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N-Heterocyclic Silyl Pincer Ligands

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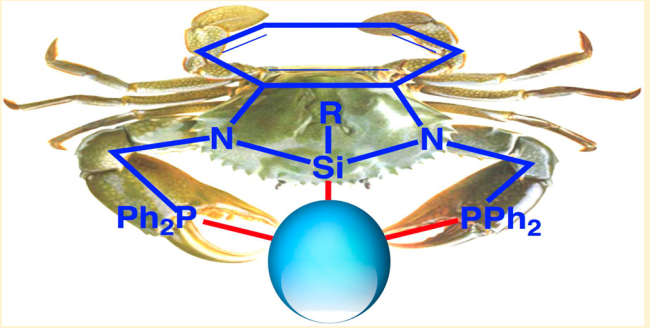
Supporting Information

ABSTRACT: The reaction of 1,2-$C_6H_4(NHCH_2PPh_2)_2$ with chlorosilanes Cl_2SiHR (R = Ph, Cl) affords the benzosiladiazoles $RHSi(NCH_2PPh_2)_2C_6H_4$ (R = Ph, **1**; Cl, **2**). The phenyl derivative **1** undergoes chelate-assisted Si−H activation with $[RuPhCl(CO)(PPh_3)_2]$ and $[RhCl(PPh_3)_3]$ to afford the structurally characterized silyl pincer complexes $[RuCl(CO)(PPh_3)\{\kappa^3\text{-}P,Si,P'\text{-}SiPh(NCH_2PPh_2)_2C_6H_4\}]$ (**3**) and $[RhHCl(PPh_3)\{\kappa^3\text{-}P,Si,P'\text{-}SiPh(NCH_2PPh_2)_2C_6H_4\}]$ (**4**). The reaction of **4** with $[Et_2NH_2][S_2CNEt_2]$ affords the complex $[RhH(S_2CNEt_2)\{\kappa^3\text{-}P,Si,P'\text{-}SiPh(NCH_2PPh_2)_2C_6H_4\}]$ (**5**), structural data for which demonstrate a pronounced *trans* influence for the σ-silyl donor.

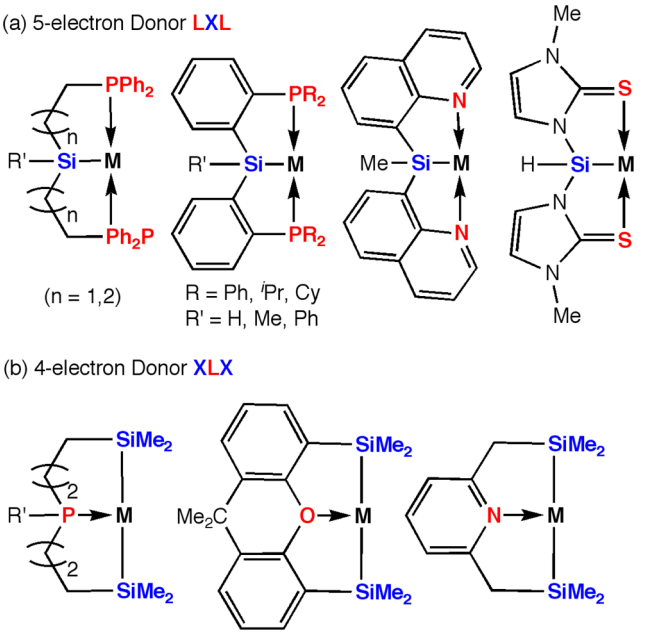


INTRODUCTION

Pincer ligands have enjoyed intense study in recent times[1] due in part to the stability that the meridional geometry confers on their complexes and because of the broad scope for modular variations in the electronic and steric features of both the axial and equatorial donors. The vast majority of pincer scaffolds involve classical phosphorus, nitrogen, oxygen, and carbon donor atoms, with the inclusion of N-heterocyclic carbene donors attracting increasing attention.[2] Recently, the possibility of incorporating highly electropositive boron as the equatorial donor has begun to be explored,[3−5] thereby drawing attention to the question of incorporating other less conventional donor atoms. Silicon as a donor is of particular interest in that electropositive σ-silyl ligands are able to stabilize higher oxidation states and through their strong *trans* influence help to labilize *trans* ligands, both features of potential utility in catalysis.

Stobart's investigations of phosphine/silyl-based pincer ligands with flexible alkyl backbones[6] predated the current focus on pincer ligands, and in the interim other more rigid silicon pincer frameworks have been developed featuring NSiN,[7,8] PSiP,[9,10] and SSiS[11] **LXL** (five-electron, Chart 1a) donor sets.[12] Alternatively, four-electron **XLX** pincer ligands have been described with SiPSi,[6] SiOSi,[13] and SiNSi[14] donor triads in which the (two) silicon donors occupy axial positions (Chart 1b). The majority of these ligands share a predilection toward adopting a facial coordination mode rather than the meridional geometry usually associated with pincer ligands, this being a corrollary of including sp^3-tetrahedral silicon within the metallabicycles. Indeed, Tilley has exploited this feature with the d^8-square planar complex $[PtCl\{\kappa^3\text{-}N,Si,N'\text{-}SiMe(quin\text{-}8)_2\}]$ (quin-8 = 9-quinon-8-yl), which activates dihydrogen, thereby allowing the strained *mer*-platinabicycle to relax to a facial geometry in the d^6-octahedral complex $[PtH_2Cl\{\kappa^3\text{-}N,Si,N'\text{-}SiMe(quin\text{-}8)_2\}]$.[7] We have therefore turned our attention to the design of silicon-based pincer ligands for which the meridional geometry might be enforced by inclusion of a suitably rigid backbone. To this end, we report herein the synthesis of the first examples of N-heterocyclic σ-silyl pincer ligands that bear a PSiP-**LXL** donor triad.

