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Preliminary communication

Hydrosilylation of an hexa-olefin star with organometallic hydrogenosilanes: ferrocenylsilylation and desilylenation☆

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Abstract

The regiospecific hydrosilylation of the star-shaped hexa-olefin $[C_6(CH_2CH_2CHCH_2)_6]$ with $[FcSiMe_2H]$ (Fc = ferrocenyl) is catalyzed by the Karstedt catalyst, giving the hexaferrocene complex $[C_6\{(CH_2)_4SiMe_2Fc\}_6]$, which was purified by chromatography and characterized by its molecular peak in the MALDI TOF mass spectrum, whereas the same reaction with the new silane $[FeCp(\eta^6\text{-}C_6Me_5CH_2SiMe_2H)][PF_6]$ gives the desilylenation product $[FeCp((\eta^6\text{-}C_6Me_6)][PF_6]$. © 1999 Elsevier Science S.A. All rights reserved.

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Hydrosilylation is a powerful tool to functionalize organic molecules [1]. For this reaction, the Karstedt catalyst of empirical formula $[Pt_2(CH_2{=}CHSi(Me)_2OSi(Me)_2CH{=}CH_2)_3]$, which follows a mechanism involving colloids, has predominated in recent years [2]. In particular, it has been used to introduce the ferrocene unit on the periphery of dendrimers [3–5].

During our research program on the synthesis and functions of redox active organometallic dendrimers [6], we have investigated the synthetic potential of the star-shaped hexaolefin core $[C_6(CH_2CH_2CHCH_2)_6]$, **1**, easily available by $FeCp^+$ induced hexa-allylation of C_6Me_6 in $[FeCp(C_6Me_6)][PF_6)]$, **2** [6a]. We now report our first results of hydrosilylation of **1** with Karstedt catalyst and the two organometallic hydrogenosilanes: $[FcSiMe_2H]$, **3**, already used by Cuadrado et al. and by Jutzi et al., and the new complex $[FeCp(\eta^6\text{-}C_6Me_5CH_2SiMe_2H)][PF_6]$, **4**.

The hydrosilylation of **1** with a two-fold excess of **3** and a few drops of the Karstedt catalyst at 40°C for 12 h gives a reaction mixture whose thin layer chromatogram analysis yields two ferrocene derivatives in addition to **3**. Column chromatography on silica using pentane/ether as eluents provided a correct separation of these orange ferrocene derivatives. The ^{1}H- and ^{13}C-NMR spectra indicated that only one compound showed a star-shape structure corresponding to branching. Further characterization by elemental analysis and MALDI TOF mass spectrum (Fig. 1, molecular peak, 100%: m/z 1867.58) confirmed the structure of the hexa-hydrosilylated reaction product and the purity of the new hexa-ferrocenyl derivative **5** obtained in 85% yield (Scheme 1). Note that no isomerization of the terminal olefin was found, as indicated by the absence of signals near δ 5.9 ppm for internal olefin protons in the ^{1}H-NMR spectrum. In addition, the cyclic voltammogram of **5** (Pt, CH_2Cl_2, $[NBu_4][PF_6]$, 0.1 M; internal

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☆ Dedicated to our friend Professor Alan H. Cowley FRS on the occasion of his 65th birthday.

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reference: [FeCp(η^6-$C_6H_5CH_3$)][PF_6]) showed the presence of only one ferrocene/ferrocenium wave at 0.475 V versus SCE as ferrocene itself ($\Delta E = E_{pa} - E_{pc} = 30$ mV at 25°C; for the reference, $\Delta E = 60$ mV). Comparison of the intensity of this wave with that of ferrocene (external reference) using the Bard–Anson formula [7] indicated that the redox process does involve 6 electrons as expected (found: 6.1 ± 0.4). This successful ferrocenylsilylation of **1** is an excellent model reaction for the analogous reactions with large poly-olefin terminated dendrimers now in progress.

Surprisingly, the analogous reaction of **1** using **4** as an hydrogenosilane agent reproducingly did not lead to any hydrosilylation product, and **1** was recovered. The organometallic compound formed in high yield was **2** resulting from the loss of the dimethylsilylene group $SiMe_2$ (Scheme 2). Since **4** is thermally stable, this reaction shows that the Karstedt catalyst induces the catalytic loss of $SiMe_2$ from **4**. This process probably occurs in a concerted way at the level of the [$ArCH_2SiPtH$] intermediate formed after oxidative addition of the Si–H bond of **4** on a silicon center (whether molecular or colloidal) of the catalyst. Note that no previous failure of such hydrosilylation was reported using neutral silanes (such as **3**). In the present case, the catalyzed desilylenation is induced clearly by the ionic nature of the silane. Since silanes are subjected to reactions of nucleophiles at the Si center and electrophiles at the C center attached to the Si atom [8], both the electrophilic cationic iron center (intramolecularly) and the weakly nucleophilic anionic PF_6^- (in the contact ion pair) are candidates to assist the process. Further work is needed, however, to establish this catalytic desilylenation mechanism, especially in order to trap the synthetically useful silylene group.

