of 25 reflections with 13.4° < $\theta$ < 17.8°, 13.4° < $\theta$ < 17.8°, 11.2° < $\theta$ < 14.4°, and 9.3° < $\theta$ < 14.6° for **2**, **4**, **5**, and **7**, respectively. The unit-cell parameters were checked for the presence of higher lattice symmetry.[37] All data were collected with the $\omega/2\theta$ scan mode. Data were corrected for Lp and for the observed linear decay of the reference reflections. Absorption corrections were applied to **4**, **5**, and **7** using the DIFABS procedure.[38] Standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (pI)^2$, with $p$ = 0.019, 0.207, 0.014, and 0.013 for **2**, **4**, **5**, and **7**, respectively.[39] The structures were solved (SHELXS86)[40] by automated Patterson methods followed by tangent expansion (**2**, **4**) or automated direct methods (**5**, **7**). Refinement on $F$ was carried out by full-matrix least-squares techniques (SHELX76).[41] The hydrogen atoms of **5** and **7** were included in the refinement on calculated positions (C–H = 0.98 Å) riding on their carrier atoms. The hydrogen atoms of **2** and **4**, and the hydroxyl hydrogen of **7**, were located on difference Fourier maps; their coordinates were included in the refinment. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms of **2**, **5**, and **7** were refined with one common isotropic thermal parameter of 0.037 (3), 0.0593 (19), and 0.067 (4) respectively. $F_c$ values of **5** and **7** were corrected for secondary extinction by refinement of an empirical isotropic parameter: $F_c' = F_c(1 - XF^2/(\sin\theta))$, with $X$ = 1.87 (10) × $10^{-6}$ and 1.54 (4) × $10^{-6}$ for **5** and **7**, respectively. Weights were introduced in the final refinement cycles. Neutral-atomic scattering factors were taken from Cromer and Mann;[42] anomalous-dispersion corrections from Cromer and Liberman.[43] Geometric calculations and illustrations were performed with PLATON[44] on a MicroVax-II cluster and a DECstation 5000. Final atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **2**, **4**, **5**, and **7** are given in Tables VII–X, respectively.

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**Supplementary Material Available:** Derivation of the Scatchard equation (text and a figure) for a compound with two binding sites and tables of fractional coordinates of the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles of the non-hydrogen and hydrogen atoms of **2**, **4**, and **7** (15 pages). Ordering information is given on any current masthead page.

OM920367F

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(37) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

(38) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(39) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *A31*, 245.

(40) Sheldrick, G. M. SHELXS86: Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany, 1986.

(41) Sheldrick, G. M. SHELX76: Program for crystal structure determination. Univ. of Cambridge, England, 1976.

(42) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(43) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(44) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

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# Nickel-Catalyzed Reactions of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene with Aromatic Compounds

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The reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (**1**) with benzene in the presence of $Ni(PEt_3)_4$ gave 1-(diethylphenylsilyl)-2-(diethylsilyl)benzene (**4a**) in high yield. Similar reaction of **1** with toluene gave 1-[diethyl(3-methylphenyl)silyl]- and 1-[diethyl(4-methylphenyl)silyl]-2-(diethylsilyl)benzene (**5a,b**). The reaction of **1** with isopropylbenzene also produced the corresponding two regioisomers. With *m*-xylene, **1** afforded 1-[diethyl(3,5-dimethylphenyl)silyl]- and 1-[diethyl(2,4-dimethylphenyl)silyl]-2-(diethylsilyl)benzene, while the reaction of **1** with *p*-xylene gave 1-[diethyl(2,5-dimethylphenyl)silyl]-2-(diethylsilyl)benzene as a main product, in addition to 1-[diethyl(4-methylbenzyl)silyl]-2-(diethylsilyl)benzene as a minor product. Similar reaction of **1** with mesitylene gave 1-[diethyl(3,5-dimethylbenzyl)silyl]-2-(diethylsilyl)benzene. The nickel-catalyzed reaction of **1** with a 1:1 mixture of benzene and toluene afforded **4a**, **5a**, and **5b** in 56, 22, and 9% yields, while, with a 1:1 mixture of benzene and mesitylene, **4a** was produced as the sole product.

## Introduction

Although considerable attention has been devoted to investigations of the strained small-ring compounds involving a silicon–silicon bond in the ring system,[1,2] much less interest has been shown in the chemistry of benzodisilacyclobutenes.[3] To our knowledge, only one paper concerning the synthesis of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobutene and its ring-opening polymerization has been reported to date.[9]

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(1) Brook, A. G. *The Chemistry of Organic Silicon Compounds. Part 2*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 15.

(2) Raabe, G.; Michl, J. Reference 1, Chapter 17.

(3) For 1,2-disilacyclobutenes, see refs. 4–6, and for 2,3-benzo-1-silacyclobutenes, see refs 7 and 8.

(4) Barton, T.; Kilgour, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7746.

(5) Sakurai, H.; Kobayashi, H.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43.

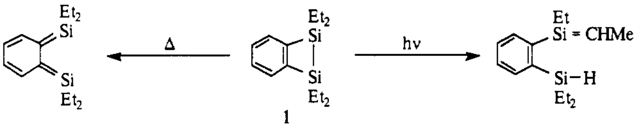
(6) Ishikawa, M.; Sugisawa, H.; Kumada, M.; Kawakami, H.; Yamabe, T. *Organometallics* **1983**, *2*, 974.

