ORGANOMETALLICS

Structural Similarities in Dinuclear, Tetranuclear, and Pentanuclear Nickel Silyl and Silylene Complexes Obtained via Si–H and Si–C Activation

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Supporting Information

ABSTRACT: The reactions of $({}^{i}Pr_{3}P)_{2}Ni^{0}$ precursors with Ph₂SiHCl, Ph₂SiH₂, PhSiH₃, and Ph₃SiH provide mononuclear, dinuclear, tetranuclear, and pentanuclear complexes with silvl and silvlene ligands. Reaction of the dinuclear Ni(0) dinitrogen complex $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-\eta^{1}:\eta^{1}-N_{2})$ with Ph₂SiHCl afforded the thermally sensitive mononuclear complex $({}^{i}Pr_{3}P)_{2}Ni(H)SiClPh_{2}$ (1), which displays considerable hydridic character in the Ni–H–Si interaction. This species



thermally converts to the dinuclear complex $[({}^{i}Pr_{3}P)Ni(\mu-SiHPh_{2})]_{2}$ (2), where the silvl ligand bridges via an agostic Si–H interaction. Alternate higher-yield routes to 2 include the rapid room-temperature reaction of Ph₂SiH₂ with $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-\eta^{1:}\eta^{1}-N_{2})$ and the reaction of Ph₂SiH₂ with Ni(1,5-cyclooctadien)₂ and ${}^{i}Pr_{3}P$ at elevated temperatures. Double Si–H activations are observed in the reaction of PhSiH₃ with $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-\eta^{1:}\eta^{1}-N_{2})$, which provides the tetranuclear C_{3} -symmetric complex $({}^{i}Pr_{3}P)Ni[({}^{i}Pr_{3}P)Ni[({}^{i}Pr_{3}P)Ni(\mu_{3}-SiHPh)]_{3}$ (3) as the major product and the pentanuclear S_{4} -symmetric complex Ni $[({}^{i}Pr_{3}P)Ni(\mu_{3}-SiHPh)]_{4}$ (4) as a minor product. Density functional theory (DFT) geometry optimizations of model complexes support the presence of agostic Ni–H–Si interactions within the tetra- and pentanuclear cores of 3 and 4. The reaction of Ph₃SiH with $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-\eta^{1:}\eta^{1-}N_{2})$ results in Si–C bond cleavage to provide the asymmetric dinuclear complex $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-C_{6}H_{5})(\mu-SiHPh_{2})$ (5), where the phenyl moiety is asymmetrically bridging. Complexes 2–5 all display similar coordination environments at one of the nickel centers, suggestive of formal oxidation state assignments of Ni(III)–Ni(I) in tetranuclear 3 and Ni(IV)–Ni(I) in pentanuclear 4.

INTRODUCTION

Transition-metal silyl and silylene complexes have attracted attention because of their importance in transition-metalcatalyzed transformations of silicon compounds¹ as well as their unique bonding and properties.² Catalytic transformations mediated by these species include hydrosilylation, dehydrocoupling, bis-silylation, silylcarbonylation, and metathesis reactions and typically involve 4d and 5d transition metals.³ Less attention has been given to nickel catalysts and complexes, but they are of current interest due to the low cost of nickel in comparison to that of the precious metals. Catalytic hydrosilylation,⁴ dehydrogenative silylation of olefins,⁵ and dehydrocoupling of organosilanes⁶ to afford polysilanes have been reported with nickel catalysts.

Isolated hydridosilyl and silylene transition-metal complexes provide insight into the intermediate stages of Si–H oxidative addition and thus are indispensable for the development of new catalytic methodologies.⁷ The majority of silylene complexes feature second- and third-row transition metals. Although mononuclear complexes have been accessed via double Si–H activation,⁸ multinuclear complexes with bridging silylene ligands are commonly formed from related reactions.^{8,9} Fewer nickel complexes bearing silane,¹⁰ silyl,¹¹ or silylene ligands¹² have been reported; particularly scarce are complexes that do not feature electronically, chelate, or sterically stabilized silylene moieties.

Our previous research has shown that with the appropriate ancillary ligands and substrates Ni complexes can both activate¹³ and catalytically functionalize C–H bonds.¹⁴ Herein we report the reaction of Ni(0) precursors with a series of silanes, which results in di-, tetra-, and pentanuclear organosilyl or silylene nickel complexes with agostic Ni–H–Si interactions derived from Si–H activation and Si–C bond breaking of simple organosilanes from reactions with low-valent nickel precursors. Despite the range of nuclearity in the structures described, all but the mononuclear complex contain centers that structurally resemble formal Ni(I) centers stabilized by metal–metal bonding interactions.

RESULTS AND DISCUSSION

The reaction of $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-\eta^{1}:\eta^{1}-N_{2})^{15}$ with 2 equiv of Ph₂SiHCl in *n*-pentane at -34 °C afforded the crystalline mononuclear complex $({}^{i}Pr_{3}P)_{2}Ni(\mu-H)(SiClPh_{2})$ (1) in 19% yield (Scheme 1). The reaction occurs within 1 min, and the modest yield is due to the thermal sensitivity of the complex. In

Received: February 14, 2012 Published: April 18, 2012 Scheme 1



aliphatic or aromatic solvents 1 decomposes in less than 1 h at 20 °C. Despite the strength of the Si–Cl bond,¹⁶ the chlorine substituent from Ph₂SiHCl is abstracted to produce NiCl- $(P^iPr_3)_2$.¹⁵ The possible transient nickel(I) diphenylsilane fragment (iPr_3P)₂Ni(SiHPh₂) is not observed, but rather the dinuclear complex [(iPr_3P)Ni(μ -SiHPh₂)]₂ (2) is isolated in low yield, from dimerization with loss of iPr_3P . In contrast to 1, complex 2 is stable under refluxing conditions in toluene. A more synthetically useful route to 2 is via the reaction of Ph₂SiH₂ with [(iPr_3P)Ni]₂(μ - η ¹: η ¹-N₂), which provides 2 in 86% yield. Similarly, the reaction of Ph₂SiH₂ with stoichiometric amounts of Ni(COD)₂ in the presence of iPr_3P provided 2 in 56% yield after heating at 55 °C for 16 h, obviating the need for [(iPr_3P)₂Ni]₂(μ - η ¹: η ¹-N₂) in the synthesis of 2. These various routes to 2 are summarized in Scheme 1.

The solid-state structure of **1** was determined by X-ray crystallography, and an ORTEP depiction is shown in Figure 1. The hydrogen atom originating from the silane was located in the electron density map, and its position was refined; the



Figure 1. Depiction of the solid-state molecular structure of 1 as determined by X-ray crystallography with 30% probability ellipsoids. Hydrogen atoms not attached to Si or Ni are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–Si(1), 2.2211(9); Ni(1)–H(1), 1.41(3); Si(1)–H(1), 1.78(3); Ni(1)–P(1), 2.2045(8); Ni(1)–P(2), 2.2375(8); P(1)–Ni(1)–P(2), 115.96(3); P(1)–Ni(1)–Si(1), 109.93(3); P(2)–Ni(1)–Si(1), 134.07(3).

magnitude of the errors in the distances to the hydrogen atom reflects the modest electron density associated with this atom in comparison to that of the adjacent Ni and Si atoms. The Ni(1)-H(1) distance of 1.41(3) Å is suitable for a nickel hydride.^{13 \hat{f} ,1⁷} Although the Si(1)–H(1) distance of 1.78(3) Å is significantly elongated in comparison to a typical Si-H bond, which are more typically in the range of 1.4-1.5 Å, it is not as long as the distances of 1.9-2.4 Å usually associated with secondary interactions between a silicon atom and an adjacent hydride.²¹ The relative position of the hydride and the silyl substituents is consistent with an elongated η^2 -SiH σ complex,¹ but related complexes with similar spectroscopic features but slightly longer Si-H distances have been described as silyl hydrido complexes.^{11c,1} It should be noted that there is a structural continuum between the limiting structures of an η^2 -SiH σ -silane complex and complete oxidative addition to the silvl hydrido complex.^{11c} The molecular structure of 1 has a near-planar nickel center, with a sum of bond angles around nickel of $360(1)^{\circ}$ for the two phosphine ligands, the silicon atom, and the bridging hydrogen atom, with an internal Si(1)-Ni(1)-H(1) angle of 52.6°. Two closely related complexes with differing degrees of H-Si interactions have been described with chelating bis-phosphine^{11c} and nonchelating NHC ligands.¹¹¹ Both of these related complexes were reported as stable at room temperature. The P(1)-Ni(1)-P(2) angle in complex 1 is $115.96(3)^\circ$, whereas the related example^{11c} which utilizes 1,2-bis(di-tert-butylphosphine)ethane features an smaller P-Ni-P angle of only 95.51(6)°; this suggests that the decreased thermal stability of 2 is possibly due to increased repulsion between the nonchelating phosphine donors. The Ni(1)-Si(1) distance of 2.2211(9) Å and Si(1)-Cl(1) distance of 2.1623(11) Å are similar to those reported for the 2-bis(di*tert*-butylphosphine)ethane analogue.^{11c} Examples are known of both a cationic analogue^{11b} and Ni(0) silane complexes with shorter Si-H interactions,^{10,11c} as determined by X-ray crystallography.

