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Note

Dehydrogenative coupling as an efficient route to ferrocene functionalized siloxanes

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Abstract

Ferrocene grafted siloxanes were prepared in high yields (~79–97%) via Rh-catalyzed dehydrogenative coupling of a series of monomeric, polymeric, and cyclic hydrosiloxanes with ferrocenemethanol. Wilkinson's catalyst was the most efficient of those surveyed (Karstedt's catalyst, H_2PtCl_6, $Co_2(CO)_8$, 10% Pd/C, 10% Pt/C, 5% Rh/C) with respect to yield and selectivity. Benzene and toluene were better solvents than tetrahydrofuran and methylene chloride.

Keywords: Polymethylhydrosiloxane; Silicones; Wilkinson's catalyst; Dehydrogenative coupling; Ferrocenemethanol, Tetramethylcyclohydrosiloxane

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1. Introduction

Recently, we reported a new protocol to graft a variety of functional organic moieties onto the backbone of poly(methylhydrosiloxane) **b** via dehydrogenative coupling assisted by Wilkinson's catalyst [1–6]. Lately, West and co-workers adapted this protocol to graft fluorescent substituents onto polysiloxanes [7]. Herein we describe the extension of this methodology to incorporate ferrocene into siloxanes.

2. Results and discussion

Ferrocenemethanol **1** was coupled with hydrosiloxanes in the presence of Wilkinson's catalyst ($RhCl(PPh_3)_3$) under mild conditions to give high yields of ferrocenyl substituted siloxanes (Scheme 1). The progress of the reaction was monitored by NMR every 6 h. ^{29}Si NMR indicated the gradual disappearance of the silicon Si–H signals at δ −36.34 ppm and the emergence of the product signals at δ −57.86, −58.48, −58.61, and −58.82 ppm. After 24 h the reaction was 97% complete. This was further confirmed by IR analysis which indicated total consumption of the OH and Si–H bands at ν 3450 cm^{-1} and ν 2160 cm^{-1}, respectively.

The reaction of the racemic α-methylferrocenemethanol **2** with the linear siloxane polymer **b** proceeded cleanly but at a slower rate (85% yield after 48 h) than the reaction of **1** with the same polymer. The results were anticipated since the former is a primary alcohol where as the latter is a secondary alcohol.

The reaction with the linear copolymer **c**, which contains 50–55 mol% of Si–H units, was carried out using excess **1**. The copolymer was isolated as a red oil by repeated precipitation from a CH_2Cl_2 solution by

