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Article

Nickel Complexes with Bis(8-quinolyl)silyl Ligands. An Unusual Ni_3Si_2 Cluster Containing Six-Coordinate Silicon[†]

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Efforts to install the bis(8-quinolyl)methylsilyl (Me-NSiN; **1** = Me-NSiNH) and bis(8-quinolyl)-phenylsilyl (Ph-NSiN; **2** = Ph-NSiNH) ligands onto nickel are described. Reaction of **1** with $NiCl_2(DME)$ and N^iPr_2Et afforded $[(^iPr_2EtNH)_2Cl][(QnH)NiCl_3]$ (**3**; Qn = quinolyl) via degradation of the silane. Reaction of **2** with $Ni(COD)_2$ in chlorobenzene yielded $[Ph\text{-}NSiN]_2Ni_3Cl_2$ (**5**), which is a rare example of a silylnickel cluster with a $[Ni_3Si_2]$ core. An X-ray structure determination reveals the presence of a triangular Ni_3 core with two face-capping silyl groups: one that is bonded symmetrically to the three nickel atoms, while the other is unsymmetrically bound. The bonding in **5** has been investigated by computational methods to obtain descriptions of the molecular orbitals. The unsymmetrical bonding of Si(1) results from a two-electron bonding interaction with Ni(1), and this explains the short Si(1)−Ni(1) contact (2.2688(6) Å). The symmetrical bonding of Si(2) appears to result from its interaction with a delocalized Ni_3 skeletal orbital. Complex **5** slowly decomposes in dichloromethane-d_2 to $(PhClSiQn_2)NiCl$ (**6**), a Ni(I) chloride complex in which the phenyl group is bonded to the nickel with an intramolecularly coordinated (silyl)arene ligand. The η^2-coordination of the aryl group involves interaction of *ipso* and *ortho* carbon atoms with the metal center. Theoretical studies of **6** support a very weak Ni−Si interaction (2−3 kcal/mol at the NBO level) that is supported by the arene coordination. The strength of the η^2-coordination of the arene was estimated at the second-order donor−acceptor NBO level to be 25 kcal/mol.

Introduction

Multidentate ligands have gained increasing popularity over the last few decades, since they have been found to impart stability and unprecedented reactivity to their organometallic complexes. Examples include PCP pincer ligands with a central aryl donor group, which have been found to support alkane dehydrogenation catalysts,[1] and PNP ligands with a central amido donor, which support both early and late transition metal complexes.[2] A less studied type of multidentate ligand involves incorporation of a silicon donor atom.[3−5] Such ligands might be expected to provide several useful functions, including strong electron donation from the silicon donor to afford an electron-rich metal center. In addition, the strong *trans* influence of silicon should promote coordinative unsaturation at a metal and facilitate substrate activation processes. Along these lines, we have reported use of the bis(8-quinolyl)methylsilyl (Me-NSiN) ligand in new chemical transformations with rhodium, iridium, and platinum.[4] This rigid tridentate silyl ligand strongly prefers *facial* coordination to transition metals and stabilizes a series of Pt(IV) alkyl and hydrido derivatives.[4d]

[†] Part of the Dietmar Seyferth Festschrift. Dedicated to Professor Dietmar Seyferth, in recognition of his many contributions to chemistry and his tireless service to the oganometallic community.

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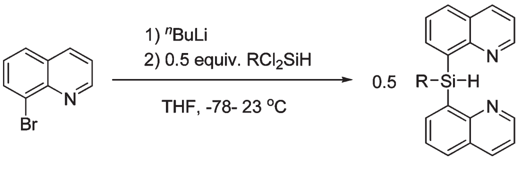
Given results from previous studies on complexes containing multidentate ligands with silicon donor atoms, it is of interest to explore their use in new chemical transformations for the first-row transition metals,[5c−f] especially since there is considerable interest in development of new catalysts based on the more abundant, and less expensive, transition metals.[6] Within this context, the studies reported here were initiated to examine the coordination chemistry of NSiN ligands with nickel. Of particular interest is the influence of a silicon donor atom on chemical properties of a nickel center. Relatively few nickel silyl complexes have been isolated;[7,8] however, the potentially analogous platinum−silicon chemistry is quite rich, with numerous platinum silyl complexes being described in the literature.[8] Of course, platinum silyl complexes play important roles in homogeneous catalysis, especially in the area of hydrosilylation.[9] In this contribution, we describe initial efforts to obtain nickel complexes of the bis(8-quinolyl)methylsilyl (Me-NSiN) and bis(8-quinolyl)phenylsilyl (Ph-NSiN) ligands. These studies have led to isolation of several structurally unusual nickel complexes including a silicon−nickel cluster with an unusual [Ni_3Si_2] core and six-coordinate silicon.

Results and Discussion

Ligand Synthesis. To examine possible electronic and steric effects in NSiN ligands, both methylsilyl and phenylsilyl derivatives were investigated. Following a previously described procedure for bis(8-quinolyl)methylsilane (Me-NSiNH, **1**),[4a,b] bis(8-quinolyl)phenylsilane (Ph-NSiNH, **2**) was obtained in 39% yield via lithiation of 8-bromoquinoline followed by addition of 0.5 equiv of dichlorophenylsilane (eq 1).



