Supporting Information

for

Significant Cooperativity Between Ruthenium and Silicon in Catalytic Transformations of an Isocyanide

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**Experimental Procedures**

**General Considerations.** All manipulations of air sensitive compounds were conducted under a nitrogen atmosphere using standard Schlenk techniques or using a nitrogen atmosphere glovebox. Proteo solvents were stored in PTFE-valved flasks after drying using JC Meyer solvent purification systems or by distillation under nitrogen from appropriate drying agents. Deuterated solvents (Cambridge Isotopes) were dried over NaK and vacuum-transferred prior to use. Xylyl isocyanide was purchased from commercial sources and purified by sublimation prior to use. Silanes were purchased from commercial sources and stored in a nitrogen atmosphere glovebox. The complexes \([\text{PhBP}^\text{Ph}_3]\text{RuH(\eta^3-H_2SiRR') (RR' = Me,Ph, 1a; RR' = Ph_2, 1b, RR' = Et_2, 1c, RR' = MeMes, 1d)^1,2}\) and \([\text{PhBP}^\text{Ph}_3]\text{Ru(H)=}[\text{C(H)(N(Xyl)(\eta^2-H—SiRR')))] (R,R' = MePh, 2a; R,R' = Ph_2, 2b)^3\) were prepared as previously reported.

NMR spectra were recorded on Bruker spectrometers at room temperature unless otherwise noted. Spectra were referenced internally to the residual proton signal relative to tetramethylsilane for \(^1\text{H}\) NMR, solvent peaks for \(^{13}\text{C}\{^1\text{H}\}\) NMR, external 85 % \(\text{H}_3\text{PO}_4\) for \(^{31}\text{P}\{^1\text{H}\}\) NMR, and tetramethylsilane for \(^{29}\text{Si}-^1\text{H}\) HMBC experiments. Assignment of certain \(^{13}\text{C}\{^1\text{H}\}\) NMR signals was made on the basis of \(^1\text{H}-^{13}\text{C}\) HSQC NMR data. The \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra for compounds 2c, 2e, and 6 feature some broad and/or overlapping resonances in the aromatic region such that each individual peak in the aromatic region could not be observed or individually identified. The \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra for these compounds also feature coupling of some resonances to \(^{31}\text{P}\) nuclei, and these doublets could not easily be distinguished from singlet resonances that happen to appear near each other. Thus, all aromatic \(^{13}\text{C}\) peaks are reported individually without regard for possible multiplicity and this results in more aromatic \(^{13}\text{C}\{^1\text{H}\}\) resonances reported than expected from the number of carbons in these complexes. The \(J_{\text{SiH}}\)
values for Ru—H—Si resonances were determined from the Ru—H resonances displayed in $^{29}$Si-filtered $^1H\{^{31}P\}$ NMR experiments. X-ray diffraction data were collected on a Bruker Platform goniometer with a Charged Coupled Device (CCD) detector (Smart Apex). Structures were solved using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI). All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library; G. Sheldrick, Bruker Analytical Systems, Madison, WI. Elemental analyses were performed by the University of California, Berkeley College of Chemistry Microanalytical Facility.

**Synthesis of [PhBP$^{Rh_3}$]Ru(H)=\{C(H)(N(Xyl)(\eta^2-H—SiEt)] (2c).** Complex 2c was prepared in a fashion similar to that previously reported for the closely related compounds 2a,b. A solution of XylNC (9.1 mg, 0.069 mmol) in benzene (1 mL) was added dropwise to a stirred yellow solution of the $\eta^3$-H$_2$SiEt$_2$ complex 1c (60.8 mg, 0.069 mmol) to provide a nearly colorless solution. The solvent was removed under reduced pressure and the resulting solids were washed with pentane (3 x 2 mL) to provide 64 mg of 2c (91% yield) as an analytically pure, off-white powder. Anal. Calcd for C_{58}H_{63}BNSiP$_3$Ru: C, 69.18; H, 6.31; N, 1.39. Found: C, 68.89; H, 6.61; N, 1.27. $^1$H NMR (C$_6$D$_6$, 600 MHz): δ 10.22 (1 H, Ru=CH), 8.21 (d, $J = 7.2$ Hz, 2 H), 7.84 (br, 4 H), 7.68 (t, $J = 7.2$ Hz, 2 H), 7.61 (br, 4 H), 7.42 (t, 7.2 Hz, 1 H), 7.07 (br, 4 H), 7.02 – 6.89 (overlapping br, 6 H), 6.85 (br, 6 H), 6.78 – 6.67 (overlapping m, 9 H), 2.27 (br, 2 H, BCH$_2$P), 1.95 (overlapping, 8 H, BCH$_2$P and ArCH$_3$), 1.66 (br, 2 H, BCH$_2$P), 1.60 (m, 2 H, SiCH$_2$Me), 1.52 (m, 2 H, SiCH$_2$Me), 1.14 (t, 7.6 Hz, 6 H, SiEt$_2$), -7.53 (m, 2 H, Ru—H—Si). $^{13}$C NMR (C$_6$D$_6$, 150.9028 MHz): 263.52 (br d, $^2J_{PH} = 54$ Hz, Ru=C), 165.82 (br), 143.66 (br), 142.62 (br), 141.86 (br), 133.76 (br), 132.80, 132.76, 132.60 (br), 132.16 (br), 129.17, 129.02,
127.63, 124.52, 19.13 (ArMe), 18.85 (br, BCP), 16.75 (br, BCP), 16.47, 8.95. \(^{31}\)P{\(^1\)H} NMR (C\(_6\)D\(_6\), 242.937 MHz): \(\delta \) 36.53 (d, \(J_{PP} = 29 \text{ Hz}\)), 28.09 (t, \(J_{PP} = 29 \text{ Hz}\)). \(^{29}\)Si-filtered \(^1\)H{\(^{31}\)P} NMR (C\(_6\)D\(_6\), 500 MHz (\(\text{^1H}\)), 99.375 MHz (\(\text{^29Si}\))): -7.53 (d, \(J_{\text{SiH}} = 43 \text{ Hz}, \text{Ru—H—Si}\)). \(^{29}\)Si NMR (C\(_6\)D\(_6\), from \(^1\)H-\(^{29}\)Si HMBC: 500 MHz (\(\text{^1H}\)), 99.375 MHz (\(\text{^29Si}\))): \(\delta \) 6.