For mononuclear complex 1, the Ni-H-Si resonance is observed at δ -10.75 as a triplet with a $J_{\rm PH}$ value of 20.5 Hz. The hydridic shift is suggestive of oxidative addition, so that an alternate view of 1 is as a Ni(II) complex. The observation of a single environment in the 121.5 MHz ³¹P{¹H} NMR as low as the freezing point of d_8 -toluene suggests a low barrier for fluxional exchange from the approximately C_s -symmetric structure observed in the solid state. The observed $J_{\rm PH}$ value is significantly smaller than coupling constants for transdisposed phosphines in Ni(II) hydrides, which are typically near 70 Hz.^{13c-f} The ²⁹Si NMR shift was observed at δ 10.2 as a triplet with a ${}^{2}J_{SiP}$ value of 62.5 Hz, but no resolved J_{SiH} . The IR spectrum of 1 features a strong absorption at 1887 cm⁻¹ that can be assigned as a stretching mode for the Ni-H moiety. This was confirmed by a DFT calculation for 1 using the B3LYP functional and the TZVP basis set in Gaussian 09, which provided an unscaled Ni-H IR stretch at 1905 cm⁻¹ as the only vibration in that region.

The solid-state structure of **2** was determined by X-ray crystallography, and an ORTEP depiction is shown in Figure 2. The molecule contains a crystallographic inversion center at the midpoint of the Ni–Ni bond. The P, Ni, and Si atoms all lie approximately within a plane. The bridging agostic interaction is almost coplanar with the $[Ni_2Si_2]$ core fragment, and the agostic hydrogen is located in the pocket afforded by the wide $P(1)-Ni(1)^i-Si(1)$ angle of $138.60(2)^\circ$, in comparison to the narrower $P(1)-Ni(1)-Si(1)^i$ angle of $108.56(3)^\circ$. The Ni(1)–



Figure 2. Depiction of the solid-state molecular structure of **2** as determined by X-ray crystallography with 30% probability ellipsoids. Hydrogen atoms not attached to Si and Ni are omitted for clarity. The superscript labels, e.g. Ni(1)ⁱ, indicate atom locations generated by a crystallographic inversion center. Selected bond distances (Å) and angles (deg): Ni(1)–Ni(1)ⁱ, 2.4878(6); Ni(1)–Si(1), 2.2654(7); Ni(1)–Si(1)ⁱ, 2.2164(8); Ni(1)–H(1), 1.55(2); Si(1)–H(1), 1.64(2); Ni(1)–P(1), 2.1681(6); Si(1)–Ni(1)–H(1), 46.5(8); P(1)–Ni(1)–Si(1), 138.60(2); P(1)–Ni(1)–Si(1)ⁱ, 108.56(3); P(1)–Ni(1)–Ni(1)–Ni(1)ⁱ, 165.14(2); P(1)–Ni(1)–H(1), 92.9(8).

Ni(1)ⁱ distance of 2.4878(6) Å is relatively long compared to the typical range of Ni–Ni single-bond distances of 2.36–2.54 Å.¹⁸ In comparison to 1, complex 2 features a 0.14(4) Å longer Ni(1)–H(1) distance of 1.55(2) Å and a 0.14(4) Å shorter Si(1)–H(1) distance of 1.64(2) Å, consistent with weaker back-donation from a Ni(I) versus a Ni(0) species. The Ni(1)– Si(1) distance for the agostic interaction of 2.2654(7) Å is 0.044(1) Å longer than that observed in 1, whereas the σ bound Ni(1)–Si(1)ⁱ distance of 2.2164(8) Å is a mere 0.005(1) Å shorter. Related dimeric structures have been previously described with nickel's heavier congeners Pt and Pd,^{9b,19,20} and a related Ni complex has recently been reported.^{11m}

The ¹H NMR spectrum of the dimeric complex 2 exhibits a Si–H shift at δ –2.05 as a doublet with a ${}^{2}J_{PH}$ coupling constant of 15.0 Hz. The 29 Si NMR shift is observed at δ 123.7 as a doublet with a ${}^{2}J_{SiP}$ value of 48.9 Hz. A ${}^{1}J_{SiH}$ value of 59.6 Hz and a ${}^{2}J_{SiH}$ value of 20.3 Hz were observed in both the ${}^{1}H$ and ²⁹Si NMR spectra of **2**; the observation of a large ${}^{2}J_{SiH}$ may be due to the trans disposition of these nuclei. Typically, ${}^{1}J_{SiH}$ coupling constants are negative and it is expected that ${}^{2}J_{SiH}$ should be positive;^{2k} interestingly, DFT predictions of NMR coupling constants using the model complex [(Me₃P)Ni(µ- $SiHPh_2$]₂ (2^{Me}) suggest that both of the observed coupling constants are negative. In 2 a stretching mode is observed for the Ni-H-Si moiety at 1582 cm⁻¹. DFT calculations on the model complex $[(Me_3P)Ni(\mu-SiHPh_2)]_2$ (2^{Me}) predict unscaled asymmetric and symmetric Ni- - -H- - -Si IR stretches at 1565 and 1577 cm⁻¹, respectively. Only the former is expected to be IR active.

Treatment of dark red solutions of $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-\eta^{1}:\eta^{1}-N_{2})$ in *n*-pentane at 20 °C with stoichiometric amounts of PhSiH₃ afforded the tetranuclear complex $({}^{i}Pr_{3}P)Ni[({}^{i}Pr_{3}P)Ni(\mu_{3}-SiHPh)]_{3}$ (3) in 54% yield as dark red crystals. The minor pentanuclear byproduct Ni $[({}^{i}Pr_{3}P)Ni(\mu_{3}-SiHPh)]_{4}$ (4) was reproducibly isolated in 3–5% yield in multiple preparations of 3. These two reaction products are shown in eq 1. Complex 4 crystallizes as black needles that are insoluble in pentane and



barely soluble in benzene. This complex is therefore readily separated from the significantly more soluble 3, which is partly soluble in pentane and soluble in benzene. The pentanuclear compound could also be isolated by manual separation of the dark brown crystalline needles of 4 from the large red crystals of 3. The stoichiometry of the reaction for the two products is slightly different. The generation of 3 requires 2 equiv of the starting dinitrogen complex reacting with 3 equiv of PhSiH₃, which liberates 4 equiv of ^{*i*}Pr₃P and 3 equiv of H₂ gas. Complex 4 is produced from $2^{1}/_{2}$ equiv of the starting dinitrogen complex reacting with 4 equiv of PhSiH₃ and produces 6 equiv of ⁱPr₃P and 8 equiv of H₂ gas. Attempts to isolate larger amounts of 4 by the addition of up to 20 equiv of PhSiH₃ to the reaction mixture failed. Attempts to synthesize 3 using Ni(COD)₂ in lieu of $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-\eta^{1}:\eta^{1}-N_{2})$ were only modestly successful; small amounts of 3 were produced, as characterized by ¹H and ³¹P{¹H} NMR spectroscopy, but only when the reaction mixture was heated to 60 °C for extended periods, and this was not a practical high-yield synthetic route to 3.

