Silylene Complexes of Late 3*d* Transition Metals Supported by *tris*-Phosphinoborate Ligands

Rex C. Handford,[®] Patrick W. Smith,[®] and T. Don Tilley*[®]

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1460, United States

Supporting Information

ABSTRACT: The complexes $[BP_3^R]MX$ ($[BP_3^R] = PhB-(CH_2PR_2)_3^-$, R = Ph, ⁱPr; M = Ni, Co, Fe; X = halide) were explored as platforms for generation of first-row metal silylene complexes. Direct silylation of $[BP_3^{Ph}]NiCl$ or $[BP_3^{iPr}]CoCl$ with (THF)₂LiSiHMes₂ resulted in formation of the silylene complexes $[BP_3^{Ph}]Ni(\mu-H)(SiMes_2)$ and $[BP_3^{iPr}]Co(\mu-H)-(SiMes_2)$, respectively. In contrast, $[BP_3^{iPr}]FeBr$ reacted with (THF)₂LiSiHMes₂ to produce the iron-alkyl $[BP_3^{iPr}]Fe(CH_2-2-(SiH_2Mes)-3,5-Me_2C_6H_2)$, a constitutional isomer of the



expected silyl or silylene complex. Preparation of the nickel benzyl complex $[BP_3^{Ph}]Ni(\eta^2-Bn)$ allowed for exploration of addition–elimination chemistry for access to silylene complexes from simple primary and secondary silanes. Heating toluene solutions of $[BP_3^{Ph}]Ni(\eta^2-Bn)$ in the presence of CySiH₃ resulted in the formation of a dimeric μ -silylene complex $[Ni(\mu-BP_2^{Ph})(\mu-SiHCy)]_2$. In the presence of 4-dimethylaminopyridine (DMAP), these conditions led to exclusive formation of the base-stabilized silylene complex $[BP_3^{Ph}]Ni(\mu-H)[SiHCy(DMAP)]$.

INTRODUCTION

To date, most reported silylene (SiR₂) complexes bear 4*d* and 5*d* transition-metal centers, while few 3*d*-metal silylene complexes have been reported.¹ These heavier-metal silylene complexes have served to develop synthetic methods to access M=Si linkages and have been instrumental in elucidating the electronic structures and reactivity patterns associated with multiple bonding between transition-metal centers and silicon.²⁻⁶ The M=Si linkage in these complexes can be accessed by abstraction of suitable leaving groups "X" bound to a silyl substituent,^{7,8} by α -H migration of a nearby Si-H bond to the metal center,⁹ or by extrusion of a silylene by direct reaction with a silane,^{3-5,10,11} among other methods (Scheme 1).^{1,6} The reactions of silylene complexes reflect substantial electrophilic character at silicon,¹² which in turn renders them prone to coordination by nucleophiles to generate base-stabilized silylene ligands.^{13,14} This electrophilicity also

Scheme 1. Some Methods To Access Transition-Metal Silylene Complexes



promotes silicon-centered hydrosilylation catalysis by silylene complexes.^{1,12,15,16}

In contrast to the well-known 4d- and 5d-metal silvlenes,¹ there is a paucity of analogous compounds based on first-row metals. This difference might be in part due to the diminished ability of 3d-metal centers to stabilize silvlene fragments, whereas the valence 4d and 5d orbitals have a large radial extension and can therefore participate in significant π -bonding stabilization of the SiR₂ fragment. The smaller 3d orbitals are less available to engage in this interaction. One consequence of this effect is the tendency of documented 3d-metal silvlenes to undergo further stabilization by interaction of M-H bonds with the electrophilic silicon center, as demonstrated in complexes such as $[BP_3^{iPr}]FeH(\eta^3-H_2SiMeR)$,¹⁷ [(dtbpe)Ni- $(\mu-H)(SiMes_2)$]⁺,¹⁸ and Cp*Fe(ⁱPr₂PMe)(H)(μ -H)(SiRR').¹⁹ Such stabilizing interactions have also been demonstrated for 4*d*-metal complexes (e.g., $[Cp*Ru(^{i}Pr_{3}P)(\mu-H)_{2}(SiRR')]^{+})$,¹⁵ albeit to a lesser extent, and such interactions are further diminished in related 5*d*-metal complexes (e.g., Cp*Os(^{*i*}Pr₃P)-(H)(=SiHTrip); Trip = 2,4,6-triisopropylphenyl).¹⁹⁻²¹ Both IR and NMR spectroscopies are consistent with the interpretation that (M)H-Si bonding decreases as Fe > Ru > Os. The lower ability of 3d metals to stabilize SiR₂ fragments might result in enhanced electrophilicity at silicon that may be exploited to promote more facile coordination of hydrosilvlation substrates to the silvlene ligand.

Silylene complexes of the late 3d transition metals were targeted in order to develop further insight into their

Received: August 31, 2018



properties and potential reactivity; late, low-valent transition metals appear to be effective in supporting the reactive M=Si linkage.^{1,12} Our investigations therefore focused on iron-, cobalt-, and nickel-based complexes of $[BP_3^R]$ ligands ($[BP_3^R = PhB(CH_2PR_2)_3^-$; R = Ph, ⁱPr). The preparation of silylene complexes based on these $[BP_3^R]M$ scaffolds, as well as their unique structural and spectroscopic properties, is detailed herein.

RESULTS AND DISCUSSION

First-row metal complexes stabilized by the $[BP_3^R]$ ligand scaffold were selected as convenient starting materials for derivatization with silyl anion sources and silanes. The sterically encumbering and strongly electron-donating coordination environment provided by the $[BP_3^R]$ ligand stabilizes reactive, low-valent 3*d*-metal complexes.²² Also, the readily prepared $[BP_3^R]MX$ (M = Mn, Fe, Co, Ni; X = halide) starting materials have served as useful precursors to an array of unusual late first-row metal complexes in a variety of oxidation states.^{22–25}

Direct Silylation of [BP₃^R]MX Complexes. Reactions with [BP₃^{Ph}]NiCl were initially explored with the goal of forming closed-shell 18 electron compounds that would be amenable to NMR characterization and analysis. The silyl anion reagent (THF)2LiSiHMes226 was employed for convenient installation of -SiHMes₂ into [BP₃^R]M platforms, where α -H-migration or hydride abstraction chemistry might be expected to generate a silvlene ligand. Thus, addition of (THF)₂LiSiHMes₂ to a toluene solution of [BP₃^{Ph}]NiCl resulted in a color change from green to dark purple, and the ³¹P{¹H} NMR spectrum of the reaction mixture indicated the formation of a single major product ($\delta_{\rm P}$ = 20.0 ppm). Single-crystal X-ray diffraction analysis of crystals of this complex grown from a saturated toluene solution layered with pentane at -30 °C reveals the product to be $[BP_3^{Ph}]Ni(\mu$ -H)(SiMes₂) (1; eq 1).



The solid-state molecular structure reveals the coordinated P and Si atoms in an approximately tetrahedral arrangement about the Ni center (Figure 1). A hydride bridging the Ni and Si centers was located in the Fourier difference map and freely refined. Complex 1 possesses a Ni–Si bond distance of 2.1415(5) Å, (cf. [(dtbpe)Ni(μ -H)(SiMes₂)]⁺; $d_{(Ni-Si)} = 2.147(2)$ Å).¹⁸ The Ni, Si, and *ipso*-C atoms of the Mes groups lie in a plane ($\Sigma(\angle) = 359^{\circ}$ about Si), while the bridging hydride lies above this plane along the Ni–Si bond vector.

