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Synthesis of new mixed ring zirconocenes and evidence of ring loss

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Abstract

The synthesis of the substituted silyl cyclopentadiene ligand [C_5H_5–$Si(CH_3)_2$(p-C_6H_4Br)] ($Cp^{Si}H$) (**1**) is described. Deprotonation of (**1**) gives ($Cp^{Si}Li$) (**2**) which reacts with 1/2 $ZrCl_4$ to produce the bent, sandwich complex $Zr(Cp^{Si})_2Cl_2$ (**3**). Compound (**3**) can be alkylated to give $Zr(Cp^{Si})_2(CH_3)_2$ (**4**). Reaction of $Cp^*ZrCl_3 \cdot (Et_2O)_{1/2}$ with (**2**) in ether produces (**3**) and $Zr(Cp^{Si})(C_5Me_5)Cl_2$ (**5**) as the minor and major products, respectively, whereas reaction in toluene produces only **5**. Et_2O and THF are found to catalyze the observed ring loss during the synthesis of **5**. Alkylation of **5** produces $Zr(Cp^{Si})(C_5Me_5)(CH_3)_2$ (**6**). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Metallocenes; Ring loss

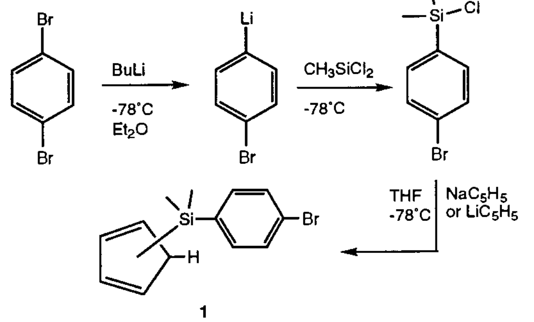
1. Introduction

The area of homogeneous metallocene-catalyzed olefin polymerization has recently received much attention, in part because ligand modifications can result in desirable changes to the properties of the resulting polymers [1]. Our most recent efforts in this area have been directed toward introducing functionalities to the cyclopentadienyl (Cp) ligand so that subsequent modifications can be performed either before or after attachment to the metal center of interest [2]. Herein we report some unusual features pertaining to the synthesis of new metallocenes bearing a bromophenyl ring bound to the Cp group via a silicon bridge. We found during the course of our syntheses that Cp* rings can be lost when attempting to prepare mixed ring metallocenes containing this group if ethereal solvents are used in even trace quantities.

2. Results and discussion

2.1. Synthesis of $(C_5H_5)Si(CH_3)_2(C_6H_4Br)$(1) (H–$Cp^{Si}$)

Halogen–lithium exchange of n-BuLi with 1,4 dibromobenzene [3] in Et_2O followed by addition to $(CH_3)_2SiCl_2$ gives $(CH_3)_2SiCl(C_6H_4Br)$ as a colorless oil in near quantitative yields (Scheme 1). Its isolation is possible, but not necessary since in situ addition of either NaCp or LiCp in THF to this species produces a yellow solution containing one major product and a



Scheme 1.

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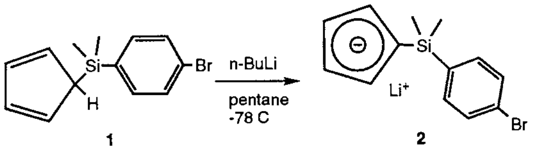
minor, colorless, lower boiling fraction which can be removed under vacuum at 100°C. The remaining yellow oil is predominantly the desired substituted cyclopentadiene $(C_5H_5)Si(CH_3)_2(C_6H_4Br)$ (**1**) (H–Cp^{Si}) as identifed by ^1H NMR spectroscopy and M/S (Scheme 1).

