Rhodium Complexes Containing a Tridentate Bis(8-quinolyl)methylsilyl Ligand: Synthesis and Reactivity

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Synthesis of a series of rhodium complexes bearing a tridentate bis(8-quinolyl)methylsilyl (NSiN) ligand is reported. Bis(8-quinolyl)methylsilane (**1**) reacted with $(PPh_3)_3RhCl$ via oxidative addition at the Si−H bond to afford $(NSiN)Rh(H)Cl(PPh_3)$ (**2**). Several coordinatively unsaturated, 16-electron complexes were synthesized, including the cationic complex $[(NSiN)Rh(H)(PPh_3)][B(C_6F_5)_4]$ (**3**) and the neutral complex $(NSiN)Rh(CH_2Ph)_2$ (**12**). The X-ray structures of **3** and **12** reveal a square-pyramidal geometry about the Rh center, with the silyl group occupying an apical position. The dicationic complex $[(NSiN)Rh(CH_3CN)_3][OTf]_2$ (**11**), synthesized by reaction of $[(NSiN)RhCl_2]_2$ (**10**) with 2 equiv of AgOTf in acetonitrile, exhibits moderate activity as a catalyst for alkene hydrogenation and for H/Cl exchange between Ph_3SiH and CH_2Cl_2. Complex **2** reacts with 2 equiv of $PhCH_2MgCl$ in benzene to afford $(NSiN)Rh(CH_2Ph)Cl(PPh_3)$ (**6**). Chlorination of **2** by DBU in CH_2Cl_2 afforded the solvent-activated Rh(III) product $(NSiN)RhCl_2(PPh_3)$ (**8**). Similarly, with PMe_3/CH_2Cl_2 as the chlorinating reagent, $[(NSiN)Rh(PMe_3)_2Cl]Cl$ (**9**) was obtained. The low-valent complex (NSiN)Rh(COD) (**14**; COD = 1,5-cyclooctadiene) was synthesized via the reaction of **1** with (COD)Rh(η^3-CH_2Ph) in benzene. The COD ligand was replaced by the phosphine-based dppe ligand, resulting in the thermally more stable complex (NSiN)Rh(dppe) (**18**; dppe = $Ph_2PCH_2CH_2PPh_2$).

Introduction

Multidentate ligands with a rigid geometry have been found to support late-transition-metal complexes that mediate interesting chemical transformations, such as the dehydrogenation of alkanes and C−H bond activation.[2−4] Such observations have generated considerable interest in the development and exploration of metal complexes containing “pincer ligands.” Despite this activity, however, only a few chelating ligand systems containing Si as a donor atom have been developed. The incorporation of a silyl group as part of the ligand framework could result in a number of interesting and useful properties for a metal complex.[5] For example, the electron-donating character of Si can give rise to an electron-rich metal center. In addition, the strong trans-labilizing ability of Si can promote the generation of coordinatively unsaturated complexes that may be useful as catalysts. Examples of chelating ancillary ligands containing the silyl group include those with a tridentate PSiP framework (e. g., $M[SiMe(CH_2CH_2CH_2PPh_2)_2]$), which Stobart and co-workers have synthesized via oxidative addition of a Si−H bond.[6] This method represents a general synthetic route to metal complexes supported by Si-containing multidentate ligands.

We have employed a related strategy to prepare complexes of a new tridentate ligand based on the bis(8-quinolyl)silyl (NSiN) framework. This method was used to synthesize a (NSiN)Ir^{III} complex, (NSiN)Ir(H)Cl(COE),[7] which possesses a distorted-octahedral geometry with the NSiN ligand bound to the Ir center in a facial manner. Preliminary reactivity studies indicate that the (NSiN)Ir fragment is chemically robust, and this presumably results from the presence of two chelate rings which stabilize the NSiN complexes against loss of the ligand.

As a formally five-electron donor, the bis(8-quinolyl)silyl ligand may be compared to more well-known ligands such as pentamethylcyclopentadienyl (Cp*), tris(pyrazolyl)borate (Tp), and 2,6-($^tBu_2PCH_2)_2C_6H_3$ (a PCP-based pincer ligand). Rhodium and iridium complexes of the last three ligands are known to engage in a number of novel bond activation processes. Thus, it should be of interest to compare the chemistry of Cp*M,[4] TpM,[2] and (PCP)M[1] (M = Rh, Ir) derivatives with that of related (NSiN)M fragments. In addition, the novel set of donor atoms associated with the NSiN ligand may provide new reaction pathways. Hard, nitrogen-based ligands, in combination with soft transition metals such as platinum and rhodium, are known to participate in a number of C−H activation processes.[2−4,8] Furthermore, it should be possible to readily access coordina-

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(1) (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083. (b) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840. (c) Brookhart, M.; Göttker-Schnetmann, I. *J. Am. Chem. Soc.* **2004**, *126*, 9330.

(2) (a) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1992**, *114*, 6087. (b) Jones, W. D.; Vetter, A. J. *Polyhedron* **2004**, *23*, 413. (c) Jones, W. D.; Wick, D. D. *Organometallics* **1999**, *18*, 495. (d) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554.

(3) Graham, W. A. G.; Ghosh, C. K. *J. Am. Chem. Soc.* **1987**, *109*, 4726.

(4) (a) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (b) Golden, J. T.; Richard, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 5837. (c) Bergman, R. G.; Burger, P. *J. Am. Chem. Soc.* **1993**, *115*, 10462.

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(6) (a) Stobart, S. R.; Joslin, F. L. *Inorg. Chem.* **1993**, *32*, 2221. (b) Stobart, S. R.; Gossage, R. A.; McLennan, G. D. *Inorg. Chem.* **1996**, *35*, 1729 and references therein.

(7) Stradiotto, M.; Fujdala, K. L.; Tilley, T. D. *Chem. Commun.* **2001**, 1200.

(8) (a) Goldberg, K. I.; Fekl, U. *J. Am. Chem. Soc.* **2002**, *124*, 6804. (b) Goldberg, K. I.; Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 8614.

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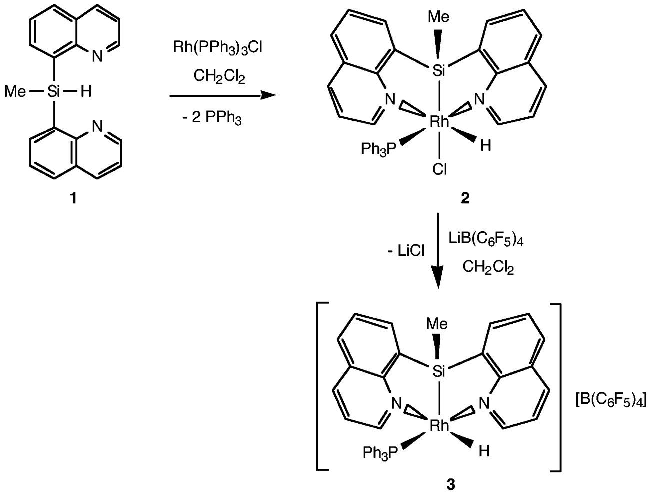
Scheme 1

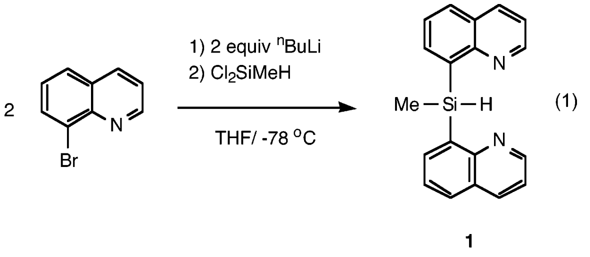


tively unsaturated metal species (due to the presence of the trans-labilizing silyl substituent) that feature a nitrogen-based ligand set.

Especially given the prominent role of Rh complexes in homogeneous catalysis, it is of interest to explore the chemistry of (NSiN)Rh complexes. Initial investigations were directed toward defining the structures that result from introduction of hydride and carbon-based ligands into the coordination sphere of such complexes. The synthetic studies reported here targeted potentially reactive hydrocarbyl hydride complexes of the type (NSiN)Rh(L)(H)(R) and coordinatively unsaturated, 16-electron complexes of the types (NSiN)RhH$_2$ and (NSiN)RhR$_2$.

Results and Discussion

Ligand Synthesis. Bis(8-quinolyl)methylsilane (**1**) was prepared via the lithiation of 8-bromoquinoline[13] by *n*-BuLi, followed by the addition of 0.5 equiv of dichloromethylsilane (eq 1). Recrystallization from toluene at -30 °C provided bis(8-quinolyl)methylsilane (**1**) as yellow crystals in 48% yield.



Synthesis of (NSiN)Rh(H)Cl(PPh$_3$) (2). Treatment of **1** with Wilkinson's catalyst, (PPh$_3$)$_3$RhCl,[10] in dichloromethane resulted in oxidative addition at the Si−H bond to give the 18-electron complex (NSiN)Rh(H)Cl(PPh$_3$) (**2**; Scheme 1). Complex **2** was isolated via crystallization from 1/1 dichloromethane/diethyl ether as a yellow crystalline solid in 82% yield. The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits a doublet at δ 59.1 ($^1J_{RhP} = 150$ Hz), and the Rh−H stretch appears at 2030 cm^{-1} in the IR spectrum. The ^1H NMR spectrum of **2** in dichloromethane-d_2 contains two sets of quinolyl protons and a hydride resonance (a doublet of doublets) at δ -15.9 ($^1J_{RhH} = 17$ Hz, $^2J_{PH} = 24$ Hz). These NMR results suggest an octahedral geometry of **2** with C_1 symmetry. As with the analogous (NSiN)Ir(H)Cl(PPh$_3$) complex,[7] the formation of **2** is stereoselective, in that a chloride ligand adopts a coordination site trans to the strong trans-influencing silyl group.

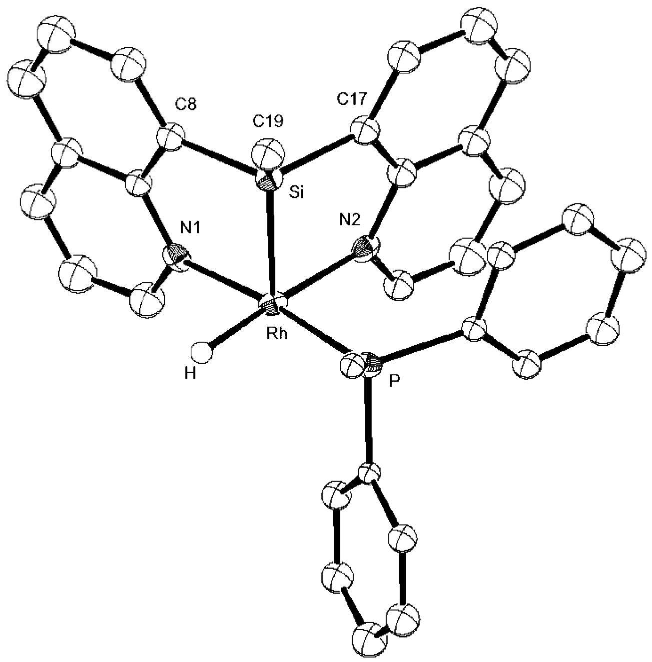


Figure 1. ORTEP diagram of the cationic complex **3** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms (except Rh−*H*), the B(C$_6$F$_5$)$_4$ counterion, one of the phenyl rings, and the solvent of crystallization are omitted for clarity.

Reactivity Studies of 2. In an attempt to generate a coordinatively unsaturated Rh(III) complex, **2** was treated with 1 equiv of LiB(C$_6$F$_5$)$_4$·2.5Et$_2$O[11] in dichloromethane at room temperature. The corresponding cationic complex, [(NSiN)Rh(H)(PPh$_3$)][B(C$_6$F$_5$)$_4$] (**3**), was isolated in 96% yield from vapor diffusion of diethyl ether into a dichloromethane solution of **3** (Scheme 1). The Rh−H group is observed as an apparent triplet at δ -13.7 in the ^1H NMR spectrum (dichloromethane-d_2) and a medium-intensity band at 2022 cm^{-1} in the IR spectrum.

For comparison, the previously reported reaction of (NSiN)Ir(H)Cl(COE) with either 0.5 or 1.0 equiv of LiB(C$_6$F$_5$)$_4$·2.5Et$_2$O produced the cationic, dinuclear complex {[(NSiN)IrH(COE)]$_2$(μ_2-Cl)}[B(C$_6$F$_5$)$_4$].[7] The mononuclear nature of **3** was established by X-ray crystallography, which revealed a square-pyramidal coordination geometry (Figure 1). As a result of its strong trans-labilizing property, the Si atom adopts the apical position, trans to an empty coordination site. The rhodium hydride ligand was located in a difference Fourier map, and its positional parameters were refined. The Rh−Si bond distance (2.237(4) Å) falls within the expected range for Rh silyl complexes (2.21−2.38 Å).[12] As observed for (NSiN)Ir complexes, significant geometric distortions at the Si center are reflected in Rh−Si−C(8) and Rh−Si−C(19) bond angles of 98.4(5) and 128.4(5)°, respectively. The other Rh−Si−C bond angles are in the range expected for an sp^3 center.

