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Chloromethylsilane functionalised dendrimers: synthesis and reactivity

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Abstract

Tetraallylsilane was functionalised using (chloromethyl)dimethylsilane to give the first generation chloromethyl terminated dendrimer **1**. The resulting dendrimer was successfully reacted with $K[CpM(CO)_2]$ ($Cp = \eta^5$-C_5H_5; M = Fe, Ru) to give $Si[(CH_2)_3SiMe_2CH_2MCp(CO)_2]_4$ functionalised dendrimers in satisfactory yield. Reaction of dendrimer **1** with NaI in acetone gave the $-SiMe_2CH_2I$ functionalised dendrimer, while reactions of **1** with $K[CpM(CO)_3]$ (M = Mo, W, Re), $Li[C_5Me_4H]$, $Na[C_5Me_4H]$, the cobaloxime nucleophile or *tert*-BuLi were not successful.

Keywords: Dendrimer; Carbosilane; Iron; Ruthenium; Silicon

1. Introduction

The rising demand for materials with improved and novel properties has shifted the emphasis in polymer research from traditional linear polymers, via cross-linked and branched polymers, to hyperbranched or dendritic polymers. This new class of highly branched three-dimensional molecules has intrigued researchers and numerous review articles have been published in recent years [1,2]. Many applications for dendrimers have been found, one of the most exciting applications being the use of dendrimers as an immobilisation phase for homogeneous catalysts [3]. From our ongoing research into dendrimers and their applications in organometallic chemistry [2,4,5], it has become clear that the number of synthetic routes available to attach an organometallic moiety to the branches of a dendrimer is limited. This limitation is mainly due to the requirement to employ reactions that have a quantitative yield in order to prevent imperfections and by-products in the dendrimer build-up [6,7].

2. Results and discussion

Dendrimers containing (chloromethyl)dimethylsilane functionalities were conveniently obtained through the catalytic hydrosilylation reaction of allyl-functionalised dendrimers with (chloromethyl)dimethylsilane [8] (Fig. 1).

We previously reported on the synthesis of $C_pRu(CO)_2$-functionalised functionalised benzylphenyl ether substituted dendrimers [4], and attempted to synthesise a carbosilane equivalent of these dendrimers. A report by Cuadrado [9] described the synthesis of a $CpFe(CO)_2$ functionalised carbosilane dendrimer. The dendrimer described in that report [9] contained a reactive Fe–Si bond and we attempted to synthesise a more robust carbosilane dendrimer by introducing a methylene group between the silicon and the metal. Reaction of the first generation chloromethyl terminated dendrimer **1** with $K[CpFe(CO)_2]$ [10] and $K[CpRu(CO)_2]$ [10] proved successful. These reactions were followed by TLC and resulted in the fully substituted dendrimers **2** and **3** in good yields (Fig. 2), after prolonged reaction times (~18 h). Dendrimers **2** and **3**

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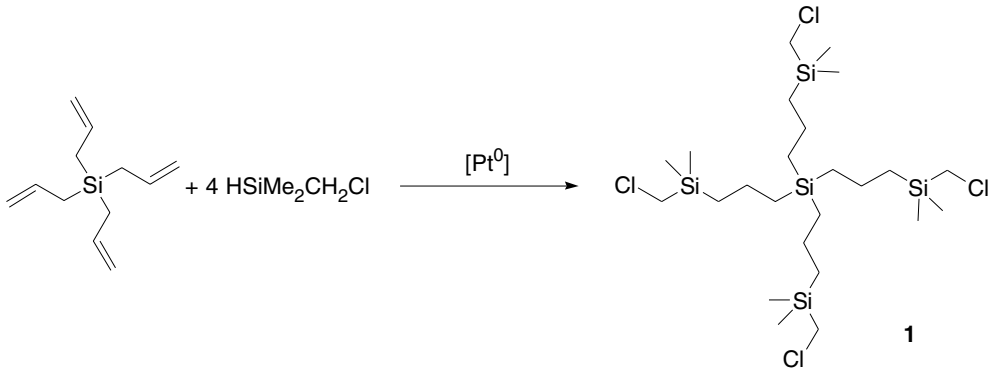

Fig. 1. Synthesis of a first generation chloromethyl terminated dendrimer.

