

E-H Bond Activation Reactions (E = H, C, Si, Ge) at Ruthenium: Terminal Phosphides, Silylenes, and Germylenes

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The placement of a strongly *trans*-influencing ligand on a ruthenium center opposite an anchoring silyl group of the tetradentate tripodal tris(phosphino)silyl ligand, $[SiP^{Ph}_3]^- ([SiP^{Ph}_3]^- = tris(2-(diphenylphosphino)phenyl)silyl), has been explored. Installation of alkyl or terminal phosphide ligands$ *trans* $to the anchoring silyl group affords the complexes <math>[SiP^{Ph}_3]RuR$ ($R = Me(2), CH_2Ph(4), PPh_2(5), P^iPr_2(6)$). Complexes **2**, **4**, and **5** are thermally unstable. Complexes **2** and **4** decay to the cyclometalated complex $[SiP^{Ph}_2P'^{Ph}]Ru$ (**3**), whereas complex **5** decays to the cyclometalated phosphine adduct $[SiP^{Ph}_2P'^{Ph}]Ru$ -(PHPh₂) (**7**). Complex **3** is found to effect E-H (E=H, C, Si, Ge) bond activation of substrates such as secondary silanes and germanes to yield the structurally unusual silylene complexes $[SiP^{Ph}_3]Ru(H)$ (SiRR') (R = R' = Ph (**10a**), R = Ph R' = Me (**10b**)) and the germylene complex $[SiP^{Ph}_3]Ru(H)(GeR_2)$ (R = Ph) (**11**) via double E-H activation transformations. Both theory and experiments suggest electrophilic character at the silylene moiety. Reaction of **3** with catecholborane, in contrast to silanes and germanes, results in insertion of the B–H unit into the M–C bond of the cyclometalated species to yield the borate complex $[SiP^{Ph}_2P'^{Ph}-B(cat)]Ru(\mu-H)$ (**14**). Complex **3** also reacts with bis(catecholato) diboron to yield a similar complex, $[SiP^{Ph}_2P^{C6H3B(cat)}-B(cat)]Ru(\mu-H)$ (**15**), with selective borylation of an *ortho* C–H bond.

Introduction

Tetradentate, tripodal ligands have a long-standing history in inorganic chemistry and continue to be exploited to prepare new types of coordination complexes and catalyst auxiliaries.¹ Recently, we reported the synthesis of the tripodal monoanionic tris(phosphino)silyl ligands $[SiP_3^R]^-$ ($[SiP_3^R] = [(2-R_2PC_6H_4)_3Si]$, R = Ph and ^{*i*}Pr) and several corresponding iron complexes, including a terminal N₂ adduct of iron(I).² A conspicuous feature of this ligand scaffold is the presence of a strongly *trans*-influencing silyl anchor,³ which is unlikely to be labile due to its anionic nature. This feature contrasts that of several topologically related ligands such as Sacconi's tris(phosphino)amine

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N(CH₂CH₂PR₂)₃ systems⁴ and Meyer's more recently developed tris(carbene)amine system,⁵ in which the apical amine donor can be hemilabile as a function of the ligand that occupies the site opposite the N atom. This article examines the properties of the $[SiP^{Ph}_{3}]^{-}$ ligand by studying a family of ruthenium complexes in which synthetic attempts are made to place strongly *trans*-influencing donor ligands at the site opposite the silyl anchor. Our studies have revealed interesting E–H bond activation transformations (E=H, C, Si, Ge). We also report the isolation and structural characterization of unusual coordination complexes including examples of terminal phosphide, silylene, and germylene complexes. These functionalities occupy positions *trans* to the silyl anchor and to our knowledge are structurally unique in this context.

Results and Discussion

Alkyl and phosphide ligands were initially targeted as candidates for the *trans*-influencing ligands opposite the silyl anchor. Heating $[SiP^{Ph}_{3}]H$, Ru(PPh_{3})_4Cl_2, and excess triethylamine at 60 °C affords purple crystals of $[SiP_{3}^{Ph}]RuCl$ (1) in 95% yield after workup (Scheme 1). The solid-state structure of 1 reveals a structure midway between a square pyramid and a trigonal bipyramid ($\tau = 0.47$; Figure 1)⁶ with a Si-Ru-Cl angle of 174.35(3)°. At room temperature the

^{(1) (}a) Macbeth, C. E.; Golombek, A. P.; Young, V. G. Jr.; Yang, C.; Kuczera, K.; Hendrich, M. P.; Borovik, A. S. *Science* 2000, 289, 938.
(b) Lim, M. H.; Rohde, J.; Stubna, A.; Bukowski, M. R.; Costas, M.; Ho, R. Y. N.; Münck, E.; Nam, W.; Que, L. Jr. *Proc. Natl. Acad. Sci. U. S.A.* 2003, 100, 3665. (c) Yandulov, D. V.; Schrock, R. R. *Science* 2003, 301. 76.

 ^{(2) (}a) Mankad, N. P.; Whited, M. T. Angew. Chem., Int. Ed. 2007,
 46, 5768. (b) Whited, M. T.; Mankad, N. P.; Lee, Y.; Peters, J. C. Inorg. Chem. 2009, 48, 2507.

⁽³⁾ Joslin et al. have previously reported a similar scaffold. See: Joslin, F. L.; Stobart, S. R. *Chem. Commun.* **1989**, 504.

^{(4) (}a) Sacconi, L.; Bertini, I. J. Am. Chem. Soc. **1967**, 89, 2235. (b) Stoppioni, P.; Mani, F.; Sacconi, L. Inorg. Chim. Acta **1974**, 11, 227. (c) Di Vaira, M.; Ghilardi, C. A.; Sacconi, L. Inorg. Chem. **1976**, 15, 1555.

^{(5) (}a) Hu, X.; Castro-Rodriguez, I.; Meyer, K. J. Am. Chem. Soc. **2003**, *125*, 12237. (b) Hu, X.; Castro-Rodriguez, I.; Meyer, K. J. Am. Chem. Soc. **2004**, *126*, 13464.

⁽⁶⁾ Addison, A. W.; Rao, T. N.; Van Rijn, J. J.; Verschoor, G. C. J. Chem. Soc., Dalton Trans. 1984, 1349.





Figure 1. Left: Solid-state structure of 1. Right: Solid-state structure of 3. Thermal ellipsoids are set at 50% probability, and solvent molecules and hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (deg): 1: Ru–Si 2.3222(11), Ru–P(1) 2.3284(11), Ru–P(2) 2.2027(11), Ru–P(3) 2.3214(12), Ru–Cl 2.5117(10), Si–Ru–Cl 174.35(3). 3: Ru–Si 2.2592(6), Ru–C(49) 2.137(2), Ru–P(1) 2.3447(6), Ru–P(2) 2.3240(6), Ru–P(3) 2.3186(6).

phosphines are equivalent on the ³¹P NMR time scale. Addition of methyllithium at -78 °C to a THF solution of 1, followed by warming to room temperature, leads to an orange solution of the thermally unstable methyl complex [SiP^{Ph}₃]RuMe (2). A ¹H NMR spectrum of the solution at room temperature, taken shortly after addition of methyllithium at -78 °C, features a quartet at $\delta = -0.98$ ppm corresponding to the methyl protons coupled to three equivalent phosphines on the NMR time scale. The corresponding ³¹P{¹H} NMR spectrum shows a singlet at $\delta = 63.7$ ppm. Both spectra indicate 3-fold symmetry for dissolved **2** on the NMR time scale, whereas its diamagnetism suggests a structure similar to **1**.