The molecular structure of **3** was determined by singlecrystal X-ray diffraction, and an ORTEP depiction is shown in Figure 3. The Ni₄Si₃ core is composed of an alternating Ni₃Si₃ fragment with a cyclohexane ring chair conformation that is capped by the unique apical Ni moiety that lies on the C_3 symmetry axis. This apical nickel is bound to three symmetryrelated SiHPh moieties, with a Ni(2)–Si(1) distance of 2.2010(7) Å. The Ni₃Si₃ ring features a short Ni(1)–Si(1) distance of 2.1935(8) Å alternating with a longer Ni(1)–Si(1)^a distance of 2.2645(8) associated with the Si–H---Ni interaction. The bridging hydrogen ligand has a Ni(1)–H(1) distance of 1.57(4) Å and a Si(1)–H(1) distance of 1.61(3) Å.

A comparison of the Ni–Si bonds in 3 with the single bonds in 2, where the Ni–Si single-bond distance is 2.2164(8) Å and the Si–H- - -Ni interaction has a Ni–Si distance of 2.2654(7) Å, suggests that the Ni(1)–Si(1) and Ni(2)–Si(1) interactions in 3 are single bonds; mononuclear Ni=Si double-bond distances are significantly shorter (2.13 Å^{11j}), although an example of a heterocyclic mononuclear silylene features a similar distance (2.20 Å^{12a}). Recently Hillhouse et al. reported a related mononuclear silylene coordination with an agostic Ni–



Figure 3. Depiction of the solid-state molecular structure of 3 as determined by X-ray crystallography with 30% probability ellipsoids. Nickel-nickel bonds are shown as open bonds, and isopropyl substituents and hydrogen atoms not attached to Si or Ni are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–H(1), 1.57(4); Si(1)–H(1), 1.61(3); Ni(1)–Ni(2), 2.5704(5); Ni(1)–Si(1), 2.1935(8); Ni(1)–Si(1)^a, 2.2645(8); Ni(2)–Si(1), 2.2010(7); Ni(1)–P(1), 2.1495(7); Ni(2)–P(2), 2.2048(12); Si(1)–Ni(2)–P(2), 108.90(2); P(1)–Ni(1)–Ni(2), 160.86(3); P(2)–Ni(2)–Ni(1), 126.47(1).

H–Si interaction, where the bridging hydrogen participates in a three-center–two-electron bond using the 1s H orbital and the π orbital of the Ni=Si core to effectively give a protonated Ni=Si double bond.^{11b} In this example, the chelating 1,2-^tBu₂PCH₂CH₂P^tBu₂ ligand presumably prevents the mononuclear species from cluster formation, in comparison to the ⁱPr₃P-supported clusters **3** and **4**. Silyl-containing clusters are rare,²¹ and only recently was an unusual cluster with a Ni₃Si₂ core with six-coordinate silicon described.^{11k} More closely related to **3** and **4** are multinuclear Pd clusters, containing a planar Pd₄Si₃ core^{20e} and a Pd₄Si₅ framework.²² Both palladium clusters show no agostic interactions.

The minor product **4** shares some structural similarities to **3**, and a depiction of the solid-state molecular structure is shown in Figure 4. The molecule has crystallographically imposed S_4



Figure 4. Depiction of the solid-state molecular structure of 4 as determined by X-ray crystallography with 30% probability ellipsoids. Hydrogen atoms not attached to Si and Ni are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–Ni(2), 2.460(1); Ni(1)–Si(1), 2.214(1); Ni(1)–Si(1)^a, 2.290(1); Ni(2)–Si(1), 2.1780(9); Si(1)–H(1), 1.65(4), Ni(1)–H(1), 1.55(4); P(2)–Ni(1)–Ni(2), 159.79(2); P(2)–Ni(1)–Si(1), 104.74(3); P(2)–Ni(1)–Si(1), 145.64(3); Si(1)–Ni(2)–Si(1), 115.34(3); Si(1)–Ni(2)–Si(1), 98.27(5).

symmetry. The core structure of the pentanuclear complex features the nickel center Ni(2) surrounded by a four Ni(1)atoms in a square-planar arrangement, with a Ni(1)-Ni(2)distance of 2.460(1) Å. The four bridging PhSi-H ligands are coordinated around the central Ni(1) atom in a distorted tetrahedron, with a $98.27(5)^{\circ}$ Si(1)-Ni(2)-Si(1)^b angle bisected by the S_4 axis and a 115.34(3)° Si-Ni(1)-Si(1)^a angle. Although the assignment of oxidation states in clusters can be subjective, due to delocalized multicenter bonding, it is interesting to consider what formal oxidation states could be assigned in these highly symmetric complexes. The Ni(2)-Si(1) bond lengths in 4 of 2.1743(2) Å are quite short. The Ni(1)-Si(1) bond length of 2.2136(10) Å is significantly longer, whereas the agostic $Ni(1)-Si(1)^{a}$ distance is 2.2901(10) Å. The Si(1)-H(1) distance is 1.65(4) Å, and the $Ni(1)-H(1)^a$ distance is 1.55(4) Å. The coordination environments for the Ni(1) centers in tetranuclear 3 and pentanuclear 4 both resemble the Ni(I) centers in 2 (vide infra); by this reasoning, one could dissect complex 3 as a Ni(III) center surrounded by and bonded to three Ni(I) centers and complex 4 as a Ni(IV) center surrounded by four Ni(I) centers. The presence of Ni–Ni bonds, which are likely significantly polarized, may aid in stabilizing such unusual formal oxidation state combinations.²³

The ${}^{1}H$, ${}^{31}P{}^{1}H$, and ${}^{29}Si{}^{1}H$ NMR spectra support the solid-state molecular structures of 3 and 4. The ¹H NMR of 3 features a characteristic upfield-shifted²⁴ doublet of doublets for the agostic Si-H at δ -1.81 with ${}^{2}J_{PH}$ and ${}^{3}J_{PH}$ values of 12.0 and 1.8 Hz, respectively. In 4 a doublet at δ –2.27 ppm with ${}^{2}J_{\rm PH}$ = 11.5 Hz was observed. In contrast, transition-metal silvlenes without agostic interactions typically feature downfield Si-H ¹H NMR resonances (δ 9.14,²⁵ 12.1,²⁶ 15.3^{20e}) in comparison to the resonances of free organosilanes. The ³¹P{¹H} NMR spectra of **3** features two ³¹P resonances in a 3:1 ratio. The resonance at δ 59.8 is a doublet, and the lower intensity resonance as δ 68.7 is a quartet attributed to the apical P atom, with a mutual ${}^{3}J_{PP}$ coupling constant of 12.5 Hz. As expected, one resonance was observed in the ³¹P{¹H} NMR spectrum of 4, at δ 61.8. The ²⁹Si{¹H} NMR spectra of 3 and 4 display characteristic downfield shifts for the silylene ²⁹Si resonances at δ 300.4 and 277.4, respectively. The former is a doublet of doublets (${}^{2}J_{PSi} = 47.9 \text{ Hz}$, ${}^{2}J_{PSi} = 10.9 \text{ Hz}$), whereas the latter is a doublet $(^{2}J_{PSi} = 45.9 \text{ Hz})$. A related diphenylsilylene bridging triangular triplatinum complex features a similar ²⁹Si{¹H} NMR shift of δ 279.4.²⁷ Downfield ²⁹Si NMR spectroscopic shifts in the range of 250–350 ppm are typically attributed to a paramagnetic shielding effect from silylene bridging metal-metal bonds.^{2g} The ¹J_{SiH} values of 45.0 and 35.9 Hz were observed for 3 and 4, respectively.

Silicon–Carbon Bond Cleavage. An unexpected Si–C bond cleavage was observed when Ph_3SiH was reacted with stoichiometric amounts of $[({}^{i}Pr_3P)_2Ni]_2(\mu-\eta^{1}:\eta^{1}-N_2)$ in *n*-pentane, as shown in eq 2. Within 20 min at 20 °C this reaction provided $[({}^{i}Pr_3P)Ni]_2(\mu-C_6H_5)(\mu-SiHPh_2)$ (5), which was isolated in 48% yield as brown needles from slow evaporation of a solution in hexamethyldisiloxane/benzene. Isolated 5 dissolved to give a pale green solution in C_6H_6 .

