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Arrested 1,2-Hydrogen Migration from Silicon to Nickel upon Oxidation of a Three-Coordinate Ni(I) Silyl Complex

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Abstract: Reaction of the dimeric Ni(I) chloride complex $[(\text{dtbpe})\text{NiCl}]_2$ (**1**) with dimesitylsilyl potassium affords the three-coordinate Ni(I) silyl complex $(\text{dtbpe})\text{Ni}(\text{SiHMes}_2)$ (**2**). Alternatively, **2** can be prepared by an oxidative-addition reaction of $\text{Mes}_2\text{Si(H)OTf}$ (Tf $= CF_3SO_3$) with the nickel(0) complex $[(\text{dtbpe})\text{Ni}]_2(\mu\text{-}C_6H_6)$ (**3**), with (dtbpe)Ni(OTf) (**4**) formed as an easily separable byproduct. The one-electron oxidation of **2** by ferrocenium affords diamagnetic $[(\text{dtbpe})\text{Ni}(\mu\text{-H})\text{SiMes}_2][\text{BAr}^F{}_4]$ (**5**), a Ni(II) complex formed by partial 1,2-H migration from silicon to nickel and featuring an unusual 3-center, 2-electron bonding motif between Ni, Si, and the bridging H. Complex **5** was also obtained from Mes_2SiH_2 activation by the neopentyl complex salt $[(\text{dtbpe})\text{Ni}(\text{CH}_2\text{CMe}_3)][\text{BAr}^F{}_4]$ (**6**) with elimination of neopentane.

Silylene complexes[1] have received considerable attention because of their participation in various transformations of organosilicon compounds, such as dehydrogenative coupling of hydrosilanes,[2] redistribution of substituents on silicon atoms,[3] Rochow's direct process,[4] and silylene transfer to unsaturated organic compounds.[5] Several synthetic strategies have been employed in the formation of silylene complexes, relying on abstraction of triflate[6] or chloride[7] from silicon to produce cationic complexes, coordination of photochemically generated silylenes,[8] and, most interestingly, 1,2-hydrogen migrations.[9] Intramolecular hydrogen migration from silicon to a late-transition metal is significant in understanding the rearrangements taking place in metal silyl complexes involved in catalysis,[1b,10,11] but only one discrete example has been reported for a group 10 metal, $[(1,2\text{-}{}^i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{P}{}^i\text{Pr}_2)\text{Pt(H)}(\text{SiMes}_2)][\text{MeB}(C_6F_5)_3]$.[12a] DFT studies on a simplified model were inconclusive on whether hydrogen bridges Pt and Si or is present as a standard Pt hydride.[12b] Herein we describe an analogous, structurally characterized Ni complex in which the H atom unambiguously bridges the metal and silicon. This report offers insight into processes taking place during Si−H activation at metals and characterizes the bonding motif in this nonclassical nickel-silyl cation.

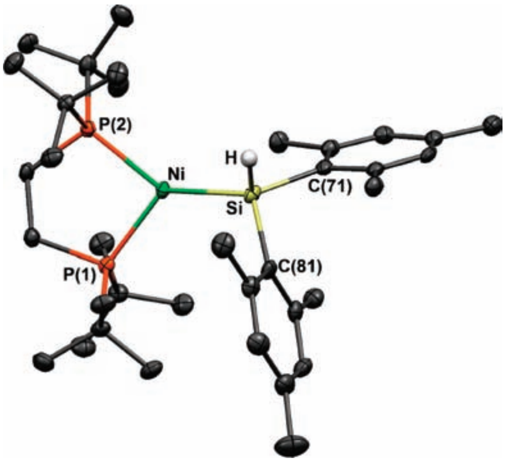
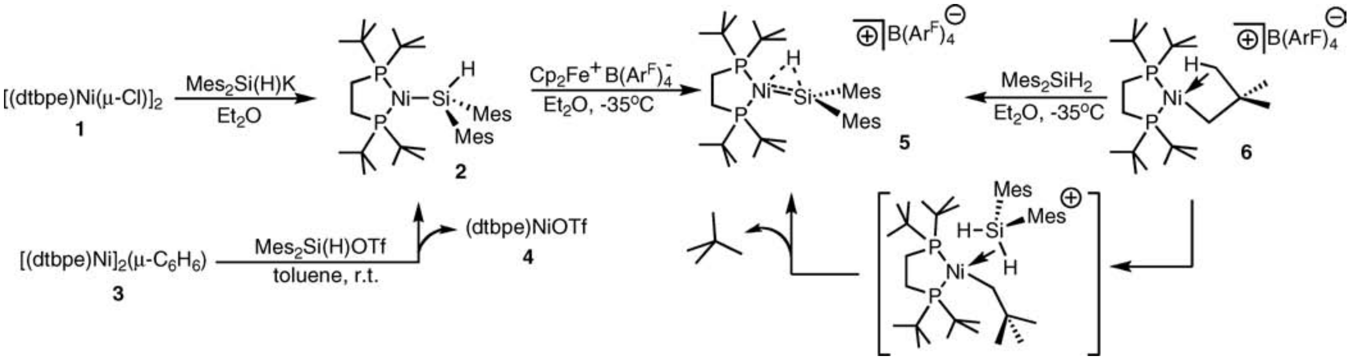


