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Reaction of 1,2-Disilylbenzene with Bis[1,2-bis(dimethylphosphino)ethane]nickel(0). Isolation and Characterization of the First Silylnickel(IV) Complex

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Summary: The first silylnickel(IV) complex was isolated from the reaction of 1,2-disilylbenzene with a nickel(0) complex and characterized by multinuclear NMR and X-ray structure analysis. Bis(silyl)nickel(II) complexes, intermediates in the formation of the silylnickel(IV) complex, were also characterized by NMR and/or X-ray analysis.

Growing interest in organosilicon compounds as functional materials and reagents for organic synthesis increases the importance of the study on silylmetals in order to develop new catalytic methodologies as well as to understand the reaction mechanism. Group 10 metals constitute useful catalysts for the transformation of organosilicon compounds, and the chemistry of silylplatinums and silylpalladiums is rapidly growing.[1] On the other hand, silylnickels are less well-known, partly because of their instability. Most of the well-characterized silylnickel complexes are SiX_3-Ni species ($X = Cl$, F).[2,3] In the catalytic cycles of group 10 metal-catalyzed reactions of organosilicon compounds, silylmetal(IV) species can be considered to play an important role. Silylplatinum(IV)[4] and silylpalladium(IV)[5] complexes have indeed been isolated and characterized, while no silylnickel(IV) species has been isolated or even detected spectroscopically.[6] Related nickel(IV) species with organyl ligands have only recently been isolated.[7] Here we report the reaction of 1,2-disilylbenzene (**1**)[4d,8] with $Ni(dmpe)_2$ (**2**) (dmpe = 1,2-bis(dimethylphophino)eth-

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[1] Recent reviews: (a) Yamashita, H.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 403−419. (b) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317−1350. (c) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351−1374. (d) Braunstein, P.; Knorr, M. *J. Organomet. Chem.* **1995**, *500*, 21−38. (e) Suginome, M.; Ito, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 1925−1934.

[2] For examples of silylnickel complexes: (a) Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1974**, *76*, 95−103. (b) Liu, C.-S.; Cheng, C.-W. *J. Am. Chem. Soc.* **1975**, *97*, 6746−6749. (c) Janikowski, S. K.; Radonovich, L. J.; Groshens, T. J.; Klabunde, K. J. *Organometallics* **1985**, *4*, 396−398. (d) Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108* (8), 7147−7419. (e) Bierschenk, T. R.; Guerra, M. A.; Juhlke, T. J.; Larson, S. B.; Lagow, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 4855−4860. (f) Choe, S.-B.; Schneider, J. J.; Klabunde, K. J.; Radonovich, L. J.; Ballintine, T. A. *J. Organomet. Chem.* **1989**, *376*, 419−439. (g) Brezinski, M. M.; Schneider, J.; Radonovich, L. J.; Klabunde, K. J. *Inorg. Chem.* **1989**, *28*, 2414−2419.

[3] Silylene−nickel complexes have been reported recently, see: (a) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33−34. (b) Nlate, S.; Herdtweck, E.; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1861−1863.

[4] For recent examples: (a) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917−1919. (b) Michalczyk, M. J.; Recatto, C. A.; Calabrese, J. C.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7955−7957. (c) Levy, C. J.; Puddephatt, R. J.; Vittal, J. J. *Organometallics* **1994**, *13*, 1559−1560. (d) Shimada, S.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8289−8290. (e) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. *J. Organomet. Chem.* **1996**, *521*, 405−408.

[5] (a) Shimada, S.; Tanaka, M.; Shiro, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1856−1858. (b) Suginome, M.; Kato, Y.; Takeda, N.; Oike, H.; Ito, Y. *Organometallics* **1998**, *17*, 495−497.

[6] Intermediacy of silylnickel(IV) species has been proposed: (a) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050−2054. (b) Ishikawa, M.; Nomura, Y.; Tozaki, E.; Kunai, A.; Ohshita, J. *J. Organomet. Chem.* **1990**, *399*, 205−213. (c) Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1992**, *11*, 3004−3008.

