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Snapshots of the oxidative-addition process of silanes to nickel(0)

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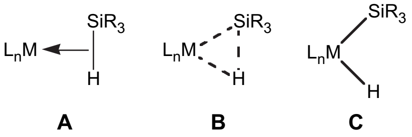
Dedicated to Professor Günther Wilke who has nurtured the field of organonickel chemistry from its infancy to its present state of maturity and importance

Abstract—Addition of hydridosilanes, Ar_2SiHX, to the labile Ni(0) benzene complex $[(dtbpe)Ni]_2(C_6H_6)$ (**1**; dtbpe=1,2-bis(di-*tert*-butylphosphino)ethane) gives mononuclear Ni(II) hydride silyl complexes of the formulation $(dtbpe)Ni(\mu\text{-}H)SiAr_2X$ (**2**, X=H, Ar=Mes; **3**, X=H, Ar=Ph; **4**, X=Me, Ar=Ph; **5**, X=Cl, Ar=Ph). Although the crystal structures of two representatives of the series indicate square-planar coordination around nickel, in solution structures having apparent C_{2v} symmetry are observed. We propose that this behavior is due to a fluxional process that involves η^2-SiH intermediates. Other data are also consistent with the facile reductive elimination of the silane to regenerate nickel(0) products. Oxidation of **2** and **3** with triphenylcarbenium tetrakis(pentafluorophenyl)borate results in silane elimination and formation of $[(dtbpe)Ni(\eta^3\text{-}C_6H_5CPh_2)^+][B(C_6F_5)_4^-]$ (**6**), the structure of which shows the CPh_3^- ligand bound to a Ni(II) center through a phenyl ring in an η^3-allylic fashion.

1. Introduction

Due to interest in silicon-containing materials, the chemistry of metal silyl–silylene complexes has received increased attention in recent years. Silyl complexes show distinct differences when compared to corresponding alkyl complexes, an important one being the facility of addition of Si–H bonds compared to the more problematical addition of C–H bonds to transition metal fragments.[1] Unlike C–H activation processes, which although known, are difficult, the oxidative addition of silanes is one of the main methods of preparing silyl complexes. The nature of the metal–SiH interaction has been intensively studied, but there is a structural continuum between the limiting extremes of η^2-SiH bonding (**A**) and complete oxidative addition (**C**); computational methods are also ambiguous (Scheme 1).[1a,c]



Scheme 1.

Due to the reactivity of most $[M](SiR_3)(H)$ species, there are very few instances where the primary product of Si–H oxidative addition has been isolated, that being even more true for the transition metals of the nickel triad. Moreover, complexes containing agostic or nonclassical Si–H interactions are relatively rare for the late-transition metals and few examples are known for mononuclear compounds.[2] Thus, insight into this process could be obtained from the isolation and characterization of complexes proposed to be intermediates in metal-hydrosilylation reactions. Our work with low valent nickel complexes supported by a bulky diphosphine ligand has provided us with the appropriate framework to study the direct interaction of a secondary silane and a Ni(0) species. The Ni(dtbpe) fragment (dtbpe=1,2-bis(di-*tert*-butylphosphino)ethane) has been shown to be effective in supporting unusual low valent metal functionalities such as nitrene, phosphinidene, and carbene,[3] and we were intrigued by the possibility of accessing silylene analogues ($(dtbpe)Ni{=}SiR_2$) by double Si–H activation of hydridosilanes in processes similar to those reported by Tilley and co-workers in Pt, Ir, and W systems.[4] Herein, we present our findings on the interactions of $HSiXR_2$ (X=H, CH_3, Cl; R=phenyl, 2,4,6-trimethylphenyl) with the labile Ni(0) complex $[(dtbpe)Ni]_2(C_6H_6)$ (**1**)[5] and the characterization of nickel silyl hydride reaction products.

2. Experimental

2.1. General considerations

Unless otherwise stated, all manipulations were performed under an inert atmosphere using an MBraun Lab Master dry box, under a purified nitrogen atmosphere; *n*-pentane

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was dried via passage through activated alumina and Q-5 columns and then stored over 4 Å molecular sieves. [(dtbpe)-Ni]$_2$(C_6H_6) (**1**) and dimesitylsilane were synthesized according to the literature;[5,6] [Ph_3C^+][$B(C_6F_5)_4^-$] by adaptation of a published procedure.[7] All other chemicals were used as received. Infrared data (Nujol mulls on CaF_2 plates) were measured with a Nicolet 670-FTIR instrument. ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on Bruker 500 and 400 MHz NMR spectrometers. ^{1}H and ^{13}C NMR are reported with reference to solvent resonances (for residual C_6D_5H, δ_H=7.16 and δ_C=128.0 in C_6D_6; for residual C_4HD_7O, δ_H=3.58 and δ_C=67.8; for residual $CHDCl_2$, δ_H=5.32 and δ_C=53.8 in CD_2Cl_2). ^{31}P NMR spectra are reported with respect to external 85% H_3PO_4 (0 ppm). ^{29}Si NMR spectra are reported with respect to external neat TMS (0 ppm). X-ray diffraction data were collected on a Siemens Platform goniometer with a Charged Coupled Device (CCD) detector. Structures were solved by direct methods using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