Figure 1. A perspective view of complex **2** (35% probability ellipsoids; H atoms except on Si omitted for clarity). Selected metrical parameters (distance, Å; angle, deg): Ni−Si = 2.3731(10), Ni−P(1) = 2.2502(10), Ni−P(2) = 2.2507(9), Si−H = 1.53(3); P(1)−Ni−P(2) = 90.60(3), P(1)−Ni−Si = 126.68(4), P(2)−Ni−Si = 138.75(4), Ni−Si−H = 110.0(12), Ni−Si−C(71) = 124.35(12), Ni−Si−C(81) = 112.88(11), C(71)−Si−C(81) = 104.65(15).

A Ni(I) silyl complex, in which one of the silyl substituents is hydrogen, was targeted as a precursor to a possible nickel-silylene fragment. The reaction between $[(\text{dtbpe})\text{Ni}(\mu\text{-Cl})]_2$ (**1**, dtbpe = $1,2\text{-}{}^t\text{Bu}_2\text{PCH}_2\text{CH}_2\text{P}{}^t\text{Bu}_2$)[13] and Mes_2SiHK (Mes = $2,4,6\text{-Me}_3C_6H_2$) allowed for the isolation of $(\text{dtbpe})\text{Ni}(\text{SiHMes}_2)$ (**2**) as green dichroic crystals in 86% yield (Scheme 1). This method was higher yielding and had better reproducibility than the oxidative addition of $\text{Mes}_2\text{Si(H)OTf}$ (Tf $= CF_3SO_3$) to a nickel(0) complex, $[(\text{dtbpe})\text{Ni}]_2(\mu\text{-}C_6H_6)$ (**3**, Scheme 1).[14] Although other silanes give arrested oxidative addition of the Si−H bond to the Ni(0) center,[15] two products were formed in the reaction of **3** with $\text{Mes}_2\text{Si(H)OTf}$: (dtbpe)Ni(OTf) (**4**)[13b] and **2**.

Scheme 1



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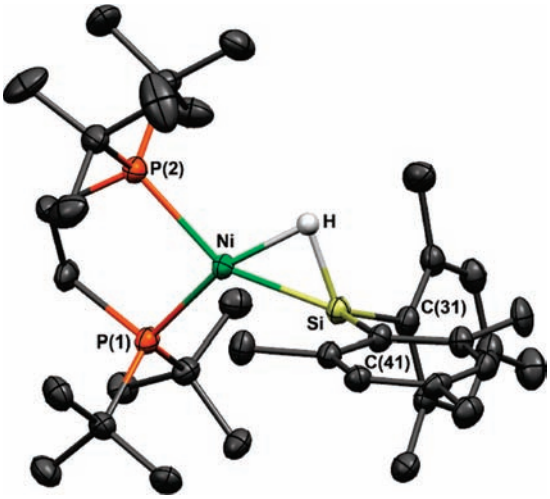

Figure 2. A perspective view of the complex cation of **5** (35% probability ellipsoids; H atoms except on Si omitted for clarity). Select metrical data (distance, Å; angle, deg): Ni−Si = 2.147(2), Ni−H = 1.70(7), Ni−P(1) = 2.189(2), Ni−P(2) = 2.254(2), Si−H = 1.64(7); P(1)−Ni−P(2) = 92.56(6), P(1)−Ni−Si = 115.17(7), P(2)−Ni−H = 103(2), Si−Ni−H = 49(2), Ni−Si−C(31) = 121.2(2), Ni−Si−C(41) = 124.5(2), C(31)−Si−C(41) = 114.3(3).

