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A Versatile and Efficient Hydrosilylation Route to Functionalized Polyferrocenylsilanes

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Experimental Part

Materials. All manipulations were performed under an inert atmosphere using standard Schlenk techniques or an N_2 filled glove box. Solvents, silanes, amines and alcohols were purchased from commercial vendors, dried by standard methods and distilled prior to use. Karstedt's catalyst (2.1 – 2.4 wt-% Pt in xylenes), *n*-butyllithium (1.6 M in hexanes) and sodium cyclopentadiene (NaCp) (2 M in THF) were used as received. Compounds **1a**, **1d**, and **2** were synthesized as reported elsewhere.[1, 2]

Equipment. NMR spectra were taken on either Varian Gemini 200 or 300, Varian Mercury 300 or 400 or Unity 500 spectrometers. ^{1}H- and ^{13}C-NMR chemical shifts were referenced internally to residual solvent peaks, and ^{29}Si-NMR chemical shifts were referenced externally to $Si(CH_3)_4$. All NMR data are reported for C_6D_6 solutions. Molecular weights were estimated by gel permeation chromatography (GPC) using equipment as described elsewhere,[3] and are reported relative to polystyrene standards. Mass spectra were obtained with a VG 70-250S mass spectrometer operating in electron impact (EI) mode. Differential scanning calorimetry (DSC) was performed using equipment as described elsewhere.[4]

Hydrosilylation Reactions. Hydrosilylation reactions were carried out using 50 – 100 mg of polymer in toluene solution, with a 2 – 3 fold excess of silane, and using ca. 0.2 – 0.3 mol-% Pt, relative to olefinic groups, as catalyst. Reactions with the chlorosilanes were performed at r.t., and those with Et_3SiH were performed at 60 °C. NMR characterization data are given only for those products which were 100 % hydrosilylated.

*Reaction of **4** with Et_3SiH.* To a solution of **4** (80 mg, 0.28 mmol) in toluene (3 mL), Et_3SiH (65 µL, 0.76 mmol) and Karstedt's catalyst (6 µL) were added. The mixture was stirred overnight at 60 °C, concentrated, precipitated into methanol and pumped dry to give 81mg (75%) of a red solid. ^{1}H NMR analysis indicated 76 % conversion of the olefin groups. GPC: M_n = 17 100; M_w = 41 600; PDI = 2.43.

*Reaction of **4** with Ph_2ClSiH.* A toluene (8 mL) solution of **4** (80 mg, 0.28 mmol), Ph_2ClSiH (100 µL, 0.48 mmol) and Karstedt's catalyst (6 µL) was stirred overnight at room temperature, concentrated, precipitated into hexanes and pumped dry to give 73 mg (52 %) of a red solid.

^{1}H-NMR: δ 0.65 (s, 3H, Si-C*H*$_3$); 1.34 (s, 2H, Si-C*H*$_2$); 1.80 (s, 2H, Si-CH$_2$-C*H*$_2$); 3.64 (s, 2H, Si-O-C*H*$_2$), 4.1-4.45 (m, 8H, Cp-*H*); 7.02 (m, 4H, *m*-Ph); 7.50 (m, 4H, *o*-Ph); 7.62 (m, 2H, *p*-Ph)). ^{13}C-NMR: δ -1.34 (Si-*C*H$_3$); 13.48 (Si-*C*H$_2$); 27,14 (Si-CH$_2$-*C*H$_2$); 65.71 (Si-O-*C*H$_2$); 70.08 (Cp: Si-*C*); 72.85 (Cp: C^2, C^5); 74.66 (Cp: C^3, C^4); 128.91 (*ipso*-Ph); 131.57 (*o,p*-Ph); 135.21 (*m*-Ph). ^{29}Si-NMR: δ 2.70 (1Si, *Si*Cp$_2$); 11.38 (1Si, *Si*Ph$_2$).

*Reaction of **4** with $MeCl_2SiH$.* Performed similar to that above, using a solution of **4** (65 mg, 0.23 mmol), $MeCl_2SiH$ (150 µL, 0.97 mmol) and Karstedt's catalyst (10 µL) in toluene (3 mL). ^{1}H NMR analysis indicated that 100 % conversion of the olefin groups occurred during the hydrosilylation reaction.

^{1}H-NMR: δ 0.45 (s, 3H, CpSi-C*H*$_3$); 0.73 (s, 3H; Cl_2Si-C*H*$_3$); 1.00 (s, 2H, Si-C*H*$_2$); 1.67 (s, 2H, Si-CH_2-C*H*$_2$); 3.62 (s, 2H, Si-O-C*H*$_2$); 4.05-4.65 (m, 8H, Cp-*H*). ^{13}C-NMR: δ -1.43 (Si-*C*H$_3$); 5.30 (Si-(*C*H$_3$)$_2$); 18.43 (Si-*C*H$_2$); 26.41 (Si-CH_2-*C*H$_2$); 64.90 (Si-O-*C*H$_2$); 69.99 (Cp: Si-*C*); 72.92 (Cp: C^2, C^5); 74.36 (Cp: C^3, C^4). ^{29}Si-NMR: δ 2.99 (1Si, *Si*Cp$_2$); 33.41 (1Si, *Si*Cl$_2$).

Reaction of **5** *with Et_3SiH.* A toluene (3 mL) solution of **5** (75 mg, 0.28 mmol), Et_3SiH (65 µL, 0.79 mmol) and of Karstedt's catalyst (6 µL) was stirred overnight at 60 °C, concentrated, precipitated into methanol and pumped dry to give 65 mg (64%) of a red solid. ^{1}H-NMR analysis of the product indicated that ca. 12 % conversion of the allyl groups had occurred.

Reaction of **5** *with Ph_2ClSiH.* A solution of **5** (75 mg, 0.28 mmol), Ph_2ClSiH (100 µL, 0.48 mmol) and Karstedt's catalyst (6 µL) in toluene (3 mL) was stirred overnight at room temperature, concentrated, precipitated into hexanes and pumped dry to give 82 mg (64%) of a red solid. ^{1}H-NMR analysis of the product indicated 38 % conversion of the allyl groups.

Reaction of **5** *with $MeCl_2SiH$.* A solution of 50mg of **5** (50 mg, 0.19 mmol), $MeCl_2$SiH (100 µL, 0.65 mmol) and Karstedt's catalyst (6 µL) in toluene (2 mL) was stirred overnight at room temperature, concentrated, precipitated into hexanes and pumped dry to afford a red gum. ^{1}H-NMR analysis indicated 75 % conversion of the allyl groups in the hydrosilylation reaction.

References for Supporting Information

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