Chart 1. Representative LXL[6−12] and XLX[6,13,14] Silyl Pincer Ligands



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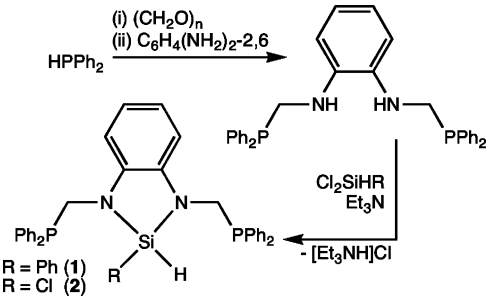
RESULTS AND DISCUSSION

N-Heterocyclic σ-boryl pincer ligand complexes of iridium, rhodium, and ruthenium have been described previously,[3b,4] resulting from chelate-assisted B−H activation of the diazaboroles $HB(NCH_2PR_2)_2C_6H_4$-1,2 (R = Ph, Cy). Setting the stage for a similar strategy, the reactions of $C_6H_4(NHCH_2PPh_2)_2$-1,2[4] with chlorosilanes $RHSiCl_2$ (R = Ph, Cl) in the presence of triethylamine were explored and found to readily afford the 2,1,3-siladiazoles $HSiR(NCH_2PPh_2)_2C_6H_4$ (R = Ph, **1**; Cl, **2**, Scheme 1). Among

Scheme 1. Synthesis of Silyl Pincer Pro-ligands



the spectroscopic data for **1**, the most noteworthy are (i) a strong absorption in the infrared spectrum (KBr: 2176 cm^{-1}) corresponding primarily to the ν_{SiH} mode; (ii) a silicon hydride resonance at δ_H = 5.52 ($^4J_{PH}$ = 4, $^1J_{SiH}$ = 245 Hz) in the ^1H NMR spectrum; and (iii) a broadened resonance at δ_{Si} = −12.4 in the $^{29}Si\{^1H\}$ NMR spectrum. Similar data were obtained for **2**. The characterization of **1** included a crystallographic study, the results of which are summarized in Figure 1, confirming the

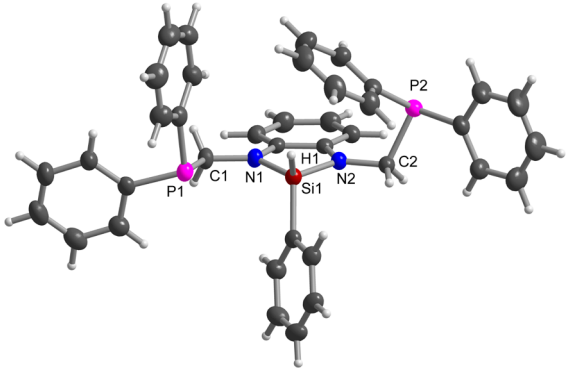
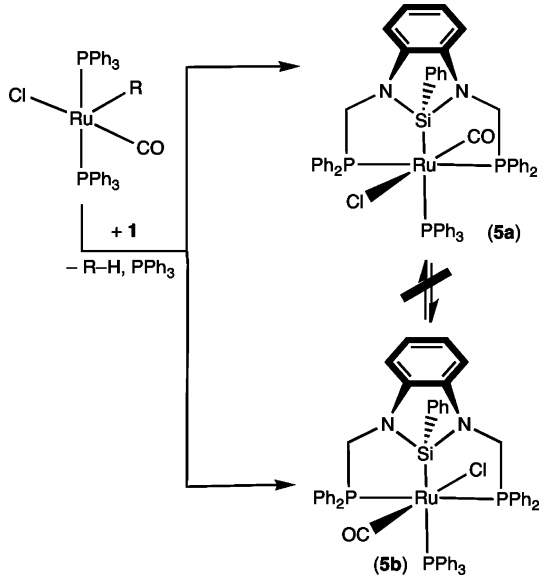


Figure 1. Molecular structure of **1** (50% displacement ellipsoids). Selected bond distances (Å) and angles (deg): N1−Si1 1.7311(13), N2−Si1 1.7420(12), Si1−H1 1.460(17), Si1−N1−C1 129.09(10), Si1−N2−C2 126.26(10), N2−Si1−N1 91.61(6), N2−Si1−H1 115.9(7), N1−Si1−H1 116.6(7), Σ°(N1) 359.6, Σ°(N2) 259.9.

formation of the desired pro-ligand. Both the crystal structure and the computationally optimized (DFT-B3LYP-6-31G*) geometry of **1** involve an essentially coplanar arrangement of the $C_6H_4(NC)_2Si$ unit (mean Σ°(N) = 359.8°), presaging a geometrically induced reluctance of σ-silyl complexes derived from **1** to adopt facial coordination geometries.

We have previously employed the complexes $[RuRCl(CO)(PPh_3)_2]$ (R = CH=CHPh, **3**;[15] Ph, **4**[16]) for the synthesis of N-heterocyclic σ-boryl and borane complexes of ruthenium via chelate-assisted B−H activation[3] while **4** has been shown to react with conventional silanes, $HSiR_3$, to afford coordinatively unsaturated σ-silyl complexes $[Ru(SiR_3)Cl(CO)(PPh_3)_2]$.[17] Accordingly, the reactions of these substrates with **1** were investigated. In contrast to simple silanes, which require heating (benzene reflux), **1** reacted with either **3** or **4** at room temperature. Given the steric clutter about the silicon center in **1**, this increase in reactivity may be attributed to rapid initial coordination of a phosphine arm prior to, and assisting, Si−H activation. Over a period of 24 h, the starting complexes and **1** were consumed accompanied by the liberation of one equivalent of triphenylphoshine and the corresponding hydrocarbon (C_6H_6, $PhCH{=}CH_2$). The reaction did not however provide a single product, but rather a mixture of two noninterconverting diastereomers, **5a** and **5b**, the ratio of which varied depending on the precursor (Scheme 2), allowing

