Hydrosilane σ-Adduct Intermediates in an Adaptive Zinc-Catalyzed Cross-dehydrocoupling of Si–H and O–H Bonds

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General Experimental Section

All manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Water and oxygen were removed from benzene and pentane solvents using an IT PureSolv system. Benzene-$d_6$ and THF-$d_8$ were heated to reflux over Na/K, and vacuum-transferred. Dimethyl zinc and diethyl zinc were purchased from Sigma Aldrich and were used as received. Products of catalytic hydroboration were assigned based on comparison with authentic samples and/or literature values. $^1$H, $^{13}$C{$^1$H}, $^{15}$N{$^1$H} HMBC and $^{29}$Si{$^1$H} HMBC NMR spectra were collected on a Bruker DRX-400 spectrometer, a Bruker Avance III-600 spectrometer, or an Agilent MR 400 spectrometer. Infrared spectra were measured on a Bruker Vertex 80. $^{15}$N chemical shifts obtained via $^{15}$N-$^1$H HMBC experiments, originally referenced to liquid NH$_3$, were re-referenced to CH$_3$NO$_2$ by subtracting 381.9 ppm. Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S in the Chemical Instrumentation Facility (CIF) at Iowa State University.
Synthesis of Compounds

**Benzyllene-bis(4,4-dimethyl-2-oxazoline) (Ph,BOXMe2).** Ph,BOXMe2 was prepared following the literature procedure, and spectroscopic data matched literature values. Analytical data was not previously reported. Yield 17 g (59 mol, 70%). Anal. Calc. for: C, 71.30; H, 7.74; N, 9.78. Found: C, 70.94; H, 7.72; N, 9.64. Mp: 195-197 °C.

**PhBOXMe2ZnMe (2a).** Ph,BOXMe2 (0.100 g, 0.349 mmol) and ZnMe2 (0.170 mL, 0.349 mmol, 2 M in toluene) were allowed to react in a stirred benzene (5 mL) solution at room temperature over 12 h. Evaporation of the volatile materials afforded PhBOXMe2ZnMe as a white powder in good yield. This solid was recrystallized at −30 °C from a minimal amount of pentane to obtain colorless X-ray quality crystals. Yield 0.120 g, 0.331 mmol, 95%. 1H NMR (benzene-d6, 600 MHz, 25 °C): δ −0.09 (s, 3 H, ZnMe), 1.02 (s, 12 H, NCMe2CH2O), 3.42 (s, 4 H, NCMe2CH2O), 7.18 (br, 1 H, p-C6H5), 7.36 (m, 2 H, m-C6H5), 7.68 (m, 2 H, o-C6H5). 13C {1H} NMR (benzene-d6, 150 MHz, 25 °C): δ −14.68 (ZnMe), 28.80 (CNCMe2CH2O), 63.48 (CNCMe2CH2O), 74.00 (C6H5C), 77.82 (CNCMe2CH2O), 125.16 (C6H5), 127.32 (C6H5), 132.64 (C6H5), 137.20 (C6H5), 169.37 (CNCMe2CH2O). 15N NMR (benzene-d6, 60.8 MHz, 25 °C): δ −213. IR (KBr, cm−1): 663 (s), 699 (s), 742 (m), 755 (m), 816 (m), 933 (w), 1043 (s), 1171 (m), 1193 (s), 1252 (m), 1321 (m), 1365 (m), 1401 (m), 1437 (s), 1453 (s), 1490 (s), 1609 (s, νCN), 2839 (w), 2879 (m), 2902 (w), 2924 (m), 2968 (m), 2994 (s), 3053 (w), 3077 (w). Anal. Calc. for: C, 59.11; H, 6.61; N, 7.66. Found: C, 58.80; H, 6.65; N, 7.53. Mp: 208-210 °C. CCDC Deposition Number: 2062850.

**PhBOXMe2ZnEt (2b).** Ph,BOXMe2 (0.100 g, 0.349 mmol) and ZnEt2 (0.170 mL, 0.349 mmol) were allowed to react in benzene (5 mL) for 12 h at room temperature. The volatile materials were evaporated under reduced pressure to afford PhBOXMe2ZnEt as a white powder in good yield. This solid was recrystallized at −30 °C from a minimal amount of pentane to obtain colorless X-ray quality crystals (0.122 g, 0.321 mmol, 92%). 1H NMR (benzene-d6, 600 MHz, 25 °C): δ 0.77 (q, 2 H, 3JHH = 7.4 Hz, ZnCH2CH3) 1.03 (s, 12 H, NCMe2CH2O ), 1.64 (t, 3 H, 3JHH = 7.4 Hz, ZnCH2CH3), 3.42 (s, 4 H, NCMe2CH2O), 7.17 (d, 1 H, 3JHH = 7.1 Hz, p-C6H5), 7.37 (m, 2 H, m-C6H5), 7.69 (d, 2 H, 3JHH = 8.5 Hz, o-C6H5). 13C {1H} NMR (benzene-d6, 150 MHz, 25 °C): δ −0.44 (ZnCH2CH3), 13.12 (ZnCH2CH3), 28.88 (CNCMe2CH2O), 63.44 (CNCMe2CH2O), 73.95 (C6H5C), 77.79 (CNCMe2CH2O), 125.18 (C6H5), 127.35 (C6H5), 132.66 (C6H5), 137.22 (C6H5),
169.32 (CNCMe₂CH₂O). ¹³N NMR (benzene-d₆, 60.8 MHz, 25 °C): δ –214. IR (KBr, cm⁻¹): 661 (m), 697 (m), 760 (w), 802 (w), 851 (w), 990 (w), 1008 (m), 1051 (s), 1107 (s), 1117 (w), 1137 (w), 1180 (w), 1212 (w), 1235 (w), 1248 (w), 1278 (w), 1312 (w), 1337 (w), 1388 (m), 1413 (m), 1457 (s), 1491 (s), 1606 (s), 2872 (m), 2904 (m), 2924 (m), 2962 (s), 3030 (w), 3054 (w), 3080 (w). Anal. Calc. for: C, 60.09; H, 6.90; N, 7.38. Found: C, 59.88; H, 6.90; N, 7.17. Mp: 210-212 °C. CCDC Deposition Number: 2062849.