The 16-electron, cationic complex **3** is surprisingly inert, as indicated by its stability in the presence of H$_2$, C$_6$H$_6$, or Ph$_3$SiH in 1:1 PhF/benzene-d_6 solvent at 80 °C over 1 week. However, complex **3** did react in dichloromethane solvent at 80 °C to quantitatively produce the cationic complex [(NSiN)Rh(Cl)(PPh$_3$)][B(C$_6$F$_5$)$_4$] (**4**) via H/Cl exchange. Complex **4** was

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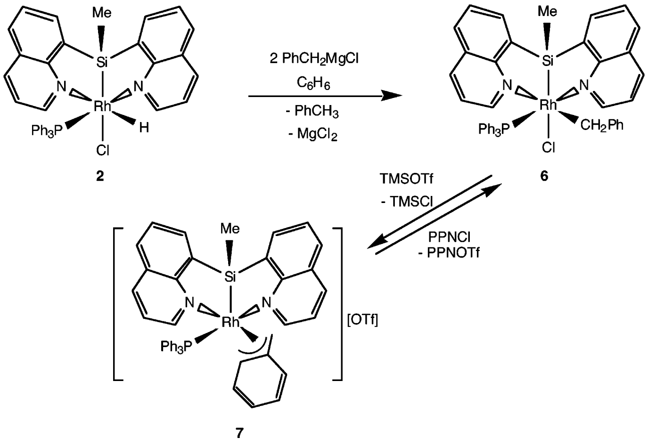
(9) Butler, J. L.; Gordon, M. *J. Heterocycl. Chem.* **1975**, *12*, 1015.

(10) Wilkinson, G.; Osborn, J. A. *Inorg. Synth.* **1990**, *28*, 77.

(11) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

(12) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

Scheme 2



isolated in 92% yield via vapor diffusion of diethyl ether into a dichloromethane solution of **4**.

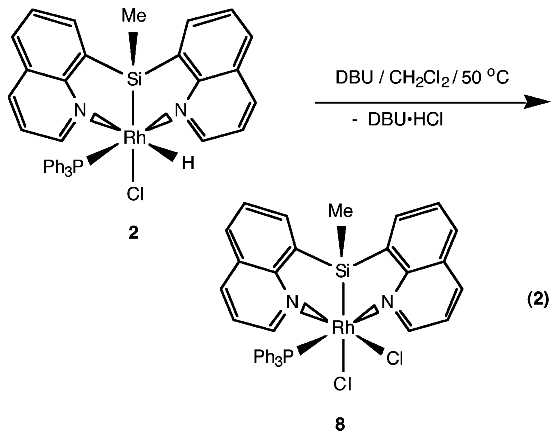
In an attempt to render the rhodium center of **3** more reactive, the synthesis of [(NSiN)Rh(H)(PMe$_3$)][B(C$_6$F$_5$)$_4$], which should be more electron rich and less sterically crowded, was targeted. Treatment of bis(8-quinolyl)methylsilane (**1**) with (COD)Rh(PMe$_3$)Cl[13] gave the complex (NSiN)Rh(H)Cl(PMe$_3$) (**5**) in 59% yield. Complex **5** was isolated from concentrated THF solution as a yellow powder. The Rh−H resonance of **5** appears in the ^{1}H NMR spectrum (dichloromethane-d_2) as a doublet of doublets at δ −16.6 ($^1J_{\mathrm{RhH}} = 22$ Hz, $^2J_{\mathrm{PH}} = 29$ Hz). In the IR spectrum, the Rh−H group gives rise to a band at 2045 cm^{-1}.

Chloride abstraction from **5** using LiB(C$_6$F$_5$)$_4$·2.5Et$_2$O in dichloromethane-d_2 resulted in a mixture of products. Interestingly, the ^{1}H NMR spectum of the reaction mixture did not contain a hydride resonance that could be assigned to a Rh−H species. On the basis of results described below, it seems possible that, upon chloride abstraction, PMe$_3$ dissociates and acts as a dehydrohalogenation reagent, to remove the rhodium hydride ligand (vide infra).

Alkyl hydride complexes of the type (NSiN)RhH(R)(PPh$_3$) were targeted, as such complexes were expected to exhibit a rich reaction chemistry. These compounds could potentially eliminate RH to generate the unsaturated species (NSiN)Rh(PPh$_3$) and should provide information regarding the stability of C−H activation products derived from (NSiN)Rh(PPh$_3$). The addition of 1 equiv of PhCH$_2$MgCl to **2** in benzene resulted in partial conversion to a new product. To obtain complete conversion, 2 equiv of PhCH$_2$MgCl was required, and this gave the neutral complex (NSiN)Rh(CH$_2$Ph)(Cl)(PPh$_3$) (**6**). The reaction is quantitative by ^{1}H NMR spectroscopy (using Si(SiMe$_3$)$_4$ as standard) and produces 1 equiv of toluene and 1 equiv of **6** (Scheme 2). The ^{1}H NMR spectrum of **6** in benzene-d_6 exhibits two apparent triplets at δ 2.20 and 1.77, assigned as diastereotopic hydrogens of the benzyl group. On a preparative scale, **6** was obtained as a somewhat impure, crystalline material in approximately 50% yield. From this reaction, an analytically pure sample of **6** could not be obtained, as recrystallizations invariably yielded product that was contaminated by small amounts of MgCl$_2$. In one particular sample, 0.89% of Mg was present according to Mg analysis. However, FAB-MS allowed observation of a m/z^+ peak at 755.3, which corresponds to the (NSiN)Rh(CH$_2$Ph)(PPh$_3$)$^+$ fragment. Further confirmation of the identity of **6** comes from the reaction chemistry described below.

Complex **6** reacts with Me$_3$SiOTf in benzene to give [(NSiN)Rh(η^3-CH$_2$Ph)(PPh$_3$)]OTf (**7**), as an orange microcrystalline precipitate in 58% yield. Once isolated, complex **7** is sparingly soluble in benzene and only partially dissolves in THF. In THF-d_8, the ^{1}H NMR spectrum of **7** contains a broad singlet peak at δ 5.63, which can be assigned to the benzyl group. A 2D ^{13}C−^{1}H HMQC NMR experiment correlated these benzyl CH_2 protons to a ^{13}C{^{1}H} NMR resonance at δ 108.6 (br m). Both ^{1}H and ^{13}C{^{1}H} NMR peaks are consistent with a structure containing an η^3-benzyl group.[14] In addition, complex **7** underwent an anionic exchange with PPNCl in benzene, resulting in an analytically pure sample of **6** (Scheme 2). The process by which **2** is alkylated to form **6** is clearly unusual and is not fully understood. In addition, successful alkylation of **2** is limited to PhCH$_2$MgCl. Intractable products were obtained from reactions between **2** and other alkylating reagents such as MeLi and PhMgCl, under the same conditions. Hopefully, further investigations of this system will reveal mechanistic information concerning the formation of **6**.

Another possible synthetic route to (NSiN)Rh(PPh$_3$) involves dehydrochlorination of **2** with a base. Refluxing **2** in the presence of 1 equiv of DBU in dichloromethane resulted in an elimination of HCl, as the ^{1}H NMR spectrum of the crude reaction mixture indicated the formation of DBU·HCl. However, the rhodium-containing product, crystallized from a mixture of dichloromethane and diethyl ether in 68% yield, was characterized as (NSiN)RhCl$_2$(PPh$_3$) (**8**), the presumed product of dichloromethane activation (eq 2). The ^{1}H NMR spectrum of **8** contains two sets of quinolyl protons, suggesting C_1 symmetry. This chlorination of **2** does not occur in nonhalogenated solvents under comparable conditions. For example, no reaction was observed when **2** and 1 equiv of DBU was refluxed in benzene or THF, over 2 days. This result supports the involvement of dichloromethane as a reagent in the reaction of eq 2. The crystallographically determined structure of **8** is shown in Figure 2. As expected, the Rh−Cl bond trans to the silyl group (2.640(2) Å) is significantly longer than the bond trans to the quinolyl N atom (2.356(2) Å).



(2)

In addition to DBU/CH$_2$Cl$_2$, PMe$_3$/CH$_2$Cl$_2$ acts as a chlorinating reagent for complex **2**. Reaction of **2** with an excess of PMe$_3$ (3 equiv) in dichloromethane at room temperature afforded the dichloromethane-activated Rh(III) product [(NSiN)Rh(PMe$_3$)$_2$-

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[13] Andersen, R. A.; Kulzick, M. A.; Price, R. T.; Muetterties, E. L. *J. Organomet. Chem.* **1987**, *333*, 105.

[14] (a) Fryzuk, M. D.; McConville, D. H.; Rettig, S. J. *J. Organomet. Chem.* **1993**, *445*, 245. (b) Gatti, G.; Lopez, J. A.; Mealli, C.; Musco, A. *J. Organomet. Chem.* **1994**, *483*, 77. (c) Crascall, L. E.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, *24*, 3445.

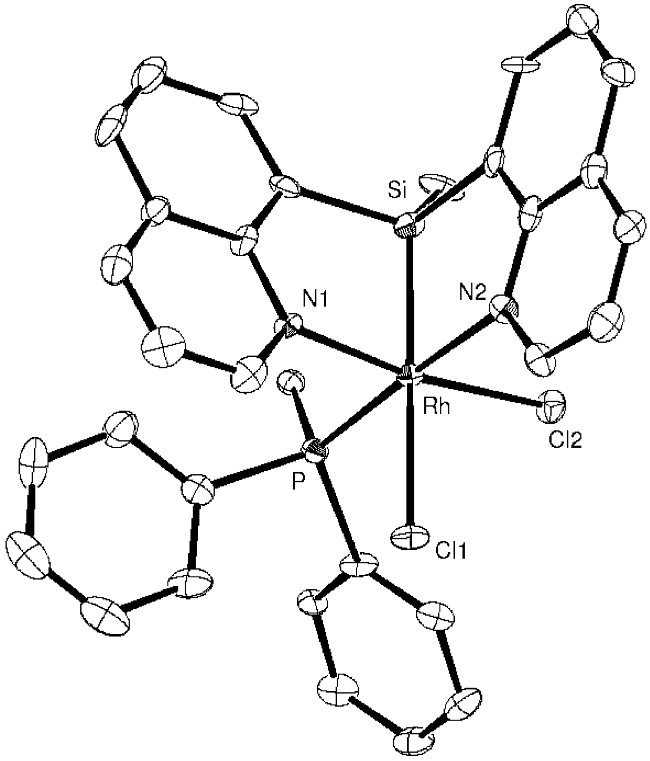
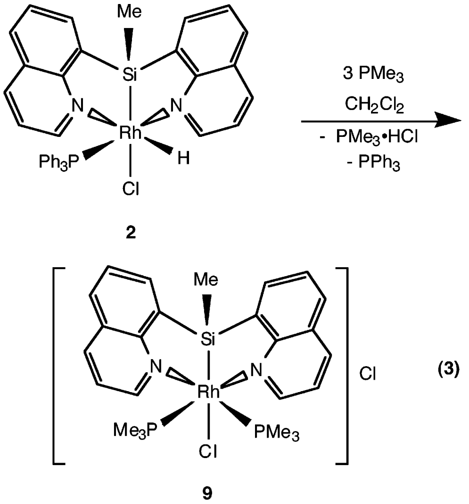


Figure 2. ORTEP diagram of complex **8** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms, one of the phenyl rings, and the dichloromethane molecule are omitted for clarity.

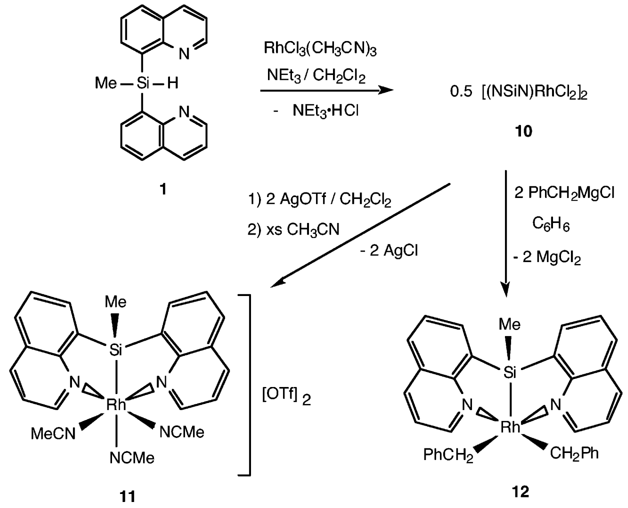
Cl][Cl] (**9**), which was crystallized from dichloromethane in 54% yield (eq 3). The ^{1}H NMR resonances corresponding to two PMe_3 groups appear at δ 1.26, and a single set of quinolyl resonances in the ^{1}H NMR spectrum indicates C_s symmetry for the molecule.