The solid-state molecular structure of 5 was determined by X-ray crystallography, and an ORTEP depiction is shown in Figure 5. Complex 5 has a Ni(1)–Ni(2) bond length of 2.4075(9) Å, which is in the typical range for single bonds, but much shorter than in 2 (2.4878(6) Å). The cleaved phenyl



Figure 5. Depiction of the solid-state molecular structure of 5 as determined by X-ray crystallography with 30% probability ellipsoids. Hydrogen atoms not attached to Si and Ni are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–Ni(2), 2.4075(9); Ni(1)–H(1), 1.46(6); Si(1)–H(1), 1.64(5); Ni(1)–C(1), 1.892(5); Ni(2)–C(6), 2.439(5); Ni(2)–C(1) 1.958(5); Ni(2)–Si(1), 2.2378(15); Ni(1)–Si(1), 2.2204(15); Ni(1)–P(1), 2.1966(15); Ni(2)–P(2), 2.1664(15); P(1)–Ni(1)–Ni(2), 153.19(5); P(1)–Ni(1)–Si(1), 145.47(6).

group bridges the Ni centers in an asymmetric fashion, with σ bonding to Ni(1) and an interaction of the π electrons to Ni(2). The Ni(1)–C(1) σ bond of 1.892(5) Å is only 0.066(7) Å shorter than the highly asymmetric Ni(2)–C(1) π -bonding distance of 1.958(5) Å, with a longer Ni(2)–C(6) distance of 2.439(5) Å. A similar back-donation to a formally Ni(I) center has been observed in a formally Ni(III)–Ni(I) complex.²³ The Ni(2)–Si(1) σ bond distance of 2.2378(15) Å is unexpectedly longer than the Ni(1)–Si(1) distance of 2.2204(15) Å associated with the agostic Si–H interaction. This is suggestive

of strong back-donation from the Ni(I) center to the Si–H moiety, which is supported by a short Ni(2)–H(1) distance of 1.46(6) Å, although the error is too large to draw a conclusion from these data alone.

The ¹H NMR spectrum of isolated 5 features a high-fieldshifted doublet resonance at δ -7.09 for the Si-H fragment with a ${}^{2}J_{PH}$ coupling constant of 12.0 Hz in a range similar to that for 1 but significantly less shielded in comparison to that for dinuclear complex 2, suggesting a more hydridic character in 5. In related Pt complexes of the type $(R_3P)_2Pt(H)(\mu$ -SiR₂)(μ -HSiR₂)Pt(PR₃), shifts of δ -4.9 to -7.05 have been assigned as hydrides and thus formal Pt(III)-Pt(I) structures.^{95,20a,c} In the ²⁹Si{¹H} NMR spectrum at δ 124.5 ppm a doublet of doublets with ${}^{2}J_{PSi} = 82.5$ and 3.2 Hz is observed, which correlates in the ³¹P{¹H} NMR spectrum to two different phosphorus environments at δ 55.2 and 46.3 with ${}^{3}J_{PP}$ = 24.3 Hz, respectively, suggesting that 5 is a C_1 -symmetric complex. However, the more hydridic character suggested by the upfield Ni-H shift only modestly correlates with the Si-H-Ni stretch observed at 1635 cm⁻¹, which is considerably lower than the Ni-H stretching frequency observed for 1. Such an observation is inconsistent with complete oxidative addition of the Si-H bond. In comparison, related Pt and Pd complexes are known with similar hydridic chemical shifts in the ¹H NMR spectrum that have been assigned as transition-metal hydrides from complete oxidative addition largely on the basis of NMR data.^{9b,19c,20a,c}

The cleavage of Si–C bonds by transition metals has precedent, albeit the majority of examples feature the 4d and 5d metals.^{28,29} Jones et al. were able to isolate several Si–C bond coupling products from Si–C bond activation reactions of alkynylsilanes and biphenylene with a Ni(0) precursor and postulated a *mononuclear* nickel-mediated Si–C bond formation process.³⁰ We have recently shown that C–C coupling of biphenylene with Ni(COD)₂ in the presence of ⁱPr₃P involves a formally dinuclear mixed-valent Ni(III)–Ni(I) intermediate.²³ Complex **5** suggests that dinuclear reactive intermediates in Si–C coupling are also plausible. Group 10 complexes that undergo Si–C(sp²) bond cleavage have been reported,³¹ and recently reversible intramolecular Si–C(sp³) bond activation has been observed in a nickel-silyl pincer complex^{11a} and an amidodiphosphine complex of Ni(II).³²



Figure 6. ORTEP representations selected fragments of 2-5 showing the similarity of approximately planar coordination environments to formal Ni(I) centers, shown as the rightmost Ni(1) labeled in boldface in all four depictions. In all cases 30% probability ellipsoids are shown.

| Table 1. Summary of Experi | imental and Calculated | Bond Length and NMR | R and IR Spectroscopy Data | a for Compounds 1–5 |
|----------------------------|------------------------|---------------------|----------------------------|---------------------|
|----------------------------|------------------------|---------------------|----------------------------|---------------------|

| | 1 | 2 | 3 ^{<i>a</i>} | 4 ^{<i>b</i>} | 5 |
|--|-----------|-------------------------------------|-----------------------|-----------------------|------------|
| IR stretch (Ni–H–Si) | 1887 | 1582 | 1578 | 1567 | 1635 |
| | | | | 1551 | |
| calcd IR stretch (Ni–H–Si) | 1905 | 1584 (s, A _u) | 1548 (s, E) | 1556.3 (s, B) | 1613 (s) |
| | | 1595 (A _g) ^e | 1538 (w, A) | 1551.6 (m, B) | 1602 (s) |
| | | 0 | | 1547 $(A)^{e}$ | |
| ¹ H NMR shift for Si–H (δ) | -10.75 | -2.05 | -1.81 | -2.27 | -7.07 |
| calcd ¹ H NMR shift for Si–H $(\delta)^d$ | -10.4 | -2.3 | -0.5 | -0.8 | -7.7 |
| ²⁹ Si NMR shift (δ) | 10.16 | 123.7 | 300.4 | 277.4 | 124.5 |
| calcd ²⁹ Si NMR shift $(\delta)^d$ | 54.8 | 130.1 | 298.0 | 284.0 | 130.0 |
| $ J_{\rm SiH} $ (Hz) | <7 | 59.6, 20.0 | 45.0 | 35.9 | 50.3 |
| calcd $J_{\rm SiH}$ (Hz) | 70.8 | $-53.2, -14.7^{c}$ | -35.5, -11.2 | -39.9, -9.0 | -39.8 |
| exptl Si–Ni distance (Å) | 2.2211(9) | 2.2164(8) | 2.1935(8) | 2.214(1) | 2.2378(15) |
| calcd Si-Ni distance (Å) | 2.2708 | 2.2499 | 2.23044 | 2.22961 | 2.25375 |
| exptl agostic SiNi distance (Å) ^f | n.a. | 2.2654(7) | 2.2645(8) | 2.290(1) | 2.2204(15) |
| calcd agostic SiNi distance (Å) ^f | n.a. | 2.3263 | 2.2815 | 2.3072 | 2.2552 |
| exptl Si–H distance (Å) | 1.78(3) | 1.64(2) | 1.61(3) | 1.65(4) | 1.64(5) |
| calcd Si–H distance (Å) | 1.869 | 1.597 | 1.685 | 1.672 | 1.698 |
| exptl Ni–H distance (Å) | 1.41(3) | 1.55(2) | 1.57(4) | 1.55(4) | 1.46(6) |
| calcd Ni–H distance (Å) | 1.486 | 1.661 | 1.618 | 1.621 | 1.604 |
| exptl Ni–Ni distance (Å) | n.a. | 2.4878(6) | 2.5704(5) | 2.442(3) | 2.4075(9) |
| calcd Ni–Ni distance (Å) | n.a. | 2.5390 | 2.6013 | 2.5094 | 2.4472 |
| | | | | | |

^{*a*}Calculations on model complex 3^{Me}. ^{*b*}Calculations on model complex 3^{Me}. ^{*c*}Calculated J_{SiH} for model complex 2^{Me}. ^{*d*}Relative to Me₄Si and scaled; see text for details. ^{*e*}Predicted to be IR inactive. ^{*f*}The Ni–Si distance associated with the agostic Si–H moiety.