2.1.1. Synthesis and characterization of (dtbpe)Ni(μ-H)-SiH(Mes)$_2$ (2). To a suspension of **1** (100 mg, 0.12 mmol) in 5 mL of *n*-pentane was added a cold solution of dimesitylsilane (64.43 mg, 0.24 mmol) in 2 mL of *n*-pentane. After stirring the mixture for 1 h at room temperature, precipitation was induced by cooling the solution overnight at −35 °C. The solids were separated by filtration, washed with cold *n*-pentane, and dried under vacuum to yield yellow crystalline **2** (100 mg, 0.15 mmol, 65%). ^{1}H NMR (298 K, 400.13 MHz, THF-d_8): δ 6.62 (s, 4H, $C_6H_2(CH_3)_3$), 2.40 (s, 12H, o-$C_6H_2(CH_3)_3$), 2.14 (s, 6H, p-$C_6H_2(CH_3)_3$), 1.88 (d, 4H, J_{HP}=8.6 Hz, CH_2), 1.21 (d, 36H, J_{HP}=12.0 Hz, $C(CH)_3$), −0.17 (t, 2H, J_{HP}=30.3 Hz, SiH_2). ^{13}C{^{1}H} NMR (298 K, 100.62 MHz, THF-d_8): δ 144.25 (s, Ar), 141.53 (s, Ar), 135.77 (s, Ar), 128.71 (s, Ar), 35.47 (t, J_{CP}=6.9 Hz, $C(CH_3)_3$), 31.15 (s, $C(CH_3)_3$), 25.56 (s, o-$C_6H_2(CH_3)_3$), 23.89 (t, J_{CP}=15.6 Hz, CH_2), 21.23 (s, p-$C_6H_2(CH_3)_3$). ^{31}P{^{1}H} NMR (298 K, 202.45 MHz, THF-d_8): δ 90.55 (s, J_{PSi}=53.1 Hz). ^{29}Si{^{1}H} NMR (298 K, 79.51 MHz, THF-d_8): δ 53.36 (t, J_{SiP}=53.5 Hz). IR (Nujol, CaF_2): 3041 (w), 1990 (s), 1861 (m) cm^{-1}.

2.1.2. Single-crystal X-ray structure of 2. Crystal data for **2**·1/2(C_5H_{12}): $C_{38.5}H_{64}NiP_2Si$, M=675.64, triclinic, $P\bar{1}$, a=11.283(3), b=12.291(4), c=15.994(5) Å, α=85.697(6)°, β=81.859(6)°, γ=64.003(5)°, Z=2, t=100 K, μ(Mo Kα)=0.627 mm^{-1}. A yellow prism of **2** (0.16×0.1×0.06 mm) grown from *n*-pentane at −35 °C was mounted in inert oil and transferred to the 100 K gas stream of the diffractometer. Of 9040 total reflections (1.29°<θ<23.33°), 5671 were independent and 4218 (R_{int}=4.71%) were observed with $I>2\sigma(I)$. The structure was solved using direct methods and refined by full-matrix least squares on F^2. All nonhydrogen atoms were refined anisotropically. H1 and H2 were located in the electron density map; all other hydrogen atoms were fit to idealized positions and refined isotropically. The solvation molecule of *n*-pentane is in the inversion center and is disordered over two positions. $R(F)$=5.26% and $R(wF)$=12.33%. CCDC reference no. 610081.

2.1.3. Synthesis and characterization of (dtbpe)Ni(μ-H)-SiH(C_6H_5)$_2$ (3). Complex **3** was synthesized following the protocol used for **2** except that diphenylsilane was employed. In this case, the product precipitates at room temperature and it was separated as bright yellow crystalline powder by filtration followed by washing with *n*-pentane and drying under vacuum to give pure **3** (121.28 mg, 0.22 mmol, 90%). ^{1}H NMR (298 K, 400.13 MHz, C_6D_6): δ 8.26 (d, 4H, J_{HH}=7.1 Hz, Ar), 7.33 (t, 4H, J_{HH}=7.5 Hz, Ar), 7.19 (t, 2H, J_{HH}=7.3 Hz, Ar), 1.32 (d, 4H, J_{HP}=9.4 Hz, CH_2), 1.09 (d, 36H, J_{HP}=12.0 Hz, $C(CH_3)_3$), 0.20 (t, br, 2H, J_{HP}=2.0 Hz, $SiH_2(C_6H_5)_2$). ^{13}C{^{1}H} NMR (298 K, 100.62 MHz, C_6D_6): δ 146.68 (s, Ar), 136.49 (s, Ar), 127.60 (s, Ar), 127.43 (s, Ar), 35.14 (t, J_{CP}=7.3 Hz, $C(CH_3)_3$), 30.56 (s, $C(CH_3)_3$), 23.69 (t, J_{CP}=16.2 Hz, CH_2). ^{31}P{^{1}H} NMR (298 K, 202.45 MHz, C_6D_6): δ 92.19 (s, J_{PSi}=51.6 Hz). ^{29}Si{^{1}H} NMR (298 K, 79.51 MHz, C_6D_6): δ 54.00 (t, J_{SiP}=51.6 Hz). IR (Nujol, CaF_2): 3058 (w), 3038 (w), 1993 (s), 1855 (m), 1179 (m) cm^{-1}.