(3)

Synthesis and Reactivity of 16-Electron (NSiN)RhX_2 Complexes. For previously described complexes, the NSiN ligand was introduced via Si−H oxidative addition to a low-valent Rh(I) center. To develop synthetic routes employing more readily available starting materials, the reaction of $RhCl_3(CH_3CN)_3$[15] with **1** was examined, in the presence of NEt_3 as a scavenger of HCl. In dichloromethane, this reaction gave a yellow precipitate with the empirical formula (NSiN)$RhCl_2$ (**10**) (Scheme 3).

Scheme 3



The ^{1}H NMR spectrum (dichloromethane-d_2) of the crude reaction mixture reveals the presence of $HCl{\cdot}NEt_3$ as a side product. Complex **10** exhibits poor solubility in most organic solvents, including dichloromethane and chloroform. The ^{1}H NMR spectrum of **10** in DMSO-d_6 contains one set of quinolyl protons, suggesting that, in solution, complex **10** possesses mirror symmetry. Drawing a comparison with related species containing the Tp′ (HB(3,5-$Me_2pz)_3$) and Cp* ligands, [Tp′$RhCl_2]_2$ and [Cp*$RhCl_2]_2$,[16,17] it is reasonable to assume that **6** also exists as a dimer.

Treatment of complex **10** with 2 equiv of AgOTf in dichloromethane afforded an off-white, insoluble precipitate believed to be the bis(triflate) complex (NSiN)Rh$(OTf)_2$. Subsequent addition of acetonitrile to this precipitate resulted in formation of the dicationic complex [(NSiN)Rh$(CH_3CN)_3$][OTf]$_2$ (**11**) in 68% isolated yield (Scheme 3). X-ray crystallographic analysis of **11** revealed a distorted-octahedral geometry, in which the Rh−$NCCH_3$ bond distance trans to the silyl group is approximately 0.3 Å longer than those associated with the cis-acetonitrile ligands (2.035(6), 2.011(6) Å) (Figure 3).

The ^{1}H NMR spectrum of **11** in acetonitrile-d_3 indicates the presence of only two molecules of bound acetonitrile, as a singlet at δ 1.97. The absence of a ^{1}H resonance corresponding to the acetonitrile ligand trans to the strongly trans-labilizing silyl group suggests a rapid exchange between this acetonitrile ligand and the acetonitrile-d_3 solvent. When complex **11** was dissolved in dichloromethane-d_2, the acetonitrile group trans to the silyl group appeared as free acetonitrile in the ^{1}H NMR spectrum. The IR spectrum of **11** (KBr pellet) contains two medium-intensity bands at 2304 and 2332 cm^{-1}, which can be assigned to the nitrile ligands.

It is of interest to compare the reactivity of the dicationic complex **11** with that of well-known, related species such as [Cp*Rh$(CH_3CN)_3$][X]$_2$ (X = PF_6, BF_4).[17] For the Cp*Rh complexes, partial or complete displacement of the coordinated acetonitrile ligands can be readily achieved with soft donor ligands (e.g., arene and alkene), thus making [Cp*Rh$(CH_3CN)_3$][X]$_2$ convenient precursors to a range of complexes containing the Cp*Rh^{III} fragment.[18] In contrast, no reaction was observed

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[16] Powell, J.; Reinsalu, P.; May, S. *Inorg. Chem.* **1980**, *19*, 1582.

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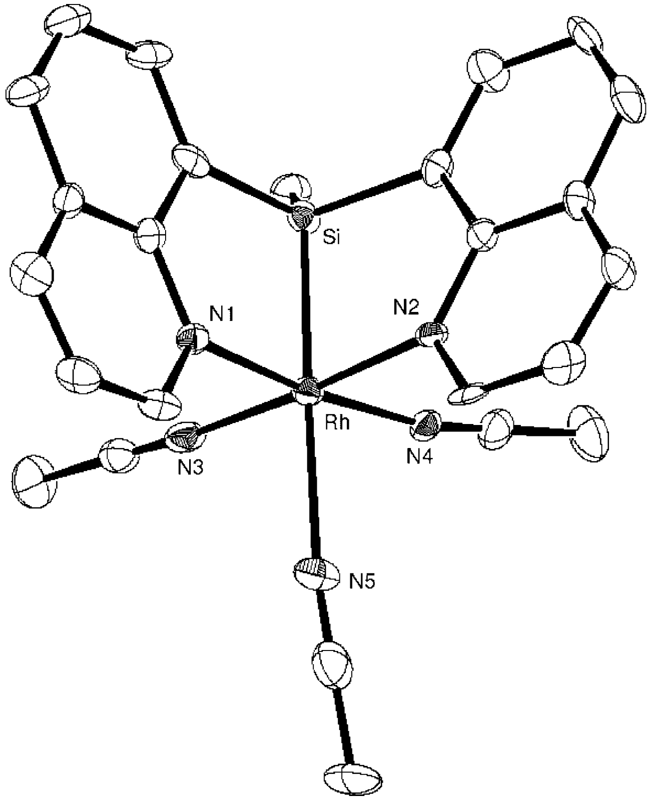

Figure 3. ORTEP diagram of the dicationic complex **11** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and two OTf counterions are omitted for clarity.

when **11** was treated with a variety of soft donors, including ethylene, (trimethylsilyl)acetylene, and benzophenone, even at 80 °C in dichloromethane-d_2. One possible explanation for this inactivity is that the harder ligand of the (NSiN)Rh fragment gives rise to a hard Rh center. Thus, complex **11** exhibits a higher affinity for hard ligands such as acetonitrile, and displacement of this ligand by softer ligands is more difficult than for $[Cp^*Rh(CH_3CN)_3][X]_2$ (X = PF_6, BF_4).

Previous studies have shown that dicationic complexes of the type $[Cp^*Rh(CH_3CN)_3][BF_4]_2$ act as a catalyst for alkene and arene hydrogenation.[19] Similarly, catalytic studies reveal that the dicationic (NSiN)Rh complex **11** is moderately active as a catalyst for alkene hydrogenations. When 5 mol % of complex **11** was combined with either cyclooctene or 1-hexene under 1−2 atm of H_2, a quantitative yield of the hydrogenated product was obtained after 1 day at 70 °C, as monitored by ^1H NMR spectroscopy. In addition, 5 mol % of complex **11** catalyzed H/Cl exchange between Ph_3SiH and dichloromethane solvent at 70 °C, resulting in the quantitative production of Ph_3SiCl and CH_3Cl after 1 day.

The 16-electron complex $(NSiN)RhH_2$ is of significant interest as a potential catalyst. Notably, a related Rh(III) species containing the 2,6-$(^tBu_2PCH_2)_2C_6H_3$ (PCP) pincer ligand, $(PCP)RhH_2$, is an active catalyst for the water-gas shift reaction and for alkane dehydrogenation.[1] However, attempts to synthesize $(NSiN)RhH_2$ have so far been unsuccessful. Reactions of **10** with 2 equiv of $LiBEt_3H$ in THF, with or without an atmosphere of H_2, under various reaction conditions, gave mixtures of products. The use of other hydride donors, such as KH and $LiBH_4$, also resulted in intractable mixtures.

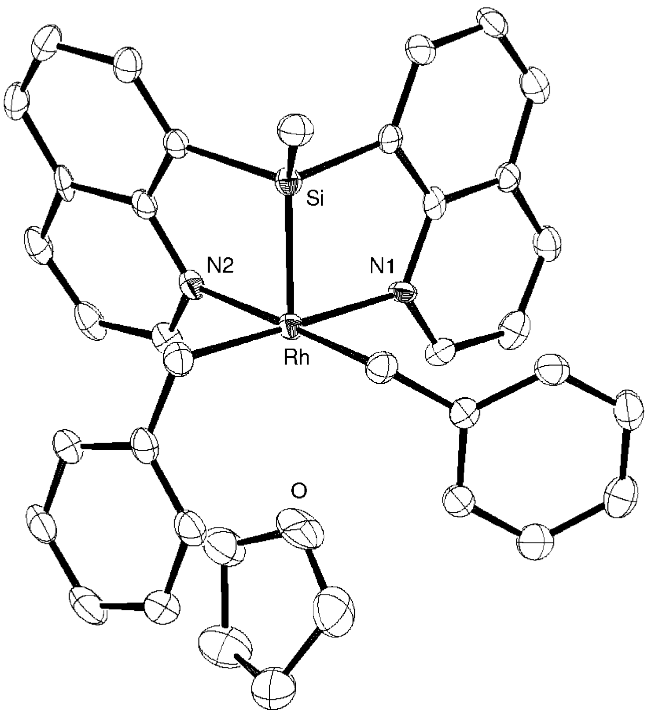

Figure 4. ORTEP diagram of complex **12** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

A related type of 16-electron complex, which is expected to exhibit a rich reaction chemistry and possibly serve as a precursor to $(NSiN)RhH_2$, is a dialkylrhodium(III) complex supported by the NSiN ligand. Thus, it was found that the reaction of **10** with 2 equiv of $PhCH_2MgCl$ in benzene generated the 16-electron, neutral complex $(NSiN)Rh(CH_2Ph)_2$ (**12**). The ^1H NMR spectrum of **12** in THF-d_8 exhibits one set of quinolyl protons, indicative of C_s symmetry. The diastereotopic protons of the methylene groups of the benzyl rings are observed as two distinct doublet of doublets at δ 2.47 ($^2J_{HH} = 9.0$ Hz, $^2J_{RhH} = 3.0$ Hz) and 2.11 ($^2J_{HH} = 9.0$ Hz, $^2J_{RhH} = 1.0$ Hz). The Rh−CH_2 resonance in the $^{13}C\{^1H\}$ NMR spectrum appears as a doublet at δ 23.30 ($^1J_{RhC} = 12.5$ Hz).

Complex **12** crystallized from a 3/2 mixture of THF and diethyl ether as yellow crystals, and the X-ray structure reveals a square-pyramidal geometry about the Rh center with a THF molecule located near the Rh atom and trans to the silyl group (Figure 4). However, the Rh−O distance of 4.384(4) Å is too long to represent a bonding interaction. The Rh−C bond distances (2.093(4) and 2.079(4) Å) fall within the expected range for such Rh−C(benzyl) bonds.[20]

The possibility that the coordinatively unsaturated, 16-electron dibenzyl complex **12** might participate in bond activations with small molecules led us to examine the reactivity of **12** with H_2, benzene-d_6, and Et_3SiH. However, at 80 °C, no reaction of **12** with either H_2 or Et_3SiH was observed in benzene-d_6 after 3 days. Complex **12** began to decompose at 120 °C in benzene-d_6, to give a black precipitate and toluene as products. Attempts to generate an 18-electron complex by treating **12** with two-electron donors, such as PPh_3 and CO, were also unsuccessful. We attribute this unusual stability of the 16-electron complex

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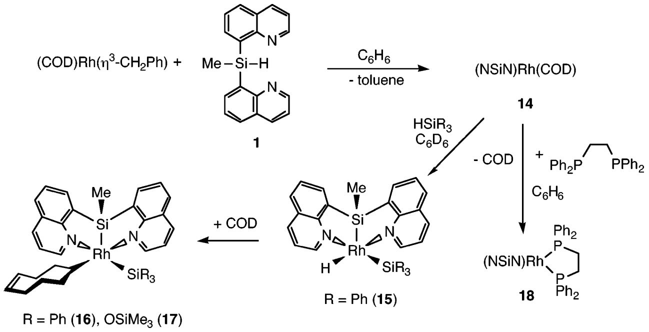
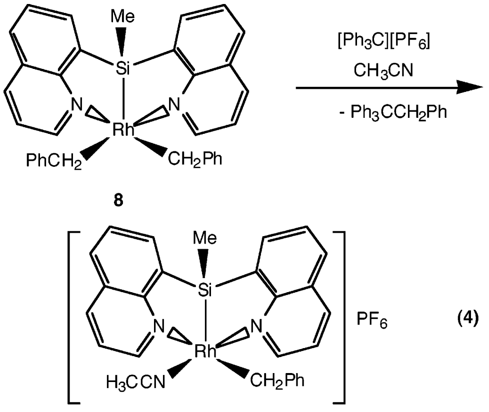
Scheme 4



12 to the strong trans-labilizing silyl group of the NSiN ligand.

