



Note

Asymmetric activation of dialkyl zirconocenes

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ABSTRACT

Asymmetric alkylmethyl zirconocene derivatives were readily synthesised from $\text{Cp}_2\text{ZrCl}(\text{CH}_3)$, and the appropriate alkylolithium reagent. The alkyl groups contain a silyl functionality on the β -position. These asymmetric dialkyl zirconocenes were successfully activated by $\text{B}(\text{C}_6\text{F}_5)_3$, selectively abstracting the methyl group. The clear difference in the ^{13}C NMR resonances, due to the alkyl groups on the cationic zirconocene made it possible to conclude that selective activation of this class of compounds was possible.

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1. Introduction

We reported previously on the hydrozirconation of alkene-terminated dendrimers and dendrimer model compounds [1] as part of our quest towards the synthesis of star-shaped polymers using zirconocene type polymerisation catalysts. The (selective) activation of these hydrozirconated dendrimers using the normal polymerisation co-catalysts, e.g. MAO, proved unsuccessful. Therefore, we decided to turn our attention to the selective activation of dialkyl zirconocene complexes.

Dialkyl zirconocene complexes that contain β -hydrogen atoms give rise to a number of problems, including thermal instability. In addition, cationic zirconocene complexes that contain β -hydrogen atoms are likely to undergo β -hydrogen elimination reactions to give a cationic zirconocene hydride and an alkene. Therefore we focussed on zirconocenes that do not contain any β -hydrogen atoms. With these considerations in mind, we decided to generate dialkyl zirconocenes that were sterically congested at the β -position. We tuned our attention to methylalkyl zirconocenes with a methyl-enedimethylsilyl group ($-\text{CH}_2\text{Si}(\text{CH}_3)_2\text{R}$) as the alkyl group. The reasoning behind investigating this class of zirconocenes was that the bulky dimethylsilyl group should give selective activation after reaction with alkyl abstraction reagents such as $\text{B}(\text{C}_6\text{F}_5)_3$ [2].

2. Results and discussion

Reaction of zirconocene dichloride, **1**, with excess methylolithium in diethyl ether afforded dimethyl zirconocene, **2** [3,4], in 80% yield.

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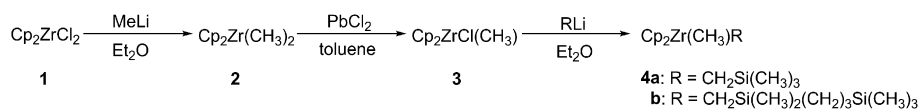
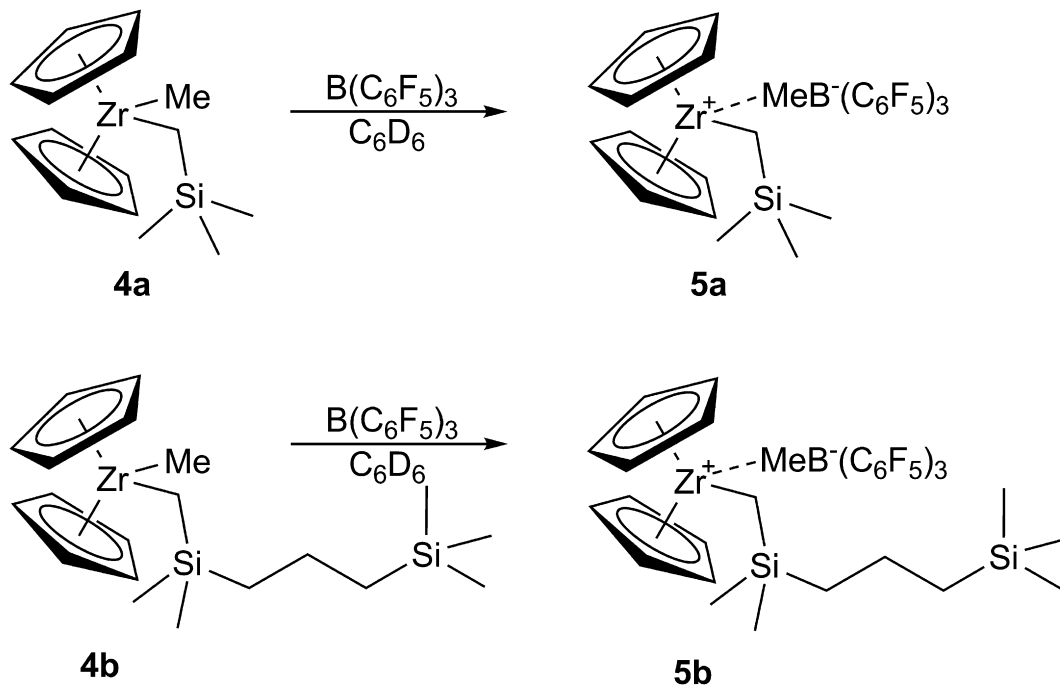
The dimethyl zirconocene, **2**, was purified by sublimation, and analysed by ^1H and ^{13}C NMR spectroscopy. Reaction of dimethyl zirconocene, **2**, with lead(II)chloride in toluene afforded the chloromethyl zirconocene, **3** [4,5], in 78% yield. This route led to a higher yield than the reaction of zirconocene dichloride, **1**, with one equivalent of methyl Grignard in dichloromethane (Scheme 1).