(1)

1: R = Me, ref 4b

2: R = Ph, 39% yield

Isolation of [(^{i}Pr$_2$EtNH)$_2$Cl][(QnH)NiCl$_3$] (3). Treatment of **1** with $NiCl_2$(DME) and excess N^{i}Pr$_2$Et in refluxing THF did not afford the desired chelate-assisted, Si−H bond activation product (NSiN)NiCl. Instead, an unexpected product was isolated in low yield (11%) by crystallization from THF/pentane, and single-crystal X-ray crystallography established this compound as [(^{i}Pr$_2$EtNH)$_2$Cl][(QnH)NiCl$_3$] (**3**; Qn = quinolyl; eq 2). This Ni(II) product likely results from C(sp^2)−Si cleavage of the NSiN ligand by a protic species generated by interaction of the silane with a Ni−Cl bond.

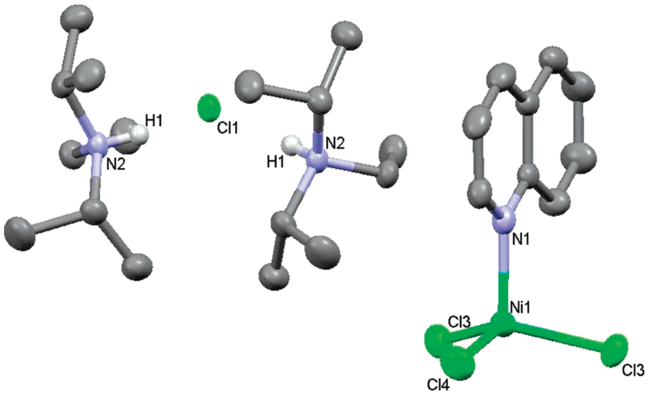
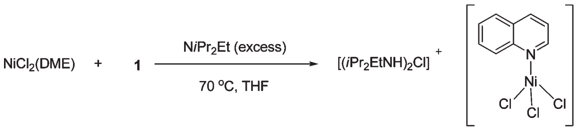


Figure 1. Molecular structures of **3** with thermal ellipsoids drawn at the 50% probability level. Key bond distances (Å) and angles (deg): Ni(1)−N(1)=2.029(3), Ni(1)−Cl(3)= 2.245(1), Ni(1)−Cl(4) = 2.231(1), Cl(1)···H(1) = 2.336(6), H(1)···Cl(1)···H(1) = 130.4(15).



3

(2)

As shown in Figure 1, the (QnH)NiCl$_3^-$ anion adopts a tetrahedral geometry about the Ni center, with the Ni(II) atom coordinated by quinoline and three chlorides. In the [(^{i}Pr$_2$EtNH)$_2$Cl]$^+$ complex cation, two ^{i}Pr$_2$EtNH$^+$ units are symmetrically hydrogen-bonded to a chloride anion, with crystallographically equivalent H···Cl distances of 2.336(6) Å and an H···Cl···H angle of 130.4(15)°. A similar structure, in which two R_3NH^+ cations are bound via hydrogen bonds to one chloride ion, was previously proposed for [(^{n}Oct$_3$NH)$_2$Cl][FeCl$_4$] on the basis of infrared spectroscopy. The H···Cl···H arrangement in this structure was suggested to have a linear geometry.[10]

Reaction of 1 with (tmeda)NiPhCl. The complex (tmeda)-NiPhCl[11] (tmeda = tetramethylethylenediamine) was envisioned as a potential precursor to (R-NSiN)NiCl complexes, as it was anticipated that Si−H oxidative addition followed by reductive elimination of C_6H_6 would lead to formation of the desired (R-NSiN)NiCl complex. Reaction of **1** with (tmeda)NiPhCl in 1,2-dichloroethane (or dichloromethane)

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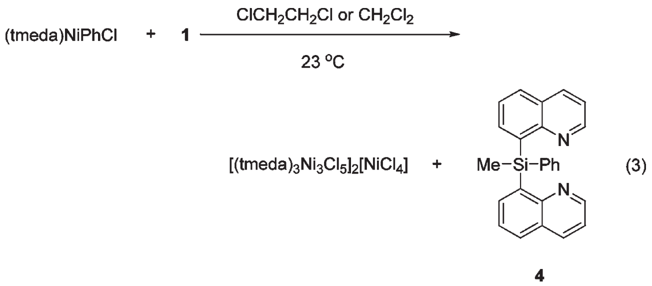
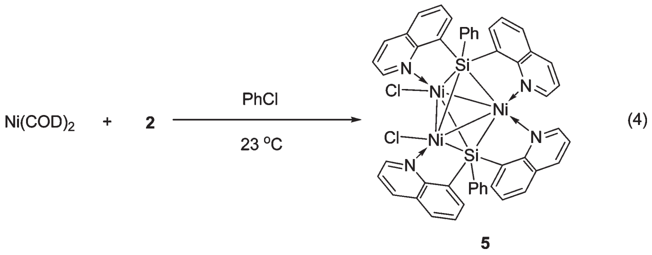
at room temperature afforded an off-white solid (74% yield), which was characterized by multinuclear NMR spectroscopy and GC-MS as bis(8-quinolyl)methylphenyl silane (**4**). This reaction also provided green crystals from dichloromethane/pentane, identified by single-crystal X-ray diffraction as $[(\mathrm{tmeda})_3\mathrm{Ni}_3\mathrm{Cl}_5]_2[\mathrm{NiCl}_4]$[12] (46% yield). Presumably, this reaction proceeds by a chelate-assisted, Si−H bond oxidative addition of **1**, followed by C−Si reductive elimination of **4** (eq 3). This C−Si bond formation is likely driven by the eventual formation of the trinuclear nickel species $[(\mathrm{tmeda})_3\mathrm{Ni}_3\mathrm{Cl}_5]_2[\mathrm{NiCl}_4]$.



