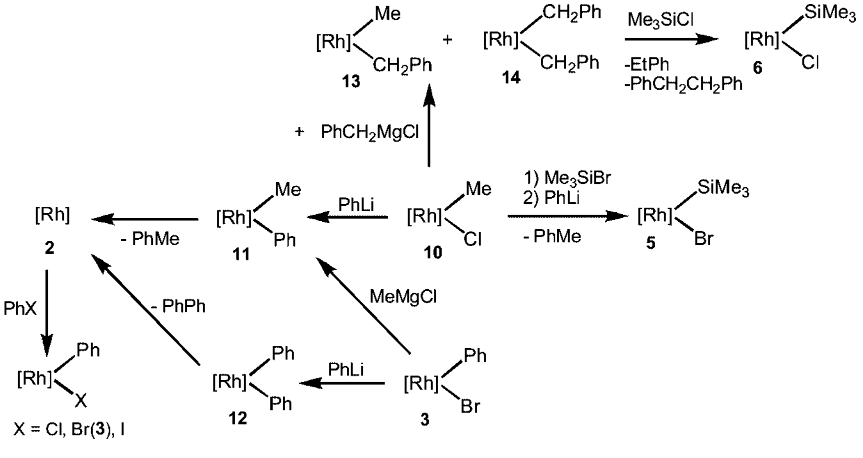


**Table 1. Selected NMR Data for 4−9**

| compd | $\delta$, $^{31}$P, ppm | $^{1}J_{\text{P-Rh}}$, Hz | $\delta$, $^{29}$Si, ppm | $^{1}J_{\text{Si-Rh}}$, Hz | $^{2}J_{\text{Si-P}}$, Hz |
|---|---|---|---|---|---|
| **4** | 39.5 | 113 | 60.7 | 28 | 8 |
| **5** | 37.2 | 110 | 59.5 | 28 | 8 |
| **6** | 36.4 | 112 | 58.5 | 29 | 8 |
| **7** | 38.7 | 109 | 66.7 | 39 | 8 |
| **8** | 40.8 | 104 | 42.5 | 57 | 10 |
| **9** | 42.1 | 100 | −12.5 | 87 | 12 |

(PNP)Rh(Me)(Cl) (**10**, apical Me).[10a,11c] The environment about Si is pseudotetrahedral (angles about Si range from 102° to 118°) with no structural evidence of interaction between Rh and the substituents on Si. The Rh−P, Rh−N, and Rh−Cl distances are unremarkable and comparable to those observed in **3** and **10**.[10a,11c] The Rh−Si distance in **7** (2.2777(9) Å) is only slightly shorter than the Rh−Si distance of 2.314(2) Å in $(Me_3P)_3Rh(H)_2(SiClPh_2)$ reported by Osakada et al.[19]

**Reaction of (PNP)Rh(SPr$^{i}_{2}$) (1) with Me$_2$SiHCl and the Structure of 15.** The reaction of **1** with $Me_2SiHCl$ offered insight into the competition between Si−H and Si−Cl OA. Complex **15** was formed exclusively after thermolysis (18 h, 70 °C). Given the conditions, it is reasonable to assume that the preference for **15** over the unobserved Si−Cl OA product is thermodynamic and not merely kinetic.

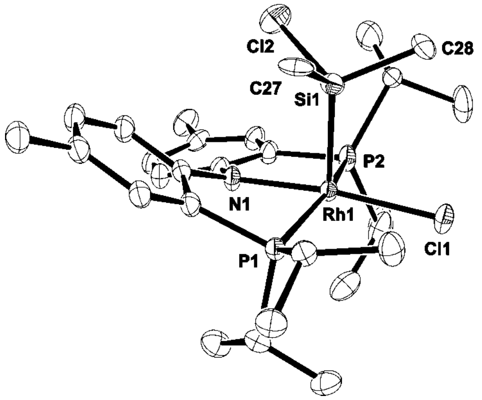
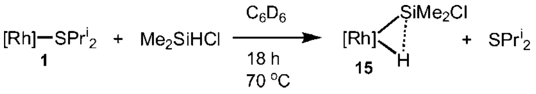


**Figure 1.** ORTEP[20] drawing (50% probability ellipsoids) of **7** showing selected atom labeling. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) follow: Rh1−Si1, 2.2777(9); Rh1−P1, 2.3249(8); Rh1−P2, 2.3256(8); Rh1−N1, 2.027(2); Rh1−Cl1, 2.3511(7); Si1−Rh1−P1, 96.46(3); Si1−Rh1−P2, 97.43(3); P1−Rh1−P2, 159.42(3); Si1−Rh1−N1, 91.56(8); P1−Rh1−N1, 80.38(7); P2−Rh1−N1, 84.13(7); Si1−Rh1−Cl1, 96.24(3); P1−Rh1−Cl1, 99.42(3); P2−Rh1−Cl1, 94.09(3); N1−Rh1−Cl1, 172.17(8).

