

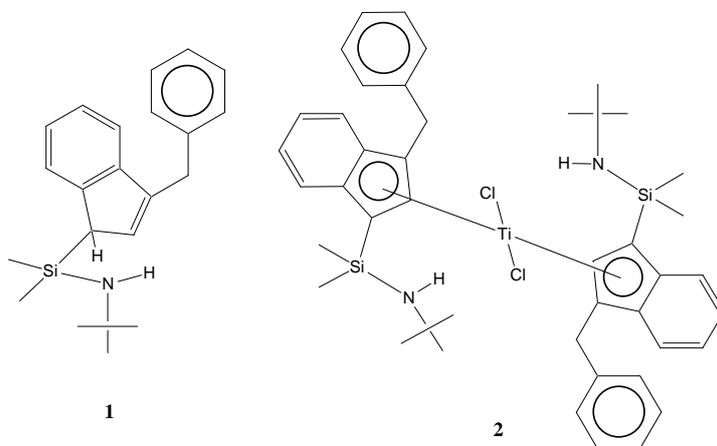
SYNTHESIS AND CHARACTERIZATION OF THE DISUBSTITUTED INDENE DERIVATIVE 3-BENZYL-1-t-BUTYLAMINE(DIMETHYLSILYL)INDENE AND ITS SANDWICH COMPLEX WITH DICHLOROTITANIUM

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Abstract

The synthesis of the disubstituted indene derivative 3-benzyl-1-t-butylamine(dimethylsilyl)-indene, 3-C₆H₅CH₂-1-SiMe₂(NHBu^t)-C₉H₆, **1** and its sandwich complex with dichlorotitanium, [η⁵-{3-C₆H₅CH₂-1-SiMe₂(NHBu^t)-C₉H₅}]₂TiCl₂ **2**, and their characterization using ¹H, ¹³C & ²⁹Si-NMR and mass spectroscopy have been described.



Introduction

Sandwich and half-sandwich complexes of titanium and zirconium are receiving much interest now-a-days because of their use as catalyst precursors for catalytic polymerization of alkenes.¹⁻⁵ We also have reported several amido functionalized half-sandwich complexes of the two metals and their successful use as catalyst precursors for homogeneous polymerization of ethylene.⁶ Recently we reported several sandwich complexes of zirconium with disubstituted indenyl ligands.⁷ As an extension of the work the synthesis and characterization of a similar sandwich complex of titanium is now reported.

Experimental

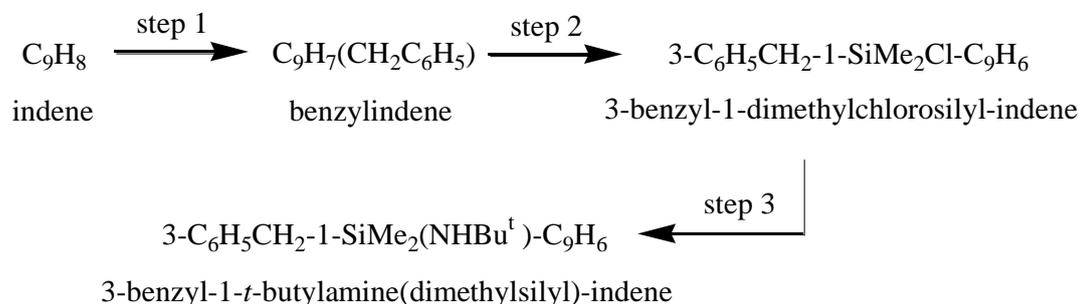
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All experimental work was carried out using Schlenk technique under an atmosphere of dried argon. Et₂O, THF and n-pentane were purified by distillation over LiAlH₄. Commercial indene, C₉H₈, was distilled prior to use and stored at -30°C. All other reagent grade chemicals were used without further purification.