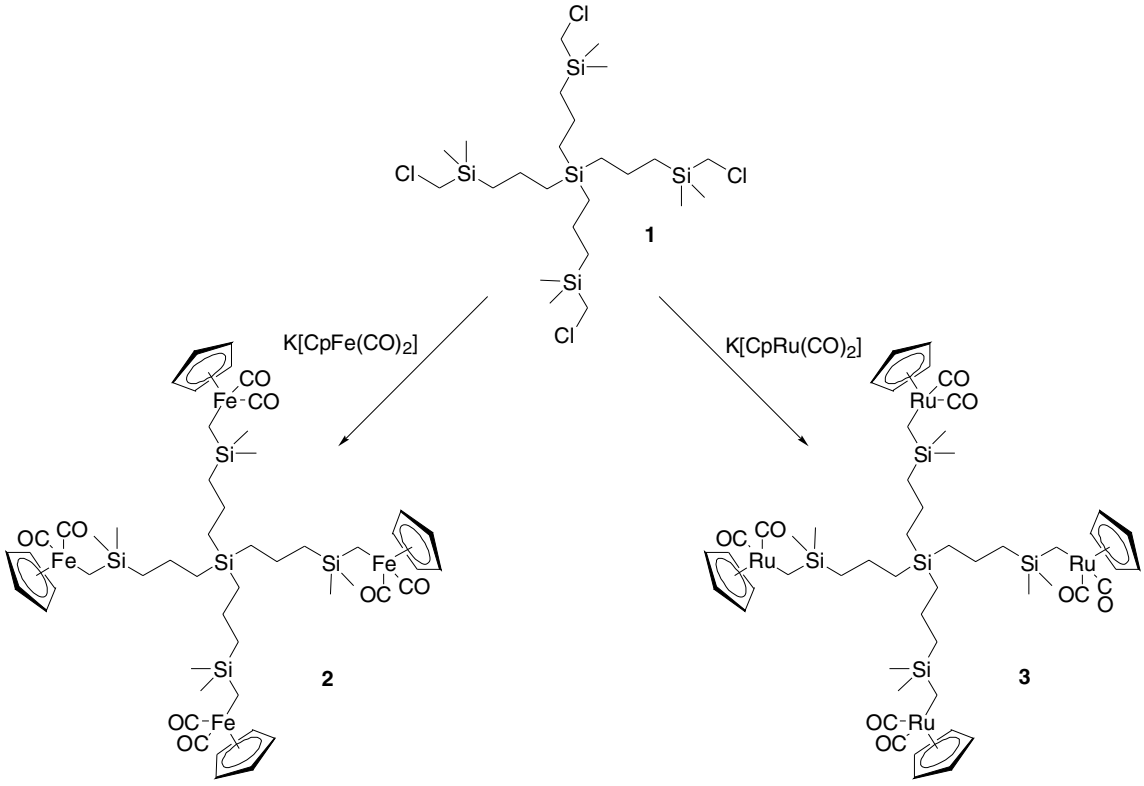

Fig. 2. Synthesis of iron and ruthenium containing dendrimers **2** and **3**.

were purified by column chromatography and were isolated as air-stable oils. ^{1}H and ^{13}C NMR spectroscopy revealed that full substitution of the chlorine for the $CpM(CO)_2$ (M = Fe, Ru) dendrimers had occurred and no traces of the CH_2Cl signal at δ 2.76 (400 MHz) were observed. FT-IR spectroscopy also confirmed the purity of the products; no traces of the dimeric starting material $[CpM(CO)_2]_2$; (M = Fe, Ru) were present. IR and NMR spectroscopy also confirmed the stability of the compounds as no traces of decomposition products were observed. Unfortunately, mass spectrometry (EI and FAB) resulted in decomposition products, and neither the parent ion nor any identifiable fragments were found.