Synthesis of (Ph-NSiN)$_2$Ni$_3$Cl$_2$ (5). An additional approach to the synthesis of an NSiN-Ni complex utilized COD as a leaving group and was based on the known reaction of PhCl, Ni(COD)$_2$, and a bidentate *N*,*N*-ligand (NN) such as tmeda or 2,2′-bipyridyl to form a (NN)Ni(Ph)Cl complex.[11] It was reasoned that a nickel-phenyl derivative formed in solution might then react via Si−H oxidative addition followed by C−H reductive elimination to install the NSiN ligand onto nickel. Indeed, treatment of silane **2** with Ni(COD)$_2$ and excess PhCl resulted in isolation of a new nickel silyl species, **5** (eq 4). Further purification by crystallization afforded **5** as dark red crystals in 38% yield. The ^{1}H NMR spectrum of **5** in dichloromethane-d_2 contains four different sets of quinolyl protons, suggesting an unsymmetrical structure. The ^{29}Si NMR spectrum of **5** exhibits two signals at 11.1 and 9.0 ppm, corresponding to inequivalent silicon environments.



X-ray quality crystals of **5** were obtained by layering pentane onto a solution of **5** in 1,2-dichloroethane at room temperature. The ORTEP diagram of **5** is shown in Figure 2. The three Ni atoms form a triangle, and the central Ni$_3$Cl$_2$ moiety is capped by two bis(8-quinolyl)phenylsilyl groups to form an unusual [Ni$_3$Si$_2$] core. The Ni(2)−Ni(3) distance (involving the Ni atoms with Ni−Cl bonds) is 2.3203(4) Å, while the other two Ni−Ni distances are slightly longer, averaging ca. 2.39 Å. One silyl group is primarily bonded to Ni(1), as indicated by a Ni(1)−Si(1) distance (2.2688(6) Å) that is shorter than the other two Ni−Si(1) distances (av 2.52 Å). The other silyl group is bound more symmetrically to the Ni$_3$ triangle and exhibits roughly equivalent Ni−Si(2) bond distances, which average 2.37 Å. Note that this distance is longer than those typically associated with Ni−Si bonds (2.14−2.30 Å[13,7]).

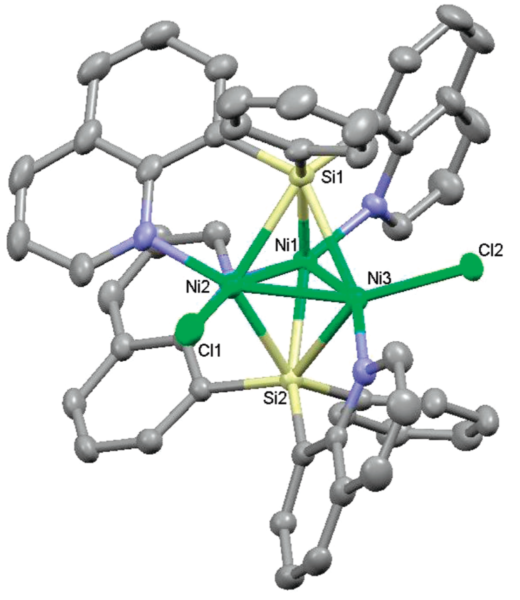


Figure 2. Molecular structure of **5** with thermal ellipsoids drawn at the 50% probability level (hydrogens omitted). Key bond distances (Å): Ni(1)−Ni(2) = 2.3947(4), Ni(1)−Ni(3) = 2.3847(4), Ni(2)−Ni(3) = 2.3203(4), Si(1)−Ni(1) = 2.2688(6), Si(1)−Ni(2) = 2.4592(6), Si(1)−Ni(3) = 2.5769(6), Si(2)−Ni(1) = 2.3496(6), Si(2)−Ni(2) = 2.4011(6), Si(2)−Ni(3) = 2.3563(6).

