

Supporting Information

A New Alternative to Stryker's Reagent in Hydrosilylation: Synthesis, Structure, and Reactivity of a Well-Defined Carbene–Copper Acetate Complex

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Experimental

General Methods. Toluene was distilled from sodium benzophenone ketyl under nitrogen. Cu(OAc)₂, hydrosilanes and other commercial substrates were purchased from Aldrich and used as received. (*E*)-Cinnamionitrile (**2a**) was purchased from Aldrich and other nitrile substrates (**2b-2g**) were prepared from the corresponding aldehydes or ketones with diethyl (cyanomethyl)phosphonate by the literature procedure.¹ All reactions were carried out under a nitrogen atmosphere, in an oven-dried Schlenk tube and run two or more times. Flash chromatography was performed on silica gel from Merck (70–230 mesh). All ¹H NMR spectra were obtained on Varian Mercury 400 systems and reported parts per million (ppm) downfield from tetramethylsilane. ¹³C NMR spectra are reported in ppm referenced to deuteriochloroform (77.2 ppm). Infrared spectra (IR) were obtained on Magma-IR560 and are recorded in cm⁻¹.

Synthesis of 1: Cu(OAc)₂ (90.8 mg, 0.50 mmol) and IPr (214.8 mg, 0.55 mmol) were placed in a Schlenk flask and 3 mL of toluene was added. The reaction mixture was stirred at room temperature for 12 h and blue precipitate formed. The resulting precipitate was isolated by filtration, washed with toluene, and dried in vacuo to afford [Cu(IPr)(OAc)₂] as a blue solid (229 mg, 80%). Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of pentane to a concentrated CH₂Cl₂ solution of the complex. (Found: C, 65.34; H, 7.48; N, 4.98. Calc. for C₃₁H₄₂CuN₂O₄: C, 65.30; H, 7.42; N, 4.91%).

General Procedure for the 1,2-reduction of carbonyl compounds (Table 1, entries 1 and 2): **1** (5.7 mg, 0.01 mmol) was placed in an oven-dried Schlenk tube and PMHS (0.15 mL, 2.5 mmol) and toluene (0.5 mL) were added under nitrogen. The reaction mixture was stirred for 5 min at room temperature and then, carbonyl compound (aldehydes or ketones) (1.0 mmol) was added. The reaction tube was washed with toluene (0.5 mL), sealed, and stirred until no starting material was detected by TLC. The reaction mixture was quenched with water and transferred to a round-bottom flask with an aid of Et₂O (10 mL), and NaOH (2.5 M, 1.2 mL) was added. The biphasic mixture was stirred vigorously for 0.5 h. The layers were separated and the aqueous layer was extracted with Et₂O (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated. The product was purified by silica gel chromatography and its ¹H spectrum was compared with either literature data or that of

¹ Wadsworth, W. S.; Emmons, W. D. *J. Am. Chem. Soc.* 1961, **83**, 1733.

authentic material.

(4-Methoxyphenyl)-methanol (Table 1, entry 1): The title compound was isolated as a colorless oil in 97% yield: δ_{H} (400 MHz; CDCl₃; Me₄Si) 1.88 (1 H, br s), 3.79 (3 H, s), 4.58 (2 H, s), 6.86 (2 H, d, *J* 8.3), 7.25 (2 H, d, *J* 8.3).

1-Phenylpropanol (Table 1, entry 2): The title compound was isolated as a colorless oil in 96% yield: δ_{H} (400 MHz; CDCl₃; Me₄Si) 0.90 (3 H, t, *J* 7.3), 1.84–1.70 (2 H, m), 1.92 (1 H, br s), 4.56 (1 H, t, *J* 6.6), 7.32–7.22 (5 H, m).

General procedure for the 1,4-reduction of enones (Table 1, entries 3 and 4): **1** (5.7 mg, 0.010 mmol) was placed in an oven-dried Schlenk tube and 1,1,3,3-tetramethyl disiloxane (1.5 or 0.55 mmol) and toluene (0.5 mL) were added under nitrogen. The reaction mixture was stirred for 30 min at room temperature and then, enone was added. The reaction tube was washed with toluene (0.5 mL), sealed, and stirred until no starting material was detected by TLC. The reaction mixture was concentrated in vacuo and the product was isolated by Kugelrohr distillation or silica gel chromatography and its ¹H spectrum was compared with literature data.

(3-Methyl-1-cyclohexenyloxy)-tetramethyldisiloxane (Table 1, entry 3): The title compound was isolated as a colorless oil in 30% yield and 1,3-bis(3-methyl-1-cyclohexenyloxy)-tetramethyldisiloxane in 49% yield. The following is the ¹H NMR of the monomeric product: δ_{H} (400 MHz; CDCl₃; Me₄Si) 0.23–0.21 (12 H, m), 0.95 (3 H, d, *J* 7.0), 1.60–1.52 (1 H, m), 1.78–1.66 (3 H, m), 2.02–1.96 (2 H, m), 2.25–2.22 (1 H, m), 4.71 (1 H, sept, *J* 2.7), 4.80 (1 H, m).