**Scheme 4**



For **15**, it is conceivable to propose two bonding descriptions: either a classical silyl hydride formalism (true OA product) or an $\eta^2$-Si−H nonclassical $\sigma$-complex. $\eta^2$-Si−H complexes of Rh have been characterized for addition of Si−H to Rh(III),[21] but not Rh(I), as is the case here. Both the solution NMR data and the results of a solid-state X-ray diffraction on a single crystal of **15** (Figure 2) point to the identity of **15** being a borderline case. The hydridic resonance in **15** was found at $\delta$ −15.6 ppm in the $^1$H spectrum as a doublet of doublets of triplets, owing to the coupling to $^{29}$Si (31 Hz), $^{103}$Rh (24 Hz), and $^{31}$P (11 Hz), respectively. The $^{29}$Si resonance of **15** ($\delta$ 49.3 ppm) displays coupling to the hydride (31 Hz), $^{103}$Rh (23 Hz), and $^{31}$P (6 Hz). $J_{\text{Si-H}}$ values have been proposed as indicators of the presence of a residual Si−H interaction. Schubert's arbitrary proposal of 10−20 Hz as the lower limit for Si−H bonding is frequently used.[22] The value of 31 Hz falls slightly above this criterion. However, in a more recent review,[23]Nikonov cogently argued

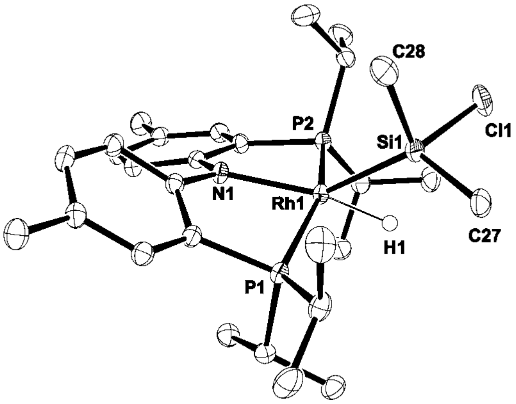
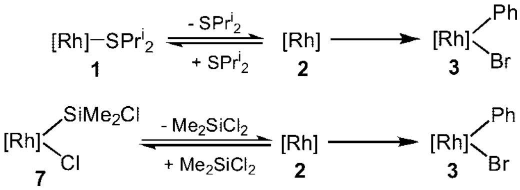


**Figure 2.** ORTEP[20] drawing (50% probability ellipsoids) of **15** showing selected atom labeling. Hydrogen atoms (except Rh-H) and the rotational disorder of the $Me_2SiCl$ group are omitted for clarity. Rotational disorder of the $SiClMe_2$ group is not shown. Selected bond distances (Å) and angles (deg) follow: Rh1−P1, 2.3081(4); Rh1−P2, 2.3056(4); Rh1−N1, 2.0642(13); Rh1−Si1, 2.2600(5); Rh1−H1, 1.50(2); Si1−H1, 1.93(2); P1−Rh1−P2, 156.195(16); P1−Rh1−N1, 80.62(4); P2−Rh1−N1, 82.58(4); P1−Rh1−Si1, 100.928(17); P2−Rh1−Si1, 102.866(17); N1−Rh1−Si1, 136.83(4); P1−Rh1−H1, 97.3(8); P2−Rh1−H1, 94.8(8); N1−Rh1−H1, 165.7(8).

**Scheme 5**



that $J_{Si-H}$ values should be evaluated with caution and that several factors need to be taken into account. For example, $J_{Si-H}$ values in free trialkylsilanes are intrinsically smaller than $J_{Si-H}$ values in silanes bearing electron-withdrawing substituents on Si (such as Cl). It is thus unreasonable to apply the same arbitrary "cutoff" value for different silanes.

For a true silyl hydride structure for **15**, a Y-shaped geometry is expected with an acute H−Rh−Si angle.[18] It is worth noting that acute H−Ta−PMe$_3$ and H−Re−PMe$_3$ angles have been previously shown to result in $J_{H-P}$ coupling as large as 75 Hz; nonclassical H−P interactions were not invoked.[24]

The $^{29}$Si−$^{103}$Rh coupling in **15** (23 Hz) is lower than for a presumably classical single Rh−Si bond in **7** (39 Hz); however, comparison of these values should also be made with caution because of the different structures of **15** and **7**. In the square-pyramidal **7**, the silyl ligand is trans to the empty site, which may lead to enhanced Rh−Si bonding.

The solid-state structure of **15** was determined by X-ray diffractometry (Figure 2). The N1−Rh1−Si1 angle of 136.83(4)° is consistent with both a Y-shaped OA product structure and a nonclassical silane complex. The hydrogen atom in question was located and its position was refined isotropically. Applying caution appropriate to the determination of hydrogen positions by X-ray diffractometry, we note that the Si−H distance is quite long (1.93(2) Å) and is near 2 Å, another arbitrary "cutoff" criterion introduced by Schubert.[22] At the same time the Rh−Si distance in **15** (2.2600(5) Å) is actually slightly shorter than the unambiguous Rh−Si single bond in **7** (2.2777(9) Å). The chemistry of Si−H addition to transition metals truly offers a continuum of structures in terms of the bonding situation. Our data indicate that **15** is at the end of this continuum, approaching or embodying an OA product.