From the substitution reactions using $K[CpFe(CO)_2]$ and $K[CpRu(CO)_2]$ it was concluded that nucleophilic substitution reactions using metal nucleophiles on dendrimer **1** should be feasable. We therefore endeavored to react dendrimer **1** with weaker nucleophiles such as $K[CpW(CO)_3]$ [10] and $K[CpMo(CO)_3]$ [10]. Reaction of dendrimer **1** with these nucleophiles was, however, not successful. Some substitution on the dendrimer occurred, but we were not able to quantitatively drive the substitution reaction to completion, despite a large excess of nucleophiles and prolonged reaction times. Since we have previously been successful to synthesising a zeroth generation functionalised dendrimer of the benzylphenyl ether type [11], we opted to react dendrimer **1** with the

strong cobaloxime nucleophile. Surprisingly the reaction of dendrimer **1** with the cobaloxime nucleophile was not successful. Since we performed this reaction using the normal reaction conditions, and negligible nucleophilic substitution occurred, we did not investigate the reaction further. We also previously reported on the synthesis of $CpRe(CO)_3$ functionalised benzylphenyl ether dendrimers [12] and decided to investigate the reaction of $K[CpRe(CO)_3]$ with dendrimer **1** but unfortunately the reaction of dendrimer **1** with $K[CpRe(CO)_3]$ was also proved unsuccessful. Reaction of dendrimer **1** with tetramethylcyclopentadienyllithium or -sodium in refluxing THF did not give the expected tetramethylcyclopentadiene terminated dendrimer, nor did reaction of **1** with eight equivalents of *tert*-BuLi in diethyl ether at −78 °C result in the lithiated dendrimer [13]. We attributed these unsuccessful reactions to the relative inertness of the chlorine atom on the methylene functionality since apparently the chloro group was stabilised by the silicon atom, which removed sufficient electron density from the chloro group. However, by heating **1** in dry acetone under reflux in the presence of sodium iodide, the chloro group was replaced by the more reactive iodo group. Prolonged reaction times were again necessary to drive this reaction to completion. The iodomethyl-substituted dendrimer, $Si[(CH_2)_3\text{-}SiMe_2CH_2I]_4$ (**4**) was readily identified from its ^1H NMR spectrum. There was an upfield shift of the CH_2X (X = Cl, I) proton resonance from δ 2.76 to δ 2.00 ppm. By comparison, we performed the same reaction with a model compound, $Me_3Si(CH_2)_3\text{-}SiMe_2CH_2Cl$, and found the same reactivity trend.

3. Conclusions

Three new dendrimers were synthesised on the basis of chloromethyl terminated dendrimer **1**. The new $CpFe(CO)_2CH_2$- and $CpRu(CO)_2CH_2$-terminated dendrimers were characterised by ^1H, ^{13}C and IR spectroscopy. Mass spectrometry proved inconclusive on these dendrimers. Several reactions of dendrimer **1** were performed but proved unsuccessful due to the relative inertness of the chloromethyl group. The chloromethyl group can, however, be replaced by an iodomethyl group through reaction of the **1** by reaction with NaI in acetone.

4. Experimental details

4.1. General remarks

Manipulations of sensitive compounds were carried out under purified nitrogen using glovebox (MBraun Unilab) or standard Schlenk line techniques under purified argon [14]. Solvents were dried by passage through a column containing alumina (neutral, Brockmann grade I) and distilled from sodium/benzophenone ketyl prior to use [15]. All reagents were stored under argon. Tetraallylsilane and allyltrimethylsilane were purchased from Sigma Aldrich. $[CpFe(CO)_2]_2$ and $Ru_3(CO)_{12}$ were purchased from Strem. (Chloromethyl)dimethylsilane [16], $Si[(CH_2)_3SiMe_2CH_2Cl]_4$ [8] and $[CpRu(CO)_2]_2$ [17] were prepared by literature methods. Karstedt catalyst [18] was prepared according to literature methods and stored under argon as a 1% Pt solution in toluene.

NMR spectra were recorded on either a Varian Unity-400 (^1H: 400 MHz; ^{13}C: 100.6 MHz) spectrometer or a Varian Mercury-300 (^1H: 300 MHz; ^{13}C: 75.5 MHz) spectrometer at ambient temperature. Chemical shifts were referenced to TMS using either the residual protio impurities in the solvent (^1H NMR), the solvent resonances (^{13}C NMR) or external TMS (^{29}Si NMR). Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer in the range 450–4400 cm^{-1}. Spectra were recorded on neat samples between NaCl plates. Mass spectra were determined by Dr P. Boshoff of the mass spectrometry unit at the Cape Technikon. The selected m/z values given refer to the isotopes ^1H, ^{12}C and ^{28}Si. In all cases, the isotopic distribution pattern was checked against the theoretical distribution. Elemental analyses were performed using a Carlo Erba EA1108 elemental analyzer at the microanalytical laboratory of the University of Cape Town.

