

Dichloro(methyl)silyl-substituted cyclopentadienyl titanium complexes ¹

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Received 20 May 1997

Abstract

The synthesis of $(C_5H_4)(SiMeCl_2)(SiMe_3)$ is described. The reaction of a dichloromethane solution of this compound with one equivalent of titanium tetrachloride leads to the monocyclopentadienyl complex $[TiCl_3\{\eta^5-C_5H_4(SiMeCl_2)\}]$. Treatment of this complex with the lithium amides $LiN(SiMe_3)_2$ and $LiNH^tBu$ affords $[TiCl_2\{N(SiMe_3)_2\}\{\eta^5-C_5H_4(SiMeCl_2)\}]$ and $[TiCl_2\{\eta^5-C_5H_4[SiMeCl(\eta-N^tBu)]\}]$, respectively. Alkylation of the trichlorotitanium derivative with 1.5 equivalents of $Mg(CH_2C_6H_5)_2(THF)_2$ leads to the tribenzyl derivative $[Ti(CH_2C_6H_5)_3\{\eta^5-C_5H_4(SiMeCl_2)\}]$. Hydrolysis of the trichloro- and tribenzyl-complexes leads to the μ -oxo dititanium compounds $[TiX_2\mu\{\eta^5-C_5H_4(\eta-OSiMeCl)\}]_2$ ($X = Cl, CH_2Ph$). All of the new complexes were characterized by elemental analysis and NMR spectroscopy. © 1998 Elsevier Science S.A.

Keywords: Titanium; [Dichloro(methyl)silyl]cyclopentadienyl; Amidosilyl

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{¹H} NMR spectroscopy. Its ¹H and ¹³C{¹H} 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 sp² carbon atoms were observed at ambient temperature.

Compound **1** reacted with one equivalent of $TiCl_4$ at room temperature in dichloromethane to give the monocyclopentadienyl derivative $[TiCl_3\{\eta^5-C_5H_4(SiMeCl_2)\}]$ **2** with highly selective elimination of the $SiMe_3$ group as $SiClMe_3$ instead of the more electronegative $SiCl_2Me$ (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°C . The ^1H and $^{13}\text{C}\{^1\text{H}\}$ 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°C . The ^1H 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 $\text{LiN}(\text{SiMe}_3)_2$ in hexane at room temperature gave the amido complex $[\text{TiCl}_2\{\text{N}(\text{SiMe}_3)_2\}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMeCl}_2)\}]$ **3** (Scheme 1). Compound **3** was isolated as orange crystals by cooling a hexane solution to -30°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_3 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.

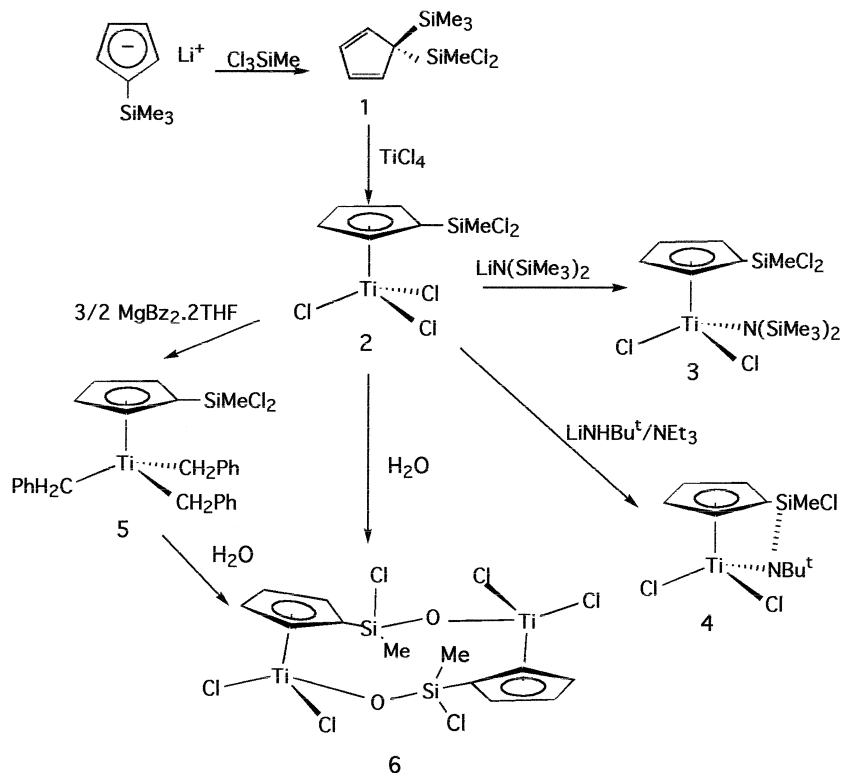
A similar reaction of **2** with one equivalent of