The ¹H NMR resonance for the bridging hydride of 1 in benzene- d_6 (at -6.22 ppm) is a quartet due to coupling to phosphorus (² J_{HP} = 11.7), with satellites for coupling to silicon (¹ $J_{(Ni)H-Si}$ = 70 Hz). The latter coupling constant is larger than that for [(dtbpe)Ni(μ -H)(SiMes₂)]⁺ (¹ $J_{(Ni)H-Si}$ = 43 Hz; dtpbe = ¹Bu₂PCH₂CH₂P^tBu₂), indicative of a greater bonding interaction between Si and the bridging hydride. The ²⁹Si-¹H HMBC NMR spectrum of 1 shows correlation between the upfield hydride resonance and a silicon resonance



Figure 1. Solid-state molecular structure of 1. Thermal ellipsoids are drawn at 50% probability. Most H atoms and all carbon atoms of the molecule's arene rings, with the exception of the *ipso*-C atoms, are omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1–Si1: 2.1415(5), Fe1–H1: 1.58(2), Si1–H1: 1.56(2), Fe1–P1: 2.2564(4), Fe1–P2: 2.1773(5), Fe1–P3: 2.2866(4), Ni1–H1–Si1: 85.7(12), Ni1–Si1–C1: 120.33(5), Ni1–Si1–C2: 126.69(5), C1–Si1–C2: 112.38(7), B1–Ni1–Si1: 164.66(3).

at 192.2 ppm; this chemical shift is similar to those of silylene and η^3 -silane complexes reported in the literature.^{1,13,17-19} While the solid-state and solution spectroscopic properties of **1** are consistent with silylene character in the Ni–Si linkage, a Si–H bonding interaction is still clearly present. Thus, **1** is also an example of "arrested" α -migration of the hydride from the silicon atom to the metal center, as observed in [(dtbpe)Ni(μ -H)(SiMes₂)]^{+,18} The singlet observed in the ³¹P{¹H} NMR spectrum at 20.0 ppm indicates that the three phosphorus donor atoms of the [BP₃^{Ph}] ligand are equivalent in solution at room temperature, likely as the result of an intramolecular dynamic process.

Given this success with the $[BP_3^{Ph}]$ NiCl system and its silylation with $(THF)_2$ LiSiHMes₂, silylations of the corresponding $[BP_3^R]MX$ (M = Fe, Co) complexes were examined. Initial investigations focusing on reactions of $[BP_3^{Ph}]MX$ (M =Fe, X = Br; M = Co, X = I) with $(THF)_2$ LiSiHMes₂ were not fruitful, and in all cases resulted in complex, intractable product mixtures. Suspecting that this may be a result of the relatively diminished electron-donating ability of $[BP_3^{Ph}]$ and the resulting instability of electronically unsaturated $[BP_3^{Ph}]Fe^{II}$ and $[BP_3^{Ph}]Co^{II}$ complexes, attention was turned to complexes of $[BP_3^{IPr}]$. In the past, this more donating *tris*phosphinoborate ligand has been observed to stabilize highly electronically and coordinatively unsaturated metal complexes that were inaccessible using the $[BP_3^{Ph}]$ congener.^{22,23,25} Also, the greater steric protection afforded by the ⁱPr groups over Ph should help stabilize reactive metal centers containing silylene ligands.²²

Treatment of a pentane suspension of $[BP_3]^{iPr}]CoCl$ with 1 equiv of $(THF)_2LiSiHMes_2$ at -30 °C resulted in a gradual color change from aquamarine to purple (eq 2). The ¹H NMR spectrum of the product mixture indicated formation of a paramagnetic product, along with trace amounts of Mes_2SiH₂ and (Mes_2SiH)₂. Maintenance of (Me_3Si)_2O solutions of the reaction mixture at -30 °C for 2 weeks resulted in precipitation of the silane byproducts, leaving behind a dark purple complex in solution in spectroscopically pure form. The ¹H NMR spectrum of this species revealed 11 broadened and shifted resonances consistent with a paramagnetic complex formulated as $[BP_3]^{iPr}]Co(SiHMes_2)$ or $[BP_3]^{iPr}]Co(\mu-H)$ -(SiMes₂) (2). The low isolated yield (28%) of 2 could be the result of various 1-electron processes resulting in

disproportionation of the starting materials, as indicated by the formation of Mes₂SiH₂ and (Mes₂SiH)₂. An Evans method measurement of 2 revealed a magnetic moment of 1.5 $\mu_{\rm B}$, which is closest to that expected for an S = 1/2 complex and most consistent with the 17-electron silylene complex $[BP_3^{iPr}]Co(\mu-H)(SiMes_2)$ (2), since all reported 15-electron complexes of the type $[BP_3^{iPr}]CoX$ (X = Cl, I) have been found to possess quartet ground states at room temperature,²² likely the spin state that would be adopted by the hypothetical silvl complex [BP₃^{iPr}]Co(SiHMes₂). The IR spectrum of 2 contains a medium-intensity absorption band at 1604 cm⁻¹, which is similar in frequency to the Ni(μ -H)Si band in the IR spectrum of 1 ($\nu = 1602$ cm⁻¹). This suggests closely related $M(\mu-H)$ Si bonding for both complexes (M = Co, Ni). Unfortunately, crystals suitable for X-ray diffraction analysis were not obtained, due to the extremely high solubility of 2 in all solvents tested. In the absence of such data, the molecular structure assigned to 2 must remain somewhat tentative.



As for the $[BP_3^{R}]Fe^{II}$ systems, previous investigations of these complexes have concluded that species of the type $[BP_3^{iPr}]$ FeSiR₃ (R = SiMe₃, Ph) can be readily prepared by metathesis of the Fe-Br bond in [BP3^{iPr}]FeBr with KSi- $(SiMe_3)_3$ or $[(THF)_3Li]SiPh_3$, respectively.²⁷ A complex originally formulated as [BP3^{iPr}]Fe(SiHMes2) was also prepared, but its solid-state molecular structure was not determined. To interrogate the nature of the Fe-Si bond, and to compare its bonding metrics relative to the nickel congener 1, this complex was again prepared with the goal of obtaining crystalline material suitable for single-crystal X-ray diffraction analysis. Surprisingly, the structure obtained from X-ray studies of single crystals of "[BP₃^{iPr}]Fe(SiHMes₂)" was not that of the expected iron silyl complex, but rather that of the isomeric iron benzyl complex $[BP_3^{iPr}]$ Fe $(CH_2-2-(SiH_2Mes)-3,5-Me_2C_6H_2)$ (3, eq 3; Figure 2).



No Fe–Si bond is apparent in the solid-state structure of 3 $(d_{(Fe-Si)} = 4.5503(10) \text{ Å})$, and both hydrogen atoms bound to the Si atom were located in the Fourier difference map and isotropically refined. On the basis of this structure, the original spectroscopic data reported for " $[BP_3^{Pr}]Fe(SiHMes_2)$ " can be better rationalized. The solution magnetic moment of 4.81 μ_B corresponding to an S = 2 ground state is consistent with a tetrahedrally coordinated high-spin d^6 metal center, and the Si–H stretching frequency of 2151 cm⁻¹ is typical for silanes. The rearrangement of the initial Fe–Si bond to the Fe–C bond present in 3 is unexpected, given that bond strengths for the former are typically greater than for the latter, though Fe–Si to Fe–C rearrangements have been observed in the



Figure 2. Solid-state molecular structure of **3**. Most H atoms have been omitted, and isopropyl- and phenyl-groups of the $[BP_3^{\cdot Pr}]$ ligand have been truncated for clarity. Fe1–C1: 2.062(3), Fe1–S1: 4.5503(10), C1–H1: 0.91(3), C1–H2: 0.93(3), Si1–H3: 1.40(3), Si1–H4: 1.42(3), Fe1–P1: 2.4733(8), Fe1–P2: 2.4257(8), Fe1–P3: 2.4806(7), B1–Fe1–C1: 167.99(10).

literature.²⁸ At present, it remains unclear what the driving force for this transformation is, though it is possible that the reduction in steric interactions during the conversion of " $[BP_3]^{Pr}$]Fe(SiHMes₂)" into 3 is a major factor.

Reactions of [BP_3^{R}]Ni^{II} Complexes with Silanes. $[BP_3^{R}]MR$ complexes (R = alkyl, aryl) were examined to evaluate whether silyl and silylene complexes could be generated by direct reaction with primary and secondary silanes through the release of R-H with formation of a new M– Si bond. Initially, $[BP_3^{Ph}]Ni(Bn)$ (4; Bn = benzyl) was targeted, envisioning its use in addition–elimination reactivity with silanes. Treatment of $[BP_3^{Ph}]NiCl$ with 0.5 equiv of $Bn_2Mg(THF)_2$ afforded a magenta-colored solid following precipitation from a saturated THF solution of the reaction mixture with pentane. Multinuclear NMR spectroscopy of benzene- d_6 solutions of the solid indicated the formation of a diamagnetic complex whose spectroscopic features are consistent with those expected for complex 4 (eq 4).