Scheme 2. Synthesis of Ruthenium Silyl Pincer Complexes (R = Ph, CH=CHPh)



us to conclude that the isomers are not in equilibrium. The difference in ratio resulting from different precursors (**5a**:**5b** = 1:3.2 (R = Ph), cf. 1:7.62 R = CH=CHPh) presumably reflects the relative rates of benzene compared with styrene elimination from a fluxional intermediate. These isomers, each of which involve a *mer*-RuP_3 geometry on the basis of $^{31}P\{^1H\}$ and ^1H NMR data, arise from the various possible arrangements of the three unidentate ligands Cl, CO, and PPh_3 and their relationship (*syn*, *anti*) to the silicon phenyl substituent (six isomers are conceivable). Two of these, **5a** and **5b**, are related by exchange of chloride and carbonyl ligands and cocrystallized.[18]

A crystallographic analysis on one such crystal was successfully modeled by a $\mathbf{5a}_{0.7}\cdot\mathbf{5b}_{0.3}$ composition, with the molecular geometry of the major isomer **5a** being depicted in Figure 2.[19] The crystal structure confirms that the pincer ligand does indeed adopt the meridional geometry, although this is accompanied by some distortions from ideality. These include slightly pyramidalized nitrogen centers (mean Σ°(N) = 347°), a splayed Ru1−Si1−C31 linkage (128.27(8)°), and contraction from linearity of the *trans* bisaxial P1−Ru1−P2 arrangement (152.49(2)°). These Ru−P bonds are significantly (ca. 170 esd) shorter than that *trans* to the *trans*-influential silyl donor (Ru1−P3 = 2.5007(6) Å). The ruthenium−silicon separation

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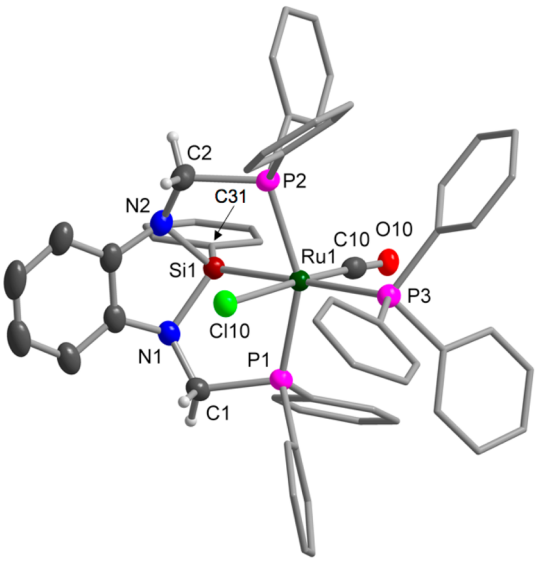


Figure 2. Molecular structure of **5a** in a crystal of $\mathbf{5a}_{0.7}\cdot\mathbf{5b}_{0.3}$ (50% displacement ellipsoids; hydrogen atoms omitted). **5b** is related to **5a** by positional disorder of chloride and carbonyl ligands. Selected bond distances (Å) and angles (deg): Cl10–Ru1 2.475(2), N1–Si1 1.770(2), N2–Si1 1.767(2), P1–Ru1 2.3573(6), P2–Ru1 2.3998(6), P3–Ru1 2.5007(6), Ru1–Si1 2.3723(6), Si1–N2–C2 119.27(16), Si1–N2–C8 109.54(17), P2–Ru1–P1 152.49(2), P2–Ru1–Si1 77.44(2), P1–Ru1–Si1 77.98(2), Ru1–Si1–C31 128.27(8), $\sum^{\circ}$(N1) = 345.1, $\sum^{\circ}$(N2) = 348.4.

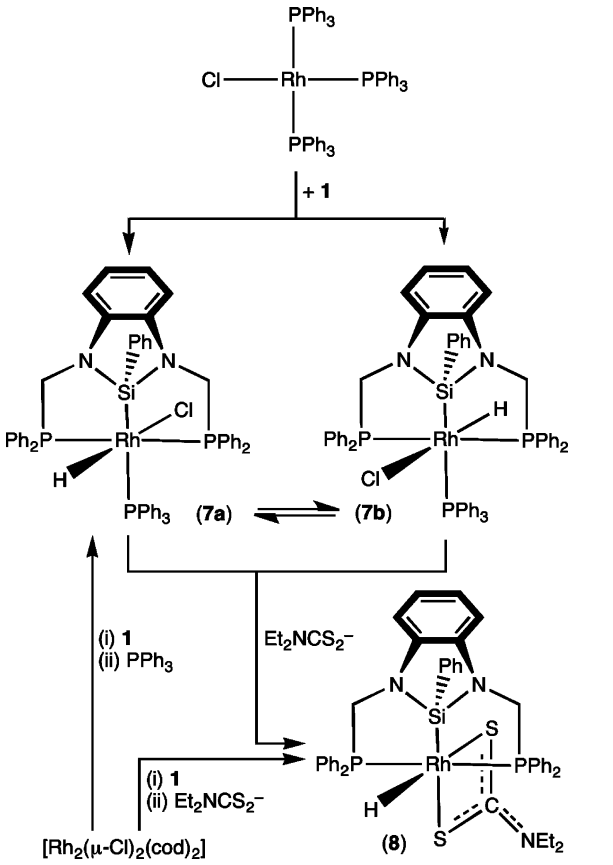
(2.3723(6) Å) is somewhat short when compared with data for nonchelated octahedral ruthenium silyl complexes (2.41–2.48 Å),[20] although similarly shortened Ru–Si bonds are observed when electronegative silicon substituents (Cl, OEt) are involved,[21] a feature attributed, on the basis of *ab initio* calculations, to the importance of M–Si π-interactions.[22]

The complex $[RhCl(PPh_3)_3]$ (**6**) is an effective alkene hydrosilyation catalyst, with the first step in such a cycle being the oxidative addition of the Si–H bond to rhodium(I).[23] It therefore seemed that **6** would provide a suitable entry point into rhodium complexes based on **1**. A smooth reaction ensues between **1** and **6** at room temperature to afford two isomers of the complex $[RhHCl(PPh_3)\{\kappa^3\text{-}P,Si,P'\text{-}SiPh(NCH_2PPh_2)_2C_6H_4\}]$ (**7a**/**7b**) in addition to two equivalents of liberated PPh_3, the ^{31}P resonance for which is broadened, indicating exchange with the coordinated phosphine on the ^{31}P NMR time scale (Scheme 3).