(7) Okazaki, R.; Kang, K.-T.; Inamoto, N. *Tetrahedron Lett.* **1981**, *22*, 235.

(8) Kang, K.-T.; Seo, H.-C.; Kim, K.-N. *Tetrahedron Lett.* **1985**, *26*, 4761.

0276-7333/92/2311-4135$03.00/0

Recently, we demonstrated that the thermolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (1) that can be readily obtained by sodium condensation of 1,2-bis(chlorodiethylsilyl)benzene gives an *o*-quinodisilane as a reactive intermediate. The *o*-quinodisilane thus formed reacts with acetylenes and carbonyl compounds to give [4 + 2] cycloadducts.[10] In contrast to the thermolysis, the photolysis of 1 affords a silene arising from homolytic scission of a silicon–silicon bond, followed by intramolecular disproportionation of the resulting diradical.[11] During the course of our investigation concerning the reaction of the silicon-containing small-ring compounds with a transition metal complex,[12-14] we found that treatment of 1 with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in benzene gives a benzene adduct derived from the C–H bond activation of a benzene molecule. In this paper we report the reaction of 1 with aromatic compounds in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0).

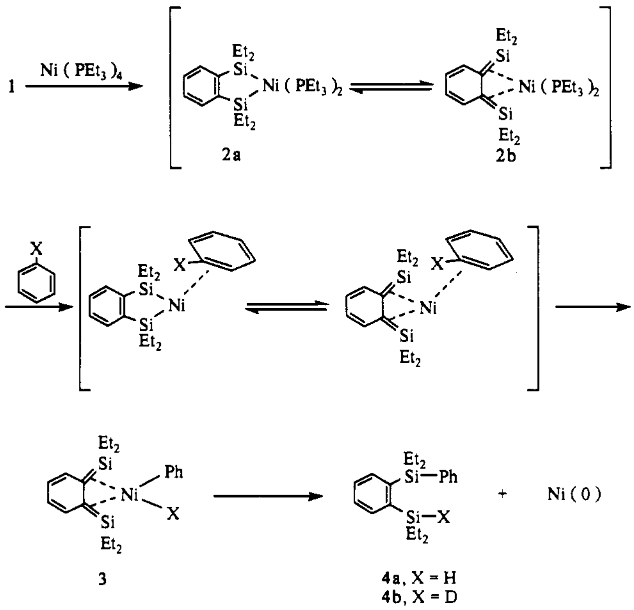


## Results and Discussion

In order to learn more about the chemical behavior of 3,4-benzodisilacyclobutene toward nickel complexes, we treated 1 with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in hexane in a degassed sealed tube at 150 °C for 24 h. GLC analysis of the reaction mixture showed no appreciable amount of volatile products. GPC analysis of the mixture, however, indicated the presence of a polymeric substance whose molecular weight was determined to be $M_w = 2900$, relative to the polystyrene standards. The $^{1}$H NMR spectrum of the polymeric substances reveals broad resonances due to ethylsilyl protons, hydrosilyl protons, and phenylene ring protons. Its IR spectrum shows a strong absorption due to stretching frequencies of an Si–H group. To our surprise, similar reaction of 1 in refluxing benzene afforded a benzene adduct as the sole volatile product. Thus, the reaction of 1 with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in refluxing benzene for 17 h gave 1-(diethylphenylsilyl)-2-(diethylsilyl)benzene (**4a**) in 97% yield. The structure of **4a** was confirmed by spectrometric analysis, as well as by elemental analysis. The IR spectrum of **4a** shows a strong absorption band at 2139 cm$^{-1}$, due to Si–H stretching frequencies. Its $^{13}$C NMR spectrum reveals 10 resonances in the aryl region, attributed to phenyl and phenylene carbons. The $^{29}$Si NMR spectrum shows two resonances at $\delta$ −9.78 and −3.32 ppm, due to two nonequivalent silicon atoms. These results are wholly consistent with the structure proposed for **4a**.

In order to confirm whether or not the hydrogen attached to a silicon atom in compound **4a** was originated from the benzene molecule, we carried out the reaction of 1 with deuteriobenzene. In this reaction, 2-(deuteriodiethylsilyl)-1-[diethyl(pentadeuteriophenyl)silyl]benzene (**4b**) was produced in 59% yield, in addition to 12% of the starting compound 1. The mass spectrum of **4b** indicates a fragment (M$^+$ − Et) at $m/e$ 303, and the $^2$H NMR spectrum reveals broad signals at 4.3 and 7.2 ppm, due to a D–Si bond and a pentadeuteriophenyl group. These results clearly indicate that the hydrogen on the silicon atom comes from the benzene molecule.

### Scheme I



The formation of 4 may be best explained in terms of C–H bond activation of benzene by a nickel complex. The C–H bond activation of arenes by transition metal complexes has been extensively investigated, and many types of the complexes involving the Zr, Rh, Ta, and Re metals have been used as catalysts.[15-25] However, nickel-catalyzed C–H bond activation is rather rare and is limited only to silicon compounds. We found that sp-hybridized C–H bond of ethynylsilanes[26] can be activated by a nickel(0) catalyst giving dienynes and that the thermolysis of 2-mesityl-4-phenyl-1,1-bis(trimethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-2-silacyclobut-3-ene affords two isomers of a 5,6-benzo-1,3-disilacyclohexene derivative arising from intramolecular C–H bond activation of a mesityl methyl group.[27,28] We also found similar intramolecular C–H bond activation of a tolyl methyl group in the reaction of 2-(*o*-tolyl)-2-(phenylethynyl)hexamethyl-

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(9) Shiina, K. *J. Organomet. Chem.* **1986**, *310*, C57.

