Cationic Copper(I) Complexes as Efficient Pre-catalysts for the Hydrosilylation of Carbonyl Compounds

Silvia Díez-González, Natalie M. Scott and Steven P. Nolan*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

snolan@uno.edu

Supporting Information

General Considerations

All ketones were used as received. All solid reagents were stored under argon in a glovebox containing less than 1 ppm O₂. Tetrakis(acetonitrile)copper(I) hexafluorophosphate and tetrafluoroborate,¹ IPr·HCl and free IPr² were synthesized according to literature procedures. Solvents were distilled from appropriate drying agents. Flash column chromatography was performed on silica gel 60 (320-400 mesh). ¹H NMR and ¹³C NMR were recorded on a 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported with respect to tetramethylsilane as internal standard in ppm. All reported yields are isolated yields and are average of at least two runs.

Synthesis of [(IPr)₂Cu] X Complexes (X = PF₆ or BF₄)

In an oven-dried vial fitted with a septum screw cap, tetrakis(acetonitrile)copper(I) hexafluoroborate (0.186 g, 0.5 mmol) or tetrafluoroborate (0.157 g, 0.5 mmol) IPr·HCl (0.424 g, 1 mmol) and sodium *tert*-butoxide (96 mg, 1 mmol) were loaded inside a glovebox and stirred in dry THF (10 mL) outside the glovebox for 6 hours. After filtering the reaction mixture through a plug of celite (THF), the filtrate was mixed with hexane to form a precipitate. A second filtration led to the isolation of the expected complexes.

Bis[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper hexafluorophosphate (1). From tetrakis(acetonitrile)copper(I) hexafluorophosphate and following the general procedure, 0.474 g of the title compound were isolated as a pure white solid (96%). ¹H NMR (400 MHz, acetone-*d*₆): δ = 7.54 (t containing a singlet at 7.55, *J* = 7.8 Hz, 8H, *p*-CH + NCH), 7.25 (d, *J* = 7.8 Hz, 8H, *m*-CH), 2.42 (septet, *J* = 6.8 Hz, 8H, (CH₃)₂CH), 1.04 (d, *J* = 6.8 Hz, 18H, CH₃), 0.94 (d, *J* = 6.8 Hz, 18H, CH₃); ¹³C NMR (100 MHz; CDCl₃): δ = 178.4 (N–C–N), 145.0 (CH aromatic), 134.6 (C aromatic), 130.6 (C aromatic), 125.2 (=CH–N), 124.5 (CH aromatic), 28.6 (CH(CH₃)₂), 24.25 (CH₃), 24.12 (CH₃); Elemental analysis calcd for C₅₄H₇₂CuF₆N₄P (985.69): C, 65.80; H, 7.36; N, 5.68. Found: C, 65.49; H, 7.42; N, 5.99.

Bis[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper tetrafluoroborate (2). From tetrakis(acetonitrile)copper(I) tetrafluoroborate and following the general procedure, 0.452 g of the title compound were isolated as a pure white solid (92%). ¹H NMR (400 MHz, acetone-*d*₆): δ = 7.54 (t containing a singlet at 7.55, *J* = 7.5 Hz, 8H, *p*-CH + NCH), 7.25 (d, *J* = 7.5 Hz, 8H, *m*-CH), 2.40 (septet, *J* = 6.8 Hz, 8H, CH(CH₃)₂), 1.04 (d, *J* = 6.8 Hz, 24H, CH₃), 0.94 (d, *J* = 6.8 Hz, 24H, CH₃); ¹³C

NMR (100 MHz, CDCl₃): δ = 177.4 (N–C–N), 145.0 (CH aromatic), 134.7 (C aromatic), 130.6 (C aromatic), 125.3 (=CH–N), 124.5 (CH aromatic), 28.6 (CH(CH₃)₂), 24.3 (CH₃), 24.2 (CH₃); Elemental analysis calcd for C₅₄H₇₂BCuF₄N₄ (927.53): C, 69.93; H, 7.82; N, 6.04. Found: C, 69.57; H, 7.60; N, 5.87.

General Procedure for the Hydrosilylation of Carbonyl Compounds

In an oven-dried vial fitted with a septum screw cap, **2** (27 mg, 0.03 mmol, 3 mol%) and sodium *tert*-butoxide (12 mg, 12 mol%) were charged inside a glove box and stirred in dry THF (2 mL) at room temperature or at 55 °C outside of the glove box for 10 minutes before adding triethylsilane (0.33 mL, 2 mmol, 2 equiv) through the septum using a syringe. After 10 more minutes of stirring, the carbonyl compound (1 mmol) was added. When the starting material was a solid, it was added as a solution in THF. The reaction was monitored by GC, after consumption of the starting material or no further conversion, the reaction mixture was opened to air and filtered through a plug of active charcoal and celite using ethyl acetate as solvent. The organic phase was concentrated *in vacuo* and the purity of the residue checked on GC and ¹H NMR. Flash chromatography was then performed unless crude product was estimated to be greater than 95% pure.