[PhBOXMe₂Zn(μ-OMe)]₂ (3a). Methanol (0.026 g, 0.820 mmol, 0.032 mL) was added to a solution of PhBOXMe₂ZnMe (0.100 g, 0.273 mmol) in benzene. The reaction mixture was stirred for 30 min. at room temperature. Evaporation of the volatile materials afforded [PhBOXMe₂Zn(μ-OMe)]₂ as a white powder in good yield (0.1 g, 0.259 mmol, 95%). ¹H NMR (chloroform-d, 600 MHz, 25 °C): δ 1.45 (s, 12 H, CNCMe₂CH₂O), 3.65 (s, 3 H, OMe), 3.87 (s, 4 H, CNCMe₂CH₂O), 7.09 (m, 1 H, C₆H₅), 7.31-7.20 (m, 4 H, C₆H₅). ¹³C{¹H} NMR (chloroform-d, 150 MHz, 25 °C): δ 29.02 (CNCMe₂CH₂O), 54.49 (OMe), 63.89 (CNCMe₂CH₂O), 71.33 (C₆H₅C), 78.67 (CNCMe₂CH₂O), 124.99 (p-C₆H₅), 127.20 (C₆H₅), 132.14 (C₆H₅), 137.32 (C₆H₅), 168.96 (CNCMe₂CH₂O). ¹⁵N NMR (chloroform-d, 60.8 MHz, 25 °C): δ –225. IR (KBr, cm⁻¹): 699 (m), 743 (m), 756 (m), 818 (m), 936 (w), 962 (w), 1056 (s), 1194 (s), 1251 (m), 1318 (s), 1365 (m), 1387 (m), 1407 (m), 1458 (s), 1494 (s), 1608 (s, vCN), 2802 (m), 2874 (m), 2926 (m), 2967 (m), 3027 (s), 3043 (m), 3079 (w). Anal. Calc. for: C, 56.63; H, 6.34; N, 7.34. Found: C, 56.61; H, 6.41; N, 7.22. Mp: 235 °C (dec). CCDC Deposition Number: 2062852.

[PhBOXMe₂Zn(μ-OiC₃H₇)]₂ (3b). iC₃H₇OH (0.050g, 0.820mmol, 0.062mL) was added to a solution of PhBOXMe₂ZnMe (0.100 g, 0.273 mmol) in benzene. The reaction was stirred for 30 min. at room temperature. Evaporation of the volatile materials afforded [PhBOXMe₂Zn(μ-OiC₃H₇)]₂ as a white powder in good yield (0.103 g, 0.251 mmol, 92%). This solid was recrystallized from a minimal amount of methylene chloride at –30 °C to obtain colorless X-ray quality crystals. ¹H NMR (chloroform-d, 600 MHz, 25 °C): δ 1.08 (d, 3JHH = 5.9 Hz, 2 H, ZnOCHMe₂), 1.40 (s, 12 H, CNCMe₂CH₂O), 3.78 (s, 4 H, CNCMe₂CH₂O), 4.13 (sep, 1 H, ZnOC₃H₇), 7.04 (m, 1 H, C₆H₅), 7.19-7.15 (b, 4 H, C₆H₅). ¹³C{¹H} NMR (chloroform-d, 150 MHz, 25 °C): δ 28.56 (ZnOCHMe₂), 29.64 (CNCMe₂CH₂O), 64.35 (CNCMe₂CH₂O), 78.67 (ZnOCHMe₂), 71.60 (C₆H₅C), 125.04 (C₆H₅), 127.31 (C₆H₅), 132.44 (C₆H₅), 137.75 (C₆H₅), 168.89.
(CNCMe₂CH₂O). $^{15}$N NMR (chloroform-$d$, 60.8 MHz, 25 °C): δ –225. IR (KBr, cm$^{-1}$): 501 (w), 522 (w), 577 (w), 662 (w), 699 (w), 740 (w), 759 (w), 817 (w), 935 (m), 970 (s), 1021 (m), 1057 (s), 1129 (m), 1193 (m), 1252 (m), 1318 (m), 1366 (m), 1406 (m), 1441 (m), 1461 (m), 1495 (s), 1606 (s, νCN), 2876 (w), 2925 (m), 2961 (s). Anal. Calc. for: C, 58.61; H, 6.89; N, 6.84. Found: C, 58.37; H, 6.84; N, 6.68. Mp: 295 °C (dec). CCDC Deposition Number: 2062851.