**Synthesis of [PhBP\(^{\text{Ph}_3}\)]Ru(H)=[C(H)(N(2,6-diphenyl-p-tolyl))(\(\eta^2\)-H—SiMePh)] (2e).** Complex 2e was prepared as previously reported for the closely related compounds 2a,\(^{3}\)b. A solution of 2,6-diphenyl-p-tolylisocyanide (11.8 mg, 0.043 mmol) in benzene (1 mL) was added to a stirred yellow suspension of the \(\eta^3\)-H\(_2\)SiMePh complex 1a (39 mg, 0.043 mmol) in benzene (1 mL). All of 1a had dissolved after 1 h to provide a clear, colorless solution. Volatiles were removed by evaporation under reduced pressure to provide an off-white solid that was washed with pentane (3 x 2 mL) to provide 44 mg of 2e (ca. 87 % yield) as a white powder containing minor impurities as indicated by \(^1\)H NMR spectroscopy. Satisfactory elemental analysis was obtained on a sample of 2e that was prepared by vapor diffusion of pentane into a toluene solution of 2e at \(\text{–} 30^\circ\text{C}\). Anal. Calcd for C\(_{72}\)H\(_{67}\)BNSiP\(_3\)Ru: C, 73.34; H, 5.73; N, 1.19. Found: C, 73.01; H, 5.74; N, 1.21. \(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz): \(\delta \) 11.04 (m, Ru=CH), 8.18 (d, \(J = 7.1 \text{ Hz}, 2 \text{ H})\), 7.85 (t, \(J = 8.5 \text{ Hz}, 2 \text{ H})\), 7.79 (d, \(J = 7.1 \text{ Hz}, 2 \text{ H})\), 7.67 (t, \(J = 7.1 \text{ Hz}, 2 \text{ H})\), 7.39 (overlapping m, 3 H), 7.29 (br t, \(J = 7.3 \text{ Hz}, 2 \text{ H})\), 7.15 (br m, 8 H), 7.05 (br m, 8 H), 6.96 (br m, 5 H), 6.76 (br m, 10 H), 6.66 (m, 6 H), 6.49 (br, 2 H), 2.18 (overlapping m, 4 H, BCH\(_2\)P), 2.00 (br, 1 H, BCH\(_2\)P), 1.86 (3 H, ArCH\(_3\)), 1.83 (br, 1 H, BCH\(_2\)P), 1.61 (br, 1 H, BCH\(_2\)P), 1.51 (br, 1 H, BCH\(_2\)P), 0.61 (3 H, SiCH\(_3\)), -7.19 (br, 2 H, Ru—H—Si). \(^{13}\)C{\(^1\)H} NMR (C\(_6\)D\(_6\), 150.9028 MHz): \(\delta \) 265.35 (br, Ru=CH), 166.14 (br), 144.10, 143.91, 142.84, 142.73, 142.62, 142.10,
142.07, 141.91, 141.69 (br), 140.34, 140.05, 139.79, 139.54 (br), 139.23, 138.42, 137.63, 137.49, 137.13, 136.38, 134.70, 133.91, 133.83, 133.32, 133.25, 132.88, 132.84, 132.81, 132.75, 132.51, 132.47, 132.43, 131.91, 131.84, 130.97 (br), 130.26, 130.11, 129.68 (br), 129.31, 128.89 (br), 128.02 (br), 127.80 (br), 127.69 (br), 124.50, 20.86 (ArCH3), 20.32 (br, BCP), 17.61 (br, BCP), 11.97 (SiCH3).

$^{31}$P{$^1$H} NMR (C6D6, 161.975 MHz): $\delta$ 34.80 (t, $J_{PP}$ = 33 Hz), 27.57 (d, $J_{PP}$ = 33 Hz).

$^{31}$P{$^1$H} NMR (toluene-d8, 202.497 MHz): $\delta$ 35.09 (t, $J_{PP}$ = 33 Hz), 27.30 (t, $J_{PP}$ = 33 Hz), 26.95 (t, $J_{PP}$ = 33 Hz).

$^1$H-$^{29}$Si HMBC ( -30 °C in toluene-d8, 500 MHz ($^1$H), 99.375 MHz ($^{29}$Si)): $^{29}$Si $\delta$ 4.