Crystals of both **7a** and **7b** were obtained and crystallographically analyzed (see Supporting Information). The topologies of the molecular structures of **7a** and **7b** are very similar to that of **5a** with further indications that although the meridional geometry is enforced, this is accompanied by some strain, reflected in the modest pyramidalization at nitrogen and bending of the phosphine chelate arms toward the sterically unassuming hydride ligand. The Rh1–P3 (PPh_3) bond length of 2.5047(10) Å (cf. 2.3572(11), 2.3276(11) Å for the axial donors) is somewhat long for octahedral rhodium, indicating perhaps, as with **5a**/**5b**, the operation of a significant *trans* influence by the σ-silyl donor, implicitly manifest as a *trans* effect with respect to phosphine dissociation.

The two isomers are in dynamic equilibrium with very little difference in relative energy, as indicated by ^1H NMR integration of the hydride signals ($CDCl_3$: K_{298} = 1.5; C_6D_6: K_{298} = 2.7). The two isomers most likely interconvert via

Scheme 3. Synthesis of Rhodium Silyl Pincer Complexes



dissociation/recoordination of the phosphine ligand via the coordinatively unsaturated species "$RhHCl\{SiPh(NCH_2PPh_2)_2C_6H_4\}$", and the magnitude of the $^2J_{PH}$ couplings[15] suggests that both isomers involve *cis* coordination of the hydride and PPh_3 ligands (Scheme 3). It should however be noted that this alone does not account for the *syn*/*anti*-periplanar interchange of the Ph–Si–Rh–H positions, raising the possibility that either reversible Si–H elimination/addition operates or that dissociation of one pincer arm allows access to stereochemically less constrained geometries. For **5a** and **5b**, which do not interconvert, a Si–H elimination/addition sequence is precluded. To obviate problems associated with the separation of **7a**/**7b** from liberated PPh_3, *the same isomeric mixture* was obtained in two steps via the sequential reaction of **1** with half an equivalent of $[Rh_2(\mu\text{-}Cl)_2(\eta^4\text{-}cod)_2]$ (cod = cycloocta-1,5-diene) and one equivalent of PPh_3.

To more definitely assess the *trans* influence of the silyl donor,[7,22,24] the synthesis of a chelate dithiocarbamate derivate $[RhH(S_2CNEt_2)\{SiPh(NCH_2PPh_2)_2C_6H_4\}]$ (**8**) was developed via the reaction of the **7a**/**7b** isomeric mixture with $[Et_2NH_2][S_2CNEt_2]$ or of **1** with $[Rh_2(\mu\text{-}Cl)_2(\eta^4\text{-}cod)_2]$ and $[Et_2NH_2][S_2CNEt_2]$. A single isomer of **8** was formed in spectroscopically quantitative yield in each case, and both synthetic routes presumably proceed via the 16-electron five-coordinate species "$RhHCl\{SiPh(NCH_2PPh_2)_2C_6H_4\}$", wherein the different steric impact of the chloride and hydride ligands most likely accounts for the ultimately observed regiochemistry.

The molecular structure of **8** is depicted in Figure 3, which in addition to reproducing the geometric features observed for the "$M\{SiPh(NCH_2PPh_2)_2C_6H_4\}$" (M = Ru, Rh) units of **5a**/**5b** and **7a** also offers the internally standardized opportunity for

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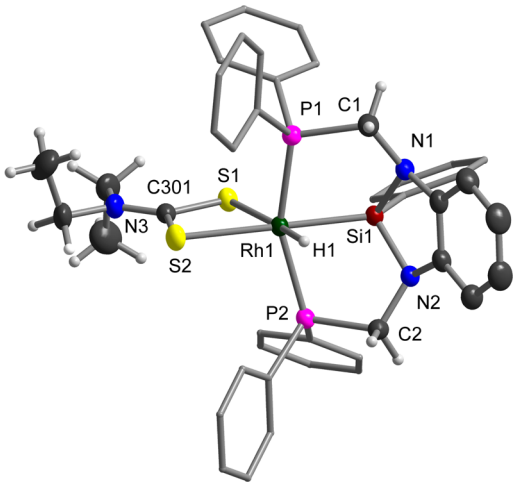

Figure 3. Molecular structure of **8** in a crystal (50% displacement ellipsoids; hydrogen atoms and solvate omitted). Selected bond distances (Å) and angles (deg): N1−Si1 1.7664(13), N2−Si1 1.7658(13), P1−Rh1 2.2885(4), P2−Rh1 2.2991(4), Rh1−S1 2.4387(4), Rh1−S2 2.4940(4), Rh1−Si1 2.2796(4), Rh1−H1 1.532, P2−Rh1−P1 156.077(15), P2−Rh1−Si1 78.678(15), P1−Rh1−Si1 80.574(15), N1−Si1−N2 93.46(6), N1−Si1−Rh1 109.79(5), N2−Si1−Rh1 108.20(5), N1−Si1−C31 107.45(7), N2−Si1−C31 110.40(7), Rh1−Si1−C31 123.41(5), ∑°(N1) = 344.9, ∑°(N2) = 344.3°.

comparing the relative *trans* influences of the hydride and *σ*-silyl donors within the same complex. The Rh1−S2 bond length (2. 2.4940(4) Å) *trans* to silicon is significantly (138 esd) longer than that *trans* to the hydride ligand (Rh1−S1 = 2.4387(4) Å), indicating that the *σ*-silyl donor exerts a remarkably strong *trans* influence, even relative to the hydride ligand.

In conclusion, a straightforward synthetic route to N-heterocyclic silyl pincer pro-ligands has been demonstrated. These pro-ligands readily install the tridentate silyl pincer ligand via facile Si−H bond activation. Although the rigid NHSi framework reinforces the meridional coordination geometry, there are attendant geometric distortions associated with including an sp^3-hybridized silyl group as the equatorial donor group. Furthermore, the ligand appears prone to forming isomeric mixtures when coordinated to octahedral centers bearing disparate ligands. Each of these issues would be obviated in the case of N-heterocyclic *silylene* pincer ligands, a challenge we are currently addressing.