Examples of unstrained Si–C bond activation within the nickel coordination sphere are limited, and dinuclear Ni(I) complexes such as 5 from such processes are unprecedented. It is noteworthy that the Si–C bond activation that produces 5 occurs even in the presence of a typically more reactive Si–H bond.

Comparison of Formally Ni(I) Centers. Complexes 2 and 5 are both formally Ni(I)-Ni(I) species, with a Ni-Ni bond, albeit with varying degrees of back-donation to the bound Si-H, so that 5 could be viewed as nearing a formal Ni(I) - Ni(III)oxidation state assignment. The formal oxidation states of the nickel centers in 3 and 4 are not absolutely defined, although by connectivity they can be assigned as formally Ni(III)-Ni(I)²³ and Ni(IV)-Ni(I) complexes, respectively, where the central atom in each complex has the high formal oxidation state. Although in many clusters oxidation state assignments are not particularly useful due to electron delocalization, in some cases geometries combined with other spectroscopic parameters allows a useful assignment to be made. A comparison of complexes 2-5 shows similarities in both geometries and spectroscopic parameters for the formally Ni(I) centers. Significant polarization of the Ni-Ni bonds may stabilize such species with apparently incompatible oxidation states.²³ Figure 6 shows a comparison of the Ni(I) bonding environments in these molecules, using fragments of the solid-state structures of 2-5. The views are shown so that the similarities between the rightmost Ni(I) centers, labeled in boldface, are evident. The donor environment around each of these nickel centers is approximately planar and features a Ni-Ni bond, a Si-H interaction suggestive of significant back-donation, a phosphine donor, and a σ bond to either Si or C. The silicon centers all feature an approximately tetrahedral arrangement of σ bonds. The Ni–Ni–P bond is always significantly less than 180° and is always bent away from the adjacent bound Si-H moiety.

A comparison of bond lengths and spectroscopic parameters for complexes 1-5 is shown in Table 1. Due to the inherent difficulties in locating hydrogen atoms by X-ray crystallography, as well as the significant errors in bond lengths to hydrogen, bond lengths from DFT calculations performed with the B3LYP functional and the TZVP basis set are included to support the experimental data. Optimized structures with zero imaginary stretching frequencies were used for all complexes. For 3 and 4 the model complexes $(Me_3P)Ni[(Me_3P)Ni(\mu_3-$ SiHPh)]₃ (3^{Me}) and Ni[(Me₃P)Ni(μ_3 -SiHPh)]₄ (4^{Me}) were used for computational efficiency. Similarly, the model complex $[(Me_3P)Ni(\mu-SiHPh_2)]_2$ (2^{Me}) was used for the calculated NMR coupling constants for complex 2. All the optimized structures gave complexes with the same geometrical features and connectivity predicted from the X-ray crystallographic data, thus confirming the location of the silicon-bound hydrogen atoms in these complexes.

A comparison of the IR stretching frequencies in complexes 1-5 reveals that complexes 2-5 feature Si-H-Ni stretching frequencies that range from 1551 to 1635 cm⁻¹. The unique complex is 1, which displays a stretching frequency at 1887 cm⁻¹ appropriate for a Ni-H moiety. The DFT calculated stretch of 1905 cm^{-1} for 1 revealed that the motion of the H moiety in this vibration occurs nearly coincident with the Ni-H bond vector. In complexes 2-5 the calculated motion of the hydrogen atoms for these strong absorptions lies between the Ni-H and H-Si vectors. The highest stretching frequency for the formally Ni(I) complexes is for 5, suggestive of stronger back-bonding to the Si-H moiety in this complex. DFT calculations predict that high-intensity lower frequency vibrations associated with the Ni-H-Si moiety should be observed at 1326, 1207, 1270, and 1158 cm⁻¹ for 2, 3^{Me}, 4^{Me}, and 5, respectively, but the experimental spectra all contained too many peaks in this region to allow assignment.

The ¹H NMR shift of the Si-H-Ni moiety supports the greater degree of back-donation to the Si-H moiety in 5 relative to 2-4, consistent with the IR data. Complex 1 displays a strongly upfield shifted resonance at δ –10.75. In contrast, the shifts in 2-4 are in the range of δ -1.81 to -2.27. The ¹H NMR shift of the Si-H-Ni moiety in 5 at δ -7.07 is significantly shifted toward the range expected for a nickel hydride. Most notably, clusters 3 and 4 do not feature ¹H NMR Si-H-Ni shifts that are significantly different from those of the verifiably Ni(I) complex 2. DFT calculations approximate the trends in the chemical shifts reasonably well. The ²⁹Si NMR shifts are nearly identical for the Ph2Si-H silvl moieties in 2 and 5, but the PhSi-H silylene moieties of 3 and 4 are clearly distinct. The experimental ${}^{1}J_{SiH}$ values range from 35.5 to 59.6 Hz in complexes 2-5; however, there appears to be no strong correlation between the value of this coupling constant and the degree of back-donation to the Si-H moiety. Clusters 3 and 4 do not feature unusual coupling constants in comparison to the verifiably Ni(I) centers in 2 and 5. DFT calculations predict that these observed coupling constants are negative, as anticipated for one-bond Si-H coupling. The smaller ${}^{2}J_{Si-H}$ value observed for 2 is also predicted to be negative. It should be noted that the basis sets used are not optimized to describe electron density near the nucleus and thus should provide only approximate NMR coupling constants. The largest error is for 1, where a large positive coupling constant is predicted, but no J_{SiH} value is resolved in either the ¹H or ²⁹Si spectrum.

The σ -bound Ni–Si bond distances do not seem to strongly correlate to the proposed oxidation state. The Ni–Si distance in the formally Ni(II) complex 1 is 2.2211(9) Å, which is similar to those in the formally Ni(I) containing complexes 2–4, which have distances in the range of 2.1935(8)–2.2164(8) Å. The Ni–Si distance of 2.2378(15) Å in 5 is the longest and may be due to a more electron rich Ni center, due to the poorer π -accepting ability of the aryl substituent in comparison to a Si–H moiety in 2. The agostic Ni- - Si interactions fall in the range of 2.228(15)–2.290(1) Å. The shortest of these interactions are in the same range as the Ni–Si σ bonds, suggesting that the Si–H moiety is a very good acceptor. As previously noted, in complex 5 the degree of back-donation could be interpreted as nearing a formally Ni(I)–Ni(III) compound.²³

Calculations on the model complexes 2, 3^{Me} , 4^{Me} , and 5 suggest that back-donation is greatest in 5, with a Si–H bond distance of 1.698 Å. By this measure, complexes 3^{Me} and 4^{Me} feature similar degrees of back-donation, with Si–H bond distances of 1.685 and 1.672 Å, respectively. The least activated complex is 2. The complexes with the longest calculated Si–H distances also feature the shortest Ni–H distances. The Ni–H distance of 1.604 Å in 5 is only ~0.1 Å longer than typical crystallographically determined nickel–hydride bond distances.^{13f} Similar short distances of 1.621 and 1.618 Å are calculated for 3^{Me} and 4^{Me} , whereas 2 features the longest calculated Ni–H distance of 1.661 Å.

These parameters all suggest that complexes 3 and 4 possess Ni(I) sites similar to those in 2 and 5. The degree of backbonding suggested from the IR and NMR data does not correlate exactly with the calculated lengthening of the Si–H bond; similar observations have been noted before in σ complexes of silanes.^{2k,33}

The central Ni atoms in complexes **3** and **4** also feature interesting bonding environments. Excluding bonding interactions with the peripheral nickel atoms, the arrangement of

donors around the central atom is a distorted tetrahedron in both complexes. The bonding in 4 is particularly interesting from an orbital overlap point of view because of the perfect square-planar arrangement of bonded nickel atoms in S_4 symmetry. The formation of four bonds to the nickel atoms requires molecular orbitals of A, B, and E symmetry on the central atom. The pairs of both p_x/p_y and d_{xz}/d_{yz} orbitals on the central nickel have E symmetry; however, due to the squareplanar arrangement of nickel centers, the actual overlap with the d_{xz}/d_{yz} pair is nearly 0. Thus, nickel–nickel metal bonds can be expected to have a relatively large p orbital contribution from the central atom. As a result, the bonds from the central atom to the silylene moieties in 4 should feature significantly more d orbital character.

