Supporting Information

Catalytic Hydrosilylation of Carbonyl Compounds with Cationic Oxorhenium(V) Salen

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Materials and Instruments. All manipulations were performed under air unless stated otherwise. Solvents were generally purified with a solvent purification system prior to use. Organosilanes and carbonyl compounds were obtained from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were recorded on 300 or 200 MHz spectrometers at 20 °C. Proton resonances were referenced internally to residual solvent peaks (CHCl_3 , 7.26; CHDCl_2 , 5.32).

General Procedure for Catalytic Hydrosilylation of Carbonyl Compounds. The following is a typical procedure. To a small vial or NMR tube with a magnetic stir bar was added with ReO^+ catalyst (1 mol%), ketone or aldehyde (0.7 mmol, ~ 1 M) and CD_2Cl_2 (0.5 mL) unless stated otherwise. After the catalyst was dissolved, organosilane (1.5 equiv) was added. The resulting solution was stirred under ambient temperature and monitored by ^1H NMR or TLC until the carbonyl compounds were consumed completely. For slow reactions, it was monitored for several days or until >90% conversion. The reaction mixture was then directly subject to flash chromatography on a silica gel column, eluted with 2% Et_3N in hexanes. The isolated silyl ether products of >95% purity (by NMR and/or GC-MS) were identified by comparing the ^1H NMR spectra with literature reports and confirmed by GC-MS analysis. The impurities, usually less than 3%, are disiloxanes, as confirmed by GC-MS analysis. The byproducts in hydrosilylation, ether and alkane, are identified by comparison of characteristic NMR signals with literature reports and by GC-MS analysis.

Triethyl(1-phenyl ethoxy)silane ($\text{PhCH}(\text{CH}_3)\text{OSiEt}_3$).¹ ^1H NMR (300 MHz, CDCl_3): δ 7.20-7.40 (m, 5H, Ph), 4.92 (q, 1H), 1.43 (d, J = 6.0 Hz, 3H), 0.93 (t, J = 7.8 Hz, 9H), 0.58 (q, J = 7.8 Hz, 6H). GC-MS: m/z 236.

***t*-Butyl dimethyl(1-phenyl ethoxy)silane** ($\text{PhCH}(\text{CH}_3)\text{OSi}^t\text{BuMe}_2$).² ^1H NMR (300 MHz, CDCl_3): δ 7.20-7.40 (m, 5H, Ph), 4.88 (q, J = 6.3 Hz, 1H), 1.42 (d, J = 6.3 Hz, 3H), 0.91 (s, 9H), 0.06 (s, 3H), -0.02 (s, 3H). GC-MS (EI): m/z 235 ($(\text{M}-1)^+$, 1), 221 (1), 179 (24), 105 (8), 75 (100).

Dimethyl phenyl (1-phenyl ethoxy)silane ($\text{PhCH}(\text{CH}_3)\text{OSiPhMe}_2$).³ ^1H NMR (300 MHz, CDCl_3): δ 7.56 (m, 2H), 7.20-7.40 (m, 8H, Ph), 4.92 (q, $J = 6.3$ Hz, 1H), 1.43 (d, $J = 6.3$ Hz, 3H), 0.34 (s, 3H), 0.30 (s, 3H). GC-MS (EI): m/z 256 (3), 241 (40), 178 (67), 167 (31), 137 (100), 105 (18).

Methyl diphenyl (1-phenyl ethoxy)silane ($\text{PhCH}(\text{CH}_3)\text{OSiPh}_2\text{Me}$).⁴ ^1H NMR (300 MHz, CDCl_3): δ 7.58 (m, 5H), 7.25-7.45 (m, 10H, Ph), 4.95 (q, $J = 6.3$ Hz, 1H), 1.46 (d, $J = 6.3$ Hz, 3H), 0.57 (d, 3H, $J = 9.9$ Hz). GC-MS (EI): m/z 318 (3), 303 (7), 240 (90), 199 (100), 167 (29), 135 (28), 105 (28).

Triethyl(1-methyl *n*-propoxy)silane ($\text{EtCH}(\text{Me})\text{OSiEt}_3$).⁵ ^1H NMR (300 MHz, CDCl_3): δ 3.71(m, 1H), 1.43 (m, 2H), 1.13 (d, 3H, $J = 5.7$ Hz), 0.96 (t, $J = 7.8$ Hz, 9H), 0.88 (t, $J = 7.5$ Hz, 3H), 0.59 (q, $J = 7.8$ Hz, 6H). GC-MS (EI): m/z 188 (M^+).