**Oxidative Addition of PhBr.** We previously showed that the OA reaction of PhBr with **1** proceeds via a dissociative mechanism (Scheme 5).[10b] We surmised that the Si−Cl OA products may enter a similar reaction (Scheme 5), where the initial step, analogous to the simple SPr$^i_2$ dissociation, would be the loss of the chlorosilane via Si−Cl RE. To test this hypothesis, we performed thermolyses of **1**, **7**, and **8** with 1.1 equiv of PhBr in C$_6$D$_6$. After 40 min at 75 °C, the reactions with **1** and **7** resulted in similar conversions to **3** (88% and 80%, respectively), whereas no conversion was detected in the reaction with **8** ($^{31}$P NMR evidence). Since the activation energy for a dissociative reaction (be that plain ligand dissociation or loss of a molecule via RE) should be similar to the binding energy of the fragment being lost,[25] these results are consistent with the greater thermodynamic preference for the OA of MeSiCl$_3$ to the (PNP)Rh fragment compared to the OA of Me$_2$SiCl$_2$ and coordination of SPr$^i_2$. **1** is roughly isoergic with **7** (vide supra), and the similarity of their apparent rates of reaction with PhBr is consistent with a dissociative mechanism in both cases. At this point, however, we cannot conclusively establish the intrinsic mechanism of the reaction of (PNP)Rh (**2**) with silyl halides.

## Conclusion

Investigation of Si-Hal oxidative addition reactions to the (PNP)Rh fragment led to a few interesting findings. The thermodynamic favorability of the oxidative addition reactions increases for Me$_3$Si-Hal compounds in the series Cl < Br < I. The oxidative addition of the Si−Cl bond becomes more favorable with the increasing number of Cl substituents on the Si atom. On the other hand, Si−H addition is preferred over the Si−Cl addition when Me$_2$SiHCl is used as a substrate. (PNP)Rh(SPr$^i_2$) (**1**) serves as a convenient precursor for the (PNP)Rh fragment **2** (via SPr$^i_2$ dissociation) only for those reactions where oxidative addition of Si-Hal is more favorable than coordination of SPr$^i_2$. The less thermodynamically stable oxidative addition products can nonetheless be prepared by using C−C reductive elimination to access (PNP)Rh (**2**) irreversibly. Oxidative addition of PhBr proceeds at similar rates with (PNP)Rh(SPr$^i_2$) (**1**) and with (PNP)Rh(SiMe$_2$Cl)(Cl) (**7**). By analogy with the earlier studies of the reactivity of **1**,[10b] a dissociative mechanism is proposed for the reaction of PhBr with **7**, intimating initial loss of Me$_2$SiCl$_2$.

The rigid PNP ligand ensures that the (PNP)Rh framework endures a wide variety of ligand exchange, oxidative addition, and reductive elimination reactions and thus permits us to concentrate on straightforward kinetic and thermodynamic comparisons. The present study allows us to not only analyze the Si-Hal oxidative addition reactivity but also place it into the context of other reactions of (PNP)Rh.

## Experimental Section

**General Considerations.** Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Ethyl ether and pentane were dried and deoxygenated (by purging) using a solvent purification system by MBraun and stored over molecular sieves in an Ar-filled glovebox. C$_6$D$_6$ was dried over NaK/Ph$_2$CO, distilled, and stored over molecular sieves in an Ar-filled glovebox. Fluorobenzene was dried with CaH$_2$, then distilled and stored over molecular sieves in an Ar-filled glovebox. (PNP)Rh(Cl)(Me)[11c] and (PNP)Rh(SPr$^i_2$)[10b] were prepared according to modified published procedures. Silicon tetrachloride, MeSiCl$_3$, Me$_2$SiCl$_2$, Me$_3$SiCl, Me$_3$SiBr, Me$_3$SiI, Me$_2$SiHCl, Me$_3$SiSiMe$_3$, Me$_3$SiOTf, and Me$_3$SiOSiMe$_3$ were degassed prior to use and stored over molecular sieves in an Ar-filled glovebox. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 ($^1$H NMR, 399.755 MHz; $^{13}$C NMR, 100.518 MHz; $^{31}$P NMR, 161.822 MHz) and a Varian iNova 500 ($^{29}$Si NMR,

---

(19) Osakada, K.; Sarai, S.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16*, 3973.

(20) Ortep-3 for Windows. Farugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(21) Taw, F. L.; Bergman, R. G.; Brookhart, M. *Organometallics* **2004**, *23*, 886.

(22) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

(23) Nikonov, G. I. *Adv. Organomet. Chem.* **2005**, *53*, 217.

(24) (a) Ozerov, O. V.; Watson, L. A.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 6363. (b) Clark, J. R.; Pulvirenti, A. L.; Fanwick, P. E.; Sigalas, M.; Eisenstein, O.; Rothwell, I. P. *Inorg. Chem.* **1997**, *36*, 3623. (c) Parkin, B. C.; Clark, J. C.; Visciglio, V. M.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1995**, *14*, 3002.

(25) 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.

100 MHz) spectrometer. For $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra, the residual solvent peak was used as an internal reference. $^{31}$P{$^{1}$H} NMR spectra were referenced externally using 85% $H_3PO_4$ at 0 ppm. $^{29}$Si{$^{1}$H} NMR were referenced internally using tetramethylsilane at 0 ppm. The signal-to-noise ratios of the $^{29}$Si{$^{1}$H} NMR spectra of (PNP)Rh(I)($SiMe_3$) (**4**), (PNP)Rh(Br)($SiMe_3$) (**5**), and (PNP)Rh(Cl)($SiMe_3$) (**6**) were dramatically improved by addition of the relaxation agent $Cr(acac)_3$ (5−10 mg) to the sample.[26]