**Synthesis of [PhBPPh3]Ru[CH2(3,5-(CH3)2-2-(η2-H—Si(NMeXyl)Me)C6H2])** (6). The yellow η3-H2SiMeMes complex 1d (15.4 mg, 0.016 mmol) was dissolved in a solution of XylNC (2.1 mg, 0.016 mmol) in C6D6 (0.7 mL) to give a colorless solution that became yellow after 5 minutes. The reaction was monitored by $^1$H NMR spectroscopy until a broad Ru—H resonance corresponding to the intermediates 2d and 7d ($^1$H $\delta$ -4.5 to -7.5 ppm) was no longer observed (ca. 12 h at 23 °C). After this point, the solvent was removed under vacuum to give a yellow solid. The crude product was dissolved in toluene, layered with pentane, and stored at -20 °C to provide 6 as an analytically pure yellow microcrystalline powder (12 mg, 69 % yield). A single crystal of 6 suitable for X-ray diffraction analysis was obtained by vapor diffusion of pentane into a solution of 6 in THF at -30 °C. Anal. Calcd for C64H67BNSiP3Ru: C, 70.97; H, 6.23; N, 1.29. Found: C, 70.59; H, 6.23; N, 1.35. $^1$H NMR (C6D6, 500 MHz): $\delta$ 8.17 (br, 2 H), 8.06 (d, $J$ = 7.1 Hz, 2 H), 7.78 (br, 4 H), 7.61 (t, $J$ = 7.3 Hz, 2 H), 7.37 (t, $J$ = 7.3 Hz, 1 H), 7.09 (br, 1 H), 7.04 – 6.84 (br m, 11 H), 6.84 – 6.62 (br m, 9 H), 6.55 (br, 2 H), 5.99 (br, 2 H), 5.83 (br, 2 H),
5.21 (1 H), 3.41 (dd, \( J = 5.8 \) Hz, 2 Hz, 1 H, Ru—CH), 2.65 (3 H, NCH\(_3\)), 2.44 (br, 1 H, BC(H)P), 2.31 (3 H, ArCH\(_3\)), 2.25 (3 H, ArCH\(_3\)), 2.18 (1 H, BC(H)P), 2.13 (d, \( J = 5.8 \) Hz, 1 H, Ru—CH), 2.06 (br, 1 H, BC(H)P), 2.03 (3 H, ArCH\(_3\)), 1.77 (3 H, ArCH\(_3\)), 1.50 (3 H, BC(H)P), 0.99 (3 H, SiCH\(_3\)), -8.73 (d, \( J_{PH} = 11 \) Hz, Ru—H—Si). \(^{29}\)Si NMR (C\(_6\)D\(_6\), from \(^1\)H-\(^{29}\)Si HMBC: 500 MHz (\(^1\)H), 99.375 MHz (\(^{29}\)Si)): \( \delta -8.73 \). \(^{29}\)Si-filtered \(^1\)H{\(^{31}\)P} NMR (C\(_6\)D\(_6\), 500 MHz (\(^1\)H), 99.375 MHz (\(^{29}\)Si)): 2.65 (d, \( J_{SiH} = 3.4 \) Hz, Si—N—CH\(_3\)), 0.99 (dd, \( J_{SiH} = 7 \) Hz, \( J_{HH} = 2.9 \) Hz, Si—CH\(_3\)) -8.73 (d, \( J_{SiH} = 108 \) Hz, Ru—H—Si). \(^1\)H NMR (CD\(_2\)Cl\(_2\), -10 °C, 600 MHz): \( \delta 7.91 \) (t, \( J = 8 \) Hz, 2 H), 7.84 (t, \( J = 8.5 \) Hz, 2 H), 7.58 (t, \( J = 8.5 \) Hz, 2 H), 7.51 (d, \( J = 7.5 \) Hz, 2 H), 7.46 (overlapping m, 3 H), 7.33 (t, \( J = 7.3 \) Hz, 1 H), 7.27 (t, \( J = 7.3 \) Hz, 2 H), 7.13 (t, \( J = 7 \) Hz, 1 H), 7.08 (t, \( J = 7.4 \) Hz, 1 H), 7.06 – 6.99 (overlapping m, 4 H), 6.97 (d, \( J = 7.5 \) Hz, 1 H), 6.92 (t, \( J = 7.4 \) Hz, 2 H), 6.88 (t, \( J = 7.4 \) Hz, 2 H), 6.82 (t, \( J = 7.5 \) Hz, 2 H), 6.74 (m, 3 H), 6.56 (t, \( J = 8.1 \) Hz, 2 H), 5.86 (br, 2 H), 5.43 (t, \( J = 8.4 \) Hz, 2 H), 4.73 (1 H), 3.07 (1 H, Ru—CH), 2.83 (3 H, NCH\(_3\)), 2.16 (3 H, ArCH\(_3\)), 1.99 (3 H, ArCH\(_3\)), 1.90 (br t, \( J = 16 \) Hz, 1 H, BC(H)P), 1.79 (3 H, 1.71 (t, \( J = 17 \) Hz, 1 H, BC(H)P), 1.57 (1 H, Ru—CH), 1.44 (t, \( J = 15 \) Hz, 1 H, BC(H)P), 1.09 (br, 1 H, BC(H)P), 0.99 (br, 3 H, SiCH\(_3\)), 0.97 (br, 1 H, BC(H)P), 0.87 (br, 1 H, BC(H)P), -8.92 (d, \( J_{PH} = 26 \) Hz, Ru—H—Si). \(^{13}\)C NMR (CD\(_2\)Cl\(_2\), -10 °C, 150.9028 MHz): 147.45, 146.37, 146.09, 144.72, 144.68, 144.64, 144.42, 144.39, 143.45, 143.30, 141.71, 141.51, 139.58, 139.36, 138.29, 136.99, 136.41, 135.05, 135.01, 134.77, 134.74, 134.25, 134.18, 133.12 (br), 132.72, 132.65, 132.43, 132.38, 131.88, 131.50, 131.44, 130.76, 130.39, 130.34, 130.10, 130.08, 129.28, 129.18, 129.11, 128.87, 128.68, 128.63, 128.54, 128.48, 128.34, 128.28, 128.22, 128.16, 128.07, 127.93, 127.76, 127.46, 127.40, 127.33, 127.27, 127.12, 127.07, 126.98, 126.93, 125.54, 125.27, 125.12, 123.59, 39.47, 28.83 (d, \( J_{CP} = 25 \) Hz, Ru—C), 24.16 (ArCH\(_3\)), 23.32 (br, BCP), 21.55 (ArCH\(_3\)), 19.51 (br, BCP), 19.19 (ArCH\(_3\)), 19.16 (ArCH\(_3\)), 18.08, 5.78 (SiCH\(_3\)). \(^{31}\)P{\(^1\)H} NMR
(CD₂Cl₂, -10 °C, 242.937 MHz): δ 50.76 (dd, Jₚₚ = 42 Hz, 14 Hz), 39.28 (t, Jₚₚ = 37 Hz), 23.46 (dd, Jₚₚ = 33 Hz, 14 Hz).

Variable temperature ¹H NMR spectra of 6 (CD₂Cl₂, 600 MHz; top to bottom: -70 °C to 20 °C). Boxes are drawn around the ¹H NMR resonances observed at –70 °C for the dearomatized C—H bonds of the η³-benzyllic ligand derived from activation of the Si—Mes group.
$^{13}$C-$^{1}$H HSQC NMR spectrum of 6 (CD$_2$Cl$_2$, $^1$H: 600 MHz, $^{13}$C: 150.9028 MHz, -10 °C; upfield region displayed: $^1$H δ -0.5 to 4.5 ppm, $^{13}$C δ -7.5 to 52.5). Signals corresponding to the SiCH$_3$, ArCH$_3$, and NCH$_3$ methyl groups are labeled. Boxes are drawn around signals corresponding to diastereotopic methylene groups (e.g. the Ru—CH$_2$—Ar and B—CH$_2$—P groups) to emphasize the coupling of inequivalent $^1$H NMR resonances to the same $^{13}$C NMR resonances as part of these methylene groups.
$^1$H-$_2$H COSY NMR spectrum of 6 (CD$_2$Cl$_2$, 500 MHz, upfield region displayed: $^1$H δ -1.0 to 4.0 ppm on both axes). Boxes are drawn to highlight cross peaks corresponding to the proton resonances of the diastereotopic methylene groups.
\(^{29}\text{Si}-^{1}\text{H} \) HMBC NMR spectrum for 6 (C\(_6\)D\(_6\); \(^{1}\text{H} \) : 500 MHz, \(^{29}\text{Si} \) : 99.375 MHz) optimized for large \(J_{\text{SiH}}\) coupling between \(^{29}\text{Si} \) NMR resonance and \(^{1}\text{H} \) NMR resonance of the Ru—H—Si bridging hydride ligand.