(10) Ishikawa, M.; Sakamoto, H.; Tabuchi, T. *Organometallics* **1991**, *10*, 3173.

(11) Sakamoto, H.; Ishikawa, M. *Organometallics* **1992**, *11*, 2580.

(12) Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040.

(13) Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417.

(14) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050.

(15) Barefield, E. K.; Parshall, G. W.; Tabbe, F. N. *J. Am. Chem. Soc.* **1970**, *92*, 5234.

(16) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

(17) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.

(18) Jones, W. D.; Feher, F. J. (a) *J. Am. Chem. Soc.* **1982**, *104*, 4240; (b) *Organometallics* **1983**, *2*, 563; (c) *J. Am. Chem. Soc.* **1984**, *106*, 1650; (d) *Acc. Chem. Res.* **1989**, *22*, 91.

(19) Jones, W. D.; Maguire, J. A. *Organometallics* **1986**, *5*, 590.

(20) Stella, S.; Chiang, M.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1987**, 161.

(21) (a) Berry, D. H.; Jiang, Q. *J. Am. Chem. Soc.* **1989**, *111*, 8049. (b) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952.

(22) Tanaka, M.; Sakakura, T. *Pure Appl. Chem.* **1990**, *62*, 1147.

(23) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221.

(24) Boese, W. T.; Goldman, A. S. *Organometallics* **1991**, *10*, 782.

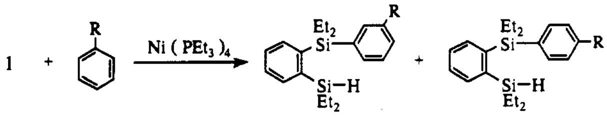
(25) Kunin, A. J.; Eisenberg, R. *Organometallics* **1988**, *7*, 2124.

(26) Ishikawa, M.; Ohshita, J.; Ito, Y.; Minato, A. *J. Chem. Soc., Chem. Commun.* **1988**, 804.

(27) Ishikawa, M.; Ohshita, J.; Ito, Y. *Organometallics* **1986**, *5*, 1518.

(28) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050.

**Scheme II**



5a, R = Me
6a, R = Me$_2$CH

5b, R = Me
6b, R = Me$_2$CH

trisilane with a catalytic amount of tetrakis(triethylphosphine)nickel(0).[29]

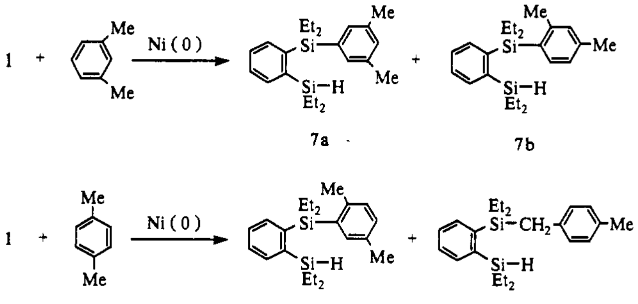
Scheme I illustrates a possible mechanistic interpretation of the observed reaction course. We suggest that o-quinodisilane–nickel complex **2b**, which would be produced from 3,4-benzo-2,2,5,5-tetraethyl-1-nickela-2,5-disilacyclopent-3-ene (**2a**) is involved as a key intermediate in C–H bond activation of benzene. Benzene would coordinate to the nickel atom in **2a** or **2b** in an $\eta^2$ fashion, and then the oxidative addition of a C–H bond of the coordinated benzene to the nickel atom takes place to give complex **3**. Finally reductive elimination of a nickel(0) species from complex **3** gives the observed product **4**.

The formation of 3,4-benzo-1-metala-2,5-disilacyclopent-3-enes, analogous to **2a**, from the reaction of 1,2-bis(dimethylsilyl)benzene with transition metal complexes has been reported.[30-34] Evidence for the production of **2b** has not yet been obtained so far. The coordination of arenes to the metal in an $\eta^2$ fashion is well-known, and evidence for the intermediacy of the $\eta^2$-arene complex has been reported by Jones and Feher.[18c,d]

Toluene also reacted with **1** in the presence of the nickel(0) catalyst to give two isomers of an adduct, which could be identified as 1-[diethyl(3-methylphenyl)silyl]-2-(diethylsilyl)benzene (**5a**) and 1-[diethyl(4-methylphenyl)silyl]-2-(diethylsilyl)benzene (**5b**), in 69 and 14% yields, respectively. Similar reaction of **1** with isopropylbenzene again produced two isomers of an adduct, 1-[diethyl(3-isopropylphenyl)silyl]-2-(diethylsilyl)benzene (**6a**) and 1-[diethyl(4-isopropylphenyl)silyl]-2-(diethylsilyl)benzene (**6b**), in 55 and 19% yields, respectively (Scheme II). In both cases, meta-substituted isomers **5a** and **6a** were produced as abundant isomers, and no products derived from ortho and benzylic C–H bond activation of toluene and isopropylbenzene were detected in the reaction mixture either by spectroscopic analysis or GLC analysis. Jones and Feher have reported that heating $(C_5Me_5)Rh(PMe_3)(Ph)H$ in toluene gives only the meta and para isomers of $(C_5Me_5)Rh(PMe_3)(tolyl)H$, although the photolysis of $(C_5Me_5)Rh(PMe_3)H_2$ in toluene affords *m*-, *p*-, and *o*-tolyl derivatives, along with a trace of a benzyl derivative.[18a] In these reactions, it has been found that the *m*-tolyl isomer is an abundant species, as observed in the present nickel-catalyzed reaction.