The spectrometers JEOL FX 90Q and Bruker ARX 250, AC 300 and DRX 500 were used for recording NMR spectra. The chemical shifts in ¹H-NMR spectra are referred to the residual proton signal of the solvent (δ = 7.24 ppm for CDCl₃, δ = 7.15 ppm for C₆D₆) and in ¹³C-NMR spectra to the solvent signal (δ = 77.0 ppm for CDCl₃, δ = 128.0 ppm for C₆D₆). SiMe₄ (δ = 0.0) was used as an external standard for ²⁹Si-NMR spectra. The mass spectra were recorded with a Varian MAT CH7 instrument.

Synthesis of the disubstituted indene derivative 3-benzyl-1-t-butylamine(dimethylsilyl)indene, 3-C₆H₅CH₂-1-SiMe₂(NHBu^t)-C₉H₆ 1

The preparation of this compound involved the following three steps:



Step 1: Preparation of benzylindene, C₉H₇(CH₂C₆H₅)

Indene, C₉H₈, (250 mmol) was dissolved in a mixture of 100 ml Et₂O and 30 ml THF and the solution was cooled to -78°C. n-Butyllithium (250 mmol) was added using a syringe and the reaction mixture was stirred for 6 h at room temperature. 250 mmol of benzylbromide was next added dropwise at -78°C and the mixture was stirred for another 12 h at room temperature. It was then hydrolysed with 50 ml water, the organic layer was filtered over Na₂SO₄ and the clear filtrate was evaporated to dryness. Distillation of the crude product in vacuo gave 82% yield of C₉H₇(CH₂C₆H₅). GC showed it to be about 100% pure.

Step 2: Preparation of 3-benzyl-1-dimethylchlorosilyl-indene, 3-C₆H₅CH₂-1-SiMe₂Cl-C₉H₆

The benzyl substituted indene derivative (50 mmol) was dissolved in 100 ml Et₂O and cooled to -78°C. An equimolar amount (50 mmol) of n-butyllithium was then added slowly and the mixture was stirred for 4 h at room temperature. The evolution of n-butane was completed in this period. The solution was again cooled to -78°C and added to 3 molar excess of Me₂SiCl₂ solution in 80 ml Et₂O at -78°C. This was left stirred overnight. To remove the precipitated LiCl, the suspension was filtered over Na₂SO₄ and the clear filtrate was evaporated in vacuo to remove solvent and excess Me₂SiCl₂. The disubstituted indenylchlorosilane derivative, 3-C₆H₅CH₂-1-SiMe₂Cl-C₉H₆, was obtained in about 90% yield as a light yellow viscous liquid. GC showed it to be about 98% pure.

*Step 3: Preparation of 3-benzyl-1-*t*-butylamine(dimethylsilyl)-indene, 3-C₆H₅CH₂-1-SiMe₂(NHBu^t)-C₉H₆ **1***

To an ether solution of 3-C₆H₅CH₂-1-SiMe₂Cl-C₉H₆ (50 mmol) 3 molar excess of *tert*-butylamine, H₂NBu^t, was added at room temperature and the mixture was left stirred over-night. The hydrogen chloride formed in this step was eliminated by excess amine and precipitated as ammonium hydrochloride. The solvent was removed in vacuo and the residue was treated with about 100 ml pentane. The suspension was filtered over Na₂SO₄/SiO₂ and the clear filtrate was evaporated to remove pentane and excess of *tert*-butylamine. The product **1** was obtained almost quantitatively as a light yellow viscous oil. GC showed it to be about 96% pure. [Spectral data: ¹H-NMR: δ 0.10 (s, 3H), 0.17 (s, 3H), 1.36 (s, 9H), 3.69 (s, 1H), 4.15 (s, 2H), 6.50 (s, 1H), 7.36-7.49 (m, 10H); ¹³C-NMR: C_q (negative phase) δ 49.6, 140.1, 140.3, 144.4, 146.2; CH (positive phase) δ 46.9, 119.4, 123.1, 123.6, 123.8, 124.5, 126.0, 128.3, 128.9, 130.0, 131.1, 132.8; CH₂ (negative phase) δ 34.6; CH₃ (positive phase) δ - 0.7, 0.3, 33.9; ²⁹Si-NMR: δ -1.65. Mass spectrum: m/z 335 [M⁺], 320 [M⁺-Me], 263 [M⁺-2 Cl], 205 [M⁺-SiMe₂NHBu^t], 130 [SiMe₂NHBu^t]⁺.