**(PNP)Rh(I)(SiMe$_3$) (4).** (PNP)Rh($SPr^i_2$) (**1**) (60.0 mg, 0.092 mmol) was treated with $Me_3SiI$ (14.4 $\mu$L, 0.101 mmol) in $C_6D_6$ (0.7 mL) in a J. Young NMR tube and heated at 70 °C for 18 h, resulting in a color change from orange to black. Analysis by $^{31}$P{$^{1}$H} NMR showed only **4**. The resultant solution was evaporated to dryness, and the residue was extracted with ether and filtered through Celite. The filtrate was evaporated to dryness to yield a green solid residue. This residue was dissolved in pentane and recrystallized at −35 °C to afford **4** by precipitation. Yield: 0.040 g (60%). $^{1}$H NMR ($C_6D_6$): $\delta$ 7.72 (d, 2H, 8 Hz, Ar-*H* of PNP), 7.12 (s, 2H, Ar-*H* of PNP), 6.78 (d, 2H, 8 Hz, Ar-*H* of PNP), 2.92 (m, 2H, C*H*Me$_2$), 2.72 (m, 2H, C*H*Me$_2$), 2.16 (s, 6H, Ar−C*H*$_3$ of PNP), 1.68 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.40 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.18 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.10 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 0.41 (s, 9H, Si*Me*$_3$). $^{13}$C{$^{1}$H} NMR ($C_6D_6$): $\delta$ 160.0 (vt, 10 Hz, *C*-N of PNP), 132.2 (s, $C_{Ar}$ of PNP), 131.4 (s, $C_{Ar}$ of PNP), 125.6 (vt, 3 Hz, $C_{Ar}$ of PNP), 123.4 (vt, 18 Hz, $C_{Ar}$ of PNP), 117.5 (vt, 5 Hz, $C_{Ar}$ of PNP), 28.5 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 27.2 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 22.8 (s, Ar-*C*H$_3$), 20.5, 20.3, 19.9, 18.9 (four s, CH(*C*H$_3$)$_2$), 11.1 (s, Si(*C*H$_3$)$_3$). $^{31}$P{$^{1}$H} NMR ($C_6D_6$): $\delta$ 39.5 (d, 113 Hz). $^{29}$Si{$^{1}$H} NMR ($C_6D_6$): $\delta$ 60.7 (dt, $J_{Rh-Si}$ = 28 Hz, $J_{P-Si}$ = 8 Hz, Rh−Si). Anal. Found (Calcd) for $C_{29}H_{49}INP_2RhSi$: 47.46 (47.61); 6.59 (6.75).

**(PNP)Rh(Br)(SiMe$_3$) (5).** (PNP)Rh(Me)(Cl) (**10**) (30.0 mg, 0.052 mmol) was treated with $Me_3SiBr$ (7.0 $\mu$L, 0.057 mmol) in $C_6D_6$ (0.7 mL) in a J. Young NMR tube followed by addition of PhLi (28.4 $\mu$L, 0.057 mmol). After 24 h at ambient temperature, **5** was the main product observed by $^{1}$H and $^{31}$P{$^{1}$H} NMR. The solution was treated with a drop of water and then evaporated to dryness, and the residue was extracted with $Et_2O$ and filtered through Celite. The filtrate was evaporated to dryness to yield a green residue. This residue was dissolved in $Et_2O$ and recrystallized at −35 °C to afford **5**. Yield: 14 mg (40%). $^{1}$H NMR ($C_6D_6$): $\delta$ 7.72 (d, 2H, 8 Hz, Ar-*H* of PNP), 7.12 (s, 2H, Ar-*H* of PNP), 6.78 (d, 2H, 8 Hz, Ar-*H* of PNP), 2.86 (m, 2H, C*H*Me$_2$), 2.72 (m, 2H, C*H*Me$_2$), 2.16 (s, 6H, Ar-C*H*$_3$ of PNP), 1.65 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.34 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.23 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.11 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 0.40 (s, 9H, Si*Me*$_3$). $^{13}$C{$^{1}$H} NMR ($C_6D_6$): $\delta$ 160.3 (vt, 10 Hz, *C*-N of PNP), 132.2 (s, $C_{Ar}$ of PNP), 131.4 (s, $C_{Ar}$ of PNP), 125.6 (vt, 3 Hz, $C_{Ar}$ of PNP), 123.4 (vt, 18 Hz, $C_{Ar}$ of PNP), 117.6 (vt, 5 Hz, $C_{Ar}$ of PNP), 27.8 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 27.0 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 21.7 (s, Ar-*C*H$_3$), 20.4, 20.2, 19.6, 18.9 (four s, CH(*C*H$_3$)$_2$), 9.5 (s, Si(*C*H$_3$)$_3$). $^{31}$P{$^{1}$H} NMR ($C_6D_6$): $\delta$ 37.2 (d, 110 Hz). $^{29}$Si{$^{1}$H} NMR ($C_6D_6$): $\delta$ 59.5 (dt, $J_{Rh-Si}$ = 28 Hz, $J_{P-Si}$ = 8 Hz, Rh-*Si*). Anal. Found (Calcd) for $C_{29}H_{49}BrNP_2RhSi$: 50.81 (50.88); 7.11 (7.21).