Solutions of **2** cleanly convert over approximately 30 min at room temperature to the new species $[SiP^{Ph}_2P'^{Ph}]Ru$ (**3**) via cyclometalation of an *ortho* phenyl C–H bond with concomitant loss of methane. The solid-state structure of **3**, shown in Figure 1, shows a square-pyramidal geometry ($\tau = 0.07$) with the silicon atom occupying the apical position and an open coordination site *trans* to the silyl anchor. The Ru–Si bond length in **3** is shorter than that in **1** (2.2592(6) vs 2.3222(11) Å), which is in accordance with the absence of a *trans* ligand opposite the silyl anchor in **3**. The ³¹P{¹H} NMR spectrum of **3** features three sets of peaks, with the resonance of the phosphine in the metallacycle shifted significantly upfield at $\delta = -11.3$ ppm relative to the others at $\delta = 64.9$ and 62.0 ppm. Upfield shifts for the ³¹P{¹H} NMR spectrum of cyclometalated phosphine complexes are well precedented.⁷

The reaction between benzyl magnesium chloride and 1 results in the corresponding benzyl complex [SiP^{Ph}₃]Ru- (CH_2Ph) (4). NMR spectroscopy suggests that the benzyl moiety is not bound in an η^1 fashion. At room temperature complex 4 exhibits two broad resonances at $\delta = 81.4$ and 58.3 ppm in a 1:2 ratio in the ${}^{31}P{}^{1}H{}$ spectrum in addition to several broad $[SiP_{3}^{Ph}]^{-}$ resonances in the ¹H and ¹³C{¹H} spectra. An η^3 assignment of the benzyl ligand in 4 is suggested by the large ${}^{1}J_{CH}$ value of 145 Hz at the benzylic carbon in the ¹³C spectrum of 4, though η^2 coordination cannot be rigorously excluded from the NMR data available.⁸ The upfield resonance of the *ortho* hydrogens of the benzyl ligand in the ¹H NMR spectrum, which appears as a doublet at $\delta = 5.97$ (J = 7.6 Hz) in d_8 -THF, provides strong evidence against η^1 coordination.⁸ Although broadening of the ortho hydrogen resonance is observed upon cooling, decoalescence is not observed at temperatures as low as -90 °C. Decoalescence of the ortho carbons on the benzyl ligand is likewise not attained in the ${}^{13}C{}^{1}H$ spectrum at -90 °C. The benzyl species shows thermal instability akin to 2 and decays to 3 via loss of toluene over several days at 22 °C.

The addition of lithium diphenylphosphide to 1 at -78 °C immediately leads to a dark green solution of the phosphide

^{(7) (}a) Cole-Hamilton, D. J.; Wilkinson, G. J. J. Chem. Soc., Dalton Trans. 1977, 797. (b) Pez, G. P.; Grey, R. A.; Corsi, J. J. Am. Chem. Soc. 1981, 103, 7528.

^{(8) (}a) Cámpora, J.; López, J. A.; Palma, P.; Ruíz, C.; Carmona, E. Organometallics 1997, 16, 2709. (b) Brookhart, M.; Buck, R. C.; Danielson, E. III J. Am. Chem. Soc. 1989, 111, 567. (c) Winter, M. J.; Woodward, S. J. Chem. Soc., Chem. Commun. 1989, 457. (d) Braun, T.; Münch, G.; Windmüller, B.; Gevert, O.; Laubender, M.; Werner, H. Chem.—Eur. J. 2003, 9, 2516. (e) Boardman, B. M.; Valderrama, J. M.; Muñoz, F.; Wu, G.; Bazan, B. C.; Rojas, R. Organometallics 2008, 27, 1671. (f) Gielens, E. E. C. G.; Tiesnitsch, J. Y.; Hessen, B.; Teuben, J. H. Organometallics 1998, 17, 1652.



Figure 2. Left: Solid-state structure of **5**. Right: Solid-state structure of **6**. Thermal ellipsoids are set at 50% probability, and solvent molecules and hydrogen atoms have been removed for clarity. Only one molecule in the asymmetric unit for **5** is shown. Selected bond lengths (Å) and angles (deg): **5**: Ru(1)–Si (1): 2.3783(3), Ru(1)–P(4) 2.2700(3), Ru(1)–P(1) 2.3522(3), Ru (1)–P(2) 2.3404(3), Ru(1)–P(3) 2.2567(3), Si(1)–Ru(1)–P(4) 176.42(1), P(1)–Ru(1)–P(2) 130.47(1), P(2)–Ru(1)–P(3) 109.54(1), P(1)–Ru(1)–P(3) 108.87(1). **6**: Ru–Si 2.3690(4), Ru–P(4) 2.2592(4), Ru–P(1) 2.3354(4), Ru–P(2) 2.3368(4), Ru–P(3) 2.2827(4), Si(1)–Ru–P(4) 161.88(2), P(1)–Ru–P(2) 142.46(2), P(2)–Ru–P(3) 102.64(2), P(1)–Ru–P(3) 104.55(2).

complex $[SiP^{Ph}_{3}]RuPPh_{2}$ (5). The ${}^{31}P{}^{1}H{}$ spectrum exhibits one species with resonances at $\delta = 214.1$ and 75.0 ppm corresponding to the phosphide and phosphine P nuclei, respectively. The highly downfield chemical shift of the phosphide P nucleus indicates the presence of a terminal phosphide ligand with a planar geometry about the phosphorus atom,9 a rare feature for ruthenium phosphide complexes; there is only one other structurally characterized example.¹⁰ The solid-state structure (Figure 2) contains two molecules in the asymmetric unit and shows that the angles about the terminal phosphide ligand sum to average values of 357°. In contrast to 1, the geometry of 5 more closely approximates a trigonal bipyramid, with an average τ value of 0.74. Notably, the Ru-P (phosphide) bond lengths of 2.2700(3) and 2.2525(3) Å are significantly shorter than the Ru–P (phosphine) bond lengths that average to 2.32 Å, despite the presence of the trans-silyl group. This observation points to multiple-bond character between the phosphide ligand and the ruthenium center, especially in light of the planar geometry about the phosphide P atom. Complex 5 is also structurally distinctive in that the terminal phosphide and silvl ligands are *trans* disposed in the solid state with Si-Ru-P angles of 176° and 174° for the two molecules in the asymmetric unit. The diisopropyl phosphide complex, [SiP^{Ph}₃]RuPⁱPr₂ (6), is prepared analogously to 5 and exhibits similar spectroscopic characteristics but different structural parameters, with a geometry closer to that of 1 (Figure 2). The Ru-Si bond in 6 is appreciably longer than in 1 (2.369 vs 2.322 Å), reflecting the stronger trans influence of the phosphide ligand. Similarly to solutions of 2 and 4, solutions of 5 decay to an isolable cyclometalated phosphine adduct complex, 7 (Scheme 1). The identity of 7 is confirmed by elemental analysis, an (ν_{P-H}) IR stretch at 2288 cm⁻¹, and a $J_{\rm PH}$ of 302 Hz in the ³¹P NMR spectrum for





the coordinated PPh_2H . Complex 7 is also accessible via addition of diphenylphosphine to 3.

The decay of 5 follows clean first-order kinetics with activation parameters of $\Delta H^{\ddagger} = 20(2)$ kcal/mol and $\Delta S^{\ddagger} =$ 16(4) eu. A kinetic isotope effect was obtained by the use of a deuterated ligand, d_{30} -[SiP^{Ph}₃]H, in which the phenyl sub-stituents on the phosphine arms are fully deuterated. The synthesis of d_{30} -[SiP^{Ph}₃]H is outlined in Scheme 2 and is accompliated in form at is accomplished in four steps in an overall yield of 42%. d_{10} -PPh₂H,¹¹ prepared in 81% yield by lithium metal reduction of d_{15} -PPh₃ followed by acidic workup, is coupled with 2-iodobromobenzene through a palladium-catalyzed reaction to yield d_{10} -[2-(diphenylphosphino)phenylbromide] in 95% yield. Lithiation of d_{10} -[2-(diphenylphosphino)phenylbromide], followed by addition of trichlorosilane, yields the desired deuterated product in 85% yield. The ¹H NMR spectrum of the prepared d_{30} -[SiP^{Ph}₃]H shows resonances attributable to the protons on the ligand backbone with very little (< 3%) incorporation of ¹H nuclei in the phenyl substituents of the phosphine. d_{30} -[SiP^{Ph}₃]Ru(PPh₂) was prepared analogously to 5, and its thermal decay behavior at 35 °C shows a kinetic isotope effect of 5.5(3). Collectively, the kinetic data suggest a highly ordered transition state with significant C-H bond cleavage.

The clean conversion of 2 to 3 and 5 to 7 via C-H activation of a phenyl ring inspired us to examine the installation of a silyl ligand *trans* to the $[SiP^{Ph}_{3}]^{-}$ silyl anchor. Structurally characterized mononuclear complexes with trans silyl ligands are not known for group 8 metals, with a small number reported for the earlier metals¹² and the rest comprised of group 10 or later metals.¹³ The first approach we examined involved addition of silanes to the dinitrogen hydride complex $[SiP^{Ph}_{3}]Ru(H)(N_{2})$ (8). Complex 8 is readily prepared by addition of sodium triethylborohydride to 1. Our assignment of 8 is based upon the presence of a hydride resonance at $\delta = -7.95$ ppm in the ¹H NMR spectrum and an $(\nu_{\rm N-N})$ IR stretch at 2167 cm⁻¹, which shifts to 2095 cm⁻¹ upon use of ${}^{15}N_2$ (calcd: 2093 cm⁻¹). The Ru-H stretch is not observed in the IR spectrum. In accordance with the high-frequency N2 stretch, the N2 ligand is appreciably labile. Solutions of 8 change color from yellow to orange under reduced pressure, and the ¹⁵N NMR spectrum of an

^{(9) (}a) Baker, R. T.; Whitney, J. F.; Breford, S. S. *Organometallics* **1983**, *2*, 1049. (b) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.