Complex **2** represents the first example of a three-coordinate Ni(I) silyl complex. The solid-state structure of **2** (Figure 1) features a trigonal-planar nickel center and tetrahedral silicon. The Ni−Si distance of 2.3731(10) Å is slightly longer than other reported Ni−Si bonds (2.21−2.30 Å),[15,16] presumably due to sterics. The hydrogen connected to the silicon atom was located in the electron-density map at 1.50 Å from Si and refined isotropically. The assignment of a nickel(I) center is supported by the effective magnetic moment of 2.1 μ_B, determined in solution (22 °C, C_6D_6), corresponding to one unpaired electron and consistent with a d^9 electronic configuration.

A cyclic voltammogram of **2** shows a quasi-reversible wave for the Ni(I)/Ni(II) couple at $E_{1/2} = -0.48$ V (THF; vs Cp_2Fe/Cp_2Fe^+). Oxidation of **2** with $[Cp_2Fe][B(Ar^F)_4]$ (Scheme 1, Ar^F = 3,5-$(CF_3)_2C_6H_3$) allowed for the isolation of diamagnetic [(dtbpe)Ni(μ-H)SiMes$_2$][BAr$^F_4$] (**5**) in 85% yield. X-ray crystallography (Figure 2) reveals that a hydrogen atom is located in the P_2NiSi plane of **5**, bridging nickel and silicon (Ni−H = 1.70(7) Å, Si−H = 1.64(7) Å) and resulting in distorted square-planar coordination geometry at nickel. The Ni−Si distance (2.147(2) Å) is 9% shorter than the corresponding distance in **2** and is close in value to that reported for Ni silylene complexes (∼2.14 Å).[16d] The {C(31), C(41), Si} plane is perpendicular to the {P(1), P(2), Ni} plane (∠87.75°). There are similarities in the structures of Ni(0) boryl complexes[17a] and a Mo hydrosilylene complex[17b] and **2**.

In agreement with its solid-state structure, features of the μ-H resonance in the ^1H NMR spectrum of **5** are indicative of hydridic character. It appears at δ −8.64 (dd, J_{HP} = 4.8, 47.1 Hz) with a J_{HP} smaller than those found in other d^8 square-planar nickel hydrides.[18] In addition, the J_{HSi} at 43.4 Hz is smaller than those in conventional hydrosilyls and hydrosilanes (∼60−150 Hz).[19] The $^{29}Si\{^1H\}$ NMR spectrum shows a resonance at δ 292 (dd, J_{PSi} = 12, 146 Hz). Attempts to deprotonate **5** to give a silylene complex ((dtbpe)Ni═SiMes$_2$) were unsuccessful, perhaps also reflective of its hydridic character.

Reaction of Mes_2SiH_2 with the neopentyl complex salt [(dtbpe)Ni(CH_2CMe_3)][BAr$^F_4$] (**6**; Scheme 1)[13c] also affords **5**, indicating the structural motif found in **5** is not a consequence of peculiar reaction conditions in its synthesis. This likely proceeds by silane coordination to the electrophilic Ni center,[15] replacing a weak C−H agostic interaction,[13c] to give an intermediate that undergoes intramolecular H-abstraction with neopentane elimination to generate **5**. This metathesis route is attractive as it uses a secondary silane that is more accessible than Mes$_2$SiHK and would appear to be the more general synthetic approach.

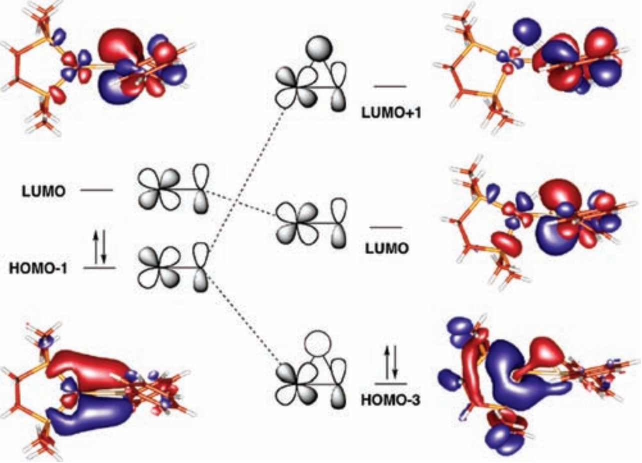

Figure 3. Frontier molecular π-symmetry orbitals for a hypothetical nickel silylene (dmpe)Ni═SiPh$_2$ (left) and for the three-center bond of (dmpe)Ni(μ-H)SiPh$_2^+$ (right).