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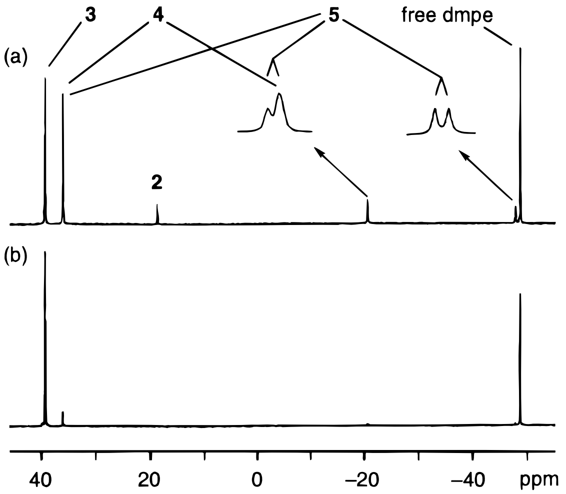
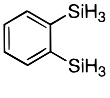


Figure 1. ^{31}P NMR spectra of the reaction mixture of **1** and **2** at 80 °C in C_6D_6 after (a) 7 h and (b) 66 h.

ane), which resulted in the isolation of a dimeric silylnickel(II) complex and the first silylnickel(IV) complex.



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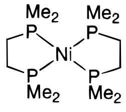

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The reaction of **1** with **2** (**1**:**2** = 2:1) proceeded at 80 °C in C_6D_6. Figure 1 shows the ^{31}P NMR spectra of the reaction mixture after 7 and 66 h heating. After 7 h, five new signals (δ = 39.41, 36.06, −20.43, −20.56, −47.83 ppm) were found in addition to those of **2** (δ = 18.72 ppm) and uncoordinated dmpe (δ = − 48.72 ppm). After 66 h, only the signals at 39.41 ppm and of uncoordinated dmpe remained and the others almost had disappeared. The structure of the final product (81% isolated yield) was assigned as the tetrakis(silyl)nickel(IV) complex **3**[9] by comparing its ^{1}H, ^{31}P, ^{13}C, and ^{29}Si NMR data with those of the corresponding tetrakis(silyl)palladium(IV) complex.[5a] Its ^{29}Si NMR spectrum displayed two characteristic signals at $\delta = 4.61$ (t, $^{2}J_{P-Si}$ = 18 Hz) and − 0.36 (dd, $^{2}J_{Pcis-Si} = 20$ Hz, $^{2}J_{Ptrans-Si} =$ 116 Hz). Furthermore, the structure was unambiguously confirmed by X-ray structure analysis (Figure 2).[10] The Ni−Si1 bond is longer than the Ni−Si2 bond, because of the stronger trans influence of silicon than that of phosphorus. The Ni−Si2 bond length is within the range of reported values, while the Si1−Ni bond length is the longest so far reported.[2c,e−g,3a,b]

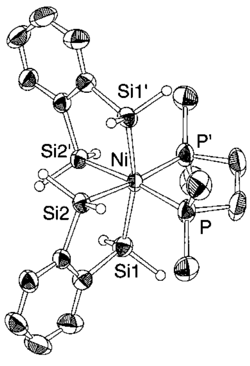
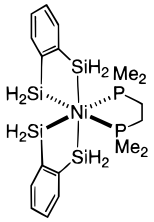


Figure 2. Molecular structure of complex **3** (40% probability). Selected bond lengths (Å) and angles (deg): Ni−Si1 2.2900(9), Ni−Si2 2.2522(7), Ni−P 2.1973(7), Si1−Ni−Si2 86.70(3), Si1−Ni−Si1′ 164.91(4), Si2−Ni−P 93.40(3), Si2−Ni−Si2′ 84.44(4), P−Ni−P′ 89.25(4).



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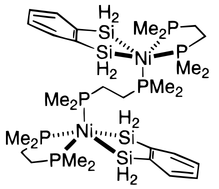

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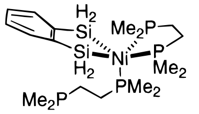

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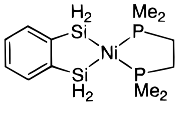

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The intermediate species observed in the ^{31}P NMR spectrum (Figure 1a) were assigned to a mixture of bis(silyl)nickel(II) complexes **4** and **5** based on the following results. To isolate the intermediate species, the reaction of **1** with **2** (**1**:**2** = 1:1.5) was carried out at 80 °C for 5 h. The crude mixture contained **2** and the intermediate species as well as a small amount of **3**. One of the intermediate species could be isolated as slightly yellow, thin plates (42% isolated yield) upon cooling the reaction mixture.[11] The molecular structure was confirmed to be dimeric bis(silyl)nickel(II) complex **4** by X-ray structure analysis (Figure 3).[12] The Si−Ni bond lengths are within the range of reported values.[2c,e−g,3a,b] The Ni−P3 bond

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[7] (a) Klein, H.-F.; Bickelhaupt, A.; Jung, T.; Cordier, G. *Organometallics* **1994**, *13*, 2557−2559. (b) Klein, H.-F.; Bickelhaupt, A.; Lemke, M.; Jung, T.; Röhr, C. *Chem. Lett.* **1995**, 467−468. (c) Klein, H.-F.; Bickelhaupt, A.; Lemke, M.; Sun, H.; Brand, A.; Jung, T.; Röhr, C.; Flörke, U.; Haupt, H.-J. *Organometallics* **1997**, *16*, 668−676.