$[^{12}$BOX$^{Me2}$Zn($μ$-O-2,6-C$_6$H$_3$Me$_2$)]$_2$ (3e)$_2$. 3,5-Dimethyl phenol (0.050 g, 0.410 mmol) was added to a solution of $[^{12}$BOX$^{Me2}$ZnMe (0.100 g, 0.273 mmol) in benzene. The reaction was stirred for 30 minutes at room temperature. Evaporation of the volatile materials afforded $[^{12}$BOX$^{Me2}$Zn($μ-OC_6H_3Me_2$)]$_2$ as a white powder in good yield (0.122 g, 0.259 mmol, 95%). $^1$H NMR (chloroform-$d$, 600 MHz, 25 °C): δ 1.33 (s, 12 H, NCMe$_2$CH$_2$O), 2.26 (s, 6 H, C$_6$H$_3$Me$_2$), 3.94 (s, 4 H, NCMe$_2$CMe$_2$O), 6.37 (s, 2 H, OC$_6$H$_3$Me$_2$), 6.43 (s, 1 H, OC$_6$H$_3$Me$_2$), 7.24 (m, 1 H, p-C$_6$H$_5$), 7.38 (m, 2 H, m-C$_6$H$_5$), 7.44 (d, $^3$J$_{HH}$ = 7.6 Hz, 2 H, o-C$_6$H$_3$). $^{13}$C{$^1$H} NMR (chloroform-$d$, 150 MHz, 25 °C): δ 21.54 (OC$_6$H$_3$Me$_2$), 29.12 (NCMe$_2$CH$_2$O), 64.24 (NCCMe$_2$CH$_2$O), 72.28 (C$_6$H$_3$C), 78.85 (NCMe$_2$CH$_2$O), 116.57 (C$_6$H$_3$Me$_2$), 119.70 (OC$_6$H$_3$), 125.45 (C$_6$H$_5$), 127.51 (C$_6$H$_5$), 132.40 (C$_6$H$_5$), 137.15 (C$_6$H$_3$), 138.71 (m-C$_6$H$_3$Me$_2$), 160.60 (C$_6$H$_3$Me$_2$), 169.48 (NCMe$_2$CH$_2$O). $^{15}$N NMR (chloroform-$d$, 60.8 MHz, 25 °C): δ –227.28. IR (KBr, cm$^{-1}$): 522 (w), 602 (w), 621 (m), 662 (m), 698 (m), 740 (m), 759 (m), 817 (m), 828 (m), 939 (m), 949 (m), 1059 (s), 1167 (s), 1194 (s), 1252 (s), 1316 (s), 1369 (s), 1382 (s), 1408 (w), 1442 (w), 1459 (m), 1492 (s), 1594 (s, νCN), 2892 (m), 2919 (m), 2969 (m), 3023 (m), 3051 (m), 3080 (m), 3594 (w), 3626 (w), 3705 (w), 3731 (w). Anal. Calc. for: C, 63.63; H, 6.41; N, 5.94. Found: C, 63.48; H, 6.32; N, 5.78. Mp: 340 °C (dec).
Catalytic Dehydrocoupling Experiments

A representative procedure for the catalytic dehydrocoupling of silanes and alcohols using $^{1}$PhBOX$^{Me2}$ZnMe in benzene as solvent is given. Methanol (0.100 g, 3.15 mmol, 0.127 mL) was added to a solution of $2a$ (0.032 g, 0.09 mmol) in benzene-$d_{6}$ containing tetrakis(trimethylsilyl)silane (0.01 M) as an internal standard. Phenylsilane (0.100 g, 0.9 mmol, 0.110 mL) was added to the reaction mixture, and the homogeneous solution was mixed on a vortex stirrer at room temperature. The progress of the reaction was monitored using $^{1}$H NMR spectroscopy, specifically observing the appearance of new signals assigned to the alkoxy groups of the product and disappearance of SiH signal of the phenylsilane.

**Solvent-free conditions**: A mixture of methanol (0.100 g, 3.15 mmol, 0.127 mL) and phenylsilane (0.100 g, 0.9 mmol, 0.110 mL) was added to $2a$ (0.032 g, 0.09 mmol). The reaction mixture becomes effervescent. The progress of the homogeneous reaction was monitored by removing small aliquots for analysis by $^{1}$H NMR spectroscopy.

**Conditions for high turnovers**: Methanol (0.100 g, 3.15 mmol, 0.127 mL) and phenylsilane (0.100 g, 0.9 mmol, 0.110 mL) were added to $^{1}$PhBOX$^{Me2}$ZnMe (diluted to $9 \times 10^{-8}$ mmol; $3.8 \times 10^{-7}$ M). The homogeneous reaction mixture was allowed to stir for 5 d at room temperature.

Silane Products from Catalytic Dehydrocoupling Reactions

$\text{PhSi(OMe)}_{3}$. $^{1}$H NMR matches literature report in chloroform-$d$.\textsuperscript{[2]} $^{1}$H NMR given here in benzene-$d_{6}$. $^{1}$H NMR (benzene-$d_{6}$, 600 MHz, 25 °C): $\delta$ 3.48 (s, 9 H, OMe), 7.20 (m, 3 H, C$_{6}$H$_{5}$), 7.80 (m, 3 H, C$_{6}$H$_{5}$) $^{13}$C ($^{1}$H) NMR (benzene-$d_{6}$, 150 MHz, 25 °C): $\delta$ 50.25 (OMe). 127.89 (C$_{6}$H$_{5}$), 127.98 (C$_{6}$H$_{5}$), 130.39 (C$_{6}$H$_{5}$), 134.89 (C$_{6}$H$_{5}$).

