Reversing the Role of the Metal-oxygen π-bond. Chemoselective Catalytic Reductions with a Rhenium(V)-Dioxo Complex

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Supporting Information

General Information. Unless otherwise noted all commercial materials were used without purification. Reactions were carried out open to atmospehere in Fisher Scientific disposable borosilicate culture tubes. ACS grade (0.05 % H_2O) benzene and tetrahydrofuran (THF) were obtained from EM Science. Silanes were purchased from Aldrich Chemical Company. Iododioxo(bistriphenylphosphine)rhenium(V) (**1**) was prepared in two steps from potassium rhennate as described below. Alternatively it could be purchased from Aldrich Chemical Company at lower purity. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F_{254} TLC plates. Chromatography was carried out on ICN SiliTech 32-63 D 60 Å silica gel. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AMX-300 and AMX-400 spectrometers and referenced to $CDCl_3$ unless otherwise noted. IR spectra were recorded on NaCl plates with an ATI Mattson Gemini FTIR spectrometer. Mass spectral and CHN data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

Preparation of Iododioxo(bistriphenylphosphine)rhenium(V) (1). To a white suspension of potassium perhennate (3.54g, 12.3 mmol) in absolute ethanol (105 mL)

was added triphenylphosphine (17.70g, 67.5 mmol) followed by 47% hydriodic acid (18 mL). The reaction mixture was then brought to reflux in an oil bath and allowed to stir for 1h. After this time the brownish-green slurry was removed from the heat and cooled to room temperature. The mixture was then filtered over a Buchner funnel, washed copiously with 95% ethanol, and air dried on the funnel to oxodiiodo(ethoxo)bis(triphenylphosphine)rhenium(V) (~11.5 g) as an olive green powder.

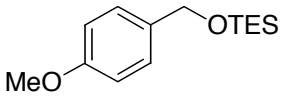
This solid was then suspeneded in acetone (575 mL) and water (23 mL) was added. The reaction mixture was then stirred and at which point a noticeable color change occurs within 5 min. After 1h the purple slurry was filtered over a Buchner funnel, washed with acetone (2 x 250 mL) and then ethanol (250 mL). The solid was dried *in vacuo* to provide **1** (6.4 g, 60% two steps) as a purple powder.

General Procedure for Hydrosilyation of Aldehydes with 1 in Benzene. To a small test tube equipped with a magnetic stir bar and charged with a solution of aldehdyde (100 mg or 100 μL, 1 eq) in benzene (1M) was added silane (1.2 eq) followed by catalyst **1** (2 mol%). The reaction mixture was then placed in a pre-heated oil bath (60 °C) and monitored periodically by TLC. Upon completion the reaction mixture was diluted with hexanes (~.4 mL), loaded directly on to a silica gel column and chromatographed with the appropriate mixture of hexanes and diethyl ether to give the silyl ether.

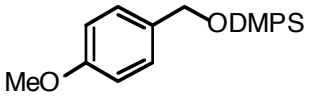
General Procedure for Hydrosilyation of Aldehydes with 1 in THF. To a small test tube equipped with a magnetic stir bar and charged with a solution of aldehdyde (100 mg

or 100 μL, 1 eq) in THF (1M) was added silane (1.2 eq) followed by **1** (2 mol%). The reaction mixture was then placed in a pre-heated oil bath (60 ºC) and monitored periodically by TLC. Upon completion the reaction mixture was concentrated *in vacuo*, diluted with a small amount hexanes and diethyl ether (~.5 mL), loaded on to a silica gel column, and chromatographed with the appropriate mixture of hexanes and diethyl ether to give the silyl ether.

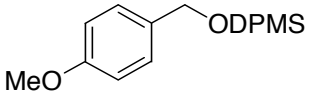
General Procedure for Hydrosilyation of Ketones with 1 in Benzene. To a small test tube equipped with a magnetic stir bar and charged with a solution of ketone (100 mg or 100 μL, 1 eq) in benzene (1M) was added silane (1.2 eq) followed by **1** (2 mol%). The reaction mixture was then placed in a pre-heated oil bath (80 ºC) and monitored periodically by TLC. Upon completion the reaction mixture was diluted with hexanes (~.4 mL), loaded directly on to a silica gel column, and chromatographed with the appropriate mixture of hexanes and diethyl ether to give the silyl ether.