Complex **5** represents a rare example of a structurally characterized silicon−transition metal cluster containing six-coordinate silicon. Indeed, clusters that incorporate more than two metal atoms and bridging Si ligands have only a few precedents, most of which involve metal carbonyl fragments.[14−19] For example, a series of pseudo-octahedral Co$_4$Si$_2$ clusters incorporating five-coordinate silicon have

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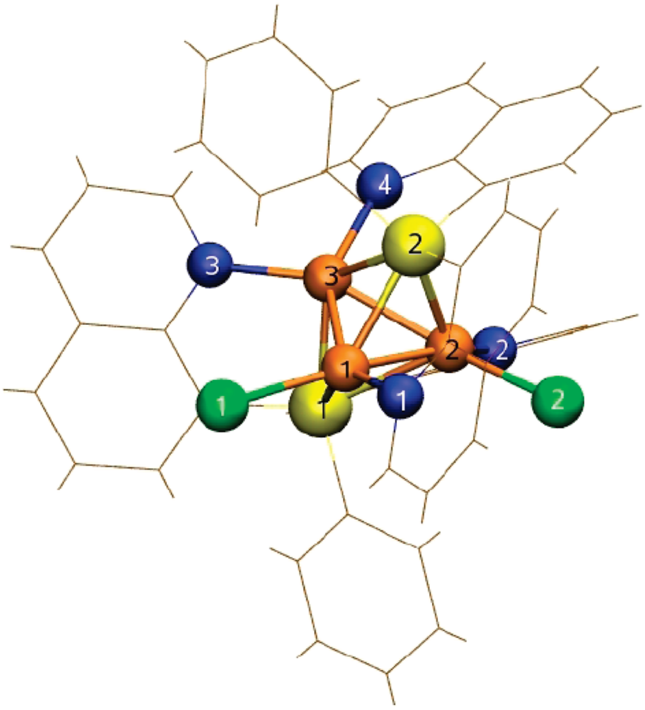


Figure 3. Optimized DFT structure of **5**.

Table 1. Selected Bond Lengths of 5 in Å

bond	optimized structure	X-ray
Ni2−Ni3	2.310	2.320
Ni1−Ni3	2.361	2.385
Ni1−Ni2	2.412	2.395
Si1−Ni2	2.524	2.459
Si1−Ni3	2.549	2.577
Si1−Ni1	2.248	2.269
Si2−Ni2	2.357	2.401
Si2−Ni3	2.341	2.356
Si2−Ni1	2.396	2.350
Cl1−Ni2	2.228	2.240
Cl2−Ni3	2.239	2.213
N1−Ni2	1.971	1.957
N4−Ni3	1.927	1.940
N3−Ni1	2.000	1.981
N2−Ni1	1.988	1.951

been synthesized via oxidative additions of hydrosilanes to $Co_2(CO)_8$.[14] An Fe_3Si_2 cluster involving four-coordinate silicon, $[(\mu^3\text{-Si}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$, has been prepared by reaction of SiH_4, $Fe(CO)_5$, and $[CpFe(CO)_2]_2$ under harsh conditions.[15a] A somewhat related copper complex containing a bridging silyl ligand, $Cu_2[Si(SiMe_3)_3]_2BrLi(THF)_3$, was synthesized by reaction of $(Me_3Si)_3SiLi(THF)_3$ with CuBr.[16a] Trinuclear M_3 complexes (M = Pd, Pt)[17] as well as dinuclear nickel complexes[7d] with edge-bridged silylene ligands have also been reported.

Computational Studies of 5. In order to gain better insight into the bonding in this unusual nickel−silicon cluster, a theoretical investigation of **5** at the DFT(B3PW91/SDD(Ni, Si,Cl), 6-31G(d,p) for the other atoms) level was undertaken. First of all, the geometry was successfully optimized without symmetry restrictions (Figure 3).

The comparison between the experimental and theoretical bond lengths is excellent (Table 1), which demonstrates the ability of the computational method to model the complex. The electronic ground state was determined to be a closed-shell singlet, leading to a diamagnetic complex as observed by NMR experiments.

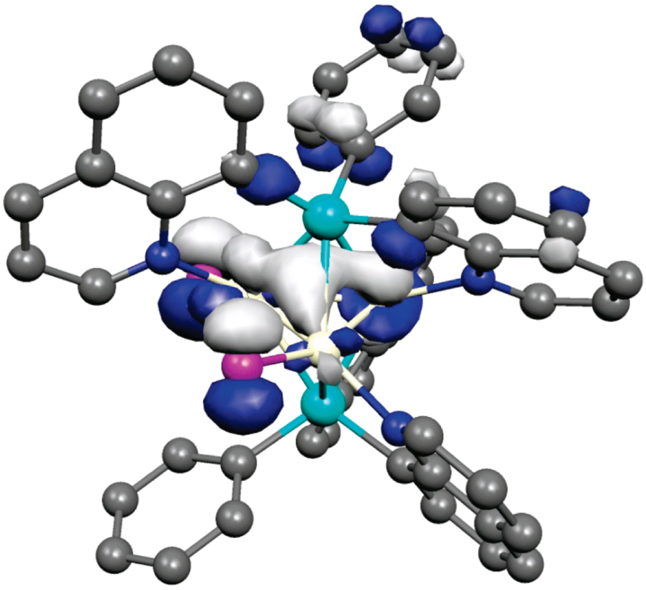
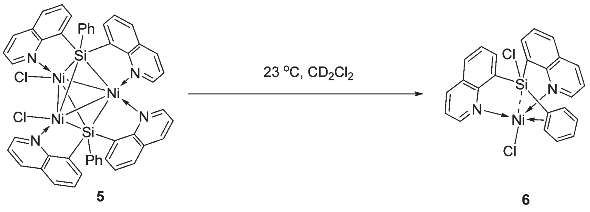


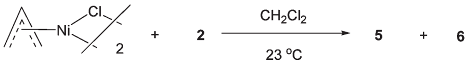
Figure 4. Ni_3 skeletal orbital that ensures the symmetrical coordination with Si.

