Supplementary Material (ESI) for Chemical Communications

Supplementary Information For:

Silver-Catalyzed Hydrosilylation of Aldehydes

Bradley M. Wile and Mark Stradiotto*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3 (Canada)

Fax: 1-902-494-1310; E-mail: mark.stradiotto@dal.ca

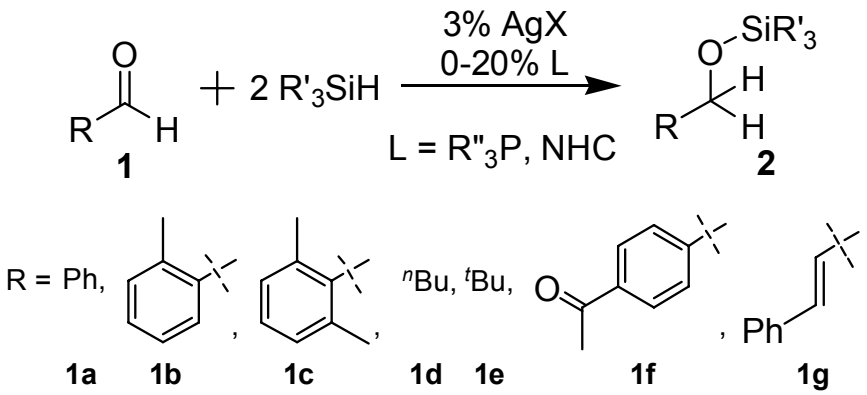
Contents

General Experimental Considerations. Except where noted, all manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 ºC) and evacuated while hot prior to use. Non-deuterated solvents benzene, tetrahydrofuran, and toluene were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system (mBraun). Tetrahydrofuran was purified over two alumina-packed columns, while toluene and benzene were purified over one alumina-packed column and one column packed with copper-Q5 reactant. Solvents dimethylsulfoxide (Aldrich) and 1,2-dichloroethane (Aldrich) were degassed using three repeated freeze-pump-thaw cycles and then dried over 4 Å molecular sieves for 24 h prior to use. All liquid reagents (including the silanes, Aldrich) were degassed using three repeated freeze-pump-thaw cycles prior to use, unless noted. Benzaldehyde (ACP) was washed with 10 % aqueous sodium bicarbonate until no further CO_2 was evolved, followed by saturated aqueous sodium sulfite, then dried over magnesium sulfate and distilled under reduced pressure. All other aldehydes were obtained from Aldrich in high purity. Phosphines were obtained in high purity from Strem (tri-n-butylphosphine, tri-t-butylphosphine, triisopropylphosphine, tricyclohexylphosphine, 1,2-bis(diethylphosphino)ethane) or Aldrich (triethylphosphine, triphenylphosphine). 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene was prepared using literature procedures (Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561). AgCl (Fisher) and all other silver salts (Aldrich) were dried in vacuo for a minimum of 48 h prior to use. GC-MS and GC-FID were performed on a Perkin Elmer AutoSystem XL gas chromatograph equipped with a TurboMass mass spectrometer. GC-MS analyses were performed using a Supelco 30 m x 0.25 mm MDN-5S 5% phenyl methylsiloxane, film thickness 0.50 μm, temperature programmed: 60

°C, 1 min; 20 °C/min to 200 °C, 7 min; 45 °C/min to 280 °C, 7 min. GC-FID analyses were done in a similar way except on a Supelco DB200 column.

General Protocol for Hydrosilylation Experiments. The protocol used for the hydrosilylation of benzaldehyde with dimethylphenylsilane, employing 3 mol% AgOTf and 20 mol% Et_3P in tetrahydrofuran is provided as a representative procedure. To a solution of AgOTf in THF (0.018 g, 0.072 mmol in 1.6 mL THF) was added triethylphosphine (0.071 mL, 0.057 g, 0.48 mmol). The clear, colorless solution was allowed to equilibrate for 5 min under the influence of magnetic stirring, at which point benzaldehyde (0.25 mL, 2.4 mmol) was added by use of an Eppendorf pipette. The resultant solution was stirred for an additional 5 min to ensure equilibration of the benzaldehyde with the catalyst, after which dimethylphenylsilane (0.73 mL, 0.65 g, 4.8 mmol) was added. Subsequently, 0.7 mL aliquots were placed in 13 x 100 mm borosilicate tubes and sealed with a PTFE valve. Reactor cells were immediately transferred to a temperature-controlled mineral oil bath. Magnetic stirring of the solutions was initiated and the headspace vapor pressure was reduced to approximately 0.5 mmHg. Occasionally, color changes and/or formation of Ag metal precipitate was noted during the course of the reaction, as noted in Tables S1 and S2. At the desired sampling time the reactor cells were opened and filtered through a short Al_2O_3 column (5 cm long x 0.5 cm diameter) from which clear, colorless solutions eluted. Benzene was passed through the column to increase the total eluted volume to between 1.0 and 1.5 mL. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS and quantitative data were obtained from GC-FID analysis. Tabulated data represent the average of two runs. In some reactions in which no ligand was employed, polymerization of the THF solvent was observed at reaction times greater than 6 hours. In some instances tetramethyldiphenyldisiloxane was observed as a side-product. The ratio of disiloxane

formed to aldehyde reacted was found to vary between undetectable and 1:6 when a ligand was employed, and between undetectable and 3:1 in the absence of ligand. We view this disiloxane as arising from a competing pathway involving adventitious water, as has been observed previously (Eaborn, C.; Odell, K.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 93). Control experiments show that the Ag salt is required to generate disiloxane, the identity of which was confirmed by comparison with a rationally prepared sample (Goldberg, Y.; Alper, H. *Organometallics* **1995**, *14*, 804).