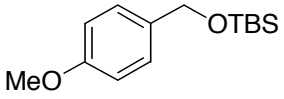
Triethyl-(4-methoxy-benzyloxy)-silane (3a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 2H), 6.87 (m, 2H), 4.67 (s, 2H), 3.81 (s, 3H), 0.97 (t, *J* = 7.8, 3H), 0.64 (q, *J* = 7.9, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 133.5, 127.8, 113.7, 64.5, 55.3, 6.8, 4.5; IR (neat) 2954, 1613, 1513, 1246 ν max cm^{-1}; HRMS (EI) calc. for $[C_{14}H_{24}O_2Si]^+$ 252.1546, found 252.1549; CHN calc.: C, 66.61; H, 9.58, found: C, 66.28; H, 9.61.



(4-Methoxy-benzyloxy)-dimethyl-phenyl-silane (3b). ^{1}H NMR (300 MHz, $CDCl_3$) 7.27-7.24 (m, 2H), 7.41-7.33 (m, 3H), 7.21 (m, 2H), 6.85 (m, 2H), 4.62 (s, 2H), 3.80 (s, 3H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 159.0, 136.0, 134.5, 132.8, 129.9, 128.2, 128.0, 113.7, 65.1, 55.3, -2.8; IR (neat) 3068, 1613, 1513, 1247 max cm^{-1}; HRMS (EI) calc. for $[C_{21}H_{22}O_2Si]^+$ 334.1389, found 334.1384; CHN calc.: C, 75.41; H, 6.63, found: C, 75.26; H, 6.88.

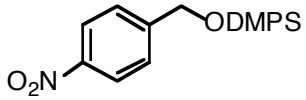


(4-Methoxy-benzyloxy)-methyl-diphenyl-silane (3c). ^{1}H NMR (300 MHz, $CDCl_3$) 7.64-7.61 (m, 4H), 7.46-7.35 (m, 6H), 7.24 (m, 2H), 6.86 (m, 2H), 4.74 (s, 2H), 3.81 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 158.9, 136.0, 127.8, 113.7, 64.5, 55.3, 6.8, 4.5; IR (neat) 2954, 1613, 1513, 1246 max cm^{-1}; HRMS (EI) calc. for $[C_{14}H_{24}O_2Si]^+$ 252.1546, found 252.1549; CHN calc.: C, 66.61; H, 9.58, found: C, 66.28; H, 9.61.

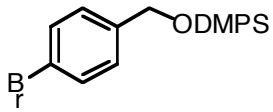


***tert*-Butyl-(4-methoxy-benzyloxy)-dimethyl-silane (3d).** ^{1}H NMR (300 MHz, $CDCl_3$) 7.25 (m, 2H), 6.88 (m, 2H), 4.68 (s, 2H), 3.81 (s, 3H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 158.7, 133.6, 127.5, 113.6, 64.7, 55.3, 26.0, 18.4, -5.2; IR

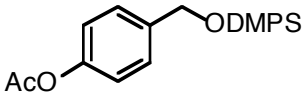
(neat) 1513, 1464, 1248, 1087, 837 □ max cm^{-1}; HRMS (EI) calcd for $[C_{14}H_{24}O_2Si]^+$ 252.1553, Found 252.1546; CHN calc.: C, 66.61; H 9.58, found C 66.52; H 9.89



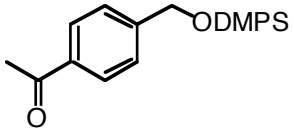
Dimethyl-(4-nitro-benzyloxy)-phenyl-silane (5a). ^1H NMR (300 MHz, $CDCl_3$) □8.18 (m, 2H), 7.60-7.57 (m, 2H), 7.47-7.37 (m, 5H), 7.05-7.01 (m, 2H), 4.77 (s, 2H), 0.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) □148.8, 147.4, 137.2, 133.8, 130.4, 128.4, 127.0, 123.9, 64.2, -1.5; IR (neat) 2958, 1521, 1346 □ max cm^{-1}; HRMS (EI) calc. for $[C_{15}H_{17}NO_3Si]^+$ 300.1182, found 300.1185; CHN calc.: C, 62.69; H, 5.96; N, 4.87, found: C, 62.58; H, 6.24; N, 5.01.