CONCLUSIONS

In summary, a series of mono-, di-, tetra-, and pentanuclear nickel complexes (1-5) with bridging organosilyl/silylene ligands and agostic Ni-H-Si interactions have been obtained under relatively mild reaction conditions by reaction of $[({}^{i}\mathrm{Pr}_{3}\mathrm{P})_{2}\mathrm{Ni}]_{2}(\mu-\eta^{1}:\eta^{1}-\mathrm{N}_{2})$ with a series of silanes. The syntheses of these complexes include some remarkable transformations, including the cleavage of a Si-C bond in the presence of a typically more reactive Si-H bond. Silylene complexes of nickel prepared from simple sterically unencumbered silanes are uncommon. The tetranuclear and pentanuclear complexes 3 and 4 with Si-H agostic interactions are without precedent. Furthermore, the peripheral nickel coordination environments in these complexes are strikingly similar to those of the verifiable Ni(I) complexes 2 and 5. The similarity of these environments suggests that complexes 3 and 4 can be formally described as mixed-valent Ni(I)-Ni(III) and Ni(I)-Ni(IV) complexes, though the polarization of Ni-Ni bonds in these complexes undoubtedly allows for the presence of such apparently incompatible oxidation states, and the electronic structures of the central atoms in these complexes are not expected to be the same as those of mononuclear organo-metallic Ni(III) and Ni(IV) complexes.^{12i,34} Regardless, the silicon-nickel bonds to these formally high-valent central nickel atoms are interesting to compare to other related highvalent congeners, such as Pd.35 The reactivities of these bridging silvlene nickel clusters are of continuing interest in our studies.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glovebox. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Aldrich, sparged with dinitrogen, and passed through activated alumina under a positive pressure of nitrogen gas; toluene and hexanes were further deoxygenated using using a Grubbs type column system.¹ Benzene- d_6 was dried by heating at reflux with Na/K alloy in a sealed vessel under partial pressure andthen trap-to-trap distilled and freeze-pump-thaw degassed three times. Toluene- d_8 was purified in an analogous manner by heating at reflux over Na. THF-d₈ was purified in an analogous manner by heating at reflux over K. ${}^{1}H$, ${}^{31}P{}^{1}H$, and ${}^{13}C{}^{1}H$ spectra were recorded on a Bruker AMX spectrometer operating at 300 or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in hertz. ¹H NMR spectra were referenced to residual protons (C₆D₅H, δ 7.16; C₇D₇H, δ 2.09; C₄D₇HO, δ 1.73) with respect to tetramethylsilane at δ 0.00. ³¹P{¹H} NMR spectra were referenced to external 85% H_3PO_4 at δ 0.00.

¹³C{¹H} NMR spectra were referenced relative to solvent resonances (C₆D₆, δ 128.0; C₇D₈, δ 20.4; C₄D₈O, δ 25.37). ²⁹Si{³¹P} NMR spectra were referenced to an external sample of 50% Si(CH₃)₄ in C₆D₆ at δ 0.0. Infrared spectra (IR) were recorded on a Bruker Tensor 27 instrument operating from 4000 to 400 cm⁻¹. Elemental analyses were performed at the Center for Catalysis and Materials Research, Windsor, Ontario, Canada. [Ni₂N₂(PⁱPr₃)₄] was prepared by the Mg reduction of (PⁱPr₃)₂NiCl in THF, followed by extraction into and crystallization from pentanes. Ni(COD)₂ (COD = 1,5-cyclooctadiene) was synthesized according to literature methods. The compounds benzene-*d*₆ toluene-*d*₈, and THF-*d*₈ were purchased from Cambridge Isotope Laboratory. The compounds nickel dichloride, chlorodiphenylsilane, phenylsilane, diphenylsilane, and triphenylsilane were purchased from Aldrich and used as received. Triisopropylphosphine was purchased from Strem and used as received.

Synthesis and Characterization of (¹Pr₃P)₂Ni(H)SiClPh₂ (1). Chlorodiphenylsilane (100 mg, 0.45 mmol) dissolved in 2 mL of npentane was slowly added to a stirred solution of $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-N_{2})$ (175 mg, 0.22 mmol) in 2 mL of *n*-pentane at -34 °C. The low temperature was maintained, and after 1 min, the reaction mixture turned green-brown. Stirring was stopped and pale yellow cubic shaped crystals formed. The crystals were separated from the solution by decantation, and the residual solvent was removed using vacuum. The pale yellow crystals were washed with cold n-pentane and dried under vacuum to provide 1 (yield 52 mg, 19%). Complex 1 is thermally sensitive, and solutions of 1 cannot be handled for extensive periods at room temperature. ¹H NMR (298 K, C₆D₆, 500 MHz): δ -10.75 ppm (t, ²J_{PH} = 20.5 Hz, 1H, Ni-H-Si), 1.11 (dd, ³J_{HH} = 7.0 Hz, ${}^{3}J_{PH} = 13.0$ Hz, 36H, P(CH(CH₃)₂)₃), 2.15 (sept, ${}^{3}J_{HH} = 7.0$ Hz, 6H, P(CH(CH₃)₂)₃), 7.07 (t, ${}^{3}J_{HH} = 7.0$ Hz, 2H, para-H), 7.28 (apparent t, ${}^{3}J_{HH} = 6.5$ Hz, 4H, Ar-H), 8.10 (apparent t, ${}^{3}J_{HH} = 7.0$ Hz, 4H, Ar-H). ${}^{31}P{}^{1}H{}$ NMR (298 K, C₆D₆, 121.5 MHz): δ 47.3 (s). ²⁹Si{¹H} NMR (298 K, C₆D₆, 59.6 MHz): δ 10.16 (t, ²J_{PSi} = 62.5 Hz). IR (Nujol, KBr): 3130 m, 1887 s (br, Ni-H), 1645 w, 1583 w, 880 s, 1297 w, 1240 s, 1184 s, 1156 w, 1090 s, 1053 s, 1029 s, 966 w, 922 m, 802 s, 735 s, 572 m, 564 m, 522 s, 494 vs, 475 vs, 431 s cm⁻¹. Anal. Calcd for C30H53ClNiP2Si (597.92): C, 60.26; H, 8.93. Found: C, 59.86; H, 8.76.

Synthesis and Characterization of $[({}^{i}Pr_{3}P)Ni(\mu-SiHPh_{2})]_{2}$ (2). Method a. To a solution of $[({}^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-N_{2})$ (190 mg, 0.24 mmol) in 5 mL of *n*-pentane was added a solution of diphenylsilane (88 mg, 0.48 mmol) in 2 mL of *n*-pentane at 20 °C. Gas evolution was observed immediately. After the mixture was stirred for 10 min at room temperature, precipitation was induced by cooling the solution overnight at -33 °C. The crystals were separated by decanting off the solution, followed by washing the solid with 1 mL of ice-cold *n*-pentane and drying under vacuum to afford red rhombic crystals of 2. A second crop from the mother liquor delivered a combined yield of 165 mg (86%) of the product.