\(^{29}\text{Si}-^{1}\text{H} \) HMBC NMR spectrum for 6 (C\(_6\)D\(_6\); \(^{1}\text{H} \) : 500 MHz, \(^{29}\text{Si} \) : 99.375 MHz) optimized for small \(J_{\text{SiH}}\) coupling between \(^{29}\text{Si} \) NMR resonance and \(^{1}\text{H} \) NMR resonances of the Si—N—CH\(_3\) group (\(^{1}\text{H} \, \delta \, 2.64 \, \text{ppm}\)) and Si—CH\(_3\) group (\(^{1}\text{H} \, \delta \, 0.99 \, \text{ppm}\)).
Synthesis of 1,2,7-trimethyl-2-phenyl-2-silacycloindoline (3a). Complex 1a (16 mg, 0.018 mmol) was dissolved in a solution of PhMeSiH₂ (27 mg, 0.22 mmol) in THF-\(d_8\) (0.5 mL) to give a colorless solution of 1a-THF. A 750 mM stock solution of XylNC in THF-\(d_8\) was prepared by dissolving 26.5 mg of XylNC in 0.27 mL of THF-\(d_8\). A portion of the XylNC solution (20 µL, 0.015 mmol) was transferred by microliter syringe to the solution of 1a-THF and PhMeSiH₂. After 15 minutes at 23 °C, the reaction mixture was heated to 70 °C for 1.5 h. The mixture was examined by \(^1\)H NMR to confirm the formation of 3a and the regeneration of 1a-THF. The reaction mixture was subjected to four more cycles of adding 20 µL of the XylNC solution and then heating to 70 °C for 1.5 h. At this point, examination of the reaction mixture by \(^1\)H NMR spectroscopy revealed that only 18 % of 1a-THF remained present in solution. A 70 % yield of 3a was determined by integration of the \(^1\)H NMR resonances for 3a against a ferrocene internal standard. The solvent and excess PhMeSiH₂ were removed under vacuum to provide a red oil from which 3a was isolated as a colorless oil by vacuum distillation (5 mg, 38 % yield). \(^1\)H NMR (\(C_6D_6\), 500 MHz): \(\delta 7.44\) (d, \(J = 7.3\) Hz, 2 H), 7.17 (m, 3 H), 7.03 (d, \(J = 7.2\) Hz, 1 H), 6.90 (d, \(J = 7.5\) Hz, 1 H), 6.75 (t, \(J = 7.3\) Hz, 1 H), 2.82 (3 H, NCH₃), 2.40 (3 H, ArCH₃), 2.12 (d, \(J = 18\) Hz, 1 H, ArC(H)Si), 1.97 (d, \(J = 18\) Hz, 1 H, ArC(H)Si), 0.34 (3 H, SiCH₃). \(^{29}\)Si-filtered \(^1\)H NMR (\(C_6D_6\), 500 MHz (\(^1\)H), 99.375 MHz (\(^{29}\)Si)): \(\delta 2.82\) (d, \(J_{SiH} = 3.2\) Hz, Si—N—CH₃), 2.12 (dd, \(J_{HH} = 18\) Hz, \(J_{SiH} = 7.4\) Hz, Si—C(H)Ar), 1.97 (dd, \(J_{HH} = 18\) Hz, \(J_{SiH} = 7.4\) Hz, Si—C(H)Ar), 0.34 (d, \(J_{SiH} = 6.9\) Hz, Si—CH₃). \(^{29}\)Si (\(C_6D_6\), from \(^{29}\)Si-\(^1\)H HMBC: 600 MHz (\(^1\)H), 119.250 MHz (\(^{29}\)Si)): \(\delta 14.7\) ppm. \(^1\)H NMR (CD₂Cl₂, 600 MHz): 7.58 (d, \(J = 7.4\) Hz, 2 H), 7.44 – 7.35 (overlapping m, 3 H), 6.94 (d, \(J = 7.3\) Hz, 1 H), 6.76 (d, \(J = 7.7\) Hz, 1 H), 6.49 (t, \(J = 7.5\) Hz, 1 H), 3.08 (3 H, NCH₃), 2.51 (3 H, ArCH₃), 2.16 (d, \(J = 18\) Hz, 1 H, ArC(H)Si), 2.11 (d, \(J = 18\) Hz, 1 H, ArC(H)Si), 0.60 (3 H, SiCH₃). \(^{13}\)C\(^{\{1\}}\)H NMR (CD₂Cl₂, 150.903 MHz): 151.27,
136.46, 133.86, 131.06, 129.88, 128.77, 127.89, 127.13, 120.93, 116.97, 33.42 (NCH$_3$), 20.62 (ArCH$_3$), 15.91 (ArCH$_2$Si), -4.38 (SiCH$_3$). GC-MS $m/z$ 253 (M$^+$), 238, 222, 207, 194, 175, 160, 146, 132, 119, 105.

$^{29}$Si-filtered $^1$H NMR spectrum of 3a prepared in situ from 2a (C$_6$D$_6$, 500 MHz ($^1$H), 99.375 MHz ($^{29}$Si)). Insets display resonances for the Si—N—CH$_3$ methyl group (left), the Si—CH$_2$—Ar methylene group (middle), and the Si—CH$_3$ methyl group (right). The small resonance at 1.5 ppm is due to small amounts of 2a remaining in the sample.

$^{29}$Si—$^1$H HMBC NMR spectrum of 3a (C$_6$D$_6$, 600 MHz ($^1$H), 119.250 MHz ($^{29}$Si)). Displays coupling of the SiCH$_3$, SiCH$_2$Ar, NCH$_3$, and o-H of the SiPh group to $^{29}$Si.
Catalytic formation of [(CH)$_2$(NXyl)$_2$]SiEt$_2$ (4). Complex 2a (5.0 mg, 0.0055 mmol) was dissolved in a solution of Et$_2$SiH$_2$ (125 mg, 1.42 mmol) in C$_6$D$_6$ (0.6 mL) containing ferrocene as an internal standard. An initial $^1$H NMR spectrum was recorded in a sealed J-Young NMR tube prior to the addition of XylNC (7.0 mg, 0.053 mmol). Another $^1$H NMR spectrum was obtained prior to heating the mixture to 60 °C. After 20 h at 60 °C, $^1$H NMR spectroscopy revealed the formation of 4 in 54 % yield. Volatiles were removed under reduced pressure and the remaining residue was redissolved in C$_6$D$_6$. The $^1$H NMR spectrum of this latter solution displayed resonances that were identical to those of a sample of 4 that was prepared independently from glyoxal, XylNH$_2$, and Et$_2$SiCl$_2$. 