⁽¹⁰⁾ Derrah, E. J., Pantazis, D. A.; McDonald, R.; Rosenberg, L. Organometallics 2007, 26, 1473.

⁽¹¹⁾ Gulyás, H.; Benet-Buchholz, J.; Escudero-Adan, E. C.; Freixa, Z.; van Leeuwen, P. W. N. M. *Chem.—Eur. J.* **2007**, *13*, 3424.

^{(12) (}a) Wu, Z.; Diminnie, J. B.; Xue, Z. J. Am. Chem. Soc. 1999, 121,
4300. (b) Qiu, H.; Woods, J. B.; Wu, Z.; Chen, T.; Yu, X.; Xue, Z. Organometallics 2005, 24, 4190.

⁽¹³⁾ Selected examples: (a) Ilsley, W. H.; Sadurski, E. A.; Schaaf, T. F.; Albright, M. J.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. J. Organomet. Chem. **1980**, 190, 257. (b) Biershenk, T. R.; Guerra, M. A.; Juhlke, T. J.; Larson, S. B.; Lagow, R. J. J. Am. Chem. Soc. **1987**, 109, 4855. (c) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. Inorg. Chem. **1987**, 26, 2106. (d) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. J. Organomet. Chem. **1996**, 521, 405.



isotopically enriched sample features a single broad resonance centered at $\delta = -65$ ppm (ref to MeNO₂) with no signal for free N₂, indicating facile exchange. Judging from the ²J_{PH} values of 60 and 28 Hz, the structure of **8** is most consistent with a pseudooctahedral complex featuring a dinitrogen ligand *trans* disposed to the silyl anchor. Such an arrangement is rare and renders the N₂ ligand labile, as has been observed by our group for the iron complex [SiP^{Ph}₃]Fe(N₂).²

As outlined in Scheme 3, the addition of diphenylsilane to 8 cleanly leads to one species by ¹H NMR spectroscopy. The solid-state structure of the product¹⁴ reveals Ru-Si bond lengths of 2.4808(4) and 2.4103(4) Å for the silicon derived from diphenylsilane and that from the [SiP^{Ph}₃]⁻ ligand, respectively. Although a signature resonance in the hydride region of the ¹H NMR spectrum is easily discerned, hydrogen atom(s) bound to the ruthenium center could not be assigned from the XRD data (see Supporting Information). At -20 °C, a resonance at $\delta = 5.46$ ppm is observed that integrates in a 1:2 ratio against the hydridic resonance at $\delta = -7.18$ ppm. The former resonance appears close to the silicon hydride resonance of diphenylsilane in the same solvent (δ = 4.88 ppm, d_8 -THF) and is assigned to a terminal silicon hydride. The latter resonance could be assigned to two hydride ligands, giving a dihydride/silvl formulation for the product 9, or alternatively to a resonance arising from a terminal Ru hydride and a bridging Ru-H-Si hydride in rapid exchange. Further cooling of 9 to -80 °C does not lead to decoalescence of this resonance. To establish the possibility of a direct hydride interaction with the new silicon-containing ligand, a ¹H-²⁹Si HSQC experiment was undertaken. The spectrum at -20 °C reveals coupling constants of ${}^{1}J_{\text{SiH}} = 80$ Hz at $\delta = -7.18$ ppm¹⁵ and ${}^{1}J_{\text{SiH}} =$ 210 Hz at $\delta = 5.46$ ppm at -20 °C. These data suggest the most reliable assignment to be a terminal hydride/ η^2 -silane adduct complex, $[SiP_3]Ru(H)(\eta^2-H_2SiPh_2)$ (9), instead of a

dihydride/silyl complex. While **9** is six-coordinate, the ${}^{31}P{}^{1}H{}$ NMR spectrum features a single resonance even at -80 °C, indicative of fluxional behavior and potential scrambling of the hydride and silane hydrogen atoms. Scrambling in **9** was examined through ¹H NMR analysis of a deuterated analogue synthesized by the addition of D₂SiPh₂ to a solution of d_{30} -[SiP^{Ph}₃]Ru(H)(N₂).¹⁶ The presence of a single exchangeable ¹H nucleus enables facile examination of scrambling. The ¹H NMR spectrum at -20 °C indeed shows resonances at both 5.46 and -7.18 ppm in a 1:2.8 ratio, pointing to facile scrambling between the three hydrogen atoms in **9** (Scheme 3) and to the slight preference for deuterium to occupy the position on the silane that is not interacting with the metal.¹⁷

To explore related Si-H bond activation processes, the reaction between diphenylsilane and the cyclometalated species 3 was examined. While many cyclometalated complexes are stable to ring-opening under a variety of conditions, several systems have been found to ring open upon addition of substrates.¹⁸ Accordingly, the addition of diphenylsilane to 3 at -78 °C quantitatively produces a single product according to the ¹H NMR spectrum. The spectrum features an upfield singlet resonance at $\delta = -8.97$ ppm. Moreover, the 29 Si $\{{}^{1}$ H $\}$ spectrum shows a singlet resonance at $\delta = 374$ ppm, which is significantly downfield of known silyl complexes,¹⁹ in addition to the quartet resonance for the $[\text{SiP}^{\text{Ph}}_3]^-$ ligand at $\delta = 104 \text{ ppm} (^2 J_{\text{SiP}} = 15 \text{ Hz})$. Taken together, the spectra support the formulation of the silylene complex [SiP^{Ph}₃]Ru(H)(SiPh₂) (10a). The solid-state structure, shown in Figure 3, corroborates this assignment and reveals a terminal silvlene ligand *trans* disposed to the silvl anchor of the [SiP^{Ph}₃]⁻ ligand, providing a Si1-Ru-Si2 angle of 175.58(2)°. As for the case of the phosphide complex 5, this arrangement of ligands is to our knowledge unprecedented.²⁰ The angles about the silylene silicon sum to 359.9 (1)°, confirming sp² hybridization at the Si atom. The hydride ligand can be located in the difference map and resides at a position that is nearly coplanar with the plane defined by the silylene moiety, providing evidence against direct Si-H interactions. The Ru-Si bond length between the metal and the silvlene moiety is 2.2842(5) Å and is slightly longer than other base-free ruthenium silvlene complexes,²¹ manifesting the trans influence of the silyl donor. The addition of methylphenylsilane to 3 similarly results in the facile conversion to the silvlene complex [SiP^{Ph}₃]Ru(H)(SiMePh) (10b), featuring ²⁹Si{¹H} resonances at $\delta = 359$ and 101 ppm (² $J_{SiP} = 18$ Hz). As in 10a, the hydride resonance at $\delta =$ -9.21 ppm in the ¹H spectrum shows no coupling with the phosphines. Both 10a and 10b exhibit a single resonance in the ³¹P{¹H} NMR spectrum at 22 °C despite being six coordinate, as in 9. We presume that complexes 10a and

⁽¹⁴⁾ See Supporting Information.

⁽¹⁵⁾ $J_{\text{SiH}} = 40$ Hz from the spectrum, but this value is doubled to account for the rapid exchange with the hydride, which is assumed to have a $J_{\text{Si-H}} = 0$ Hz. The reader is referred to Taw, F. L.; Bergman, R. G. Brookhart, M. Organometallics **2004**, 23, 886 for further details.

⁽¹⁶⁾ d_{30} -[SiP^{Ph}₃]Ru(H)(N₂) is prepared analogously to **8**.

⁽¹⁷⁾ A small amount of free diphenylsilane is also observed in the spectrum. This indicates that free diphenylsilane can exchange with the η^2 -coordinated silane.

⁽¹⁸⁾ Selected examples: (a) Leucke, H. F.; Bergman, R. G. J. Am. Chem. Soc. **1997**, *119*, 11538. (b) Mork, B. V.; Tilley, T. D. J. Am. Chem. Soc. **2001**, *123*, 9702.

⁽¹⁹⁾ Corey, J. Y.; Braddock-Wilking, J. Chem. Rev. 1999, 99, 175.

⁽²⁰⁾ Okazaki et al. have reported a complex in which a base-stabilized silylene and a silyl ligand are at an angle of 160.34(2)° and 159.89(3)° from each other. See: Okazaki, M.; Minglana, J. J. G.; Yamahira, N.; Tobita, H.; Ogino, H. *Can. J. Chem.* **2003**, *81*, 1350.