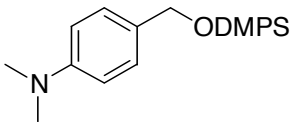
(4-Bromo-benzyloxy)-dimethyl-phenyl-silane (5b). ^1H NMR (300 MHz, $CDCl_3$) □7.61-7.57 (m, 2H), 7.48-7.38 (m, 5H), 7.17 (m, 2H), 4.64 (s, 2H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) □139.8, 137.3, 133.6, 131.38, 129.9, 128.3, 128.0, 120.9, 64.3, -1.7; IR (neat) 2957, 1591, 1486, 1252 □ max cm^{-1}; HRMS (EI) calc. for $[C_{15}H_{17}BrOSi]^+$ 320.0235, found 320.0236; CHN calc.: C, 56.08; H, 5.33, found: C, 56.25; H, 5.50.



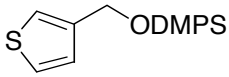
Acetic acid 4-(dimethyl-phenyl-silanyloxymethyl)-phenyl ester (5c). ^{1}H NMR (300 MHz, $CDCl_3$) 7.62-7.58 (m, 2H), 7.45-7.35 (m, 3H), 7.38-7.22 (m, 2H), 7.05-7.01 (m, 2H), 4.67 (s, 2H), 2.30 (s, 3H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 217.1, 169.9, 150.1, 138.7, 137.8, 133.9, 130.1, 128.4, 128.3, 121.7, 64.9, -1.3; IR (neat) 2958, 1765, 1213 max cm^{-1}; HRMS (EI) calc. for $[C_{17}H_{20}O_3Si]^+$ 300.1182, found 300.1185; CHN calc.: C, 67.96; H, 6.71, found: C, 67.94; H, 6.92.



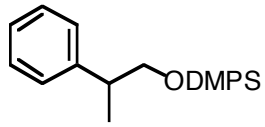
1-[4-(Dimethyl-phenyl-silanyloxymethyl)-phenyl]-ethanone (5d). ^{1}H NMR (400 MHz, $CDCl_3$) 7.93 (m, 2H), 7.57 (m, 2H), 7.42 (m, 5H), 4.76 (s, 2H), 2.59 (s, 3H), 0.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.9, 146.4, 137.2, 136.1, 133.5, 129.9, 128.5, 128.0, 126.3, 64.4, 26.7, -1.7; IR (neat) 3585, 1679, 1607, 1262, 1116, 1086 max cm^{-1}; HRMS (EI) calc. for $[C_{17}H_{20}O_2Si]^+$ 285.1307, found: 285.1311.



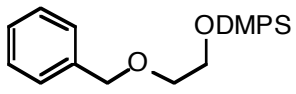
[4-(Dimethyl-phenyl-silanyloxymethyl)-phenyl]-dimethyl-amine (5e). ^{1}H NMR (300 MHz, C_6D_6) 7.60 (m, 2H), 7.15 (m, 5H), 6.57 (m, 2H), 4.65 (s, 2H), 2.47 (s, 6H), 0.32 (s, 6H); ^{13}C (300 MHz, C_6D_6), 161.3, 138.5, 133.9, 129.7, 129.3, 128.4, 128.3, 128.1, 127.7, 122.8, 65.6, 40.5, -1.1; IR (neat) 2957, 1615, 1524 max cm^{-1}.



Dimethyl-phenyl-(thiophen-3-ylmethoxy)-silane (5f). Starting material was chromatographed prior to use. ^{1}H NMR (300 MHz, $CDCl_3$) 7.63-7.58 (m, 2H), 7.45-7.36 (m, 3H), 7.28-7.25 (m, 1H), 7.14-7.12 (m, 1H), 7.00 (m, 1H), 4.69 (s, 2H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 142.1, 137.6, 133.6, 129.8, 128.0, 126.8, 125.9, 121.5, 61.05, -1.6; IR (neat) 2957, 1427, 1252 max cm^{-1}; HRMS (EI) calc. for $[C_{15}H_{16}OSSi]^+$ 248.0691, found 248.0696; CHN calc.: C, 62.85; H, 6.49, found: C, 62.53; H, 6.64.