The reaction of **1** with *m*-xylene also afforded two regioisomers in 58 and 24% yields. The abundant product was identified as 1-[diethyl(3,5-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**7a**), and a minor product, as 1-[diethyl(2,4-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**7b**). With *p*-xylene, compound **1** reacted to give 1-[diethyl(2,5-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**8a**) in 40% yield, in addition to a 6% yield of 1-[diethyl(4-methylbenzyl)silyl]-2-(diethylsilyl)benzene (**8b**) (Scheme III).

**Scheme III**



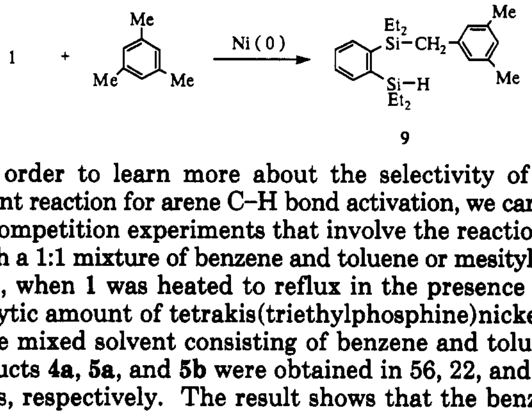
7a

7b

8a

8b

The formation of **8b**, in which C–H bond activation of a xylyl methyl group is involved, is of considerable interest because no product arising from the benzylic C–H bond is detected in the reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with *p*-xylene under thermal conditions. We carried out the reaction of **1** with mesitylene. Thus, the reaction of **1** with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in refluxing mesitylene for 30 h gave 1-[diethyl(3,5-dimethylbenzyl)silyl]-2-(diethylsilyl)benzene (**9**) in 28% yield, as the sole volatile product, indicating that C–H bond activation on an sp$^3$ carbon occurs in the present system.[35]



9

In order to learn more about the selectivity of the present reaction for arene C–H bond activation, we carried out competition experiments that involve the reaction of **1** with a 1:1 mixture of benzene and toluene or mesitylene. Thus, when **1** was heated to reflux in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) in the mixed solvent consisting of benzene and toluene, products **4a**, **5a**, and **5b** were obtained in 56, 22, and 9% yields, respectively. The result shows that the benzene C–H bond is more reactive than that of toluene. Similar nickel-catalyzed reaction of **1** with a 1:1 mixture of benzene and mesitylene gave **4a** in 69% yield as the sole volatile product. No product **9** could be detected in the reaction mixture. Such a trend is consistent with the result obtained from the reaction of other metal complexes.[18d]

The structures of all new compounds reported here were verified by mass, IR, and $^1$H, $^{13}$C, and $^{29}$Si NMR spectrometric analysis, as well as by elemental analysis (see Experimental Section).

## Experimental Section

**General Procedure.** All reactions were carried out under an atmosphere of dry argon. Yields were determined by GLC using an internal standard. NMR spectra were recorded on a JEOL Model EX-270 spectrometer using a deuteriochloroform solution containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument. Gas chromatographic separations were carried out using a column (3 m × 10 mm) packed with 30%

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[29] Ishikawa, M.; Nomura, Y.; Tozaki, E.; Kunai, A.; Ohshita, J. *J. Organomet. Chem.* **1990**, *399*, 205.

[30] Tilley, T. D. *The Chemistry of Organic Silicon Compounds. Part 2*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24.

[31] Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 107.

[32] Fink, W. *Helv. Chim. Acta* **1976**, *59*, 606.

[33] Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *Organometallics* **1985**, *4*, 623.

[34] Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16.

[35] Intramolecular sp$^3$ C–H bond activation of a mesityl group has been reported.[28,36]

[36] Albert, J.; Ceder, R. M.; Gomez, M.; Granell, J.; Sales, J. *Organometallics* **1992**, *11*, 1536.

SE-30 silicone on Chromosorb P. Gel permeation chromatographic separation was performed with a Model LC-908 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.). Tetrakis(triethylphosphine)nickel(0) was prepared by the method reported in the literature.[37]

**Materials.** 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (**1**) was prepared as reported previously.[10] Benzene and hexane used as solvents were dried over lithium aluminum hydride and distilled before use. Toluene, *m*-xylene, *p*-xylene, and mesitylene were dried over sodium and distilled just before use under an argon atmosphere.

