**Intermolecular and Intramolecular, Platinum-Catalyzed,
Acceptorless Dehydrogenative Coupling of Hydrosilanes
with Aryl and Aliphatic Methyl C–H Bonds**

Supporting Information

Naofumi Tsukada and John F. Hartwig*

*Yale University, Department of Chemistry,
P.O. Box 208107, New Haven, Connecticut 06520-8107*

General. All manipulations were conducted under a nitrogen atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven-dried for approximately 1 h prior to use. Benzene and toluene were purged with nitrogen for 45 min and dried with a solvent purification system containing a 1 m column of activated alumina. Other arenes were purified by distillation from the appropriate drying agents. $\text{TpPt}(\text{Me})_2\text{H}$,¹ $\text{Tp}'\text{Pt}(\text{Me})_2\text{H}$,² $\text{Tp}'\text{Pt}(\text{Me})(\text{H})_2$ ³ and $\text{Tp}'\text{Pt}(\text{Ph})_2\text{H}$ ² (Tp=hydridotrispyrazolylborate, Tp'=hydridotris(3,5-dimethylpyrazolyl)borate) were prepared according to literature procedures. Unless noted otherwise, all other reagents were used as received from commercial suppliers. ^1H NMR spectra were obtained at 400 MHz using tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained at 100.6 MHz using tetramethylsilane as an internal standard. GC analyses were performed using a DB-1301 narrow bore column.

General procedure for the intermolecular dehydrogenative coupling of silanes with arenes. $\text{Tp}'\text{Pt}(\text{Me})_2\text{H}$ (3.3 mg, 6.3 μmol), a silane (0.125 mmol) and an arene (0.50 ml) were placed into an NMR tube, and the tube was sealed under vacuum. The tube was heated at 200 °C for 24 h (for benzene) or 48 h (other arenes). The tube was opened, dodecane (10 μl , 44 μmol) was added as internal standard, and an aliquot was removed and analyzed by GC. Results for substituted benzenes are summarized in Table S1.

Table S1. Dehydrogenative Coupling of silanes with substituted benzenes

silane	arene	yield(%)
HSiEt_3	toluene	54 (meta), 28 (para), 3 (ortho)
HSiEt_3	trifluorotoluene	41 (meta), 20 (para), <1 (ortho)
HSiEt_3	<i>o</i> -xylene	43 (4-Si), 2 (3-Si)
HSiEt_3	<i>m</i> -bis(trifluoromethyl)benzene	38 (5-Si)
HSiEt_3	toluene + trifluorotoluene	26 (CF_3 , meta), 12 (CF_3 , para), 16 (CH_3 , meta), 9 (CH_3 , para)
HSiPr^n_3	<i>m</i> -xylene + <i>m</i> -bis(trifluoromethyl)benzene	39 (CF_3 , 5-Si), 12 (CH_3 , 5-Si)

The products PhSiEt_3 ,⁴ PhSiPr^n_3 ,⁵ and Ph_2SiMe_2 ⁶ have been prepared previously. To calculate response factors, we independently prepared these compounds as follows. To a solution of R_3SiCl (10.0 mmol) in ether (10 ml) was added PhMgBr (11.0 mmol, 1.0 M in THF) at 0 °C. The reaction mixture was stirred 15 h at room temperature. Saturated aqueous ammonium chloride (5 ml), followed by water (1 ml) and ether (10 ml), was added, and the organic layer was separated. The aqueous layer was extracted with ether (10 ml). The combined organic layers were dried over MgSO_4 , and the solvents were removed in vacuo. The crude oil was purified by flash chromatography using hexane as eluent, followed by bulb-to-bulb distillation.

The product Ph_3SiMe has been prepared previously.⁷ To calculate response factors for GC, we independently prepared Ph_3SiMe as follows. Ph_3SiH (2.60g, 10.0 mmol) was placed in a flask. MeLi (16.5 mmol, 1.5 M in ether) was added at room temperature, and the mixture was stirred overnight at room temperature. Saturated aqueous ammonium

chloride (5 ml) followed by water (1 ml) and ether (10 ml) were added, and the organic layer was separated. The aqueous layer was extracted with ether (10 ml). The combined organic layers were dried over MgSO_4 , and the solvent was removed in vacuo. The crude product was recrystallized twice from ethanol. The yield was 37%.