Method b. Under vigorous stirring, a mixture of $Ni(COD)_2$ (220) mg, 0.8 mmol) in the presence of 1 equiv of ${}^{i}Pr_{3}P$ (128 mg, 0.8 mmol) in 5 mL of toluene was combined dropwise with a solution of diphenylsilane (147 mg, 0.8 mmol) in 5 mL of toluene at 20 °C. After the reaction mixture was heated for 16 h at 55 °C, the volatiles were removed under vacuum and the reddish residue was extracted with npentane $(2 \times 5 \text{ mL})$ and filtered through a sintered-glass disk. Crystals were isolated by cooling the solution to -33 °C, affording 161 mg (56%) of 2. ¹H NMR (298 K, C₆D₆, 500 MHz): δ -2.05 (d, ²J_{PH} = 15.0 Hz, 2H, Ni–H–Si), 0.87 (dd, ${}^{3}J_{PH} = 13.0$ Hz, ${}^{3}J_{HH} = 7.0$ Hz, 36H, $P(CH(CH_3)_2)_3)$, 1.79 (sept, ${}^{3}J_{HH} = 7.0$ Hz, 6H, $P(CH(CH_3)_2)_3)$, 7.19 (t, ${}^{3}J_{HH} = 7.0$ Hz, 2H, Ar-H), 7.30 (t, ${}^{3}J_{HH} = 7.0$ Hz, 4H, Ar-H), 8.38 (t, ${}^{3}J_{HH} = 7.0$ Hz, 4H, Ar-H). ${}^{13}C{}^{1}H{}^{1}$ NMR (298 K, C₆D₆, 75.5 MHz): δ 19.9 (s, Ni–P(CH(CH₃)₂)₃), 25.87 ppm (vt, ¹J_{PC} + ³J_{PC} =18.2 Hz, Ni-P(CH(CH₃)₂)₃), 127.4 (s, Ar-CH), 127.7 (s, Ar-C), 136.3 (s, Ar-CH), 144.11 (s, Ar-C). ³¹P{¹H} NMR (298 K, C₆D₆, 121.5 MHz): δ 57.8 (s, 2P, NiPⁱPr₃). ²⁹Si¹H} (298 K, C₆D₆, 59.6 MHz): δ 123.7 (d, ²J_{SiP} = 48.9 Hz). ²⁹Si NMR (298 K, C₆D₆, 59.6 MHz): δ 123.7 (ddd, ² J_{SiP} = 48.9 Hz, J_{SiH} = 59.6, 20.3 Hz). IR (Nujol, KBr): 3045 w, 1582 m, 1425 m, 1243 m, 1090 m, 1043 w, 881 w, 735

s, 698 vs, 653 s, 614 m, 496 s, 479 s, 429 m cm $^{-1}$. Anal. Calcd for $C_{42}H_{64}Ni_2P_2Si_2$ (804.46): C, 62.71; H, 8.02. Found: C, 62.35; H, 8.67.

Synthesis of (ⁱPr₃P)Ni[(ⁱPr₃P)Ni(μ_3 -SiHPh)]₃ (3) and Ni[(ⁱPr₃P)-Ni(μ_3 -SiHPh)]₄ (4). To an ice-cold solution of $[(^iPr_3P)_2Ni]_2(\mu$ -N₂) (250 mg, 0.31 mmol) in 10 mL of *n*-pentane was added a solution of phenylsilane (68 mg, 0.62 mmol) in 5 mL of *n*-pentane. Immediately, the solution turned from dark red to brown and gas evolution (N₂) was observed. After the mixture was stirred for 1 h at room temperature, the mixture was put aside for crystallization. Over the course of 5 days at room temperature, dark red-brown cubic crystals precipitated. The crystals were filtered off and the mother liquor reduced by half its volume under vacuum, and a second crop of 3 was obtained. The combined yield afforded between 102 and 115 mg (54–61%) of an analytically pure sample of 3. Black needlelike crystals of 4 (13 mg, 5% yield) were manually separated from the accompanying crystals of 3. Complex 4 could also be isolated by dissolving the more soluble 3 in benzene and filtering.

Characterization of **3**. ¹H NMR (298 K, C_6D_{67} 500 MHz): δ –1.81 (dd, $J_{\rm PH}$ = 12.0 Hz, 1.8 Hz, 3H, Ni-H-Si), 0.90 and 0.93 (dd, ${}^{3}J_{\rm PH}$ = 13.0 Hz, ${}^{3}J_{HH} = 7.0$ Hz, 9H each, P(CH(CH_3)_2)_3), 1.19 (dd, ${}^{3}J_{PH} =$ 12.0 Hz, ${}^{3}J_{\text{HH}} = 7.0$ Hz, 27H, P(CH(CH₃)₂)₃), 1.35 (dd, ${}^{3}J_{\text{PH}} = 13.5$ Hz, ${}^{3}J_{\text{HH}} = 7.0$ Hz, 27H, P(CH(CH₃)₂)₃), 1.47 (sept, ${}^{3}J_{\text{HH}} = 7.0$ Hz, 3H, $P(CH(CH_3)_2)_3)$, 2.10 (sept, ${}^{3}J_{HH} = 7.0$ Hz, 9H, $P(CH(CH_3)_2)_3)$, 7.19 (t, ${}^{3}J_{HH} = 7.0$ Hz, 3H, para-H), 7.36 (apparent t, ${}^{3}J_{HH} = 7.5$ Hz, 6H, Ar-H), 8.38 (apparent t, ${}^{3}J_{HH} = 7.0$ Hz, 6H, Ar-H). ${}^{13}C{}^{1}H$ NMR (298 K, C₆D₆, 75.5 MHz): δ 19.5 (s, 9C, CH₃), 20.2 (s, 3C, CH₃), 20.5 (s, 3C, CH₃), 21.2 (d, 9C, ${}^{1}J_{PC}$ =4.5 Hz, CH₃), 25.9 (d, J_{PC} =18.2 Hz, P-CH), 126.6 (s, Ar-CH), 128.6 (s, Ar-C), 136.6 (s, Ar-CH), 150.4 (s, Ar-C). ³¹P{¹H} NMR (298 K, C₆D₆, 121.5 MHz): δ 68.7 (q, ³J_{PP} = 12.5 Hz, 1P, NiPⁱPr₃), 59.8 (d, ³J_{PP} = 12.5 Hz, 3P, NiPⁱPr₃). ²⁹Si{¹H} NMR (298 K, C₆D₆, 59.6 MHz): δ 300.4 (dd, ²J_{SiP} = 47.9 Hz, 10.9 Hz). ²⁹Si NMR (298 K, C₆D₆, 59.6 MHz): δ 300.4 (ddd, ³J_{SiH} = 45.0 Hz). IR (Nujol, KBr): 3157 w, 3125 w, 2032 w, 1946 w, 1887 w, 1819 w, 1578 (Ni-H-Si), 1359 s, 1298 m, 1245 s, 1156 s, 1086 s, 1053 s, 1043 s, 1023 s, 997 s, 960 w, 925 m, 880 w, 852 vw, 733 vs, 697 vs, 653 vs, 607 s, 563 m, 521 vs, 481 vs, 456 s, 410 s cm⁻¹. Anal. Calcd for C54H102Ni4P4Si3 (1194.31): C, 54.31; H, 8.61. Found: C, 54.17; H, 8.99

Characterization of **4**. ¹H NMR (298 K, C₆D₆, 500 MHz): δ –2.27 (d, ²J_{PH} = 11.5 Hz, 4H, Ni–H–Si), 1.17 and 1.20 (m, 24 H, CH₃), 1.83 (sept, ³J_{HH} = 7.0 Hz, 12H, P(CH(CH₃)₂)₃), 6.97 (m, 4H, *para*-H), 7.40 (m, 8H, *meta*-H), 7.80 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 2.1 Hz, 8H, *ortho*-H). ³¹P{¹H} NMR (298 K, C₆D₆, 121.5 MHz): δ 61.8 (s). ²⁹Si{¹H} NMR (298 K, C₆D₆, 59.6 MHz): δ 277.4 (d, ²J_{SiP} = 45.9 Hz). ²⁹Si{¹H} NMR (298 K, C₆D₆, 59.6 MHz): δ 277.4 (dd, ¹J_{SiH} = 35.9 Hz). Anal. Calcd for C₆₀H₁₀₈Ni₅P₄Si₄ (1359.20): C, 53.02; H, 8.01. Found: C, 53.12; H, 7.52. IR (Nujol, KBr): 3217 vw, 3061 m, 3046 m, 2027 vw, 1939 vw, 1882 vw, 1805 vw, 1567 m, 1551 m, 1427 m, 1297 w, 1246 m, 1179 m, 1157 w, 1092 s, 1045 s, 964 vw, 928 w, 883 m, 824 vw, 729 s, 695 vs, 654 vs, 636 m, 612 vs, 557 m, 522 vw, 495 vs, 458 s cm⁻¹.