4.2. Synthesis of $Si[(CH_2)_3Si(CH_3)_2CH_2Fe(CO)_2\text{-}C_5H_5]_4$ (2)

$[CpFe(CO)_2]_2$ (0.300 g, 0.85 mmol) was cleaved over NaK-melt (from 0.200 g K and 0.060 g Na) in THF in 2.5 h in a H-type Schlenk-tube [19]. The mixture was filtered and a solution of $Si[(CH_2)_3Si(CH_3)_2CH_2Cl]_4$ (0.100 g, 0.16 mmol) in THF (2.0 cm^3) was added via syringe. The mixture was stirred overnight and the solvent distilled off *in vacuo*. Extraction with pentane gave a yellow solution. The product was purified through column chromatography (silica/CH_2Cl_2:hexane = 1:1) and the first yellow band was collected. Evaporation of the solvent gave a yellow oil: $Si[(CH_2)_3Si(CH_3)_2\text{-}CH_2Fe(CO)_2C_5H_5]_4$ (**2**) (0.169 g, 89%), Rf(silica/CH_2Cl_2:hexane = 1:1) 0.79; ν_{max}/cm^{-1} 2011 (s, ν(CO)) and 1959 (s, ν(CO)) (hexane); $\delta_H(CDCl_3$, 400 MHz) 4.79 (20 H, s, 4 C_5H_5), 1.36 (8 H, m, 4 $CH_2CH_2CH_2$), 0.59 (16 H, m, ^3J(HCCH) 8 Hz, 8 $SiCH_2$), 0.01 (24 H, s, 8 CH_3) and −0.32 (8 H, s, 4 CH_2Fe); $\delta_{C\{H\}}(CDCl_3$, 100.6 MHz) 217.45 (8 C, 8 CO), 84.84 (20 C, 4 C_5H_5), 24.04 (4 C), 19.02 (4 C), 17.95 (4 C), 0.24 (8 C, 8 CH_3) and −24.99 (4 C, 4 CH_2Fe).

4.3. Synthesis of $Si[(CH_2)_3Si(CH_3)_2CH_2Ru(CO)_2\text{-}C_5H_5]_4$ (3)

$[CpRu(CO)_2]_2$ (0.300 g, 0.68 mmol) was cleaved over NaK-melt (from 0.200 g K and 0.060 g Na) in THF in

2.5 h in a H-type Schlenk-tube [19]. The mixture was filtered and a solution of $Si[(CH_2)_3Si(CH_3)_2CH_2Cl]_4$ (0.100 g, 0.16 mmol) in THF (2.0 cm^3) was added via syringe. The mixture was stirred overnight and the solvent distilled off *in vacuo*. Extraction with pentane gave a colourless solution. The product was purified through column chromatography (silica/CH_2Cl_2:hexane = 1:1) and the first band was collected. Evaporation of the solvent gave a colourless oil: $Si[(CH_2)_3Si(CH_3)_2CH_2Ru(CO)_2C_5H_5]_4$ (**3**) (0.165 g, 75%)*Rf* 0.73(silica/CH_2Cl_2:hexane = 1:1) 0.81; ν_{max}/cm^{-1} 2011 (s, ν(CO)) and 1959 (s, ν(CO)) (hexane); δ_H($CDCl_3$, 400 MHz) 4.81 (20 H, s, 4 C_5H_5), 1.36 (8 H, m, 4 $CH_2CH_2CH_2$), 0.59 (16 H, m, ^3J(HCCH) 8 Hz, 8 $SiCH_2$), 0.01 (24 H, s, 8 CH_3) and −0.22 (8 H, s, 4 CH_2Ru); $\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 217. 5 (8 C, 8 CO), 84.8 (20 C, 4 C_5H_5), 24.0 (4 C), 19.02 (4 C), 18.0 (4 C), 0.2 (8 C, 8 CH_3) and −23.8 (4 C, 4 CH_2Ru).