1,3-Bis((*R*)-5-isopropenyl-2-methyl-1-cyclohexenyloxy)-tetramethyl-disiloxane (Table 1, entry 4): The title compound was isolated as a colorless oil in 93% yield: δ_{H} (400 MHz; CDCl₃; Me₄Si) 0.19–0.18 (12 H, m), 1.42 (2 H, qd, *J* 11.7 and 6.2), 1.59 (6 H, s), 1.75 (6 H, s), 1.79–1.77 (2 H, m), 2.25–1.95 (10 H, m), 4.73–4.72 (4 H, m).

General procedure for the conjugate reduction of α,β -unsaturated nitriles (Table 2): **1** (5.7 mg, 0.01 mmol) was placed in an oven-dried Schlenk tube and PMHS (0.18 mL, 3.0 mmol) and toluene (0.5 mL) were added under nitrogen. The reaction mixture was stirred for 5 min at room temperature and then, α,β -unsaturated nitrile (1.0 mmol)

was added, followed by *t*-BuOH (0.18 mL, 2.0 mmol). The reaction tube was washed with toluene (0.5 ml), sealed, and stirred until no starting nitrile was detected by TLC or GC. The reaction mixture was quenched with water and transferred to a round-bottom flask with an aid of Et₂O (10 mL), and then NaOH (2.5 M, 1.2 mL) was added. The biphasic mixture was stirred vigorously for 0.5 h. The layers were separated and the aqueous layer was extracted with Et₂O (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated. The product was purified by Kugelrohr distillation or silica gel chromatography.

3-Phenyl-propionitrile (Table 2, 3a): Using the general procedure, the title compound was isolated as a colorless oil by silica gel chromatography in 91% yield: δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.61 (2 H, t, *J* 7.3), 2.95 (2 H, t, *J* 7.3), 7.33–7.20 (5 H, m).

3-Furan-2-yl-propionitrile (Table 2, 3b): Using the general procedure, the title compound was isolated as a colorless oil by silica gel chromatography in 87% yield: δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.66 (2 H, t, *J* 7.3), 2.98 (2 H, t, *J* 7.3), 6.15 (1 H, d, *J* 2.2), 6.29 (1 H, d, *J* 2.2), 7.32 (1 H, s).

3-Methyl-nonanenitrile (Table 2, 3c): Using the general procedure, the title compound was isolated as a colorless oil by Kugelrohr distillation in 88% yield: δ_{H} (400 MHz; CDCl₃; Me₄Si) 0.90 (3 H, t, *J* 6.9), 1.08 (3 H, d, *J* 6.6), 1.42–1.22 (10 H, m), 1.86–1.81 (1 H, m), 2.26 (1 H, dd, *J* 16.5 and 6.9), 2.31 (1 H, dd, *J* 16.5 and 5.5).

3-Phenyl-butyronitrile (Table 2, 3d): Using the general procedure, the title compound was isolated as a colorless oil by silica gel chromatography in 88% yield: δ_{H} (400 MHz; CDCl₃; Me₄Si) 1.44 (3H, d, *J* 6.9), 2.55 (1 H, dd, *J* 10.2 and 7.3), 2.57 (1 H, dd, *J* 10.2 and 6.6), 3.16–3.11 (1 H, m), 7.33–7.20 (5 H, m).

4-(2-Cyano-1-methyl-ethyl)-benzonitrile (Table 2, 3e): Using the general procedure, the title compound was isolated as a white solid by silica gel chromatography in 94% yield: δ_{H} (400 MHz; CDCl₃; Me₄Si) 1.47 (3 H, d, *J* 6.9), 2.60 (1 H, dd, *J* 5.6 and 1.8), 2.62 (1 H, dd, *J* 5.6 and 1.4), 3.25–3.20 (1 H, m), 7.36 (2 H, d, *J* 7.5), 7.64 (2 H, d, *J* 7.5).

(1,2,3,4-Tetrahydro-naphthalen-1-yl)-acetonitrile (Table 2, 3f): Using the general procedure, the title compound was isolated as a colorless oil by silica gel

chromatography in 87% yield; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2928, 2215, 1603, 1450, 757; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.07–1.78 (4 H, m), 2.79–2.56 (4 H, m), 3.22–3.18 (1 H, m), 7.22–7.06 (4 H, m); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.7, 25.1, 28.4, 29.7, 35.1, 119.2, 126.3, 127.0, 128.2, 129.7, 136.7, 137.3.

3,4,4-Trimethyl-pentanenitrile (Table 2, 3g): Using the general procedure, the title compound was isolated as a colorless oil by Kugelrohr distillation in 82% yield; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3547, 2949, 2247, 1473, 1344; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.89 (9 H, s), 1.08 (3 H, d, J 6.6), 1.70–1.66 (1 H, m), 2.06 (1 H, dd, J 16.5 and 10.0), 2.46 (1 H, dd, J 16.5 and 3.6); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 14.9, 15.3, 20.4, 27.0, 40.5, 120.1.