The bonding in **5** may be analyzed by inspection of the molecular orbitals derived from the calculation. Orbitals corresponding to the Ni−Cl bonds are readily apparent, as are three Ni−Ni bonding orbitals and two-center, two-electron Ni−N bonds. The unsymmetrical bonding of Si(1) appears to result from a strong two-electron bonding interaction with Ni(1), which results in the short Si(1)−Ni(1) contact. The symmetrical bonding of Si(2) to the trinickel core can be understood according to the Wade−Mingos rules for metal clusters.[20] These rules indicate that a facial coordination of a ligand is possible, as one of the Ni_3 skeletal orbitals (formed by a combination of d orbitals) is oriented toward the silicon center (Figure 4). Moreover, there is only one orbital of this type for a triangle, so that only one bridging ligand may be accommodated in this way. Thus, all other ligands must bind to the cluster in terminal positions, as edge coordination appears to be disfavored for both steric and electronic factors.

Degradation of 5. Complex **5** slowly decomposes in dichloromethane-d_2 to give a new paramagnetic species (**6**) over several days at room temperature (eq 5). A mixture of **5** and **6** was also obtained from the reaction of **2** with allyl nickel chloride in dichloromethane (eq 6). Analysis of the crude products by ^1H NMR spectroscopy suggested a ∼1:3 ratio of **5** and **6**. Species **6** was separated from **5** by successive crystallizations from dichloromethane/pentane and was structurally characterized as an unusual Ni(I) chloride complex with an intramolecularly coordinated (silyl)arene ligand.



(5)



(6)

Crystallographic data for **6** revealed a roughly tetrahedral geometry about the Ni center (Figure 5). The reaction

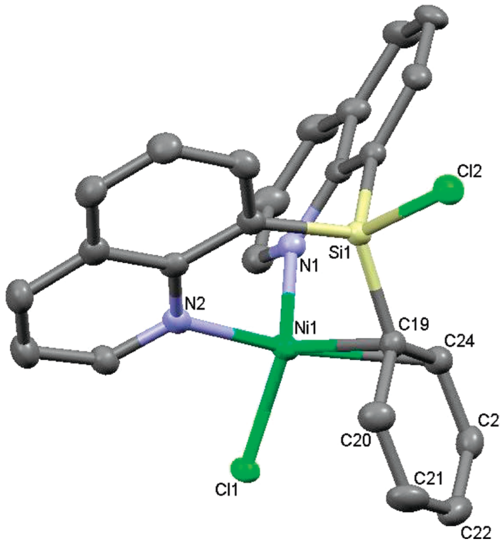


Figure 5. Molecular structures of **6** with thermal ellipsoids drawn at the 50% probability level (hydrogens omitted). Key bond distances (Å) and angles (deg): Ni(1)−C(19) = 2.068(3), Ni(1)−C(24) = 2.369(3), Ni(1)−Cl(1) = 2.3307(8), Si(1)···Ni(1) = 2.6772(10), Si(1)−Cl(2) = 2.1142(11), C(19)−Si(1) = 1.839(3), C(19)−C(24) = 1.429(4), C(20)−C(21) = 1.380(5), C(22)−C(23) = 1.376(5), Ni(1)···Si(1)−Cl(2) = 156.00(4).

involves conversion of the Si−H group of **2** to a Si−Cl group. The resulting bis(8-quinolyl)phenylchlorosilane ligand is bonded to the Ni(I) center in a chelated fashion through two N donors of the quinolyl groups and a π interaction with the (silyl)phenyl ring. The latter interaction results in Ni−C(19) and Ni−C(24) distances of 2.068(3) and 2.369(3) Å, respectively, and the C(19)−C(24) distance (1.429(4) Å) is significantly longer than the C(20)−C(21) (1.380(5) Å) and C(22)−C(23) (1.376(5) Å) distances, suggesting an η^2-coordination of the phenyl ring. The Ni···Si distance of 2.677(1) Å is much less than the sum of the van der Waals radii of Ni and Si (4.1 Å),[21] but is greater than the sum of the covalent radii (2.35 Å).[22] The geometry about the silicon atom (including Ni as a substituent) may be described as a distorted trigonal bipyramid ($\sum$(C−Si−C) = 342.8° and Ni···Si−Cl = 156.00(4)°), and the Si−Cl distance (2.114(1) Å) is longer than that of a typical Si−Cl bond (e.g., that of Ph_3SiCl is 2.077(1) Å[23]). These findings suggest the presence of a weak Ni→Si donor interaction.