$\text{PhSi(OiPr)}_{3}$. $^{1}$H NMR matches literature report.\textsuperscript{[3]} $^{1}$H NMR (benzene-$d_{6}$, 600 MHz, 25 °C): $\delta$ 1.23 (d, $^{3}$J$_{HH}$ = 6.2 Hz, 18 H, Me), 4.35 (m, 3 H, CH), 7.24 (m, 3 H, C$_{6}$H$_{5}$), 7.93 (m, 2 H, C$_{6}$H$_{5}$). $^{13}$C ($^{1}$H) NMR (benzene-$d_{6}$, 100 MHz): $\delta$ 134.9 (C$_{6}$H$_{5}$), 133.4 (C$_{6}$H$_{5}$), 129.9 (C$_{6}$H$_{5}$); 65.3 (OCH/Me$_{2}$), 25.4 (OCHMe$_{2}$).
PhMeSi(OMe)$_2$. $^1$H NMR matches literature report in chloroform-$d$.\[1\] $^1$H NMR (benzene-$d_6$, 600 MHz, 25 °C): δ 0.30 (s, 3 H, SiMe), 3.39 (s, 6 H, OMe), 7.22 (m, 3 H, C$_6$H$_3$), 7.72 (m, 2 H, C$_6$H$_5$). $^{13}$C ($^1$H) NMR (benzene-$d_6$, 150 MHz, 25 °C): δ –5.18 (SiHMe), 49.90 (OMe), 127.98 (C$_6$H$_3$), 129.43 (C$_6$H$_5$), 134.12 (C$_6$H$_5$), 134.41 (C$_6$H$_5$).

PhMeHSiOiPr. $^1$H NMR matches literature report.\[3\] $^1$H NMR (benzene-$d_6$, 600 MHz, 25 °C): δ 0.37 (s, 3 H, SiHMe), 1.09 (m, 6 H, OCHMe$_2$), 3.94 (m, 1 H, OCHMe$_2$), 5.28 (s, 1 H, SiH), 7.21 (m, 3 H, C$_6$H$_3$), 7.63 (m, 2 H, C$_6$H$_5$). $^{13}$C ($^1$H) NMR (benzene-$d_6$, 150 MHz, 25 °C): δ –2.23 (SiHMe), 25.07 (OCHMe$_2$), 66.56 (OCHMe$_2$), 127.91 (C$_6$H$_3$), 129.87 (C$_6$H$_5$), 133.86 (C$_6$H$_3$), 136.69 (C$_6$H$_5$).

PhMeHSiOiBu.\[5\] $^1$H NMR (benzene-$d_6$, 600 MHz, 25 °C): δ 0.39 (d, $^3$J$_{HH}$ = 3.1 Hz, 3 H, SiMe), 1.22 (s, 9 H, OCMMe$_3$), 5.41 (m, 1 H, SiH), 7.22 (m, 3 H, C$_6$H$_3$), 7.66 (m, 2 H, C$_6$H$_5$). $^{13}$C ($^1$H) NMR (benzene-$d_6$, 150 MHz, 25 °C): δ –0.47 (SiHMe), 31.21 (OCMe$_3$), 72.67 (OCMe$_3$), 128.07 (C$_6$H$_3$), 129.61 (C$_6$H$_5$), 133.71 (C$_6$H$_5$), 138.11 (C$_6$H$_5$).

PhMeHSiOC$_6$H$_3$Me$_2$.\[6\] $^1$H NMR (benzene-$d_6$, 600 MHz, 25 °C): δ 0.43 (d, $^2$J$_{HH}$ = 3.25 Hz, 3 H, SiHMe), 2.05 (s, 6 H, C$_6$H$_3$Me$_2$), 5.54 (q, $^3$J$_{HH}$ = 3.2 Hz, 1 H, SiHMe), 6.50 (s, 1 H, C$_6$H$_3$Me$_2$), 6.73 (s, 2 H, C$_6$H$_3$Me$_2$), 7.16 (m, 3 H, C$_6$H$_3$), 7.62 (m, 2 H, C$_6$H$_5$). $^{13}$C ($^1$H) NMR (benzene-$d_6$, 150 MHz, 25 °C): δ –2.23 (SiHMe), 20.91 (C$_6$H$_3$Me$_2$), 127.45 (C$_6$H$_3$Me$_2$), 127.69 (C$_6$H$_3$Me$_2$), 130.25 (C$_6$H$_5$), 133.86 (C$_6$H$_5$), 135.09 (C$_6$H$_5$), 139.11 (C$_6$H$_5$), 155.63 (ipso-C$_6$H$_3$Me$_2$).

Ph$_2$Si(OMe)$_2$. $^1$H NMR spectrum in chloroform-$d$ matches literature report.\[7\] $^1$H NMR (benzene-$d_6$, 600 MHz, 25 °C): δ 3.46 (s, 6 H, OMe), 7.20 (m, 6 H, C$_6$H$_3$), 7.81 (m, 4 H, C$_6$H$_5$). $^{13}$C ($^1$H) NMR (benzene-$d_6$, 150 MHz, 25 °C): δ 50.26 (OMe), 127.98 (C$_6$H$_3$), 130.23 (C$_6$H$_5$), 132.74 (C$_6$H$_5$), 135.03 (C$_6$H$_5$).

Ph$_2$HSiOiPr. $^1$H NMR matches literature report.\[3\] $^1$H NMR (benzene-$d_6$, 600 MHz, 25 °C): δ 1.13 (d, $^3$J$_{HH}$ = 7.1 Hz, 6 H, OCHMe$_2$), 4.07 (m, 1 H, OCHMe$_2$), 5.71 (s, 1 H, SiH), 7.18 (m, 5 H, C$_6$H$_5$),
7.71 (m, 5 H, C₆H₅). ¹³C{¹H} NMR (benzene-d₆, 150 MHz, 25 °C): δ 25.09 (OCHMe₂), 67.08 (OCHMe₂), 27.95 (C₆H₅), 130.11 (C₆H₅), 134.69 (C₆H₅), 134.89 (C₆H₅).

**Ph₂HSiOrBu.** ¹H NMR spectrum in chloroform-d matches literature report.¹⁸ ¹H NMR (benzene-d₆, 600 MHz, 25 °C): δ 1.26 (s, 9 H, OCMes), 5.82 (s, 1 H, SiH), 7.18 (m, 6 H, C₆H₅), 7.72 (m, 4 H, C₆H₅). ¹³C{¹H} NMR (benzene-d₆, 150 MHz, 25 °C): δ 31.22 (OCSMe₃), 73.23 (OCMe₃), 127.89 (C₆H₅), 129.86 (C₆H₅), 134.57 (C₆H₅), 136.21 (C₆H₅).