Reaction of chloromethyl zirconocene, **2**, with one equivalent of the appropriate lithium reagents $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$ [6], and $\text{LiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$, respectively, afforded the asymmetrically substituted dialkyl zirconocenes **4** in reasonable yields ($\sim 80\%$). It would have been advantageous to attach either a Si–H or an allylsilane functionality to the zirconocene. However, upon trying to convert either $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{H}$ or $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}=\text{CH}_2$ into the respective lithium reagents, various side reactions occurred, such as deprotonation of the allyl group, and reaction of the produced lithium reagent with the acidic Si–H bond. It appeared to be not possible to generate either $\text{LiCH}_2\text{Si}(\text{CH}_3)_2\text{H}$ or $\text{LiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}=\text{CH}_2$.

Both asymmetric dialkyl zirconocene compounds (see Fig. 1) were positively characterised by ^1H and ^{13}C NMR spectroscopy. Unfortunately we could not obtain suitable crystals of **4b** for X-ray crystallography. Attempts to obtain satisfactory elemental analyses for any of the dialkyl zirconocenes were not successful, due to the sensitivity of the dialkyl zirconocenes towards oxygen and water.

The asymmetric dialkyl zirconocenes, **4a** and **4b**, described above have to be activated in order to be able to polymerise alkenes. For our purposes, we required this activation to be selectively directed towards abstraction of the methyl group.

Reaction of the model compounds with excess $\text{B}(\text{C}_6\text{F}_5)_3$ resulted in the selective abstraction of the methyl group (Fig. 1) [7], as was

Scheme 1. Synthesis of asymmetric dialkyl zirconocenes **4a** and **4b**.Fig. 1. Selective activation of the asymmetric dialkyl zirconocenes **4a** and **4b**.

concluded from both ^1H and ^{13}C NMR spectroscopy. In order to conclude this, we also needed the ^1H and ^{13}C NMR data for $[\text{Cp}_2\text{ZrCH}_3]^+$, **5**, and $[\text{Cp}_2\text{ZrCH}_2\text{Si}(\text{CH}_3)_3]^+$, **6**. The Zr–C signal in the ^{13}C NMR spectra provided the clearest distinction between these two compounds. The ^{13}C signal for $[\text{Cp}_2\text{ZrCH}_3]^+$ (**5**) was found at δ 45 whereas the ^{13}C signal for $[\text{Cp}_2\text{ZrCH}_2\text{Si}(\text{CH}_3)_3]^+$ (**6**) appeared at δ 70. This large difference in shift is due to the electron-withdrawing properties of the silicon atom.

The compound $[\text{Cp}_2\text{ZrCH}_3]^+$, **5**, was easily obtained [2] by reacting dimethyl zirconocene, **2**, with an excess $\text{B}(\text{C}_6\text{F}_5)_3$ in benzene at room temperature. The yellow cationic methyl zirconocene, **5**, was formed instantaneously. As starting material for $[\text{Cp}_2\text{ZrCH}_2\text{Si}(\text{CH}_3)_3]^+$, **6**, the reaction of zirconocene dichloride, **1**, with excess $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$, was performed. The compound $\text{Cp}_2\text{Zr}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$, was isolated as large off-white crystals after work-up.