To provide insight into the bonding characteristics of **6**, DFT studies were performed on the real complex. A Ni−Si interaction of 2−3 kcal/mol was found at the NBO level. This interaction is quite small and has to be supported by the arene coordination. The strength of the η^2-coordination of the arene can be estimated at the second-order donor−acceptor NBO level and is much higher than that of the Ni−Si interaction (25 vs 2−3 kcal/mol). An AIM analysis was carried out in order to further characterize the interaction between the Ni center and the SiPh fragment. A bond critical point was located between Ni and Si (ρ = 0.052), which is closer to Si (0.72 Å) than Ni (1.98 Å). Another bond critical point was located (ρ = 0.072) at a position equidistant between C(19) (1.04 Å) and Ni (1.06 Å). The density at the bond critical point is higher in the latter case, which is consistent with the NBO analysis. Drawings of molecular orbitals corresponding to the Ni−phenyl and Ni−Si interactions are provided in the Supporting Information. A similar bonding situation has been reported very recently for $\{[o\text{-}{}^{i}Pr_2P(C_6H_4)BPh_2]Cu(\mu\text{-}Cl)\}_2$,[24,25] in which a weak Cu→B interaction supported by arene coordination has been thoroughly studied by NMR spectroscopy, X-ray crystallography, and DFT calculations.

Conclusion

Reactions of the bis(8-quinolyl)silanes **1** and **2** with simple nickel complexes have led to unusual coordination complexes of nickel rather than simple mononuclear, four-coordinate species of the type (R-NSiN)NiX. Addition of **2** to $Ni(COD)_2$ in the presence of PhCl results in incorporation of the Ph-NSiN ligand into a nickel complex, the silylnickel cluster **5**. Bonding analysis by inspection of the molecular orbitals suggests that one silyl ligand plays a central role in stabilizing the trinickel core, by functioning as a triply bridging ligand bonding symmetrically to a metal cluster skeletal orbital that is bonding with respect to the three nickel atoms. This unusual cluster with a $[Ni_3Si_2]$ core and silicon atoms with expanded coordination spheres suggests a new role for NSiN ligands in the assembly of multinuclear metal complexes. The NSiN ligands also appear to have the potential to allow access to low-valent nickel species such as **6**. The mechanisms of the reactions providing nickel cluster **5** and the nickel(I) complex **6** are currently unknown, but they may involve the intermediacy of simple divalent (Ph-NSiN)NiX species. Thus, compounds of the latter type may be highly reactive and represent interesting targets for future synthetic studies.

Experimental Section

General Considerations. All manipulations were carried out using Schlenk techniques under a purified N_2 atmosphere or in a Vacuum Atmospheres drybox. Solvents were distilled under N_2 from appropriate drying agents and stored in Straus flasks. Benzene-d_6 was dried by vacuum distillation from Na/K alloy. Dichloromethane-d_2 was dried with CaH_2 and vacuum transferred prior to use. Ethyldiisopropylamine, tetramethylethylene diamine (tmeda), 1,2-dichloroethane, dichloromethylsilane, and dichlorophenylsilane were dried over CaH_2 and vacuum transferred to a sealed storage flask. All other reagents were

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purchased from Aldrich, Strem, or Gelest and used as received. Allyl nickel chloride dimer,[26] (tmeda)NiPhCl,[11a] and 8-bromoquinoline[27] were prepared according to literature procedures. Bis(8-quinolyl)methylsilane (**1**) was synthesized as previously described.[4a,b] NMR spectra were recorded on Bruker AV-600, DRX-500, AV-500, AVB-400, AVQ-400, and AV-300 spectrometers at room temperature. ^{1}H NMR spectra were referenced to residual protio solvent peaks. ^{13}C{^{1}H} NMR spectra were referenced to solvent resonances (δ 128.39 for C_6D_6, δ 54.00 for CD_2Cl_2, δ 43.6 for $ClCD_2CD_2Cl$). ^{29}Si chemical shifts were referenced to internal $(CH_3)_4Si$. Elemental analyses were carried out by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. GC-MS analysis was performed on an Agilent Technologies 6890N GC system with an HP-5MS column.

Synthesis of Bis(8-quinolyl)phenylsilane (Ph-NSiNH, 2). *N*-Butyllithium (1.6 M in hexanes, 6.5 mL, 10.4 mmol) was added dropwise to a stirred solution of 8-bromoquinoline (2.05 g, 9.9 mmol) in THF (50 mL) at −78 °C. The mixture was stirred for 10 min at this temperature before phenyldichlorosilane (neat, 0.74 mL, 5.1 mmol) was added via syringe. The reaction mixture was stirred for another 15 min at −78 °C before being warmed to room temperature and stirred for an additional 19 h. All volatile materials were removed *in vacuo*, and the resulting residue was extracted with toluene (100 mL). The yellow extract was concentrated to about 25 mL and filtered. The filtrate was stored at −30 °C for 2 days to give the product as a pale yellow solid in 39% yield (0.7 g, 1.93 mmol). ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 8.80 (d, $J_{HH} = 4.2$ Hz, of d, $J_{HH} = 1.8$ Hz, 2H), 8.19 (d, $J_{HH} = 8.1$ Hz, of d, $J_{HH} = 1.8$ Hz, 2H), 7.92 (d, $J_{HH} = 8.1$ Hz, of d, $J_{HH} = 1.5$ Hz, 2H), 7.70 (d, $J_{HH} = 6.9$ Hz, of d, $J_{HH} = 1.5$ Hz, 2H), 7.65 (m, 2H), 7.47 (m, 2H), 7.41−7.30 (m, 5H) (aryl hydrogens, total 17H), 6.32 (s, 1H, Si*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.77 MHz): δ 153.02, 150.12, 139.76, 136.75, 136.71, 136.54, 136.14, 130.42, 129.57, 128.30, 128.17, 126.76, 121.59. ^{29}Si{^{1}H} NMR (CD_2Cl_2, 119.23 MHz): δ −23.8. Anal. Calcd (%) for $C_{24}H_{18}N_2Si$ (362.50): C, 79.52, H, 5.00, N, 7.73. Found: C, 79.66, H, 4.80, N, 7.34.