**Computational Details**

The ground state geometry optimization, IR frequency and saddle point calculations were performed using Truhlar’s Minnesota 06-2X meta-GGA functional,¹⁹ as implemented in NWChem.¹⁰ The Los Alamos National Laboratory double-ζ valence basis set (LANL2DZ)¹¹ was used along with effective core potentials (ECPs) for Zn and Si. Grimme’s dispersion corrections were empirically added through a long-range contribution (DFT-D3) for all calculations.¹² Hessians were performed on all optimized structures. Starting materials, intermediates, and products contain no imaginary (negative) modes. Transition-state structures (saddle points) contained exactly one negative frequency mode. All ground state structures IR frequencies were corrected by a scaling factor of 0.960.
NMR and IR spectra of 2a-b and 3a-c

Figure S1. $^1$H NMR spectrum of PhBOX$^{Me_2}$ZnMe (2a) acquired in benzene-$d_6$. 
Figure S2. $^{13}$C{$^1$H} NMR spectrum of PhBOXMe$^2$ZnMe (2a) acquired in benzene-$d_6$. 
Figure S3. $^{15}$N-$^1$H HMBC spectrum of PhBOXMe$_2$ZnMe (2a) acquired in benzene-$d_6$. Recalibration to nitromethane as an external standard gives $\delta_N = -213$. 
Figure S4. Infrared spectrum of $^{\text{Ph}}\text{BOX}^{\text{Me}_2}\text{ZnMe}$ (2a; KBr).
Figure S5. $^1$H NMR spectrum of PhBOXMe2ZnEt (2b) in acquired in benzene-$d_6$. 
Figure S6. $^{13}$C{${}^1$H} NMR spectrum of $^Ph$BOX$^Me_2ZnEt$ (2b) acquired in benzene-$d_6$. 
Figure S7. $^{15}$N-$^1$H HMBC spectrum of $^{c}$PhBOX$^{Me_2}$ZnEt (2b) acquired in benzene-$d_6$. Recalibration to nitromethane as an external standard gives $\delta_N = -214$. 
Figure S8. Infrared spectrum of PhBOXMe2ZnEt (2b, KBr).
Figure S9. $^1$H NMR spectrum of $^{\text{Ph}}\text{BOX}^{\text{Me}_2}\text{ZnOMe}$ (3a) acquired in chloroform-$d$. 
Figure S10. $^{13}$C{$^1$H} NMR spectrum of PhBOXMe$_2$ZnOMe (3a) acquired in chloroform-$d$. 
Figure S11. Infrared spectrum of $^{\text{Ph}}$BOX$^{\text{Me}_2}$ZnOMe (3a, KBr).
Figure S12. $^1$H NMR spectrum of $^{3b}$PhBOXMe$_2$ZnOiPr (3b) acquired in chloroform-$d$. 
Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $^{\text{Ph}}\text{BOX}^{\text{Me}_2}\text{ZnOiPr}$ (3b) acquired in chloroform-$d$. 
Figure S14. Infrared spectrum of $^{3b}_{\text{Ph}}$BOX$^{\text{Me}_2}$ZnOiPr (3b, KBr).
Figure S15. $^1$H NMR spectrum of $^{Ph}$BOXMe$_2$ZnOC$_6$H$_3$Me$_2$ (3c) acquired in chloroform-$d$. 
Figure S16. $^{13}$C{${}^1$H} NMR spectrum of $^{\text{Ph}}$BOX$^{\text{Me}_2}$ZnOC$_6$H$_3$Me$_2$ (3c) acquired in chloroform-$d$. 
Figure S17. Infrared spectrum of $^{\text{PhBOX}}^\text{Me}_2\text{ZnOC}_6\text{H}_3\text{Me}_2$ (3c, KBr).
**Figure S18.** $^1$H NMR spectrum of PhSi(OMe)$_3$ acquired in benzene-$d_6$ obtained from PhBOX$^{Me2}$ZnMe-catalyzed dehydrocoupling of phenyl silane and methanol.
Figure S19. $^{13}$C{$^1$H} NMR spectrum of PhSi(OMe)$_3$ acquired in benzene-$d_6$, obtained from PhBOX$_{Me}ZnMe$-catalyzed dehydrocoupling of phenyl silane and methanol.
Figure S20. $^1$H NMR spectrum of PhSi(OiPr)$_3$ acquired in benzene-$d_6$, obtained from PhBOX$^\text{Me}_2$ZnMe-catalyzed dehydrocoupling of phenyl silane and isopropanol.
Figure S21. $^{13}$C$\{^1\text{H}\}$ NMR spectrum of PhSi(OiPr)$_3$ acquired in benzene-$d_6$, obtained from PhBOXMe$_2$ZnMe-catalyzed dehydrocoupling of phenyl silane and isopropanol.
Figure S22. $^1$H NMR spectrum of PhMeSi(OMe)$_2$ acquired in benzene-$d_6$, obtained from PhBOX$^{Me2}$ZnMe-catalyzed dehydrocoupling of phenyl methyl silane and methanol.
Figure S23. $^{13}$C{H} NMR spectrum of PhMeSi(OMe)$_2$ acquired in benzene-$d_6$, obtained from PhBOXMe$_2$ZnMe-catalyzed dehydrocoupling of phenyl methyl silane and methanol.
Figure S24. $^1$H NMR spectrum of PhMeHSiOiPr acquired in benzene-$d_6$, obtained from \textbf{PhBOX}^{Me_2}ZnMe-catalyzed dehydrocoupling of phenyl methyl silane and isopropanol.
Figure S25. $^{13}$C\{^1H\} NMR spectrum of PhMeHSiOiPr acquired in benzene-$d_6$, obtained from PhBOXMe$_2$ZnMe-catalyzed dehydrocoupling of phenyl methyl silane and isopropanol.
Figure S26. $^1$H NMR spectrum of PhMeHSiOtBu acquired in benzene-$d_6$, obtained from PhBOXMe$_2$ZnMe-catalyzed dehydrocoupling of phenyl methyl silane and tert-butanol.
Figure S27. $^{13}\text{C}^{'\text{H}}$ NMR spectrum of PhMeHSiOrBu acquired in benzene-$d_6$, obtained from PhBOXMe2ZnMe-catalyzed dehydrocoupling of phenyl methyl silane and tert-butanol.
Figure S28. $^1$H NMR spectrum of PhMeHSiOC$_6$H$_3$Me$_2$ acquired in benzene-$d_6$, obtained from PhBOX$_{Me}^2$ZnMe-catalyzed dehydrocoupling of phenyl methyl silane and 2,5-dimethylphenol.
Figure S29. $^{13}$C{1H} NMR spectrum of PhMeHSiOC₆H₃Me₂ acquired in benzene-$d_6$, obtained from PhBOXMe²ZnMe-catalyzed dehydrocoupling of phenyl methyl silane and 2,5-dimethylphenol.
Figure S30. $^1$H NMR spectrum of Ph$_2$Si(OMe)$_2$ acquired in benzene-$d_6$, obtained from PhBOX$^{Me2}$ZnMe-catalyzed dehydrocoupling of diphenyl silane and methanol.
Figure S31. $^{13}$C{${}^{1}$H} NMR spectrum of Ph$_2$Si(OMe)$_2$ acquired in benzene-$d_6$, obtained from PhBOXM$_2$ZnMe-catalyzed dehydrocoupling of diphenylsilane and methanol.
Figure S32. $^1$H NMR spectrum of Ph$_2$HSiOiPr acquired in benzene-$d_6$, obtained from PhBOXMe$_2$ZnMe-catalyzed dehydrocoupling of diphenylsilane and isopropanol.
Figure S33. $^{13}$C$\{{}^1\text{H}\}$ NMR spectrum of Ph$_2$HSiOiPr acquired in benzene-$d_6$, obtained from PhBOXMe$_2$ZnMe-catalyzed dehydrocoupling of diphenylsilane and isopropanol.
Figure S34. $^1$H NMR spectrum of Ph$_2$HSiOtBu acquired in benzene-$d_6$, obtained from Ph$_2$BOXMe$_2$ZnMe-catalyzed dehydrocoupling of diphenylsilane and tert-butanol.
Figure S35. $^{13}$C$^1$H NMR spectrum of Ph$_2$HSiOtBu acquired in benzene-$d_6$, obtained from PhBOX$^{Me_2}$ZnMe-catalyzed dehydrocoupling of diphenyl silane and tert-butanol.
Procedure for Kinetic Experiments