As with 1, the ³¹P{¹H} NMR spectrum of 4 at room temperature contains only a sharp singlet corresponding to the three phosphorus nuclei of the $[BP_3^{Ph}]$ ligand, indicative of approximate $C_{3\nu}$ symmetry in solution. The η^2 -coordination of the benzyl ligand in 4, with net donation of three electrons, has been documented in the literature,²⁹ and in this case likely results from steric crowing about the metal center resulting from the Ph-substituents of the $[BP_3^{Ph}]$ ligand which precludes η^3 -coordination. Consistent with this, the solid-state structure of 4 (Figure 3) shows Ni–CH₂ and Ni–C_{ipso} distances of 1.982(2) and 2.226(3) Å, while the nonbonding Ni–C_{ortho} distances are 2.644(3) and 3.149(3) Å.

Mixtures of 4 and a secondary silane (1 equiv of Ph_2SiH_2 , Mes₂SiH₂, or Cy₂SiH₂) in benzene- d_6 underwent no reaction, even after several hours at temperatures up to 100 °C. In contrast, the primary silanes PhSiH₃ and CySiH₃ reacted with 4 at 65 °C in benzene- d_6 to produce 1 equiv of toluene, as indicated by ¹H NMR spectroscopy. In the case of PhSiH₃,



Figure 3. Solid-state molecular structure of 4. Thermal ellipsoids are drawn at 50% probability. Most H atoms and all carbon atoms of the Ph rings on the $[BP_3^{Ph}]$ ligand, with the exception of the *ipso*-C atoms, are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–C1: 1.982(2), Ni1–C2: 2.226(3), C1–C2: 1.455(4), Ni1–C3: 2.644(3), Ni1–C7: 3.149(3), C1–H1: 0.91(3), C1–H2: 0.94(3), Ni1–P1: 2.2302(8), Ni1–P2: 2.2325(8), Ni1–P3: 2.2490(7). Ni1–C1–C2: 79.10(15), Ni1–C2–C1: 60.95(14), B1–Ni1–C1: 135.80(9), B1–Ni1–C2: 175.74(8).

monitoring of the reaction mixture by ¹H NMR spectroscopy indicated intermediate formation of hydride-containing products, as evidenced by the appearance of several upfield multiplets. Unfortunately, these species decayed over time even as the amount of evolved toluene increased. The ¹H NMR spectrum of the dark-brown colored final reaction mixture after 4 h at 65 °C indicated a complex mixture, with small quantities of the redistribution products Ph₂SiH₂ (27% yield) and trace PhSiH₃ being the only tractable species (no SiH₄ was evident in the ¹H NMR spectrum).

In contrast, the reaction of 4 with an excess of CySiH₃ at 65 °C for 5 h (eq 5) produced a dark brown solution which, following removal of the solvent and subsequent ether washes, yielded a purple powder whose ¹H and ³¹P{¹H} NMR spectra in benzene-*d*₆ indicated the presence of a single diamagnetic product bearing a hydride resonance at -7.17 ppm. Recrystallization of the complex from THF layered with pentane at -30 °C provides small single-crystals suitable for X-ray diffraction analysis. The molecular structure (Figure 4) reveals a dinuclear nickel silylene complex, [Ni(μ -BP₂^{Ph})(μ -SiHCy)]₂ (5; [BP₂^{Ph}] = PhB(CH₂PPh₂)₂) wherein the metal centers are bridged by SiHCy and [BP₂^{Ph}] ligands.



Complex 5 possesses a diamond-shaped Ni₂Si₂ core, with two of the opposing Ni–Si bonds being bridged by hydride ligands. The Ni–Si distances ($d_{(Ni(\mu-H)Si)} = 2.2104(8)$ Å and $d_{(Ni-Si)} = 2.1800(8)$ Å) are shorter than those found in the related nickel μ -silylene [(depe)Ni(HSi(2-H₂Si-C₆H₄))]₂ ($d_{(Ni-Si)} = 2.210(1)$ Å; depe = 1,2-bis(diethylphosphino)ethane).³⁰ Solution NMR spectra of 5 in benzene- d_6 are



Figure 4. Solid-state molecular structure of **5**. Thermal ellipsoids are drawn at 50% probability. Most H atoms and all carbon atoms of the Ph rings on the $[BP_2^{Ph}]$ ligands, with the exception of the *ipso*-C atoms, are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–Si1: 2.1800(8), Si1–Ni1': 2.2104(8), Ni1–H1: 1.53(3), H1–Si1': 1.73(3), Ni1–P1: 2.1753(7), Ni1–P2': 2.2277(7), Ni1–Ni1': 2.6825(6), Ni1–Si1–Ni1': 75.33(3), Ni1–Si1–H1': 118.2(9), Ni1'-H1'-Si1: 85.7(13), P1–Ni1–P2': 127.89(3).

consistent with a C_i -symmetric complex, suggesting that the dimeric structure is conserved in solution. The ¹H NMR spectrum of 5 contains a multiplet corresponding to the bridging hydride ligand at -7.17 ppm and another resonance belonging to the cyclohexyl methine proton at 2.03 ppm. A cross-peak between both resonances and a ²⁹Si nucleus is observed at 220.9 ppm in the ²⁹Si-¹H HMBC NMR spectrum. The moderate coupling constant $({}^{1}J_{(Ni)H-Si} = 52 \text{ Hz})$ for the bridging hydride indicates a diminished H-Si interaction relative to 1, possibly indicating that 5 has progressed further along the reaction coordinate for the α -H migration. Thus, the degree of Si-H bond activation in 5 suggests that the complex is intermediate between μ -silylene and μ -silylyne descriptions. The ³¹P{¹H} NMR spectrum of 5 exhibits resonances consistent with an AA'BB' spin system (Figure S1); using the same numbering scheme presented in Figure 4, nuclei P1/ P1' and P2/P2' comprise the two sets of nuclei that are mutually chemically inequivalent, thereby giving rise to the observed coupling.

Given the moderate isolated yield of **5** (46%), the reaction of **4** with CySiH₃ was monitored by ¹H NMR spectroscopy. Integration against an internal standard of Si(SiMe₃)₄ showed formation of 1 equiv of toluene relative to the starting material, which was consumed after 5 h at 65 °C, indicating that the addition–elimination reaction to form toluene is quantitative. However, the fate of the CH₂PPh₂ side arm formally lost in the conversion of **4** to **5** remains unknown, and no MePPh₂ was observed in the ³¹P{¹H} NMR spectrum of the reaction mixture at any point during the thermolysis. Any MePPh₂ generated in the reaction mixture may have been quickly consumed by other reactive species, contributing to the low yield of **5**.

The thermolysis of complex 4 in the presence of $CySiH_3$ and 4-dimethylaminopyridine (DMAP) was examined, to potentially trap a coordinatively unsaturated monomeric complex. Maintenance of a mixture containing 4, an arbitrary excess of $CySiH_3$ (6 equiv), and 1 equiv DMAP in toluene at 80 °C for 6 h resulted in precipitation of a bright yellow flocculent solid. The ¹H NMR spectrum of the final reaction mixture in the

presence of an internal standard (Si(SiMe₃)₄) indicated that 1 equiv of CySiH₃ was consumed with concomitant evolution of 1 equiv of toluene. Though the yellow powder isolated from the reaction mixture was insoluble in pentane, ether, and arenes, it was highly soluble in THF. Thus, single-crystal X-ray diffraction analysis of crystals of the complex grown by vapor diffusion of ether into a concentrated THF solution at $-30 \,^{\circ}$ C over several days reveals that this complex can be formulated as the base-stabilized silylene complex [BP₃^{Ph}]Ni(μ -H)[SiHCy-(DMAP)] (6, eq 6).



