Dichloro(methyl)silyl-substituted cyclopentadienyl titanium complexes

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Abstract

The synthesis of (C₅H₅)(SiMeCl₂)₂ is described. The reaction of a dichloromethane solution of this compound with one equivalent of titanium tetrachloride leads to the monocyclopentadienyl complex TiCl₅-C₅H₅SiMeCl₂. Treatment of this complex with the lithium amides LiN(SiMe₃)₂ and LiNH₂Bu affords TiCl₅-C₅H₅(SiMeCl₂) and TiCl₅-C₅H₅(SiMeCl(N-Bu)), respectively. Alkylation of the trichlorotitanium derivative with 1.5 equivalents of Mg(CH₂C₅H₅)THF leads to the tribenzyl derivative Ti(C₅H₅)₅-C₅H₅-Mg(CH₂C₅H₅)THF. Hydrolysis of the trichloro- and tribenzyl-complexes leads to the μ-oxo dititanium compounds TiX₂-M-C₅H₅-C₅H₅(X=Cl, CH₂Ph). All of the new complexes were characterized by elemental analysis and NMR spectroscopy. © 1998 Elsevier Science S.A.

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1. Introduction

The study of homogeneous metallocene-based catalysts for the polymerization of α-olefins is one of the most active fields of research and many different types of modified systems have been investigated [1,2]. Monocyclopentadienyl-type compounds and particularly amido(dimethylsilyl)-bridged cyclopentadienyl complexes [3–6] are being intensively studied because these constrained-geometry catalysts are less restricted and able to polymerize and co-polymerize different bulkier olefins [7–9]. Recently, there has been a growing interest in the development of catalytic systems based on supported cyclopentadienyl ligands and metal complexes [10,11]. In this regard, the synthesis of group 4 transition metal complexes containing functionalized cyclopentadienyl ligands is of great interest [2]. A large number of compounds containing silyl-substituted cyclopentadienyl ligands have been prepared [12,13], but only a few examples of group 4 derivatives with active silicon–halogen bonds have been reported [3] [5,14,15]. Here, we describe the synthesis, chemical behaviour and characterisation of novel titanium derivatives containing a dichloro(methyl)silyl-substituted cyclopentadienyl ligand.

2. Results and discussion

The novel silyl-disubstituted 1-[dichloro(methyl)silyl]-1-(trimethylsilyl) cyclopentadiene 1 was prepared by reaction of (trimethylsilyl)cyclopentadienyl lithium with one equivalent of trichloromethylsilane in hexane (Scheme 1). Compound 1 was isolated as a pale yellow liquid in 84% yield and was characterized by ¹H and ¹³C NMR spectroscopy. Its ¹H and ¹³C NMR spectra showed the expected singlets for the trimethylsilyl and dichloro(methyl)silyl groups along with two resonances for the two pairs of non-equivalent protons of an AA′BB′ spin system and carbon atoms, respectively, and one weak resonance corresponding to the sp³ carbon. Very small amounts of the other possible isomers with the silyl ligands bonded to sp³ carbon atoms were observed at ambient temperature.

Compound 1 reacted with one equivalent of TiCl₄ at room temperature in dichloromethane to give the monocyclopentadienyl derivative [TiCl₅-C₅H₅(SiMeCl₂)] 2 with highly selective elimination of the SiMe₃ group as SiClMe₃ instead of the more electronegative SiCl₂Me (Scheme 1).

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1 Dedicated to an excellent scientist and a good friend, Peter M. Maitlis on the occasion of his 65th birthday.
Compound 2 was isolated as a yellow solid in 83% yield by cooling a hexane solution to $-30^\circ$C. The $^1$H and $^{13}$C($^1$H) NMR spectra of 2 showed a resonance for the methyl group bonded to silicon and an AA'BB' spin system for the cyclopentadienyl ring protons.

The titanium complex 2 was air-and-moisture-sensitive, but could be stored under argon for months as a solid. Its hexane or toluene solutions turned dark green after one week at $-30^\circ$C. The $^1$H NMR spectra of these green solutions indicated the formation of very small amounts of transformation products, which were not studied. Compound 2 was readily soluble in aromatic hydrocarbons.

Reaction of 2 with one equivalent of Li(N(SiMe)$_3$)$_2$ in hexane at room temperature gave the amido complex [TiCl$_2$(N(SiMe)$_3$)$_2$](η$^3$-C$_5$H$_4$(SiMeCl$_3$)) 3 (Scheme 1). Compound 3 was isolated as orange crystals by cooling a hexane solution to $-30^\circ$C. This selective reaction of lithium salts with the more polar Ti–Cl bonds leading to the metal–amido complex has been observed for other related groups 4 and 5 metal compounds [3]. In spite of the bulkiness of the bis(trimethylsilyl) amido ligand compound 3 did not eliminate SiClMe$_2$ even by refluxing its toluene solution. Thermal decomposition of 3 occurred on heating at 100°C, to give a mixture of decomposition products which was not further studied.