One of the benzyl groups in **12** was abstracted by 1 equiv of $[Ph_3C][PF_6]$ in acetonitrile to afford the 16-electron, cationic Rh(III) complex $[(NSiN)Rh(CH_2Ph)(CH_3CN)][PF_6]$ (**13**) in 69% yield (eq 4). The ^{1}H NMR spectrum (dichloromethane-d_2) contains two diastereotopic protons for the benzyl group as two doublets of doublets at δ 3.02 ($^2J_{HH'} = 8.5$ Hz, $^2J_{RhH} = 2.5$ Hz) and 2.15 ($^2J_{H'H} = 8.5$ Hz, $^2J_{RhH'} = 1.5$ Hz). Similar to complex **11**, the acetonitrile ligand trans to the quinolyl N atom binds strongly to the Rh(III) center (vide supra). Treatment of **13** with 1−2 atm of ethylene, diphenylacetylene, or benzophenone in benzene-d_6 did not result in displacement of acetonitrile at 80 °C after 2 days.



(4)

The reaction chemistry of **13** was briefly explored. At room temperature, a benzene-d_6 solution of **13** and 1 equiv of Ph_3SiH yielded no reaction. When the reaction mixture was heated to 50 °C for 12 h, the ^{1}H NMR spectrum indicated the formation of toluene and a complex mixture of products. Similar results were observed for the interactions of **13** with 1-pentyne, phenylacetylene, and hydrogen (1 atm). In each case, no reaction was observed at room temperature in benzene-d_6, and heating the reaction mixture to 60 °C resulted in formation of a black precipitate. Heating a benzene-d_6 solution of **13** to 80 °C, with or without NEt_3, resulted in formation of toluene-*d* after 1 day, according to ^{1}H NMR spectroscopy. This result indicates that an activation of benzene-d_6 occurred; however, other products from this reaction were not identifiable by NMR spectroscopy.

Neutral (NSiN)Rh^{I} Complexes. The investigations described above suggest that (NSiN)Rh^{I} complexes do not form readily and may be reactive in nature. Therefore, an additional attempt was made to synthesize an isolable (NSiN)Rh^{I} complex, directly from a Rh(I) reagent. Reaction of (COD)Rh(η^3-CH_2Ph)[17] with 1 equiv of **1** quantitatively produced toluene and (NSiN)Rh(COD) (**14**) as a dark brown solid (Scheme 4). The ^{1}H NMR spectrum of **14** in benzene-d_6 contains one set of quinolyl protons and broad singlets at δ 5.25 and δ 3.32 (for bound COD), indicating mirror symmetry for the molecule. The ^{13}C{^{1}H} NMR spectrum reveals two olefinic carbon resonances at δ 106.3 and 46.1, both of which couple to ^{103}Rh with *J* values of 3.8 and 17 Hz, respectively. These coupling constants suggest that, in solution, both olefinic groups of the COD ligand are bound to the Rh center, resulting in a five-coordinate Rh(I) complex.

Examples of 18-electron, five-coordinate Rh(I) complexes have been characterized both in solution[21] and in the solid state.[22] The crystal structures of these compounds reveal a trigonal-bipyramidal geometry at the Rh center. In observed chemistry based on TpRh(LL) complexes, both 16- and 18-electron complexes are known. In the solid state, (κ^2-Tp)Rh(NBD) (NBD = norbornadiene) and (κ^2-Tp)Rh(COD) exist as 16-electron complexes, while (κ^3-Tp)Rh(DQ) (DQ = duroquinone) is assigned as an 18-electron, 5-coordinate species.[22a] In addition, recent studies have shown that complexes of the type Tp^{Me}Rh(LL) (LL = 2CO, NBD, COD) display $\kappa^2-\kappa^3$ isomerism of the Tp^{Me} ligand in solution.[23] Therefore, to investigate any $\kappa^2-\kappa^3$ isomerism for the NSiN ligand in **14**, variable-temperature ^{1}H NMR experiments of a toluene-d_8 solution of **14** were performed. These studies revealed no decoalescence of the ^{1}H NMR resonances at temperatures as low as −80 °C.

Complex **14** is thermally unstable in solution and decomposes within a few hours at 70 °C in benzene-d_6. It reacts immediately with H_2 (1 atm) in benzene-d_6 to produce cyclooctene and a black precipitate. Neither $(NSiN)RhH_2$ nor $(NSiN)RhH_2(COE)$ was observed by NMR spectroscopy. However, the reaction with Ph_3SiH (1 equiv, benzene-d_6, room temperature) immediately resulted in the clean formation of $(NSiN)Rh(H)(SiPh_3)$ (**15**), as indicated by a hydride resonance at δ 13.2 (d, $^1J_{RhH} = 28$ Hz), with the elimination of COD. On the basis of ^{1}H NMR spectroscopy, complex **15** is unstable in benzene solution and reacted further with COD to yield the olefin-insertion product (NSiN)Rh(η^1-C_8H_{13})($SiPh_3$) (**16**) (Scheme 4).

An analogous olefin-insertion product was also obtained from reaction of **14** with $HSi(OSiMe_3)_3$ in benzene, which gave the neutral Rh(III) complex (NSiN)Rh(η^1-C_8H_{13})[$Si(OSiMe_3)_3$] (**17**) (Scheme 4). However, the olefin insertion step is more rapid and the rhodium hydride intermediate (NSiN)Rh(H)[$Si(OSiMe_3)_3$] could not be observed during the course of the reaction. To investigate the potential hydrosilylation catalytic activity of **14**, 10 mol % of **14** was combined with Ph_3SiH and COD in benzene and the mixture heated to 50 °C. After 18 h, several isomers of the hydrosilylation product $C_8H_{13}SiPh_3$ were observed (>90% yield) by GC/MS.

In an attempt to generate more thermally stable Rh(I) complexes, phosphine derivatives of the type $(NSiN)Rh(PR_3)_n$ were targeted. Treatment of **14** with 1 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) gave the corresponding Rh(I) complex (NSiN)Rh(dppe) (**18**) in a quantitative yield on the basis of ^{1}H NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum of **18** contains two doublet of doublets at δ 70.6 ($^1J_{RhP} = 190$ Hz, $^2J_{PP'} = 15$ Hz) and δ 43.3 ($^1J_{RhP'} = 125$ Hz, $^2J_{P'P} = 15$

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Hz). These results indicate that both phosphine groups bind to the Rh center, as evidenced by the large Rh−P coupling constants, and are consistent with a trigonal-bipyramidal or a distorted-square-pyramidal structure. Complex **18** was thermally stable in benzene-d_6 solution and inactive toward Ph_3SiH and H_2, even at 80 °C over 3 days.

Conclusions

This paper describes synthetic pathways to various rhodium complexes containing a tridentate NSiN ligand and initial reactivity studies for (NSiN)Rh compounds. Reliable methods for introduction of the NSiN ligand are based on oxidative addition of the Si−H bond of bis(8-quinolyl)methylsilane, as employed in the synthesis of (NSiN)Rh(H)(Cl)(PPh_3) (**2**) from the silane and $(PPh_3)_3RhCl$. A related process, involving reaction of $RhCl_3(CH_3CN)_3$ with the silane **1** in the presence of NEt_3, provided the useful starting material [(NSiN)$RhCl_2$]$_2$ (**10**). The reactivity studies completed thus far indicate that the (NSiN)-Rh^{III} fragment is rather chemically robust.

Investigations with the (NSiN)Rh^{III} fragment have produced several coordinatively unsaturated 16-electron complexes, including [(NSiN)RhH(PPh_3)][$B(C_6F_5)_4$] (**3**) and (NSiN)Rh($CH_2Ph)_2$ (**12**). Despite their coordinative unsaturation, these complexes are thermally stable and chemically inert. This stability may result, in part, from the strong trans effect of Si, which prevents the binding of molecular substrates trans to the silyl group.

Similarities between the NSiN ligand and the more well-known Cp* and Tp ligands are reflected in the formation of complexes such as [(NSiN)$RhCl_2$]$_2$ (**10**) and [(NSiN)Rh-$(MeCN)_3$][OTf]$_2$ (**11**). However, the chemical behaviors of the (NSiN)Rh complexes are quite distinct from those of their Cp*Rh and TpRh counterparts. For example, although [Cp*Rh-$(MeCN)_3$][OTf]$_2$ possesses highly labile acetonitrile ligands, the analogous [(NSiN)Rh$(MeCN)_3$][OTf]$_2$ (**11**) is inert toward substitution of its acetonitrile ligands by soft donors such as arenes and alkenes. Nonetheless, like its Cp*Rh analogue, complex **11** exhibits moderate activity as a catalyst for alkene hydrogenation. Interestingly, **11** catalyzes H/Cl exchange between Ph_3SiH and CD_2Cl_2, to quantitatively give Ph_3SiCl and CD_2HCl.

Reactive Rh(I) complexes bearing the NSiN ligand were obtained via the (COD)Rh(η^3-CH_2Ph) starting material, to initially give (NSiN)Rh(COD) (**14**), which is thermally unstable in solution at 70 °C. In general, the isolation and characterization of additional (NSiN)Rh^I complexes has proven difficult, due to their lack of thermal stability. A notable aspect of this chemistry concerns the predominance of 5-coordinate Rh(I) complexes, which is apparently enforced by the tripodal nature of the NSiN ligand. The Rh(I) complex **14** activates the Si−H group of Ph_3SiH to give the Rh(III) intermediate (NSiN)Rh(H)($SiPh_3$) (**15**), which then undergoes COD insertion to produce (NSiN)Rh-(η^1-C_8H_{13})($SiPh_3$) (**16**). This chemistry is undoubtedly related to the behavior of **14** as a hydrosilylation catalyst.

Future investigations will focus on stoichiometric and catalytic transformations of substrates containing hard donor atoms (e.g., O and N) at (NSiN)Rh^{III} centers.

Experimental Section

General Procedures. All manipulations were conducted under an N_2 atmosphere using standard Schlenk or glovebox techniques. In general, solvents were distilled under N_2 from appropriate drying agents and stored in PTFE-valved flasks. Deuterated solvents (Cambridge Isotopes) were dried with appropriate drying agents and vacuum transferred prior to use. The reagents 8-bromoquinoline,[9] $(PPh_3)_3RhCl$,[10] (COD)RhCl(PMe_3),[13] (COD)Rh(η^3-CH_2Ph),[14a] $RhCl_3(CH_3CN)_3$,[15] $Mg(CH_2Ph)_2(THF)_2$,[24] and $LiB(C_6F_5)_4 \cdot 2.5Et_2O$[11] were prepared according to literature procedures. $Me(H)SiCl_2$ (Gelest) was distilled under N_2 and degassed before use. All other chemicals were purchased from Aldrich or Gelest and used without further purification. Ethylene (Air Gas) and dihydrogen (Praxair) were used as received. The NMR spectra were recorded at 500 MHz (^1H), 202 MHz ($^{31}P\{^1H\}$), 125 MHz ($^{13}C\{^1H\}$), 376.5 MHz (^{19}F), or 99 MHz ($^{29}Si\{^1H\}$) on Bruker DRX-500 and AVQ-400 spectrometers at ambient temperature, with chemical shifts reported in ppm downfield of tetramethylsilane (^1H, ^{13}C, and ^{29}Si), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P). Elemental analyses were performed by the Micro-Mass Facility in the College of Chemistry at the University of California, Berkeley. Infrared spectra were recorded as KBr pellets on a Mattson FTIR 3000 instrument.

Qn_2SiHMe (1). This synthesis represents an improvement over that previously described in the literature. *n*-Butyllithium (1.6 M in hexane, 13.5 mL, 21.6 mmol) was added dropwise to a magnetically stirred solution of 8-bromoquinoline (4.32 g, 20.8 mmol) in 70 mL of THF at −78 °C over 5 min, and stirring was continued for an additional 5 min at this temperature. $Me(H)SiCl_2$ (1.13 mL, 10.8 mmol) was then slowly added dropwise, causing a color change from light brown to yellow. The resulting mixture was stirred at room temperature for 12 h. After removal of the solvent and other volatile materials in vacuo, the yellow residue was redissolved in toluene (120 mL) and cannula-filtered. The remaining off-white solid was washed with 2 × 15 mL of toluene. The extracts were combined and concentrated to 50 mL, at which point an off-white solid (LiCl) started to form. The toluene solution was filtered again, and the filtrate was concentrated to approximately 30 mL and stored under N_2 at −30 °C for 48 h. Compound **1** was obtained as pale yellow crystals in 48% yield (1.50 g, 4.99 mmol). ^1H NMR (C_6D_6, 500 MHz): δ 8.64 (d, $J_{HH} = 4.1$ Hz, of d, $J_{HH} = 1.8$ Hz, 2 H, Ar *H*), 7.99 (d, $J_{HH} = 6.7$ Hz, of d, $J_{HH} = 1.5$ Hz, 2 H, Ar *H*), 7.47 (d, $J_{HH} = 8.2$ Hz, of d, $J_{HH} = 1.8$ Hz, 2 H, Ar *H*), 7.39 (d, $J_{HH} = 8.2$ Hz, of d, $J_{HH} = 1.5$ Hz, 2 H, Ar *H*), 7.13 (d, $J_{HH} = 8.2$ Hz, of d, $J_{HH} = 6.7$ Hz, 2 H, Ar *H*), 6.67 (d, $J_{HH} = 8.2$ Hz, of d, $J_{HH} = 4.1$ Hz, 2 H, Ar *H*), 6.34 (q, $J_{HH} = 3.8$ Hz, 1 H, Si*H*), 1.32 (d, $J_{HH} = 3.8$ Hz, 3 H, SiCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 153.3, 149.5, 139.1, 138.6, 135.9, 129.5, 127.9, 126.4, 120.8 (aryl carbons), −2.7 (SiCH_3). $^{29}Si\{^1H\}$ NMR (C_6D_6, 99 MHz): δ −18.9. Anal. Calcd for $C_{19}H_{16}N_2Si$: C, 75.96; H, 5.37; N, 9.32. Found: C, 75.63; H, 5.50; N, 9.24. IR (cm^{-1}): ν_{SiH} 2131 s.