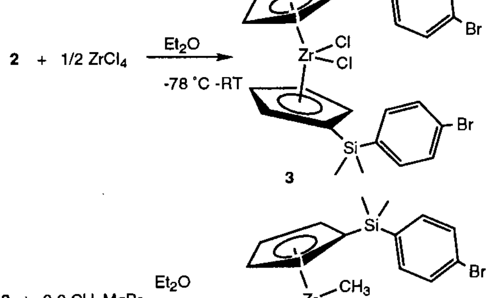
The ^1H NMR of (**1**) displays two broadened Cp ring resonances and we attribute this to rapid sigmatropic shifts of either the methine proton, the silyl group or both [4]. The spectrum is qualitatively very similar to that of C_5H_5–$Si(CH_3)_3$ [5]. Sigmatropic rearrangements are well known in related silyl substituted cyclopentadienyl systems [4], and we have not investigated the features of this fluxionality in greater detail. Compound (**1**) is readily deprotonated by n-BuLi in pentane to give the base-free lithium salt $Li(C_5H_4)Si(CH_3)_2(C_6H_4Br)$ (**2**) (Li–Cp^{Si}) in good yield as an air sensitive, white solid that is insoluble in aliphatic and aromatic hydrocarbons and soluble in ethers (Eq. 1). Exposure of **2** to moisture produces **1** as observed by ^1H NMR.



(1)

2.2. The synthesis of $(Cp^{Si})_2ZrCl_2$ (3) and $(Cp^{Si})_2Zr(CH_3)_2$ (4)

The reaction of two eq of **2** with one eq of $ZrCl_4$ in Et_2O produces $(Cp^{Si})_2ZrCl_2$ (**3**) as an air-stable white solid that is soluble in most common organic solvents (**3**, Eq. 2). Alkylation of (**3**) with CH_3MgBr produces the dimethyl complex $(Cp^{Si})_2Zr(CH_3)_2$ (**4**) as a colorless solid (**4**, Eq. 3). Compound **4** is air sensitive and has solubility properties similar to **3**, thus limiting isolated yields. ^1H NMR analysis of the crude product indicates near quantitative conversion to **4**. It is noteworthy that use of CH_3MgCl does not afford complete alkylation to the dimethyl **4** but yields the tentatively characterized monomethyl species $(Cp^{Si})_2Zr(CH_3)Cl$ as the major product. Use of excess CH_3MgCl to drive the reaction is ineffective and leads to decomposition.



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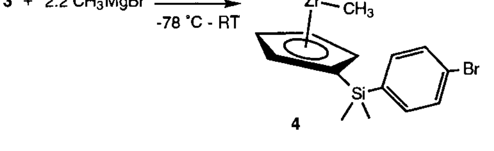
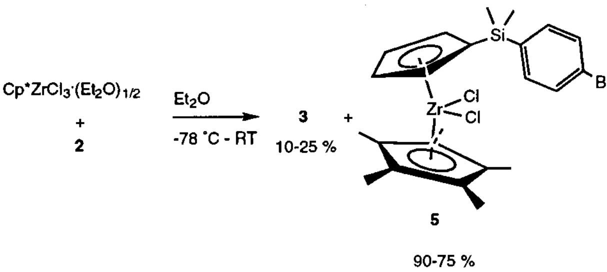


(3)

2.3. The synthesis of $(Cp^*)(Cp^{Si})Zr(Cl)_2$ (5)

Reaction of $Cp^*ZrCl_3 \cdot (Et_2O)_{1/2}$ with **2** produces $(Cp^*)(Cp^{Si})Zr(Cl)_2$ (**5**) and $(Cp^{Si})_2ZrCl_2$ (**3**) in as large as a 3:1 ratio (isolated yields) when the reactions are performed in Et_2O (**3** and **5**, Eq. 4). Relative ratios vary between batches but significant amounts of **3** are always produced.