EXPERIMENTAL SECTION

General Considerations. All manipulations of air-sensitive compounds were carried out under a dry and oxygen-free argon atmosphere using standard Schlenk and vacuum line techniques, with dry and degassed solvents. NMR spectra were recorded at 25 °C on Varian Mercury 300 (^{1}H at 300.1 MHz, ^{31}P at 121.5 MHz) and Varian Inova 300 (^{1}H at 299.9 MHz, ^{13}C at 75.42 MHz, ^{31}P at 121.4 MHz, ^{29}Si at 59.6 MHz) spectrometers. The chemical shifts (δ) for ^{1}H and ^{13}C spectra are given in ppm relative to residual signals of the solvent, ^{29}Si relative to an internal $SiMe_4$ reference, and ^{31}P relative to an external H_3PO_4 reference. Low- and high-resolution mass spectra were obtained on a ZAB-SEQ4F spectrometer by positive ion ESI techniques using an acetonitrile matrix by the mass spectrometry service of the Australian National University. Assignments were made relative to M, where M is the molecular cation. Assignments were verified by simulation of isotopic composition both for low- and high-resolution levels. Elemental microanalysis was performed by the microanalytical service of the Australian National University. Data for X-ray crystallography were collected with a Nonius Kappa CCD diffractometer. The compounds $[Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2]$,[15] $[Ru(Ph)Cl(CO)(PPh_3)_2]$,[16] $[RhCl(PPh_3)_3]$,[25] and $[Rh_2(\mu\text{-}Cl)_2(\eta^4\text{-}COD)_2]$[26] were prepared according to published procedures. The salt $[H_2NEt_2][S_2CNEt_2]$ was prepared from diethylamine and carbon disulfide in diethyl ether. Other reagents were used as received from commercial suppliers.

The compound $C_6H_4(NHCH_2PPh_2)_2$-1,2 was prepared via minor modifications of the method described by Yamashita:[4] A stirred suspension of paraformaldehyde (3.90 g, 0.130 mol) in diphenylphosphine (24.2 g, 0.130 mol) was heated to 100 °C until all the paraformaldehyde had dissolved (40 min). The solution was left to cool to 25 °C before being dissolved in dichloromethane (150 mL) and transferred to a solution of *o*-phenylenediamine (7.03 g, 0.065 mol). The resultant solution was covered with aluminum foil and stirred for 2 days. After the solvent was removed *in vacuo*, diethyl ether (100 mL) was added to the crude, yellow solid. Stirring for 5 min afforded a white precipitate, which was isolated by filtration. Yield: 24.15 g (0.048 mol, 74%). NMR (C_6D_6, 25 °C) ^{1}H: δ_H 3.27 (s br, 2 H, NH), 3.51 (d, 4 H, NCH_2, $^2J_{HP}$ = 4), 6.68, 6.93 (dd × 2, 2 H × 2, C_6H_4, ^3JHH = 6, $^4J_{HH}$ = 4 Hz), 7.02−7.04 (m, 12 H, C_6H_5), 7.33−7.39 (m, 8 H, C_6H_4). ^{31}P{^{1}H}: δ_P −17.9 (s). These data were consistent with those previously published.[4]

Synthesis of $PhHSi(NCH_2PPh_2)_2C_6H_4$ (1). Triethylamine (3.00 mL, 21.0 mmol) was added to a stirred solution of $C_6H_4(NHCH_2PPh_2)_2$ (5.00 g, 9.90 mmol) in THF (100 mL). Dichlorophenylsilane (1.50 mL, 10.2 mmol) was added dropwise to the stirred solution. The resultant suspension was stirred for 4 days, then stored at 4 °C for 2 h. The supernatant was isolated by cannula filtration, and volatiles were removed *in vacuo*, leaving a sticky solid. This was extracted with benzene, and the residual precipitate was removed by cannula filtration. The benzene was removed *in vacuo*; then trituration of the solid in diethyl ether (50 mL) yielded a white precipitate, which was isolated by cannula filtration. Yield: 5.31 g (8.72 mmol, 88%). NMR (C_6D_6, 25 °C) ^{1}H: δ_H = 3.85 (dd, 2 H, PCH_aH_bN, $^2J_{PH}$ = 30, $^2J_{HaHb}$ = 14), 3.86 (dd, 2 H, PCH_bH_aN, $^2J_{PH}$ = 37, $^2J_{HaHb}$ = 14), 5.52 (t, 1 H, SiH, $^4J_{PH}$ = 4, $^1J_{HSi}$ = 245 Hz), 6.85−7.53 (m, 29 H, C_6H_5 and C_6H_4). ^{31}P{^{1}H}: δ_P = −22.0. ^{13}C{^{1}H}: δ_C = 45.9 (d, NCH_2, $^1J_{CP}$ = 8), 108.8 [d, $C^{2,5}(C_6H_4)$, $^4J_{CP}$ = 2 Hz), 118.7 [$C^{3,4}(C_6H_4)$], 128.5−138.3 (m, C_6H_5). ^{29}Si{^{1}H}: δ_{Si} = −12.4 (s br). IR (KBr): ν_{SiH} = 2176 cm^{-1}. ESI-MS (positive ion): m/z = 532 [M − Ph]$^+$, 331.4 [M − Ph + CH_2PPh_2]$^+$, 319.4 [M − Ph − NCH_2PPh_2]$^+$, 133.1 [M − Cl − NCH_2PPh_2 − PPh_2]$^+$. Anal. Found: C, 75.20; H, 5.77; N, 4.42. Calcd for $C_{38}H_{34}N_2P_2Si$: C, 74.98; H, 5.63; N, 4.60. NB: The obtention of an analytically pure sample required multiple tedious recrystallizations to remove traces (2−3%) of the corresponding dioxide (δ_P −18.03, C_6D_6). For practical purposes, the crude material is suitable for further use because the solubility of the dioxide differs more markedly from that of the derived complexes and is easily removed during workup. Crystals suitable for X-ray crystallography were obtained by recrystallization from diethyl ether. Crystal data for **1**: $C_{38}H_{34}N_2P_2Si$, M_w = 608.72, T = 200(2) K, triclinic, $P\bar{1}$ (No. 2), a = 10.5915(3) Å, b = 13.0298(3) Å, c = 13.0621(3) Å, α = 71.6251(16)°, β = 78.7715(16)°, γ = 68.7673(14)°, V = 1587.97(7) Å^3, Z = 2, D_{calcd} = 1.273 Mg m^{-3}, μ(Mo Kα) = 0.21 mm^{-1}, colorless prism, 0.45 × 0.18 × 0.14 mm, 48 779 measured reflections with $2\theta_{max}$ = 60.1°, 9282 independent reflections, 9282 absorption corrected data used in F^2 refinement, 524 parameters, 250 restraints, R = 0.044, R_w = 0.109 for 6994 reflections with $I > 2\sigma(I)$. (CCDC 898193).