To calculate response factors for GC, the products *m*- $\text{CH}_3\text{C}_6\text{H}_4\text{SiEt}_3$ and *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SiEt}_3$ were prepared according to literature procedures.⁸ Other di- or tri-substituted arene products such as $\text{CF}_3\text{C}_6\text{H}_4\text{SiEt}_3$,⁹ 3,4- $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{SiEt}_3$,¹⁰ 3,5- $(\text{CF}_3)_2\text{C}_6\text{H}_3\text{SiEt}_3$, 3,5- $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{SiPr}_3$ and 3,5- $(\text{CF}_3)_2\text{C}_6\text{H}_3\text{SiPr}_3$ were prepared in a similar manner. To a solution of ArBr (3.0 mmol) in ether (5.0 ml) was added dropwise *n*-BuLi (3.3 mmol, 1.6 M in hexanes) at -78°C . After stirring for 2 h at -78°C , R_3SiCl (3.0 mmol) was added, and then the mixture was stirred overnight at room temperature. Saturated aqueous ammonium chloride (2 ml), followed by water (1 ml) and ether (5 ml), was added, and the organic layer was separated. The aqueous layer was extracted with ether (5 ml). The combined organic layers were dried over MgSO_4 , and the solvents were removed in vacuo. The crude oil was purified by flash chromatography using hexane as eluent, followed by bulb-to-bulb distillation.

[(3,5-bis(trifluoromethyl)phenyl)triethylsilane. ^1H NMR (CDCl_3) δ 7.88 (s, 2H), 7.85 (s, 1H), 0.99 (t, $J = 7.9$ Hz, 9H), 0.86 (q, $J = 7.9$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 141.3, 133.8, 130.6 (q, $J_{\text{FC}} = 32$ Hz), 123.7 (q, $J_{\text{FC}} = 273$ Hz), 122.6 (septet, $J_{\text{FC}} = 4$ Hz), 7.2, 3.1; Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{F}_6\text{Si}$: C, 51.21; H, 5.53. Found: C, 51.21; H, 5.55.

(3,5-dimethylphenyl)tri-*n*-propylsilane. ^1H NMR (CDCl_3) δ 7.08 (s, 2H), 6.98 (s, 1H), 2.31 (s, 6H), 1.35 (m, 6H), 0.96 (t, $J = 7.2$ Hz, 9H), 0.76 (m, 6H); ^{13}C NMR δ 138.0, 136.8, 131.8, 130.4, 21.5, 18.6, 17.5, 15.3; Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{Si}$: C, 77.78; H, 11.52. Found: C, 77.59; H, 11.77.

[(3,5-bis(trifluoromethyl)phenyl)tri-*n*-propylsilane. ^1H NMR (CDCl_3) δ 7.88 (s, 2H), 7.84 (s, 1H), 1.35 (m, 6H), 0.98 (t, $J = 7.3$ Hz, 9H), 0.85 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 142.1, 133.8, 130.7 (q, $J_{\text{FC}} = 32$ Hz), 123.8 (q, $J_{\text{FC}} = 273$ Hz), 122.6 (septet, $J_{\text{FC}} = 4$ Hz), 18.4, 17.3, 14.9; Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{F}_6\text{Si}$: C, 55.12; H, 6.53. Found: C, 55.21; H, 6.50.

Dehydrogenative cyclization of (2-phenylethyl)dimethylsilane. Yield determined by ^1H NMR spectroscopy: $\text{Tp}^*\text{Pt}(\text{Me})_2\text{H}$ (3.8 mg, 7.3 μmol), (2-phenylethyl)dimethylsilane (24 μl , 0.125 mmol), dodecahydrotriphenylene (3.7 mg, 15 μmol) and cyclohexane- d_{12} (0.50 ml) were placed into an NMR tube, and then the tube was sealed under vacuum. An initial ^1H NMR spectrum of the sample was recorded. The tube was heated at 200°C for 48 h. A second ^1H NMR spectrum was obtained after this time. The yield (70%) of 1,1-dimethyl-1-silaindan¹¹ was determined from the ^1H NMR spectra by integration against the dodecahydrotriphenylene internal standard.