$^{13}$C-$^1$H HSQC NMR spectrum of 3a (C$_6$D$_6$, 150.903 MHz (\(^{13}\)C), 600 MHz (\(^1\)H).
Stoichiometric synthesis of [(CH)$_2$(NXyl)$_2$]SiEt$_2$ (4). Samples of compound 4 were prepared from glyoxal, XylNH$_2$, and Et$_2$SiCl$_2$ following a published procedure for preparing the related compound [(CH)$_2$(NXyl)$_2$]SiHCl.$^4$ First, the bis-imino compound (XylN=C(H))$_2$ was prepared by condensation of XylNH$_2$ with glyoxal following a published procedure.$^5$ A yellow solution of (XylN=C(H))$_2$ (0.67 g, 2.5 mmol) in THF (30 mL) was transferred via cannula into a Schlenk tube containing lithium pellets (60 mg, 8.6 mmol). After 15 minutes, the solution had darkened from yellow to red. After stirring for 48 h, the dark red solution was separated from excess lithium via cannula transfer into a new Schlenk tube. The reaction solution was cooled to −78 °C (dry ice/iPrOH) and a solution of Et$_2$SiCl$_2$ (0.40 g, 2.5 mmol) in benzene (10 mL) was added via cannula. The resulting solution was removed from the cooling bath and stirred for 16 h at room temperature. The solvent was removed under vacuum and the resulting red oil was dissolved in pentane (7 mL), filtered from insoluble material, and evaporated under reduced pressure to provide 0.768 g of a dark red oil that was ca. 80 % pure by $^1$H NMR. A sample of the crude product (50 mg) was dissolved in pentane (2 mL) and passed through a plug of silica to provide a pure sample of 4 (26 mg) that was fully characterized. $^1$H NMR (C$_6$D$_6$, 500 MHz): δ 7.03 (d, $J$ = 7.3 Hz, 4 H), 6.98 (m, 2 H), 5.51 (2 H, =CH), 2.41 (12 H, ArCH$_3$), 0.90 (q, $J$ = 7.6, 4 H, Et), 0.66 (t, $J$ = 7.6 Hz, 6 H, Et). $^{13}$C{$_1^1$H} NMR (C$_6$D$_6$, 150.903 MHz): 143.40, 137.97, 129.13, 126.10, 119.22, 19.49, 8.76, 6.95. GC-MS m/z 350 (M+), 321, 218, 188, 160, 132, 105.
In situ observation of 1d⇄CNXyl, 2d and 7d.

Sample Preparation. A solution of the η³-H₂SiMeMes complex 1d (12 mg, 13 mmol) in toluene-d₈ (0.4 mL) and a solution of XylNC (1.8 mg, 14 mmol) in toluene-d₈ (0.3 mL) were cooled in a glovebox equipped with a cold well (cooled from outside with dry ice/iPrOH and using ball bearings inside to conduct heat). The two solutions were layered in a J-Young NMR tube, sealed, and the NMR tube was quickly transferred to a dry ice/iPrOH bath outside of the glovebox. The solutions were mixed by shaking immediately prior to inserting the sample into an NMR probe that was cooled to -40 °C and the reaction mixture was monitored by NMR spectroscopy at a variety of temperatures. Select NMR data for 1d⇄CNXyl, 2d, and 7d are tabulated, and spectra are presented below:

In Situ Observation of 1d⇄CNXyl. The adduct between 1d and XylNC was observed as the predominant [BP₃]Ru species in solution after mixing solutions of 1d and XylNC while keeping the temperature at ≤ -40 °C. ¹H NMR (toluene-d₈, -40 °C, 500 MHz): δ 8.20 ppm (d, J = 6.9 Hz, 2 H), 7.73 (t, J = 7.3 Hz, 2 H), 7.55 – 7.45 (overlapping br, 13 H), 6.84 (t, J = 6.9 Hz, 8 H), 6.76 (t, J = 6.9 Hz, 12 H), 6.63 (t, J = 7.4 Hz, 1 H, Xyl), 6.38 (d, J = 7.4 Hz, 2 H, Xyl), 2.62 (6 H, mesityl ArCH₃), 2.20 (3 H, mesityl ArCH₃), 1.86 (6 H, xylyl ArCH₃), 1.79 (br, 6 H, BCH₂P), 1.48 (3 H, SiCH₃), -7.97 (m, 3 H, Ru—H—Si). ³¹P{¹H} (toluene-d₈, - 40 °C, 202.497 MHz): δ 42.01 (br).
$^{31}$P{$^1$H} NMR (toluene-$d_8$, -40 °C, 202.497 MHz). The broad $^{31}$P{$^1$H} NMR resonance centered at 41.96 ppm corresponds to 1d$\leftrightarrow$CNXyl and is consistent with the $^{31}$P{$^1$H} NMR resonances observed for adducts of XylNC or other Lewis bases with the $\eta^3$-H$_2$SiRR’ complexes 1a-c.$^{1,3}$

$^1$H NMR (toluene-$d_8$, -40 °C, 500 MHz). The initial adduct formation between 1d and XylNC proceeded cleanly enough to allow identification and proper integration of all $^1$H NMR resonances. The Ru—H resonance at $^1$H $\delta$ -7.97 ppm is consistent with the Ru—H resonances observed for adducts of XylNC or other Lewis bases with the $\eta^3$-H$_2$SiRR’ complexes 1a-c.$^{1,3}$
$^1$H NMR (toluene-$d_8$, -40 °C, 500 MHz). Aromatic region. Note that XylNC was present in small excess and thus the resonances labeled Xylyl correspond to free and bound XylNC that exchange rapidly on the NMR timescale.

$^1$H NMR (toluene-$d_8$, -40 °C, 500 MHz). Aliphatic region.
$^1$H NMR (toluene-$d_8$, -40 °C, 500 MHz). Hydride region. The large Ru—H resonance at $^1$H $\delta$ - 7.97 ppm corresponds to 1d$\leftarrow$CNXyl and the smaller resonances at ca. -1.5 ppm and ca. -5.0 ppm respectively correspond to the SiCH$_2$—H$\rightarrow$Ru and Si—H$\rightarrow$Ru groups of 7d that had formed from 1d$\leftarrow$CNXyl.