Upon reacting $\text{Cp}_2\text{Zr}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$, with excess $\text{B}(\text{C}_6\text{F}_5)_3$ in C_6D_6 , the formation of a yellow-brown oil was observed. Upon analysis by ^1H and ^{13}C NMR spectroscopy, it appeared that there was nothing more than a residue of starting material present in the solution. Apparently, a solvent-separated ion pair was formed—and these are known to have low solubility in benzene. When the NMR spectrum of this compound was measured in the more polar $\text{C}_6\text{D}_5\text{Br}$, a mixture of unidentified zirconocenes was observed, indicating that decomposition might have occurred. Once again, suitable crystals for X-ray crystallography could unfortunately not be obtained.

3. Conclusions

Asymmetric dialkyl zirconocene derivatives were readily synthesised from $\text{Cp}_2\text{ZrCl}(\text{CH}_3)$, and the appropriate alkyl lithium

reagent. These asymmetric dialkyl zirconocenes were successfully activated by $\text{B}(\text{C}_6\text{F}_5)_3$, selectively abstracting the methyl group. The clear difference in the ^{13}C NMR resonances, due to the alkyl groups on the cationic zirconocene made it possible to conclude that selective activation of this class of compounds was possible.

4. Experimental

4.1. General procedures

All manipulations of air- and/or moisture sensitive compounds were carried out under an inert atmosphere of argon using standard Schlenk techniques [8] or in an inert atmosphere M Braun Unilab glovebox containing dinitrogen. Inert gases were purified by passage through columns filled with molecular sieves (5 Å) and BASF catalyst [9]. Sublimations were performed according to the technique described by Pool and Teuben [10]. Syringes were stored at 60°C and all other glassware was thoroughly dried for minimal 4 h at 210°C before use.

All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of argon. Solvents were pre-dried by passage through a column containing alumina (neutral, Brockmann grade I) followed by distillation from the appropriate drying/deoxygenating agent [11], transferred into dry vessels equipped with Teflon valve closures, and stored under argon.

Allyltrimethylsilane, Cp_2ZrCl_2 and methyl lithium were obtained from Sigma–Aldrich and stored under Ar. (Chloromethyl)dime-thylsilane [12] (Found: C, 33.0; H, 8.6. $\text{C}_3\text{H}_9\text{SiCl}$ (108.6) requires C, 33.2; H, 8.4%), $\text{Cp}_2\text{ZrCl}(\text{CH}_3)$ [13] and $\text{Cp}_2\text{Zr}(\text{CH}_3)[\text{CH}_2\text{Si}(\text{CH}_3)_3]$ [14] were prepared according to literature procedures.

Microanalysis data were obtained from the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer in the range 450–4400 cm^{-1} . Samples were either prepared neat between NaCl discs for liquids. NMR spectra were recorded on a Varian Unity-400 (^1H : 400 MHz; ^{13}C : 100.6 MHz; ^{29}Si : 79.5 MHz) spectrometer at ambient temperature. ^1H NMR spectra were referenced internally using the residual protonated impurities in the solvent (CDCl_3 : δ 7.27; C_6D_6 : δ 7.16;) and reported relative to tetramethylsilane (δ 0.00). ^{13}C NMR spectra were internally referenced to solvent resonances (CDCl_3 : δ 77.0; C_6D_6 : δ 128.0) and reported relative to tetramethylsilane (δ 0.0).

4.2. (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 under 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, eluting with hexane. Evaporation of the hexane gave $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Cl}$, as a colourless oil (3.41 g; 87%). (Found: C, 48.4; H, 10.6. $\text{C}_9\text{H}_{23}\text{Si}_2\text{Cl}$ (222.9) requires C, 48.5; H, 10.4%; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 2955 (s, $\nu_{\text{as}}(\text{CH}_3)$), 2914 (s, $\nu_{\text{as}}(\text{CH}_2)$), 2875 (s, $\nu_{\text{s}}(\text{CH}_3)$), 2792, 1450 (s, $\delta_{\text{as}}(\text{CH}_3)$), 1396 (m, $\delta_{\text{as}}(\text{CH}_2)$), 1337, 1249 (m, $\delta_{\text{s}}(\text{CH}_3)$), 1217, 1175, 1143, 1079, 1024, 944, 909, 836 (s, $\nu(\text{Si}(\text{CH}_2)_4)$), 747, 692 and 643 (neat); $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 1.39 (2 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.71 (2H, m, $^3\text{J}(\text{HCCCH})$ 8 Hz, CH_2Si), 0.58 (2 H, m, $^3\text{J}(\text{HCCCH})$ 8 Hz, CH_2Si), 0.11 (6 H, s, $\text{Si}(\text{CH}_3)_2$) and 0.01 (9 H, s, $\text{Si}(\text{CH}_3)_3$); $\delta_{\text{C}}(\text{H})$ ($\text{CDCl}_3, 100.6 \text{ MHz}$) 30.52, 21.19, 18.18, 18.14, -1.61 (2 C, $\text{Si}(\text{CH}_3)_2$) and -4.53 (3 C, $\text{Si}(\text{CH}_3)_3$); m/z (EI) 209 (97), 208 (28), 207 (31) and 181 (25%) (M^+ 222 was not observed).

