

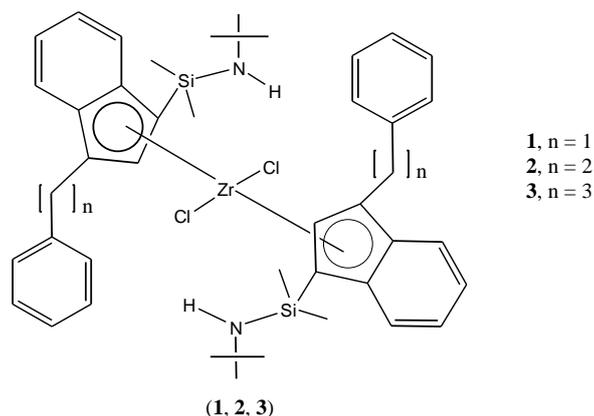
SYNTHESIS AND CHARACTERIZATION OF THREE SANDWICH COMPLEXES OF ZIRCONIUM WITH DISUBSTITUTED INDENYL LIGANDS

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Abstract

The preparation of three sandwich complexes of zirconium (**1,2,3**) with disubstituted indenyl ligands and their characterization using ^1H , ^{13}C and ^{29}Si -NMR and mass spectroscopy is described.



Introduction

The chemistry of sandwich and half-sandwich complexes of zirconium and titanium is gaining increasing interest for their application as catalyst precursors for catalytic polymerization of olefins¹⁻⁵. We have earlier reported several amido functionalized half-sandwich complexes of these metals and their use as catalyst precursors for homogeneous ethylene polymerization⁶. In this paper we report the synthesis and spectroscopic characterization of another three new sandwich complexes of zirconium.

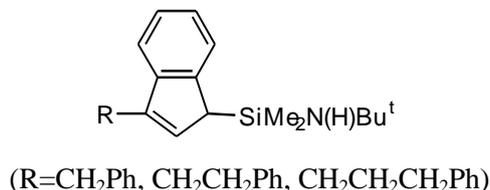
Experimental

The work was carried out using the standard Schlenk technique and dried argon was used to make inert atmosphere. The solvents were dried and distilled before use. All starting materials were commercially available and used without further purification. The spectrometers Bruker ARX 250, AC 300 and DRX 500 were used for recording the NMR spectra. The chemical shifts in the ^1H -NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for CDCl_3 , $\delta = 7.15$ ppm for C_6D_6) and in the ^{13}C -

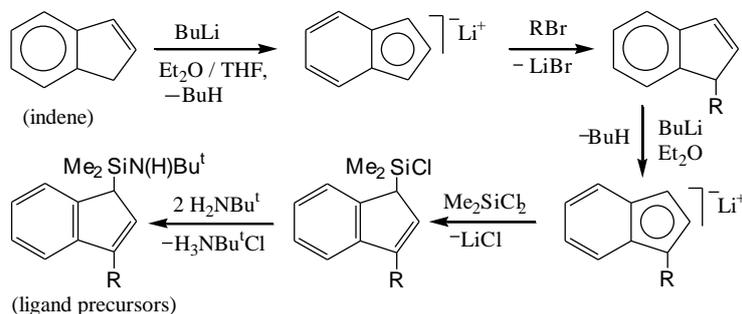
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NMR spectra to the solvent signal ($\delta = 77.0$ ppm for CDCl_3 , $\delta = 128.0$ ppm for C_6D_6). SiMe_4 ($\delta = 0.0$) was used as an external standard for ^{29}Si -NMR spectra. The mass spectra were recorded with a varian MAT CH7 instrument.

General procedure for the preparation of the ligand precursors (disubstituted indenenes),



These were prepared by successive reactions shown in Scheme 1 following the procedure described in ref⁶.