^{(21) (}a) Ochiai, M.; Hashimoto, H.; Tobita, H. *Angew. Chem.* **2007**, *119*, 8340; *Angew. Chem., Int. Ed.* **2007**, *46*, 8192. (b) Grumbine, S. K.; Tilley, T. D. J. Am. Chem. Soc. **1994**, *116*, 5495.



Figure 3. Left: Solid-state structure of **10a**. Right: LUMO of **10a**. Thermal ellipsoids are set at 50% probability, and hydrogens on phenyl rings and solvent molecules have been removed for clarity. Selected bond lengths (Å) and angles (deg): **10a**: Ru–Si(2) 2.2842(5), Ru–P(1) 2.3698(5), Ru–P(2) 2.2920(5), Ru–P(3) 2.3130(5), Si(1)–Ru–Si(2) 175.58(2).



10b result from α -hydrogen migration from a five-coordinate silyl intermediate, $[SiP^{Ph}_{3}]Ru(SiHR_{2})$, by analogy with the proposed manner by which several other silylenes derived from silanes are thought to be formed.²²

The germylene analogue of **10a** is similarly obtained through the addition of diphenylgermane to **3** (Scheme 4). Such a reaction cleanly affords $[SiP^{Ph}_{3}]Ru(H)(GePh_{2})$ (**11**). As expected, complex **11** exhibits spectroscopic characteristics closely resembling that of **10a**, and an XRD study establishes that it is nearly isostructural. The only significant difference arises from the Ru–Ge bond length of 2.3579(3) Å. This bond length is difficult to compare with other systems due to the dearth of ruthenium germylene complexes, but is similar to the reported bond length of 2.339 (1) Å in the related iridium complex, $[PhB(CH_2PPh_2)_3]Ir-(H)_2(GeMes_2).^{23}$

While bona fide examples of terminal silylene complexes have gained increasing prominence in the literature,²⁴ those that feature a strongly donating ligand *trans* to the silylene



Figure 4. Solid-state structure of **11**. Thermal ellipsoids are set at 50% probability, and hydrogens on phenyl rings and solvent molecules are removed for clarity. Selected bond lengths (A) and angles (deg): Ru–Ge 2.3579(3), Ru–P(1) 2.3709(5), Ru–P(2) 2.2955(5), Ru–P(3) 2.3136(5), Si–Ru–Ge 176.25(1).

moiety are quite rare²⁵ and may be expected to be unstable. Typical examples of complexes featuring a strong donor *trans* to a silylene ligand possess two heteroatom-stabilized cyclic silylenes opposite one another.²⁶ Accordingly, solutions of **10a** and **10b** decompose slowly to unknown products at room temperature over a few days but are stable in the solid state at -35 °C. For comparison, the related six-coordinate iridium silylene complexes [PhBP^{Ph}₃] Ir(H)₂(SiR₂) (R = Mes, Ph, Et, Me)^{22,23} are prepared at elevated temperatures and are appreciably more stable ([PhBP^{Ph}₃] = [PhB(CH₂PPh₂)₃]⁻).

The addition of excess H_2 gas to **10a** affords two products, with the silane adduct **9** being the major species present. The minor product is obtained quantitatively via an independent route through the addition of excess H_2 gas to **3** and is

⁽²²⁾ Peters, J. C.; Feldman, J. D.; Tilley, T. D. J. Am. Chem. Soc. 1999, 121, 9871.

⁽²³⁾ Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4065.

⁽²⁴⁾ Waterman, R.; Hayes, P. G.; Tilley, T. D. Acc. Chem. Res. 2007, 40, 712.

⁽²⁵⁾ An example of a base-stabilized silylene complex with a *trans* hydride ligand has been reported. The reader is referred to: Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884.

^{(26) (}a) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704. (b) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1998**, *17*, 5599.



Figure 5. Left: ¹H NMR (300 MHz) of the hydride resonance of 8 at RT. Right: ¹H NMR (500 MHz) of 13 in the hydride region at -90 °C.

assigned as the dihydrogen hydride complex [SiP₃]Ru(H)-(H₂) (12). Complex 12 features a broad upfield resonance at $\delta = -4.3$ ppm that exhibits coalescence even at -80 °C, making a specific structural assignment difficult. However, the short $T_{1 \text{ min}}$ value of 33 ms recorded at 0 °C (500 MHz ¹H NMR) is consistent with a dihydrogen/hydride formulation.^{27,28} The dihydrogen ligand is labile, and 12 can hence be converted to 8 upon prolonged exposure to dinitrogen. The formation of 12 likely results from silane displacement by dihydrogen, as exposure of excess H₂ gas to 9 results in partial conversion of 9 to 12 with loss of free silane. Further, addition of approximately 1 equiv of H₂ gas to 10a results in formation of 12.

The addition of methyllithium to 10a at -78 °C was examined to try to generate a species exhibiting trans disposition of silyl ligands. The LUMO of 10a, obtained from a single-point DFT calculation and shown in Figure 3, reveals significant contribution from the p orbital on the silicon of the silylene moiety,²⁹ which suggests it should have electrophilic character. Our data for the addition of methyllithium to 10a is consistent with nucleophilic attack at the silvlene to generate a MePh₂Si⁻ ligand, as opposed to deprotonation of the metal-bound hydride. The ¹H NMR spectrum of the product formed shows a singlet hydride resonance at $\delta =$ -9.77 ppm, which exhibits no coupling to the phosphine P atoms as in 10a and 10b, and a resonance at $\delta = 0.21$ that is assigned to the methyl group. The absence of satellites at the upfield resonance indicates little interaction between the hydride and either silyl Si atom, suggesting the hydride silyl product $\{[SiP^{Ph}_3]Ru(H)(SiMePh_2)\}\{Li(THF)_x\}$ (13). The structure of 13 is presumed to feature the silvl ligand trans to the $[SiP^{Ph}_{3}]^{-}$ silvl anchor on the basis of variable-temperature NMR analysis. As shown in Figure 5, upon cooling to -90 °C, partial decoalescence of the hydride resonance to a broad five-line pattern with a coupling constant of $J_{\rm HP} = 28$ Hz is observed. This splitting pattern is reminiscent of that observed for the hydride resonance in 8, with ${}^{2}J_{\rm HP} = 60$ Hz, 28 Hz due to coupling with the cis and trans phosphines, respectively. We rationalize the broad five-line pattern of 13 as resulting from the superposition of a doublet of triplets with similar coupling constants.

We have also attempted the installation of a boryl ligand opposite the silyl anchor. While unsuccessful, the reaction products (Scheme 5) are interesting and worthy of



brief comment. Addition of catecholborane at -78 °C to **3** followed by warming gives rise to a light orange solution (Scheme 5). Its ¹H NMR spectrum shows clean formation of one product featuring a broad resonance at $\delta = -6.24$ ppm, and a broad resonance at $\delta = 12$ ppm is observed in the ¹¹B {¹H} spectrum. The solid-state structure for complex **14**, shown in Figure 6, depicts formal insertion of the B–H bond into the M–C bond of the metallacycle, revealing a bridging B–(μ -H)–Ru hydride.³⁰ The Ru–B distance of 2.468(2) Å indicates very little, if any, direct interaction between the boron atom with the metal. One of the oxygen atoms from the catecholborane is coordinated to the metal, with a Ru–O distance of 2.376(2) Å, completing the coordination sphere.

The above reaction suggested to us that replacement of the bridging hydride unit with a boryl ligand might be possible through addition of bis(catecholato)diboron. However, such a reaction instead affords a product with a ¹H NMR spectrum closely resembling 14. The solid-state structure of the product, 15, indeed reveals an analogous structure to 14, but moreover shows that a phenyl ring has been selectively borylated at the *ortho* position. A number of mechanisms are conceivable for this transformation,³¹ and a plausible intermediate might be the intended boryl complex, which subsequently activates the aryl C–H bond.

Concluding Remarks

The tetradentate $[SiP^{Ph}_3]^-$ ligand has been exploited in the preparation of a family of new ruthenium complexes.

^{(27) (}a) Hamilton, D. G.; Crabtree, R. H. J. Am. Chem. Soc. **1988**, *110*, 4126. (b) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. J. Am. Chem. Soc. **1991**, *113*, 4173.

⁽²⁸⁾ A partial deuteration experiment of **12** using HD has been performed to try to obtain the H–D coupling constant according, but overlap of the H₃ and H₂D isotopomer resonances at 0 °C complicates the determination. Further cooling results in the gradual merging of the resonances until at -50 °C a single broad resonance is observed. This method of analysis follows: Oldham, W. J. Jr; Hinkle, A. S.; Heinekey, D. M. J. Am. Chem. Soc. **1997**, 119, 11028.