The solid-state molecular structure of **6** (Figure 5) possesses a Ni–Si distance of 2.173(2) Å, which is between the



Figure 5. Solid-state molecular structure of **5.** Thermal ellipsoids are drawn at 50% probability. All carbon atoms of the Ph rings on the [BP₃^{Ph}] ligand, with the exception of the *ipso*-C atoms, are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–Si1: 2.1731(15), Si1–H1: 1.51(5), Si1–N1: 1.908(5), Ni1–P1: 2.2016(13), Ni1–P2': 2.2235(13), Ni1–P3: 2.1694(11), B1–Ni1–Si1: 149.13(9).

corresponding values found in complexes 1 and 5. The Ni-Si linkage in 6 is highly distorted away from the Ni-B axis $(\theta_{(Si-Ni-B)} = 149.13(9)^{\circ})$, in contrast to the nearly linear Si– Ni-B unit observed in 1. This distortion is due to steric interactions between the silicon-bound DMAP and the Ph substituents of the [BP3^{Ph}] ligand, which would be brought into close contact for Si-Ni-B angles approaching 180°. Though the presence of a nickel-bound hydride ligand could not be confirmed crystallographically, the ¹H NMR spectrum of **6** in THF- d_8 exhibits a resonance at -7.85 ppm (${}^{1}J_{(Ni)H-Si} =$ 28 Hz) corresponding to the Ni-H nucleus. This spectrum also displays a Si-H resonance at 5.10 ppm (${}^{1}J_{SiH} = 173.0$ Hz). Both Ni-H and Si-H nuclei exhibit coupling to a silicon nucleus at 53.4 ppm in the ²⁹Si-¹H HMBC NMR spectrum of 6, indicating that the hydride ligand interacts with the silicon center in a manner similar to those in complexes 1 and 5. However, the diminished value of the (Ni)H-Si coupling constant for this interaction $({}^{1}J_{(Ni)H-Si} = 28 \text{ Hz})$ relative to

related parameters for 1 and 5 (${}^{1}J_{(Ni)H-Si} = 70$, 52 Hz, respectively) suggests that the strength of the bridging hydride-silicon interaction is diminished in 6.

A probable mechanism for the formation of 6 (Scheme 2) involves oxidative addition of a Si-H bond in $CySiH_3$ to give

Scheme 2. Possible Mechanism for the Formation of Proposed Intermediate C, and Further Reactivity of C To Form Complexes 5 and 6 ($[Ni] = [BP_3^{Ph}]Ni$)



 $[BP_3^{Ph}]Ni(H)(Bn)(SiH_2Cy)$ (A). As thermolysis of a C_6D_6 solution containing only 4 and DMAP did not result in the consumption of either species, it is likely that Si–H activation in the presence of CySiH₃ initiates the reaction leading to 6. Next, elimination of toluene from A leads to the transient generation of $\{[BP_3^{Ph}]Ni(SiH_2Cy)\}$ (B), which then rapidly isomerizes via partial α -migration to $[BP_3^{Ph}]Ni(\mu-H)(SiHCy)$ (C). The evolution of toluene during the course of this reaction is quantitative, as determined by ¹H NMR spectroscopy in the presence of an internal standard (Si(SiMe_3)_4). The electrophilic silylene moiety of C is trapped in the presence of DMAP to give 6 as the final product. In the absence of DMAP, C is a potential intermediate for the formation of 5, though the mechanism of the remaining steps leading to 5 remain elusive.

An examination of the reactivity of 6 with several unsaturated organic substrates demonstrated that the Si-H bond is not prone toward direct insertions. Thermolysis of THF solutions of 6 in the presence of 1-octene, 3-hexyne, benzophenone, or benzaldehyde at 40-50 °C for 1 h did not result in any consumption of the starting materials. Evidently, the strong binding of DMAP inhibits the coordination of an unsaturated substrate, a step that precedes Si-H insertion in related complexes.¹² The lack of electrophilic character at silicon is also consistent with the ²⁹Si chemical shift of 6 (53.4 ppm), which is substantially upfield from the region commonly observed for silvlene complexes (~150-400 ppm),¹ and is similar to those commonly observed for metal-silyl complexes (-100 to 100 ppm).¹⁰ Previous reports of base-stabilized silvlene complexes have indicated substantial sp^3 (i.e., silvl) character at silicon and M-Si single-bond character;¹ the aforementioned properties of 6 are consistent with this characterization.

A closely related complex to **6** bearing a Si-coordinated 4morpholinopyridine (MorPy) ligand, $[BP_3^{Ph}]Ni(\mu-H)[SiHCy-(MorPy)]$ (**6**'), was also prepared. As DMAP is more basic than MorPy (p $K_a = 10.06, 9.01$, respectively),³¹ thermolysis of **6'** in the presence of DMAP might be expected to furnish **6**. However, heating of a benzene- d_6 solution containing **6'** and 1 equiv of DMAP at 70 °C for 1 h did not result in any conversion of **6'** to **6**; heating to 100 °C resulted only in the partial decomposition of **6'** to release unbound MorPy as the only tractable product, with no consumption of DMAP. Likewise, no reaction was observed following thermolysis of a THF- d_8 solution of **6** in the presence of MorPy (3 equiv) at 70 °C for 1 h. The substantial silyl characters of **6** and **6'** are likely responsible for the substitutional inertness of the coordinated Lewis bases.

CONCLUDING REMARKS

The complexes described here illustrate the general utility of α -H migration steps in forming first-row metal-silylene complexes, even with high-spin metal centers. Both an anionic silyl source and a hydrosilane have proven to be useful precursors for introduction of silylene-type ligands. The residual M–H…Si interactions observed in some of these complexes further emphasize a growing theme for 3*d*-metal silylene complexes, in that hydride ligands can be important for stabilization of reactive silylene moieties. With respect to the $[BP_3^{R}]$ scaffolds, investigations targeting cobalt and iron complexes indicate that the $[BP_3^{iPr}]$ ligand enables access to silylene and alkyl complexes that could not be generated with the less sterically protecting $[BP_3^{Ph}]$ ligand. Future efforts will focus on the influence of such ancillary ligands on 3*d*-metal silylene reactivity.

EXPERIMENTAL SECTION

All manipulations were carried out using standard Schlenk techniques or in inert atmosphere gloveboxes filled with dry dinitrogen. Solvents were stored over molecular sieves (4 Å) after collection from a JC Meyers Phoenix solvent purification system. Benzene- d_6 was degassed with 3 freeze-pump-thaw cycles and stored over activated molecular sieves (4 Å) for 1 d prior to use. The compounds Tl[BP₃^{Ph}],³² $(THF)Li[BP_{3}^{Pr}]$, ²⁷ $[BP_{3}^{Ph}]NiCl$, ²⁴ $[BP_{3}^{Pr}]FeBr$, ²⁷ $Bn_{2}Mg(THF)_{2}$, ³³ $(THF)_{2}LiSiHMes_{2}$, ²⁶ $CySiH_{3}$, ³⁴ and $[BP_{3}^{Pr}]Fe(CH_{2}-2-(SiH_{2}Mes) 3,5-Me_2C_6H_2$ ²⁷ (3) were prepared according to literature procedures. The purity of 3 following purification via recrystallization was verified by ¹H NMR spectroscopy, which indicated the exclusive formation of one species (3) whose spectroscopic features are identical to those reported previously.²⁷ The NMR spectra were recorded on Bruker Avance 400, 500, and 600 MHz spectrometers, and spectra were referenced to solvent residual signals (¹H, ¹³C),³⁵ or to external references (³¹P, ¹¹B, ²⁹Si). The IR spectra were collected on a Bruker Vertex spectrometer, with samples prepared as Nujol mulls sandwiched between NaCl plates; absorption bands in spectra that are masked by peaks for Nujol are not reported.