*Experimental procedure and selected physical data for **4** and **5**.* (**4**) Me_2SiHCl (0.70 g, 7.48 mmol) was added at 20°C to a THF (10 ml) solution of [FeCp(η^5-$C_6Me_5CH_2$)] (1.92 g, 6.8 mmol). A yellow precipitate appeared instantaneously. The solution was allowed to stir for 15 min, the solvent was then removed under vacuum. After metathesis with aqueous HPF_6, the yellow solid was redissolved in CH_2Cl_2 and dried over Na_2SO_4; reprecipitation by addition of excess ether gave **4** as a yellow powder (yield: 62%). IR (KBr, Si–H stretch): $\nu = 2122$ cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 4.45$ (s, 5H, C_5H_5), 3.87 (m, 1H, SiH), 2.54 (d, ^3J(HH) = 3.6 Hz, 2H, CH_2Si), 2.45 (s, 6H, ArMe), 2.43

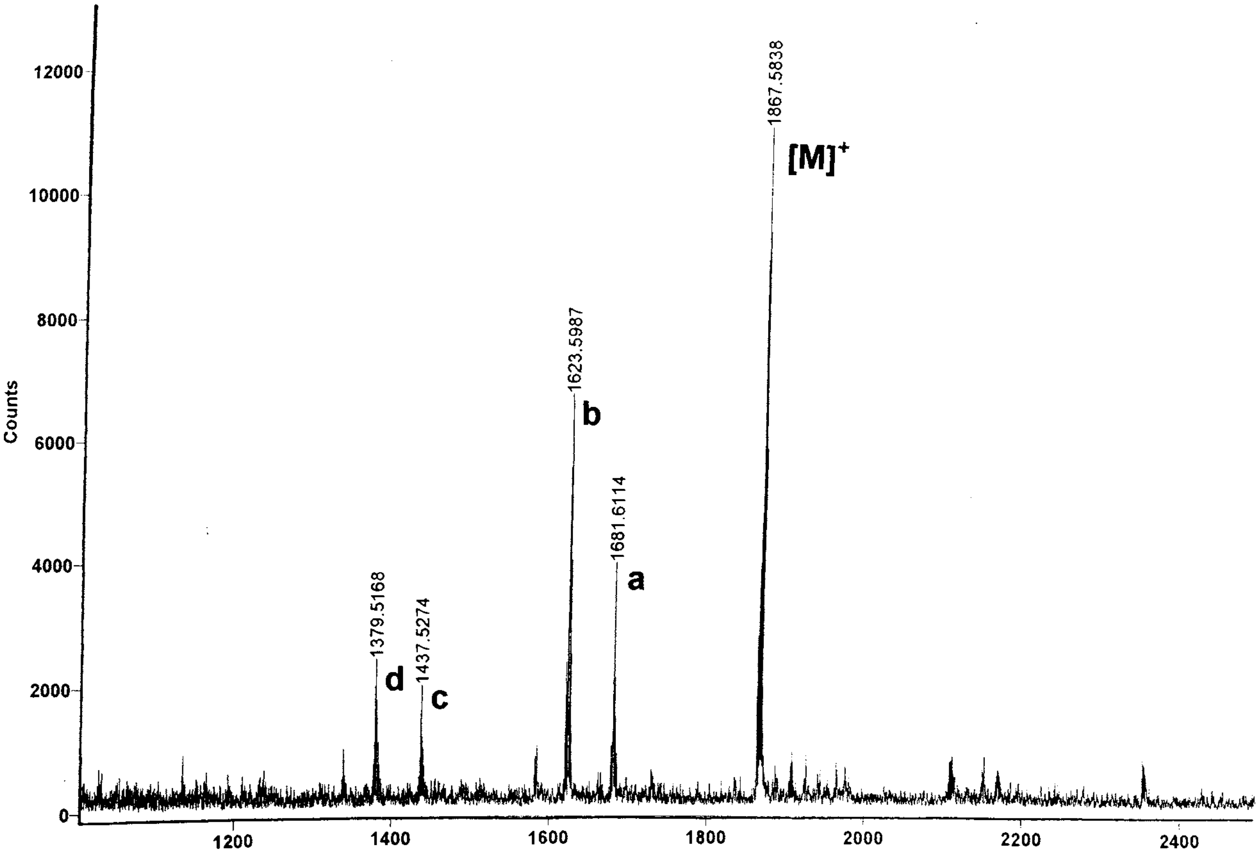
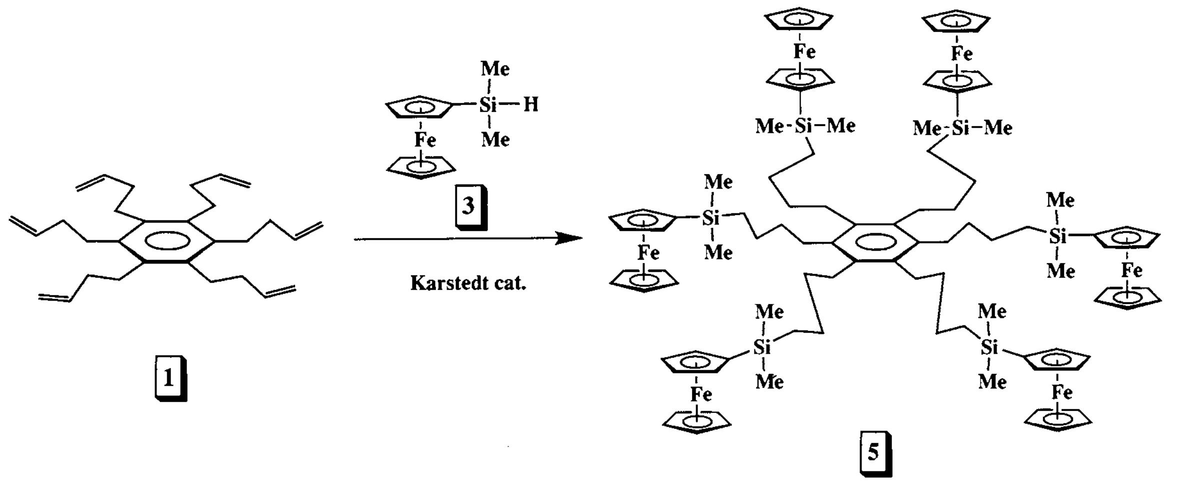
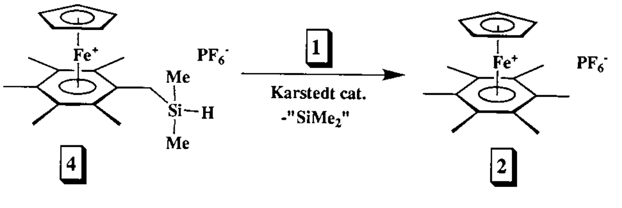