2.1.4. Synthesis and characterization of (dtbpe)Ni(μ-H)-Si(CH_3)(C_6H_5)$_2$ (4). Complex **4** was synthesized following the protocol used for **2** except that diphenylmethylsilane was employed, yielding orange crystalline **4** (96.68 mg, 0.17 mmol, 70%). ^{1}H NMR (298 K, 500.13 MHz, THF-d_8): δ 7.52 (m, 4H, C_6H_5), 7.15–6.95 (m, 6H, C_6H_5), 1.83 (d, 4H, J_{HP}=8.8 Hz, CH_2), 1.19 (d, 36H, J_{HP}=12.0 Hz, $C(CH)_3$), 0.71 (s, 3H, $SiCH_3$), −6.49 (t, 1H, br, NiH). ^{13}C{^{1}H} NMR (298 K, 100.62 MHz, THF-d_8): δ 150.27 (s, C_6H_5), 135.99 (s, C_6H_5), 126.97 (s, C_6H_5), 126.03 (s, C_6H_5), 35.29 (t, J_{CP}=7.3 Hz, $C(CH_3)_3$), 30.96 (s, $C(CH_3)_3$), 24.41 (t, J_{CP}=16.9 Hz, CH_2), ^{31}P{^{1}H} NMR (298 K, 202.45 MHz, THF-d_8): δ 93.16 (s, br). ^{29}Si{^{1}H} NMR (298 K, 79.51 MHz, THF-d_8): δ 59.22 (t, J_{SiP}=51.2 Hz). IR (Nujol, CaF_2): 1845 (m), 1425 (s), 1181 (m) cm^{-1}.

2.1.5. Synthesis and characterization of (dtbpe)Ni(μ-H)-SiCl(C_6H_5)$_2$ (5). To a suspension of **1** (100 mg, 0.12 mmol) in 5 mL of *n*-pentane was added a 2 mL *n*-pentane solution of diphenylchlorosilane (55 mg, 0.25 mmol). The reaction mixture was stirred for 1 h at room temperature. The bright yellow precipitate was filtered and washed with 2 mL of *n*-pentane and vacuum dried to yield pure **5** (120 mg, 0.20 mmol, 84%). For **5**: ^{1}H NMR (298 K, 400.13 MHz, C_6D_6): δ 8.26 (dd, 4H, J_{HH}=8.0 Hz, J_{HH}=1.3 Hz, Ar), 7.31 (td, 4H, J_{HH}=7.7 Hz, J_{HH}=1.3 Hz, Ar), 7.18 (tt, 2H, J_{HH}=5.6 Hz, J_{HH}=1.3 Hz, Ar), 1.32 (d, 4H, J_{HP}=9.6 Hz, CH_2), 1.10 (d, 36H, J_{HP}=9.6 Hz, $C(CH_3)_3$), −8.29 (t, 1H, J_{HP}=29.8 Hz, J_{HSi}=5.0 Hz, $SiH(C_6H_5)_2$); (200 K, 500.13 MHz, C_7D_8): δ 1.20 (d, 18H, J_{HP}=11.0 Hz, $C(CH_3)_3$), 0.95 (d, 18H, J_{HP}=10.5 Hz, $C(CH_3)_3$), −8.19 (dd, 1H, J_{HP}=20.0 Hz, J_{HP}=90.0 Hz, $SiH(C_6H_5)_2$). ^{13}C{^{1}H} NMR (298 K, 100.62 MHz, C_6D_6): δ 147.98 (s, Ar), 135.53 (s, Ar), 129.06 (s, Ar), 127.44 (s, Ar), 34.82 (t, J_{CP}=7.4 Hz, $C(CH_3)_3$), 30.54 (s, $C(CH_3)_3$), 23.70 (s, br, CH_2). ^{31}P{^{1}H} NMR (298 K, 202.45 MHz, C_6D_6): δ 92.65 (s, J_{PSi}=77 Hz). ^{29}Si{^{1}H} NMR (298 K, 79.51 MHz, C_6D_6): δ 24.00 (t, J_{SiP}=77.6 Hz). IR (Nujol, CaF_2): 1883 (w), 1425 (w) cm^{-1}.