4.3. $\text{LiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$

A solution of (chloromethyl)dimethyl(3-(trimethylsilyl)propyl)silane, (0.409 g, 1.8 mmol) in diethyl ether (3 cm^3) was slowly added to a vigorously stirred suspension of lithium pieces (0.450 g, 65 mmol) in diethyl ether (10 cm^3). The formation of a white solid was observed and the surface of the lithium pieces started shining. The mixture was stirred for an additional 2 h. and filtered over Celite to give a clear colourless solution. The concentration was determined using the Gilman 'double titration' to be 0.26 M. Yield: 6 cm^3 , 1.56 mmol, 87%.

Quenching the solution with D_2O , followed by evaporation of the volatiles gave $\text{DCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ as determined by NMR:

$\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 1.27 (2 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.49 (4 H, m, $^3\text{J}(\text{HCCCH})$ 8 Hz, 2 CH_2Si), -0.10 (15 H, s, 5 CH_3) and -0.12 (2 H, t, $^2\text{J}(\text{DCH})$ 2 Hz, CH_2D); $\delta_{\text{C}}(\text{H})$ ($\text{CDCl}_3, 100.6 \text{ MHz}$) 21.6 (1 C, 4 $\text{CH}_2\text{CH}_2\text{CH}_2$), 18.6 (2 C, 4 CH_2Si), -1.6 (5 C, 5 CH_3) and -1.9 (1 C, t, $^1\text{J}(\text{CD})$ 18 Hz, CH_2D).

4.4. $\text{Cp}_2\text{Zr}(\text{CH}_3)[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3]$

Chloromethyl zirconocene, **3** (0.178 g, 0.65 mmol) was dissolved in diethyl ether (2.0 cm^3) in a centrifuge tube and cooled to -78°C by means of an alcohol/ CO_2 bath. A solution of $\text{LiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ in diethyl ether (2.5 cm^3 , 0.26 M, 0.65 mmol) was added *via* syringe. Upon stirring the mixture a white precipitate formed. The mixture was heated to 0°C by removing the alcohol/ CO_2 bath. The volatiles were removed *in*

vacuo to leave a white liquid. The liquid was stripped with pentane ($2 \times 0.5 \text{ cm}^3$) before it was extracted into pentane (10 cm^3). The solids were centrifuged off and the supernatant colourless liquid was transferred to a Schlenk-tube. The extraction was repeated ($2 \times 5 \text{ cm}^3$). The volatiles were removed *in vacuo* to give a slightly yellow liquid. The liquid was dissolved in pentane and cooled to -78°C , at which temperature a white solid separated. The supernatant liquid was syringed off at -78°C and the product dried under vacuum. The product was identified as **4b**, $\text{Cp}_2\text{Zr}(\text{CH}_3)[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3]$ by ^1H and ^{13}C NMR.

$\delta_{\text{H}}(\text{C}_6\text{D}_6, 400 \text{ MHz})$ 5.75 (10 H, s, 2 C_5H_5), 1.25 (2 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.87 (4 H, m, 2 SiCH_2), 0.12 (2 H, s, ZrCH_2), 0.09 (6 H, s, $\text{Si}(\text{CH}_3)_2$), 0.04 (9 H, s, $\text{Si}(\text{CH}_3)_3$) and -0.15 (3 H, ZrCH_3); $\delta_{\text{C}}(\text{H})$ ($\text{C}_6\text{D}_6, 100.6 \text{ MHz}$) 110.10 (10 C, 2 C_5H_5), 46.73 (1 C, ZrCH_2), 28.28 (1 C, ZrCH_3), 25.05, 21.73, 19.29, 1.55 (3 C, $\text{Si}(\text{CH}_3)_3$) and -1.45 (2 C, $\text{Si}(\text{CH}_3)_2$).