Fig. 1. MALDI TOF mass spectrum of **5**. M: molecular peak; (a) [M–FcH]$^+$; (b) [M–$FcSiMe_2H$]$^+$; (c) [M–Fc–$FcSiMe_2H$]$^+$; (d) [M–2$FcSiMe_2H$]$^+$. Note that the peaks **a** and **c** correspond to silylene terminated branches.



Scheme 1.



Scheme 2.

(s, 9H, Ar*Me*), 0.12 (d, ^3J(HH) = 3.7 Hz, 6H, Si*Me*$_2$). ^{13}C{^{1}H}-NMR (50.32 MHz, CDCl$_3$): $\delta = 96.41$, 97.98, 98.58, 103.65 (Cq, *Ar*), 78.42 (C_5H_5), 19.83 (CH$_2$Si), 17.47, 17.70, 18.04 (Ar–CH$_3$), -3.99 (SiCH$_3$). Anal. Calc. for $C_{19}H_{29}Fe_1Si_1P_1F_6$: C, 46.92; H, 6.01. Found: C, 46.78; H, 5.94. (**5**) A 1% solution of the Karstedt catalyst in xylene (0.5 ml) was added to a solution of **1** (40 mg, 0.1 mmol) in toluene (10 ml). Air was passed briefly through the solution, then dimethylferrocenylsilane **3** (293 mg, 1.2 mmol) in a small amount of toluene was added dropwise. The mixture was stirred overnight at 40°C and the solvent and excess of ferrocenylsilane were removed under high vacuum. The residue was purified by chromatography (pentane/ether, silica) to give **5** as an orange, waxy solid (yield: 85%). ^{1}H-NMR (200 MHz, CDCl$_3$): $\delta = 4.35$ (bs, 12H, C_5H_4), 4.15 (s, 30H, C_5H_5), 4.11 (bs, 12H, C_5H_4), 2.47 (m, 12H, CH_2Ar), 1.54 (m, 24H, CH_2CH_2Ar + CH_2CH_2Si), 0.73 (m, 12H, CH_2Si), 0.26 (s, 36H, SiMe$_2$). ^{13}C{^{1}H}-NMR (50.32 MHz, CDCl$_3$): $\delta = 137.11$ (Cq, Ar), 73.24 (Cq, C_5H_4), 73.08, 70.38 (C_5H_4), 68.18 (C_5H_5), 35.39 (CH_2Ar), 29.70 (CH_2CH_2Ar), 25.17 (CH_2CH_2Si), 16.19 (CH_2Si), -2.75 (SiCH$_3$). Anal. Calc. for $C_{102}H_{138}Fe_6Si_6$: C, 65.59; H, 7.45. Found: C, 65.89; H, 7.64. MS (MALDI-TOF): *m*/*z* (%) 1867.58 [M$^+$] (100%).

Acknowledgements

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