2.1.6. Single-crystal X-ray structure of 5. Crystal data for **5**: $C_{30}H_{51}ClNiP_2Si$, M=595.90, triclinic, $P\bar{1}$, a=9.8023(13), b=10.5891(13), c=16.608(2) Å, α=90.328(3)°, β=92.863(3)°, γ=113.578(2)°, Z=2, t=100 K, μ(Mo Kα)=0.856 mm^{-1}. A yellow block of **5** (0.1×0.08×0.08 mm) grown from *n*-pentane at −35 °C was mounted in inert oil and transferred to the 100 K gas stream of the diffractometer. Of 9984 total reflections ($1.23° < \theta < 28.27°$), 7059 were independent and 4893 (R_{int}=5.17%) were observed with $I > 2\sigma(I)$. The structure was solved using direct methods and refined by full-matrix least squares on F^2. All nonhydrogen atoms were refined anisotropically. The hydride hydrogen atom was located in the electron density map, all other hydrogen atoms were fit to idealized positions and refined isotropically. $R(F)$=9.86% and $R(wF)$=14.64%. CCDC reference no. 610082.

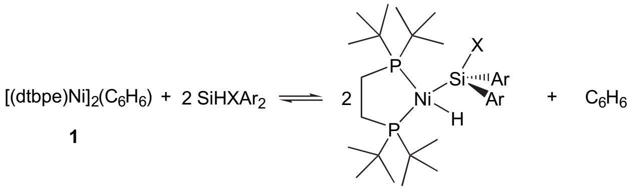
2.1.7. Synthesis of $[Ph_3C^+][B(C_6F_5)_4^-]$. This compound was synthesized adapting a published procedure for triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate by using $Na^+[B(C_6F_5)_4^-]$ instead of sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate.[7]

2.1.8. Synthesis and characterization of $[(dtbpe)Ni(\eta^3\text{-}C_6H_5CPh_2)^+][B(C_6F_5)_4^-]$ (6). *Method A*: To a cold solution of **2** (64.56 mg, 0.1 mmol, in 5 mL diethyl ether at −35 °C), a 5 mL solution of $[Ph_3C^+][B(C_6F_5)_4^-]$ (92.24 mg, 0.1 mmol) at −35 °C was added dropwise. The mixture was allowed to warm to room temperature and stir for another 30 min. After removal of solvent under vacuum, the solids were triturated with *n*-pentane (3×5 mL). The ^{1}H NMR of this fraction shows recovered silane in 95%. The yellow crude solid was recrystallized from a 1:1 diethyl ether–*n*-pentane mixture affording (**6**) in 80% isolated yield (103.96 mg, 0.08 mmol). Complex **3** reacts with $[Ph_3C^+][B(C_6F_5)_4^-]$ in an analogous fashion to give **6** in 80% isolated yield. *Method B*: To a cold solution of **1** (41.62 mg, 0.05 mmol, in 5 mL diethyl ether at −35 °C), a 5 mL solution of $[Ph_3C^+][B(C_6F_5)_4^-]$ (92.24 mg, 0.1 mmol) at −35 °C was added dropwise. The mixture was allowed to warm to room temperature and stir for another 30 min. After removal of solvent under vacuum, the solids were triturated with *n*-pentane (3×5 mL). The yellow crude solid was recrystallized from a 1:1 diethyl ether–*n*-pentane mixture affording **6** in 90% isolated yield (116.95 mg, 0.09 mmol). For **6**: ^{1}H NMR (298 K, 400.13 MHz, CD_2Cl_2): δ 7.39 (t, 2H, J_{HH}=7.0 Hz, Ph), 7.23–7.33 (m, 8H, Ph), 6.89 (dd, 2H, J_{HH}=8.8 Hz, J_{HH}=2.5 Hz, Ph), 6.23 (t, 1H, J_{HH}=5.1 Hz, Ph), 5.93 (t, 2H, J_{HH}=6.9 Hz, Ph), 1.87 (sextet, 2H, J=8.1 Hz, CH_2), 1.71 (sextet, 2H, J=8.0 Hz, CH_2), 1.90 (d, 18H, J_{HP}=13.1 Hz, $C(CH_3)_3$), 1.15 (d, 18H, J_{HP}=13.2 Hz, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (298 K, 100.62 MHz, CD_2Cl_2): δ 148.45 (d, J_{HF}=241.5 Hz, C_6F_5), 142.81 (s, CPh_3), 138.56 (d, J_{HF}=247.8 Hz, C_6F_5), 167.65 (d, J_{HF}=244.8 Hz, C_6F_5), 136.55 (s, C_6F_5), 129.60 (s, Ph), 128.92 (s, Ph), 128.31 (s, Ph), 112.75 (s, Ph), 107.59 (d, J_{CP}=9.0 Hz, Ph), 71.35 (d, J_{CP}=9.2 Hz, Ph), 37.57 (d, J_{CP}=14.5 Hz, $C(CH_3)_3$), 36.07 (d, J_{CP}=13.6 Hz, $C(CH_3)_3$), 30.28 (d, J_{CP}=13.4 Hz, $C(CH_3)_3$), 22.96 (m, CH_2). $^{31}P\{^1H\}$ NMR (298 K, 202.45 MHz, CD_2Cl_2): δ 89.17 (d, J_{PP}=12.1 Hz), 86.12 (d, J_{PP}=12.2 Hz).