In situ observation of 2d. The solution of 1d$\leftarrow$CNXyl was allowed to warm to room temperature for 20 minutes before returning to the NMR probe at 20 °C. The reaction mixture was examined by $^1$H NMR spectroscopy at a variety of temperatures, which indicated the formation of 2d and that it exists in equilibrium with complex 7d. Overlap of resonances for 2d and 7d resulted in complex aromatic and aliphatic regions in the $^1$H NMR spectra of solutions containing 2d such that most resonances of 2d could not be clearly identified and assigned. Thus, 2d was identified by distinctive $^1$H NMR resonances for the Ru=CH—a proton and for the Ru—H—Si hydride ligands that were very similar to those previously reported for the closely related carbene compound 2a.$^3$ $^1$H NMR (toluene-$d_8$, -40 °C, 500 MHz): $\delta$ 10.67 (1 H, Ru=CH), -7.02 (dt, $J_{PH}$ = 44 Hz, 11 Hz, 1 H, Ru—H—Si), -7.42 (dt, $J_{PH}$ = 39 Hz, 14 Hz, 1 H, Ru—H—Si).

$^{31}$P{$^1$H} NMR (toluene-$d_8$, -20 °C, 202.497 MHz): $\delta$ 38.3 (br), 32.6 (br), 23.4 (br).
$^1$H NMR (toluene-$d_8$, -40 to 20 °C, 500 MHz): Hydride region of reaction mixture after warming to room temperature and upon cooling back to -40 °C. At 20 °C, the only Ru-H resonance observed for 2d and 7d is very broad and centered around $^1$H $\delta$ -6.3 ppm. At lower temperatures this signal undergoes decoalescence and sharpens into distinct signals for 2d and 7d. Note that minor hydride species are present as impurities and the [BP$_3$]RuH(CNXyl)$_2$ complex was identified by the similarity of its Ru—H resoance to that of the closely related [BP$_3$]RuH(CO)$_2$ complex, but was not isolated. The presence of an additional hydride complex is also evident from the $^1$H NMR signal at -6.85 ppm at 20 °C, but this species could not be identified.

$^1$H NMR (toluene-$d_8$, -40 °C, 500 MHz): Full $^1$H NMR spectrum recorded at -40 °C. Peak heights are optimized for observing key resonances originating from 2d.
In Situ observation of 7d. Unlike for 1d-CNXYl and 2d, complex 7d could not be identified *in situ* by comparison of its NMR data with those of analogous compounds since compounds analogous to 7d were not observed to form from \( \eta^3 \)-H\(_2\)SiRR’ complexes other than the \( \eta^3 \)-H\(_2\)SiMeMes complex 1d. Thus, a variety of 1D and 2D NMR experiments were used to clearly establish the primary coordination environment surrounding ruthenium in 7d. \( ^1 \)H NMR (toluene-\( d_8 \), -50 °C, 500 MHz): \( \delta \) 3.72 (br, 1 H, Ru—CH\(_2\)—N), 3.15 (3 H, ArCH\(_3\)), 2.87 (br, 1 H, Ru—CH\(_2\)—N), 2.42 (3 H, ArCH\(_3\)), 2.20 (3 H, ArCH\(_3\)), 2.05 (3 H, ArCH\(_3\)), 2.01 (3 H, ArCH\(_3\)), -1.51 (3 H, SiCH\(_3\)), -4.97 (m, 1 H, Ru—H—Si). \( ^31 \)P\{\( ^1 \)H\} NMR (toluene-\( d_8 \), -50 °C, 202.497 MHz): \( \delta \) 55.5 (dd, \( J_{PP} = 46, 31 \) Hz), 42.5 (br), 8.2 (br).
$^1$H NMR (toluene-$d_8$, -50 °C, 500 MHz): Full $^1$H NMR spectrum for 7d recorded at -50 °C.

Upfield region of $^1$H NMR spectrum for 7d. Resonances that could be assigned are labeled.
$^{31}$P-$^1$H NMR spectrum of 7d (toluene-$d_8$, -50 °C, 202.497 MHz):

$^1$H-$^1$H COSY NMR spectrum of 7d (toluene-$d_8$, -30 °C, 500 MHz, upfield region displayed: $^1$H $\delta$ 0 to 4.5 ppm on both axes). Boxes are drawn to highlight cross peaks between the diastereotopic Ru—CH$_2$—N resonances.
$^{13}$C-$^1$H HMBC NMR spectrum of 7d (toluene-$d_8$, -50 °C $^1$H: 500 MHz, $^{13}$C: 125.783 MHz). The presence of an agostic SiCH$_2$—H---Ru interaction is indicated by the upfield $^1$H and $^{13}$C resonance that is highlighted. A $^1J_{CH}$ value of ca. 115 – 118 Hz was determined from this signal, which is similar to that of the SiCH$_3$ group of the organosilicon species 3a ($^1J_{CH} = 120$ Hz, determined by examining satellite signals in the $^1$H NMR of 3a). These observations provide no insight into the nature of the agostic interaction in 7d due to the opposite effects that agostic interactions have on the $^1J_{CH}$ value for the bridging and terminal C—H bonds of the methyl group, and the rapid exchange between these positions on the NMR timescale.\(^6\)
$^{13}$C-$^1$H HSQC NMR spectrum of 7d (toluene-$d_8$, -50 °C, $^1$H: 500 MHz, $^{13}$C: 125.783 MHz). Upfield region is displayed ($^1$H δ -2.5 to 5 ppm; $^{13}$C δ -50 to 50 ppm).
$^{31}\text{P}-^1\text{H}$ HMBC NMR spectrum of 7d (toluene-$d_8$, -50 °C, $^1\text{H}$: 500 MHz, $^{31}\text{P}$: 202.497 MHz). Note that the $^{31}\text{P}$ NMR resonance at δ 55.6 ppm exhibits coupling with the Ru—H resonance ($^1\text{H}$ δ -4.97 ppm), the SiCH$_3$ resonance ($^1\text{H}$ δ -1.51 ppm), and both resonances of the diastereotopic aminomethyl (Ru-CH$_2$-N) moiety which confirms that these $^1\text{H}$ NMR resonances correspond to a single [BP$_3$]Ru species. The aminomethyl resonances and the Si—H$\rightarrow$Ru resonance are also displayed as coupled to other $^{31}\text{P}$ NMR resonances ($^{31}\text{P}$ δ 8.2, 42.5 ppm) which confirms that all three of these $^{31}\text{P}$ resonances are part of the same complex. The aminomethyl ligand, the agostic SiCH$_2$—H$\rightarrow$Ru interaction, the Si—H$\rightarrow$Ru interaction, and the tridentate [BP$_3$]$^-$ ligand provide an electronically and coordinatively saturated ruthenium center if the agostic C—H bond is regarded as a 2 e$^-$ donor. This confirms that no other ligands are bound to the ruthenium center in 7d.