 $[BP_3^{Ph}]Ni(\mu-H)(SiMes_2)$ (1). In a glovebox, a 20 mL vial was charged with [BP3^{Ph}]NiCl (0.045 g; 0.058 mmol), a stir bar, and toluene (2 mL). The contents of the vial were then rapidly stirred to afford a clear emerald solution, and then chilled to -30 °C. Separately, a solution of (THF₂)LiSiHMes₂ (0.024 g; 0.058 mmol) in toluene (1.5 mL) was prepared, and also chilled to -30 °C. At this temperature, the (THF₂)LiSiHMes₂ solution was added to the stirred [BP₃^{Ph}]NiCl solution dropwise over 2 min, resulting in a color change to dark purple. The mixture was stirred for a further 5 min, and then the volatile components were removed in vacuo. The dark purple paste was suspended in pentane (4 mL), affording a purple solution containing suspended brown solids. Toluene (1.5 mL) was added to increase the solubility of 1 in the extracts. The mixture was filtered through Celite $(0.5 \times 3 \text{ cm})$ to afford a dark purple solution, and the reaction mixture was washed further with pentane $(3 \times 2 \text{ mL})$. The clear purple washes were also filtered. The volatile components of the

combined filtrate were removed in vacuo to produce 1 as an analytically pure purple solid. Yield: 0.027 mg; 46%. Crystals of 1 suitable for single-crystal X-ray diffraction analysis were grown by layering a concentrated toluene solution of the complex with pentane, and maintaining the mixture at -30 °C for 18 h. ¹H NMR (400 MHz, benzene- d_6): $\delta - 6.22$ (q, ${}^{2}J_{HP} = 12$ Hz, ${}^{1}J_{(Ni)H-Si} = 70$ Hz, 1H, μ -H), 1.95 (d, ${}^{2}J_{HP} = 3.50$, 6H, PhB(CH₂PPh₂)₃), 2.07 (s, 6H, Mes para-CH₃), 2.28 (s, 12H, Mes ortho-CH₃), 6.65 (s, 4H, Mes meta-H), 6.75 $(t, {}^{3}J_{HH} = 7.2 \text{ Hz}, 12\text{H}, PPh_{2} \text{ meta-H}), 6.84 (t, {}^{3}J_{HH} = 7.4 \text{ Hz}, 6\text{H},$ PPh₂ para-H), 7.24 (m, 1H, BPh para-H), 7.36 (t, J = 7.2 Hz, 12H, PPh_2 ortho-H), 7.66 (t, ${}^{3}J_{HH} = 7.4$ Hz, 2H, BPh meta-H), 8.18 (d, ${}^{3}J_{HH}$ = 6.4 Hz, 2H, BPh ortho-H). ¹³C NMR (151 MHz, benzene- d_6) δ 20.2 (m, PhB(CH₂PPh₂)₃) 21.0 (Mes para-CH₃), 24.6 (Mes ortho-CH₃), 124.1 (s), 125.5 (s), 128.2 (s), 128.4 (s), 129.4 (s), 132.1 (s), 132.5 (d, ${}^{2}J_{CP}$ = 4.2 Hz), 132.5 (d, ${}^{2}J_{CP}$ = 4.9), 137.7 (s), 139.8 (s), 140.5 (m), 141.0 (m), 141.5 (s), 145.1 (s). ${}^{31}P{}^{1}H$ NMR (160 MHz, benzene- d_6): δ 20.0 (s). ¹¹B NMR (193 MHz, benzene- d_6): δ -13.6 (s). ²⁹Si–¹H HMBC NMR (500 MHz; 99 MHz, benzene- d_6): δ 192.2. Anal. Calcd for C₆₃H₆₄BNiP₃Si: C, 74.79; H, 6.40. Found: C, 74.46; H, 6.40. IR (cm⁻¹): 1602 (m), 1584 (m), 1433 (s), 1307 (w), 1263 (w), 1158 (m), 1091 (s), 1027 (m), 919 (m), 891 (m), 861 (m), 740 (s), 697 (s), 619 (m), 603 (m).

[BP₃^{iPr}]CoCl. In a glovebox, (THF)Li[BP₃^{iPr}] (0.181 g; 0.32 mmol) was loaded into a 20 mL vial and dissolved in THF (5 mL). Separately, another 20 mL vial was charged with $CoCl_2$ (0.043 g; 0.33 mmol), THF (2 mL), and a stir bar. Both mixtures were chilled to -30 °C, and at this temperature, the clear, colorless solution of (THF)Li[BP₃^{iPr}] was added dropwise to the rapidly stirred suspension of CoCl₂. Over the course of 4 h, the mixture became a dark, clear aquamarine color with some suspended CoCl₂ settling out of solution. The reaction mixture was dried in vacuo to produce a dark blue paste, which was subsequently extracted into toluene (3×2) mL) and filtered through Celite (0.5×2 cm). The filtrate was dried in vacuo, and the resulting solid was crystallized by layering a saturated toluene solution with pentane, and maintaining the mixture at -30 °C for 18 h, depositing dark blue blocks of $[BP_3^{iPr}]CoCl$. Yield: 0.147 g; 87%. The spectroscopic properties of this complex are consistent with those reported in the literature.²²

 $[BP_3^{iPr}]Co(\mu-H)(SiMes_2)$ (2). In a glovebox, a 20 mL vial was charged with [BP₃^{iPr}]CoCl (0.028 g; 0.048 mmol) and a stir bar. The powder was suspended in pentane (5 mL), and the resulting aquamarine suspension was chilled to -30 °C. At this temperature, solid (THF)₂LiSiHMes₂ (0.020 g; 0.048 mmol) was added to the suspension, causing the reaction mixture to change to a purple color with suspended brown solids after 3 min. The reaction mixture was stirred for a further 30 min, and then filtered through Celite (0.5×2 cm) to afford a clear purple filtrate, which was dried in vacuo to give a sticky purple solid. The residue was again extracted in pentane (5 mL), and filtered through Celite (0.5 \times 1 cm). The clear purple filtrate was dried in vacuo, and the sticky purple oil was redissolved in $(Me_3Si)_2O$ (2 mL). The resulting solution was maintained at -30 °C for 2 weeks to induce the deposition of small colorless crystals, presumably the silane byproducts (Mes₂SiH₂ and (Mes₂SiH)₂). A final filtration of the purple solution through a glass wool plug afforded 2 as a sticky purple oil after drying in vacuo. Yield: 0.011 g; 28%. ¹H NMR (500 MHz; benzene- d_6): δ –2.68 (v br), 2.16 (s), 2.20 (s), 2.38 (s), 3.14 (s), 6.05 (s), 6.36 (s), 7.64 (s), 8.04 (s), 8.81 (br), 13.6 (br). μ_{eff} (Evans method; benzene- d_6): 1.5 μ_{B} . Anal. Calcd for C45H76BCoP3Si: C, 66.91; H, 9.48. Found: C, 68.51; H, 9.08. The inaccurate elemental analysis of oily samples of 4 is presumably due to the tenacious retention of (Me₃Si)₂O solvent molecules, as indicated by ¹H NMR analysis of samples of the complex. IR (cm^{-1}) : 1604 (m), 1551 (w), 1412 (w), 1288 (w), 1261 (w), 1241 (w), 1154 (w).

 $[BP_3^{Ph}]Ni(\eta^2-Bn)$ (4). In a glovebox, a 20 mL vial was charged with $[BP_3^{Ph}]NiCl$ (0.097 g; 0.12 mmol), a stir bar, and toluene (5 mL). The contents of the vial were then rapidly stirred to afford a clear emerald solution of $[BP_3^{Ph}]NiCl$. To this was added a toluene (1 mL) solution of $Bn_2Mg(THF)_2$ (0.022 g; 0.063 mmol) dropwise over 2 min. A clear magenta-colored reaction mixture resulted, which became cloudy after 2 min. After being allowed to stir for another