General. Reactions were monitored by $^1$HNMR spectroscopy using Bruker Avance-III 600 NMR spectrometer. The temperature of the NMR probe was preset to 333.2 K before each experiment and was calibrated using a thermocouple inserted through a septum into an NMR tube containing benzene. The concentration of $^{Ph}$BOX$^{Me_2}$ZnMe pre-catalyst was determined by integration vs. a standard of accurately known concentration of tetrakis(trimethylsilyl)silane Si(SiMe$_3$)$_4$ dissolved in benzene-$d_6$ prior to the addition of substrate. During catalytic conversions, single-scan $^1$HNMR spectra were acquired at preset intervals (1 min or 3 min). Peak areas of signals assigned to reactants, products, and the Si(SiMe$_3$)$_4$ standard was used as the basis to calculate concentrations. Concentrations of PhMeSiH$_2$ or ArylOH vs time were fit via non-linear least squares regression analysis to appropriate second-order, first-order (exponential), or zero-order equations.

Representative kinetic experiment for the catalytic dehydrocoupling of PhMeSiH$_2$ and 3,5-dimethylphenol using $^{Ph}$BOX$^{Me_2}$ZnMe. The samples were prepared by adding a measured volume (0.5 mL) of a stock benzene-$d_6$ solution of Si(SiMe$_3$)$_4$ (10.0 mM) to pre-weighed $^{Ph}$BOX$^{Me_2}$ZnMe, giving solutions of pre-catalyst ranging from 0.61 mM to 25.1 mM. The NMR spectrometer probe was preset and calibrated to 60.1 °C. The pre-catalyst solution was placed in a septa-capped NMR tube and inserted into the NMR spectrometer to determine the concentration of the precatalyst. The NMR tube was ejected from the spectrometer. A substrate mixture (0.1 mL) containing 0.09 mL of PhMeSiH$_2$ and 0.1 g of 3,5-dimethylphenol in 1 mL of the stock benzene-$d_6$ solution of Si(SiMe$_3$)$_4$ was added to the NMR tube through the septa using microliter syringe. The hole in the septa was then covered with silicon grease to provide an additional seal. The sample was re-inserted into the pre-heated NMR spectrometer probe to commence the kinetics experiment. The concentration of PhMeSiH$_2$ and 3,5-dimethylphenol were determined by comparison of weighted integrals of appropriate resonances to the known concentration of the internal standard Si(SiMe$_3$)$_4$.