**Determination of $K_{eq}$ for the Reaction of (PNP)Rh($S^iPr_2$) (1) with Me$_3$SiBr.** (PNP)Rh($S^iPr_2$) (**1**) (20.0 mg, 30.8 $\mu$mol) in $C_6D_6$ (total volume brought to 0.70 mL) was treated with $Me_3SiBr$ (three different experiments were conducted for three different amounts of $Me_3SiBr$: 20 $\mu$L, 0.15 mmol, 0.22 M; 41 $\mu$L, 0.31 mmol, 0.44 M; 81 $\mu$L, 0.62 mmol, 0.88 M) in a J. Young NMR tube. The samples were placed in an oil bath, which was preheated to 65 °C. The reaction was monitored by $^{31}$P{$^{1}$H} NMR and $^{1}$H NMR at regular intervals until the ratio of products remains unchanged over time (<27 h at 65 °C). The ratio of free isopropyl sulfide to free bromotrimethylsilane was determined by integrating signals of the CH protons of isopropyl sulfide against the methyl protons of bromotrimethylsilane for each experiment. Trace amounts of (PNP)Rh(H)(Br) and an unknown product were detected in the $^{31}$P{$^{1}$H} NMR. The equilibrium constant was determined to be $K_{eq}$ = 0.8(1); the error was taken to be double the standard deviation calculated by MS Excel.

**(PNP)Rh(Cl)(SiMe$_3$) (6).** (PNP)Rh(Me)(Cl) (**10**) (50.0 mg, 0.086 mmol) was treated with $PhCH_2MgCl$ (95 $\mu$L of a 1.0 M solution in $Et_2O$, 0.095 mmol) in $C_6D_6$ (0.7 mL) in a J. Young NMR tube. After 10 min at ambient temperature, **13** (95%) and **14** (5%) were observed by $^{1}$H and $^{31}$P{$^{1}$H} NMR. The solution passed through a short plug of silica using fluorobenzene as eluent, and the resulting solution was evaporated to dryness. The residue was redissolved in $C_6D_6$ (0.7 mL) and treated with $Me_3SiCl$ (12 $\mu$L, 0.095 mmol). After 3 days at ambient temperature, NMR analysis revealed the formation of **6** as well as ethylbenzene (selected data: $^{1}$H NMR ($C_6D_6$): $\delta$ 2.43 (q, 2H, 8 Hz, C$_6$H$_5$-C*H*$_2$-CH$_3$), 1.06 (t, 3H, 8 Hz, C$_6$H$_5$-CH$_2$-C*H*$_3$)) and bibenzyl (selected data: $^{1}$H NMR ($C_6D_6$): $\delta$ 2.73 (s, 4H, C$_6$H$_5$-C*H*$_2$-C*H*$_2$-C$_6$H$_5$)). Complex **6** was not isolated but characterized by NMR in solution instead; data for **6** follow. $^{1}$H NMR ($C_6D_6$): $\delta$ 7.72 (d, 2H, 8 Hz, Ar-*H* of PNP), 7.12 (s, 2H, Ar-*H* of PNP), 6.78 (d, 2H, 8 Hz, Ar-*H* of PNP), 2.77 (m, 2H, C*H*Me$_2$), 2.69 (m, 2H, C*H*Me$_2$), 2.15 (s, 6H, Ar-C*H*$_3$ of PNP), 1.62 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.32 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.25 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.11 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 0.40 (s, 9H, Si*Me*$_3$). $^{13}$C{$^{1}$H} NMR ($C_6D_6$): $\delta$ 160.4 (vt, 10 Hz, *C*-N of PNP), 132.2 (s, $C_{Ar}$ of PNP), 131.3 (s, $C_{Ar}$ of PNP), 125.5 (vt, 3 Hz, $C_{Ar}$ of PNP), 123.1 (vt, 18 Hz, $C_{Ar}$ of PNP), 117.6 (vt, 5 Hz, $C_{Ar}$ of PNP), 27.4 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 26.7 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 21.1 (s, Ar-*C*H$_3$), 20.4, 20.1, 19.4, 18.9 (four s, CH(*C*H$_3$)$_2$), 8.6 (s, Si(*C*H$_3$)$_3$). $^{31}$P{$^{1}$H} NMR ($C_6D_6$): $\delta$ 36.4 (d, 112 Hz, *P*(Pr$^i$)$_2$). $^{29}$Si{$^{1}$H} NMR ($C_6D_6$): $\delta$ 58.5 (dt, $J_{Rh-Si}$ = 29 Hz, $J_{P-Si}$ = 8 Hz, Rh-*Si*).

**Attempted Reaction of (PNP)Rh($SPr^i_2$) (1) with TMSCl.** (PNP)Rh($SPr^i_2$) (**1**) (20.0 mg, 0.031 mmol) was dissolved in neat $Me_3SiCl$ (0.7 mL) in a J. Young NMR tube. After 48 h at 85 °C, **1** was the only compound observed by $^{31}$P{$^{1}$H} NMR.