Isolation of the product by dehydrogenative coupling: $\text{Tp}^*\text{Pt}(\text{Me})_2\text{H}$ (3.8 mg, 7.3 μmol), (2-phenylethyl)dimethylsilane (24 μl , 0.125 mmol), and cyclohexane (0.50 ml) were placed into an NMR tube, and the tube was sealed under vacuum. The tube was heated at 200°C for 24 h. The tube was opened, the solvent was evaporated under reduced pressure, and the resulting oil was purified by column chromatography on silica gel, eluting with *n*-hexane to give 13 mg (61%) of 1,1-dimethyl-1-silaindan.¹¹

Synthesis of (3-phenylpropyl)diethylsilane. A mixture of $\text{RhCl}(\text{PPh}_3)_3$ (14 mg, 15

μmol), allylbenzene (0.40 ml, 3.0 mmol), and diethylsilane (0.77 ml, 6.0 mmol) in benzene (10 ml) was stirred overnight at room temperature. The volatile materials were removed under reduced pressure, and the resulting oil was purified by column chromatography on silica gel, eluting with *n*-hexane to give 0.56 g (90%) of (3-phenylpropyl)diethylsilane. ^1H NMR (CDCl_3) δ 7.27 (m, 2H), 7.19–7.15 (m, 3H), 3.66 (septet, $J = 3.1$ Hz, 1H), 2.64 (t, $J = 7.7$ Hz, 2H), 1.67 (m, 2H), 0.96 (t, $J = 7.8$ Hz, 6H), 0.65 (m, 2H), 0.58 (dq, $J = 7.8, 3.1$ Hz, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 142.6, 128.5, 128.2, 125.7, 39.6, 26.8, 10.5, 8.2, 2.8; Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{Si}$: C, 75.65; H, 10.74. Found: C, 75.37; H, 10.85.

Dehydrogenative cyclization of (3-phenylpropyl)diethylsilane. $\text{Tp}^*\text{Pt}(\text{Me})_2\text{H}$ (3.8 mg, 7.3 μmol), (3-phenylpropyl)diethylsilane (30 μl , 0.125 mmol), dodecahydrotriphenylene (5.0 mg, 21 μmol) and cyclohexane (0.50 ml) were placed into an NMR tube, and the tube was sealed under vacuum. An initial ^1H NMR spectrum of the sample was recorded. The tube was heated at 200 $^\circ\text{C}$ for 48 h. A second NMR spectrum was obtained after this time. The yield (64%) of 1,1-diethyl-1,2,3,4-tetrahydro-1-silanaphthalene was determined from the ^1H NMR spectra by integration against the dodecahydrotriphenylene internal standard. To obtain isolated material for spectral and analytical data, the product was independently prepared as follows.¹² Magnesium turnings (182 mg, 7.50 mmol) and THF (1.0 ml) were placed in a flask. A solution of 1-bromo-2-(3-bromopropyl)benzene (834 mg, 3.00 mmol) in THF (8.0 ml) was added dropwise, and the mixture was stirred for 18 h at room temperature. The supernatant was transferred dropwise by syringe to a solution of dichlorodiethylsilane (377 mg, 2.4 mmol) in THF (1.0 ml). The mixture was heated at reflux for 2.5 h and cooled to room temperature. Saturated aqueous ammonium chloride (5 ml), followed by water (1 ml) and ether (1 ml), was added, and the organic layer was separated. The aqueous layer was extracted with ether (10 ml). The combined organic layers were dried over Na_2SO_4 , and the solvents were removed in vacuo. The crude oil was purified by flash chromatography with hexane as eluent, followed by bulb-to-bulb distillation. The yield was 36%. ^1H NMR (CDCl_3) δ 7.42 (m, 1H), 7.24 (m, 1H), 7.17 (m, 1H), 7.09 (m, 1H), 2.73 (m, 2H), 1.91 (m, 2H), 0.94 (t, 6H), 0.88 (m, 2H), 0.73 (q, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 149.4, 134.3, 133.7, 128.6, 128.5, 125.1, 35.6, 22.9, 8.7, 7.5, 5.7; Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{Si}$: C, 76.40; H, 9.86. Found: C, 76.13; H, 10.04.