[8] Schröck, R.; Sladek, A.; Schmidbaur, H. *Z. Naturforsch. B* **1994**, *49*, 1036−1040.

[9] To a toluene solution (5 mL) of Ni(dmpe)$_2$ (500 mg, 1.39 mmol) was added **1** (530 μL, 488 mg, 3.51 mmol), and the resulting solution was heated at 80 °C for 10 days under N_2. After removal of volatiles under vacuum, the residue was dissolved in hot C_6H_6 (20 mL) and insoluble materials were filtered off. Upon cooling the filtrate to room temperature, colorless crystals (containing two molecules of benzene per **3**) formed, from which some crystals were taken for X-ray analysis. After an addition of hexane (10 mL) to complete the crystal formation, the crystals were filtered and dried under vacuum (benzene molecules in the crystals are easily removed upon evacuation) to give **3** as white powder (540 mg, 81% based on Ni(dmpe)$_2$). **3**: ^{1}H NMR (C_6D_6) δ 0.76 (6H, d, $J = 9$), 1.01 (6H, d, $J = 9$), 1.0−1.4 (4H, m), 4.75−5.10 (8H, m), 7.10−7.25 (4H, m), 7.72 (2H, d, $J = 7$), 7.98 (2H, d, $J = 7$); ^{31}P NMR (C_6D_6) δ 39.27; ^{13}C NMR δ 10.75 (m, PMe), 12.17 (m, PMe), 28.08 (t, $J_{P-C} = 24$, PCH_2CH_2P), 127.63, 127.72, 133.45, 133.88, 147.42 (t, $^{3}J_{P-C} = 3$), 152.02 (t, $^{3}J_{P-C} = 2$); ^{29}Si NMR (C_6D_6) δ −0.35 (dd, $^{2}J_{Pcis-Si} = 20$, $^{2}J_{Ptrans-Si} = 116$), 4.62 (t, $^{2}J_{P-Si} = 18$); IR (KBr) 3042, 2974, 2908, 2056, 2024, 1423, 1303, 1288, 1263, 1243, 1114, 942, 833, 808, 764, 710, 652, 522, 447, 420; EI-MS (70 eV) *m/z* 480 (M^{+}, 2), 450 (25), 448 (46), 210 (40), 208 (100, Ni(dmpe)), 180 (46). Anal. Calcd for $C_{18}H_{32}Ni_1P_2Si_4$: C, 44.91; H, 6.70. Found: C, 45.41; H, 6.84.

[10] Crystal data for **3**·2C_6H_6: $C_{30}H_{44}Ni_1P_2Si_4$, fw = 637.67, monoclinic, *C*2/*c*, $a = 23.810(7)$ Å, $b = 9.092(3)$ Å, $c = 17.982(5)$ Å, $\beta = 118.75(2)°$, $V = 3412(1)$ Å^3, $Z = 4$, $D_{calc} = 1.24$ g cm^{-3}, $R = 0.036$, $R_w = 0.055$.

[11] To a toluene solution (6 mL) of Ni(dmpe)$_2$ (800 mg, 2.23 mmol) was added **1** (224 μL, 206 mg, 1.49 mmol), and the resulting solution was heated at 80 °C for 5 h under N_2. Upon cooling the mixture at room temperature, light yellow crystals settled. Filtration, washing with a small amount of toluene, and drying under vacuum gave **4** in 42% yield (260 mg) based on **1**. **4**: ^{1}H NMR (C_6D_6) δ 0.76 (12H, d, $J =$ 3.5), 1.02−1.30 (36H, m), 5.28−5.38 (8H, m, Si−H), 7.23 (4H, dd, $J =$ 3, 5), 7.98 (4H, d, J = 3, 5); ^{31}P NMR (C_6D_6) δ −20.48 (s), 35.82 (s); ^{29}Si (C_6D_6) NMR δ −7.7 (t, J = 35); IR (KBr) 3038, 2970, 2904, 2010, 1421, 1296, 1280, 1139, 1104, 944, 895, 820, 760, 717, 499, 447. Anal. Calcd for $C_{30}H_{64}Ni_2P_6Si_4$: C, 42.87; H, 7.68. Found: C, 43.10; H, 7.70.