5 min, the volatile components of the reaction mixture were removed in vacuo to produce a shiny magenta solid. The solid was redissolved in THF (3 mL) and rapidly stirred to give a clear magenta solution. A THF (1 mL) solution of 1,4-dioxane (0.023 g; 0.26 mmol) was added in one portion to the reaction mixture, which was stirred for a further 30 min and then filtered through Celite $(0.5 \times 3 \text{ cm})$ to give a clear magenta filtrate. The volume of the filtrate mixture was reduced in vacuo to 3 mL and subsequently layered with pentane (9 mL). This mixture was maintained at -30 °C for 1 d to induce the deposition of 4 as an analytically pure microcrystalline magenta solid. Yield: 0.084 g; 73%. Crystals of 4 were grown from a saturated toluene solution of 4 which was layered with pentane and stored at room temperature for 2 d. ¹H NMR (400 MHz, benzene- d_6): δ 1.95 (br s, 6H, PhB(CH₂PPh₂)₃), 2.48 (q, ${}^{3}J_{HP}$ = 4.8 Hz, 2H, η^{2} -CH₂Ph), 6.85-6.94 (m, 13H, Ar-H), 6.85-6.94 (m, 7H, Ar-H), 7.11-7.23 (obscured m, 11H, Ar-H), 7.27–7.52 (m, 5H, Ar-H), 7.62 (t, ${}^{3}J_{HH} = 7.4$ Hz, 2H, B-Ph meta-H), 8.10 (d, ${}^{3}J_{HH} = 7.4$ Hz, 2H, B-Ph ortho-H). ${}^{13}C{}^{1}H{}$ NMR (150 MHz, 1.0 mL 9:1 THF: benzene- d_6): δ 20.8 (m, PhB(CH₂PPh₂)₃), 34.6 (q, ${}^{2}J_{CP}$ = 5.9 Hz, η^{2} -CH₂Ph), 119.2, 123.4, 127.4, 128.3, 129.3, 129.5, 131.7, 132.5 (m), 140.1 (m). ³¹P{¹H} NMR (162 MHz, benzene- d_6): δ 15.0. ¹¹B{¹H} NMR (193 MHz, 1.0 mL 9:1 THF: benzene- d_6): δ –14.5. Anal. Calcd for C₅₂H₄₈BNiP₃: C₆ 74.76; H, 5.79. Found: C, 74.39; H, 5.96. IR (cm⁻¹): 1305 (m), 1154 (m), 1087 (m), 1068 (w), 1025 (w), 907 (m), 860 (m), 765 (s), 748 (s), 730 (s).

 ${\rm Ni}(\mu-{\rm BP_2}^{\rm Ph})(\mu-{\rm SiHCy})_2$ (5). In a glovebox, a 50 mL reaction vessel was charged with 4 (0.063 g; 0.075 mmol), CySiH₃ (0.024 g; 0.21 mmol), and a stir bar. To this mixture was added toluene (10 mL) to afford a magenta-colored mixture. The vessel was sealed with a Teflon stopcock and then immersed in an oil bath heated to 65 °C. The rapidly stirred contents were maintained at this temperature for 5 h, in which time the reaction mixture became a dark-brown color. In a glovebox, the volatile components of the reaction mixture were removed in vacuo to afford a dark brown paste. Washing the paste with ether $(5 \times 1 \text{ mL})$ produced a dark purple solid, which was dried in vacuo to afford 5 as a purple powder. Yield: 0.023 g; 46%. Crystals of 5 suitable for X-ray diffraction analysis were grown from a saturated THF solution of 5 layered with pentane, which was maintained at -30 °C for 4 d. ¹H NMR (600 MHz, benzene- d_6): δ -7.17 (m, 2H, Si-H), 0.58 (m, 2H, Cy-H), 1.13 (m, 4H, Cy-H), 1.36 (m, 6H, Cy-H), 1.43-1.51 (overlapping m, 1H, Cy-H), 1.43-1.51 (overlapping m, 2H, CH₂PPh₂), 1.55-1.62 (overlapping m, 1H, Cy-H), 1.55-1.62 (overlapping m, 2H, CH₂PPh₂), 1.71 (m, 2H, Cy-H), 2.03 (m, 2H, Si-C-H), 2.08 (br d, J = 13.1 Hz, 2H, Cy-H), 2.24 (m, 2H, CH₂PPh₂), 2.45 (br d, J = 15.4 Hz, 2H, CH₂PPh₂), 6.79 (t, J = 7.5 Hz, 4H, B-Ph meta-H), 6.90 (t, J = 7.4 Hz, 2H, B-Ph para-H), 6.96 (d, J = 7.1 Hz, 2H, CH₂PPh₂), 6.97-7.03 (m, 16H, CH₂PPh₂), 7.04-7.07 (m, 6H, CH₂PPh₂), 7.08–7.12 (overlapping m, 4H, CH₂PPh₂), 7.28 (t, J = 7.7 Hz, 4H, B-Ph ortho-H), 7.61 (tm, J = 7.6 Hz, 4H, CH₂PPh₂), 7.86 $(tm, J = 8.9 Hz, 4H, CH_2PPh_2), 8.09 (tm, J = 8.3 Hz, 4H, CH_2PPh_2).$ ¹³C{¹H} NMR (150 MHz, benzene- d_6): δ 26.9 (Cy-C), 28.2 (Cy-C), 29.0 (Cy-C), 29.4 (Cy-C), 31.1 (Cy-C), 38.6 (Cy-C), 125.6, 126.9, 127.5 (m), 127.6, 128.5 (d, J = 10.2), 128.9 (d, J = 13.2), 129.3, 131.9 (m), 132.9 (m), 133.1 (m), 133.2, 134.9 (m). Note: a resonance for the carbon nucleus in each PCH₂B unit was not found by direct or indirect detection methods. ³¹P{ ^{1}H } NMR (160 MHz, benzene- d_6): δ 28.6 (AA'BB' m), 31.9 (AA'BB' m). ²⁹Si-¹H HMBC NMR (500 MHz; 99 MHz, benzene- d_6): δ 220.8 (¹ $J_{(Ni)H-Si}$ = 52 Hz). Anal. Calcd for C₇₆H₈₂B₂Ni₂P₄Si₂: C, 69.44; H, 6.29. Found: C, 65.55; H, 6.64. Repeated combustion analyses of spectroscopically pure samples of 5 gave consistently low carbon content, possibly due to the formation of nickel carbides during combustion. IR (cm⁻¹): 1886 (w), 1744 (w), 1649 (m), 1584 (w), 1263 (w), 1180 (w), 1087 (m), 1025 (m), 977 (w), 884 (w), 794 (m), 757 (m), 738 (m), 721 (m).

 $[BP_3^{Ph}]Ni(\mu-H)[SiHCy(DMAP)]$ (6). In a glovebox, a 25 mL vessel was charged with a magenta-colored toluene suspension (10 mL) containing 4 (0.055 g; 0.065 mmol), 4-dimethylaminopyridine (DMAP) (0.008 g; 0.065 mmol), CySiH₃ (0.045 g; 0.39 mmol), and a stir bar. The vessel was sealed with a Teflon stopcock and immersed in an oil bath maintained at 80 °C for 6 h, resulting in a

color change to bright yellow-orange. After this time, the vessel was returned to a glovebox and the volatile components of the reaction mixture were removed in vacuo, producing a yellow-orange powder. The powder was redissolved in THF (4 mL) and layered with Et₂O (10 mL). Maintenance of the mixture at -30 °C for 18 h resulted in deposition of **6** as an analytically pure microcrystalline powder. Yield: 0.058 g; 91%. Crystals of 6 suitable for X-ray diffraction analysis were grown by slow vapor diffusion of Et₂O into a THF solution of **6**. ¹H NMR (600 MHz, THF- d_8): δ –7.85 (qd, ${}^2J_{\rm HP}$ = 26 Hz, ${}^3J_{\rm HH}$ = 12 Hz, ${}^{1}J_{(Ni)H-Si} = 28$ Hz, 1H, Ni-H), 0.83 (pentet d, J = 12.6, 3.2, 1H, Cy-H), 0.91 (tt, J = 13, 2.4 Hz, 1H, Cy-H), 0.98 (qd, J = 13, 3.3 Hz, 1H, Cy-H), 1.04 (tt, J = 13, 3.7 Hz, 1H, Cy-H), 1.15 (qt, J = 13, 3.3 Hz, 1H, Cy-H), 1.25 (qt, J = 13, 3.6 Hz, 1H, Cy-H), 1.33 (m, 6H, PhB(CH_2PPh_2)₃), 1.58 (d, J = 14 Hz, 1H, Cy-H), 1.62 (d, J = 12 Hz, 1H, Cy-H), 1.74 (overlapping with solvent residual, 2H, Cy-H), 2.36 (d, J = 13 Hz, 1H, Cy-H), 3.23 (s, 6H, N(CH₃)₂), 5.10 (qd, ${}^{3}J_{HP} = 21$ Hz, ${}^{3}J_{HH} = 12$ Hz, ${}^{1}J_{SiH} = 173.0$, 1H, Si-H), 6.77 (q, J = 8.2 Hz, 12H, PPh_2 meta-H), 6.77 (overlapping, 2H, DMAP meta-H), 6.83 (t, J = 7.5Hz, 1H, BPh para-H), 6.87 (q, J = 6.7 Hz, 6H, PPh₂ para-H), 7.05 (t, J = 7.5 Hz, 2H, BPh meta-H), 7.15 (dt, J = 29, 7.4 Hz, 12H, PPh₂ ortho-H), 7.56 (d, J = 7.3 Hz, 2H, BPh ortho-H), 8.42 (d, ${}^{3}J = 7.1$ Hz, 2H, DMAP ortho-H). ¹³C{¹H} NMR (151 MHz, THF-d₈): 21.4 (1:1:1:1 q, ${}^{1}J_{CB} = 41.5$, PhB(CH₂PPh₂)₃), 28.0 (Cy-C), 29.4 (Cy-C), 29.7 (Cy-C), 30.3 (Cy-C), 32.0 (Cy-C), 34.7 (q, ${}^{3}J_{CP} = 4.2$ Hz, Cy-Csi), 39.6 (N(CH₃)₂), 107.6 (s), 123.0 (s), 127.1 (s), 127.3 (d, J = 6.8), 127.6 (m), 132.5 (s), 133.2 (m), 144.8 (m), 146.6 (s), 157.5 (s). ${}^{11}B{}^{1}H{}$ NMR (193 MHz, THF- d_8): $\delta - 14.2$ (s). ³¹P{¹H} NMR (243 MHz, THF-d₈): δ 25.0 (s). ²⁹Si-¹H HMBC NMR (600 MHz; 120 MHz, THF-d₈): δ 53.4. Anal. Calcd for C₅₈H₆₄BN₂NiP₃Si: C, 71.11; H, 6.59; N, 2.86. Found: C, 70.73; H, 6.72; N, 2.95. IR (cm^{-1}) : 2048 (m), 1768 (w), 1624 (s), 1556 (m), 1301 (w), 1205 (m), 1157 (w), 1089 (w), 1064 (s), 1024 (s), 917 (m), 857 (m), 733 (s), 696 (s).