**Reaction of 1 with Benzene.** In a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.5616 g (2.26 mmol) of **1** and 59 mg (0.11 mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry benzene. The mixture was heated to reflux for 17 h. GLC analysis of the reaction mixture indicated the presence of 1-(diethylphenylsilyl)-2-(diethylsilyl)benzene (**4a**) (97% yield) and the starting compound **1** (1% yield). Pure **4a** was isolated by preparative GLC: MS *m/e* 297 ($M^+$ − Et); IR 2139, 1429, 1225, 1112, 1004 cm$^{-1}$; $^1$H NMR 0.51–1.24 (m, 20H, EtSi), 4.22 (quint, 1 H, HSi, $J$ = 3.3 Hz), 7.27–7.67 (m, 9H, phenyl and phenylene ring protons); $^{13}$C NMR 4.26, 5.01, 7.51, 8.19 (EtSi), 127.48, 127.80, 127.92, 128.59, 134.90, 134.99, 136.10, 138.47, 143.07, 143.67 (phenyl and phenylene ring carbons); $^{29}$Si NMR −9.78, −3.32. Anal. Calcd for $C_{20}H_{30}Si_2$: C, 73.55; H, 9.26. Found: C, 73.50; H, 9.20.

**Reaction of 1 with Benzene-$d_6$.** In a 15-mL glass tube fitted with a stirrer and reflux condenser was placed 0.4593 g (1.85 mmol) of **1** and 46 mg (8.62 × $10^{-2}$ mmol) of tetrakis(triethylphosphine)nickel(0) in 1 mL of dry benzene-$d_6$. The mixture was heated to reflux for 15 h. GLC analysis of the resulting mixture showed the presence of 2-(deuteriodiethylsilyl)-1-[diethyl(pentadeuteriophenyl)silyl]benzene (**4b**) (59% yield) and 12% of the starting compound **1**. Pure **4b** was isolated by preparative GLC: MS *m/e* 303 ($M^+$ − Et); IR 2270, 1567, 1556, 1462, 1455, 1416, 1260, 1233, 1118, 1056, 1007 cm$^{-1}$; $^1$H NMR 0.51–1.26 (m, 20H, EtSi), 7.33–7.67 (m, 4H, phenylene ring protons); $^{13}$C NMR 4.19, 5.03, 7.53, 8.18 (EtSi), 126.97 (t, $J_{C-D}$ = 23 Hz), 127.80, 127.92, 128.55 (t, $J_{C-D}$ = 23 Hz), 134.47 (t, $J_{C-D}$ = 23 Hz), 135.00, 136.10, 138.20, 143.11, 143.67 (deuteriophenyl and phenylene ring carbons); $^2$H NMR (δ, in $(CD_3)_2CO$) 4.3 (broad s, DSi), 7.2 (broad s, $C_6D_5$).

**Reaction of 1 with Toluene.** In a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed 0.4707 g (1.89 mmol) of **1** and 52 mg (9.79 × $10^{-2}$ mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry toluene. The mixture was heated to reflux for 4 h. The reaction mixture was analyzed by GLC as being 1-[diethyl(3-methylphenyl)silyl]-2-(diethylsilyl)benzene (**5a**) (69% yield) and 1-[diethyl(4-methylphenyl)silyl]-2-(diethylsilyl)benzene (**5b**) (14% yield). Pure **5a** and **5b** were isolated by preparative GLC. Data for **5a**: MS *m/e* 311 ($M^+$ − Et); IR 3043, 2954, 2873, 2155, 1458, 1414, 1232, 1117, 1008, 971, 813, 738, 714 cm$^{-1}$; $^1$H NMR 0.49–1.21 (m, 20H, EtSi), 2.28 (s, 3H, Me), 4.19 (quint, 1H, HSi, $J$ = 3.3 Hz), 7.11–7.64 (m, 8H, tolyl and phenylene ring protons); $^{13}$C NMR 4.28, 5.07, 7.57, 8.20 (EtSi), 21.48 (Me), 127.39, 127.76, 127.87, 129.36, 131.91, 134.97, 135.54, 136.12, 136.66, 138.24, 143.20, 143.68 (tolyl and phenylene ring carbons); $^{29}$Si NMR −9.78, −3.34. Anal. Calcd for $C_{21}H_{32}Si_2$: C, 74.04, H, 9.47. Found: C, 74.01; H, 9.33. Data for **5b**: MS *m/e* 311 ($M^+$ − Et); IR 3037, 2954, 2873, 2156, 1458, 1414, 1232, 1117, 1007, 972, 806, 708 cm$^{-1}$; $^1$H NMR 0.45–1.25 (m, 20H, EtSi), 2.33 (s, 3H, Me), 4.21 (quint, 1H, HSi, $J$ = 3.3 Hz), 7.10–7.65 (m, 8H, tolyl and phenylene ring protons); $^{13}$C NMR 4.32, 5.16, 7.57, 8.20 (EtSi), 21.46 (Me), 127.76, 127.84, 128.32, 131.91, 134.95, 135.54, 136.12, 138.35, 143.32, 143.68 (tolyl and phenylene ring carbons); $^{29}$Si NMR −9.83, −3.39. Anal. Calcd for $C_{21}H_{32}Si_2$: C, 74.04; H, 9.47. Found: C, 73.95; H, 9.36.