Scheme 1. Synthesis of the ligand precursors, disubstituted indenenes

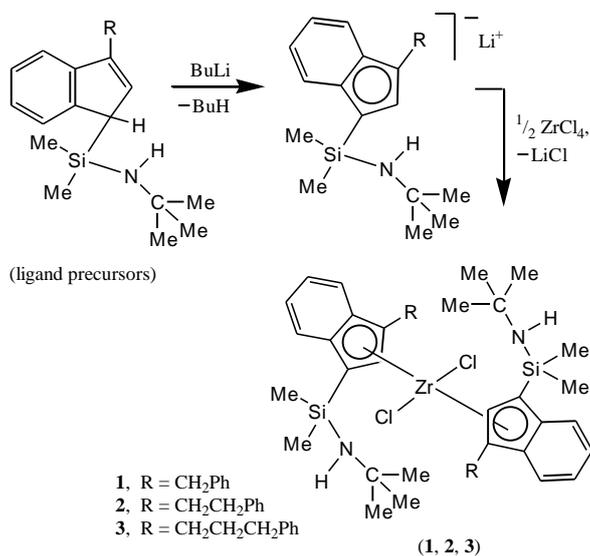


General procedure for the preparation of the sandwich complexes

Diethyl ether solution of the appropriate ligand precursor (100 mmol) was taken in a Schlenk flask and was cooled to -78°C by immersing the flask in a bath of dry ice/acetone. Equimolar amount of n-butyllithium was slowly added to it and the mixture was stirred for 8hrs at room temperature. The solution of the resulting lithiated ligand was again cooled to -78°C and ether solution of ZrCl_4 (50 mmol) was slowly added with stirring. After completion of addition, the reaction mixture was allowed to reach room temperature and stirred for another 12hrs. The precipitated LiCl was removed by filtration over Na_2SO_4 and the clear filtrate was concentrated and left overnight at -78°C for crystallization. Orange yellow crystals of the sandwich complex separated which were collected and dried under vacuum. Yield: 62-75%. Table-1 shows their mass and NMR spectroscopic data.

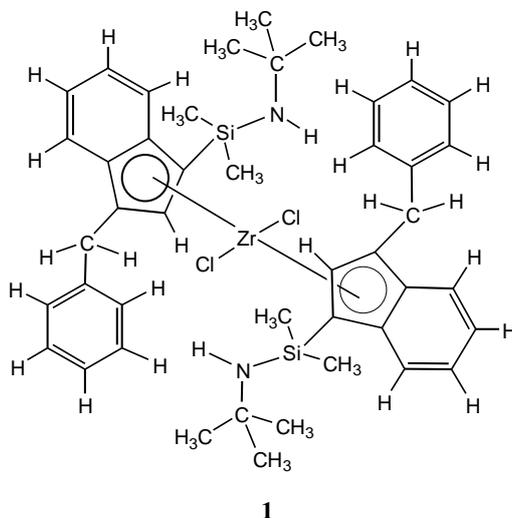
Results and Discussion

Three new sandwich complexes of zirconium (**1**, **2**, **3**) were prepared from reactions of ZrCl_4 with 2 molar equivalents of the lithiated ligands (details given in the experimental section). Scheme 2 shows the reactions involved in their preparation. In the first step the ligand precursor is reacted with equimolar amount of butyllithium to form the lithiated ligand which in the second step reacts with half molar equivalent of zirconium tetrachloride to form the corresponding sandwich complex.



Scheme 2. Reactions involved in the preparation of complexes **1**, **2**, **3**

^1H , ^{13}C and ^{29}Si -NMR and mass spectroscopy were used for the characterization of these complexes. The data are listed in Table 1 and characterization of complex **1** is discussed below in details.



In the aliphatic region of the $^1\text{H-NMR}$ spectrum of **1** signals for the two diastereotopic methyl groups attached to silicon were detected at $\delta = 0.75$ and 0.88 ppm as two sharp single peaks of equal intensity. The three methyl groups of the *tert*-butyl group were homotopic and form one singlet with a signal intensity of nine protons at $\delta = 1.31$ ppm. The signal for the N–H proton was at $\delta = 6.65$ ppm. The peak for the CH_2 protons was a multiplet centered at $\delta = 4.36$ ppm and signals for all C–H (aromatic) protons were observed in the region $\delta = 7.23 - 8.32$ ppm as another multiplet with the proper intensity ratio for ten protons.

In the J-modulated $^{13}\text{C-NMR}$ spectrum of **1** (Fig.1) the signals with negative phase at $\delta = 141.8, 138.2, 135.1, 132.1$ and 124.0 ppm were attributed to the quaternary carbon atoms present in the cyclopentadienyl and phenyl rings and signals for CH resonances of these rings appeared with positive phase at $\delta = 128.3, 128.2, 128.0, 127.7, 126.6, 126.5, 126.4, 126.0, 125.3$ and 124.3 ppm. The aliphatic area exhibited the singlet signal with positive phase at $\delta = 33.8$ ppm for the three homotopic methyl carbon atoms of the *tert*-butyl group. Signals for the diastereotopic carbon atoms of the two methyl groups attached to silicon appeared with positive phase at $\delta = 3.1$ and 3.7 ppm and the signal for the CH_2 carbon appeared with negative phase at $\delta = 34.5$ ppm. The quaternary carbon of the *tert*-butyl group gave a signal with negative phase at $\delta = 49.8$ ppm.