⁽²⁹⁾ Tilley and co-workers have reported related results: (a) Hayes, P. G.; Beddie, C.; Hall, M. B.; Waterman, R.; Tilley, T. D. J. Am. Chem. Soc. **2006**, *128*, 428. (b) Calimano, E.; Tilley, T. D. J. Am. Chem. Soc. **2008**, *130*, 9226.

⁽³⁰⁾ Such an insertion has been observed previously. The reader is referred to: Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Marder, T. B. *J. Am. Chem. Soc.* **1995**, *117*, 8777.

^{(31) (}a) Hartwig, J. F.; Cook, K. S.; Hapke, M.; Incarvito, C. D.; Fan,
Y.; Webster, C. E.; Hall, M. B. J. Am. Chem. Soc. 2005, 127, 2538.
(b) Wan, X.; Wang, X.; Luo, Y.; Takami, S.; Kubo, M.; Miyamoto, A. Organometallics 2002, 21, 3703. (c) Ishiyama, T.; Miyaura, N. J. Organomet. Chem. 2003, 680, 3. (d) Tamura, H.; Yamazaki, H.; Sato,
H.; Sakaki, S. J. Am. Chem. Soc. 2003, 125, 16114.



Figure 6. Left: Solid-state structure of **14**. Right: Solid-state structure of **15**. Thermal ellipsoids are set at 50% probability, and hydrogens on phenyl rings and solvent molecules have been removed for clarity. The bridging hydride was not found in **15**. Selected bond lengths (A) and angles (deg): **14**: Ru–Si 2.2913(6), Ru–P(1) 2.3288(5), Ru–P(2) 2.3250(5), Ru–P(3) 2.3382(6), Ru–O(1) 2.3757 (15), Ru–B 2.4684(2), Si–Ru–O(1) 167.47(4). **15**: Ru–Si 2.2952(3), Ru–P(1) 2.3400(3), Ru–P(2) 2.3108(3), Ru–P(3) 2.3497(3), Ru–O(1) 2.3265(6), Ru–B 2.449(1), Si–Ru–O(1) 167.65(2).

Most notably, the cyclometalated derivative **3** is a reactive synthon that activates E-H bonds, allowing the preparation of structurally distinctive silylene and germylene complexes. In addition, phosphide/silyl and disilyl complexes can be prepared using the $[SiP^{Ph}_{3}]Ru$ scaffold. All of these complexes are unusual by virtue of the placement of two strongly *trans*-influencing ligands in approximate *trans* positions to one another. As such, these species are thermally unstable, as is manifest in the thermal conversion of phosphide **5** to phosphine **7**. Studies in our lab continue to map the reactivity patterns of this $[SiP_{3}]Ru$ system and to exploit its properties in the context of homogeneous catalysis.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of dinitrogen. Unless otherwise noted, solvents were degassed and dried by thoroughly sparging with N2 gas followed by passage through an activated alumina column. Pentane, benzene, toluene, tetrahydrofuran, and diethyl ether were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran. All reagents were purchased from commercial vendors and used without further purification unless otherwise noted. Celite (Celite 545) was dried at 150 °C overnight before use. Methyllithium was purchased in a solution form and concentrated, redissolved in tetrahydrofuran, and titrated. Ru-(PPh₃)₄Cl₂,³² tris(2-(diphenylphosphino)phenyl)silane ([SiP^{Ph}₃]-H),² and diphenylphosphine were synthesized according to literature procedures.¹¹ d_{15} -Triphenylphosphine was prepared by a modification of a literature procedure³³ in which purification was attained by column chromatography (eluent 1:1 hexane/EtOAc). d_{10} -Diphenylphosphine was prepared analogously to diphenylphosphine. d_{30} -[SiP^{Ph}₃]H was synthesized analogously to [SiP^{Ph}₃]H using d_{10} -[2-(diphenylphosphino)phenyl bromide] (prepared analogously to 2-(diphenylphosphino) phenyl bromide³⁴). LiPⁱPr₂·THF was synthesized by the addition of lithium pellets to a THF solution of chlorodiisopropylphosphine. LiPPh₂·Et₂O was synthesized by the addition of butyllithium to a diethyl ether solution of diphenylphosphine. Triethylamine was dried over calcium hydride and distilled. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and stored over 3 Å molecular sieves prior to use. Elemental analyses were performed by Desert Analytics, Tuscon, AZ, and by Columbia Analytical Services, Tuscon, AZ (formerly Desert Analytics).

X-ray Crystallography Procedures. X-ray diffraction studies were carried out at the Beckman Institute Crystallography Facility and at the MIT Department of Chemistry X-ray Diffraction Facility on a Bruker Smart 1000 CCD diffractometer or Bruker three-circle Platform diffractometer, equipped with a CCD detector. Data was collected at 100 K using Mo Ka ($\lambda = 0.710$ 73 Å) radiation for all structures except for **6** and Cu Ka ($\lambda = 1.541$ 78 Å) for **6** and solved using SHELXL.³⁵ X-ray quality crystals were grown as described in the experimental procedures. The crystals were mounted on a glass fiber or nylon loop with Paratone N oil.

Spectroscopic Measurements. Varian Mercury-300, Bruker Avance-400, and Varian Inova-500 were used to collect ¹H, ¹¹B, ¹³C, ²⁹Si, and ³¹P spectra at room temperature unless otherwise noted. ¹H and ¹³C spectra were referenced to residual solvent resonances. ¹¹B spectra were referenced to external boron trifluoride etherate ($\delta = 0$ ppm), ¹⁵N spectra were referenced to external neat nitromethane ($\delta = 0$ ppm), ²⁹Si spectra were referenced to external tetramethylsilane ($\delta =$ 0 ppm), and ³¹P spectra were referenced to external 85% phosphoric acid ($\delta = 0$ ppm).

Kinetic Measurements. In a typical experiment, 0.5 mL of a solution of **5** (approximately 50 mM) was added to a J. Young tube containing a sealed internal integration standard (PPh₃), and the sealed tube was heated on a temperature-equilibrated hot plate, which was kept to within 0.5 °C at all times. The reaction was followed by ³¹P NMR, and the ratio of **5** to PPh₃ was obtained through comparison of the peak height of **5** (peak at 75.0 ppm) to that of PPh₃. The resulting data were fit to first-order decay. The rate constants reported are the average of two experiments, and the error reported is the standard deviation of the two rate constants obtained. A kinetic isotope effect was obtained by performing an analogous reaction at 35 °C using d_{30} -[SiP^{Ph}₃]Ru(PPh₂) (prepared similarly to **5**) and

⁽³²⁾ Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. Inorg. Synth. 1970, 12, 237.

⁽³³⁾ Baldwin, J. E.; Barden, T. C.; Pugh, R. L.; Widdison, W. C. J. Org. Chem. **1987**, *52*, 3303.

⁽³⁴⁾ Whited, M. T.; Rivard, E.; Peters, J. C. Chem. Commun. 2006, 1613.

⁽³⁵⁾ Sheldrick, G. M. Acta Crystallogr. A 2008, 64, 112.

comparing the rate constants of the decay of 5 and d_{30} -[SiP^{Ph}₃]-Ru(PPh₂).

DFT Calculations. A single-point calculation on 10a was run on the Gaussian03³⁶ suite of programs with the B3LYP³⁷ level of theory with the LANL2DZ basis set for Ru,³⁸ Si, and P with diffuse and polarization functions for Si and P.³⁹ The 6-31G-(d,p) basis set was used for C and H.

Synthesis of [SiP^{Ph}_3]RuCl (1). H[SiP^{Ph}_3] (1.90 g, 2.34 mmol) and Ru(PPh₃)₄Cl₂ (2.86 g, 2.34 mmol) were charged into a flask, and benzene (120 mL) was added. Triethylamine (1.01 mL, 7.26 mmol) was added, and the flask was heated at 60 °C for 18 h. The mixture was filtered through Celite, and the volatiles were removed in vacuo. Layering diethyl ether over a concentrated CH₂Cl₂ solution resulted in large purple blocks. The crystals were dissolved in benzene, and lyophilization yielded an analytically pure, red-purple solid (2.12 g, 95.6%). Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a concentrated benzene solution. ¹H NMR (C_6D_6, δ) : 8.38 (d, J = 7.5 Hz, 3H), 7.38 (m, 11H), 7.24 (t, 3H), 7.15 (m, 7H), 6.87 (t, 3H), 6.77 (t, 5H), 6.66 (t, 10H). ¹³C{¹H} NMR (C₆D₆, δ): 155.0, 154.9, 147.9, 135.7, 134.2, 132.7, 132.5, 129.8, 129.2, 128.8. ${}^{31}P{}^{1}H{}$ NMR (C₆D₆, δ): 68.1 (s). ${}^{29}Si{}^{1}H{}$ NMR (CDCl₃, δ): 77.6 (q, J = 16 Hz). Anal. Calcd for C₅₄H₄₂SiP₃ClRu: C, 68.38; H, 4.46. Found: C, 68.44; H, 4.23.