2.1.9. Single-crystal X-ray structure of 6. Crystal data for **6**: $C_{69}H_{67}BF_{24}NiP_2$, M=1483.69, triclinic, $P\bar{1}$, a=13.579(3), b=15.064(4), c=17.160(4) Å, α=97.363(5)°, β=104.497(5)°, γ=96.744(5)°, Z=2, t=100 K, μ(Mo Kα)=0.449 mm^{-1}. A yellow block of **5** (0.04×0.04×0.08 mm) grown from 1:1 diethyl ether–*n*-pentane at −35 °C was mounted in inert oil and transferred to the 100 K gas stream of the diffractometer. Of 15,032 total reflections ($1.24° < \theta < 23.34°$), 9516 were independent and 7362 (R_{int}=7.69%) were observed with $I > 2\sigma(I)$. The structure was solved using direct methods and refined by full-matrix least squares on F^2. All nonhydrogen atoms were refined anisotropically, hydrogen atoms were fit to idealized positions and refined isotropically. $R(F)$=4.91% and $R(wF)$=12.16%. CCDC reference no. 610083.

3. Results and discussion

Reaction of pentane solutions of $[(dtbpe)Ni]_2(C_6H_6)$ (**1**) with dimesitylsilane (Mes_2SiH_2) at room temperature affords (dtbpe)Ni(μ-H)SiH(Mes)$_2$ (**2**) in 65% isolated yield (Scheme 2). The solid-state structure of **2** was determined by X-ray crystallography and a perspective view of the complex is shown in Figure 1. The structure of **2** shows a square-planar nickel coordinated to the chelating dtbpe ligand, silicon, and hydrogen. The relative position of the hydride and the silyl fragments is consistent with arrested oxidative addition of the silane, i.e., a structure intermediate between **B** and **C** in Scheme 1. As expected, the Si–H(2) bond involving the bridging hydrogen at 1.92(4) Å is much longer than the terminal Si–H(1) bond distance of 1.42(4) Å. The Ni–Si bond length (2.245(2) Å) is in the range of known Ni–Si single bonds.[8]



2: X = H, Ar = 2,4,6-trimethylphenyl
3: X = H, Ar = C_6H_5
4: X = CH_3, Ar = C_6H_5
5: X = Cl, Ar = C_6H_5

Scheme 2.

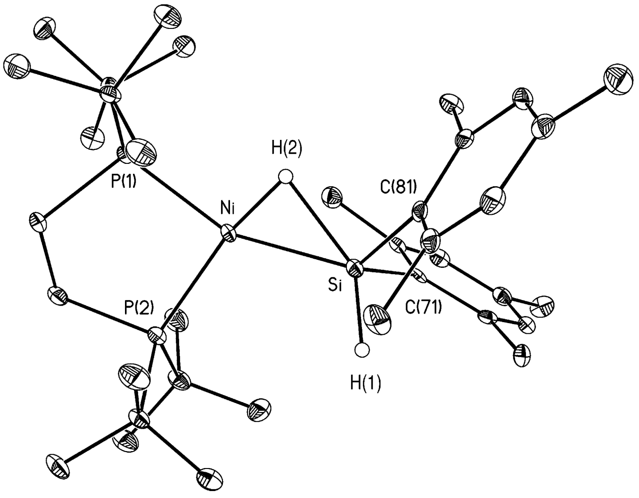


Figure 1. ORTEP view of complex **2** (35% probability thermal ellipsoids, H atoms except those attached to Si and Ni omitted for clarity). Selected bond distances (Å) and angles (°): Ni–P1=2.184(2), Ni–P2=2.195(2), Ni–Si=2.245(2), Ni–H(2)=1.41(4), Si–H(1)=1.42(4), Si–H(2)=1.92(4), Si–C(71)=1.936(4), Si–C(81)=1.918(4) Å; P(1)–Ni–P(2)=93.09(5), P(1)–Ni–H(2)=97(2), P(2)–Ni–Si=111.06(5), Si–Ni–H(2)=58(2), C(71)–Si–C(81)=106.3(2), C(71)–Si–Ni=116.42(15), C(81)–Si–Ni=119.63(13)°.