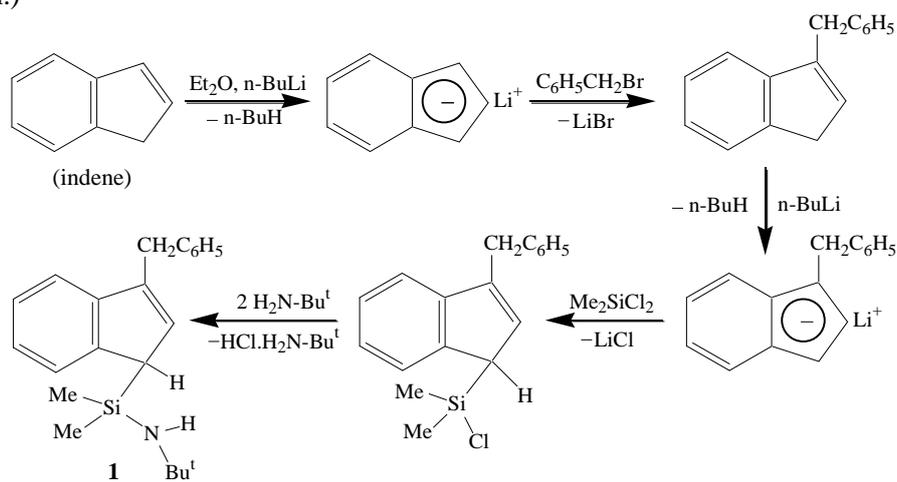
*Synthesis of the sandwich complex, [η⁵-{3-C₆H₅CH₂-1-SiMe₂(NHBu^t)-C₉H₅}]₂TiCl₂ **2***

The ligand precursor 3-C₆H₅CH₂-1-SiMe₂(NHBu^t)-C₉H₆ (10 mmol) was dissolved in Et₂O (150 ml) and the solution was cooled to -78°C. A solution of n-BuLi (10 mmol) was slowly added to it and the mixture was stirred for 5 h at room temperature. The lithium salt of the ligand was thus obtained. This was slowly added to a THF solution of TiCl₃.THF (5 mmol) at -78°C and the mixture was stirred for 12 h at room temperature. For oxidation, the titanium(III) compound thus formed was mixed with 6 mmol (1.66 g) PbCl₂ at room temperature and the reaction mixture was stirred for 1h. When stirring was stopped, the precipitated elemental Pb and PbCl₂ settled at the bottom of the reaction flask. The clear solution from the top was separated using a cannula and the solvent was evaporated in vacuo. The residue was treated with n-pentane, filtered over Na₂SO₄ and

the clear solution was evaporated to dryness in vacuo. The complex **2** was thus obtained as a red solid (yield 62%).

Results and discussion

The disubstituted indene derivative **1** was used as the ligand precursor for the preparation of the sandwich complex **2**. Compound **1** was synthesized from indene, C_9H_8 , first by substitution with a benzyl group, $CH_2C_6H_5$, next by another substitution with a dimethylchlorosilyl group, Me_2SiCl , and finally by conversion of the chlorosilyl group into the aminosilyl group, $Me_2Si(NHBu^t)$. The reactions involved in these conversion processes are shown in Scheme 1. (Details of the process are given in the experimental section.)