Isolation of [(^{i}Pr$_2$EtNH)$_2$Cl][(QnH)NiCl$_3$] (3). A PTFE-valved sealable reaction flask was charged with $NiCl_2$(DME) (0.088 g, 0.40 mmol). A solution of **1** (0.120 g, 0.40 mmol) and ethyldiisopropylamine (0.25 mL, 1.51 mmol) in THF (10 mL) was added. The flask was sealed and stirred at 70 °C for 37 h. The mixture was filtered to give a clear green solution, which was layered with pentane (10 mL). At −30 °C, blue crystals were obtained in 11% yield (0.025 g, 0.0424 mmol). Anal. Calcd (%) for $C_{25}H_{47}N_3Cl_4Ni$ (590.16): C, 50.88, H, 8.03, N, 7.12. Found: C, 51.18, H, 8.90, N, 7.10. A crystalline sample of **3** (blue needle $0.30 \times 0.05 \times 0.05$ mm^3) was used for X-ray crystallographic analysis.

Reaction of 1 with (tmeda)NiPhCl in 1,2-Dichloroethane. A solution of **1** (0.032 g, 0.107 mmol) in 1,2-dichloroethane (3 mL) was added to (tmeda)NiPhCl (0.031 g, 0.108 mmol) with stirring. The resulting solution was stirred at room temperature for 18 h. All volatile materials were removed *in vacuo*, and the resulting residue was extracted with benzene (4 mL). The benzene solution was filtered through Celite and a glass fiber filter, and the solvent was then removed under vacuum to yield crude **4** as a pale orange powder (0.039 g). Crude **4** was exposed to air and extracted into benzene (3 mL). The benzene solution was filtered through silica gel, and then the solvent was removed under vacuum to give spectroscopically pure **4** as an off-white solid in 74% yield (0.030 g, 0.080 mmol). A byproduct from this reaction, crystallized from CH_2Cl_2/pentane, was identified by single-crystal X-ray analysis as the previously known compound $[(tmeda)_3Ni_3Cl_5]_2[NiCl_4]\cdot CH_2Cl_2$[12] (0.012 g, 0.0071 mmol, 46% yield).

Complex **4** was characterized by NMR spectroscopy and GC-MS. ^{1}H NMR (C_6D_6, 600.13 MHz): δ 8.51 (d, $J_{HH} = 4.2$ Hz, of d, $J_{HH} = 1.8$ Hz, 2H), 7.81 (m, 4H), 7.51 (d, $J_{HH} = 7.8$ Hz, of d, $J_{HH} = 1.8$ Hz, 2H), 7.44 (d, $J_{HH} = 7.8$ Hz, of d, $J_{HH} = 1.2$ Hz, 2H), 7.22−7.10 (m, 5H), 6.65 (d, $J_{HH} = 7.8$ Hz, of d, $J_{HH} = 4.2$ Hz, 2H) (aryl hydrogens, total 17H), 1.80 (s, 3H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 153.16, 149.56, 139.50, 139.47, 139.28, 136.63, 135.85, 129.95, 129.03, 128.36, 127.95, 126.51, 121.26 (aryl carbons), −0.49 (Si-*C*H$_3$). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 119.23 MHz): δ −9.0. GC-MS: *m*/*z* 376 (M$^+$), 361, 299, 248.