(NSiN)Rh(H)(Cl)(PPh_3) (2). To a stirred solution of **1** (0.0650 g, 0.216 mmol) in 10 mL of CH_2Cl_2 was added a solution of Rh-$(PPh_3)_3$Cl (0.200 g, 0.216 mmol) in 10 mL of CH_2Cl_2 at room temperature. After 18 h of stirring, the solvent was removed in vacuo. The yellow residue was washed with pentane (2 × 10 mL), and then it was taken up in 15 mL of CH_2Cl_2; this solution was filtered through Celite and concentrated to a volume of 7 mL. Vapor diffusion of diethyl ether into this solution at room temperature for 48 h produced **2** as yellow crystals in 82% yield (0.135 g, 0.177 mmol). ^1H NMR (CD_2Cl_2, 500 MHz): δ 10.79 (m, 1 H, Ar *H*), 10.00 (m, 1 H, Ar *H*), 8.10 (d, $J_{HH} = 8.0$ Hz, 1 H, Ar *H*), 8.00 (d, $J_{HH} = 6.4$ Hz, 1 H, Ar *H*), 7.83 (d, $J_{HH} = 19$ Hz, of d, $J_{HH} = 6.6$ Hz, 2 H, Ar *H*), 7.68 (d, $J_{HH} = 7.2$ Hz, 1 H, Ar *H*), 7.54−7.51 (m, 8 H, Ar *H*), 7.40 (m, 2 H, Ar *H*), 7.13−7.05 (m, 10 H, Ar *H*), 0.419 (s, 3 H, SiCH_3), −15.9 (d, $J_{RhH} = 24$ Hz, of d, $J_{PH} = 17$ Hz, 1 H, Rh*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 155.4, 154.3, 153.3, 152.7, 148.3, 147.8, 137.9, 137.3, 135.1, 134.8, 134.6, 134.5, 133.8 (d, $J = 11.2$ Hz), 129.4 (d, $J = 2.5$ Hz), 129.1, 128.9, 128.5 (d, $J = 17.5$ Hz), 127.7 (d, $J = 10.0$ Hz), 127.5, 127.0, 122.2 (d, $J = 3.8$ Hz), 121.8 (aryl carbons), −2.48 (d, $J = 1.0$ Hz, SiCH_3).

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^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 40.3 (m). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 59.1 (d, J_{RhP} = 150 Hz). Anal. Calcd for $C_{37}H_{31}N_2SiPClRh$: C, 63.39; H, 4.46; N, 4.00. Found: C, 63.02; H, 4.43; N, 3.78. IR (cm^{-1}): ν 2030 (m, Rh−H).

[(NSiN)Rh(H)(PPh$_3$)][B(C$_6$F$_5$)$_4$] (3). A solution of **2** (0.150 g, 0.214 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a stirred solution of Li(OEt$_2$)$_{2.5}$B(C$_6$F$_5$)$_4$ (0.185 g, 0.212 mmol) in 10 mL of CH_2Cl_2 at room temperature. The stirring was continued for 1 h before all volatiles were removed under vacuum. The remaining yellow solid was redissolved in diethyl ether and filtered through Celite. Vapor diffusion of pentane into the concentrated diethyl ether solution gave pale yellow crystals in 96% yield (0.305 g, 0.204 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.21 (m, 1 H, Ar *H*), 8.73 (d, J_{HH} = 5.0 Hz, 1 H, Ar *H*), 8.39 (d, J_{HH} = 8.0 Hz, of d, J_{HH} = 1.0 Hz 1 H, Ar *H*), 8.12 (d, J_{HH} = 11.0 Hz, of d, J_{HH} = 1.0 Hz, 1 H, Ar *H*), 8.05 (d, J_{HH} = 8.2 Hz of, d, J_{HH} = 1.2 Hz, 1 H, Ar *H*), 7.93 (d, J_{HH} = 6.0 Hz, of d, J_{HH} = 1.5 Hz, 1 H, Ar *H*), 7.90 (d, J_{HH} = 7.5 Hz, 1 H, Ar *H*), 7.69 (m, 2 H, Ar *H*), 7.57 (d, J_{HH} = 8.0 Hz, of d J_{HH} = 5.0 Hz, 1 H, Ar *H*), 7.52 (d, J_{HH} = 7.5 Hz, of d J_{HH} = 6.5 Hz 1 H, Ar *H*), 7.40−7.36 (m, 9 H, Ar *H*), 7.28−7.22 (m, 7 H, Ar *H*), 3.46 (q, J_{HH} = 7.0 Hz, 8 H, OCH_2CH_3), 1.18 (t, J_{HH} = 7.0 Hz, 12 H, OCH_2CH_3), 0.88 (s, 3 H, SiCH_3), −13.5 (t, J_{RhH} = J_{PH} = 22 Hz, 1 H, Rh*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 154.4, 150.4, 150.0, 149.7, 148.1 (br d, J_{CF} = 241 Hz, B(C_6F_5)$_4$), 142.9, 142.3, 139.2, 138.7, 138.2 (br d, J_{CF} = 248 Hz, B(C_6F_5)$_4$), 136.2 (br d, J_{CF} = 239 Hz, B(C_6F_5)$_4$), 135.8, 135.6, 132.6 (d, J_{CP} = 11.0 Hz), 131.2 (d, *J* = 2.5 Hz), 129.9, 129.7, 129.6, 129.2 (d, J_{CP} = 81 Hz), 128.9 (d, J_{CP} = 7.5 Hz), 128.8, 128.3, 127.7, 125−122 (v br, B-*C*), 122.0 (d, *J* = 2.5 Hz), 121.8 (aryl carbons), 65.9 (s, OCH_2CH_3), 14.7 (s, OCH_2CH_3), −2.0 (s, SiCH_3). ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −130.8 (t, J_{FF} = 18.0 Hz, 8 F, *o*-F), −161.6 (t, J_{FF} = 20.0 Hz, 4 F, *p*-F), −165.9 (br s, 8 F, *m*-F). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 52.95 (d, $^{1}J_{SiRh}$ = 40 Hz, of d $^{2}J_{SiP}$ = 11 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 50.8 (d, $^{1}J_{RhP}$ = 144 Hz). Anal. Calcd for $C_{69}H_{51}N_2SiPBO_2F_{20}Rh$: C, 55.51; H, 3.44; N, 1.88. Found: C, 55.71; H, 3.05; N, 1.96. IR (cm^{-1}): ν 2022 (w, Rh−H).

[(NSiN)Rh(Cl)(PPh$_3$)][B(C$_6$F$_5$)$_4$] (4). A CD_2Cl_2 solution of **3** was heated to 50 °C for 48 h. The reaction was quantitative on the basis of ^{1}H NMR spectroscopy. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 10.1 (m, 1 H, Ar *H*), 9.34 (d, J_{HH} = 5.0 Hz, 1 H, Ar *H*), 8.16 (d, J_{HH} = 11.6 Hz, of d J_{HH} = 6.8 Hz, 2 H, Ar *H*), 8.04 (d, J_{HH} = 6.4 Hz, 1 H, Ar *H*), 7.86 (d, J_{HH} = 8.0 Hz, 1 H, Ar *H*), 7.81 (d, J_{HH} = 8.0 Hz, 1 H, Ar *H*), 7.65−7.55 (m, 9 H, Ar *H*), 7.50 (m, 1 H, Ar *H*), 7.33 (m, 3 H, Ar *H*), 7.16 (m, 6 H, Ar *H*), 6.86 (m, 1 H, Ar *H*), 0.96 (s, 3 H, SiCH_3). ^{13}C{^{1}H} (CD_2Cl_2, 125 MHz): 153.0, 152.4, 151.4, 151.0, 148.6 (br d, J_{CF} = 239 Hz), 142.4, 141.9, 140.3, 139.8, 138.7 (br d, J_{CF} = 251 Hz), 136.9, 136.7 (br d, J_{CF} = 243 Hz), 136.4, 134.1 (d, *J* = 10 Hz), 131.9 (d, *J* = 2.5 Hz), 130.6, 130.4, 129.8, 129.7, 129.3, 129.1 (d, J_{PC} = 10 Hz), 128.8 (d, J_{PC} = 52.8 Hz), 128.8, 124.9 (v br, B−*C*), 123.0 (d, *J* = 4.5 Hz), 122.8 (aryl carbons), −1.29 (s, SiCH_3). ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −131.3 (t, J_{FF} = 23 Hz, 8 F, *o*-F), −162.1 (t, J_{FF} = 23 Hz, 4 F, *p*-F), −166.3 (br s, 8 F, *m*-F). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 64.6 (d, $^{1}J_{SiRh}$ = 29.5 Hz, of d $^{2}J_{SiP}$ = 10.0 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 26.4 (d, $^{1}J_{RhP}$ = 126 Hz). Anal. Calcd for $C_{61}H_{30}N_2SiPBClF_{20}Rh$: C, 53.12; H, 2.19; N, 2.03. Found: C, 53.42; H, 2.54; N, 2.37.

(NSiN)Rh(H)(Cl)(PMe$_3$) (5). A 150 mL Schlenk flask equipped with a stir bar was charged with **1** (0.600 g, 2.00 mmol) and (COD)-Rh(PMe$_3$)Cl (0.612 g, 1.90 mmol). To this solid mixture was added 50 mL of C_6H_6, and the reaction mixture was stirred at room temperature for 12 h. Then, all volatiles were removed in vacuo to produce a yellow solid. Recrystallization from a concentrated THF solution of **5** at −30 °C resulted in a yellow powder in 59% yield (0.576 g, 1.12 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 10.56 (m, 1 H, Ar *H*), 10.15 (m, 1 H, Ar *H*), 8.12−8.05 (m, 4 H, Ar *H*), 7.69 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.0 Hz, 1 H, Ar *H*), 7.65 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.0 Hz, 1 H, Ar *H*), 7.54−7.49 (m, 2 H, Ar *H*), 7.40 (d J_{HH} = 8.2 Hz, of d J_{HH} = 4.8 Hz, 1 H, Ar *H*), 7.36 (m, 1 H, Ar *H*), 1.21 (d J_{PH} = 10 Hz, of d J_{RhH} = 1.5 Hz, 9 H, Ar *H*), 1.18 (s, 3 H, SiCH_3), −16.6 (d J_{RhH} = 29 Hz, of d J_{PH} = 22 Hz, 1 H, Rh*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 155.0, 154.2, 153.4, 153.2, 148.4, 147.9, 137.9, 137.6, 135.1, 134.9, 129.2, 129.0, 128.7, 128.5, 127.4, 127.3, 122.1, 122.0 (d, *J* = 3.8 Hz) (aryl carbons), 20.1 (d $^{1}J_{PC}$ = 35 Hz, of d $^{2}J_{RhC}$ = 2.5 Hz, PCH_3), −1.58 (d, $^{2}J_{RhC}$ = 3.9 Hz, SiCH_3). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 38.6 (m). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 6.80 (d, $^{1}J_{RhP}$ = 138 Hz). Anal. Calcd for $C_{22}H_{25}N_2SiPClRh$: C, 51.32; H, 4.89; N, 5.44. Found: C, 51.58; H, 4.96; N, 5.52. IR (cm^{-1}): ν 1986 (m, Rh−H).

(NSiN)Rh(CH$_2$Ph)Cl(PPh$_3$) (6). (1) To a stirred slurry of **2** (0.155 g, 0.221 mmol) in 10 mL of benzene was added a 1.0 M diethyl ether solution of $PhCH_2MgCl$ (0.24 mL, 0.240 mmol). The reaction mixture was stirred at room temperature for 20 min, after which it became homogeneous and dark red. The resulting solution was filtered through Celite, and the benzene solvent was slowly removed under vacuum. When the solvent volume reached approximately 3 mL, a yellow microcrystalline solid was obtained. The solid was washed with 2 × 3 mL of cold toluene to afford the crude product in 48% yield (0.087 g, 0.106 mmol).