Because of unusual solution behavior of **2** (vide infra), we prepared several analogues of **2** using the same synthetic protocol. Thus, diphenylsilane, diphenylmethylsilane, and chlorodiphenylsilane react with **1** to yield (dtbpe)Ni(μ-H)-$SiH(C_6H_5)_2$ (**3**), (dtbpe)Ni(μ-H)$Si(CH_3)(C_6H_5)_2$ (**4**), and (dtbpe)Ni(μ-H)$SiCl(C_6H_5)_2$ (**5**), respectively (Scheme 2).

The solid-state structure of **5** was determined by X-ray crystallography and a perspective view of the complex is shown in Figure 2. Like that of **2**, the structure of **5** shows a square-planar nickel coordinated to the chelating dtbpe ligand, silicon, and hydrogen. Key metrical parameters in the nickel coordination sphere of **5**, Si–H=1.90(5) Å and Ni–Si=2.222(2) Å, are essentially the same as those found in **2**. IR spectra confirm the crystal data, and a typical strong Si–H stretching vibration at ~2000 cm^{-1} is observed in **2** and **3** but is absent in **4** and **5.**

Solution NMR data for **2** indicate interesting dynamic, fluxional behavior. ^1H and ^{31}P measurements taken in benzene-d_6 show **2** to be in equilibrium with free Mes_2SiH_2 (^1H δ 5.29, SiH_2) and **1**-d_6, with **2** predominating at lower temperatures. NMR spectra of **2** in THF-d_8 show the presence of a C_{2v} symmetrical environment. Four equivalent *tert*-butyl groups are observed at δ 1.21 for the phosphine ligand and two equivalent protons at δ −0.17 for the coordinated silane in the ^1H NMR spectrum, and a singlet resonance is seen at δ 90.55 (with ^{29}Si satellites) in the ^{31}P spectrum. The observation of J_{PH}~30 Hz (SiH_2) in the ^1H spectrum and J_{SiP}~53 Hz in the ^{29}Si and ^{31}P spectra indicate that Mes_2SiH_2 is not undergoing dissociation from the nickel center on the NMR timescale in tetrahydrofuran solution, unlike in benzene. In the case of compound **2**, we were not able to freeze out (by NMR) a static solution structure on cooling. Consistent with these observations, spectra of (dtbpe)Ni$(SiHD(Mes)_2$ (**2**-d_1), prepared from **1** and Mes_2SiHD, show the same chemical shift for the Si–H proton in the ^1H NMR spectrum as for the Si–D deuteron in the ^2H NMR spectrum indicating that these two are exchanging on the NMR timescale.

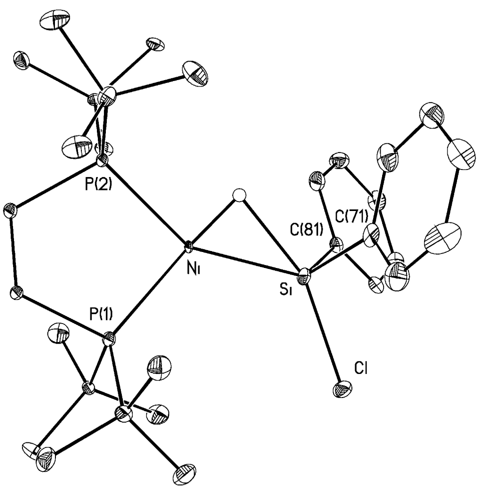
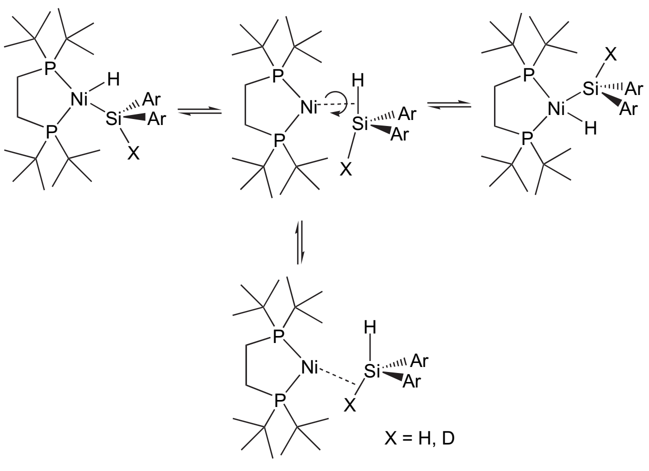