Moderate to high concentration of 3,5-dimethylphenol (>1.5 equiv. vs. PhMeSiH$_2$). Here we describe the procedure for kinetic measurements giving initial rates of 3,5-dimethylphenol product formation (d[P]/dt) vs [ArylOH]. Saturation behavior was tested by measuring these initial rates with increasing concentrations of 3,5-dimethylphenol. The samples were prepared by adding a measured volume (0.6 mL) of a stock solution of Si(SiMe$_3$)$_4$ in benzene-$d_6$ to $^{Ph}$BOX$^{Me_2}$ZnMe to
generate a 0.011 M pre-catalyst solution. The sample was transferred to an NMR tube, capped with a septum, and 3,5-dimethylphenol was added (in quantities ranging from 0.013 g to 0.183 g) by injecting through the rubber septum. The NMR tube was placed in a pre-heated NMR probe at 60 °C, and a $^1$H NMR spectrum was acquired to determine a precise initial concentration of 3,5-dimethylphenol. The sample was removed from the probe, PhMeSiH$_2$ (0.112 ± 0.005 M) was added through the septum using a microliter syringe into NMR tube, the tube was quickly returned to the probe, and single scan spectra were acquired automatically at preset time intervals. The concentration of products at each time point was determined by integration of appropriate resonances relative and the internal standard. Linear least squares regression analysis of PhMeHSiOC$_6$H$_3$Me$_2$ concentration vs time provided rates $d[P]/dt$ for each initial 3,5-dimethylphenol concentration. Then, the plot of $d[P]/dt$ vs $[C_6H_3Me_2OH]_{ini}$ (Figure 5) revealed saturation, then decrease in rate as $[C_6H_3Me_2OH]_{ini}$ increased.

**Moderate to high concentration of PhMeSiH$_2$.** A related method, first adding excess PhMeSiH$_2$ to the solution of PhBOX$^{Me^2-ZnMe}$ containing Si(SiMe$_3$)$_4$ as an internal standard, measuring its initial concentration, then adding 3,5-dimethylphenol, and acquiring spectra at preset time intervals provided initial rates for saturation experiments in PhMeSiH$_2$. Linear least squares regression analysis of PhMeHSiOC$_6$H$_3$Me$_2$ concentration vs time provided rates $d[P]/dt$ for each initial PhMeSiH$_2$ concentration. Then, the plot of $d[P]/dt$ vs $[PhMeSiH_2]_{ini}$ (Figure 7) revealed saturation in rate as $[PhMeSiH_2]_{ini}$ increased.
**Chart S1.** Concentration ranges for Kinetic Regimes 1 and 2 and their corresponding experimental rate laws. $k_1^{obs}$ rate constants referring to Kinetic Regime 1 and $k_2^{obs}$ rate constants referring to Kinetic Regime 2, with primed (') experimental rate constants obtained from the slope of $k_{obs}$ vs. $[^{13}C_6H_4]BOXMe^2ZnMe$.

### A. Reaction Mechanism

\[
\text{PhMeSiH}_2 + \text{ArylOH} \xrightarrow{\text{H}_2} \text{PhMeSi–OAr}_2
\]

### B. Rate laws and reactant concentration ratios

#### Kinetic Regime 1:
- [ArylOH]:[PhMeSiH$_2$] $> 1.5:1$
- Rate law: \[ \text{rate} \sim k^{1\text{INHIB}}_{\text{obs}}[^{13}C_6H_4]^{1}\text{ZnMe}[^{13}C_6H_4]^{1}\text{SiMe}_2 \]
- Experimental rate laws:
  - $k^{1\text{A}}_{\text{obs}}$ = \( \frac{k^{1A}k^{1B}}{k^{1A}[\text{ArylOH}] + k^{-1A} + k^{1B}[\text{PhMeSiH}_2] + K>[\text{ArylOH}]^2} \)
  - $k^{1\text{SAT}}_{\text{obs}}$ = \( k^{1B} \)
  - $k^{1\text{INHIB}}_{\text{obs}}$ = \( \frac{k^{1A}k^{1B}}{K>[\text{ArylOH}]^2} \)

#### Kinetic Regime 2:
- [ArylOH]:[PhMeSiH$_2$] $< 1.4:1$
- Rate law: \[ \text{rate} \sim k^{2\text{SAT}}_{\text{obs}}[^{13}C_6H_4]^{1}\text{ZnMe}[^{13}C_6H_4]^{1}\text{SiMe}_2 \]
- Experimental rate laws:
  - $k^{2\text{A}}_{\text{obs}}$ = \( \frac{k^{2A}k^{2B}}{k^{2A}[\text{PhMeSiH}_2] + k^{-2A} + k^{2B}} \)
  - $k^{2\text{SAT}}_{\text{obs}}$ = \( k^{2B} \)

### C. Relationship between experimental and derived rate constants

#### Kinetic Regime 1:
- \( k^{1\text{A}}_{\text{obs}} \gg k^{1\text{INHIB}}_{\text{obs}} \)
- \( k^{1\text{A}}_{\text{obs}} \gg k^{1\text{B}}[^{13}C_6H_4]^{1}\text{ZnMe}[^{13}C_6H_4]^{1}\text{SiMe}_2 + K>[\text{ArylOH}]^2 \)
- \( k^{1\text{A}}_{\text{obs}} \gg k^{-1A} + k^{1B}[\text{PhMeSiH}_2] + K>[\text{ArylOH}]^2 \)
- \( k^{1\text{INHIB}}_{\text{obs}} \ll K>[\text{ArylOH}]^2 \)

#### Kinetic Regime 2:
- \( k^{2\text{A}}_{\text{obs}} \ll (k^{-2A} + k^{2B})/k^{2A} \)
- \( k^{2\text{SAT}}_{\text{obs}} \ll (k^{-2A} + k^{2B})/k^{2B} \)
- \( [\text{PhMeSiH}_2] \ll (k^{-2A} + k^{2B})/k^{2A} \)
Figure S36. Representative plot of [PhMeSiH$_2$] vs time, showing second-order behavior. 