(2) Complex **6** can also be generated by adding 10 mL of benzene to a solid mixture of **7** (0.075 g, 0.082 mmol) and PPNCl (0.049 g, 0.085 mmol). The reaction slurry was stirred at room temperature for 8 h, after which it became more homogeneous. The reaction mixture was filtered through Celite, and the orange filtrate was concentrated to approximately 2 mL, at which point a yellow solid started to form. Slow evaporation of benzene further yielded analytically pure **6** in 22% yield (0.014 g, 0.018 mmol). ^{1}H NMR (C_6D_6, 500 MHz): δ 9.74 (d J_{HH} = 4.5 Hz, of d J_{HH} = 2.0 Hz, 1 H, Ar *H*), 9.68 (d J_{HH} = 4.8 Hz, of d J_{HH} = 1.8 Hz, 1 H, Ar *H*), 8.16 (d, J_{HH} = 7.0 Hz, 1 H, Ar *H*), 7.78 (d J_{HH} = 6.2 Hz, of d J_{HH} = 2.2 Hz, 1 H, Ar *H*), 7.36 (m, 6 H, Ar *H*), 7.19 (m, 2 H, Ar *H*), 7.08 (m, 3 H, Ar *H*), 6.84 (m, 2 H, Ar *H*), 6.76 (m, 9 H, Ar *H*), 6.64 (m, 1 H, Ar *H*), 6.52 (d J_{HH} = 8.2 Hz, of d J_{HH} = 5.2 Hz, 1 H, Ar *H*), 6.44 (d J_{HH} = 8.2 Hz, of d J_{HH} = 4.8 Hz, 2 H, Ar *H*), 6.35 (m, 2 H, Ar *H*), 3.59 (m, 4 H, THF), 2.20 (t, $^{2}J_{RhH} \approx {}^{2}J_{HH'} \approx$ 6.0 Hz, 1 H, RhC*H*H′), 1.77 (t, $^{2}J_{RhH'} \approx {}^{2}J_{H'H} \approx$ 6.0 Hz, 1 H, RhC*H′*H), 1.40 (m, 4 H, THF), 1.15 (s, 3 H, SiCH_3). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 150.6, 150.0, 149.7, 145.9, 140.4, 139.9, 137.9 (d, *J* = 32.5 Hz), 137.3, 135.3, 135.0, 135.3, 135.0, 134.1, 133.9 (d, *J* = 12.5 Hz), 130.3, 129.5, 129.2, 128.9, 128.4, 127.5, 127.2 (d, *J* = 8.8 Hz), 127.0, 126.9, 122.0, 120.1, 119.4 (aryl carbons), 33.3 (d, $^{2}J_{PC}$ = 36.5 Hz, of d $^{1}J_{RhC}$ = 11.3 Hz, RhCH_2Ph) 4.41 (s, SiCH_3). ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): δ 4.0 (d, $^{1}J_{RhSi}$ = 74 Hz, of d $^{2}J_{SiP}$ = 15 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 43.4 (d, $^{1}J_{RhP}$ = 167 Hz). Anal. Calcd for $C_{44}H_{37}N_2SiPRhCl$: C, 66.42; H, 4.69; N, 3.52. Found: C, 66.21; H, 4.33; N, 3.48.

[(NSiN)Rh(η^3-CH$_2$Ph)(PPh$_3$)][OTf] (7). At ambient temperature, 1 equiv of neat TMSOTf (0.030 g, 0.135 mmol) was added to a stirred 15 mL benzene suspension of **6** (0.100 g, 0.122 mmol). The reaction mixture became homogeneous within 10 min. After 2 h, the dark red mixture was concentrated to 5 mL. An orange microcrystalline solid precipitated from solution after 24 h. The supernatant was decanted, and the remaining precipitate was washed with 2 × 3 mL of benzene. The product **7** was isolated in 58% yield (0.066 g, 0.0708 mmol). ^{1}H NMR (THF-d_8, 500 MHz): δ 9.06 (d J_{HH} = 5.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 8.97 (d J_{HH} = 5.0 Hz, of d J_{HH} = 2.0 Hz, 1 H, Ar *H*), 8.43 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 8.20 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 8.10 (d J_{HH} = 7.0 Hz, of d J_{HH} = 1.0 Hz, 1 H, Ar *H*), 7.77 (m, 2 H, Ar *H*), 7.55 (m, 4 H, Ar *H*), 7.25 (t, J_{HH} = 7.5 Hz, 1 H, Ar *H*), 6.98 (m, 9 H, Ar *H*), 6.92 (m, 6 H, Ar *H*), 6.38 (br s, 1 H, Ar *H*), 6.27 (t, J_{HH} = 7.5 Hz, 1 H, Ar *H*), 6.21 (br s, 1

H, Ar *H*), 5.63 (br s, 1 H, Ar *H*), 1.50 (t, $^{2}J_{\mathrm{RhH}} \approx {}^{2}J_{\mathrm{HH'}} \approx 5.0$ Hz, 1 H, RhC*H*$_2$), 1.17 (t, $^{2}J_{\mathrm{RhH'}} \approx {}^{2}J_{\mathrm{H'H}} \approx 5.0$ Hz, 1 H, RhC*H*$_2$), 0.87 (s, 3 H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (THF-*d*$_8$, 125 MHz): δ 150.3, 150.2, 150.1, 150.0, 149.5, 148.9, 144.5 (d, $J = 3.0$ Hz), 142.6, 142.1, 138.7, 138.0, 137.7, 136.0, 134.1 (d, $J = 13.8$ Hz), 130.8, 130.4, 129.2, 129.1, 128.3 (d, $J = 64$ Hz), 127.9 (d, $J = 8.8$ Hz), 122.5, 121.6, 121.5, 120.6 (m), 119.3 (m), 108.6 (br m) (aryl carbons), 31.3 (d $^{2}J_{\mathrm{PC}} = 37.5$ Hz, of d $^{1}J_{\mathrm{RhC}} = 11.3$ Hz, Rh*C*H$_2$Ph) 4.47 (d, $J = 3.8$ Hz, Si*C*H$_3$). ^{19}F NMR (THF-*d*$_8$, 376.5 MHz): δ −78.02 (s). ^{29}Si{^{1}H} NMR (THF-*d*$_8$, 99 MHz): δ 4.1 (d $^{1}J_{\mathrm{RhSi}} = 70$ Hz, of d $^{2}J_{\mathrm{SiP}} = 15$ Hz). ^{31}P{^{1}H} NMR (THF-*d*$_8$, 162 MHz): δ 41.2 (d, $^{1}J_{\mathrm{RhP}} = 167$ Hz). Anal. Calcd for $C_{45}H_{37}N_2SiPO_3F_3SRh$: C, 59.73; H, 4.12; N, 3.10. Found: C, 59.37; H, 4.03; N, 2.83.

(NSiN)RhCl$_2$(PPh$_3$) (8). A 250 mL two-neck round-bottom flask was equipped with a stir bar and a reflux condenser. Under N$_2$, **2** (0.400 g, 0.570 mmol) and 50 mL of CH$_2$Cl$_2$ were added, followed by neat DBU (0.100 mL, 0.669 mmol). The reaction mixture was refluxed for 12 h at 65 °C, at which point all volatile materials were removed under reduced pressure. The remaining yellow residue was then redissolved in 25 mL of CH$_2$Cl$_2$, and filtration provided a yellow filtrate. Recrystallization from a 1/1 mixture of CH$_2$Cl$_2$ and diethyl ether (20 mL in total) afforded the desired product in 68% yield (0.312 g, 0.388 mmol). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 10.98 (m, 1 H, Ar *H*), 10.18 (d, $J_{\mathrm{HH}} = 5.0$ Hz, 1 H, Ar *H*), 8.13 (d $J_{\mathrm{HH}} = 8.0$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 1 H, Ar *H*), 8.04 (d $J_{\mathrm{HH}} = 7.0$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 1 H, Ar *H*), 8.00 (d $J_{\mathrm{HH}} = 6.5$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 1 H, Ar *H*), 7.78 (d $J_{\mathrm{HH}} = 8.0$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 1 H, Ar *H*), 7.72 (d $J_{\mathrm{HH}} = 8.0$ Hz, 1 H, Ar *H*), 7.63−7.59 (m, 7 H, Ar *H*), 7.53 (q, $J_{\mathrm{HH}} = 7.0$ Hz, 2 H, Ar *H*), 7.45 (m, 1 H, Ar *H*), 7.24−7.22 (m, 3 H, Ar *H*), 7.10−7.06 (m, 6 H, Ar *H*), 6.79 (d $J_{\mathrm{HH}} = 8.5$ Hz, of d $J_{\mathrm{HH}} = 5.5$ Hz, 1 H, Ar *H*), 0.45 (s, 3 H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125 MHz): δ 157.7, 155.4, 154.4, 152.5, 146.9, 146.2, 138.7, 138.1, 135.6, 135.4, 134.9 (d, $J = 8.8$ Hz), 137.7, 133.3, 130.0 (d, $J = 2.5$ Hz), 129.7 (d, $J = 2.5$ Hz), 129.3, 129.2, 127.8 (d, $J = 38$ Hz), 127.9, 127.8, 122.5, 122.4 (aryl carbons), −5.27 (Si*C*H$_3$). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, 99 MHz): δ 45.1 (d, $^{1}J_{\mathrm{SiRh}} = 24.2$ Hz, of d $^{2}J_{\mathrm{SiP}} = 11.4$ Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202.5 MHz): δ 24.2 (d, $^{1}J_{\mathrm{RhP}} = 128$ Hz). Anal. Calcd for $C_{37}H_{30}N_2SiPCl_2Rh\cdot CH_2Cl_2$: C, 55.62; H, 3.93; N, 3.47. Found: C, 55.44; H, 3.97; N, 3.49.

[(NSiN)Rh(PMe$_3$)$_2$(Cl)][Cl] (9). To a 20 mL solution of CH$_2$Cl$_2$ solution of **2** (0.200 g, 0.285 mmol) was added 0.3 mL of neat PMe$_3$ (2.90 mmol). After 8 h, the yellow reaction mixture was cannula-filtered and the filtrate was dried in vacuo. Recrystallization from a 1/1 mixture of CH$_2$Cl$_2$ and diethyl ether (20 mL in total) resulted in colorless crystals in 54% yield (0.096 g, 0.154 mmol). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 10.36 (m, 2 H, Ar *H*), 8.37 (d $J_{\mathrm{HH}} = 8.0$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 2 H, Ar *H*), 8.19 (d $J_{\mathrm{HH}} = 7.0$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 2 H, Ar *H*), 7.89 (d $J_{\mathrm{HH}} = 7.5$ Hz, of d $J_{\mathrm{HH}} = 1.2$ Hz, 2 H, Ar *H*), 7.68 (d $J_{\mathrm{HH}} = 8.0$ Hz, of d $J_{\mathrm{HH}} = 6.5$ Hz, 2 H, Ar *H*), 7.56 (d $J_{\mathrm{HH}} = 8.2$ Hz, of d $J_{\mathrm{HH}} = 5.0$ Hz, 2 H, Ar *H*), 1.41 (s, 3 H, SiC*H*$_3$), 1.26 (m, 18 H, P(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125 MHz): δ 154.7, 152.4 (d, $^{2}J_{\mathrm{RhC}} = 1.4$ Hz), 143.4, 140.4, 136.9, 130.3, 129.6, 128.7, 123.1 (aryl carbons), 17.5 (m, P(*C*H$_3$)$_3$), −2.81 (d, $^{3}J_{\mathrm{RhC}} = 2.3$ Hz, Si*C*H$_3$). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, 99 MHz): δ 46.1 (d $^{1}J_{\mathrm{SiRh}} = 28$ Hz, of t $^{2}J_{\mathrm{SiP}} = 12$ Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202.5 MHz): δ 2.44 (d, $^{1}J_{\mathrm{PRh}} = 117$ Hz). Anal. Calcd for $C_{25}H_{33}N_2SiP_2RhCl_2$: C, 48.01; H, 5.32; N, 4.48. Found: C, 47.65; H, 5.30; N, 4.14.