Scheme 1: Synthesis of the disubstituted indene derivative **1**

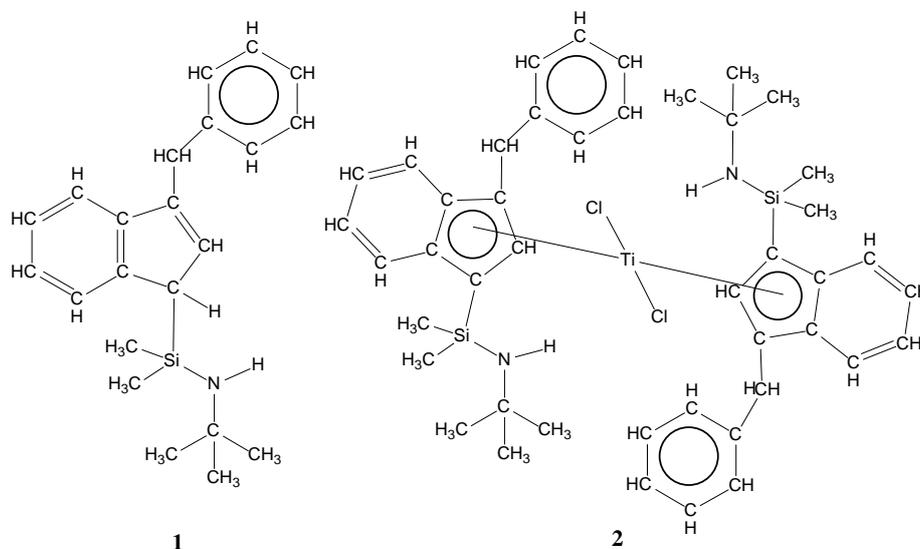


Fig. 1. The detailed structural view of **1** and its sandwich complex **2**.

Structures of the ligand precursor **1** and its sandwich complex **2** with titanium dichloride are elaborately shown in Fig.1. In the ¹H-NMR spectrum of **1** (Fig.2) the aliphatic area showed two singlets of equal intensity at δ 0.10 and 0.17 for the two diastereotopic methyl groups attached to silicon. The three methyl groups of the *tert*-butyl group, CMe₃, are homotopic and showed a singlet for nine protons at δ 1.36. The two methylene (CH₂) protons of the benzyl group showed a signal at δ 4.15, the silicon-attached CH proton of the cyclopentadiene ring at δ 3.69 and the NH proton at δ 6.50. Signals for all aromatic protons appeared in the region δ 7.36 – 7.49.

In the J-modulated ¹³C-NMR spectrum of **1** (Fig.3) the aromatic region showed four resonance signals with negative phase at δ 140.1, 140.3, 144.4, 146.2 for the four quaternary carbon atoms (C_q) present in the cyclopentadiene and phenyl rings and eleven signals with positive phase at δ 119.4, 123.1, 123.6, 123.8, 124.5, 126.0, 128.3, 128.9, 130.0, 131.1, 132.8 for the CH carbons present in these rings. The aliphatic area showed one signal with negative phase at δ 49.6 for the quaternary carbon atom present in the *tert* butyl group (CMe₃) and another at δ 34.6 for the CH₂ carbon of the benzyl group. Two resonance signals with positive phase were observed at δ -0.7, 0.3 for the two diastereotopic carbon atoms present in the two methyl groups attached to silicon (SiMe₂) and another at δ 33.9 for the three homotopic carbon atoms of the methyl groups present in the *tert*-butyl group (CMe₃).