(Cyclohexyloxy)triethylsilane (Table 1, entry 1). Using the general procedure at room temperature, cyclohexanone (0.100 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.211 g, 98% yield). Spectroscopic data were consistent with previously reported data for this compound.³

(2-Methylcyclohexyloxy)triethylsilane (Table 1, entry 2). Using the general procedure at room temperature, 2-methylcyclohexanone (0.120 mL, 1 mmol) was hydrosilylated by triethylsilane. After concentration of the filtrate, a colorless oil was obtained as the pure product in a mixture 85:15 of *trans:cis* diastereoisomers (0.206 g, 90% yield). Spectroscopic data were consistent with previously reported data for this compound.⁴

Bicyclo[2.2.1]hept-2-yloxytriethylsilane (Table 1, entry 3). Using the general procedure at room temperature, norcamphor (0.110 g, 1 mmol) was hydrosilylated by triethylsilane. After concentration of the filtrate, a colorless oil was obtained as the pure product in a mixture 97:3 of *endo:exo* isomers (0.217 g, 96% yield). Spectroscopic data were consistent with previously reported data for this compound.⁵

Triethyl(octan-2-yloxy)silane (Table 1, entry 4). Using the general procedure at room temperature, 2-octanone (0.156 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.224 g, 92% yield). Spectroscopic data were consistent with previously reported data for this compound.⁶

Triethyl(undecan-2-yloxy)silane (Table 1, entry 5). Using the general procedure at room temperature, 2-undecanone (0.210 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.273 g, 97% yield). Spectroscopic data were consistent with previously reported data for this compound.⁴

(4-Phenylbutan-2-yloxy)triethylsilane (Table 1, entry 6). Using the general procedure at room temperature, benzylacetone (0.150 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.252 g, 95% yield). Spectroscopic data were consistent with previously reported data for this compound.⁴

(1-Phenylethoxy)triethylsilane (Table 1, entry 7). Using the general procedure at room temperature, acetophenone (0.117 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.231 g, 98% yield). Spectroscopic data were consistent with previously reported data for this compound.⁷

(1-Phenylpropoxy)triethylsilane (Table 1, entry 8). Using the general procedure at room temperature, propiophenone (0.133 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.232 g, 93% yield). Spectroscopic data were consistent with previously reported data for this compound.⁵

[1-(Naphthalen-1-yl)ethoxy]triethylsilane (Table 1, entry 9). Using the general procedure at room temperature, 1'-acetonaphnone (0.154 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.269 g, 94% yield). Spectroscopic data were consistent with previously reported data for this compound.⁵

Triethyl(hex-5-en-2-yloxy)silane (Table 1, entry 10). Using the general procedure at room temperature, hex-5-en-2-one (0.117 mL, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.220 g, 98% yield). Spectroscopic data were consistent with previously reported data for this compound.⁸

(1-Isopropyl-2-methylpropoxy)triethylsilane (Table 2, entry 1). Using the general procedure at 55 °C, 2,4-dimethylpentanone (0.140 mL, 1 mmol) was hydrosilylated by triethylsilane. The residue was purified by flash chromatography on silica gel (pentane) to afford 0.214 g (93% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.⁹

(2,6-Dimethylcyclohexyloxy)triethylsilane (Table 2, entry 2). Using the general procedure at 55 °C with 19.3 mg (20 mol %) of NaO^tBu, 2,6-dimethylcyclohexanone (0.140 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford two diastereoisomers of the title compound (0.052 g of the *meso trans/trans* isomer and 0.174 g of the *meso cis/cis*, 93% yield)¹⁰ as colorless oils. Spectroscopic data were consistent with previously reported data for this compound.¹¹

(Dicyclopropylmethoxy)triethylsilane (Table 2, entry 3). Using the general procedure at 55 °C, dicyclopropyl ketone (0.114 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.211 g the title compound as a colorless oil (94% yield). Spectroscopic data were consistent with previously reported data for this compound.⁵

(Dicyclohexylmethoxy)triethylsilane (Table 2, entry 4). Using the general procedure at 55 °C with 0.50 mL (3 mmol) of triethylsilane, dicyclohexyl ketone (0.200 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.304 g the title compound as a colorless oil (98% yield). Spectroscopic data were consistent with previously reported data for this compound.¹¹

Triethyl-(1-*o*-tolylethoxy)silane (Table 2, entry 5). Using the general procedure at 55 °C, 2'-methylacetophenone (0.175 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 95:5) to afford 0.241 g (96% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.¹¹