[(NSiN)RhCl$_2$]$_2$ (10). To a solid mixture of **1** (0.650 g, 2.16 mmol) and RhCl$_3$(CH$_3$CN)$_3$ (0.720 g, 2.16 mmol) was added CH$_2$Cl$_2$ (75 mL), followed by 0.35 mL of neat NEt$_3$ (2.51 mmol). After 18 h, the resulting orange suspension was allowed to settle. Then, the orange filtrate was removed via cannula filtration to leave a yellow precipitate. The yellow residue was washed with CH$_2$Cl$_2$ (2 × 20 mL) and dried in vacuo to give the desired product in 62% yield (0.630 g, 1.33 mmol). ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ 10.50 (m, 2 H, Ar *H*), 8.50 (d $J_{\mathrm{HH}} = 20$ Hz, of d $J_{\mathrm{HH}} = 7.5$ Hz, 2 H, Ar *H*), 8.32 (d $J_{\mathrm{HH}} = 18$ Hz, of d $J_{\mathrm{HH}} = 6.0$ Hz, 2 H, Ar *H*), 7.95 (t, $J_{\mathrm{HH}} = 9.0$ Hz, 2 H, Ar *H*), 7.68 (m, 4 H, Ar *H*), 1.36 (s, 3 H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (DMSO-*d*$_6$, 125 MHz): δ 157.7, 155.4, 154.4, 152.5, 146.9, 146.2, 138.7, 138.1, 135.6, 135.4, 134.9 (d, $J = 8.8$ Hz), 137.7, 133.3, 130.0 (d, $J = 2.5$ Hz), 129.7 (d, $J = 2.5$ Hz), 129.3, 129.2, 127.8 (d, $J = 3.8$ Hz), 127.9, 127.8, 122.5, 122.4 (aryl carbons), −5.27 (s, Si*C*H$_3$). ^{29}Si{^{1}H} NMR (DMSO-*d*$_6$, 99 MHz): δ 51.6 (d, $^{1}J_{\mathrm{SiRh}} = 22.0$ Hz). Anal. Calcd for $C_{19}H_{15}N_2SiCl_2Rh$: C, 48.22; H, 3.20; N, 5.92. Found: C, 47.89; H, 3.40; N, 5.89.

[(NSiN)Rh(CH$_3$CN)$_3$][OTf]$_2$ (11). A 200 mL Schlenk flask, covered with aluminum foil, was charged with [(NSiN)RhCl$_2$]$_2$ (0.500 g, 0.528 mmol) and AgOTf (0.570 g, 2.22 mmol). To this was added 50 mL of CH$_2$Cl$_2$, and the reaction mixture was stirred at ambient temperature for 8 h. After the reaction suspension was allowed to settle, the yellow filtrate was removed by cannula filtration to leave an off-white precipitate, to which 30 mL of CH$_3$CN was added. The CH$_3$CN solution was stirred for 3 h, at which point the solution became yellow as a fluffy white precipitate (AgCl) formed. The reaction solution was concentrated to 5 mL, and vapor diffusion of diethyl ether into this solution at room temperature produced **11** as colorless crystals in 68% yield (0.591 g, 0.718 mmol). ^{1}H NMR (CD$_3$CN, 500 MHz): δ 9.63 (d, $J_{\mathrm{HH}} = 5$ Hz, 2 H, Ar *H*), 8.48 (d $J_{\mathrm{HH}} = 1.5$ Hz, of t $J_{\mathrm{HH}} = 7$ Hz, 4 H, Ar *H*), 8.00 (d $J_{\mathrm{HH}} = 8$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 2 H, Ar *H*), 7.78 (d $J_{\mathrm{HH}} = 8$ Hz, of d $J_{\mathrm{HH}} = 7$ Hz, 2 H, Ar *H*), 7.66 (d $J_{\mathrm{HH}} = 8.5$ Hz, of d $J_{\mathrm{HH}} = 5.5$ Hz, 2 H, Ar *H*), 1.97 (s, 6 H, C*H*$_3$CN), 1.61 (s, 3 H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (CD$_3$CN, 125 MHz): δ 157.0, 154.4, 142.2, 140.6, 138.6, 131.7, 130.5, 129.7, 124.1 (aryl carbons), 126.2 (CH$_3$*C*N), 1.8 (*C*H$_3$CN), −3.9 (Si*C*H$_3$). ^{19}F NMR (CD$_3$CN, 376.5 MHz): δ −79.7 (s). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, 99 MHz): δ 63.1 (d, $^{1}J_{\mathrm{RhSi}} = 20.3$ Hz). Anal. Calcd for $C_{33}H_{29}N_2O_6S_2F_6SiRh$: C, 39.37; H, 2.94; N, 8.50, S, 7.78. Found: C, 39.42; H, 2.58; N, 8.31, S, 7.67. IR (cm^{-1}): ν(CN) 2332, 2304.

(NSiN)Rh(CH$_2$Ph)$_2$ (12). To a solid mixture of **10** (0.250 g, 0.264 mmol) and Mg(CH$_2$Ph)$_2$(THF)$_2$ (0.143 g, 0.550 mmol) was added 30 mL of C$_6$H$_6$ at room temperature. After 18 h of stirring, the reaction mixture was taken to dryness under reduced pressure. The remaining brownish yellow residue was dissolved in 20 mL of THF and filtered through Celite. Recrystallization from a 1/1 mixture of THF:diethyl ether (6 mL in total) at −30 °C produced a yellow powder in 66% yield (0.203 g, 0.348 mmol). ^{1}H NMR (THF-*d*$_8$, 500 MHz): δ 8.47 (d $J_{\mathrm{HH}} = 4.5$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 2 H, Ar *H*), 8.07 (d $J_{\mathrm{HH}} = 4.5$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 2 H, Ar *H*), 7.99 (d $J_{\mathrm{HH}} = 8.5$ Hz, of d $J_{\mathrm{HH}} = 1.5$ Hz, 2 H, Ar *H*), 7.64 (d $J_{\mathrm{HH}} = 8$ Hz, of d $J_{\mathrm{HH}} = 1$ Hz, 2 H, Ar *H*), 7.44 (d $J_{\mathrm{HH}} = 8$ Hz, of d $J_{\mathrm{HH}} = 7$ Hz, 2 H, Ar *H*), 7.06 (d $J_{\mathrm{HH}} = 7.5$ Hz, of d $J_{\mathrm{HH}} = 5$ Hz, 2 H, Ar *H*), 6.63 (m, 6 H, Ar′ *H*), 6.42 (m, 4 H, Ar′ *H*), 2.47 (d $J_{\mathrm{HH}} = 9$ Hz, of d $J_{\mathrm{RhH}} = 3$ Hz, 2 H, C*H*$_2$Ar′), 2.11 (d $J_{\mathrm{HH}} = 9$ Hz, of d $J_{\mathrm{RhH}} = 1$ Hz, 2 H, C*H*$_2$Ar′), 1.11 (s, 3 H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (THF-*d*$_8$, 125 MHz): δ 153.5, 152.7, 152.6, 152.3, 147.8, 136.5, 134.8, 129.5, 129.1, 128.8, 127.9, 127.5, 127.4, 122.0, 121.2 (aryl carbons), 23.3 (d, $J_{\mathrm{RhC}} = 12.5$ Hz, Rh*C*H$_2$), −5.5 (d, $J_{\mathrm{RhC}} = 3.8$ Hz, Si*C*H$_3$). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, 99 MHz): δ 43.7 (d, $J_{\mathrm{RhSi}} = 60.3$ Hz). Anal. Calcd for $C_{33}H_{29}N_2SiRh$: C, 67.80; H, 5.00; N, 4.79. Found: C, 67.84; H, 5.08; N, 4.49.

[(NSiN)Rh(CH$_2$Ph)(CH$_3$CN)][PF$_6$] (13). To a 5 mL CH$_3$CN solution of **8** (0.150 g, 0.273 mmol) was added a 5 mL CH$_3$CN solution of Ph$_3$CPF$_6$ (0.112 g, 0.288 mmol). The reaction mixture was stirred at room temperature for 24 h to produce a milky yellow solution. The resulting mixture was filtered through Celite, and the yellow precipitate was extracted with 2 × 10 mL of CH$_3$CN. The clear yellow filtrate was dried under vacuum. Recrystallization by vapor diffusion of diethyl ether into a concentrated THF solution (3 mL) of the product produced a yellow crystalline solid in 69% yield (0.128 g, 0.188 mmol). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 9.23

(d J_{HH} = 5.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 8.38 (d J_{HH} = 5.5 Hz, of t J_{HH} = 1.0 Hz, 1 H, Ar *H*), 8.37 (m, 1 H, Ar *H*), 8.27 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 8.22 (d J_{HH} = 6.8 Hz, of d J_{HH} = 1.2 Hz, 1 H, Ar *H*), 8.19 (d J_{HH} = 6.8 Hz, of d J_{HH} = 1.2 Hz, 1 H, Ar *H*), 8.14 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 7.87 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 7.79 (d J_{HH} = 8.2 Hz, of d J_{HH} = 1.2 Hz, 1 H, Ar *H*), 7.64 (m, 2 H, Ar *H*), 7.53 (d J_{HH} = 8.2 Hz, of d J_{HH} = 4.8 Hz, 1 H, Ar *H*), 7.27 (d J_{HH} = 8.2 Hz, of d J_{HH} = 5.2 Hz, 1 H, Ar *H*), 7.06 (m, 3 H, Ar *H*), 6.72 (m, 2 H, Ar *H*), 3.02 (d $^2J_{RhH}$ = 2.5 Hz, of d $^2J_{HH'}$ = 8.5 Hz, 1 H, RhCH_2), 2.20 (s, 3 H, CH_3CN), 2.14 (d $^2J_{RhH}$ = 1.5 Hz, of d $^2J_{HH'}$ = 8.5 Hz, 1 H, RhCH_2), 1.34 (d, $^3J_{RhH}$ = 0.5 Hz, 3 H, SiCH_3). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 125 MHz): δ 153.4 (d, $^2J_{RhC}$ = 2.5 Hz), 152.8, 152.7, 152.5, 152.0, 145.0, 142.5, 142.4, 142.3, 139.1, 138.5, 136.0, 135.9, 130.1, 129.8, 129.4, 129.0, 128.5, 128.1, 127.9, 124.2, 122.7, 122.2 (aryl carbons), 128.9 (d, $^2J_{RhC}$ = 1.8 Hz, $\mathrm{CH_3}$*C*N), 20.0 (d, $^1J_{RhC}$ = 20.4 Hz, Rh$C\mathrm{H_2}$), 4.18 (s, $C\mathrm{H_3}$CN), −4.01 (d, $^3J_{RhC}$ = 2.4 Hz, Si$C\mathrm{H_3}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 376.5 MHz): δ 73.4 (d, $^1J_{FP}$ = 43.3 Hz). ^{29}Si{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 99 MHz): δ 57.3 (d, J_{SiRh} = 40 Hz). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 162 MHz): δ −145.1 (septet, $^1J_{PF}$ = 711 Hz). Anal. Calcd for $\mathrm{C_{28}H_{25}N_3SiPRhF_6}$: C, 49.49; H, 3.71; N, 6.18. Found: C, 49.30; H, 3.58; N, 5.99.

(NSiN)Rh(COD) (14). A 5 mL $\mathrm{C_6H_6}$ solution of **1** (0.163 g, 0.542 mmol) was added dropwise to a 8 mL $\mathrm{C_6H_6}$ solution of (COD)Rh(η^3-$\mathrm{CH_2Ph}$) (0.172 g, 0.569 mmol) at ambient temperature. The reaction mixture was stirred for 4 h, when it was filtered through Celite. The dark brown filtrate was reduced to dryness under vacuum. The resulting dark brown solid was washed with pentane (2 × 5 mL) and dried in vacuo. Product **16** was obtained in 92% yield (0.254 g, 0.499 mmol). ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz): δ 8.99 (d J_{HH} = 4.5 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar *H*), 7.99 (d J_{HH} = 6.5 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar *H*), 7.27 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar *H*), 7.12 (d J_{HH} = 8.0 Hz, of d J_{HH} = 6.5 Hz, 2 H, Ar *H*), 7.06 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar *H*), 6.59 (d J_{HH} = 8.0 Hz, of d J_{HH} = 4.5 Hz, 2 H, Ar *H*), 5.25 (br s, 2 H, *H*C═C*H*), 3.56 (br s, 2 H, *H*C═C*H*), 2.46 (m, 4 H, CH_2 of COD), 2.34 (m, 2 H, CH_2 of COD), 2.27 (m, 2 H, CH_2 of COD), 1.05 (s, 3 H, SiCH_3). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz): δ 155.2 (d, $^2J_{RhC}$ = 2.5 Hz), 152.3, 150.3, 135.7, 134.5, 129.0, 128.5, 127.4, 126.9, 121.0 (aryl carbons), 106.3 (d, $^2J_{RhC}$ = 3.8 Hz, *C*═C of COD), 46.1 (d, $^2J_{RhC}$ = 16.8 Hz, C═*C* of COD), 36.7, 28.9 (s, $C\mathrm{H_2}$ of COD), −6.5 (d, $^3J_{RhC}$ = 3.2 Hz, Si$C\mathrm{H_3}$). ^{29}Si{^{1}H} NMR ($\mathrm{C_6D_6}$, 99 MHz): δ 35.2 (d, $^1J_{SiRh}$ = 33 Hz). Anal. Calcd for $\mathrm{C_{27}H_{27}N_2SiRh}$: C, 63.52; H, 5.33; N, 5.49. Found: C, 63.32; H, 5.40; N, 5.67.