[BP₃^{Ph}]Ni(µ-H)[SiHCy(MorPy)] (6'). A J. Young NMR tube was charged with a benzene suspension containing 4 (0.011 g; 0.013 mmol), MorPy (0.002 g; 0.012 mmol), and CySiH₃ (0.004 g; 0.035 mmol). Thermolysis of the mixture at 70 °C for 1 h resulted in a color change from magenta to clear orange-brown. The mixture was brought to a glovebox, and the volatile components were removed in vacuo, giving a dark orange powder. The powder was redissolved in toluene (1 mL) and layered with pentane (3 mL). Maintenance of the mixture at -30 °C for 18 h resulted in the precipitation of a yellow powder. The supernatant was decanted from the solids, which were then washed with pentane $(3 \times 1 \text{ mL})$ to afford 6' as a spectroscopically pure yellow powder. Yield: 0.010 g; 73%. ¹H NMR (600 MHz, benzene- d_6): $\bar{\delta}$ -7.95 (qd, ${}^2J_{\rm HP}$ = 26 Hz, ${}^3J_{\rm HH}$ = 12 Hz, $J_{(Ni)Si-H} = 51$ Hz, 1H, Ni-H), 1.13 (dq, J = 14, 3 Hz, 1H, Cy-H), 1.24 (qm, J = 13, 2H, Cy-H), 1.37 (tm, J = 13 Hz, 1H, Cy-H), 1.41 (tt, J = 13, 4 Hz, 1H, Cy-H), 1.52 (qt, J = 13, 4 Hz, 1H, Cy-H), 1.80 (tm, J = 16, 2H, Cy-H), 1.91-2.04 (overlapping m, 7H = 6H, PhB(CH₂PPh₂)₃ and 1H, Cy-H), 2.15 (dm, J = 14 Hz, 1H, Cy-H), 2.23 (dd, J = 6, 4 Hz, 4H, Mor CH_2), 3.01 (t, J = 5 Hz, 4H, Mor CH_2), 5.54 (qd, ${}^3J_{\rm HP} = 21$ Hz, ${}^3J_{\rm HH} = 12$ Hz, ${}^1J_{\rm HSi} = 169$ Hz, 1H, Si-H), 5.63 (d, J = 7 Hz, 2H, Py meta-H), 6.88 (tm, J = 8 Hz, 12 H, PPh₂ meta-H), 6.91 (dd, J = 7, 5 Hz, 6H, PPh₂ para-H), 7.43 (tt, J = 7, 1 Hz, 1H, BPh para-H), 7.52 (dt, J = 32, 8 Hz, 12 H, PPh₂ ortho-H), 7.69 (t, J = 7 Hz, 2H, BPh meta-H), 8.30 (d, J = 7 Hz, 2H, Py ortho-H), 8.32 (br d, J = 7 Hz, 2H, BPh ortho-H). ¹³C{¹H} NMR (126 MHz, benzene-d₆): δ 22.1 (m, PhB(CH₂PPh₂)₃), 27.6 (Cy-C), 28.9 (Cy-C), 29.1 (Cy-C), 30.1 (Cy-C), 31.8 (Cy-C), 34.3 (m, Cy-C), 45.0 (Mor CH_2), 65.4 (Mor CH_2), 106.7 (Py meta-C), 123.7, 127.1 (d, J =8 Hz), 127.5 (m), 132.9 (m), 137.9, 144.4, 146.5, 155.8. $^{11}\mathrm{B}\{^{1}\mathrm{H}\}$ NMR (193 MHz, THF- d_8): δ -13.5 (s). ³¹P{¹H} NMR (243 MHz, THF-d₈): δ 26.3 (s). ²⁹Si-¹H HMBC NMR (600 MHz; 120 MHz, THF- d_8): δ 56.1.

X-ray Crystallography. Data for **3** and **4** were collected at the UC Berkeley CheXRay crystallographic facility on a Bruker APEX-II CCD area detector using Mo K α ($\lambda = 0.7107$ Å) monochromated using QUAZAR multilayer mirrors. Data for **1**, **5**, and **6** were collected at the Advanced Light Source beamline 12.2.1 using a Bruker D85 three-circle diffractometer equipped with an PHOTON II

CCD area detector using synchrotron radiation ($\lambda = 0.7288$ Å) monochromated by channel-cut Si(111). Structure solution, modeling, and refinement was performed using OLEX2³⁶ with the SHELX^{37,38} suite of programs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00635.

³¹P{¹H} NMR spectrum of **5** and details of X-ray crystallography (PDF)

Accession Codes

CCDC 1864939–1864943 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tdtilley@berkeley.edu.

ORCID 🔍

Rex C. Handford: 0000-0002-3693-1697 Patrick W. Smith: 0000-0001-5575-4895 T. Don Tilley: 0000-0002-6671-9099

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the National Science Foundation under grant no. CHE-1566538. UC Berkeley ChexRay is funded by the National Institutes of Health under grant no. S10-RR027172. We thank Simon J. Teat and Laura J. McCormick of the Advanced Light Source for their expertise and assistance. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

REFERENCES

(1) Waterman, R.; Hayes, P. G.; Tilley, T. D. Synthetic Development and Chemical Reactivity of Transition-Metal Silylene Complexes. *Acc. Chem. Res.* **2007**, *40*, 712–719.

(2) Feldman, J. D.; Mitchell, G. P.; Nolte, J. O.; Tilley, T. D. Isolation and Characterization of Neutral Platinum Silylene Complexes of the Type $(R_3P)_2Pt = SiMes_2$ (Mes = 2,4,6-Trimethylphenyl). J. Am. Chem. Soc. **1998**, 120, 11184–11185.

(3) Peters, J. C.; Feldman, J. D.; Tilley, T. D. Silylene Extrusion from a Silane: Direct Conversion of Mes₂SiH₂ to an Iridium Silylene Dihydride. *J. Am. Chem. Soc.* **1999**, *121*, 9871–9872.

(4) Mork, B. V.; Tilley, T. D. High Oxidation-State (Formally d^0) Tungsten Silylene Complexes via Double Si-H Bond Activation. J. Am. Chem. Soc. 2001, 123, 9702–9703.

(5) Mork, B. V.; Tilley, T. D. Synthons for Coordinatively Unsaturated Complexes of Tungsten, and Their Use for the Synthesis of High Oxidation-State Silylene Complexes. *J. Am. Chem. Soc.* **2004**, *126*, 4375–4385.