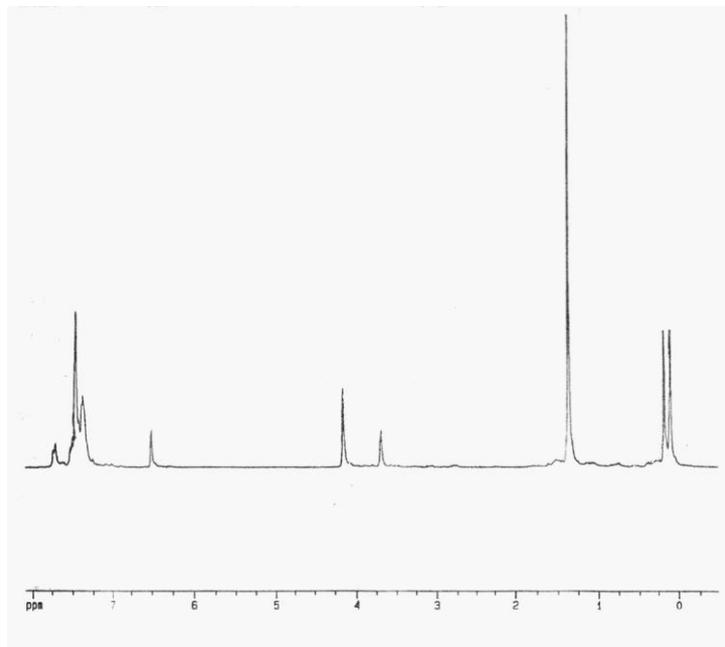


Fig. 2. ^1H -NMR spectrum of the ligand precursor **1**.

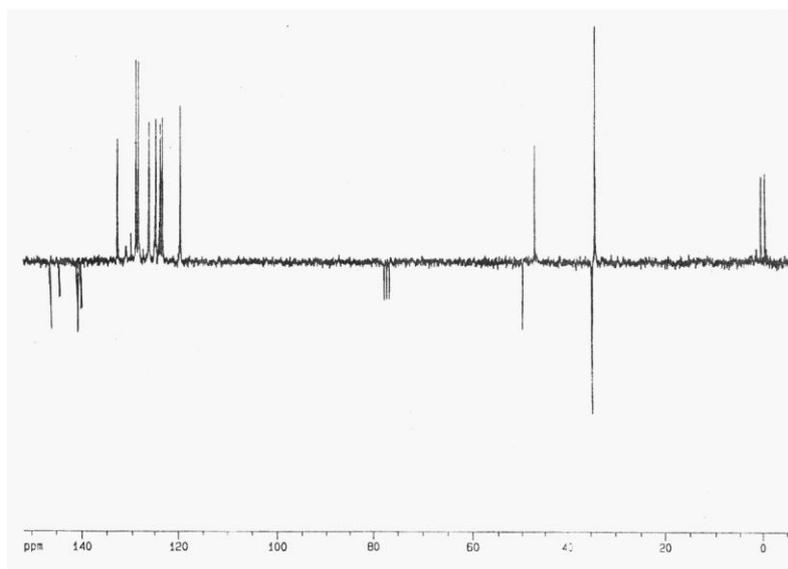
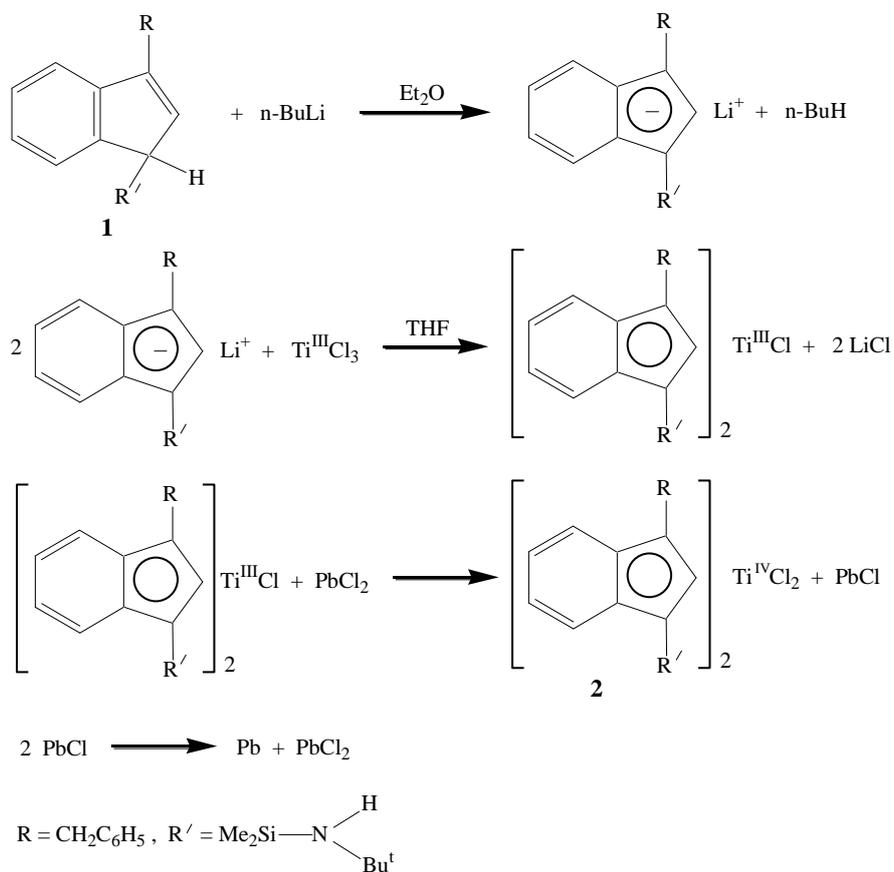