Synthesis of [SiP^{Ph}₃]RuMe (2). [SiP^{Ph}₃]RuCl (10 mg, 0.011 mmol) was charged into a J-Young tube and dissolved in d_8 -THF. The tube was cooled to -78 °C, and MeLi (11 μ L, 0.011 mmol) was syringed in. The tube was quickly capped, and a NMR spectrum of the sample was taken immediately afterward. ¹H NMR (THF- d_8 , δ): 8.34 (d, J = 7.2 Hz, 3H), 7.36–6.71 (m, 39H), -0.98 (q, J = 4.8 Hz, 3H, Ru-CH₃). ³¹P NMR $(\text{THF-}d_8, \delta): 63.7$

Synthesis of $[SiP_2^{Ph}P'_1]Ru$ (3). $[SiP_3^{Ph}]RuCl$ (0.93 g, 0.98 mmol) was dissolved in THF (60 mL) in a flask and cooled to -78 °C. MeLi (0.95 mL, 0.98 mmol) was added dropwise via syringe. The red solution was warmed to room temperature, yielding an orange solution. The solvent was removed in vacuo, and benzene (50 mL) was added to the resulting orange solid. The resulting solution was stirred for 1 h, and the mixture was filtered through Celite and concentrated. Recrystallization from layering diethyl ether over a concentrated THF solution yielded orange needles that analyzed for $[SiP^{Ph}_2P'^{Ph}]Ru \cdot Et_2O$. These crystals were suitable for X-ray diffraction, and the solid-state structure includes one molecule of diethyl ether, consistent with the elemental analysis. The diethyl ether could be removed by prolonged exposure of the crushed crystals to vacuum (0.76 g, 85%). ¹H NMR (C₆D₆, δ): 8.32 (m, 2H), 8.16 (d, J=7.5 Hz, 1H),

8.03 (d, J = 6.6 Hz, 1H), 7.73 (m, 3H), 7.53 (t, J = 7.5 Hz, 1H), 7.27–6.38 (m, 31H), 6.22 (td, J = 13.0 Hz, 1.8 Hz, 2H). ¹³C{¹H} NMR (THF-*d*₈, δ): 167.8, 167.2, 157.0, 156.6, 153.8, 153.3, 151.6, 151.3, 149.7, 149.3, 146.8, 146.5, 146.4, 146.3, 145.9, 140.0, 139.8, 137.6, 136.5, 136.4, 135.7, 135.6, 135.0, 134.9, 132.3, 132.1, 131.3, 131.3, 131.2, 131.1, 131.1, 130.8, 129.9, 128.8, 129.7, 128.4, 128.2, 127.8, 127.6, 127.5, 127.2, 127.0, 126.8, 126.7, 126.4, 126.2, 126.0, 125.9, 125.7, 125.6, 125.4, 125.2, 124.7, 124.3, 124.2, 122.5, 119.7. ²⁹Si{¹H} NMR (THF d_8, δ): 71.4. ³¹P{¹H} NMR (C₆D₆, δ): 64.9 (dd, J = 19 Hz, 14 Hz), 62.0 (dd, J=235 Hz, 14 Hz), -11.3 (dd, J=235 Hz, 19 Hz). Anal. Calcd for C₅₈H₅₁OSiP₃Ru: C, 70.65; H, 5.21. Found: C, 70.77; H, 5.40.

Synthesis of $[SiP^{Ph}_{3}]Ru(\eta^{3}-CH_{2}Ph)$ (4). $[SiP^{Ph}_{3}]RuCl$ (50 mg, 0.053 mmol) was dissolved in THF (5 mL) and cooled to -78 °C. BnMgCl (27 µL, 0.053 mmol) was added by syringe, and the resulting solution was allowed to warm to room temperature. The solvent was removed in vacuo, the residue was redissolved in benzene, and the resulting solution was filtered through Celite. Pentane was added to a concentrated solution to precipitate out the product, which was pure by NMR (48 mg, 91%). ¹H NMR (d_8 -THF, δ): 7.8–6.5 (br, overlapping peaks), 6.96 (t, J = 7.2 Hz, 1H), 6.63 (t, J = 7.6 Hz, 2H), 5.97 (d, J = 7.6 Hz, 2H), 2.52 (q, J = 4.4 Hz, 2H). ¹H NMR (d_8 -THF, δ , -20 °C): 7.93 (d, J = 7.2 Hz, 2H), 7.63 (s, 4H), 7.45–7.12 (m, 12H), 6.97–6.85 (m, 10H), 6.72–6.6 (m, 8H), 6.41 (s, 4H), 6.40 (d, J = 8.4 Hz, 4H), 5.88 (d, J = 8 Hz, 2H), 2.49 (br, 2H). ¹³C NMR (C₆D₆, δ): 152.1 (br), 139.3 (br), 134.4, 132.5, 131.1 (br), 129.2, 127.7, 126.1, 121.3, 38.4. ¹³C NMR (*d*₈-THF, δ, -20 °C): 157.9, 157.4, 152.4 (m), 147.0, 146.7, 140.0 (br), 139.4 (br), 136.9, 135.6, 134.4, 134.3, 133.8, 132.8, 132.6, 132.4, 130.7, 129.8, 128.9, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.7, 125.7, 38.2 (m). ³¹P NMR (C_6D_6 , δ): 81.4 (br), 58.3 (br).

Synthesis of [SiP^{Ph}₃]Ru(PPh₂) (5). [SiP^{Ph}₃]RuCl (0.30 g, 0.32 mmol) was dissolved in THF (5 mL) and cooled to -78 °C. LiPPh₂·Et₂O (84 mg, 0.32 mmol) was added in one portion, resulting in an immediate color change to dark green. Solvent was removed, and the resulting solid was redissolved in benzene, followed by filtration through Celite. The dark green solution was lyophilized to yield a green solid (0.34 g, 97%). Crystals suitable for X-ray diffraction were grown from layering diethyl ether over a concentrated solution of dichloromethane at -35 °C. ¹H NMR (C₆D₆, δ): 8.48 (d, J = 7.2 Hz, 3H), 7.25-6.67 (m, 52H). ¹³C NMR (C_6D_6 , δ): 156.0 (m), 151.6, 150.9 (m), 143.2 (m), 133.6, 132.8, 132.5, 132.3 (m), 129.4, 128.9, 128.7, 128.5, 128.3, 128.1, 128.0, 128.0, 127.9, 126.9. ³¹P NMR (C₆D₆, δ): 214.1 (q, J = 15 Hz, 1P), 75.0 (d, J = 15 Hz).

Synthesis of $[SiP^{Ph}_{3}]Ru(P'Pr_{2})$ (6). $[SiP^{Ph}_{3}]RuCl$ (0.20 g, 0.21 mmol) was suspended in benzene (10 mL), and an excess of $\text{LiP}^{i}\text{Pr}_{2}$ ·THF (0.082 g, 0.42 mmol) was added in one portion. The resulting mixture was stirred for 7 h, at which time the color of the solution had turned from purple to dark green. The mixture was filtered through Celite, and pentane was layered over a concentrated solution to yield green crystals that analyzed for $[SiP^{Ph}_{3}]Ru(P^{i}Pr_{2}) \cdot 1.5C_{6}H_{6}$ (0.17 g, 71%). These crystals were suitable for X-ray diffraction and showed the correct number of benzene molecules, as indicated by the elemental analysis. ¹H NMR (C_6D_6, δ): 8.36 (d, J = 6.9 Hz, 3H), 7.24–7.20 (m, 15H), 6.96 (m, 3H), 6.82 (q, J = 7.5 Hz, 21H), 3.04 (2H, J = 7.2 Hz, 2H), 1.18 (d, J = 7.2 Hz, 6H), 1.15 (d, J = 7.2 Hz, 6H). ¹³C NMR (C_6D_6 , δ): 155.6 (m), 151.2 (m), 143.7 (m), 133.5, 133.3(m), 132.1, 129.0, 128.9, 128.7, 128.5, 128.3, 128.0, 127.9, 46.3 (d, J = 8.0 Hz), 21.7, 21.6. ³¹P NMR (C₆D₆, δ): 295.0 (q, J = 18 Hz, Ru- P^{i} Pr₂), 77.0 (d, J = 18 Hz). Anal. Calcd for C₆₉H₆₅SiP₄Ru: C, 72.23; H, 5.71. Found: C, 72.45; H, 5.72.