4.4. Synthesis of (chloromethyl)dimethyl(3-(trimethylsilyl)propyl)silane

A solution of (chloromethyl)dimethylsilane (2.0 g, 18.4 mmol) in THF (5.0 cm^3) was slowly added to a cooled (ice/water) solution of allyltrimethylsilane (2.0 g, 17.5 mmol) and Karstedt catalyst solution (1% Pt in toluene, 100 mm^3) in tetrahydrofuran (5.0 cm^3). After the addition was complete, the mixture was stirred at room temperature for 1 h and heated with reflux for 3 days. The volatiles were removed *in vacuo* to give a colourless oil mixed with a black precipitate. The solids were removed by filtration over a pad of silica and eluted with hexane. Evaporation of the hexane gave $(CH_3)_3Si(CH_2)_3Si(CH_3)_2CH_2Cl$, as a colourless oil (3.41 g; 87%) (Found: C, 48.4; H, 10.6. $C_9H_{23}Si_2Cl$ (222.9) requires C, 48.5; H, 10.4%); ν_{max}/cm^{-1} 2955 (s, $\nu_{as}(CH_3)$), 2914 (s, $\nu_{as}(CH_2)$), 2875 (s, $\nu_s(CH_3)$), 2792, 1450 (s, $\delta_{as}(CH_3)$), 1396 (m, $\delta_{as}(CH_2)$), 1337, 1249 (m, $\delta_s(CH_3)$), 1217, 1175, 1143, 1079, 1024, 944, 909, 836 (s, $\nu(Si(CH_2)_4)$), 747, 692 and 643 (neat); δ_H($CDCl_3$, 400 MHz) 1.39 (2 H, m, $CH_2CH_2CH_2$), 0.71 (2H, m, ^3J(HCCH) 8 Hz, CH_2Si), 0.58 (2 H, m, ^3J(HCCH) 8 Hz, CH_2Si), 0.11 (6 H, s, $Si(CH_3)_2$) and 0.01 (9 H, s, $Si(CH_3)_3$); $\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 30.52, 21.19, 18.18, 18.14, −1.61 (2 C, $Si(CH_3)_2$) and −4.53 (3 C, $Si(CH_3)_3$); *m/z* (EI) 209 (97), 208 (28), 207 (31) and 181 (25%) (M^+ 222 was not observed).

4.5. Synthesis of $ICH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3$

Sodium iodide (2.0 g, 13.3 mmol) and $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2Cl$, (1.500 g, 6.7 mmol) were dissolved in acetone (20 cm^3). The mixture was heated under reflux for 2 h, during which time a white solid precipitated. The volatiles were removed *in vacuo*. The remaining solids were partitioned between hexane (25 cm^3) and water (25 cm^3). The aqueous layer was extracted with hexane (3×25 cm^3). The combined organic layers were washed with water (3×25 cm^3) and brine (3×25 cm^3), dried over $MgSO_4$ and filtered. Removal of the volatiles in vacuo gave $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2I$ (1.8 g, 78%); δ_H($CDCl_3$, 400 MHz) 1.99 (2 H, s, CH_2I), 1.35 (2 H, m, $CH_2CH_2CH_2$), 0.70 (2 H, m, ^3J(HCCH) 8 Hz, $SiCH_2$), 0.55 (2 H, m, ^3J(HCCH) 8 Hz, $SiCH_2$), 0.10 (6 H, s, $Si(CH_3)_2$) and −0.03 (9 H, s, $Si(CH_3)_3$); $\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 21.2 (1 C, $CH_2CH_2CH_2$), 19.3 (1 C, $SiCH_2$), 18.3 (1 C, $SiCH_2$), −1.6 (3 C, $Si(CH_3)_3$), −3.0 (2 C, $Si(CH_3)_2$) and −13.1 (1 C, CH_2I).

4.6. Synthesis of $Si[(CH_2)_3SiMe_2CH_2I]_4$ (**4**)

This compound was prepared from $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Cl]_4$ in a similar to the preparation of $ICH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3$. Yield: 93%. ^1H and ^{13}C similar to that of the starting material except that the CH_2I resonance could be found at δ 2.00 (^1H) and δ 30.45 (^{13}C).

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