Figure 2. ORTEP view of the structure of complex **5** (35% probability thermal ellipsoids, H atoms except those attached to Si and Ni omitted for clarity). Selected bond distances (Å) and angles (°): Ni–P1=2.186(2), Ni–P2=2.189(2), Ni–Si=2.222(2), Ni–H=1.32(5), Si–H=1.90(5), Si–Cl=2.166(2), Si–C(71)=1.928(7), Si–C(81)=1.906(7) Å; P(1)–Ni–P(2)=95.51(6), P(2)–Ni–H=91(2), P(1)–Ni–Si=117.77(7), Si–Ni–H=59(2), C(71)–Si–C(81)=108.2(3), C(71)–Si–Ni=106.5(2), C(81)–Si–Ni=117.9(2), Cl–Si–Ni=122.22(9)°.

Similar solution fluxionality was observed for **3** and **4**, giving apparent C_{2v} symmetrical structures in solution. Interestingly, in contrast to **2**, complexes **3**, **4**, and **5** in benzene solution appear not to be in equilibrium with the free silane and **1**-d_6, perhaps a consequence of the smaller size of their aryl substituents compared with the two bulky mesityl silyl substituents in **2**. Moreover, in the case of compound **5**, this fluxional process is sufficiently slow at 200 K in the ^1H NMR spectrum (toluene-d_8) that the asymmetric solution structure consistent with the solid-state structure could be observed. The upfield triplet (δ −8.29, J_{PH}=30 Hz) for the hydride ligand observed at room temperature resolves on cooling (200 K) into the expected doublet-of-doublets (δ −8.19, J_{PH}=20 Hz, J_{PH}=90 Hz) due to coupling with the two inequivalent (*cis* and *trans*) ^{31}P nuclei. The *tert*-butyl resonances behave in a similar manner, splitting into two doublets at 200 K corresponding to pairwise inequivalent *tert*-butyls in the static structure. Chen et al. have reported similar fluxionality in $(Et_2PCH_2CH_2PEt_2)Ni\{[2-(SiH_3)-C_6H_4]_2SiH_2\}$ in which the hydride ligand resonances partially resolve at 193 K.[9]

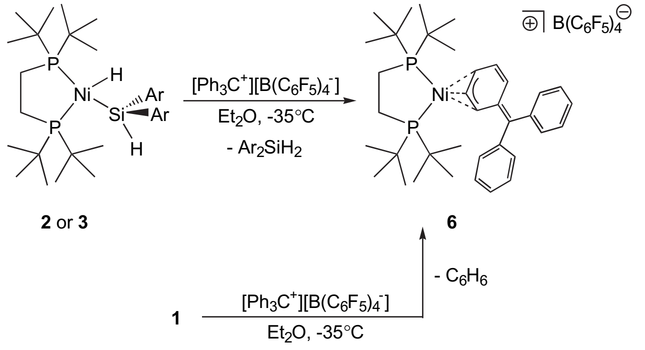
These data are consistent with dynamic processes illustrated in Scheme 3. The key feature is reversible oxidative addition via a Ni(0)-η^2 silane intermediate. Rapid rotation about the Ni–(H–Si) bond followed by oxidative addition allows equilibration of the two sides of phosphine ligand. When a secondary silane is employed, a second process that interchanges the two hydrogen positions is also occurring. This is reflected in the ^1H chemical shifts of the unique proton(s). In **4** and **5** in which there is no second (exchangeable) hydrogen, the resonances occur in the normal upfield hydride region (δ −6.5 and −8.3, respectively), whereas in **2** and **3** the exchanging protons resonate at δ~0, and average of the upfield hydride resonance and the downfield resonance for a typical Si–H moiety (δ~5).



Scheme 3.

We have surveyed the reactions of complexes **2–5** with alkenes and alkynes in anticipation that they might participate in hydrosilylation of the unsaturated carbyl substrates, but the reactions invariably led to elimination of the original silane. For example, **3** reacts with ethylene to give Ph_2SiH_2 and (dtbpe)Ni(C_2H_4),[10] and with alkynes to give the corresponding (dtbpe)Ni(C_2R_2) adducts.[11]

Given the stability of cationic Ni(II) alkyls in this system, like [(dtbpe)Ni(CH_2CMe_3)$^+$],[12] we attempted to prepare silyl analogues [(dtbpe)Ni($SiAr_2X$)$^+$] by hydride abstraction from **2** and **3**. Silane elimination also confounded our efforts here. Reaction of **2** or **3** with triphenylcarbenium tetrakis(pentafluorophenyl)borate in diethyl ether results in silane elimination and formation of the unusual 'triphenylmethyl' complex [(dtbpe)Ni(η^3-$C_6H_5CPh_2$)$^+$][$B(C_6F_5)_4^-$] (**6**) in high yield (Scheme 4; Fig. 3). Complex **6** was characterized by NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy and by single-crystal X-ray diffraction. Instead of hydride abstraction by trityl, elimination of Mes_2SiH_2 or Ph_2SiH_2 occurs to give a Ni(0) intermediate that undergoes two-electron oxidation by trityl with coordination of the resulting 'Ph_3C^-' fragment. Analysis of the organic fraction of the reaction mixture showed only Mes_2SiH_2 or Ph_2SiH_2. Consistent with this scenario is the observation that **6** alternatively can be prepared by the reaction of [CPh_3^+][$B(C_6F_5)_4^-$] with the benzene complex **1**.