Synthesis of $[SiP^{Ph}_{2}P'^{Ph}]Ru(PHPh_{2})$ (7). $[SiP^{Ph}_{2}P'^{Ph}]Ru$ (0.025 g, 0.027 mmol) was dissolved in THF (4 mL) and cooled to -78 °C. To the stirring solution was added diphenylphosphine via syringe. The resulting yellow solution was warmed to room temperature, and the solvent was removed to yield

⁽³⁶⁾ Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; , Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; M. A. Al-Laham, Peng C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C. Pople, J. A. Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford, CT, $20\bar{0}4.$

^{(37) (}a) Becke, A. D. J. Chem. Phys. 1993, 98, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785.

^{(38) (}a) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 270. (b) Wadt, W. R.; Hay, P. J. J. Chem. Phys. 1985, 82, 284. (c) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.

⁽³⁹⁾ Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. J. Chem. Phys. 2001, 105, 8111.

a yellow solid. Analytically pure material was obtained by recrystallization from layering pentane over a concentrated THF solution to yield yellow microcrystals (0.023 g, 76%). 1 H NMR (C_6D_6 , δ): 8.44 (d, J = 7.0 Hz, 1H), 8.26 (d, J = 7.0 H, 1H), 8.10 (m, 3H), 7.65 (t, J=7.5 Hz, 1H), 7.59 (t, J=7.5 Hz, 2H), 7.56 (dt, J = 303 Hz, 9.5 Hz, 1H, PHPh₂), 7.40 (t, J = 8.0 Hz, 2H), 7.33-6.39 (m, 38H), 5.65 (t, J = 8.0 Hz, 2H). ¹³C NMR (C₆D₆, δ): 161.3, 160.8, 158.0, 157.6, 154.9, 154.5, 152.2, 151.8, 151.5, 150.8, 150.5, 150.3, 149.9, 145.7, 145.3, 142.4, 142.1, 141.5, 140.1, 139.4, 139.3, 137.6, 137.4, 135.4, 135.3, 135.1, 134.9, 134.2, 134.0, 133.9, 133.4, 133.3, 132.6, 132.5, 130.5, 130.3, 129.7, 129.4, 129.3, 129.3, 129.2, 128.9, 128.0, 127.9, 127.8, 127.5, 127.4, 127.1, 127.0, 126.4, 126.3. $^{31}\mathrm{P}$ NMR (C₆D₆, δ): 67.6 (dm, J = 226 Hz), 62.3 (m), 8.4 (q, J = 21 Hz), -13.0 (dm, J = 226 Hz). IR (KBr, cm⁻¹): 3046, 2956, 2924, 2869, 2288 (v[P-H]), 1954, 1558, 1479, 1434, 1309, 1273, 1183, 1156, 1090. Anal. Calcd for C₆₆H₅₂SiP₄Ru: C, 72,18; H, 4.77. Found: C, 71.59; H, 4.82.

Alternatively, a solution of $[SiP^{Ph}_3]Ru(PPh_2)$ can be left standing at room temperature for several days and cleanly decays to 7.

Synthesis of [SiP^{Ph}₃]Ru(H)(N₂) (8). [SiP^{Ph}₃]RuCl (0.60 g, 0.63 mmol) was dissolved in THF (60 mL) and cooled to -78 °C. Sodium triethylborohydride (1 M in THF, 0.63 mL, 0.63 mmol) was added dropwise to the solution, and the resulting solution was warmed to room temperature. The solvent was removed, and the resulting solid was redissolved in benzene, followed by filtration through Celite. Pentane was layered over a concentrated benzene solution to yield white needles (0.53 g, 88%). ¹H NMR (C_6D_6, δ) : 8.59 (d, J = 7.2 Hz, 2H), 8.32 (d, J = 7.5 Hz, 1H), 7.87 (m, 4H), 7.44 (m, 2H), 7.31 (td, *J* = 6.0 Hz, 1.2 Hz, 2H), 7.20-6.46 (m, 32H), -7.95 (dt, J=60.9 Hz, 27.6 Hz, 1H, Ru-H). ¹³C NMR (C_6D_6, δ) : 156.8, 156.2, 155.8, 155.4, 155.0, 150.8, 150.5, 150.1, 149.1, 148.5, 147.4, 142.1, 141.8, 141.5, 140.3, 140.0, 137.5 (t), 134.4 (t), 133.7, 133.2, 133.1 (d), 132.9, 132.5, 132.3, 129.3 (d), 129.2, 127.7, 127.4 (d). ¹⁵N NMR (C_6D_6, δ): – 65.1. ³¹P NMR (C₆D₆, δ): 67.5 (d, J = 12 Hz, 2P), 59.4 (t, J =12 Hz, 1P). IR (KBr, cm⁻¹): 3050, 2929, 2869, 2167 (ν [N₂]), 1896, 1482, 1436, 1118.

Synthesis of $[\text{SiP}^{\text{Ph}}_3]\text{Ru}(\text{H})(\eta^2-\text{H}_2\text{SiPh}_2)$ (9). $[\text{SiP}^{\text{Ph}}_3]\text{Ru}(\text{H})-(\text{N}_2)$ (0.15 g, 0.16 mmol) was dissolved in benzene (7 mL), and diphenylsilane (0.030 mL, 0.16 mmol) was added dropwise to the stirring solution. The mixture was stirred for 5 min, and the solvent was removed. Layering pentane over a concentrated benzene solution yielded yellow crystals suitable for X-ray diffraction (0.15 g, 85%). ¹H NMR (THF- d_8 , δ): 8.43 (d, J = 7.0 Hz, 3H), 7.33 (t, J = 7.0 Hz, 3H), 7.03–6.70 (m, 46H), 5.49 (br, 1H, Ru-Si*H*Ph₂), -7.18 (br, 2H, Ru(*H*)(*H*SiHPh₂). ¹³C NMR (C₆D₆, δ): 153.9 (m), 150.7 (m), 143.3, 143.1, 143.0, 135.5, 133.6, 133.4, 132.8, 132.8, 132.7, 132.5, 128.8, 128.7, 128.1, 127.9, 127.7, 127.6, 127.4. ²⁹Si NMR (C₆D₆, δ): 90.3, -5.4. ³¹P NMR (C₆D₆, δ): 66.0. IR (KBr, cm⁻¹): 3055, 2086 (ν [Si-H]) 1961, 1891, 1813, 1479, 1307, 1250, 1187, 1102. Anal. Calcd for C₆₆H₅₅Si₂P₃Ru: C, 72.18; H, 5.04. Found: C, 72.79; H, 5.01.

Synthesis of $[SiP^{Ph}_{3}]Ru(H)(SiPh_{2})$ (10a). $[SiP^{Ph}_{2}P'^{Ph}]Ru$ -(0.20 g, 0.22 mmol) was dissolved in THF (10 mL) and cooled to -78 °C. Diphenylsilane (40 μ L, 0.22 mmol) was added via syringe, and the resulting red solution was allowed to warm to room temperature. The solvent was removed, and lyophilization of a benzene solution resulted in an analytically pure red solid (0.22 g, 91%). Crystals suitable for X-ray diffraction were grown from layering pentane over a concentrated benzene solution. ¹H NMR (THF- d_8 , δ): 8.66 (d, J = 7.0 Hz, 3H), 7.32 (t, J = 7.2 Hz, 3H), 7.26-6.57 (m, 46H), -8.97 (s, 1H, Ru-H). ¹³C NMR (THF- d_8 , δ): 154.9 (m), 153.9 (m), 143.3, 143.1, 143.0, 135.5, 133.6, 133.4, 132.8, 132.8, 132.7, 132.5, 128.8, 128.7, 128.1, 127.9, 127.7, 127.6, 127.4. ²⁹Si NMR (C₆D₆, δ): 373.9 (s, Ru-SiPh₂), 103.5 (q, J = 15 Hz). ³¹P NMR (C₆D₆, δ): 73.6. Anal. Calcd for C₆₆H₅₅Si₂P₃Ru: C, 72.31; H, 4.87. Found: C, 72.29; H, 4.97. **Synthesis of [SiP^{Ph}₃]Ru(H)(SiMePh) (10b).** [SiP^{Ph}₂P'^{Ph}]Ru-(0.040 g, 0.044 mmol) was dissolved in THF (5 mL) and cooled to -78 °C. Methylphenylsilane (6.0 μ L, 0.044 mmol) was added via syringe, and the resulting orange solution was allowed to warm to room temperature. The solvent was removed, and lyophilization of a benzene solution resulted in an orange solid (0.043 g, 95%). ¹H NMR (C₆D₆, δ): 8.51 (d, J = 7.0 Hz, 3H), 7.29–7.09 (m, 20H), 6.98 (t, J = 7.5 Hz, 3H), 6.90 (t, J = 7.5 Hz, 3H), 6.80 (t, J = 7.5 Hz, 6H), 6.68 (t, J = 7.5 Hz, 12H), 1.04 (s, Ru-SiCH₃Ph, 3H), -9.21 (s, Ru-H, 1H). ¹³C NMR (C₆D₆, δ): 154.5 (m), 153.3 (m), 152.3, 142.8 (m), 134.3, 132.8, 132.3 (m), 132.0, 129.1, 128.3, 127.6, 127.4, 127.3, 19.4 (Ru-SiCH₃Ph). ²⁹Si NMR (THF-d₈, δ): 359.5 (s, Ru-*Si*MePh), 101.7 (q, J = 18 Hz). ³¹P NMR (C₆D₆, δ): 73.2.