DFT calculations (B3LYP, LANL2DZ basis sets)[20] were carried out using a (dmpe)Ni(μ-H)(SiPh$_2$)$^+$ model (dmpe = $Me_2PCH_2CH_2PMe_2$) to understand the unusual Ni−H−Si bonding motif in **5** relative to the hypothetical parent silylene (dmpe)Ni(SiPh$_2$) (Figure 3). The calculations indicate that the bridging hydrogen participates in a 3-center, 2e^- bond using the 1*s* H orbital and the π orbital of the Ni═Si core to effectively give a “protonated” Ni═Si double bond, and an NBO analysis is consistent with this picture. Optimized metrical parameters for the (dmpe)Ni(μ-H)(SiPh$_2$)$^+$ model (e.g., Ni−H = 1.731 Å, Si−H = 1.616 Å, Ni−Si = 2.177 Å) agree well with actual values observed in the structure of **5** and converge to the bridging structure from either initial hydrido silylene or σ-silyl models (see Supporting Information).

In conclusion, a new three-coordinate nickel(I) silyl complex was isolated and characterized. Its oxidation leads to a 1,2-hydrogen migration from silicon to nickel and gives an unusual cationic H-bridging species that features 3-center, 2e^- bonding.

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Supporting Information Available: Crystallographic data of **2** and **5** (CIF). Synthetic and spectroscopic characterization of all complexes and computational information (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Tilley, T. D. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1415. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; p 245. (c) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712.

(2) (a) Corey, J. Y. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 1, p 327. (b) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (c) Alcaraz, G.; Sabo-Etienne, S. *Coord. Chem. Rev.* **2008**, *252*, 2395.

(3) (a) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213. (b) Ojima, I.; Inaba, S.; Kogure, T. *J. Organomet. Chem.* **1973**, *55*, C7.

(4) (a) Clarke, M. P. *J. Organomet. Chem.* **1989**, *376*, 165. (b) Clarke, M. P.; Davidson, I. M. T. *J. Organomet. Chem.* **1991**, *408*, 149. (c) Okamoto, M.; Onodera, S.; Okano, T.; Suzuki, E.; Ono, Y. *J. Organomet. Chem.* **1997**, *531*, 67.

(5) (a) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227. (b) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1995**, *14*, 530. (c) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824.

(6) (a) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801. (b) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 358. (c) Grumbine, S. D.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 5607.

(7) Wanandi, P. W.; Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 972.

(8) Feldman, J. D.; Mitchell, G. P.; Nölte, J.-O.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184.

(9) (a) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871. (b) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4065.

(10) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351.

(11) (a) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1996**, *15*, 3477. (b) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635. (c) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326.

(12) (a) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2524. (b) Besora, M.; Maseras, F.; Lledos, A.; Eisenstein, O. *Inorg. Chem.* **2002**, *41*, 7105.

(13) (a) Mindiola, D. J.; Waterman, R.; Jenkins, D. M.; Hillhouse, G. L. *Inorg. Chim. Acta* **2003**, *345*, 299. (b) Iluc, V. M.; Miller, A. J. M.; Hillhouse, G. L. *Chem. Commun.* **2005**, 5091. (c) Kitiachvili, K. D.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2004**, *126*, 10554.

(14) Bach, I.; Pörschke, K.-R.; Goddard, R.; Kopiske, C.; Krüger, C.; Rufinska, A.; Seevogel, K. *Organometallics* **1996**, *15*, 4959.

(15) Iluc, V. M.; Hillhouse, G. L. *Tetrahedron* **2006**, *62*, 7577.

(16) (a) Shimada, S.; Rao, M. L. N.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 213. (b) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Millevolte, A. J.; Powell, D. R.; West, R. *J. Organomet. Chem.* **2001**, *636*, 17. (c) Shimada, S.; Rao, M. L. N.; Tanaka, M. *Organometallics* **1999**, *18*, 291. (d) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Millevolte, A. J.; Powell, D. R.; West, R. *Organometallics* **2000**, *19*, 3263.

(17) (a) Crestani, M. G.; Muñoz-Hernández, M.; Arévalo, A.; Acosta-Ramírez, A.; García, J. J. *J. Am. Chem. Soc.* **2005**, *127*, 18066. (b) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 10428.

(18) (a) Clark, H. C.; Shaver, A. *Can. J. Chem.* **1975**, *53*, 3462. (b) Green, M. L. H.; Saito, T.; Tanfield, P. J. *J. Chem. Soc., A* **1971**, 152.

(19) (a) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (b) Williams, E. A.; Cargioli, J. D. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1979; Vol. 9, p 221.

(20) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

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