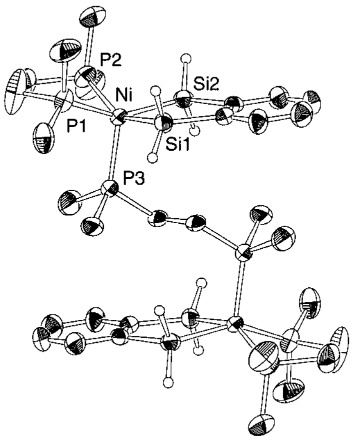

Figure 3. Molecular structure of complex **4** (40% probability). Selected bond lengths (Å) and angles (deg): Ni−Si1 2.247(3), Ni−Si2 2.255(3), Ni−P1 2.163(3), Ni−P2 2.163(3), Ni−P3 2.248(2), Si1−Ni−Si2 80.86(9), P1−Ni−P2 85.6(1), Si1−Ni−P3 102.45(9).

(2.26 Å) is much longer than Ni−P1 (2.16 Å) and Ni−P2 (2.16 Å). The ^{31}P NMR spectrum of **4** showed two singlets at 35.82 and − 20.48 ppm; these were assigned to the chelating and the bridging phosphines, respectively, on the basis of the integration in the ^{31}P NMR spectrum and the following variable-temperature ^{31}P NMR experiment. As suggested by the longer Ni−P3 bond length than those of Ni−P1 and Ni−P2, the bridging phosphine is expected to decoordinate more easily than the chelating phosphines. ^{31}P NMR measurement showed the signal at 35.82 ppm did not change upon heating to 70 °C, while the signal at −20.48 ppm broadened at 40 °C and almost disappeared at 70 °C. Accordingly, we conclude that, in Figure 1a, the signal at 36.06 ppm corresponds to the chelating phosphine in **4** and the signal at −20.43 or −20.56 ppm corresponds to the bridging phosphine. The relative intensity of the signal at 36.06 ppm to the signal at −20.43 or −20.56 ppm in Figure 1a is much greater than that of the signal at 35.82 ppm to the signal at −20.48 ppm in the ^{31}P NMR spectrum of **4**. This suggests that the signal at 36.06 ppm is due not only to **4** but also to a species with a structure similar to that of **4**. The signal at −47.83 ppm in Figure 1a appeared as a doublet (J = 20 Hz)[13] and had almost the same chemical shift as that due to uncoordinated dmpe. It most likely is assignable to the uncoordinated phosphine terminus of complex **5**, which can be formed by the reaction of **4** with free dmpe. Indeed, the addition of 1 equiv of dmpe to **4** in C_6D_6 resulted in the emergence of the same signals as those at −20.43 and −47.83 ppm in Figure 1a. Further addition of dmpe (9 equiv) reduced the signals of **4** and the signal around −20.5 ppm became a doublet (J = 20 Hz) having almost the same intensity as that at −47.83 ppm. The signal corresponding to the chelating phosphines of **5** has the same chemical shift as that of **4**. At intermediate stages of the reaction of **1** with **2**, an equilibrium among **4**, **5**, and **6** probably exists, although the concentration of **6** would be very low. Complex **4** reacted with **1** more easily than **2** to form complex **3**; even at room temperature the reaction proceeded slowly.

The mechanism of the formation of **3** is envisioned to be similar to that leading to the platinum complex.[4d] Oxidative addition of two Si−H bonds and reductive elimination of H_2 form complex **6**, which exists mainly as pentacoordinated species **4** and **5** in the presence of free dmpe. The subsequent transformation presumably involves a tris(silyl)hydridonickel(IV) intermediate formed by the oxidative addition of a third Si−H bond and subsequent intramolecular dehydrogenative cyclization to form the final product **3**. Further investigation is necessary to clarify the mechanism.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for complexes **3** and **4** (15 pages). See any current masthead page for ordering information and Internet access instructions.

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[12] Crystal data for **4**: $C_{30}H_{64}Ni_2P_6Si_4$, fw = 840.44, monoclinic, $C2/c$, a = 19.316(4) Å, b = 12.652(3) Å, c = 18.138(4) Å, β = 101.05(2)°, V = 4350(2) Å^3, Z = 4, D_{calc} = 1.28 g cm^{-3}, R = 0.042, R_{w} = 0.064.

[13] This J value is consistent with $^3J_{p-p}$ values for $Me_2PCH_2CH_2PR_2$: King, R. B.; Cloyd, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 53−60.