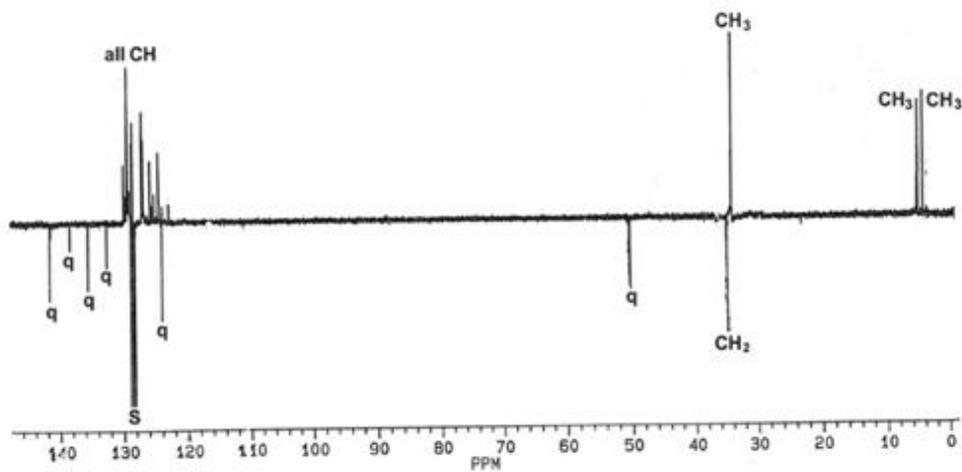


Fig. 1. J-modulated ^{13}C -NMR spectrum of complex 1

Table 1: ^1H , ^{13}C , ^{29}Si -NMR and mass spectral data of the prepared sandwich complexes.

Complex	^1H -NMR (ppm)	^{13}C -NMR (ppm)	^{29}Si -NMR (ppm)	Mass spectrum (m/z)
1	0.75 (s, SiMe), 0.88 (s, SiMe), 1.31 (s, CMe_3), 4.36 (m, CH_2), 6.65 (s, NH), 7.23-8.32 (m, Ar-H)	C_q : 141.8, 138.2, 135.1, 132.1, 124.0, 49.8; CH: 128.3, 128.2, 128.0, 127.7, 126.6, 126.5, 126.4, 126.0, 125.3, 124.3; CH_2 : 34.5; CH_3 : 33.8, 3.7, 3.1	-11.1	830 [M^+], 700 [M^+ - $\text{Me}_2\text{SiNHBu}^{\dagger}$], 685 [M^+ - $\text{Me}_2\text{SiNHBu}^{\dagger}\text{-Me}$]
2	0.74 (s, SiMe), 0.87 (s, SiMe), 1.40 (s, CMe_3), 2.70-3.61 (m, $\text{CH}_2\text{-CH}_2$), 6.25 (s, NH), 6.85-8.21 (m, Ar-H)	C_q : 141.2, 139.8, 138.6, 134.3, 131.7, 49.4; CH: 128.7, 128.3, 128.1, 127.6, 126.4, 126.2, 125.0, 124.4, 123.3, 118.6; CH_2 : 35.3, 29.8; CH_3 : 33.6, 3.7, 2.0	-11.2	858 [M^+], 808 [M^+ -Me-Cl], 728 [M^+ - $\text{Me}_2\text{SiNHBu}^{\dagger}$], 642 [M^+ - $\text{Me}_2\text{SiNHBu}^{\dagger}\text{-Me-2Cl}$]
3	0.76 (s, SiMe), 0.86 (s, SiMe), 1.35 (s, CMe_3), 1.81-2.92 (m, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 6.46 (s, NH), 7.20-8.12 (m, Ar-H)	C_q : 141.6, 135.0, 131.4, 125.4, 115.4, 49.6; CH: 128.5, 128.1, 127.5, 127.3, 126.5, 125.3, 124.1, 122.3, 119.1, 115.3; CH_2 : 35.4, 33.0, 27.4; CH_3 : 33.5, 3.6, 2.8	-11.1	886 [M^+], 871 [M^+ -Me], 835 [M^+ -Me-Cl], 798 [M^+ -Me-2Cl], 756 [M^+ - $\text{Me}_2\text{SiNHBu}^{\dagger}$]

The ^{29}Si -NMR spectrum of **1** showed a sharp single resonance at $\delta = -11.1$ ppm.

The mass spectrum of **1** showed the molecular ion peak at m/z 830 and other peaks for its fragments at m/z 700 [M^+ - $\text{SiMe}_2\text{N(H)Bu}^{\dagger}$], 685 [M^+ - $\text{Me}_2\text{SiN(H)Bu}^{\dagger}\text{-Me}$] which were characteristic for the formulation of complex **1**.

Thus all the experimental evidences strongly support the proposed structure of the sandwich complex **1**. Spectroscopic data of the remaining two complexes **2** and **3** (Table 1) can be similarly explained.

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