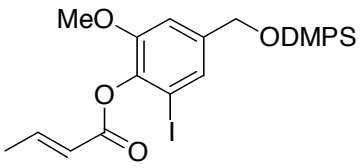


Dimethyl-phenyl-(2-phenyl-propoxy)-silane (5g). ^{1}H NMR (300 MHz, $CDCl_3$) 7.51-7.58-7.48 (m, 2H), 7.41-7.16 (m, 8H), 3.69 (dd, *J* = 9.9, 6.1, 2H), 3.58 (dd, *J* = 9.9, 7.6, 2H), 2.91 (app h, *J* = 7.0, 1H), 1.27 (d, *J* = 7.0, 3H), 0.30 (s, 3H), 0.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.4, 138.0, 133.5, 129.6, 128.3, 127.9, 127.6, 126.4, 69.2, 42.4, 17.6, -1.8, -1.8; IR (neat) 2960, 1428, 1252 max cm^{-1}; LRMS (EI) calc. for $[C_{17}H_{20}O_3Si\text{-}CH_3]^+$ 255, found 255 ; CHN calc.: C, 75.50; H, 8.20, found: C, 75.29; H, 8.09.



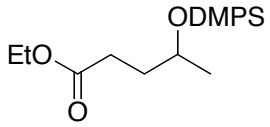
(2-Benzyloxy-ethoxy)-dimethyl-phenyl-silane (5h). ^{1}H NMR (300 MHz, $CDCl_3$) 7.60-7.57 (m, 2H), 7.39-7.26 (m, 8H), 4.53 (s, 2H), 3.78 (t, *J* = 5.2, 2H), 3.55 (t, *J* = 5.2, 2H), 0..39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.4, 137.8, 133.6, 129.6, 129.9,

128.4, 127.9, 127.7, 127.6, 73.2, 71.4, 62.6, -1.7; IR (neat) 2864, 1428, 1252 □ max cm^{-1}; HRMS (EI) calc. for $[C_{17}H_{22}O_2Si]^+$ 286.1389, found 286.1381; CHN calc.: C, 71.28; H, 7.74, found: C, 71.10; H, 7.92.

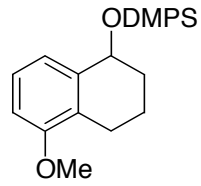


But-2-enoic acid 4-(dimethyl-phenyl-silanyloxymethyl)-2-iodo-6-methoxyphenyl ester (5i). ^{1}H NMR (300 MHz, $CDCl_3$) □ 7.59 (m, 2H), 7.39 (m, 3H), 7.32-7.22 (m, 2H), 6.86 (s, 1H), 6.11 (dq, *J* = 15.5, 1.7, 1H), 4.55 (s, 2H), 3.78 (s, 3H), 1.99 (dd, *J* = 6.9, 1.7), 1H), 0.44 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 163.3, 151.6, 147.7, 141.0, 139.6, 137.2, 133.6, 129.9, 128.0, 128.0, 121.5, 110.7, 91.5, 64.0, 56.1, 18.4, -1.8; IR (neat) 2957, 1745, 1139 □ max cm^{-1}; HRMS (EI) calc. for $[C_{20}H_{23}IO_4Si]^+$ 482.0410, found 482.0417; CHN calc.: C, 49.80; H, 4.81, found: C, 49.59; H, 4.71.

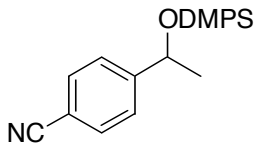
(4-*tert*-Butyl-cyclohexyloxy)-dimethyl-phenyl-silane (5j). ^{1}H NMR (300 MHz, $CDCl_3$) □ 7.57 (m, 2H), 7.37 (m, 3H), 3.50 (m, 1H), 1.87 (d, *J* = 12.9, 2H); 1.71 (m, 2H); 1.26 (m, 2H), 0.94 (m, 3H), 0.82 (s, 9H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 138.8, 133.5,129.4, 127.8, 72.3, 47.1, 36.2, 32.3, 27.6, 25.8, -0.9484; IR 1251, 1116, 1087 □ max cm^{-1}; HRMS (EI) calc. for $[C_{18}H_{30}OSi]^+$ 290.2063, found 290.2066.