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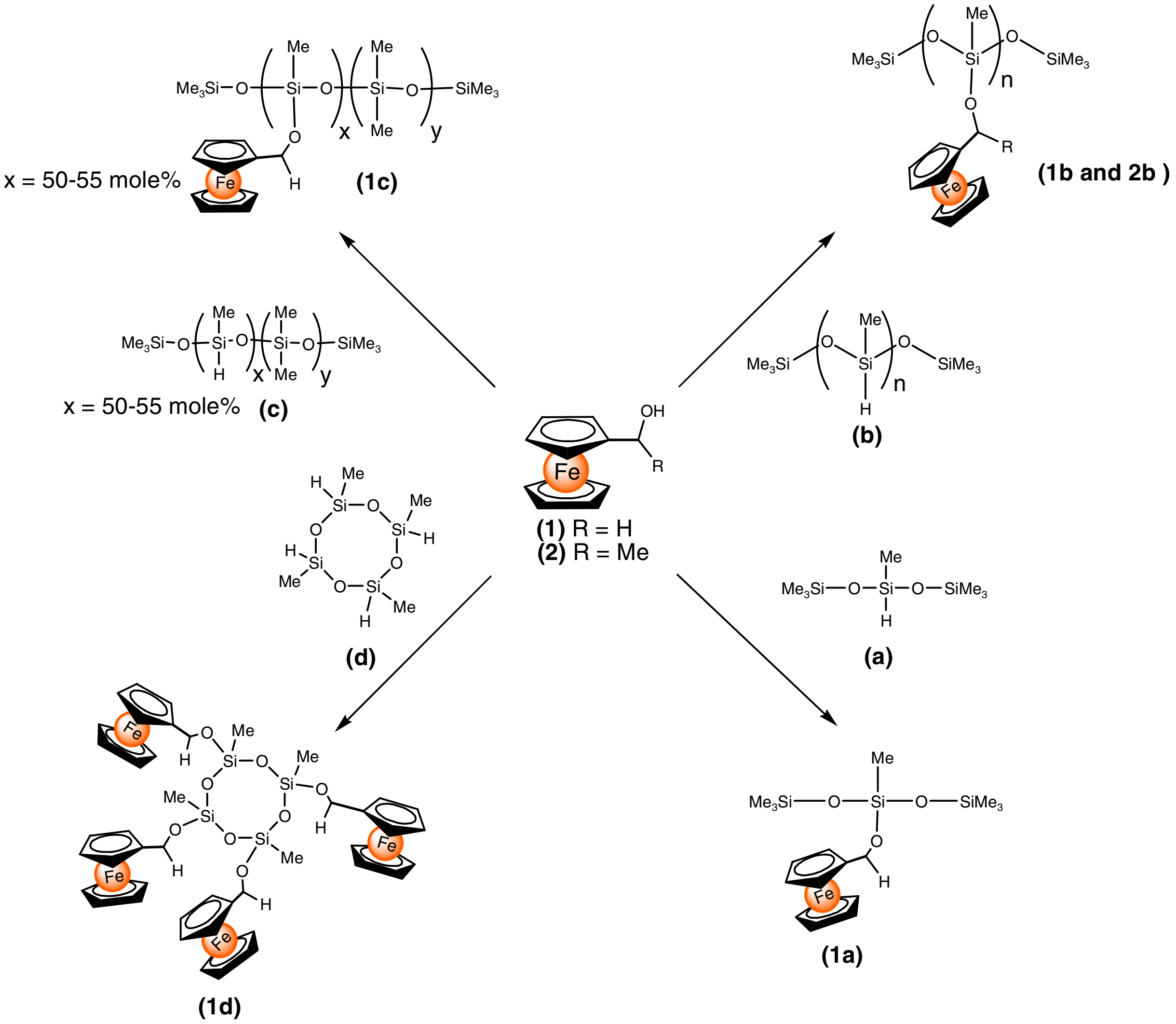

Scheme 1.

dropwise addition into large excess of acetonitrile at room temperature. The red oil copolymer was obtained after solvent removal. ^{29}Si NMR analysis of the final product shows signals at δ +7.27 (terminal $OSiMe_3$); −20.00 to −22.00 (m, broad, $SiMe_2$); −56.04 to −58.84 (m, broad, SiMe).

Ferrocene substituted tetramethylcyclohydrosiloxane **1d** was obtained in 80% yield using the same approach. The polymers were stable for several months in toluene and in the solid state under an inert atmosphere at ambient temperature. This was confirmed by IR and NMR analyses of the polymer, the latter showing no change in the ^{1}H, ^{13}C and ^{29}Si spectra. In all cases, the ferrocene substituted siloxanes were soluble in dichloromethane, THF, toluene, benzene, and chloroform and insoluble in acetonitrile, methanol, and hexane.

Several other catalysts were investigated for the dehydrogenative coupling of **1** with polymer **b** in benzene. The results are summarized in Table 1. The efficiency and selectivity of Wilkinson's catalyst were excellent, giving rise to a 97% yield of **1b**. Catalysts used in entries 2 and 3 were less selective and gave low yield. The byproducts isolated from entries 2 and 3 were insoluble in benzene, toluene, THF, CH_2Cl_2, and $CHCl_3$. Entries 5, 6, and 7 gave <5% of **1b** as determined by NMR.

The dehydrogenative coupling of ferrocenemethanol **1** was carried out in different solvents and found to be solvent dependent (Table 2). Benzene and toluene were the solvents of choice, giving 94–97% of poly(ferrocenylmethoxysiloxane) in ~24 h. The reaction in THF gave good yields but proceeded at a slower rate than in benzene and toluene. In dichloromethane the reaction was slower yet and gave the lowest yield.

In conclusion, our results demonstrate that dehydrogenative coupling of hydrosiloxanes with ferrocenemethanol promoted by Wilkinson's catalyst is an efficient route to ferrocenyl substituted siloxanes.