**Reaction of 1 with Isopropylbenzene.** A mixture of 0.3577 g (1.44 mmol) of **1** and 38 mg (7.15 × $10^{-2}$ mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry isopropylbenzene was heated to reflux for 7 h. GLC analysis of the reaction mixture showed the presence of 1-[diethyl(3-isopropylphenyl)silyl]-2-(diethylsilyl)benzene (**6a**) (55% yield), 1-[diethyl(4-isopropylphenyl)silyl]-2-(diethylsilyl)benzene (**6b**) (19% yield), and 2% of the starting compound **1**. Pure **6a** and **6b** were isolated by preparative GLC. Data for **6a**: MS *m/e* 368 ($M^+$); IR 2952, 2857, 2139, 1459, 1411, 1232, 1112, 1010, 807, 735, 708 cm$^{-1}$; $^1$H NMR 0.46–1.17 (m, 20H, EtSi), 1.20 (d, 6 H, $Me_2CH$–, $J$ = 6.9 Hz), 2.83 (sep, 1H, –$HCMe_2$, $J$ = 6.9 Hz), 4.24 (quint, 1H, HSi, $J$ = 3.3 Hz), 7.16–7.65 (m, 8H, cumyl and phenylene ring protons); $^{13}$C NMR 4.21, 5.10, 7.60, 8.21 (EtSi), 24.04 (Me), 34.20 (–$CHMe_2$), 126.47, 127.46, 127.74, 127.85, 132.50, 133.39, 134.98, 136.08, 138.09, 143.41, 143.65, 147.56 (cumyl and phenylene ring carbons); $^{29}$Si NMR −9.73, −3.43. Anal. Calcd for $C_{23}H_{36}Si_2$: C, 74.92; H, 9.84. Found: C, 74.87; H, 9.75. Data for **6b**: MS *m/e* 368 ($M^+$); IR 2957, 2873, 2156, 1600, 1462, 1415, 1260, 1232, 1117, 1008, 972, 820, 741, 711, 681 cm$^{-1}$; $^1$H NMR 0.45–1.18 (m, 20H, EtSi), 1.23 (d, 6 H, $Me_2CH$–, $J$ = 6.9 Hz), 2.86 (sep, 1H, –$HCMe_2$, $J$ = 6.9 Hz), 4.19 (quint, 1H, HSi, $J$ = 3.3 Hz), 7.13–7.65 (m, 8H, cumyl and phenylene ring protons); $^{13}$C NMR 4.30, 5.07, 7.60, 8.25 (EtSi), 23.94 (Me), 34.09 (–$CHMe_2$), 125.68, 127.74 (two carbons), 127.85, 134.95, 135.07, 136.03, 143.57, 143.74, 149.38 (cumyl and phenylene ring carbons); $^{29}$Si NMR −9.58, −3.66. Anal. Calcd for $C_{23}H_{36}Si_2$: C, 74.92; H, 9.84. Found: C, 74.86; H, 9.83.

**Reaction of 1 with *m*-Xylene.** A solution of 0.4845 g (1.95 mmol) of **1** and 51 mg (9.60 × $10^{-2}$ mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry *m*-xylene was heated to reflux for 27 h. The reaction mixture was analyzed by GLC as being 1-[diethyl(3,5-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**7a**) (58% yield), 1-[diethyl(2,4-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**7b**) (24% yield), and 9% of the starting compound **1**. Pure **7a** and **7b** were isolated by preparative GLC. Data for **7a**: MS *m/e* 354 ($M^+$); IR 2954, 2873, 2154, 1594, 1459, 1414, 1231, 1139, 1117, 1008, 971, 813, 739, 715, 621 cm$^{-1}$; $^1$H NMR 0.51–1.20 (m, 20H, EtSi), 2.25 (s, 6H, two Me), 4.19 (quint, 1H, HSi, $J$ = 3.3 Hz), 6.95, 7.01 (broad s, 3H, *m*-xylyl ring protons), 7.31–7.64 (m, 4H, phenylene ring protons); $^{13}$C NMR 4.35, 5.18, 7.64, 8.25 (EtSi), 21.37 (Me), 127.78, 127.85, 130.35, 132.61, 134.95, 136.15, 136.58, 138.08, 143.34, 143.72 (*m*-xylyl and phenylene ring carbons); $^{29}$Si NMR −9.78, −3.39. Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.41; H, 9.65. Data for **7b**: MS *m/e* 354 ($M^+$); IR 2954, 2872, 2154, 1604, 1458, 1413, 1229, 1116, 1007, 971, 812, 738, 708, 679 cm$^{-1}$; $^1$H NMR 0.43–1.28 (m, 20H, EtSi), 2.03 (s, 3H, Me), 2.29 (s, 3H, Me), 4.19 (quint, 1H, HSi, $J$ = 3.3 Hz), 6.88, 6.95, 6.98 (broad s, 3H, *m*-xylyl ring protons), 7.29–7.65 (m, 4H, phenylene ring protons); $^{13}$C NMR 4.21, 4.92, 7.64, 8.10 (EtSi), 21.28, 22.93 (Me), 125.53, 127.58, 127.90, 130.51, 132.59, 134.86, 135.47, 136.22, 138.72, 142.96, 143.84, 144.87 (*m*-xylyl and phenylene ring carbons); $^{29}$Si NMR −9.85, −3.78. Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.41; H, 9.60.