**(PNP)Rh(Cl)(SiClMe$_2$) (7).** (PNP)Rh($SPr^i_2$) (**1**) (30.0 mg, 0.046 mmol) was treated with $Me_2SiCl_2$ (139 $\mu$L, 1.15 mmol) in $C_6D_6$ (0.7 mL) in a J. Young NMR tube and heated at 70 °C for 24 h, resulting in a color change from orange to black. A mixture of **7** (95%) and **1** (5%) was observed by $^{31}$P{$^{1}$H} NMR. Another portion of $Me_2SiCl_2$ (56 $\mu$L, 0.46 mmol) was added, and after 24 h at 70 °C, **7** was the only compound observed by $^{31}$P{$^{1}$H} NMR. The resultant solution was evaporated to dryness, and the residue was extracted with ether and filtered through Celite. The filtrate was evaporated to dryness to yield a dark solid residue. This residue was triturated three times with pentane and dried to give (PNP)-Rh(Cl)($SiClMe_2$). Yield: 0.014 g (47%). NMR data for (PNP)-Rh(Cl)($SiClMe_2$) follow. $^{1}$H NMR ($C_6D_6$): $\delta$ 7.76 (d, 2H, 8 Hz, Ar-*H* of PNP), 7.12 (s, 2H, Ar-*H* of PNP), 6.76 (d, 2H, 8 Hz, Ar-*H* of PNP), 2.92 (m, 2H, C*H*Me$_2$), 2.77 (m, 2H, C*H*Me$_2$), 2.15 (s, 6H, Ar-C*H*$_3$ of PNP), 1.60 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.30 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.19 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.07 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 0.88 (s, 6H, SiCl*Me*$_2$). $^{13}$C{$^{1}$H} NMR ($C_6D_6$): $\delta$ 159.9 (vt, 10 Hz, *C*-N of PNP), 132.2 (s, $C_{Ar}$ of PNP), 131.5 (s, $C_{Ar}$ of PNP), 126.0 (vt, 3 Hz, $C_{Ar}$ of PNP), 122.4 (vt, 18 Hz, $C_{Ar}$ of PNP), 117.8 (vt, 5 Hz, $C_{Ar}$ of PNP), 27.4 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 26.8 (vt, 9 Hz, *C*H(CH$_3$)$_2$), 20.9 (s, Ar-*C*H$_3$), 20.4, 19.8, 19.4, 18.7 (four s, CH(*C*H$_3$)$_2$). $^{31}$P{$^{1}$H} NMR ($C_6D_6$): $\delta$ 38.7 (d, 109 Hz). $^{29}$Si{$^{1}$H}

---

[26] Utilization of $Cr(acac)_3$ for the enhancement of $^{29}$Si NMR signal-to-noise ratios in the spectra of transition metal silyl complexes has been reported by Krentz and Pomeroy; the addition of $Cr(acac)_3$ was reported to have no significant effect on chemical shifts: Krentz, R.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2976.

NMR ($C_6D_6$): $\delta$ 66.7 (dt, $J_{Rh-Si} = 39$ Hz, $J_{P-Si} = 8$ Hz, Rh-*Si*). Anal. Found (Calcd) for $C_{28}H_{46}Cl_2NP_2RhSi$: 50.80 (50.91); 6.99 (7.01).

**Determination of $K_{eq}$ for the Reaction of (PNP)Rh($S^iPr_2$) (1) with $Me_2SiCl_2$.** (PNP)Rh($S^iPr_2$) (**1**) (20.0 mg, 30.8 $\mu$mol) in $C_6D_6$ (total volume brought to 0.70 mL) was treated with $Me_2SiCl_2$ (three different experiments were conducted with three different amounts of $Me_3SiBr$: 19 $\mu$L, 0.15 mmol, 0.22 M; 37 $\mu$L, 0.31 mmol, 0.44 M; 74 $\mu$L, 0.62 mmol, 0.88 M) in a J. Young NMR tube. The samples were placed in an oil bath, which was preheated to 65 °C. The reaction was monitored by $^{31}P\{^1H\}$ NMR and $^1H$ NMR at regular intervals until the ratio of products remained unchanged over time (<27 h at 65 °C). The ratio of free isopropyl sulfide to free dichlorodimethylsilane was determined by integrating signals of the CH protons of isopropyl sulfide against the methyl protons of dichlorodimethylsilane for each experiment. Trace amounts of (PNP)Rh(H)(Cl) were detected by $^{31}P\{^1H\}$ NMR. The equilibrium constant was determined to be $K_{eq} = 1.0(1)$; the error was taken to be double the standard deviation calculated by MS Excel.

**(PNP)Rh(Cl)($SiCl_2Me$) (8).** (PNP)Rh($SPr^i_2$) (**1**) (30.0 mg, 0.046 mmol) was treated with $MeSiCl_3$ (6.0 $\mu$L, 0.051 mmol) in $C_6D_6$ (0.7 mL) in a J. Young NMR tube and heated at 70 °C for 3 h, resulting in a color change from orange to green. **8** was the only compound observed by $^{31}P\{^1H\}$ NMR. The resultant solution was evaporated to dryness, and the residue was extracted with ether and filtered through Celite. The filtrate was evaporated to dryness to yield a green solid residue. This residue was recrystallized at −35 °C from pentane to afford **8**. Yield: 0.020 g (64%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.78 (d, 2H, 8 Hz, Ar-*H* of PNP), 7.15 (s, 2H, Ar-*H* of PNP), 6.76 (d, 2H, 8 Hz, Ar-*H* of PNP), 3.07 (m, 2H, C*H*$Me_2$), 2.78 (m, 2H, C*H*$Me_2$), 2.15 (s, 6H, Ar-C$H_3$ of PNP), 1.63 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.37 (s, 3H, $SiCl_2$*Me*), 1.31 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.15 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.07 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 159.8 (vt, 10 Hz, *C*-N of PNP), 132.3 (s, $C_{Ar}$ of PNP), 131.7 (s, $C_{Ar}$ of PNP), 126.7 (vt, 3 Hz, $C_{Ar}$ of PNP), 122.3 (vt, 18 Hz, $C_{Ar}$ of PNP), 118.5 (vt, 5 Hz, $C_{Ar}$ of PNP), 27.5 (vt, 9 Hz, *C*H($CH_3$)$_2$), 27.0 (vt, 9 Hz, *C*H($CH_3$)$_2$), 20.9 (s, Ar-*C*$H_3$), 20.4, 19.6, 19.4, 18.8 (four s, CH(*C*$H_3$)$_2$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 40.8 (d, 104 Hz). $^{29}Si\{^1H\}$ NMR ($C_6D_6$): $\delta$ 42.5 (dt, $J_{Rh-Si} = 57$ Hz, $J_{P-Si} = 10$ Hz, Rh-*Si*). Anal. Found (Calcd) for $C_{27}H_{43}Cl_3NP_2RhSi$: 47.49 (47.62); 6.42 (6.36).