(4)

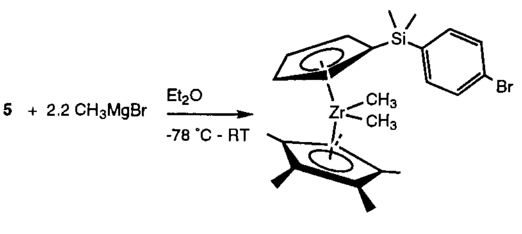
When the reaction is followed by ^1H NMR in THF-d_8, **3** and **5** are observed to form concurrently. Similar results are obtained when the reaction is run at various temperatures and reaction times. Efforts to separate **5** and **3** by chromatography or fractional crystallization were unsuccessful. Both complexes are soluble in most organic solvents and have similar retention times on alumina and silica. We initially thought that **3** was produced because varying amounts of $ZrCl_4$ may be left over from the synthesis of Cp^*ZrCl_3, but this hypothesis proved to be false. In contrast, we find that reaction of $Cp^*ZrCl_3 \cdot (Et_2O)_{1/2}$ with **2** in refluxing toluene over 5 days produces **5** exclusively (**5**, Eq. 5).

$$Cp^*ZrCl_3 \cdot (Et_2O)_2 + \mathbf{2} \xrightarrow[\text{5 day reflux}]{\text{Toluene}} \mathbf{5} \qquad (5)$$

Although we have no mechanistic information regarding this process, we speculate that loss of LiCp* is promoted by ethereal solvents. This hypothesis is further supported by the observation that if even a small amount (~4 ml) of THF is added to the toluene (~50 ml) reaction mixture, a small amount of **3** is produced, while the reaction is complete within 3 h. Although ring loss is not usually reported, it is certainly occurring in the present case.

2.4. The synthesis of $(Cp^*)(Cp^{Si})Zr(CH_3)_2$ (6)

Reaction of **5** with MeMgBr in ether produces a white solid after workup which has been identified as the dimethyl species $(Cp^*)(Cp^{Si})Zr(CH_3)_2$ (**6**) in moderate isolated yield due to its high solubility (**6**, Eq. 6). The spectroscopic properties of this compound are unremarkable, and once again the use of MeMgBr as the alkylating agent gives the best yield and most complete reaction.



(6)

Our interest in the synthesis of these metallocenes has been to functionalize the C–Br bond on the phenyl group. We anticipate that reaction of the dimethyl species **4** and **6** with n-BuLi at low temperature in ethereal solvents will result in halogen lithium exchange at the C–Br position. We have attempted to perform the halo-Li exchange reaction on compounds **4** and **6** with little success using n-BuLi as the Li source. When the exchange reaction is carried out at low temperature, trapping the resultant Li reagent with various electrophiles gave numerous products with a high degree of variability from sample to sample. The number of products observed in our halogen–lithium exchange reactions suggested that this pathway is not feasible. Negishi et al. have recently reported on their studies of reaction of metallocenes with alkyl lithiums in which half-sandwich species are formed via loss of LiCp [6]. Given the ring loss that we observed during the synthesis of **5**, it is possible that similar reactions have thwarted our attempts to lithiate the phenyl ring of the Cp^{Si} ligand.

In conclusion, our results for the synthesis of the mixed sandwich dichloride complex **5** demonstrate that the Cp* ring can easily be displaced when ethereal solvents are present even in small quantities. Although reaction times are longer when toluene is used as the solvent, loss of the Cp* ring is not observed. We also find that functionalization of Cp^{Si} via bromo-lithium exchange once it is on the metal does not appear to be a viable approach for substitution at the *para* position in zirconocene compounds.

3. Experimental details

All syntheses were performed under a dry argon atmosphere using standard Schlenk techniques. $Cp^*ZrCl_3 \cdot (Et_2O)_{1/2}$ was prepared according to a published route [7]. Tetrahydrofuran (THF), diethyl ether (Et_2O), toluene and pentane were distilled from potassium or sodium benzophenone ketyl. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a General Electric QE-300 (300 MHz) spectrometer. Elemental analyses were performed by the University of Florida Department of Chemistry Analytical Services or by Atlantic Microlabs, Norcross, GA, USA. Despite repeated attempts, elemental analyses of compounds (**4**–**6**) were consistently 1–2% low in carbon even though they were of high purity as judged by ^1H NMR spectroscopy.