Synthesis and Characterization of [(¹Pr₃P)Ni]₂(µ-C₆H₅)(µ-SiHPh₂) (5). A solution of $[Ni_2N_2(P^iPr_3)_4]$ (198 mg, 0.25 mmol) in 5 mL of *n*-pentane was combined with triphenylsilane (65 mg, 0.25 mol) dissolved in 5 mL of *n*-pentane. After the mixture was stirred for 20 min, the volatiles were removed under vacuum, which afforded a dark brown oil. The oil was taken up in a mixture of 4 mL of hexamethyldisiloxane/benzene (100/1). Brown needles of 5 suitable for analysis by X-ray crystallography precipitated via slow evaporation over 4 days and were isolated and dried under vacuum (84 mg, 48% yield). ¹H NMR (298 K, C₆D₆, 500 MHz): δ -7.07 (d, ²J_{PH} = 13.2 Hz, Ni-H-Si), 0.84 (dd, ${}^{3}J_{HH} = 6.9$ Hz, ${}^{3}J_{HP} = 6.0$ Hz, 18H, CH₃), 0.97 (dd, ${}^{3}J_{HH} = 6.9$ Hz, ${}^{3}J_{HP} = 6.0$ Hz, 18H, CH₃), 1.55 (sept, ${}^{3}J_{HH} = 6.9$ Hz,, 3H, PCH), 1.78 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 3H, PCH), 6.69 (m, 1H, Ni-C-H), 7.16-7.22 (m, 4H, Ar-H), 7.30-7.32 (m, 6H, Ar-H), 8.10–8.12 (m, 4H, Ar-H). $^{13}C\{^{1}H\}$ NMR (298 K, $C_{6}D_{6}$, 75.5 MHz): δ 19.9 (s, CH₃), 19.9 (s, CH₃); 24.5 (d, ¹J_{PC} = 17.6 Hz, Ni- $PCH(CH_3)_2)_3$, 25.0 (d, ${}^{1}J_{PC} = 16.5$ Hz, Ni $-P(CH(CH_3)_2)_3$), 120.7 (s, Ar-CH), 125.6 (s, Ar-CH), 127.2 (s, Ar-CH), 127.7 (s, Ar-C), 129.7 (s, Ar-CH), 136.0 (s, Ar-CH), 144.3 (s, Ar-CH), 183.5 (d, ${}^{2}J_{PC} = 17.6$

Article

| Table 2. (| Crystal Da | ita and | Structure | Refinement | Parameters | for | Complexes | 1 - 5 | , |
|------------|------------|---------|-----------|------------|------------|-----|-----------|-------|---|
| | | | | | | | | | |

| | 1 | 2 | 3 | 4 | 5 |
|--|----------------|---------------------------|----------------------------|----------------------------|-------------------------|
| empirical formula | C30H53ClNiP2Si | $C_{42}H_{64}Ni_2P_2Si_2$ | $C_{54}H_{102}Ni_4P_4Si_3$ | $C_{60}H_{108}Ni_5P_4Si_4$ | $C_{36}H_{58}Ni_2P_2Si$ |
| fw | 597.91 | 804.47 | 1194.35 | 1359.25 | 698.27 |
| cryst syst | monoclinic | monoclinic | cubic | cubic | monoclinic |
| a (Å) | 18.741(2) | 11.713(2) | 29.199(3) | 15.158(1) | 15.297(2) |
| b (Å) | 11.195(1) | 17.723(4) | 29.199(3) | 15.158(1) | 15.285(2) |
| c (Å) | 32.174(3) | 10.674(2) | 29.199(3) | 14.868(2) | 17.426(2) |
| α (deg) | 90 | 90 | 90 | 90 | 90 |
| β (deg) | 101.875(1) | 108.04(3) | 90 | 90 | 117.461(1) |
| γ (deg) | 90 | 90 | 90 | 90 | 90 |
| V (Å ³) | 6605.6(1) | 2106.8(10) | 24894(5) | 3416.0(7) | 3615.6(7) |
| space group | C2/c | $P2_{1}/c$ | I 4 3d | I I | $P2_1/c$ |
| Ζ | 8 | 2 | 16 | 2 | 4 |
| $D_{\rm calcd}~({\rm g/cm^3})$ | 1.202 | 1.268 | 1.275 | 1.321 | 1.280 |
| μ (Mo K α) (mm ⁻¹) | 0.818 | 1.054 | 1.384 | 1.551 | 1.186 |
| temp (K) | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) |
| $2\theta_{\max}$ (deg) | 55 | 53 | 56 | 55 | 50 |
| total no. of rflns | 34 367 | 22 104 | 133 036 | 19 186 | 34 464 |
| no. of unique rflns; R_{int} | 7456; 0.040 | 4315; 0.0236 | 5059; 0.0403 | 3871; 0.0219 | 6371; 0.119 |
| abs cor | multiscan | multiscan | multiscan | multiscan | multiscan |
| transmissn factors | 0.90-0.88 | 0.77-0.64 | 0.67-0.57 | 0.88-0.74 | 0.91-0.82 |
| no. of rflns with $I \ge 2\sigma(I)$ | 6281 | 3931 | 4833 | 3722 | 4198 |
| no. of variables | 332 | 227 | 266 | 252 | 386 |
| rflns/params | 22.4 | 17.3 | 19.0 | 15.4 | 16.5 |
| GOF on F^2 | 1.09 | 1.048 | 1.087 | 1.071 | 1.040 |
| R1; wR2 (all data) | 0.063; 0.108 | 0.0295; 0.077 | 0.0349; 0.0822 | 0.029; 0.0685 | 0.110; 0.1406 |
| residual density (e/ ų) | 0.433; -0.352 | 0.529; -0.208 | 0.867; -0.349 | 0.672; -0.308 | 0.974; -0.513 |

Hz Ni–C). ³¹P{¹H} NMR (298 K, C₆D₆, 121.5 MHz): δ 47.9 (d, ³J_{PP} = 24.5 Hz, 1P, NiPⁱPr₃), 56.8 (d, ³J_{PP} = 24.5 Hz, 1P, NiPⁱPr₃). ²⁹Si{¹H} NMR (298 K, C₆D₆, 59.6 MHz): δ 124.5 (dd, ²J_{PSi} = 82.5 Hz, ²J_{PSi} = 3.2 Hz). ²⁹Si (298 K, C₆D₆, 59.6 MHz): 124.5 (dd, ²J_{PSi} = 82.5 Hz, ²J_{SiH} = 50.3 Hz). IR (Nujol, KBr): 3037 w, 2718 w, 1950 w, 1889 w, 1818 w, 1635 s(br), 1555 s, 1526 w, 1460 vs, 1425 s, 1404 m, 1297 m, 1238 s, 1181 w, 1156 m, 1091 s, 1046 s, 1028 s, 996 m, 964 m, 925 m, 882 vs, 803 w, 727 vs, 697 vs, 655 vs, 613 s, 592 s, 506 vs, 469 s, 444 m, 423 s cm⁻¹. Anal. Calcd for C₃₆H₅₈Ni₂P₂Si (698.3): C, 61.92; H, 8.37. Found: C, 62.08; H, 8.61.

X-ray Crystallography. The X-ray structures were obtained at low temperature, with the crystals being covered in Paratone and placed rapidly into the cold N2 stream of a Kryo-Flex low-temperature device. The data were collected using the SMART³⁶ software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected using a counting time of 10-30 s per frame. A summary of crystal data, data collection, and structure refinement is given in Table 2. Data reductions were performed using the SAINT³⁷ software, and the data were corrected for absorption using SADABS.³⁸ The structures were solved by direct or Patterson methods using SHELXS-97³⁹ and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELX-97³⁹ and the WinGX⁴⁰ software package, and thermal ellipsoid plots were produced using ORTEP32.⁴¹ Complex 3 featured a 2-fold rotational disorder of two of the phosphine ligand isopropyl substituents. Complex 4 featured a disorder of the molecule about the S_4 axis that was modeled and refined to account for 10.2(1)% of the molecules. The agostic hydrogen of this disordered fragment was omitted from the model. Details of the structure solution and refinement are provided as Supporting Information for 1-5.

Calculations. Ab initio DFT calculations were performed using the hybrid functional B3LYP¹⁰ method with the Gaussian 09 package.⁴² Basis functions used were the TZVP set, provided in the Gaussian 09 program. Optimized geometries were used for all calculations. All vibrational analyses featured no imaginary frequencies. Chemical shifts and NMR coupling constants were calculated using the default options

via the NMR=spinspin keyword. Energies and optimized geometries are provided in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

Tables giving details of DFT calculations and CIF files giving X-ray crystallographic data for 1-5. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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