4-(Dimethyl-phenyl-silanyloxy)-pentanoic acid ethyl ester (5k). ^{1}H NMR (300 MHz, C_6D_6) □ 7.54 (m, 2H), 7.18 (m, 3H), 3.90 (q, *J* 7.0, 2H), 3.73 (sextet, *J* 6.1, 1H), 2.24 (m, 2H), 1.70 (m, 2H), 0.92 (m, 6H), 0.27 (2, 6H); ^{13}C NMR (300 MHz, C_6D_6) □ 172.9, 138.6, 133.8, 133.6, 133.3, 129.7, 129.6, 128.3, 128.0, 127.7, 68.1, 60.1, 34.8, 30.7, 23.8, 14.5, 1.1, -0.7, -0.9; ; IR (neat) 2963, 1735, 1253, 1118 □ max cm^{-1}.

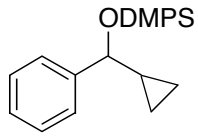


(5-Methoxy-1,2,3,4-tetrahydro-naphthalen-1-yloxy)-dimethyl-phenyl-silane (5l). ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.65 (m, 2H), 7.39 (m, 3H), 7.12 (t, *J* 7.9, 1H), 6.91 (d, *J* 7.8, 1H) 6.70 (d, *J* 8.1, 1H), 4.8 (m, 1H), 3.79 (s, 3H), 2.60 (m, 2H) 1.96 (m, 1H), 1.74 (m, 3H), 0.46 (d, *J* 3.1, 6H); ^{13}C 156.2, 141.5, 140.6, 133.2, 128.7, 127.7, 127.3, 124.2, 122.3, 108.0, 81.9, 55.5, 35.1, 22.2, 19.3, 1.0, 0.03; IR 1582.5, 1457.9, 1247.5, 1112.1, 826.1; EI HRMS calcd. for $[C_{19}H_{24}O_2Si]^+$ 312.1546, Found 312.1546; Anal. Calcd. for $C_{19}H_{24}O_2Si$: C 73.03, H 7.74; Found C 73.21, H 7.84.

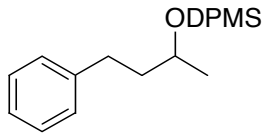


4-[1-(Dimethyl-phenyl-silanyloxy)-ethyl]-benzonitrile (5m). ^{1}H NMR (300 MHz, C_6D_6) □ 7.43 (m, 2H), 7.27 (m, 3H), 6.97 (m, 2H), 6.83 (m, 2H), 4.48 (q, 1H, *J* 6.3), 1.09

(d, 3H, *J* 6.3), 0.21 (s, 3H), 0.14 (s, 3H), ^{13}C NMR (300 MHz, C_6D_6) □ 151.2, 137.7, 133.7, 132.0, 130.1, 128.3, 128.2, 127.7, 126.0, 118.9, 111.4, 70.8, 26.8, -0.8, -1.2; ; IR (neat) 2975, 1610, 1254 □ max cm^{-1}.



(Cyclopropyl-phenyl-methoxy)-dimethyl-phenyl-silane (5n). ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.55 (d, *J* 1.5, 2 H Hz), 7.54-7.24 (m, 8H), 4.09 (d, *J* 7.3, 1H), 1.16 (m, 1H), 0.43 (m, 4H), 0.33 (s, 3 H), 0.204 (s, 3 H); ^{13}C (400 MHz, $CDCl_3$) □ 144.9, 133.7, 133.6, 129.5, 128.1, 127.7, 127.1, 126.1, 78.6, 19.9, 3.8, 2.7, -0.7, -1.2; IR (neat) 1252.2, 1116.9, 1056.5 □ max cm^{-1}; HRMS (FAB) calc. for $[C_{18}H_{22}OSi]^+$ 282.1432, found 282.1440.



Methyl-(1-methyl-3-phenyl-propoxy)-diphenyl-silane (5o). ^{1}H 7.67 (m, 4H), 7.48 (m, 7H), 7.22 (m, 4H), 4.01 (m, 1H), 2.75 (m, 1H), 2.62 (m, 1H), 1.90 (m, 1H), 1.78 (m, 1H), 1.24 (d, *J*=6.1, 3H), 0.71 (s, 3H); ^{13}C 142.4, 136.9, 136.8, 136.8, 134.5, 134.5, 129.8, 128.4, 128.4, 127.9, 125.7, 71.9, 69.0, 41.2, 32.0, 29.8, 23.7, -2.2; Anal. Calcd. for $C_{23}H_{26}OSI$: C 79.72, H 7.56; Found C 79.44, H 7.88