Synthesis of $[SiP^{Ph}_{3}]Ru(H)(GePh_{2})$ (11). $[SiP^{Ph}_{2}P'^{Ph}]Ru$ -(0.10 g, 0.11 mmol) was dissolved in THF (7 mL) and cooled to -78 °C. Diphenylgermane (21 μ L, 0.11 mmol) was added via syringe, and the resulting dark red solution was warmed to room temperature. The solvent was removed, and recrystallization from layering pentane over a concentrated benzene solution yielded red crystals suitable for X-ray diffraction. The crystals were washed with pentane, crushed, and dried under vacuum to yield an analytically pure solid (0.93 g, 74%). ¹H NMR (C₆D₆, δ): 8.60 (d, J = 7.5 Hz, 3H), 7.3–6.9(m, 31H), 6.73 (t, J = 7.5 Hz, 7H), 6.58 (t, J = 7.5 Hz, 11H), -8.95 (s, 1H, Ru-H). ¹³C NMR (THF- d_8 , δ): 163.0, 155.1, 154.7, 152.3, 151.9, 142.6 (br), 133.5 (br), 132.5, 128.7, 128.3, 127.9, 127.6 (br), 127.5, 127.4. ³¹P NMR (C₆D₆, δ): 76.2 (br). Anal. Calcd for C₆₆H₅₃SiP_{3Ge}Ru: C, 69.49; H, 4.68. Found: C, 69.23; H, 4.53.

Synthesis of $[SiP^{Ph}_{3}]Ru(H)(H_{2})$ (12). $[SiP^{Ph}_{2}P'^{Ph}]Ru$ was charged into a J. Young tube and freeze – pump–thawed three times. Excess H₂ gas (1 atm) was introduced. Analysis by NMR indicated clean conversion to product. ¹H NMR (C₆D₆, δ): 8.58 (d, J = 7.5 Hz, 3H), 7.31–7.24 (m, 18H), 6.96 (t, J = 7.5 Hz, 3H), 6.77 (t, J = 7.5 Hz, 6H), 6.63 (t, J = 7.5 Hz, 12H), -4.23 (s, 3H, Ru-(H)(H₂)). ¹³C NMR (C₆D₆, δ): 155.6 (m), 150.3 (m), 140.7 (m), 133.2, 133.2, 133.1, 132.9, 129.1, 128.9, 128.7, 128.1, 127.9, 127.8. ³¹P NMR (C₆D₆, δ): 71.2.

Synthesis of $[SiP^{Ph}_{2}P^{Ph}-B(cat)]Ru(\mu-H)$ (14). $[SiP^{Ph}_{2}P'^{Ph}]Ru$ -(0.12 g, 0.13 mmol) was dissolved in THF (7 mL) and cooled to -78 °C. Catecholborane (14 µL, 0.13 mmol) was added via syringe, and the resulting orange solution was allowed to warm to room temperature. The solvent was removed, and crystals suitable for X-ray diffraction were grown from layering pentane over a concentrated benzene solution to yield orange crystals that analyzed as $[SiP^{Ph}_2P^{Ph}-BH(O_2C_6H_4)]Ru \cdot 1.5C_6H_6$ (0.10 g, 69%). These crystals were suitable for X-ray diffraction, and the solid-state structure shows the correct number of solvent molecules. ¹H NMR (C_6D_6 , δ): 8.43 (d, J = 7.5 Hz, 1H), 8.28 (d, J = 7.2 Hz, 1H), 8.14 (m, 2H), 7.98 (m, 2H), 7.72-7.60 (m, 2H), 7.21-6.00 (m, 38H), -6.24 (br, 1H, Ru-H-B). ¹¹B NMR (THF d_8, δ): 12 (br). ¹³C NMR (THF- d_8, δ): 157.8, 157.5, 157.;1, 156.8, 156.1, 154.6, 151.2, 150.9, 150.3, 149.9, 147.8, 147.4, 144.7, 144.5, 141.6, 141.3, 139.6, 139.3, 136.6, 136.5, 136.2 (d, *J* = 3.4 Hz), 136.1, 135.8, 134.8 (d, J = 3.0 Hz), 134.2 (d, J = 4.3 Hz), 134.0 (d, J = 3.9 Hz), 133.8 (d, J = 20.8), 133.5 (m), 133.2, 132.8 (d, J = 10.4 Hz), 132.7, 132.5 (d, J = 15.3 Hz), 132.2, 131.6 (d, J=3.4 Hz), 130.7, 130.5, 130.4, 130.3 (d, J=3.4 Hz), 129.8, 129.1

(d, *J* = 21.5 Hz), 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.5 (d, J = 8.9 Hz), 121.8, 119.0, 117.6, 113.5, 112.1, 108.6. ²⁹Si NMR (C₆D₆, δ): 75.7. ³¹P NMR (C_6D_6 , δ): 72.7 (dd, J = 20.0, 15.7 Hz), 63.8 (dd, J=233.0, 20.0 Hz), 54.1 (dd, J=233.0, 15.7 Hz). Anal. Calcd for $C_{69}H_{54}BO_2SiP_3Ru: C, 72.12; H, 4.74.$ Found: C, 72.48; H, 4.65. Synthesis of $[SiP^{Ph}_2P^{C6H3B(cat)}-B(cat)]Ru(\mu-H)$ (15). [Si- $P^{Ph_2}P'^{Ph}]Ru$ (0.10 g, 0.11 mmol) was dissolved in toluene (30 mL) and cooled to -78 °C. Biscatecholatodiboron (0.026 g, 0.11 mmol) was added in one portion, and the resulting orange solution was allowed to warm to room temperature. The solvent was removed, and the residue was recrystallized twice from layering pentane over a concentrated benzene solution to yield yellow crystals suitable for X-ray diffraction (0.081 g, 64%). ¹H NMR (THF- d_8 , δ): 8.50 (d, J = 7.5 Hz, 1H), 8.22 (d, J = 7.0 Hz, 1H), 8.10 (t, J=8.5 Hz, 2H), 8.00-7.95 (m, 2H), 7.76 (d, J=7.5 Hz, 1H), 7.71 (d, J=6 Hz, 1H), 7.43-5.81 (m, 40H), -6.25 (br, 1H). ¹¹B NMR (THF- d_8 , δ): 30 (br), 11(br). ¹³C NMR (THF- d_8 , δ): 156.5,156.2, 155.8, 155.6, 154.7, 151.1, 150.7, 149.9, 149.5, 149.2, 149.0, 148.5, 148.1, 144.7, 144.4, 144.7, 144.4, 142.4, 142.2, 141.8, 137.2, 137.1, 136.6, 136.5, 136.1, 135.8, 135.5, 135.4, 134.8, 134.5, 134.3, 134.2, 134.0, 133.7, 133.6, 133.4, 133.3, 133.2, 133.0, 132.9, 132.8, 132.2, 132.1, 130.8, 130.6,

130.5, 129.7, 129.5, 129.3, 128.9, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.0, 128.0, 127.9, 127.6, 127.6, 127.4, 127.1, 127.0. ³¹P NMR (THF- d_8 , δ): 72.6 (dd, J = 19.5 Hz, 16.1 Hz), 68.8 (dd, J = 232.8 Hz, 19.5 Hz), 54.8 (dd, J = 232.7 Hz, 16.1 Hz). Anal. Calcd for C₆₆H₄₉B₂O₄SiP₃Ru: C, 68.94; H, 4.30. Found: C, 69.02; H, 3.84.

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Supporting Information Available: X-ray crystallographic data, kinetic data, and NMR spectra for 4, 5, 8, 9, 10b, 12, and 13. This material is available free of charge via the Internet at http://pubs.acs.org.