Table 1
Survey of catalysts for the dehydrogenative coupling reaction[a]

Entry	Catalyst	Catalytic loading (mmol%)	Reaction temperature (°C)	Reaction time (h)	Yield of **1b** (%)
1	$RhCl(PPh_3)_3$	1	78	24	97[b]
2	Karstedt's catalyst[c]	4×10^{-3}	rt	12	10[d]
3	$H_2PtCl_6\cdot6H_2O$	1	50	6	–[e]
4	$Co_2(CO)_8$	1	50	12	20[d]
5	10% Pd/C	1	60	24	<5%[b]
6	10% Pt/C	1	60	24	<5%[b]
7	5% Rh/C	1	60	24	<5%[b]

[a] The catalyst survey was carried out in C_6D_6.
[b] NMR yield.
[c] Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, solution in xylenes.
[d] Isolated yield.
[e] The reaction mixture formed a green gel after 6 h.

Table 2
Survey of solvents for the dehydrogenative coupling reaction

Solvent	Yield[a] (%)	Reaction time (h)
Benzene	97	24
Toluene	94	22
THF	85	36
Dichloromethane	60	72

[a] Determined by NMR.

3. Experimental

3.1. General

All reactions were carried out under argon. Air-sensitive products and reagents were handled by standard Schlenk techniques. All solvents were purified by using double column Solve-Tek Inc. (Berryville, VA) systems of activated alumina. Glassware was dried in an oven at 110–120 °C and purged with argon prior to use. Bis(trimethylsiloxy)methylsilane **a**, poly(methylhydrosiloxane) **b**, $Me_3Si–(O–SiMeH–)_n–O–SiMe_3$ ($M_w\sim2000$; $n=33–35$), poly(methylhydrodimethylsiloxane) copolymer **c**, $Me_3Si–(O–SiMeH)_x–O–(Me_2Si)_y–O–SiMe_3$ ($M_w\sim900–1200$; $x=50–55$ mol% SiH), and tetramethylhydrocyclosiloxane **d** were purchased from Gelest and used without further purification. Ferrocenemethanol, α-methylferrocenemethanol, $RhCl(PPh_3)_3$ (99.99%), Karstedt's catalyst, 10% Pd/C, 10% Pt/C, and 5% Rh/C were obtained from Aldrich and used as received. $Co_2(CO)_8$ was purchased from Strem Chemicals Inc. and used as received. ^{29}Si, ^{13}C, and ^1H NMR spectra were recorded on Varian Mercury-500 MHz and Inova-400 MHz spectrometers. ^1H and ^{13}C chemical shifts were measured against Me_4Si using solvent resonance as standard locks. ^{29}Si chemical shifts were referenced to external Me_4Si in the same solvent. IR spectra were recorded on a Matheson Instruments 2020 Galaxy Series spectrometer as KBr pellets or solutions in CaF_2 cells. Al_2O_3, activated, neutral, Brockmann I, standard grade (150 mesh) was used for purification after drying at in 110–120 °C in an oven prior to use.

*3.1.1. Synthesis of compounds **1a–1d***

In a Schlenk tube, $RhCl(PPh_3)_3$ (18 mg, 0.02 mmol) and bis(trimethylsiloxy)methylsiloxane **a** (0.55 ml, 2 mmol) were suspended in 1.00 ml of dry C_6D_6. Ferrocenemethanol **1** (0.432 g, 2.000 mmol) was added to the mixture. This mixture was degassed by three or four freeze-pump-thaw cycles and heated in an oil bath at 78 °C, under a constant flow of argon. Evolution of H_2 was observed during the entire course of the reaction. As the reaction progressed, the red reaction mixture darkened noticeably. The mixture was cooled to room temperature and eluted (toluene) through a short column of dried Al_2O_3. Solvent removal under reduced pressure provided the desired products.

*3.1.2. Bis(trimethylsiloxy)methyl(ferrocenylmethoxy)-siloxane (**1a**)*

Red oil was obtained in 90% yield. ^1H NMR ($CDCl_3$, 25 °C): δ 0.27 (s, $OSiMe_3$); 0.18 (s, SiMe); 4.62 (s, broad, OCH_2); 4.33, 4.24 (Cp). ^{13}C NMR ($CDCl_3$, 25 °C): δ 2.10 ($OSiMe_3$); −3.09 (s, SiMe); 60.77 (s, OCH_2); 87.24, 69.64, 68.82, 68.72, 68.66, 68.30 (Cp). ^{29}Si NMR ($CDCl_3$, 25 °C): δ −56.98 (SiMe); +8.34 ($OSiMe_3$). Anal. Calc. for $C_{18}H_{31}FeO_3Si_3$: C, 49.64; H, 7.17. Found: C, 49.69; H, 7.20%.