(6) Okazaki, M.; Tobita, H.; Ogino, H. Reactivity of Silylene Complexes. *Dalton. Trans.* **2003**, 493–506.

(7) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. Base-Free Silylene Complexes without π -Donor Stabilization.

Molecular Structure of $[Cp^*(PMe_3)_2Ru = SiMe_2][B(C_6F_5)_4]$. J. Am. Chem. Soc. **1994**, 116, 5495–5496.

(8) Fasulo, M. E.; Glaser, P. B.; Tilley, T. D. Cp*(PiPr₃)RuOTf: A Reagent for Access to Ruthenium Silylene Complexes. *Organometallics* **2011**, *30*, 5524–5531.

(9) Mitchell, G. P.; Tilley, T. D. Generation of a Silylene Complex by the 1,2-Migration of Hydrogen from Silicon to Platinum. *Angew. Chem., Int. Ed.* **1998**, 37, 2524–2526.

(10) Corey, J. Y.; Braddock-Wilking, J. Reactions of Hydrosilanes with Transition-Metal Complexes: Formation of Stable Transition-Metal Silyl Compounds. *Chem. Rev.* **1999**, *99*, 175–292.

(11) Corey, J. Y. Reactions of Hydrosilanes with Transition Metal Complexes. *Chem. Rev.* 2016, *116*, 11291–11435.

(12) Lipke, M. C.; Liberman-Martin, A. L.; Tilley, T. D. Electrophilic Activation of Silicon-Hydrogen Bonds in Catalytic Hydrosilations. *Angew. Chem., Int. Ed.* **2017**, *56*, 2260–2294.

(13) Lipke, M. C.; Tilley, T. D. High Electrophilicity at Silicon in η^3 -Silane σ -Complexes: Lewis Base Adducts of a Silane Ligand, Featuring Octahedral Silicon and Three Ru–H–Si Interactions. *J. Am. Chem. Soc.* **2011**, *133*, 16374–16377.

(14) Lipke, M. C.; Tilley, T. D. Hypercoordinate Ketone Adducts of Electrophilic η^3 -H₂SiRR' Ligands on Ruthenium as Key Intermediates for Efficient and Robust Catalytic Hydrosilation. *J. Am. Chem. Soc.* **2014**, 136, 16387–16398.

(15) Fasulo, M. E.; Lipke, M. C.; Tilley, T. D. Structural and Mechanistic Investigation of a Cationic Hydrogen-Substituted Ruthenium Silylene Catalyst for Alkene Hydrosilation. *Chem. Sci.* **2013**, *4*, 3882–3887.

(16) Calimano, E.; Tilley, T. D. Synthesis and Structure of PNP-Supported Iridium Silyl and Silylene Complexes: Catalytic Hydrosilation of Alkenes. *J. Am. Chem. Soc.* **2009**, *131*, 11161–11173.

(17) Thomas, C. M.; Peters, J. C. An η^3 -H₂SiR₂ Adduct of [{PhB(CH₂PiPr₂)₃}Fe^{II}H]. Angew. Chem., Int. Ed. **2006**, 45, 776–780.

(18) Iluc, V. M.; Hillhouse, G. L. Arrested 1,2-Hydrogen Migration from Silicon to Nickel upon Oxidation of a Three-Coordinate Ni(I) Silyl Complex. *J. Am. Chem. Soc.* **2010**, *132*, 11890–11892.

(19) Smith, P. W.; Tilley, T. D. Base-Free Iron Hydrosilylene Complexes via an α -Hydride Migration That Induces Spin Pairing. *J. Am. Chem. Soc.* **2018**, *140*, 3880–3883.

(20) Hayes, P. G.; Beddie, C.; Hall, M. B.; Waterman, R.; Tilley, T. D. Hydrogen-Substituted Osmium Silylene Complexes: Effect of Charge Localization on Catalytic Hydrosilation. *J. Am. Chem. Soc.* **2006**, *128*, 428–429.

(21) Hayes, P. G.; Waterman, R.; Glaser, P. B.; Tilley, T. D. Synthesis, Structure, and Reactivity of Neutral Hydrogen-Substituted Ruthenium Silylene and Germylene Complexes. *Organometallics* **2009**, *28*, 5082–5089.

(22) Betley, T. A.; Peters, J. C. The Strong-Field Tripodal Phosphine Donor, $[PhB(CH_2PiPr_2)_3]^-$, Provides Access to Electronically and Coordinatively Unsaturated Transition Metal Complexes. *Inorg. Chem.* **2003**, *42*, 5074–5084.

(23) Betley, T. A.; Peters, J. C. Dinitrogen Chemistry from Trigonally Coordinated Iron and Cobalt Platforms. J. Am. Chem. Soc. 2003, 125, 10782-10783.

(24) MacBeth, C. E.; Thomas, J. C.; Betley, T. A.; Peters, J. C. The Coordination Chemistry of " $[BP_3]NiX$ " Platforms: Targeting Low-Valent Nickel Sources as Promising Candidates to $L_3Ni=E$ and $L_3Ni\equiv E$ Linkages. *Inorg. Chem.* **2004**, 43, 4645–4662.

(25) Lu, C. C.; Peters, J. C. Pseudotetrahedral Manganese Complexes Supported by the Anionic Tris(Phosphino)Borate Ligand [PhBP^{IPr}₃]. *Inorg. Chem.* **2006**, *45*, 8597–8607.

(26) Roddick, D. M.; Heyn, R. H.; Tilley, T. D. Dimesitylsilyl Derivatives of Zirconium. *Organometallics* **1989**, *8*, 324–330.

(27) Turculet, L.; Feldman, J. D.; Tilley, T. D. Coordinatively and Electronically Unsaturated Zwitterionic Iron Silyl Complexes Featuring the Tripodal Phosphine Ligand $[PhB(CH_2P_iPr_2)_3]^-$. Organometallics **2003**, 22, 4627–4629.

(28) Windus, C.; Sujishi, S.; Giering, W. P. Relative Iron-Carbon and Iron-Silicon Bond Strengths in Derivatives of $(\eta$ -Cyclopentadienyl)-Dicarbonyliron. J. Am. Chem. Soc. **1974**, 96, 1951–1952.

(29) Dryden, N. H.; Legzdins, P.; Phillips, E. C.; Trotter, J.; Yee, V. C. Unambiguous Example of a η^2 -Benzyl Group Functioning as a Formal Three-Electron Ligand: Solid-State Molecular Structure of Cp*Mo(NO)(CH₂SiMe₃)(η^2 -CH₂C₆H₅). Organometallics **1990**, *9*, 882–884.

(30) Shimada, S.; Rao, M. L. N.; Hayashi, T.; Tanaka, M. Isolation of Dinuclear (μ -Silylene)(Silyl)Nickel Complexes and Si–Si Bond Formation on a Dinuclear Nickel Framework. *Angew. Chem., Int. Ed.* **2001**, 40, 213–216.

(31) Skoog, M. T.; Jencks, W. P. Reactions of Pyridines and Primary Amines with N-Phosphorylated Pyridines. *J. Am. Chem. Soc.* **1984**, *106*, 7597–7606.

(32) Shapiro, I. R.; Jenkins, D. M.; Thomas, J. C.; Day, M. W.; Peters, J. C. A Homoleptic Phosphine Adduct of Tl(I). *Chem. Commun.* 2001, 2152–2153.

(33) Schrock, R. R. Preparation and Characterization of $M(CH_3)_5$ (M = Nb or Ta) and Ta($CH_2C_6H_5$)₅ and Evidence for Decomposition by α -Hydrogen Atom Abstraction. J. Organomet. Chem. **1976**, 122, 209–225.

(34) Shen, Q.; Rhodes, S.; Cochran, J. C. Molecular Structure and Conformation of Cyclohexylsilane As Determined by Gas-Phase Electron Diffraction. *Organometallics* **1992**, *11*, 485–486.

(35) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179.

(36) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

(37) Sheldrick, G. M. SHELXT - Integrated Space-Group and Crystal-Structure Determination. Acta Crystallogr., Sect. A: Found. Adv. 2015, 71, 3–8.

(38) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8.