**(PNP)Rh(Cl)($SiCl_3$) (9).** (PNP)Rh($SPr^i_2$) (**1**) (30.0 mg, 0.046 mmol) was treated with $SiCl_4$ (6.0 $\mu$L, 0.051 mmol) in $C_6D_6$ (0.7 mL) in a J. Young NMR tube and heated at 70 °C for 3 h, resulting in a color change from orange to green. The resultant solution was evaporated to dryness, and the residue was extracted with ether and filtered through Celite. The filtrate was evaporated to dryness to yield a green solid residue. This residue was recrystallized from $Et_2O$ at −35 °C to afford **9**. Yield: 0.016 g (48%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.75 (d, 2H, 8 Hz, Ar-*H* of PNP), 7.11 (s, 2H, Ar-*H* of PNP), 6.77 (d, 2H, 8 Hz, Ar-*H* of PNP), 3.13 (m, 2H, C*H*$Me_2$), 2.81 (m, 2H, C*H*$Me_2$), 2.12 (s, 6H, Ar-C*H*$_3$ of PNP), 1.69 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.31 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.10 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.02 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 159.4 (vt, 10 Hz, *C*-N of PNP), 132.3 (s, $C_{Ar}$ of PNP), 131.9 (s, $C_{Ar}$ of PNP), 127.4 (vt, 3 Hz, $C_{Ar}$ of PNP), 122.3 (vt, 18 Hz, $C_{Ar}$ of PNP), 118.8 (vt, 5 Hz, $C_{Ar}$ of PNP), 27.6 (vt, 9 Hz, *C*H($CH_3$)$_2$), 26.9 (vt, 9 Hz, *C*H($CH_3$)$_2$), 20.9 (s, Ar-*C*$H_3$), 20.4, 19.4, 19.3, 18.7 (four s, CH(*C*$H_3$)$_2$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 42.1 (d, 100 Hz). $^{29}Si\{^1H\}$ NMR ($C_6D_6$): $\delta$ −12.5 (dt, $J_{Rh-Si} = 87$ Hz, $J_{P-Si} = 12$ Hz, Rh-*Si*). Anal. Found (Calcd) for $C_{26}H_{40}Cl_4NP_2RhSi$: 44.66 (44.52); 5.90 (5.74).

**(PNP)Rh(Me)($CH_2Ph$) (13) and (PNP)Rh($CH_2Ph$)$_2$ (14).** (PNP)Rh(Me)(Cl) (**10**) (25.0 mg, 0.043 mmol) was treated with $PhCH_2MgCl$ (47 $\mu$L of 1.0 M solution in $Et_2O$, 0.047 mmol) in $C_6D_6$ in a J. Young NMR tube. NMR analysis 10 min after the addition revealed formation of **13** and **14** in a 95:5 ratio, which were characterized in solution in situ. NMR data for **13** follow. $^1H$ NMR ($C_6D_6$): $\delta$ 7.85 (d, 2H, 8 Hz, Ar-*H* of PNP), 7.50 (d, 2H, 8 Hz, $C_6H_5$), 7.11 (t, 1H, 8 Hz, $C_6H_5$), 6.99 (t, 2H, 8 Hz, $C_6H_5$), 6.92 (s, 2H, Ar-*H* of PNP), 6.86 (d, 2H, 8 Hz, Ar-*H* of PNP), 3.56 (m, 2H, Rh-C*H*$_2$-$C_6H_5$), 2.35 (m, 2H, C*H*$Me_2$), 2.22 (1 multiplet + 1 singlet overlapping, 10 H, C*H*$Me_2$ + Ar-$CH_3$ of PNP), 1.58 (m, 3H, Rh-C*H*$_3$), 1.24 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 1.07 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 0.94 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$), 0.72 (app. quartet (dvt), 6H, 8 Hz, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 32.2 (d, 120 Hz). Selected NMR data for **14** follow. $^1H$ NMR ($C_6D_6$): $\delta$ 3.79 (m, Rh-C*H*$_2$-$C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 30.2 (d, 125 Hz).