**Reaction of 1 with *p*-Xylene.** A mixture of 0.2408 g (0.969 mmol) of **1** and 25 mg (4.71 × $10^{-2}$ mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry *p*-xylene was heated to reflux for 33 h. The reaction mixture was analyzed by GLC as being 1-[diethyl(2,5-dimethylphenyl)silyl]-2-(diethylsilyl)benzene (**8a**) (40% yield) and 1-[diethyl(4-methylbenzyl)silyl]-2-(diethylsilyl)benzene (**8b**) (6% yield) and 10% of unchanged **1**. Pure **8a** was isolated by preparative GLC: MS *m/e* 354 ($M^+$); IR 2954, 2872, 2156, 1458, 1415, 1378, 1232, 1117, 1007, 971, 810, 740, 706, 619 cm$^{-1}$; $^1$H NMR 0.42–1.27 (m, 20H, EtSi), 2.03 (s, 3H, Me), 2.28 (s, 3H, Me), 4.19 (quint, 1H, HSi, $J$ = 3.3 Hz), 6.92–7.65 (m, 7H, *p*-xylyl and phenylene ring protons); $^{13}$C NMR 4.17, 4.98, 7.66, 8.12 (EtSi), 21.11, 22.53 (Me), 127.60, 127.92, 129.52, 129.67, 133.58, 134.86, 135.51, 136.21, 136.80, 140.68, 142.99, 144.78 (*p*-xylyl and phenylene ring carbons); $^{29}$Si NMR −9.73, −3.62. Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.60; H, 9.54. Pure **8b** was isolated by preparative recycling HPLC: MS *m/e* 325 ($M^+$ − Et); IR 3049, 2954, 2872, 2146, 1508, 1418, 1233, 1156, 1117, 1009, 972, 817, 745, 706 cm$^{-1}$; $^1$H NMR 0.69–1.02 (m, 20H, EtSi), 2.25 (s, 3H, Me), 2.43 (s, 2H, $CH_2$), 4.63 (quint, 1H, HSi, $J$ = 3.3 Hz), 6.82–6.96 (m, 4H, *p*-xylyl ring protons), 7.14–7.56 (m, 4H, phenylene ring protons); $^{13}$C NMR 4.65, 4.69, 7.51, 8.41 (EtSi), 20.90 (Me), 22.82 ($CH_2$), 127.73, 127.87, 128.34, 128.77, 133.26, 135.06, 135.63, 136.87, 142.77, 143.68 (*p*-xylyl and phenylene ring carbons); $^{29}$Si NMR −9.69, 0.96. Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.50; H, 9.60.

**Reaction of 1 with Mesitylene.** A mixture of 0.2859 g (1.15 mmol) of **1** and 29 mg (5.46 × $10^{-2}$ mmol) of tetrakis(triethylphosphine)nickel(0) in 10 mL of dry mesitylene was heated to

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[37] Cundy, C. S. *J. Organomet. Chem.* **1974**, *69*, 305.

reflux for 30 h. The reaction mixture was analyzed by GLC as being 1-[diethyl(3,5-dimethylbenzyl)silyl]-2-(diethylsilyl)benzene (**9**) (28% yield) and unchanged **1** (3% yield). Pure **9** was isolated by preparative GLC: MS *m/e* 368 ($M^+$); IR 2955, 2874, 2146, 1602, 1457, 1417, 1117, 1016, 809 $cm^{-1}$; $^1H$ NMR 0.81–1.05 (m, 20H, EtSi), 2.18 (s, 6H, two Me), 2.40 (s, 2H, $CH_2$), 4.65 (quint, 1H, HSi, $J = 3.3$ Hz), 6.56 (broad s, 2H, mesityl ring protons), 6.67 (broad s, 1H, mesityl ring proton), 7.25–7.57 (m, 4H, phenylene ring protons); $^{13}C$ NMR 4.69 (two carbons), 7.51, 8.41 (EtSi), 21.26 (Me), 23.18 ($CH_2$), 125.64, 126.41, 127.69, 127.81, 135.04, 135.67, 137.30, 139.94, 142.71, 143.75 (mesityl and phenylene ring carbons); $^{29}Si$ NMR −9.69, 1.00. Anal. Calcd for $C_{23}H_{36}Si_2$: C, 74.92; H, 9.84. Found: C, 74.91; H, 9.81.

**Reaction of 1 with Hexane.** A mixture of 0.4229 g (1.70 mmol) of **1** and 46 mg ($8.66 \times 10^{-2}$ mmol) of tetrakis(triethylphosphine)nickel(0) in 0.6 mL of dry hexane was heated in a degassed sealed tube at 150 °C for 24 h. GLC analysis of the mixture showed the presence of 8% of the starting compound **1** and a small amount of an unidentified product (less than 4% yield). Nonvolatile products were isolated by precipitation of the mixture from methanol–chloroform: IR 3050, 2954, 2153 (H–Si), 1462, 1455, 1416, 1378, 1348, 1233, 1138, 1010, 972, 800, 704 $cm^{-1}$; $^1H$ NMR 0.45–1.12 (m, EtSi), 4.21 (broad s, HSi), 7.31–7.72 (m, phenylene ring protons).

**Reaction of 1 with a 1:1 Mixture of Benzene and Toluene.** A mixture of 0.6829 g (2.75 mmol) of **1** and 74 mg ($1.39 \times 10^{-1}$ mmol) of tetrakis(triethylphosphine)nickel(0) in the mixed solvent consisting of 5.63 g (72 mmol) of benzene and 6.63 g (72 mmol) of toluene was heated to reflux for 5 h. The mixture was analyzed by GLC as being **4a** (56% yield), **5a** (22% yield), and **5b** (9% yield). All spectral data obtained for **4a**, **5a**, and **5b** were identical with those of authentic samples.