(Diphenylmethoxy)triethylsilane (Table 2, Entry 6). Using the general procedure at 55 °C, benzophenone (0.189 g, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 95:5) to afford 0.276 g (93% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.¹¹

(2,2-Dimethyl-1-phenylpropoxy)triethylsilane (Table 2, entry 7). Using the general procedure at 55 °C, 2,2-dimethylpropiophenone (0.168 mL, 1.0 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.274 g (99% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.¹¹

(4-Methylbenzyloxy)triethylsilane (Table 3, entry 1). Using the general procedure at room temperature, *p*-tolulaldehyde (0.118 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude

product was purified by flash chromatography on silica gel (pentane:Et₂O, 98:2) to afford 0.218 g (92% yield) of the title compound as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.24 (d, *J* = 8.1 Hz, 2H, *H* aromatic), 7.15 (d, *J* = 8.1 Hz, *H* aromatic), 4.71 (s, 2H, OCH₂), 2.35 (s, 3H, CH₃), 0.99 (t, *J* = 8.0 Hz, 9H, SiCH₂CH₃), 0.66 (q, *J* = 8.0 Hz, 6H, SiCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 138.2 (*C* aromatic), 136.3 (*C* aromatic), 128.7 (CH aromatic), 126.2 (CH aromatic), 64.5 (OCH₂), 20.9 (CH₃), 6.6 (SiCH₂CH₃), 4.5 (SiCH₂CH₃); Elemental analysis calcd for C₁₄H₂₄OSi (236.43): C, 71.12; H, 10.23. Found: C, 71.33; H, 10.02.

(2-Methylbenzyloxy)triethylsilane (Table 3, entry 2). Using the general procedure at room temperature, *o*-tolulaldehyde (0.117 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 95:5) to afford 0.221 g (94% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.¹²

(4-Fluorobenzyloxy)triethylsilane (Table 3, entry 3). Using the general procedure at room temperature, *p*-fluorobenzaldehyde (0.100 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.231 g (96% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.¹²

(4-Chlorobenzyloxy)triethylsilane (Table 3, entry 4). Using the general procedure at room temperature, *p*-chlorobenzaldehyde (0.140 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 95:5) to afford 0.234 g (91% yield) of the title compound as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.32–7.18 (m, 4H, *H* aromatic), 4.70 (s, 2H, OCH₂), 0.98 (t, *J* = 8.0 Hz, 9H, SiCH₂CH₃), 0.65 (q, *J* = 8.0 Hz, 6H, SiCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 139.8 (*C* aromatic), 132.5 (*C* aromatic), 128.3 (CH aromatic), 127.4 (CH aromatic), 65.0 (OCH₂), 6.7 (SiCH₂CH₃), 4.4 (SiCH₂CH₃); Elemental analysis calcd for C₁₃H₂₁ClOSi (256.84): C, 60.79; H, 8.24. Found: C, 60.83; H, 8.31.

(2-Chlorobenzyloxy)triethylsilane (Table 3, entry 5). Using the general procedure at room temperature, *o*-chlorobenzaldehyde (0.112 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 98:2) to afford 0.242 g (94% yield) of the title compound as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (d, *J* = 7.5 Hz, 1H, *H* aromatic), 7.32–7.21 (m, 2H, *H* aromatic), 7.21–7.14 (m, 1H, *H* aromatic), 4.80 (s, 2H, OCH₂), 0.99 (t, *J* = 8.1 Hz, 9H, SiCH₂CH₃), 0.69 (q, *J* = 8.1 Hz, 6H, SiCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 138.8 (*C* aromatic), 131.3 (*C* aromatic), 128.7 (CH aromatic), 127.8 (CH aromatic), 127.4

(CH aromatic), 126.6 (CH aromatic), 61.9 (OCH₂), 6.7 (SiCH₂CH₃), 4.4 (SiCH₂CH₃); Elemental analysis calcd for C₁₃H₂₁ClOSi (256.84): C, 60.79; H, 8.24. Found: C, 60.92; H, 8.40.

(4-Bromobenzyloxy)triethylsilane (Table 3, entry 6).¹² Using the general procedure at room temperature, *p*-bromobenzaldehyde (0.185 g, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 98:2) to afford 0.281 g (93% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound. Elemental analysis calcd for C₁₃H₂₁BrOSi (301.29): C, 51.82; H, 7.03. Found: C, 52.03; H, 7.28.