**(PNP)Rh(H)($SiClMe_2$) (15).** (PNP)Rh($SPr^i_2$) (**1**) (50.0 mg, 0.077 mmol) was treated with $Me_2SiHCl$ (12.0 $\mu$L, 0.085 mmol) in $C_6D_6$ (0.7 mL) in a J. Young NMR tube. After 18 h at 70 °C, analysis by $^1H$ and $^{31}P\{^1H\}$ NMR revealed quantitative formation of **15**. The resultant solution was 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 recrystallized from $Et_2O$ at −35 °C to afford **15**. Yield: 0.031 g (62%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.57 (d, 2H, 8 Hz, Ar-*H* of PNP), 6.96 (s, 2H, Ar-*H* of PNP), 6.78 (d, 2H, 8 Hz, Ar-*H* of PNP), 2.66 (m, 2H, C*H*$Me_2$), 2.25 (s, 6H, Ar-C*H*$_3$ of PNP), 2.08 (m, 2H, C*H*$Me_2$), 1.24 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.08 (app. quartet (dvt), 12H, 8 Hz, CH*Me*$_2$), 1.04 (m, 6H, SiCl*Me*$_2$), −15.6 (dtt, $^2J_{H-Si} = 31$ Hz, $^1J_{H-Rh} = 24$ Hz, $^2J_{H-P} = 11$ Hz, Rh-*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 161.5 (vt, 10 Hz, *C*-N of PNP), 131.9 (two s, $C_{Ar}$ of PNP), 125.4 (vt, 3 Hz, $C_{Ar}$ of PNP), 122.4 (vt, 18 Hz, $C_{Ar}$ of PNP), 115.5 (vt, 5 Hz, $C_{Ar}$ of PNP), 26.5 (vt, 9 Hz, *C*H($CH_3$)$_2$), 23.9 (vt, 9 Hz, *C*H($CH_3$)$_2$), 20.4 (s, Ar-*C*$H_3$), 19.4, 18.7, 17.0, 17.4 (four s, CH(*C*$H_3$)$_2$), 15.8 (s, SiCl(*C*$H_3$)$_2$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 41.0 (d, 146 Hz). $^{29}Si$ NMR ($C_6D_6$): $\delta$ 49.3 (dtt, $^2J_{Si-H} = 31$ Hz, $^1J_{Si-Rh} = 23$ Hz, $^2J_{Si-P} = 6$ Hz, Rh-*Si*).

**Oxidative Addition of PhBr to (PNP)Rh($SPr^i_2$) (1), (PNP)Rh(Cl)($SiClMe_2$) (7), and (PNP)Rh(Cl)($SiCl_2Me$) (8).** Solutions of **1** (18.8 mg, 0.029 mmol), **7** (19.1 mg, 0.029 mmol), and **8** (20 mg, 0.029 mmol), each in 0.7 mL of $C_6D_6$, were prepared in three separate J. Young NMR tubes. Equal amounts of bromobenzene (3.2 $\mu$L, 0.032 mmol) were introduced into each NMR tube. These three samples were placed into a 75 °C oil bath. The progress of the reaction was monitored by $^{31}P$ NMR. After 40 min at 75 °C, the conversions to (PNP)Rh(Ph)(Br) (**3**) were as follows: **1**, 88%; **7**, 80%; and **8**, <3%. N.B.: (PNP)Rh(Cl)(Ph) was also observed in the $^1H$ and $^{31}P\{^1H\}$ NMR spectra of the reaction of (PNP)Rh(Cl)($SiClMe_2$) with bromobenzene, ostensibly owing to the post-OA Cl/Br exchange.

**Attempted Reaction of (PNP)Rh($SPr^i_2$) with $Me_3SiSiMe_3$.** (PNP)Rh($SPr^i_2$) (**1**) (20 mg, 0.031 mmol) and $Me_3SiSiMe_3$ (6.9 $\mu$L, 0.034 mmol) were introduced into a J. Young tube in 0.8 mL of $C_6D_6$. The sample was placed in an oil bath that was preheated at 85 °C. After 48 h at 85 °C, **1** was the only compound observed by $^1H$ and $^{31}P\{^1H\}$ NMR.

**Attempted Reaction of (PNP)Rh($SPr^i_2$) with $Me_3SiOTf$.** (PNP)Rh($SPr^i_2$) (**1**) (20 mg, 0.031 mmol) and $Me_3SiOTf$ (6.2 $\mu$L, 0.034 mmol) were introduced in a J. Young tube in 0.8 mL of $C_6D_6$. The sample was placed in an oil bath that was preheated at 85 °C. After 48 h at 85 °C, **1** was the only compound observed by $^1H$ and $^{31}P\{^1H\}$ NMR.

**Attempted Reaction of (PNP)Rh($SPr^i_2$) with $Me_3SiOSiMe_3$.** (PNP)Rh($SPr^i_2$) (**1**) (20 mg, 0.031 mmol) was introduced in a J. Young tube in neat $Me_3SiOSiMe_3$. The sample was placed in an oil bath that was preheated at 85 °C. After 48 h at 85 °C, **1** was the only compound observed by $^1H$ and $^{31}P\{^1H\}$ NMR.

**Acknowledgment.** Support of this research by the NSF (CHE-0517798), Alfred P. Sloan Foundation (Research Fellowship to O.V.O.), Department of Energy (DE-FG02-86ER13615), the donors of the Petroleum Research Fund, and Brandeis University is gratefully acknowledged. We also thank the National Science Foundation for the partial support of this work through grant CHE-0521047 for the purchase of a new X-ray diffractometer. We are grateful to Dr. Sara Kunz for assistance with NMR experiments and to Prof. Kálmán J. Szabó for useful suggestions regarding collection of the $^{29}$Si NMR spectra. We are especially thankful to Mayank Puri for the equilibrium constant data.

**Supporting Information Available:** Crystallographic information for **7** and **15** in the form of CIF files, experimental details, and pictorial NMR spectra for select compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800216H