$^{29}\text{Si}$-filtered $^1\text{H}$ NMR spectrum of 7d (toluene-$d_8$, -35 °C, 500 MHz ($^1\text{H}$), 99.375 MHz ($^{29}\text{Si}$)).
$^{29}\text{Si}-^1\text{H}$ HMBC NMR spectrum for 7d (toluene-$d_8$, $-35 ^\circ\text{C}$, $^1\text{H}$: 500 MHz, $^{29}\text{Si}$: 99.375 MHz). The signals corresponding to 7d are noted in the spectrum. The presence of an additional $^{29}\text{Si}$-containing species is evident, but this species could not be clearly identified.

Van’t Hoff Plot of $\ln([7d]/[2d])$ versus $1/T$ for the temperature range 203 – 253 K. Multiplication of the slope and intercept by the ideal gas constant ($R = 1.9872 \times 10^{-3}$ kcal/mol•K) provides thermodynamic parameters of $\Delta H_{2c \rightarrow 7d} = -3.44$ kcal/mol, and $\Delta S_{2d \rightarrow 7d} = -12.0$ eu).
X-ray Crystallography

6. Only very small single crystals of 6 could be obtained which diffracted relatively weakly. As a result, the mean I/σ value was < 2 for data collected at θ > 20.182°, and this data was not used in the solution or refinement of the structure of 6. Due to the lack of useful high angle data, the displacement parameters for atoms lighter than Si could not be refined anisotropically and the Si—H→Ru bridging hydride position could not be located. The weak data and resulting limitations of the structure model result in some unresolved ‘A-Level’, ‘B-Level’, and ‘C-Level’ alerts when the crystallographic information file is examined by CheckCIF (see below for list of alerts). Despite the relatively low intensity diffraction data, the structure for 6 was freely refined to provide bond lengths and angles for the [BP₃]Ru fragment and other common moieties (e.g. SiMes, SiMe, N(Me)(Xyl)) that were chemically reasonable and consistent with structural data for previously reported [BP₃]Ru species. Additionally, the solid state structure of 6 is fully consistent with the NMR data obtained from 6 in solution and with elemental analysis results on bulk samples of 6. Thus, the structure determined for 6 appears to provide a valid illustration of the connectivity of 6, though this conclusion relies on additional information aside from that directly obtainable from the diffraction data.
Select Bond Distances:
Ru—C1: 2.166(9) Å
Ru—C2: 2.45(1) Å
Ru—C3: 2.59(1) Å
Ru—Si: 2.680(4) Å
Crystal data and structure refinement for 6.

Empirical formula \( \text{C69 H66 B N P3 Ru Si} \)

Formula weight \( 1142.11 \)

Temperature \( 100(2) \text{ K} \)

Wavelength \( 0.71073 \text{ Å} \)

Crystal system Monoclinic

Space group \( \text{P 21/n} \)

Unit cell dimensions
\[
\begin{align*}
\text{a} &= 14.281(3) \text{ Å} \quad \alpha = 90^\circ. \\
\text{b} &= 13.986(3) \text{ Å} \quad \beta = 94.55(3)^\circ. \\
\text{c} &= 29.181(6) \text{ Å} \quad \gamma = 90^\circ.
\end{align*}
\]

Volume \( 5810(2) \text{ Å}^3 \)

\( Z \)

Density (calculated) \( 1.324 \text{ Mg/m}^3 \)

Absorption coefficient \( 0.417 \text{ mm}^{-1} \)

\( F(000) \)

Crystal size \( 0.050 \times 0.050 \times 0.010 \text{ mm}^3 \)

Theta range for data collection \( 1.400 \text{ to } 20.182^\circ. \)

Index ranges \( -13 \leq h \leq 13, -11 \leq k \leq 13, -27 \leq l \leq 28 \)

Reflections collected \( 21196 \)

Independent reflections \( 5564 \) \( \text{[R(int) = 0.2288]} \)

Completeness to theta = \( 20.182^\circ \) \( 99.7 \% \)

Absorption correction Semi-empirical from equivalents

Max. and min. transmission \( 0.7452 \text{ and } 0.6212 \)

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters \( 5564 / 0 / 341 \)

Goodness-of-fit on \( F^2 \) \( 0.948 \)

Final R indices \( [I>2\sigma(I)] \)
\( R1 = 0.0655, \text{ wR2} = 0.1273 \)

R indices (all data)
\( R1 = 0.1612, \text{ wR2} = 0.1531 \)

Extinction coefficient \( \text{n/a} \)

Largest diff. peak and hole \( 0.949 \text{ and } -0.608 \text{ e.Å}^{-3} \)
CheckCIF Alerts: The following alerts were generated by CheckCIF for the CIF of the crystallographically determined structure of 6. Despite the relatively low quality of the diffraction data leading to these alerts, all non-hydrogen atoms were freely refined to provide bond lengths and angles that were chemically reasonable. Additionally, the resulting structure depicts a composition and connectivity for 6 that is fully consistent with elemental analysis data and all NMR data obtained for bulk samples of 6.

Alert level A

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4854

Comment: Only small, weakly diffracting single-crystals of 6 could be obtained. As a result, the higher angle diffraction data was too weak (mean I/σ < 2) to be useful for structural determination. Thus, data collected at θ > 20.182° was not used for structural solution and refinement. No significant differences in the refined structure were obtained when the full data (θ max = 25.242°) was utilized.

PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s) ....... 66

Report

Comment: Due to the lack of useful high angle diffraction data, atoms lighter than silicon could not be refined anisotropically.

Alert level B

RINTA01_ALERT_3_B The value of Rint is greater than 0.18
Rint given 0.229

Comment: The high Rint value is a consequence of the relatively low quality of the diffraction data that was used for structural determination.

Alert level C

DENSD01_ALERT_1_C The ratio of the submitted crystal density and that calculated from the formula is outside the range 0.99 <> 1.01
Crystal density given = 1.324
Calculated crystal density = 1.306

PLAT046_ALERT_1_C Reported Z, MW and D(calc) are Inconsistent .... 1.306
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... Please Check

Comment: Hydrogen atoms were not placed in the disordered solvent portions of the unit cell, thus accounting for these discrepancies.