3.1. $[C_5H_5–Si(CH_3)_2(p\text{-}C_6H_4Br)]$ $(Cp^{Si}H)$ (**1**)

1,4 dibromobenzene (8.12 g, 34.4 mmol) was dissolved in ~50 ml of Et_2O and cooled to − 50°C. Once the solution had cooled, a white suspension was observed, to which 13.77 ml (2.5M, 34.4 mmol) of n-BuLi was added slowly to generate p-Li–C_6H_4Br. This mixture was left at − 50°C (~15 min), warmed to ambient temperature (10 min), recooled to − 50°C then added dropwise to $(CH_3)_2SiCl_2$ (5.12 ml) in Et_2O (25 ml) and stirred for an hour at room temperature. The solution was then cooled to − 78°C and a − 78°C solution of a stoichiometric amount (34.4 mmol) of NaCp or LiCp in THF (80 ml) was added via cannula and stirred at room temperature for 5–6 h to give a yellow solution. The reaction was quenched by pouring it into ice/cold water. The product was extracted from the aqueous layer into pentane then dried with $CaSO_4$. After filtration, the yellow solution was concentrated to leave a yellow oil. The oil was then heated to ~95°C under reduced pressure which removed a colorless unidentified fraction and left behind a thick, yellow, oil. Yield 78%. ^1H NMR (C_6D_6, 22°C): δ -0.03 (s, 6H, $Si(CH_3)_2$); 3.34 (br s, 1H, methine); 6.38 (br s, 2H, Cp ring), 6.60 (br s, 2H, Cp ring), 7.03 (d, $J_{H-H} = 8.4$ Hz, 2H, phenyl), 7.34 (d, $J_{H-H} = 8.4$ Hz, 2H, phenyl).

3.2. $[LiC_5H_4–Si(CH_3)_2(p\text{-}C_6H_4Br)]$ $(Cp^{Si}Li)$ (**2**)

Compound **1** (2.00 g, 7.16 mmol) was dissolved in ~40 ml pentane and cooled to − 50°C. 2.87 ml n-BuLi (2.5 M, 7.17 mmol) was injected slowly whereupon precipitation of a white solid was observed. The reaction was allowed to warm to room temperature and left stirring for ~5 h. The solid was cannula filtered, washed 2X with pentane, and dried under reduced pressure leaving a flocculent white solid. Yield 70%.

3.3. $Zr(Cp^{Si})_2Cl_2$ (**3**)

A flask was charged with **2** (0.900 g, 3.16 mmol) and freshly sublimed $ZrCl_4$ (0.366 g, 1.44 mmol) in a dry box and suspended in cold (− 50°C) Et_2O. Ca. 10 ml of THF was then added to this mixture and the suspension immediately dissolved to form a peach colored solution that was left to stir overnight. Solvent was removed under reduced pressure and the remaining oily solid was redissolved in 25 ml CH_2Cl_2/6 ml 4 M HCl. The product was extracted twice with CH_2Cl_2 and the combined fractions were washed with ca. 10 ml H_2O. The solution was dried over $CaSO_4$ and filtered. After the solvent was removed under reduced pressure, the remaining oily solid was triturated with pentane overnight to leave a fine white solid. Analysis of the crude reaction mixture revealed near quantitative conversion to (**3**). Due to high solubility, the isolated yield is ca. 50%. ^1H NMR (C_6D_6, 22°C): δ 0.55 (s, 12H, $Si(CH_3)_2$); 5.78 (t, $J_{H-H} = 2.6$ Hz, 4H, Cp ring), 6.27 (t, $J_{H-H} = 2.6$ Hz, 4H, Cp ring), 7.09 (d, $J_{H-H} = 8.4$ Hz, 4H, phenyl), 7.33 (d, $J_{H-H} = 8.4$ Hz, 4H, phenyl). Elemental Analysis Calc: C, 43.51; H, 4.23. Found: C, 43.53; H, 4.05.