(4-Methoxybenzyloxy)triethylsilane (Table 3, entry 7). Using the general procedure at room temperature, *p*-anisaldehyde (0.120 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 98:2) to afford 0.225 g (89% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.¹³

(Cyclohexylmethoxy)triethylsilane (Table 3, entry 8). Using the general procedure at room temperature with 0.50 mL (3 mmol, 3 equiv) of triethylsilane, cyclohexyl carbaldehyde (0.120 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 98:2) to afford 0.223 g (70% yield) of the title compound as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 3.39 (d, *J* = 6.4 Hz, 2H, OCH₂), 1.87–1.59 (m, 6H, cyclohexyl), 1.57–1.38 (m, 2H, cyclohexyl), 1.36–1.04 (m, 5H, cyclohexyl), 0.97 (t, *J* = 8.1 Hz, 9H, SiCH₂CH₃), 0.60 (q, *J* = 8.1 Hz, 6H, SiCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 68.6 (OCH₂), 40.5 (CH), 29.8 (CH₂), 26.8 (CH₂), 25.9 (CH₂), 6.8 (SiCH₂CH₃), 4.4 (SiCH₂CH₃); Elemental analysis calcd for C₁₃H₂₈OSi (228.45): C, 68.35; H, 12.35. Found: C, 68.44; H, 12.51.

(2,6-Dimethylhept-5-enyloxy)triethylsilane (Table 3, entry 9). Using the general procedure at room temperature with 0.50 mL (3 mmol, 3 equiv) of triethylsilane, 2,6-dimethylhept-5-enal (0.160 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 98:2) to afford 0.183 g (71% yield) of the title compound as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 5.13 (broad t, *J* = 7.5 Hz, 1H, C=CH), 3.47 (dd, *J* = 5.8, 9.9 Hz, 1H, OCH₂), 3.36 (dd, *J* = 6.8, 9.9 Hz, 1H, OCH₂), 2.10–1.88 (m, 2H, C=CH–CH₂), 1.69 (s, 3H, CH₃–C=), 1.65–1.53 (m containing a singlet at 1.61, 4H, CH₃–CH + CH₃–C=), 1.49–1.37 (m, 1H, CH–CH₂), 1.15–1.02 (m, 1H, CH–CH₂), 0.97 (t, 9H, *J* = 7.9 Hz, SiCH₂CH₃), 0.60 (q, *J* = 7.9 Hz, 6H, SiCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 131.1 (C=CH), 124.9 (C=CH), 68.1 (OCH₂), 35.4 (=CH–CH₂), 33.4 (CH–CH₂), 25.7 (=C–CH₃), 25.5 (=C–CH₃), 17.6 (CH₂–CH), 16.7 (CH₃), 6.8

(SiCH₂CH₃), 4.4 (SiCH₂CH₃); Elemental analysis calcd for C₁₅H₃₂OSi (256.50): C, 70.24; H, 12.57. Found: C, 70.50; H, 12.74.

Triethyl(phenethyloxy)silane (Scheme 3). Using the general procedure at 55 °C with 0.50 mL (3 mmol) of triethylsilane, ethyl phenylacetate (0.160 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane:Et₂O, 98:2) to afford 0.154 g the title compound as a colorless oil (65% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.26–7.18 (m, 2H, *H* aromatic), 7.18–7.08 (m, 3H, 2H, *H* aromatic), 3.73 (t, *J* = 7.6 Hz, 2H, OCH₂), 2.77 (t, *J* = 7.6 Hz, 2H, Ph–CH₂), 0.86 (t, 9H, *J* = 8.0 Hz, SiCH₂CH₃), 0.50 (q, *J* = 8.0 Hz, 6H, SiCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 139.1 (C), 129.1 (CH aromatic), 128.2 (CH aromatic), 126.1 (CH aromatic), 64.2 (OCH₂), 39.7 (Ph–CH₂), 6.7 (SiCH₂CH₃), 4.4 (SiCH₂CH₃); Elemental analysis calcd for C₁₄H₂₄OSi (236.43): C, 71.12; H, 10.23. Found: C, 71.27; H, 10.44.

Mechanistic studies

In an oven-dried vial fitted with a septum screw cap, [Cu(CH₃CN)₄]BF₄ (9 mg, 0.03 mmol, 3 mol %), sodium *tert*-butoxide (11.5 mg, 12 mol%) and IPr (12 mg, 3 mol% or 23 mg, 6 mol% or 35 mg, 9 mol%) were loaded inside a glove box and stirred in dry THF (2 mL) at room temperature outside of the glove box for 40 minutes¹⁴ before adding triethylsilane (0.33 mL, 2 mmol, 2 equiv) through the septum using a syringe. After 10 minutes of stirring, cyclohexanone (0.100 mL, 1 mmol) was added. The reactions were monitored by GC, the different reaction rates are presented in Figure 1. The formation of the expected silyl ether was confirmed by ¹H NMR.

Figure 1. Influence of ligand loading in the hydrosilylation of cyclohexanone

Crystallographic Data

Crystallographic information files (CIF) of complexes **1** and **2** have been deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. [fax: (+44) 1223 336033, email: deposit@ccdc.cam.ac.uk] and can be obtained on request free of charge, by quoting the publication citation and deposition number 279243 (**1**) and 279244 (**2**).

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