A similar reaction of 2 with one equivalent of LiNH'Bu in the presence of one equivalent of NEt$_3$ occurred with precipitation of LiCl and elimination of HCl to form the insoluble NEt$_3$H'Cl$^-$ salt. The constrained-geometry cyclic monomeric species [TiCl$_2$(η$^3$-C$_5$H$_4$(SiMeCl$_3$))] 4 was isolated as an orange solid from the hexane solution in 68% yield (Scheme 1). Although intermediates could not be observed, the reaction with the lithium amide probably also went through the formation of the corresponding protonated amido titanium complex which then reacted with the Si–Cl group eliminating HCl to give the final product.

Both amido compounds 3 and 4 were soluble in aromatic hydrocarbons and slightly soluble in alkanes.

The $^1$H NMR spectrum of 3 at ambient temperature showed two singlets for SiMe$_3$ and SiCl$_3$Me protons at δ 0.22 and 0.99 and two pseudotriplets for the cyclopentadienyl protons of an AA'BB' spin system at δ 6.13 and 6.70. The 6:1 intensity ratio for the SiMe$_3$ and SiCl$_3$Me protons was consistent with the formulation of 3 as [TiCl$_2$(N(SiMe)$_3$)$_2$](η$^3$-C$_5$H$_4$(SiMeCl$_3$)). The $^1$H NMR spectrum of 4 displayed two singlets for the dichloromethylsilyl and tert-butyl protons, and four resonances, one for each of the non-equivalent cyclopentadienyl protons of an ABCD spin system due to the lack of symmetry imposed by the presence of a chiral silicon atom.

Alkylation of 2 with 1.5 equivalents of

![Scheme 1](image-url)
Mg(CH\(_2\)\(_3\))\(_2\)C\(_6\)H\(_5\) in hexane at room temperature led to the trienyl derivative [Ti(CH\(_2\)\(_3\))\(_2\)C\(_6\)H\(_5\)](\(\eta^5\)-\(\eta^2\)-C\(_5\)H\(_5\))(SiMeCl\(_2\)).  

3. Experimental

3.1. Reagents and general techniques

All manipulations were performed under an inert atmosphere using Schlenk techniques or a VAC glove box Model HE 63P. Solvents were dried by standard procedures. Mg(CH\(_2\)Ph\(_2\))(THF)\(_2\) [17], LiNi(SiMe\(_3\))\(_2\) were prepared according to the literature procedures. \(\eta^5\)-C\(_5\)H\(_5\) was obtained commercially. NET\(_3\) (Merek) was distilled and stored over molecular sieves. NMR spectra were recorded at 25°C in \(\eta^5\)-C\(_5\)D\(_5\) on a Varian Unity FT-300 and 500 MHz instruments. \(\delta\) and \(\delta^c\) chemical shifts were referenced to Me\(_2\)Si, \(\delta\) 0 ppm. Elemental C, H analyses were carried out on a Perkin-Elmer 240 B microanalyzer.

3.2. Synthesis of 1-[dichloro(methyl)silyl]-1-(trimethyl silyl)cyclopentadiene (I)

Methyltrichlorosilane (6.27 ml, 53.42 mmol) was added at once to a suspension of Li[C\(_5\)H\(_5\)(SiMe\(_3\))] (7.7 g, 53.42 mmol) in 200 ml of hexane at \(-20^\circ\text{C}\). The reaction mixture was slowly warmed to room temperature and was stirred for 48 h to ensure completion of the reaction. The precipitate was allowed to settle, the supernatant liquid was filtered and volatiles were removed from the filtrate to yield a yellow-orange oil. Distillation at 70/10-2 mm Hg gave I as a pale yellow liquid (11.3 g, 45.0 mmol, 84% yield). \(\delta\) H NMR (300 MHz): \(\delta\) 0.04 (s, 9H, SiMe\(_3\)), 0.13 (s, 3H, SiMeCl\(_2\)), 6.42 (m, 2H, C\(_5\)H\(_5\)), 6.60 (m, 2H, C\(_5\)H\(_5\)) ppm. \(\delta^c\) (13\(\text{C}\)) NMR (75 MHz): \(\delta\) 1.7 (s, SiMe\(_3\)), 1.6 (s, SiMeCl\(_2\)), 59.1 [s, C\(_{ipso}\)(C\(_5\)H\(_5\))], 133.0, 133.7 [s, C\(_2\)(C\(_5\)H\(_5\))].