Diphenyl methyl(1-methyl *n*-propoxy)silane ($\text{EtCH}(\text{Me})\text{OSiPh}_2\text{Me}$).⁶ ^1H NMR (300 MHz, CD_2Cl_2): δ 7.25-7.65 (m, 10 H), 3.88 (m, 1H), 1.51 (m, 2H), 1.16 (d, 3H, $J = 6.3$ Hz), 0.89 (t, 3H), 0.66 (s, 3H). GC-MS (EI): m/z 270 (M^+).

Triethyl(1-(4-nitro-phenyl)ethoxy)silane ($4\text{-NO}_2\text{-C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{OSiEt}_3$). ^1H NMR (300 MHz, CDCl_3): δ 8.19 (d, 2H, $J = 8.7$ Hz, Ar), 7.51 (d, 2H, $J = 8.7$ Hz, Ar), 4.95 (q, 1H, $J = 6.6$ Hz), 1.44 (d, $J = 6.6$ Hz, 3H), 0.92 (t, $J = 8.1$ Hz, 9H), 0.58 (q, $J = 8.1$ Hz, 6H). ^{13}C NMR (75.438 MHz, CDCl_3): 154.4, 147.0, 126.0, 123.6, 69.9, 27.1, 6.8, 4.8. GC-MS: m/z 281 (1), 252 (100), 103 (47), 75 (24). HRMS: calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_3\text{Si}$: 281.1447, Found: 281.1448.

Triethyl((1-methyl-3-phenyl-2-propynyl)oxy)silane ($\text{PhC}\equiv\text{CCH}(\text{CH}_3)\text{OSiEt}_3$). ^1H NMR (300 MHz, CDCl_3): δ 7.34 (m, 2H, Ph), 7.24 (m, 3H), 4.70 (q, $J = 6.6$ Hz, 1H), 1.49 (d, $J = 6.6$ Hz, 3H), 0.98 (t, $J = 7.8$ Hz, 9H), 0.66 (q, $J = 7.8$ Hz, 6H). ^{13}C NMR (75.438 MHz, CDCl_3): 131.6, 128.3, 128.2, 123.2, 91.9, 83.2, 59.2, 25.6, 6.9, 4.9. GC-MS: m/z 260 (1), 245 (2), 231 (100), 203 (63), 187 (90), 159 (82), 131 (37). HRMS: calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: 260.1596, Found: 260.1599.

Triethyl(1-methyl-3-phenyl (*E*)-allyloxy)silane ($(E)\text{-PhCH=CHCH}(\text{CH}_3)\text{OSiEt}_3$).⁷ ^1H

NMR (300 MHz, CDCl₃): δ 7.35 (m, 5H, Ph), 6.53 (d, J = 15.9 Hz, 1H), 6.39 (dd, J = 15.9 Hz, 6.0 Hz, 1H), 4.49 (m, 1H), 1.34 (d, J = 6.0 Hz, 3H), 1.00 (t, J = 8.1 Hz, 9H), 0.65 (q, J = 8.1 Hz, 6H). GC-MS: m/z 262 (14), 247 (8), 233 (10), 157 (16), 131 (33), 103 (100), 75 (34).

Triethyl(1-methyl-3-phenyl *n*-propoxy)silane (PhCH₂CH₂CH(CH₃)OSiEt₃).⁸ ¹H NMR (300 MHz, CDCl₃): δ 7.15-7.35 (m, 5H, Ph), 3.85 (m, 1H), 2.65 (m, 2H), 1.75 (m, 2H), 1.19 (d, J = 6.0 Hz, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.61 (q, J = 8.0 Hz, 6H). GC-MS: m/z 263 (M-1⁺, 1), 235 (100), 159 (3), 131 (62), 115 (11), 103 (63).

Triethyl(1,2,2-trimethyl *n*-propoxy)silane ((CH₃)₃CCH(CH₃)OSiEt₃).⁹ ¹H NMR (300 MHz, CDCl₃): δ 3.46 (q, J = 6.0 Hz, 1H), 1.05 (d, J = 6.0 Hz, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.85 (s, 9H), 0.59 (q, J = 8.0 Hz, 6H). GC-MS (EI): m/z 215 ((M-1)⁺, 1), 201 (6), 187 (47), 159 (83), 103 (100), 75 (55).

Triethyl(4-^tbutyl-cyclohexyloxy)silane (^tBu-C₆H₁₀OSiEt₃).¹⁰ This product was obtained as a mixture of *trans* and *cis* isomers with *trans/cis* ratio of ca. 1:1. ¹H NMR (300 MHz, CDCl₃): mixture 3.98 (m, 1H, *cis*), 3.45 (m, 1H, *trans*), 1.90 (m, 2H), 1.74 (m, 4H), 1.1-1.5 (m, 8H), 0.90-1.05 (m, 22H), 0.85 (d, 18H), 0.60 (m, 12H). A small portion of pure *trans* isomer was isolated: δ 3.45 (m, 1H), 1.90 (m, 2H), 1.75 (m, 2H), 1.27 (m, 2H), 0.90-1.05 (m, 12H), 0.84(s, 9H), 0.59 (q, J = 7.8 Hz, 6 H). GC-MS (EI): m/z 270 (1), 241 (64), 137 (8), 103 (100), 75 (63).