(NSiN)Rh(H)(SiPh$_3$) (15). Compound **15** was generated in situ by combining **14** (9 mg, 0.0176 mmol) and $\mathrm{Ph_3SiH}$ (5 mg, 0.0192 mmol) in 0.5 mL of $\mathrm{C_6D_6}$. The reaction mixture immediately turned from dark brown to brownish yellow. Complex **15** was observed as an intermediate in the formation of **16**. ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz): δ 8.42 (d, J_{HH} = 4.5 Hz, 2 H, Ar *H*), 7.76 (br s, 6 H, Ar *H*), 7.70 (br s, 2 H, Ar *H*), 7.20 (d, J_{HH} = 2.5 Hz, 2 H, Ar *H*), 7.11 (m, 9 H, Ar *H*), 7.03 (m, 4 H, Ar *H*), 6.45 (d J_{HH} = 7.5 Hz, of d J_{HH} = 4.5 Hz, 2 H, Ar *H*), 5.57 (s, 4 H, CH_2═CH_2 of free COD), 2.20 (s, 8 H, CH_2 of free COD), 1.00 (d, J_{HH} = 1.0 Hz, 3 H, SiCH_3), −13.2 (d, J_{RhH} = 28 Hz, 1 H, Rh*H*). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz): δ 152.4, 149.6, 148.5, 137.4, 136.2, 136.1, 134.3, 130.3, 129.3, 128.8, 127.6, 127.3, 127.0, 120.8 (aryl carbons), 28.3 (s, $C\mathrm{H_2}$ of free COD), 1.40 (d, $^3J_{RhC}$ = 7.5 Hz, SiCH$_3$). ^{29}Si{^{1}H} NMR ($\mathrm{C_6D_6}$, 99 MHz): δ 36.6 (d, $^1J_{SiRh}$ = 55 Hz, *Si*CH$_3$), 18.1 (d, $^1J_{SiRh}$ = 55 Hz, *Si*Ph$_3$).

(NSiN)Rh(η^1-C$_8$H$_{13}$)(SiPh$_3$) (16). After a reaction mixture containing **15** and 1,5-cyclooctadiene in $\mathrm{C_6D_6}$ was left at room temperature for 1 day, the solution became dark red. ^{1}H NMR spectroscopy reveals **16** to be the major (>95%) product in solution. ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz): δ 8.55 (d J_{HH} = 5.0 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar *H*), 7.61 (d J_{HH} = 7.5 Hz, of d J_{HH} = 2.0 Hz, 10 H, Ar *H*), 7.46 (d, J_{HH} = 6.0 Hz, 12 H, Ar *H*), 7.13 (m, 2 H, Ar *H*), 6.94 (m, 15 H, Ar *H*), 6.85 (t, J_{HH} = 3.0 Hz, 2 H, Ar *H*), 6.73 (d, J_{HH} = 7.5 Hz, 2 H, Ar *H*), 6.37 (d J_{HH} = 8.0 Hz, of d J_{HH} = 5.0 Hz, 2 H, Ar *H*), 5.83 (m, 1 H, C*H*═CH of COD), 5.53 (m, 1 H, CH═C*H* of COD), 2.69 (m, 1 H, C*H*H of COD), 2.21 (m, 1 H, C*H*H of COD), 2.16 (m, 1 H, C*H*H of COD), 2.08 (m, 1 H, C*H*H of COD), 1.58 (m, 1 H, C*H*H of COD), 1.51 (m, 1 H, C*H*H of COD), 1.28 (s, 3 H, SiCH_3), 1.26−1.19 (m, 3 H, C*H*H of COD), 0.84 (m, 1 H, C*H*H of COD), 0.21 (m, 1 H, C*H*H of COD). ^{13}C-{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz): δ 150.7, 149.8, 149.6, 144.5, 137.1, 136.8, 136.4 (d, J_{RhC} = 2.5 Hz), 136.2, 133.8, 128.6, 128.5, 126.9, 126.8, 126.6, 120.9 (aryl carbons), 34.4, 29.5, 27.0, 26.1 (d, $^1J_{RhC}$ = 84 Hz), 22.7, 14.2, 1.02 (d, $^3J_{RhC}$ = 6.2 Hz, SiCH$_3$). ^{29}Si{^{1}H} NMR ($\mathrm{C_6D_6}$, 99 MHz): δ 35.5 (d, $^1J_{SiRh}$ = 65 Hz, *Si*CH$_3$), 11.7 (d, $^1J_{SiRh}$ = 45 Hz, *Si*Ph$_3$).

(NSiN)Rh(η^1-C$_8$H$_{13}$)[(Si(OSiMe$_3$)$_3$)] (17). Compound **17** was generated from **14** (0.100 g, 0.196 mmol) and HSi(OSiMe$_3$)$_3$ (0.060 g, 0.202 mmol) in 0.5 mL of $\mathrm{C_6D_6}$. The dark red reaction mixture yielded product **17** within 15 min at room temperature. ^{1}H NMR spectroscopy shows **17** to be the major (>95%) product in solution. The reaction solution was vacuum-dried, leaving a dark yellow solid, which was washed with 2 × 5 mL of hexanes. The analytically pure compound was obtained in 42% yield (0.066 g, 0.082 mmol). ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz): δ 9.31 (d J_{HH} = 5.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 8.48 (d J_{HH} = 5.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 8.02 (d J_{HH} = 6.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 7.89 (d J_{HH} = 6.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 7.31 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar *H*), 7.17 (m, 1 H, Ar *H*), 7.03 (m, 4 H, Ar *H*), 6.67 (d J_{HH} = 8.0 Hz, of d J_{HH} = 5.0 Hz, 1 H, Ar *H*), 6.47 (d J_{HH} = 8.0 Hz, of d J_{HH} = 5.0 Hz, 1 H, Ar *H*), 5.61 (m, 2 H, C*H*═C*H* of COD), 2.89 (m, 1 H, C*H*H of COD), 2.36−2.06 (m, 5 H, C*H*H of COD), 1.72 (m, 1 H, C*H*H of COD), 1.56 (m, 1 H, C*H*H of COD), 1.46 (d, J_{HH} = 1.5 Hz, 3 H, SiCH_3), 1.34 (m, 2 H, C*H*H of COD), 0.18 (s, 27 H, OSiCH_3), −0.14 (m, 1 H, C*H*H of COD). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz): δ 153.5, 152.8, 151.9, 151.6, 151.0, 150.1, 136.8, 136.4, 134.8, 134.7, 132.7 (*C*═C of COD), 128.8, 128.6, 128.53 (C═*C* of COD), 128.50, 127.4, 127.2, 127.0, 120.6, 120.3 (aryl carbons), 38.7, 28.7 (d, J_{RhC} = 1.0 Hz), 28.5 (d, J_{RhC} = 44 Hz), 27.6 (d, J_{RhC} = 20 Hz), 24.6 (d, J_{RhC} = 1.2 Hz), 3.01 (s, OSiCH$_3$), 2.86 (d, J_{RhC} = 7.5 Hz, SiCH$_3$). ^{29}Si{^{1}H} NMR ($\mathrm{C_6D_6}$, 99 MHz): δ 36.7 (d, $^1J_{SiRh}$ = 69 Hz, *Si*CH$_3$), −0.32 (d, $^1J_{SiRh}$ = 86 Hz, *Si*(OSiCH$_3$)$_3$), −0.66 (s, Si(O*Si*CH$_3$)$_3$). Anal. Calcd for $\mathrm{C_{36}H_{55}N_2Si_5O_3Rh}$: C, 53.45; H, 6.81; N, 3.47. Found: C, 53.08; H, 6.63; N, 3.85.

(NSiN)Rh(dppe) (18). To a stirred solution of **14** (0.100 g, 0.196 mmol) in 10 mL of benzene was added 1,2-bis(diphenylphosphino)-ethane (0.081 g, 0.203 mmol) in 5 mL of benzene at ambient temperature. After 12 h, the reaction mixture was filtered through Celite, and the light brown filtrate was taken to dryness under vacuum. The yellowish brown residue was washed with 5 mL of pentane and vacuum dried, giving the product in 89% yield (0.141 g, 0.174 mmol). ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz): δ 8.97 (d, J_{HH} = 4.5 Hz, 2 H, Ar *H*), 8.01 (t, J_{HH} = 7.0 Hz, 4 H, Ar *H*), 7.76 (d J_{HH} = 7.0 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar *H*), 7.67 (t, J_{HH} = 9.0 Hz, 4 H, Ar *H*), 7.46 (d J_{HH} = 8.7 Hz, of d J_{HH} = 1.8 Hz, 2 H, Ar *H*), 7.23 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.0 Hz, 2 H, Ar *H*), 7.08 (m, 8 H, P*Ph*$_2$), 6.93 (t, J_{HH} = 8.0 Hz, 2 H, Ar *H*), 6.85 (t, J_{HH} = 7.0 Hz, 4 H, Ar *H*), 6.50 (d J_{HH} = 8.5 Hz, of d J_{HH} = 4.5 Hz, 2 H, Ar *H*), 1.98 (m, 2 H, PCH_2), 1.85 (m, 2 H, PCH_2), 0.83 (d, J_{HP} = 2.0 Hz, 3 H, SiCH_3). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125 MHz): δ 154.9, 154.0 (d, J_{RhC} = 1.8 Hz), 152.6 (d, J_{RhC} = 8.5 Hz), 138.5 (d, J_{RhC} = 13.8 Hz), 138.2 (d, J_{RhC} = 53 Hz), 137.8, 136.2, 136.1, 134.2 (d, J_{RhC} = 13.8 Hz), 134.0 (d, J_{RhC} = 11.2 Hz), 129.0, 127.3 (d, J_{RhC} = 8.8 Hz), 126.6 (d, J_{RhC} = 43.8 Hz), 119.8 (aryl carbons), 33.2 (m, P$C\mathrm{H_2}$-CH$_2$P′), 27.8 (m, PCH$_2$$C\mathrm{H_2}$P′), 2.20 (Si$C\mathrm{H_3}$). ^{29}Si{^{1}H} NMR ($\mathrm{C_6D_6}$, 79.5 MHz): δ 22.6 (d $^1J_{SiRh}$ = 145 Hz, of d $^2J_{SiP}$ = 38 Hz, of d

$^2J_{SiP'}$ = 26 Hz, *Si*CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202.5 MHz): δ 70.6 (d $^1J_{PRh}$ = 190 Hz, of d $^2J_{PP'}$ = 15 Hz, *P*CH$_2$CH$_2$P′), 43.3 (d $^1J_{P'Rh}$ = 125 Hz, of d $^2J_{P'P}$ = 15 Hz, PCH$_2$CH$_2$*P*′). Anal. Calcd for C$_{45}$H$_{39}$N$_2$SiP$_2$Rh: C, 67.50; H, 4.91; N, 3.50. Found: C, 67.72; H, 4.82; N, 3.54.

X-ray Crystallography. General Considerations. The single-crystal X-ray analyses of compounds **3**, **8**, **11**, and **12** were carried out at the UC Berkeley CHEXRAY crystallographic facility.[25] All measurements were made on a Bruker SMART[26] CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Crystals were mounted on capillaries with Paratone-N hydrocarbon oil and held in a low-temperature N$_2$ stream during data collection. Frames were collected using ω scans at 0.3° increments, using exposures of 10 s (**8**, **11**, **12**) or 15 s (**3**). Data were integrated by the program SAINT[27] and corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP.[28] Empirical absorption corrections based on comparison of redundant and equivalent reflections were applied using SADABS.[29] Structures were solved by direct methods[30] and expanded using Fourier techniques.[31] Due to a rapid decrease in the intensity of reflections with increasing (sin θ)/λ, the structure of **3** was refined to an acceptable *R* value with all carbon atoms set to refine isotropically and all other non-hydrogen atoms were refined with anisotropic thermal parameters. In addition, the Rh−*H* atom of **3** was located in the difference Fourier map and its positional parameters were refined. For **8**, **11**, and **12**, all non-hydrogen atoms were refined anisotropically. Unless stated otherwise, all hydrogen atoms were placed in calculated positions and not refined. All calculations were performed using the teXsan crystallographic software package.[32]

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Supporting Information Available: CIF files giving crystallographic data for **3**, **8**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] http://xray.cchem.berkeley.edu.

[26] SMART: Area-Detector Software Package; Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.

[27] SAINT: SAX Area-Detector Software Package; Siemens Industrial Automation, Inc., Madison, WI 1995.

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