Dehydrogenative cyclization of tri-*n*-butylsilane. (a) Yield determined by GC. $\text{Tp}^*\text{Pt}(\text{Me})_2\text{H}$ (3.3 mg, 6.3 μmol), tri-*n*-butylsilane (32 μl , 0.125 mmol) and cyclohexane (0.50 ml) were placed into an NMR tube, and the tube was sealed under vacuum. The tube was heated at 200 $^\circ\text{C}$ for 72 h. The tube was opened, dodecane (10 μl , 44 μmol) was added as internal standard, and an aliquot was removed and analyzed by GC. The yield of 1,1-di-*n*-butyl-silacyclopentane¹³ was 80%. To calculate response factors for GC, the product was independently prepared as follows. Magnesium turnings (296 mg, 12.0 mmol) and THF (10 ml) were placed into a flask equipped with a reflux condenser. 1,4-Dibromobutane (0.657 ml, 5.50 mmol) was added dropwise, and the mixture was stirred for 1 h at room temperature and then refluxed for 0.5 h. Dibutyldichlorosilane (1.08 ml, 5.0 mmol) was added at room temperature, and the mixture was stirred for 18 h at room temperature. Saturated aqueous ammonium chloride (5 ml), followed by water (1 ml) and ether (10 ml), was added, and the organic layer was separated. The aqueous layer was extracted with ether

(10 ml). The combined organic layers were dried over MgSO_4 and the solvents were removed in vacuo. The crude oil was purified by flash chromatography using hexane as eluent and bulb-to-bulb distillation to afford 1,1-di-*n*-butylsilacyclopentane¹³ (64%).

(b) Yield determined by ^1H NMR spectroscopy. $\text{Tp}'\text{Pt}(\text{Me})_2\text{H}$ (3.4 mg, 6.5 μmol), tri-*n*-butylsilane (32 μl , 0.125 mmol), dodecahydrotriphenylene (5.0 mg, 21 μmol) and cyclohexane- d_{12} (0.50 ml) were placed into an NMR tube, and the tube was sealed under vacuum. An initial ^1H NMR spectrum of the sample was obtained. The tube was heated at 200 $^\circ\text{C}$ for 72 h. A second NMR spectrum was obtained after this time. The yield (88%) of 1,1-di-*n*-butyl-silacyclopentane¹³ was determined from the ^1H NMR spectra by integration against the dodecahydrotriphenylene internal standard.

Dehydrogenative cyclization of di-*n*-butylphenylsilane. $\text{Tp}'\text{Pt}(\text{Me})_2\text{H}$ (6.6 mg, 13 μmol), di-*n*-butylphenylsilane (33 μl , 0.125 mmol) and cyclohexane (0.50 ml) were placed into an NMR tube, and the tube was sealed under vacuum. The tube was heated at 200 $^\circ\text{C}$ for 72 h. The tube was opened, dodecane (10 μl , 44 μmol) was added as internal standard, and an aliquot was removed and analyzed by GC. The yield of 1-*n*-butyl-1-phenylsilacyclopentane¹³ was 31%. To obtain response factors for GC, the product was independently prepared as follows. Magnesium turnings (296 mg, 12.0 mmol) and THF (10 ml) were placed into a flask equipped with a reflux condenser. 1,4-dibrombutane (0.657 ml, 5.50 mmol) was added dropwise, and the mixture was stirred for 2 h at room temperature. Phenyltrichlorosilane (0.320 ml, 2.0 mmol) was added at room temperature, and the mixture was stirred for 15 h at room temperature. Saturated aqueous ammonium chloride (5 ml), followed by water (1 ml) and ether (5 ml), was added, and the organic layer was separated. The aqueous layer was extracted with ether (10 ml). The combined organic layer was dried over MgSO_4 , and the solvents were evaporated in vacuo. The crude oil was purified by flash chromatography using hexane as eluent, and bulb-to-bulb distillation to afford 1-*n*-butyl-1-phenylsilacyclopentane¹³ (70 %).

Dehydrogenative coupling of tri-*n*-propylsilane with benzene in the presence of *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{SiEt}_3$. $\text{Tp}'\text{Pt}(\text{Me})_2\text{H}$ (3.9 mg, 7.5 μmol), tri-*n*-propylsilane (26 μl , 0.125 mmol), *p*-(trifluoromethyl)triethylsilane (50.9 mg, 0.195 mmol) and benzene (0.5 ml) were placed into an NMR tube, and the tube was sealed under vacuum. The tube was heated at 200 $^\circ\text{C}$ for 24 h. The tube was opened, dodecane (10 μl , 44 μmol) was added as internal standard, and an aliquot was removed and analyzed by GC.