Synthesis of $HClSi(NCH_2PPh_2)_2C_6H_4$ (2). Triethylamine (3.00 mL, 21.0 mmol) was added to a stirred solution of $C_6H_4(NHCH_2PPh_2)_2$ (5.00 g, 9.90 mmol) in THF (100 mL). Trichlorosilane (1.00 mL, 9.90 mmol) was added dropwise to the stirred solution. The resultant suspension was stirred for 1 h, then stored at 4 °C for 2 h. The supernatant was isolated by cannula filtration, and volatiles were removed *in vacuo*, leaving a sticky solid. Subsequent trituration in diethyl ether (50 mL) yielded a pale yellow precipitate, which was isolated by cannula filtration. Yield: 3.87 g (6.80 mmol, 69%). NMR (C_6D_6, 25 °C) ^{1}H: δ_H = 3.90 (d br, 4 H, NCH_2),

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5.58 (t, 1 H, SiH, $^4J_{PH}$ = 4, $^1J_{HSi}$ = 336), 6.83, 6.95 (dd × 2, 2 H × 2, C_6H_4, $^3J_{HH}$ = 6, $^4J_{HH}$ = 4), 6.97−7.38 (m, 20 H, C_6H_5, Hz). $^{31}P\{^1H\}$: δ_P −22.7. $^{13}C\{^1H\}$: δ_C = 44.8 (d, NCH_2, $^1J_{CP}$ = 9 Hz), 109.8 [d, $C^{2,5}(C_6H_4)$, $^4J_{CP}$), 119.5 [$C^{3,4}(C_6H_4)$], 128.6−138.6 (m, C_6H_5). δ_{Si} = −25.7. IR (KBr): ν_{SiH} = 2246 cm^{-1}. ESI-MS (positive ion): m/z = 532 [M − Ph]$^+$, 319.5 [M − Cl − NCH_2PPh_2]$^+$, 133.1 [M − Cl − NCH_2PPh_2 − PPh_2)]$^+$. Anal. Found: C, 67.44; H, 5.28; N, 5.07. Calcd. for $C_{32}H_{29}ClN_2P_2Si$: C, 67.78; H, 5.15; N, 4.94.

Synthesis of [RuCl(CO)(PPh_3){SiPh(NCH_2PPh_2)$_2C_6H_4$}] (5). [Ru(CH═CHPh)Cl(CO)(PPh_3)$_2$] (0.36 g, 0.46 mmol) and **1** (0.30 g, 0.50 mmol) were dissolved in THF (40 mL). The resultant solution was stirred for 24 h. The solvent was removed *in vacuo*, and the remaining solid was suspended in diethyl ether (30 mL). Ultrasonic trituration of this suspension yielded a yellow precipitate. The reaction flask was stored at 4 °C for 2 h before the solid was isolated by cannula filtration. Yield: 0.37 g (0.36 mmol, 78%). NMR (C_6D_6, 25 °C, major isomer) ^1H: major isomer: δ_H = 4.36 (d, 2 H, PCH_aH_bN, $^2J_{HaHb}$ = 18.1), 4.56 (dt^v, 2 H, PCH_aH_bN, $^2J_{HbHa}$ = 12.0, J_{HP} = 9.0 Hz), minor isomer: δ_H = 4.02 (dt^v, 2 H, PCH_aH_bN, $^2J_{HaHb}$ = 12.0, J_{HP} = 3 Hz), 4.31 (d, 2 H, PCH_aH_bN, $^2J_{HbHa}$ = 12 Hz), both isomers: δ_H = 6.40−7.90 (m, 44 H). $^{31}P\{^1H\}$: major isomer: δ_P = 12.22 (t, 1P, $^2J_{P-P}$ = 17.0 Hz) 52.1 (d, 2P, $^2J_{P-P}$ = 17 Hz), minor isomer: δ_P = 15.17 (t, 1P, $^2J_{P-P}$ = 16.4 Hz), 54.73 (d, 2P, $^2J_{P-P}$ = 17 Hz). $^{29}Si\{^1H\}$ (HMBC): major isomer: δ_{Si} = 103.5 ($^{2,3}J_{PSi}$ = 66 Hz). $^{13}C\{^1H\}$: major isomer: δ_C = 59.0 (t_v, NCH_2PPh_2, J_{C-P} = 17 Hz), 112.9 (s, *o*-phenylene *C*, $^4J_{C-P}$ = 2 Hz), 119.8 (s, *m*-phenylene *C*), 128.8−138.2 (m, phenyl *C*), 203.7 (s, Ru-*C*O). IR (KBr): ν_{CO} = 1937 cm^{-1}. ESI-MS (positive ion): m/z = 1001.5 [M − Cl]$^+$, 736.6 [M − (Cl + PPh_3)]$^+$, 133.1 [M − (Cl, NCH_2PPh_2, PPh_2]$^+$. Accurate Mass: Found 1001.1953 [M − Cl]$^+$. Calcd for $C_{57}H_{48}ClN_2OP_3{}^{102}Ru^{28}Si$ = 1001.1949. Anal. Found: C, 66.23; H, 4.75; N, 2.64. Calcd for $C_{57}H_{48}ClN_2OP_3{}^{102}Ru^{28}Si$ C, 66.18; H, 4.68; N, 2.71. Crystals of **5a**$_{0.7}$·**5b**$_{0.3}$ suitable for X-ray crystallography were obtained by recrystallization from chloroform and ethanol. Crystal data for complex **5a**$_{0.7}$·**5b**$_{0.3}$: $C_{57}H_{48}ClN_2OP_3RuSi$ M_w = 1034.53, T = 200 K, triclinic, $P\bar{1}$ (No. 2), a = 11.6868(2) Å, b = 14.0096(2) Å, c = 15.4974(3) Å, α = 80.3054(12)°, β = 75.3846(8)°, γ = 82.5635(11)°, V = 2410.11(7) Å^3, Z = 2, D_{calcd} = 1.426 Mg m^{-3}, μ(Mo Kα) = 0.55 mm^{-1}, yellow block, 0.25 × 0.17 × 0.10 mm, 30 709 measured reflections with $2\theta_{max}$ = 55.0°, 11 076 independent reflections, 11 076 absorption corrected data used in F^2 refinement, 624 parameters, 3 restraints, R = 0.038, R_w = 0.101 for 11 076 reflections $I > 2\sigma(I)$ (CCDC 898190).