Synthesis of (Ph-NSiN)$_2$Ni$_3$Cl$_2$ (5). A slurry of **2** (0.120 g, 0.33 mmol) in chlorobenzene (3 mL) was added to $Ni(COD)_2$ (0.084 g, 0.31 mmol) with stirring. The reaction mixture was stirred at room temperature for 1 day. The reaction mixture was then concentrated to ca. 1.5 mL, and pentane (10 mL) was added to precipitate crude **5** a dark brown solid. The solid was washed with pentane (2 mL × 3) and redissolved in 1,2-dichloroethane (ca. 5 mL). This solution was filtered through Celite and a glass fiber filter and layered with pentane (ca. 15 mL). At −30 °C, **5** was obtained as dark red blocks in 38% yield (0.040 g, 0.039 mmol). ^{1}H NMR (CD_2Cl_2, 500.13 MHz): δ 9.74 (m, 1H), 9.08 (b, 2H), 8.88 (b, 2H), 8.76 (m, 2H), 8.51 (d, $J_{HH} = 6.5$ Hz, of d, $J_{HH} = 1.5$ Hz, 1H), 8.17 (m, 1H), 8.03 (m, 1H), 7.94−7.86 (m, 3H), 7.83−7.75 (m, 3H), 7.67 (m, 1H), 7.56−7.49 (m, 5H), 7.42 (m, 1H), 7.33 (m, 1H), 7.28 (m, 1H), 7.13 (m, 2H), 7.09 (d, $J_{HH} = 8.0$ Hz, of d, $J_{HH} = 5.0$ Hz, 1H), 7.05 (d, $J_{HH} = 5.0$ Hz, of d, $J_{HH} = 2.0$ Hz, 1H), 6.82 (d, $J_{HH} = 8.0$ Hz, of d, $J_{HH} = 4.5$ Hz, 1H), 6.40 (d, $J_{HH} = 8.0$ Hz, of d, $J_{HH} = 5.0$ Hz, 1H), 6.30 (d, $J_{HH} = 5.0$ Hz, of d, $J_{HH} = 1.5$ Hz, 1H), 6.11 (d, $J_{HH} = 8.0$ Hz, of d, $J_{HH} = 4.5$ Hz, 1H), 5.87 (d, $J_{HH} = 5.0$ Hz, of d, $J_{HH} = 1.5$ Hz, 1H) (aryl hydrogens, total 34 H). ^{13}C{^{1}H} NMR ($ClCD_2CD_2Cl$, 150.9 MHz): δ 155.9 (br), 155.3 (br), 153.9 (br), 153.4 (br), 152.7 (br), 150.9 (br), 150.3 (br), 147.6 (br), 147.2 (br), 144.2 (br), 141.4 (br), 139.8 (br), 139.4 (br), 139.3 (br), 138.3 (br), 138.2 (br), 138.0 (br), 137.2 (br), 137.1 (br), 137.0 (br), 136.7 (br), 136.4 (br), 129.1−126.7 (broad overlapping resonances), 121.1 (br), 120.9 (br), 120.5 (br), 120.3 (br). The broad resonances observed in the ^{13}C{^{1}H} NMR spectrum are likely due to the slow decomposition of **5**. ^{29}Si{^{1}H} NMR (CD_2Cl_2, 119.23 MHz): δ 11.1, 9.0. Anal. Calcd (%) for $C_{48}H_{34}N_4Si_2Ni_3Cl_2\cdot(ClCH_2CH_2Cl)_{0.5}$ (1019.45): C, 57.73, H, 3.56, N, 5.50. Found: C, 58.06, H, 3.45, N, 5.33. Crystals suitable for X-ray analysis were grown from layering pentane onto a 1,2-dichloroethane solution of **5** at room temperature.

Isolation of (PhClSiQn$_2$)NiCl (6). A slurry of **2** (0.080 g, 0.22 mmol) in CH_2Cl_2 (2 mL) was added dropwise to an allyl nickel chloride dimer (0.036 g, 0.13 mmol) solution in CH_2Cl_2 (2 mL). The reaction mixture was stirred at room temperature for 10 min and filtered. The dark red solution was then layered with pentane (10 mL) at room temperature for 1 day to give a brown crystalline solid as a ca. 1:3 mixture of **5** and **6** (0.073 g). The solid was redissolved in CH_2Cl_2 (ca. 7 mL), filtered, and layered with pentane (8 mL). At room temperature an analytically pure sample of **6**·(CH_2Cl_2) was obtained as dark brown crystals in 12% yield (0.015 g, 0.026 mmol). ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ 23.5, 18.1, 15.6, 13.4, 5.0. Anal. Calcd (%) for $C_{24}H_{17}N_2SiCl_2Ni\cdot(CH_2Cl_2)$ (576.02): C, 52.13, H, 3.32, N, 4.86. Found: C, 52.46, H, 3.31, N, 5.02. A crystalline sample of **6** (brown plate, 0.10 × 0.08 × 0.04 mm) was used for X-ray crystallographic analysis.

X-ray Structure Determination. The X-ray analyses of compounds **3**, **5**, and **6** were carried out at the UC Berkeley CHEXRAY crystallographic facility. All measurements were made on a Bruker SMART, APEX, or MicroStar CCD area detector with graphite-monochromated Mo or Cu Kα radiation. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by

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full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

Computational Details. All the calculations were performed with the Gaussian 03[28] suite of programs. Nickel, silicon, and chlorine were treated with a Stuttgart-Dresden pseudopotential in combination with their adapted basis set.[29,30] The basis set has been augmented by a set of f polarization functions[31,32] for the nickel atom and by a set of d polarization functions for the silicon and chlorine atoms. Carbon, nitrogen, and hydrogen atoms have been described with a 6-31G(d,p) double-ζ basis set.[33] Calculations were carried out at the density functional theory (DFT) level of theory using the hybrid functional B3PW91.[34] Geometry optimizations were carried out without any symmetry restrictions, and the nature of the extremum (minimum) was verified with analytical frequency calculations. The calculations were carried out in the gas phase. The electron density has been analyzed using the natural bonding analysis (NBO).[35]

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Supporting Information Available: CIF files giving complete crystallographic data for complexes **3**, **5**, and **6**; drawings of molecular orbitals corresponding to the Ni−phenyl and Ni−Si interactions in **6**; Cartesian coordinates of the optimized structures **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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