Reaction of 1,3- $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{SiEt}_3$ with hydrogen in the presence of the platinum catalyst. This experiment was conducted in two ways. One experiment was conducted with $\text{Tp}'\text{Pt}(\text{Me})_2\text{H}$ as catalyst and a second experiment was conducted with material from heating a combination of $\text{Tp}'\text{Pt}(\text{Me})_2\text{H}$, Et_3SiH and benzene. In the first experiment, $\text{Tp}'\text{Pt}(\text{Me})_2\text{H}$ (6.6 mg, 13 μmol), (1,3-dimethylphenyl)triethylsilane (43.5 mg, 0.197 mmol) and cyclohexane (1.0 ml) were placed into a Parr reactor, and 5 atm of hydrogen was introduced. The reactor was heated for 24 h at 200 $^\circ\text{C}$. The pressure increased to 10 atm during heating. The reactor was cooled to room temperature, and opened. Dodecane (20 μl , 88 μmol) was added as internal standard, and an aliquot was removed and analyzed by GC. No *m*-xylene was observed, and 99% of (1,3-dimethylphenyl)triethylsilane remained unreacted.

In the second experiment, A mixture of $\text{Tp}^*\text{PtMe}_2\text{H}$ (3.3 mg, 0.0063 mmol, 5 mol%), triethylsilane (20.0 μL , 0.125 mmol) and benzene (0.50 ml) was placed into an NMR tube. The tube was flame-sealed and then heated at 200 °C for 12 h. The tube was opened, and dodecane was added. An aliquot was analyzed by GC, and the yield of phenyltriethylsilane at this time was 51%. The mixture was transferred into a Parr reactor, and to the mixture was added 26.2 mg (0.119 mmol) xylyltriethylsilane and 5 atm of hydrogen. The reactor was heated at 200 °C for 24 h, and the pressure was measured to be 7 atm during heating. The reactor was cooled to room temperature, and then opened. An aliquot was analyzed by GC. The yield of phenyltriethylsilane was 59%, and 96% of m-xylyltriethylsilane remained unreacted.

- 1) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845–2847.
- 2) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg K. I. *J. Am. Chem. Soc.* **2003**, *125*, 8614–8624.
- 3) Reinartz, S.; Baik, M-H.; White, P. S.; Brookhart, M.; Templeton, J. L. *Inorg. Chem.* **2001**, *40*, 4726–4732.
- 4) Sakakura, T.; Tokunaga, Y.; Sodeyama, T.; Tanaka, M. *Chem. Lett.* **1987**, 2375–2378.
- 5) Topchiev, A. V.; Nametkin, N. S.; Gu, Chan-Li; Leonova, N. A. *Doklady Akademii Nauk SSSR* **1958**, *118*, 731–734.
- 6) van Walree, C. A.; Lauteslager, X. Y.; van Wageningen, A. M. A.; Zwikker, J. W.; Jenneskens, L. W. *J. Organomet. Chem.* **1995**, *496*, 117–125.
- 7) Seyferth, D.; Damrauer, R.; Turkel, R. M.; Todd, L. J. *J. Organomet. Chem.* **1969**, *17*, 367–378.
- 8) Nishide, K.; Miyamoto, T.; Kumar, K.; Ohsugi, S.-I.; Node, M. *Tetrahedron Lett.* **2002**, *43*, 8569–8573.
- 9) Ezbiansky, K.; Djurovich, P. I.; Laforest, M.; Sinning, D. J.; Zayers, R.; Berry, D. H. *Organometallics* **1998**, *17*, 1455–1457.
- 10) Topchiev, A. V.; Nametkin, N. S.; Gu, Chan-Li; Leonova, N. A. *Doklady Akademii Nauk SSSR* **1958**, *118* 731–4.
- 11) Benkeser, R. A.; Mozdzen, E. C.; Muench, W. C.; Roche, R. T.; Siklosi, M. P. *J. Org. Chem.* **1979**, *44*, 1370–1376.
- 12) Gilman, H.; Marrs, O. L. *J. Org. Chem.* **1965**, *30*, 325–328.
- 13) Maercker, A.; Stötzl, R. *J. Organomet. Chem.* **1984**, *273*, C57–C63.