Triethyl(benzyloxy)silane (PhCH₂OSiEt₃).³ ¹H NMR (300 MHz, CDCl₃): δ 7.33 (m, 5H, Ph), 4.74 (s, 2H), 0.99 (t, J = 7.8 Hz, 9H), 0.66 (q, J = 7.8 Hz, 6H). GC-MS: m/z 222.

Triethyl(4-chloro-benzyloxy)silane (4-Cl-C₆H₄CH₂OSiEt₃).¹¹ ¹H NMR (300 MHz, CDCl₃): δ 7.28 (m, 4H, Ar), 4.70 (s, 2H), 0.97 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). ¹³C NMR (75.438 MHz, CDCl₃): 139.9, 132.6, 128.3, 127.5, 64.1, 6.8, 4.5. GC-MS: m/z 258 (1), 256 (2), 227 (100), 197 (21), 169 (13), 125 (78).

Triethyl(2-methyl *n*-propoxy)silane (Me₂CHCH₂OSiEt₃).¹² ¹H NMR (300 MHz, CD₂Cl₂): δ 3.40 (d, J = 6.6 Hz, 2H), 1.78 (m, 1H), 0.98 (m, 15H), 0.61 (q, 6H). GC-MS (EI): m/z 188 (2), 159

(100), 131 (8), 103 (73), 75 (69), 59 (19).

Methyl diphenyl (2-methyl *n*-propoxy)silane ($\text{Me}_2\text{CHCH}_2\text{OSiPh}_2\text{Me}$).⁶ ^1H NMR (300 MHz, CDCl_3): δ 7.66 (m, 4H), 7.44 (m, 6H, Ph), 3.29 (d, $J = 6.9$ Hz, 2H), 1.99 (m, 1H), 1.03 (d, 6H, $J = 6.9$ Hz), 0.71 (s, 3H). ^{13}C NMR (75.438 MHz, CDCl_3): 137.8, 134.2, 129.8, 128.0, 78.2, 28.7, 19.7, -0.3. GC-MS (EI): m/z 270 (2), 255 (96), 227 (10), 199 (100), 183 (28), 137 (50), 105 (34).

Reaction of 2-Cyclohexen-1-one. To a small vial or NMR tube was added with ReO^+ catalyst **1a** or **1b** (1 mol%), 2-cyclohexen-1-one (0.7 mmol, ~ 1 M) and CD_2Cl_2 (0.5 mL). After the catalyst was dissolved, Et_3SiH or PhMe_2SiH (1.2 equiv) was added. The starting material 2-cyclohexen-1-one was consumed completely within 30 min as monitored by ^1H NMR. A number of reaction products, including cyclohexanone and 2-cyclohexen-1-ol, were identified in conjunction with GC-MS technique. The major species was believed to be *dl*, *meso* mixture of 3,3'-dicyclohexanone, as two close peaks with identical mass pattern was observed in GC-MS. ^{13}C ^1H NMR (300 MHz, CD_2Cl_2): δ 2.5-1.1(complex). GC-MS (EI): m/z 194 (26), 137 (12), 123 (12), 98 (100), 97 (83), 96 (28). No hydrosilylation product was observed.

General Procedure for Kinetic Studies. The progress of the reaction between PhCHO and PhMe_2SiH was followed by ^1H NMR. A NMR tube was charged with $[\text{ReO}(\text{salpn})(\text{H}_2\text{O})^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$ (**1b**) (~ 0.8 mM), Ph_3CH (50mM, internal standard), PhCHO (0.2 – 1.6 M) and CD_2Cl_2 . PhMe_2SiH (20 or 50 mM) was added and vigorously shaken immediately before the NMR tube was placed in the NMR probe. The increase of methylene peaks of the product $\text{PhCH}_2\text{OSiPhMe}_2$ and the disappearance of the SiH peak of PhMe_2SiH were monitored by integration against the methine peak of Ph_3CH . Under these conditions the reactions follows pseudo-first-order kinetics and the data were analyzed accordingly by nonlinear least-squares fitting. Figure-S1 shows a plot of normalized (by catalyst concentration) rate constants against the concentration of PhCHO .

Fig-S1: Rate constant (normalized by catalyst concentration) vs $[\text{PhCHO}]$.

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