Fig. 3. J-modulated ^{13}C -NMR spectrum of the ligand precursor **1**.

The ^{29}Si -NMR spectrum showed one sharp signal at $\delta -1.65$ for the silicon atom present in **1**. The mass spectrum showed the molecular ion peak at m/z 335 [M^+] and other mass

peaks for its different fragments. Thus the structure of **1** is satisfactorily established from its various spectroscopic investigations.

The disubstituted indene derivative **1** was successfully used as a ligand precursor for the synthesis of the sandwich complex **2**. For the purpose, **1** was first converted to its lithium salt by reaction with butyllithium and this salt was next reacted with $\text{TiCl}_3 \cdot \text{THF}$ in THF solution. An unstable titanium(III) compound with 17 valence electrons was obtained which was quickly oxidized using PbCl_2 to give the stable sandwich complex **2** with 16 electrons in the valence shell of titanium(IV). It is known from literature that titanium(IV) complexes with 16 valence electrons, e.g. $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ ⁸ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^1\text{-C}_5\text{H}_5)_2$,⁹ are sufficiently stable. The reactions involved in the synthesis of complex **2** are given below.



A comparison of the spectral data of complex **2** [$^1\text{H-NMR}$: δ 0.73 (s, 3H, SiMe), 0.87 (s, 3H, SiMe), 1.33 (s, 9H, CMe_3), 4.38 (m, 2H, CH_2), 6.62 (s, 1H, NH), 7.13 – 8.22 (m, 10H, Ar-H of indene and phenyl groups). $^{13}\text{C-NMR}$: $\delta(\text{C}_q)$ 142.3, 139.4, 135.3, 132.4,

124.8, 48.6; $\delta(\text{CH})$ 128.4, 128.3, 128.0, 127.6, 126.8, 126.3, 125.4, 125.2, 124.1, 123.7; $\delta(\text{CH}_2)$ 34.3, $\delta(\text{CH}_3)$ 3.2, 3.6, 33.7. $^{29}\text{Si-NMR}$: δ -11.8. Mass spectrum: m/z 787 (M^+) with those of the ligand precursor **1** (given in the experimental section) shows that there are changes in chemical shifts but the nature of the two spectra are very similar. A significant change in the $^{13}\text{C-NMR}$ spectrum of **2** is observed. It shows that a total of six quaternary carbon atoms (C_q) is present in **2** although five such carbon atoms are there in **1**. This is really what is expected because the ligand is coordinated in the η^5 mode in **2** and in doing so **1** has to give up the proton of the silicon-attached CH carbon of the cyclopentadiene ring, thus converting the CH carbon to a quaternary one and the cyclopentadiene ring to a negatively charged 6e-ligand. The $^{29}\text{Si-NMR}$ spectrum showed a single peak for silicon at a different chemical shift from that of **1** (δ_{Si} : -1.65 for **1**, -11.8 for **2**). The mass spectrum showed the molecular ion peak at m/z 787 and several other mass peaks for its characteristic decomposition fragments. All these spectral evidences support the proposed structure and formulation of the sandwich complex **2**.

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