Synthesis of [Rh(H)Cl(PPh_3){SiPh(NCH_2PPh_2)$_2C_6H_4$}] (7). (a) A mixture of [RhCl(PPh_3)$_3$] (0.50 g, 0.54 mmol) and **1** (0.37 g, 0.60 mmol) was dissolved in THF (70 mL). The resultant solution was stirred for 10 min before the solvent was removed *in vacuo*. The remaining solid was suspended in diethyl ether (60 mL) and triturated, yielding a yellow precipitate. The suspension was cooled to −78 °C, and the precipitate was isolated by cannula filtration. Yield: 0.23 g (0.23 mmol, 42%). Ratio of **7a**/**7b** = 1:2.7 in C_6D_6 but 1:1.5 in $CDCl_3$ (^1H NMR integration). (b) A mixture of [$Rh_2(\mu\text{-Cl})_2(\eta^4\text{-1,5-cod})_2$] (0.054 g, 0.11 mmol) and **1** (0.134 g, 0.220 mmol) were dissolved in THF (30 mL). The resultant solution was stirred for 3 h. Triphenylphosphine (0.054 g, 0.21 mmol) was added to the stirred solution. After 1 h of stirring, the solvent was removed *in vacuo*, and the remaining solid was triturated in diethyl ether (20 mL). The resultant suspension was stored at 4 °C for 2 h before the yellow precipitate was isolate by cannula filtration. A second crop of product was isolated from the filtrate. NMR analysis (^1H NMR integration) confirmed both crops were the same isomer mixture with similar proportions of **7a** and **7b**. Yield: 0.120 g (0.12 mmol, 57% yield, two crops). **7a**: NMR (C_6D_6, 25 °C) ^1H: δ_H = −19.14 (dtd, 1 H, $^1J_{RhH}$ = 17, $^2J_{HP(pin)}$ = 11, $^2J_{HP(PPh3)}$ = 4), 5.56 (dt^v, 2 H, NCH_aH_bP, $^2J_{HaHb}$ = 11, J_{HP} = 7), 5.86 (d, 2 H, NCH_aH_bP, $^2J_{HaHb}$ = 11 Hz), 6.55−7.98 (m, C_6H_5 and C_6H_4). $^{31}P\{^1H\}$: δ_P = 15.1 (dt, 1 P, PPh_3, $^1J_{PRh}$ = 77, $^2J_{PP}$ = 21), 59.1 (d.d., 2 P, CH_2PPh_2, $^1J_{PRh}$ = 117, $^2J_{PP}$ = 21 Hz). **7b**: NMR (C_6D_6, 25 °C) ^1H: δ_H = −17.22 (ddt, 1 H, $^1J_{RhH}$ = 20, $^2J_{HP(PPh3)}$ = 16, $^2J_{H-P(pin)}$ = 10), 4.24 (d, 2H, NCH_aH_bP, $^2J_{HaHb}$ = 12), 4.75 (dt^v, 2 H, NCH_aH_bP, $^2J_{HaHb}$ = 12, J_{HP} = 5 Hz), 6.55−7.98 (m, C_6H_4 and C_6H_5). $^{31}P\{^1H\}$: δ_P = 16.2 (dt, 1 P, PPh_3, $^1J_{PRh}$ = 84, $^2J_{PP}$ = 22), 56.0 (dd, 2 P, CH_2PPh_2, $^1J_{PRh}$ = 113, $^2J_{PP}$ = 22 Hz). $^{13}C\{^1H\}$: δ_C = 57.7−61.7 (m, NCH_2, **7a**/**b**), 112.2 (s, $C^{2,5}(C_6H_4)$, **7a**), 114.2 (s, $C^{2,5}(C_6H_4)$, **7b**), 119.1 (s, $C^{3,4}(C_6H_4)$, **7a**), 121.0 (s, $C^{3,4}(C_6H_4)$, **7b**), 126.9−149.5 (m, C_6H_5, **7a**/**b**).[1] IR (KBr): ν_{RhH} = 2027 s, 2051, 1966, 1894, 1821br × 4 (**7a**/**b**) cm^{-1}. ESI-MS (positive ion): m/z = 973.7 [M − Cl]$^+$, 711.4 [M − Cl − PPh_3]$^+$. Accurate Mass: Found 973.1935 [M − Cl]$^+$. Calcd for $C_{56}H_{49}N_2P_3{}^{103}RhSi$: 973.1933. Anal. Found: C, 61.69; H, 4.91; N, 3.32. Calcd for $C_{56}H_{49}ClN_2P_3RhSi$: C, 66.64; H, 4.89; N, 2.78. While there is a large discrepancy between the calculated and experimental elemental analysis, the experimental data are consistent with 7 − PPh_3 Calcd: C, 61.09, H, 4.59, N, 3.75. As the PPh_3 ligand is known to be labile, it is possible that in the process of thoroughly washing the sample to be analyzed all PPh_3 was abstracted. Crystals of **7a** suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a saturated solution of a mixture of **7a** and **7b** in chloroform. Crystal data for **7a** (RhH *anti* to SiPh): $C_{56}H_{49}ClN_2P_3RhSi$, M_w = 1009.38, triclinic, $P\bar{1}$ (No. 2) a = 11.4602(4) Å, b = 13.8696(6) Å, c = 15.3944(8) Å, α = 84.636(2)°, β = 77.551(2)°, γ = 82.766(3)°, V = 2364.80(18) Å^3, Z = 2, D_{calcd} = 1.417 Mg m^{-3}, μ(Mo Kα) = 0.59 mm^{-1}, T = 200(2) K, yellow block, 0.13 × 0.10 × 0.08 mm, F^2 refinement, R = 0.049, R_w = 0.123 for 6856 reflections ($I > 2\sigma(I)$, $\theta_{max.}$ = 25.2°), 578 parameters, CCDC 898191. Crystals of **7b**·$(C_6H_6)_{0.5}$ suitable for X-ray crystallography were obtained by slow diffusion of pentane into a saturated solution of a mixture of **7a** and **7b** in benzene. Crystal data for **7b**·$(C_6H_6)_{0.5}$ (RhH *syn* to SiPh): $C_{59}H_{52}ClN_2P_3RhSi$, M_w = 1048.44, triclinic, $P\bar{1}$ (No. 2) a = 11.74350(10) Å, b = 13.3987(2) Å, c = 17.0566(2) Å, α = 87.2376(7)°, β = 86.4154(8)°, γ = 67.1037(6)°, V = 2466.69(5) Å^3, Z = 2, D_{calcd} = 1.412 Mg m^{-3}, μ(Mo Kα) = 0.564 mm^{-1}, T = 200(2) K, yellow block, 0.14 × 0.14 × 0.22 mm, F^2 refinement, R = 0.0341, R_w = 0.0790 for 12 223 reflections ($I > 2\sigma(I)$, θ_{max} = 30.0°), 813 parameters, 394 restraints, CCDC 898194.