Scheme S1. Silver-catalyzed addition of silanes to aldehydes.

Table S1 – Addition of Silanes to Benzaldehyde[a]

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Yield **2a** (%)[b]	Yield **3a** (%)[b]	Yield other (%)[b]	TOF (h^{-1})[c]
1-1	3% $AgSbF_6$[d]	THF	24	< 1	97	3	133
1-2	3% AgOTf[d]	THF	24	94	6	< 1	133
1-3	20% Et_3P / 3% AgOTf	THF	70	98	< 1	< 1	29
1-4	3% Me_3SiOTf	THF	70	< 1	> 99	< 1	133
1-5	20% Et_3P / 3% Me_3SiOTf	THF	70	< 1	< 1	< 1	< 1
1-6	20% Et_3P / 3% AgCl	THF	70	57	< 1	< 1	1
1-7	20% Et_3P / 3% $AgBF_4$[d]	THF	70	93	< 1	< 1	7
1-8	20% Et_3P / 3% $AgSbF_6$	THF	70	95	< 1	< 1	41
1-9	20% Et_3P / 3% AgOTf	toluene	70	91	< 1	< 1	4
1-10	20% Et_3P / 3% AgOTf[d]	DMSO	70	93	< 1	< 1	51
1-11	20% Et_3P / 3% AgOTf	DCE[e]	70	36	< 1	< 1	< 1
1-12	20% Et_3P / 3% AgOTf	THF	50	89	< 1	< 1	17
1-13	10% Et_3P / 3% AgOTf	THF	70	25	< 1	< 1	< 1
1-14	10% DEPE / 3% AgOTf[e]	THF	70	45	< 1	< 1	< 1
1-15	20% DEPE / 3% AgOTf[e]	THF	70	68	< 1	< 1	< 1
1-16	20% $^{n}Bu_3P$ / 3% AgOTf[d]	THF	70	95	< 1	< 1	21
1-17	20% Cy_3P / 3% AgOTf	THF	70	13	< 1	< 1	< 1
1-18	20% $^{i}Pr_3P$ / 3% AgOTf[d]	THF	70	21	< 1	< 1	< 1
1-19	20% $^{t}Bu_3P$ / 3% AgOTf	THF	70	51	< 1	< 1	29
1-20	20% Ph_3P / 3% AgOTf	THF	70	3	9	< 1	< 1
1-21	20% NHC / 3% AgOTf[d,e]	THF	70	94	< 1	4	82
1-22	3% AgOTf[f]	THF	24	< 1	85	15	124
1-23	20% Et_3P / 3% AgOTf[f]	THF	70	59	< 1	2	1
1-24	3% AgOTf[g]	THF	24	17	< 1	83	133
1-25	20% Et_3P / 3% AgOTf[g]	THF	70	25	< 1	9	43

[a] Reactions run for 24 h employing two equivalents of Me_2PhSiH (except where noted) with respect to benzaldehyde (**1a**), with the exception of entries 1-1, 1-2, 1-4, 1-22, and 1-24, where the yield is quoted after 0.25 h. [b] Yields are quoted with respect to **1a** consumed, and are based on GC-MS and GC-FID data (average of two runs). [c] Turnover frequency (TOF) reported at 0.25 h, based on the consumption of **1a** relative to AgX employed. [d] A precipitate of Ag metal was noted to form during the course of the reaction. [e] DCE = 1,2-dichloroethane; DEPE = 1,2-bis(diethylphosphino)ethane; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene. [f] Two equivalents of Et_3SiH were used in place of Me_2PhSiH. [g] Two equivalents of Ph_2SiH_2 were used in place of Me_2PhSiH, with the double hydrosilylation product $Ph_2Si(OCH_2Ph)_2$ constituting <1% of the converted **1a**.

Table S2 – Addition of Me_2PhSiH to Aldehydes[a]

Entry	Aldehyde	% Et_3P	Yield **2** (%)[b]	Yield **3** (%)[b]	Yield other (%)[b]	TOF (h^{-1})[c]
2-1a	**1b**	20	94	< 1	1	49
2-1b	**1b**	0	88	< 1	2	121
2-2a	**1c**	20	76	< 1	1	< 1
2-2b	**1c**	0	50	< 1	40	121
2-3a	**1d**	20	86	1	12	1
2-3b	**1d**	0	9	58	20	117
2-4a	**1e**	20	48	< 1	6	1
2-4b	**1e**	0	7	< 1	1	11
2-5a	**1f**	20	> 99	< 1	< 1	37
2-5b	**1f**	0	62	< 1	24	114
2-6a	**1g**	20	99	< 1	1	37
2-6b	**1g**	0	48	< 1	17	87

[a] Reactions employing 20 mol% Et_3P were run for 24 h at 70 °C in THF, while those using no Et_3P were run for 0.25 h at 24 °C. All reactions employed two equivalents of Me_2PhSiH and 3 mol% AgOTf with respect to aldehyde (**1**). For all reactions conducted in the absence of Et_3P, the introduction of the hydrosilane resulted in rapid change of the solution color from colorless to yellow, followed by the immediate precipitation of Ag metal. [b] Yields are quoted with respect to **1** consumed, and are based on GC-MS and GC-FID data (average of two runs). [c] Turnover frequency (TOF) reported at 0.25 h, based on the consumption of **1** relative to AgOTf employed.