*3.1.3. Poly[methyl(ferrocenylmethoxy)siloxane] (**1b**)*

Red tacky material was obtained in 90% yield. ^1H NMR (C_6D_6, 25 °C): δ 0.303 (s, $OSiMe_3$); 0.54 (s, broad, SiMe); 4.90 (s, broad, OCH_2); 4.60–3.98 (m, Cp). ^{13}C NMR (C_6D_6, 25 °C): δ 2.06 (s, $OSiMe_3$); −3.01 (s, SiMe); 61.34 (broad, OCH_2); 86.93, 69.17, 68.94, 68.81, 68.55 (Cp). ^{29}Si NMR (C_6D_6, 25 °C): δ −57.86, −58.48, −58.61, −58.82 (SiMe); +9.85 (terminal $OSiMe_3$).

*3.1.4. Poly[methyl(α-methylferrocenylmethoxy)siloxane] (**2b**)*

Red tacky material was obtained in 85–80% yield. ^1H NMR (C_6D_6, 25 °C): δ 0.19 (s, broad, $OSiMe_3$, SiMe);

1.49 (s, broad, CH_3); 4.03 (broad, Cp); 4.93 (broad, OCH). ^{13}C NMR (C_6D_6, 25 °C): δ 1.50 ($OSiMe_3$); −2.81 (broad, SiMe); 24.33 (broad, CH_3); 65.91 (broad, OCH); 92.99, 68.79, 67.73, 66.88 (Cp). ^{29}Si NMR (C_6D_6, 25 °C): δ −58.94, −59.77 (SiMe); +9.87 (terminal $OSiMe_3$).

*3.1.5. Poly[methyl(ferrocenylmethoxy)dimethylsiloxane] copolymer (**1c**)*

$RhCl(PPh_3)_3$ (45 mg, 0.05 mmol) and poly(methylhydrodimethylsiloxane) copolymer (**c**) (50 mol% SiH) (0.807 g) were suspended in 6.00 ml of dry toluene. Excess ferrocenemethanol (1.900 g, 8.794 mmol) was added to the mixture. The reaction was complete after 24 h of heating at 78 °C. The copolymer was isolated by repeated precipitation from CH_2Cl_2 solution by dropwise addition into large excess of acetonitrile at room temperature. The copolymer was dried under vacuum to afford red oil material in 79% yield. ^1H NMR ($CDCl_3$, 25 °C): δ 0.15 (s, broad $SiMe_2$, SiMe); 4.58 (s, broad, OCH_2); 4.27, 4.17 (Cp). ^{13}C NMR ($CDCl_3$, 25 °C): δ 2.06 (s, $OSiMe_3$); 1.35 (broad, SiMe, $SiMe_2$); 61.05 (broad, OCH_2); 86.76, 69.60, 68.99, 68.72, 68.32, 68.20 (Cp). ^{29}Si NMR ($CDCl_3$, 25 °C): δ +7.27 (terminal $OSiMe_3$); −20.00 to −22.00 (m, broad, $SiMe_2$); −56.04 to −58.84 (m, broad, SiMe).

*3.1.6. Tetramethyltetraferrocenylmethoxycyclosiloxane (**1d**)*

$RhCl(PPh_3)_3$ (72 mg, 0.08 mmol) and tetramethylcyclohydrosiloxane (**d**) (0.48 ml, 2.00 mmol) were suspended in 5.00 ml of dry toluene. Excess ferrocenemethanol (3.456 g, 16.00 mmol) was added to the mixture. The reaction was complete after 36 h of heating at 78 °C. Isolation of the product afforded red-orange oil in 80% yield. ^1H NMR ($CDCl_3$, 25 °C): δ 0.22 (broad, MeSi); 4.60 (s, broad, OCH_2); 4.27, 4.15 (Cp). ^{13}C NMR ($CDCl_3$, 25 °C): δ −3.74 (m, broad, SiMe); 61.16 (s, OCH_2); 86.44, 69.61, 68.98, 68.82, 68.73, 68.20 (Cp). ^{29}Si NMR ($CDCl_3$, 25 °C): δ −58.60, −58.70, −58.80 (SiMe).

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