PLAT202_ALERT_3_C Isotropic non-H Atoms in Anion/Solvent ......... 5
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 3.6 Ratio
Comment: These alerts are a consequence of the relatively low quality of the diffraction data and resulting limitations in the structure model.
Kinetics study for the conversion of 2a and 2a-d$_3$ to 3a and 3a-d$_3$.

Samples for kinetics measurements were prepared by dissolving 6 mg of 2a or 2a-d$_3$ and a small amount of ferrocene (as an internal standard) in 0.6 mL of C$_6$D$_6$. The temperature of the probe was measured before and after kinetics measurements for each sample using an external standard of neat ethylene glycol to confirm a constant temperature of 78 °C. Kinetics measurements were collected for three samples each of 2a and 2a-d$_3$ which were inserted into the probe at 78 °C and allowed to equilibrate in temperature for 3 minutes prior to collecting $^1$H NMR spectra at intervals of 12 s. The conversion of 2a/2a-d$_3$ to 3a/3a-d$_3$ was monitored by integration of the SiCH$_3$ resonance ($^1$H δ 1.49 ppm) of 2a/2a-d$_3$, which for 2a-d$_3$ was the only resonance available that did not overlap significantly with other major signals observed during the kinetics experiments. Plotting ln([2a]/[2a]$_i$) versus time provided a good linear fit for the first two half-lives from the start of data collection, thus indicating that conversion of 2a to 3a was first order in 2a. At high conversion (> 4 half-lives) a small impurity resonance was evident as overlapping with the resonance of the SiCH$_3$ group. The impurity resonance was integrated and manual correction for the presence of this impurity provided a linear plot of ln([2a]/[2a]$_i$) that extended to ≥ 3 half-lives for each sample of 2a and 2a-d$_3$. These latter plots were used to determine $k_H/k_D$ for the conversion of 2a/2a-d$_3$ to 3/3a-d$_3$.

Table S1. Rate constants from $^1$H NMR kinetics measurements at 78 °C.

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<th>Sample #</th>
<th>Compound</th>
<th>Rate Constant (s$^{-1}$)</th>
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<td>Sample 1</td>
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<td>Sample 6</td>
<td>2a-d$_3$</td>
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mean $k_H = 1.45(3) x 10^{-3} \text{ s}^{-1}$; mean $k_D = 3.0(1) x 10^{-3} \text{ s}^{-1}$; $k_H/k_D = 0.48(3)$
Plots of $-\ln([2a]/[2a]_i)$ vs. Time (Samples 1 – 3) and $-\ln([2a-d_3]/[2a-d_3]_i)$ vs. Time (Samples 4 – 6) based on integration of the SiCH$_3$ resonance of 2a/2a-d$_3$ ($^1$H δ 1.49 ppm @ 78 °C):

Sample 1:

![Sample 1 graph]

Sample 2:

![Sample 2 graph]

Sample 3:

![Sample 3 graph]
Sample 4:

\[ y = 0.0029x \]
\[ R^2 = 0.9971 \]

Sample 5:

\[ y = 0.0031x \]
\[ R^2 = 0.9993 \]

Sample 6:

\[ y = 0.0029x \]
\[ R^2 = 0.9993 \]
Kinetics study for the conversion of the XylNC adducts 1a,b<–CNXyl and the CN(2,6-diphenyl-p-toly) adduct 2a<–CN(2,6-Ph2-p-toly) into the carbene complexes 2a,b,e.

Samples of the isocyanide adducts for $^1$H NMR kinetics studies were prepared in situ from the appropriate ArNC species (Ar = Xyl, 2,6-Ph2-p-toly) and 1a or 1b. Ferrocene was used as an internal standard and the conversion of the isocyanide adducts to the carbene complexes was monitored by integration of the Ru—H resonance of the adducts for ≥ 30 min. The rate of conversion at -30 °C differed in the order 1a<–CNXyl > 1b<–CNXyl > 1a<–CN(2,6-Ph2-p-toly) but spanned a relatively narrow range. These results are consistent with a previously reported computational investigation of the conversion of the isocyanide adduct 1a<–CNXyl to the carbene complex 2a. These calculations indicated a C—H bond forming rate limiting step involving a transition state in which the isocyanide carbon moves towards a hydride ligand while the SiMePh group and the N—Xyl group are relatively stationary. Since the SiMePh and N—Xyl groups do not move significantly at the transition state, it is expected that variations in the SiRR’ and N—Ar groups should have relatively minor influence on the rates of conversion of the isocyanide adducts to the carbene complexes 2a,b,e.

Plots of -ln([Adduct]/[Adduct]o) versus time (h) for the conversion of the isocyanide adducts to carbene complexes:

1a<–CNXyl:
1b$\leftrightarrow$CNXyl:

\[ y = 1.2372x \\ R^2 = 0.9984 \]

1a$\leftrightarrow$CN(2,6-Ph$_2$-$p$-tolyl):

\[ y = 1.0709x \\ R^2 = 0.9917 \]
**Computational Details.**

All calculations were performed using Gaussian ’09 suite of programs in the molecular graphics and computing facility of the College of Chemistry, University of California, Berkeley. Calculations were performed using the B3PW91 hybrid functional with the 6-31G(d,p) basis set for all main-group elements and the LANL2DZ basis set for ruthenium. The crystallographically determined atomic coordinates of 2a were used to create starting points for geometry optimization calculations of 2d-DFT and 7d-DFT. For 2d-DFT, methyl groups were added to the Si—Ph group to create an Si—Mes group, and the resulting structure was optimized to provide the final structure 2d-DFT. For 7d-DFT, the Ru—H ligand of 2d-DFT was moved from ruthenium to the carbene carbon to provide an Ru—CH2—N moiety, and the resulting structure was optimized to provide 7d-DFT. Vibrational frequencies were calculated for all converged structures and confirm that these structures lie on minima (no imaginary frequencies were determined). Images and atomic coordinates for 2d-DFT and 7d-DFT are presented below.
2d-DFT:

Select Distances:
Ru—H1: 1.781 Å
Si—H1: 1.636 Å
Ru—H2: 1.608 Å
Si—H2: 2.461 Å
Ru—Si: 2.578 Å
Ru—C1: 1.979 Å

Full atomic coordinates:

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