3.3. Synthesis of [(dichloro(methyl)silyl)-\(\eta^5\)-cyclopentadienyl] trichlorotitanium (IV) (2)

Compound 1 (4.34 g, 17.28 mmol) was added dropwise to a solution of titanium tetrachloride (2 ml, 17.28 mmol) in 75 ml of dichloromethane at \(-20^\circ\text{C}\) and the reaction mixture was stirred for 2 days. Volatiles were removed under vacuum to yield a yellow residue, which was repeatedly extracted into hexane. The hexane solution was concentrated and cooled to \(-30^\circ\text{C}\) to give 2 as a yellow microcrystalline solid (4.27 g, 12.85 mmol, 75% yield). \(\delta\) H NMR (300 MHz): \(\delta\) 0.70 (s, 3H, SiMeCl\(_2\)), 5.94 (m, 2H, C\(_5\)H\(_5\)), 6.47 (m, 2H, C\(_5\)H\(_5\)) ppm. \(\delta^c\) (13\(\text{C}\)) NMR (75 MHz): \(\delta\) 5.1 (s, SiMeCl\(_2\)), 87.0 [s, C\(_{ipso}\)(C\(_5\)H\(_5\))], 125.3, 127.9 [s, C\(_2\)(C\(_5\)H\(_5\))] ppm. Anal. Found: C, 21.80; H, 2.29%. C\(_6\)H\(_5\)Cl\(_2\)SiTi Calc.: C, 21.65; H, 2.10%. 


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3.4. Synthesis of \{dichloro(methyl)silyl-\(\eta^5\)-cyclopentadienyl\} dichloro bis(trimethylsilyl)amido titanium (IV) (3)

Solid lithium amide LiN(SiMe\(_3\))\(_2\) (0.26 g, 1.56 mmol) was added to a stirring solution of 2 (0.52 g, 1.56 mmol) in 50 ml of hexane at 20°C. The reaction mixture was stirred for 16 h. The white precipitate which formed was allowed to settle, and the supernatant liquid was filtered through Celite. The filtrate was concentrated ca. 20 ml under vacuum to ca. 30 ml. Cooling to 30°C was observed.

\(\text{CDCl}_3\) ppm. Analysis: Found: C, 35.80; H, 4.94; N, 123.6, 127.5, 127.8 [s, C=\text{C} (C\_5H\_4)]. (C\_\(\text{ipso}\) C\_5H\_4 not observed). Anal. Found: C, 64.85; H, 5.73%. C\(_{27}\)H\(_{38}\)Cl\(_2\)SiTi Calc.: C, 64.94; H, 5.65.

3.7. Synthesis of \{dichloro(methyl)silyl-\(\eta^5\)-cyclopentadienyl\} (\(\mu\)-oxo)dichlorotitanium (IV) (6)

A solution of 2 (1.40 g, 4.0 mmol) in 30 ml of toluene was treated with deoxygenated H\(_2\)O (72 \(\mu\)l, 4.0 mmol) added by syringe at ambient temperature. The reaction mixture was stirred for 5 h and then volatiles were removed under vacuum to yield a yellow microcrystalline solid which was recrystallized from toluene/hexane and identified as the title compound 6 (1.12 g, 3.20 mmol, 80% yield). \(\text{H NMR} (300 \text{ MHz}) : \delta 0.07 \text{ (s, 3H, SiMeCl)}, 5.88 \text{ (s, 1H, C\_5H\_4)}, 6.43 \text{ (s, 1H, C\_5H\_4)}, 6.80 \text{ (s, 1H, C\_5H\_4)}, 8.04 \text{ (s, 1H, C\_5H\_4),} 124.5 \text{ s, C\_C} (C\_5H\_4). (C\_\(\text{ipso}\) C\_5H\_4 not observed). Anal. Found: C, 25.33; H, 2.85%. C\(_{10}\)H\(_{16}\)Cl\(_2\)O\(_2\)Si\(_2\)Ti\(_2\) Calc.: C, 25.97; H, 2.52%.

3.8. Hydrolysis of \{dichloro(methyl)silyl-\(\eta^5\)-cyclopentadienyl\} tribenzyl titanium (IV) (7)

A solution of 5 (0.05 g, 0.1 mmol) in C\(_6\)D\(_6\) in a NMR tube was treated with deoxygenated D\(_2\)O (1.8 \(\mu\)l, 0.1 mmol) added by syringe and the tube was sealed. The reaction monitored by NMR spectroscopy was complete after 1 h giving complex 7 as the unique component in solution. \(\text{H NMR} (500 \text{ MHz}) : \delta 0.57 \text{ (s, 3H, SiMeCl)}, 2.64 \text{ (s, 2H, CH\_2Ph)}, 3.59 \text{ (s, 2H, CH\_2Ph)}, 5.97 \text{ (m, 2H, C\_5H\_4)}, 6.00 \text{ (m, 2H, C\_5H\_4),} 6.84\text{–7.13 (m, 10H, Ph).} \text{\(\text{C\_13[H NMR} (125 \text{ MHz}) : \delta 5.2 \text{ (s, SiMeCl)}, \delta 100.0 \text{ [s, C\_5H\_4], } \delta 123.1, 123.4, 124.1, 124.3 \text{ [s, C\_C (C\_5H\_4)]}, \text{(C\_\(\text{ipso}\) C\_5H\_4 not observed), } \delta 127.3, 127.7, 129.0 \text{ [s, C\_C (C\_5H\_4)]}, \delta 124.5 \text{ [s, C\_\(\text{ipso}\) C\_5H\_4]}.}

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