Scheme 4.

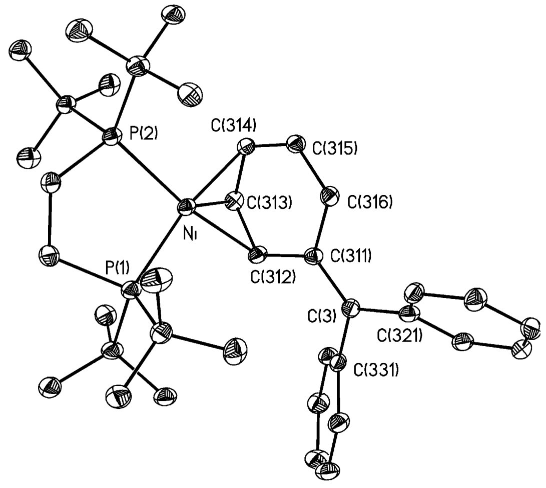


Figure 3. ORTEP view of the complex cation of **6** (35% probability thermal ellipsoids, H atoms and the counter anion omitted for clarity). Selected bond distances (Å) and angles (°): Ni–P(1)=2.2374(11), Ni–P(2)=2.224(1), Ni–C(312)=2.192(3), Ni–C(313)=1.991(3), Ni–C(314)=2.095(3), C(311)–C(312)=1.457(5), C(312)–C(313)=1.401(5), C(313)–C(314)=1.401(5), C(314)–C(315)=1.434(5), C(315)–C(316)=1.351(5), C(316)–C(311)=1.451(5), C(311)–C(3)=1.375(5), C(321)–C(3)=1.483(5), C(331)–C(3)=1.492(5) Å; P(1)–Ni–P(2)=92.03(4), C(311)–C(3)–C(321)=123.5(3), C(321)–C(3)–C(331)=114.7(3), C(331)–C(3)–C(311)=121.7(3)°.

The solid-state structure of **6** is an interesting one (Fig. 3). The CPh_3^- ligand is coordinated to nickel in an η^3-allylic fashion through adjacent *ortho*, *meta*, and *para* carbons of one of its phenyl rings, resulting in alternating C–C bond lengths in the coordinated phenyl group indicative of disruption of its 6-π aromaticity. The C(311)–C(312), C(311)–C(316), and C(314)–C(315) bond distances (1.457(5), 1.451(5), 1.434(5) Å) are in the range for C–C single bonds (~1.48 Å),[13] the C(315)–C(316) and C(311)–C(3) bond distances (1.351(5), 1.375(5) Å) are near the expected value for C=C double bonds (~1.33 Å),[13] and the bonds between the three carbon atoms bound to nickel, C(312), C(313), and C(314), exhibit intermediate bond distances (both 1.401(5) Å) as expected for a delocalized allylic fragment. The three phenyl groups of the Ph_3C^- ligand are arranged in a propeller fashion, and its central carbon (C(3)) is planar. The Ni–C bond distances range from 2.192(3) to 1.991(3) Å.

It is noteworthy that several late-transition metal complexes of Ph_3C^- have been reported, with various structures,[14] including [Pd(CPh_3)(μ-Cl)]$_2$ and Pd(acac)(CPh_3), which has an η^3-benzylic coordination mode (i.e., through the central carbon and the *ipso* and *ortho* carbons of one of the Ph rings).[14c] Structures of uncomplexed Ph_3C^- as encrypted alkali metal salts have also been reported.[15] The preference of trityl to coordinate to the Ni center in **6** through one of the phenyl rings in an allylic fashion (instead through central carbon in η^1- or η^3-modes) is probably a consequence of steric crowding engendered by the bulky dtbpe ligand.

4. Conclusions

In conclusion, the Ni complexes obtained by the reaction of **1** with several hydridosilanes allow insight into intermediate stages of the Si–H oxidative-addition reaction to a Ni(0) center. Of note is the highly fluxional nature of the η^2-SiH–Ni linkage. Reactivity studies on these compounds showed the silane addition to nickel is reversible and that the silicon-containing ligand is quite labile.

5. Crystallographic data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 610081 for compound **2**, CCDC no. 610082 for compound **5**, and CCDC no. 610083 for compound **6**.

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