**Reaction of 1 with a 1:1 Mixture of Benzene and Mesitylene.** A mixture of 0.5310 g (2.14 mmol) of **1** and 55 mg ($1.04 \times 10^{-1}$ mmol) of the nickel catalyst in the mixed solvent consisting of 5.80 g (74 mmol) of benzene and 8.85 g (74 mmol) of mesitylene was heated to reflux for 5 h. GLC analysis of the reaction mixture showed the presence of **4a** (69% yield) as the sole product. All spectral data for **4a** were identical with those of an authentic sample.

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# Heterobimetallic Complexes Containing Methylaminobis(difluorophosphine)

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The use of $cpFeCl(PNP)_2$ and $Mo(CO)_3(PNP)_2$ (cp = cyclopentadienyl; PNP = $MeN(PF_2)_2$) as precursors to heterobimetallic complexes is reported. The former generally reacts via chloride transfer to low-valent metal complexes while the latter either gives heterobimetallic complexes bridged by two PNP ligands or acts as a source of PNP ligands. $cpFeCl(PNP)_2$ with $Co_2(CO)_8$ gives $CoCl_2$ and $cpFe(\mu\text{-}PNP)_2Co(CO)_2$ (**1**) and with $Pt(C_2Ph_2)(PPh_3)_2$ forms $PtCl(PPh_3)(\mu\text{-}PF_2)(\mu\text{-}PF_2NMe)Fe(PF_2NHMe)cp$ (**2**) and $PtCl(P(O)F_2)(PPh_3)_2$ (**7**). The last is also formed from PNP and $PtCl_2(PPh_3)_2$. $Mo(CO)_3(PNP)_2$ with $Ni(CO)_2(PPh_3)_2$ or $Pt(C_2H_4)(PPh_3)_2$ gives $Mo(CO)_3(\mu\text{-}PNP)_2M(PPh_3)$ (M = Ni (**3**), Pt (**4**)) while with $MCl(CO)(PPh_3)_2$ the products are $Mo(CO)_3(\mu\text{-}PNP)_2IrCl(CO)(PPh_3)$ (M = Ir, **5**) and $Mo(CO)_3(\mu\text{-}PNP)_2RhCl(PPh_3)$ (M = Rh, **6**). Direct reaction of PNP with $Pt(C_2H_4)(PPh_3)_2$ and $cp_2Mo_2(CO)_4$ yields $Pt_2(\mu\text{-}PNP)_3(PPh_3)$ (**8**) and $cp_2Mo_2(CO)_4(\mu\text{-}PNP)$ (**9**), respectively. The $^{31}P$ NMR spectra of the complexes and related chemistry are discussed. The crystal structures of **1**, **2**, **4**, **7**, and **8** have been determined by X-ray crystallography. **1**: monoclinic; $P2_1/n$; $a = 8.750$ (1), $b = 19.908$ (2), $c = 10.719$ (2) Å; $\beta = 95.97$ (1)°; $Z = 4$. **2**: monoclinic; $P2_1/c$; $a = 12.696$ (2), $b = 13.479$ (2), $c = 21.031$ (1) Å; $\beta = 92.620$ (7)°; $Z = 4$. **4**: orthorhombic; *Pbca*; $a = 14.544$ (1), $b = 23.023$ (1), $c = 19.453$ (2) Å; $Z = 8$. **7**: monoclinic; $P2_1/c$; $a = 11.828$ (2), $b = 20.678$ (4), $c = 8.317$ (1) Å; $\beta = 95.04$ (1)°; $Z = 2$. **8**: monoclinic; $P2_1/c$; $a = 11.696$ (2), $b = 16.492$ (2), $c = 17.809$ (2) Å; $\beta = 103.465$ (2)°; $Z = 4$.

## Introduction

We have for a number of years been interested in the chemistry of bi- and trimetallic complexes stabilized by "short bite" phosphorus ligands such as $H_2C(PPh_2)_2$-(DPPM)[1] and $HC(PMe_2)_3$(tmpm).[2] The steric bulk of DPPM is such that access to the metal atoms in its bimetallic complexes is frequently quite restricted thus limiting the range of molecules which could be studied as substrates for bimetallic activation. We therefore sought less bulky ligands which could be expected to show a similar preference for bridging two metals, as opposed to forming monometallic chelates, thereby making the metal atoms accessible to a wider variety of potential substrates. An attractive class of ligands is that of formula $RN(PX_2)_2$ (R = alkyl; X = alkoxy, F).[3] Prior to our earlier work in

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[1] (a) Mague, J. T. *Organometallics* **1986**, *5*, 918 and references therein. (b) Mague, J. T. *Polyhedron* **1990**, *9*, 2635. (c) Mague, J. T. *Polyhedron* **1992**, *11*, 677.

[2] Mague, J. T.; Lloyd, C. L. *Organometallics* **1992**, *11*, 26.

[3] (a) Brown, G. M.; Finholt, J. E.; King, R. B.; Bibber, J. W. *Inorg. Chem.* **1982**, *21*, 2139. (b) Mague, J. T.; Johnson, M. P. *Organometallics* **1990**, *9*, 1254. (c) Nixon, J. F. *J. Chem. Soc. A* **1973**, 2689.

0276-7333/92/2311-4139$03.00/0