3.4. $Zr(Cp^{Si})_2(CH_3)_2$ (**4**)

Compound **3** (0.206 g, 0.286 mmol) was dissolved in ca. 15 ml Et_2O and cooled −78°C. Methyl magnesium bromide, 191 μl (3.0 M soln in Et_2O, 0.573 mmol) was added dropwise and stirred 1 h at −78°C and then warmed slowly to room temperature overnight. The product was cannula filtered and the salts were washed 2X with Et_2O. The solvent was removed from the combined fractions to leave a colorless oil which was washed 1X with pentane and then pumped dry leaving a white powder. Isolated yield ca. 80%. ^1H NMR (C_6D_6, 22°C): δ −0.13 (s, 6H, Zr–CH_3), 0.31 (s, 12H, Si(CH_3)$_2$); 5.83 (t, $J_{H-H} = 2.3$ Hz, 4H, Cp ring), 5.95 (t, $J_{H-H} = 2.3$ Hz, 4H, Cp ring), 7.08 (d, $J_{H-H} = 8.4$ Hz, 4H, phenyl), 7.34 (d, $J_{H-H} = 8.4$ Hz, 4H, phenyl).

3.5. $Zr(Cp^{Si})(C_5Me_5)Cl_2$ (**5**)

Cp*$ZrCl_3$. $(Et_2O)_{1/2}$ (1.00 g, 2.70 mmol) and **2** (0.84 g, 2.94 mmol) were mixed in a Schlenk tube and suspended in ca. 30 ml of toluene. The vessel was fitted with a condenser and refluxed for 5 days. Solvent was stripped and the remaining oily solid was redissolved in 25 ml CH_2Cl_2/ 6 ml 4 M HCl. The product was extracted twice with CH_2Cl_2 and the combined fractions were washed with ca. 10 ml of H_2O. The solution was dried over $CaSO_4$ and filtered. After the solvent was removed under reduced pressure, the remaining oily solid was triturated with pentane overnight to leave a fine white solid. Yield ca. 52% ^1H NMR (C_6D_6, 22°C): δ 0.70 (s, 6H, Si(CH_3)$_2$); 1.69 (s, 15H, Cp*), 5.67 (t, $J_{H-H} = 2.6$ Hz, 2H, Cp ring), 6.40 (t, $J_{H-H} = 2.6$ Hz, 2H, Cp ring), 7.18 (d, $J_{H-H} = 8.1$ Hz, 2H, phenyl), 7.33 (d, $J_{H-H} = 8.4$ Hz, 2H, phenyl).

3.6. $Zr(Cp^{Si})(C_5Me_5)(CH_3)_2$ (**6**)

Compound **5** (0.448 g, 0.778 mmol) was dissolved in ca. 20 ml Et_2O and cooled to −50°C. 519 μl (3.0 M, 1.56 mmol) of a solution of CH_3MgBr was syringed into the reaction mixture which was stirred at −50°C for 1 h and then warmed to room temperature and left overnight. Cannula filtration to remove the salts followed by removal of the solvent left a sticky white solid. Recrystallization from benzene/pentane at −20 gives **6** as a fine white solid. Analysis of the crude reaction mixture revealed near quantitative conversion to **6**. Owing to high solubility, the isolated yield is ca. 36%. ^1H NMR (C_6D_6, 22°C): δ −0.35 (s, 6H, Zr–CH_3); 0.47 (s, 6H, Si(CH_3)$_2$); 1.67 (s, 15H, Cp*); 5.60 (t, $J_{H-H} = 2.4$ Hz, 2H, Cp ring), 6.05 (t, $J_{H-H} = 2.4$ Hz, 2H, Cp ring), 7.16 (d, $J_{H-H} = 8.4$ Hz, 2H, phenyl), 7.34 (d, $J_{H-H} = 8.1$ Hz, 2H, phenyl).

Acknowledgements

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