\[ \text{[PhBOX$^{Me^2}$ZnMe]} = 0.00061 \text{ M, [PhMeSiH$_2$]}_{\text{ini}} = 0.1098 \text{ M, [ArylOH]}_{\text{ini}} = 0.171 \text{ M, at } 60.1 \degree \text{C in benzene-$d_6$, monitored by } ^1\text{H NMR spectroscopy.} \]
Figure S37. Plot of [PhMeSiH₂] vs time, showing second-order behavior. $[\text{PhBOX}^{\text{Me}_2}\text{ZnMe}] = 0.00061 \text{ M}$, $[\text{PhMeSiH}_2]_{\text{ini}} = 0.1098 \text{ M}$, $[\text{ArylOH}]_{\text{ini}} = 0.171 \text{ M}$, at 60.1 °C in benzene-$d_6$, monitored by $^1\text{H}$ NMR spectroscopy.
Figure S38. Plot of the concentration of the product, PhMeHSiOAr, vs time, used to determine slopes of $d[P]/dt$ for initial rates. Data from this plot correspond to the rates plotted vs [ArylOH] in Figure 5 of the main text, describing saturation behavior of ArylOH in Regime 1.
Figure S39. Plot of [PhMeSiH₂] vs time for PhBOXMe₂ZnMe-catalyzed dehydrocoupling reaction with 3,5-dimethylphenol. [PhBOXMe₂ZnMe] = 0.0011 M, [ArylOH]₀ = 0.096 M. The first-order rate constant $k²_{obs}$ is $6.37 \times 10^{-5}$ s⁻¹, determined from non-linear least squares regression analysis.
Figure S40. Plot of [PhMeSiH₂] vs time for PhBOXMe₂ZnMe-catalyzed dehydrocoupling reaction with 3,5-dimethylphenol. [PhBOXMe₂ZnMe] = 0.0020 M, [ArylOH]₀ = 0.132 M. The first-order rate constant $k^{2}_{\text{obs}}$ is $8.74 \times 10^{-5} \text{ s}^{-1}$, determined from non-linear least squares regression analysis.
Figure S41. Plot of [PhMeSiH₂] vs time for PhBOXMe₂ZnMe-catalyzed dehydrocoupling reaction with 3,5-dimethylphenol. [PhBOXMe₂ZnMe] = 0.00273 M, [ArylOH]_{ini} = 0.127 M. The first-order rate constant $k_{2obs}$ is $9.06 \times 10^{-5}$ s$^{-1}$, determined from non-linear least squares regression analysis.
Figure S42. Plot of [PhMeSiH₂] vs time for PhBOXMe₂ZnMe-catalyzed dehydrocoupling reaction with 3,5-dimethylphenol. [PhBOXMe₂ZnMe] = 0.0088 M, [ArylOH]_{ini} = 0.137 M. The first-order rate constant $k_{obs}^2$ is $1.59 \times 10^{-4}$ s$^{-1}$, determined from non-linear least squares regression analysis.
Figure S43. Plot of [PhMeSiH₂] vs time for PhBOXMe²ZnMe-catalyzed dehydrocoupling reaction with 3,5-dimethylphenol. [PhBOXMe²ZnMe] = 0.019 M, [ArylOH]ᵢᵣᵣ = 0.128 M. The first-order rate constant $k_{\text{obs}}$ is $2.46 \times 10^{-4}$ s⁻¹, determined from non-linear least squares regression analysis.
Figure S44. Plot of $[\text{PhBOX}^{\text{Me2}}\text{ZnMe}]$ vs $k^2_{\text{obs}}$, showing first-order dependence on catalyst concentration (in Kinetic Regime 2). From the slope, the observed second-order rate constant $k^2_{\text{obs}}$ equals $9.8 \pm 0.4 \times 10^{-3} \text{M}^{-1}\text{s}^{-1}$. 

$k^2_{\text{obs}} = 0.0098 \pm 0.0004 \text{M}^{-1}\text{s}^{-1}$
Figure S45. Plot of [ArylOH] vs. time under conditions with excess PhMeSiH₂ (0.85 M, 8.8 equiv. with respect to ArylOH), at a concentration range in between first-order and zero-order dependence for [PhMeSiH₂] (neither linear regression analysis nor non-linear regression analysis to an exponential decay gives a good fit).
Figure S46. Plot of [ArylOH] vs. time under conditions with excess PhMeSiH$_2$ (1.26 M, 20 equiv. with respect to ArylOH), showing zero-order dependence on both [ArylOH] and [PhMeSiH$_2$]. $k^2_{obs} = -$slope / [PhBOX$^{Me_2}$ZnMe]; [PhBOX$^{Me_2}$ZnMe] = 0.011 M.
Figure S47. Plot of [ArylOH] vs. time under conditions with excess PhMeSiH₂ (1.88 M, 27 equiv. with respect to ArylOH), showing zero-order dependence on both [ArylOH] and [PhMeSiH₂].

\[ k^{\text{SAT}_{\text{obs}}^2} = \frac{-\text{slope}}{[\text{PhBOX}^\text{MeZnMe}]}; \quad [\text{PhBOX}^\text{MeZnMe}] = 0.011 \text{ M} \]
**Figure S48.** Representative plots of product concentration [PhMeSi–OAr] vs time. Variation of [PhMeSiH$_2$]$_{ini}$ leads to saturation in rate $d[\text{PhMeSi–OAr}]/dt$, shown in Figure 7 of the main text.

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