4.5. $[\text{Cp}_2\text{ZrCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3]^+[\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3]^-$

Solid $\text{B}(\text{C}_6\text{F}_5)_3$ was added to a solution of $\text{Cp}_2\text{Zr}(\text{CH}_3)[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3]$, in C_6D_6 in an NMR tube. The tube was shaken to dissolve all of the borane and the solution turned yellow. The only compound in solution was shown to be $[\text{Cp}_2\text{ZrCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3]^+[\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3]^-$

$\delta_{\text{H}}(\text{C}_6\text{D}_6, 400 \text{ MHz})$ 5.58 (10 H, s, 2 C_5H_5), 1.36, 0.7–0.4 three overlapping triplets, 0.05 (9 H, s), -0.01 (2 H, s) and -0.17 (2 H, s); $\delta_{\text{C}}(\text{H})$ ($\text{C}_6\text{D}_6, 100.6 \text{ MHz}$) 113.62 (10 C, 2 C_5H_5), 70.85, 24.21, 21.53, 18.87, 0.86 and -1.68.

4.6. $[\text{Cp}_2\text{ZrCH}_3]^+[\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3]^-$

Dimethylzirconocene, **2**, was dissolved in C_6D_6 in a NMR tube. $\text{B}(\text{C}_6\text{F}_5)_3$ was added as a solid and the tube was shaken to dissolve the borane. The colour changed immediately from colourless to yellow.

$\delta_{\text{H}}(\text{C}_6\text{D}_6, 400 \text{ MHz})$ 5.43 (10 H, s, 2 C_5H_5), 0.27 (3 H, s, ZrCH_3) and 0.11 (3 H, br s, BCH_3); $\delta_{\text{C}}(\text{H})$ ($\text{C}_6\text{D}_6, 100.6 \text{ MHz}$) 113.96 (10 C, 2 C_5H_5) and 40.94 (1 C, Zr-CH_3). The ^{13}C NMR resonances for BCH_3 was not observed due to coupling with ^{11}B . The C_6F_5 resonances were broad due to coupling with ^{19}F .

4.7. $\text{Cp}_2\text{Zr}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$

Zirconocene dichloride, **1** (0.720 g, 2.45 mmol) was dissolved in diethyl ether (5.0 cm^3) and cooled down to -42°C . A solution of $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$, in diethyl ether (5.0 cm^3 ; 1.0 M; 5.0 mmol) was added *via* syringe. The mixture was stirred and allowed to warm to room temperature. The precipitation of a white solid was observed. The solvent was evaporated *in vacuo* and the product was extracted into pentane ($2 \times 10 \text{ cm}^3$). The resulting slightly yellow solution was concentrated and stored at -30°C to give colourless crystals of $\text{Cp}_2\text{Zr}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$ (0.448 g, %).

$\delta_{\text{H}}(\text{C}_6\text{D}_6, 400 \text{ MHz})$ 5.77 (10 H, 2 C_5H_5), 0.08 (18 H, s, 6 CH_3) and 0.03 (4 H, s, 2 CH_2); $\delta_{\text{C}}(\text{H})$ ($\text{C}_6\text{D}_6, 100.6 \text{ MHz}$) 109.85 (10 C, 2 C_5H_5), 45.50 (2 C, 2 CH_2) and 3.51 (6 C, 6 CH_3).

4.8. Attempted synthesis of $[\text{Cp}_2\text{ZrCH}_2\text{Si}(\text{CH}_3)_3]^+[(\text{CH}_3)_3\text{SiCH}_2\text{B}(\text{C}_6\text{F}_5)_3]^-$

To a solution of $\text{Cp}_2\text{Zr}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$ in C_6D_6 in a NMR tube was added solid $\text{B}(\text{C}_6\text{F}_5)_3$. The tube was shaken to dissolve the borane and immediately an orange oil separated. No signals were found in the ^1H and ^{13}C NMR spectrum, indicating that the product is insoluble in C_6D_6 . Addition of the more polar $\text{C}_6\text{D}_5\text{Br}$ did not result in the observation of any signals.

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