Synthesis of [RhH(S_2CNEt_2){SiPh(NCH_2PPh_2)$_2C_6H_4$}] (8). [$Rh_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2$] (0.050 g, 0.10 mmol) and **1** (0.130 g, 0.20 mmol) were dissolved in THF (10 mL) and stirred for 2 h. A solution of [Et_2NH_2][Et_2NCS_2] (0.052 g, 0.23 mmol) in THF (5 mL) was then added. The THF was removed *in vacuo*, and the remaining solid was resuspended in benzene (10 mL). The suspension was frozen and allowed to thaw, and the supernatant was isolated by cannula transfer. The benzene was removed *in vacuo*, and the solid remaining was resuspended in ether (15 mL) in air. Agitation of the suspension resulted in precipitation of the product. The precipitate was collected by vacuum filtration (0.095 g, 0.11 mmol, 55%). NMR (C_6D_6, 25 °C) ^1H: δ_H = −15.06 (dt, 1 H, Rh*H*, $^1J_{Rh-H}$ = 20 Hz, $^2J_{P-H}$ = 12 Hz), 0.71, 0.76 (2*t*, 2 × 3H, $S_2CNCH_2CH_3$, $^3J_{H-H}$ = 7 Hz), 3.11, 3.29 (2q, 2 × 2H, $S_2CNCH_2CH_3$, $^3J_{H-H}$ = 7 Hz), 3.59 (dt$_v$, 2H, $Ph_2PCH_aH_bN$, $^2J_{Ha-Hb}$= 13 Hz, J_{Ha-P} = 5 Hz), 4.62 (d, 2H, $Ph_2PCH_aH_bN$, $^1J_{Ha-Hb}$ = 13 Hz), 6.72−7.86 (m, 29H). $^{31}P\{^1H\}$: δ_P = 61.9 (dd, 2 P, −CH $_2PPh_2$-Rh, $^1J_{RhP}$ = 115 Hz, $^2J_{HP}$= 10 Hz). $^{13}C\{^1H\}$: δ_C = 12.4 (s, $S_2CNCH_2CH_3$), 43.4 (2s, $S_2CNCH_2CH_3$), 61.0 (t_v, Ph_2PCH_2N, J_{C-P} = 14 Hz), 113.9 (s, *o*-phenylene *C*-H), 120.1 (s, *m*-phenylene *C*-H), 130.1−136.8 (m, phenyl *C*-H), 147.3 (s, S_2CNEt_2). IR (KBr): ν_{Rh-H} = 1963 cm^{-1}. ESI-MS (positive ion): m/z = 860 [M]$^+$, 335.4 [M − (Rh + Et_2NCS_2 + CH_2PPh_2 + Ph)]$^+$, 133.1 [M − (Cl, NCH_2PPh_2, PPh_2]$^+$. Accurate Mass: Found 860.1426 [M]$^+$. Anal. Found: C, 61.88; H, 5.14; N, 4.64. Calcd for $C_{43}H_{44}N_3P_2RhS_2Si(C_3H_3)$ C, 61.46; H, 5.27; N, 4.67. Crystals suitable for X-ray crystallography were obtained by slow diffusion of ether into a saturated solution of **8** in benzene. Crystal data for complex **8**: $C_{43}H_{44}N_3P_2RhS_2Si$ M_w = 859.90, monoclinic, $P2_1/n$, a = 10.0377(1) Å, b = 19.8396(2) Å, c = 21.5427(2) Å, Z = 4, D_{calcd} = 1.394 Mg m^{-3}, μ(Mo Kα) = 0.64 mm^{-1}, T = 200 K, colorless block, 0.35 × 0.24 × 0.23 mm, F^2 refinement, R = 0.029, R_w = 0.073 for 10 766 reflections ($I > 2\sigma(I)$, θ_{max} = 30.0°), 496 parameters, CCDC 898192.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for **1** (CCDC 898193), **5a**/**5b** (CCDC 898190), **7a** (CCDC 898191), **7b** (CCDC 898194), and **8**

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(CCDC 898192) in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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