LiNH^tBu in the presence of one equivalent of NEt_3 occurred with precipitation of LiCl and elimination of HCl to form the insoluble $\text{NEt}_3\text{H}^+\text{Cl}^-$ salt. The constrained-geometry cyclic monomeric species $[\text{TiCl}_2\{\eta^5\text{-C}_5\text{H}_4[\text{SiMeCl}(\eta\text{-N}^t\text{Bu})]\}]$ **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 ^1H NMR spectrum of **3** at ambient temperature showed two singlets for SiMe_3 and SiCl_2Me 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_2Me protons was consistent with the formulation of **3** as $[\text{TiCl}_2\{\text{N}(\text{SiMe}_3)_2\}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMeCl}_2)\}]$. The ^1H NMR spectrum of **4** displayed two singlets for the dichloro(methyl)silyl 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.

$\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2(\text{THF})_2$ in hexane at room temperature led to the tribenzyl derivative $[\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_3\{\eta^5\text{-C}_5\text{H}_4(\text{SiMeCl}_2)\}]$ **5** (Scheme 1), which was isolated as a red crystalline solid in 52% yield from hexane. The ^1H NMR spectrum of **5** in C_6D_6 displayed one singlet for the chloromethylsilyl protons and one singlet for the six equivalent protons of the benzyl methylene groups, along with two multiplets due to the two pairs of non-equivalent cyclopentadienyl-ring protons.

Compound **5** was extremely moisture sensitive and had to be manipulated in an argon dry box.

Addition of one equivalent of H_2O to a toluene solution of the trichloro complex **2** resulted in the hydrolysis of two chloro bonds to give a yellow solid whose elemental analysis is consistent with the oxo derivative $[\text{TiSiCl}_3\text{OMe}(\eta^5\text{-C}_5\text{H}_4)]$. It has been reported [3] that hydrolysis of the related complex $[\text{TiCl}_3\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})\}]$ involves one Ti–Cl bond and one Si–Cl bond leading to a dinuclear compound with oxygen bridging the silicon and the titanium atoms of two $[-\text{TiCl}_2\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2-)]$ fragments which was characterized by X-ray diffraction. Similar hydrolysis of complex **2** would lead to a dimer $[\text{TiCl}_2\mu\{-\eta^5\text{-C}_5\text{H}_4(\eta\text{-OSiMeCl})\}]_2$ **6** containing two chiral silicon centers which could be expected as a mixture of the *meso* and *rac* isomers, whereas hydrolysis of two Ti–Cl or two Si–Cl bonds presumably would not induce chirality. The ^1H NMR spectrum of **6** was consistent with the first proposal indicating the presence of only one of the components as it showed four multiplets for the cyclopentadienyl ring protons of an ABCD spin system, along with one resonance due to the silyl–methyl group, and this behaviour was also confirmed by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. An analogous reaction was observed for the tribenzyl complex **5** when a solution of **5** in C_6D_6 in a NMR tube was treated with 1 equivalent of D_2O and the tube sealed. After 1 h the initial compound was totally transformed into the oxo complex $[\text{Ti}(\text{CH}_2\text{Ph})_2\mu\{-\eta^5\text{-C}_5\text{H}_4(\eta\text{-OSiMeCl})\}]_2$ **7** with elimination of PhCH_2D , observed as one triplet at δ 2.09 ($J_{\text{H-D}} = 2$ Hz). The ^1H NMR spectrum of complex **7** is consistent with the formation of a similar dimeric structure with two chiral silicon atoms which make the two pairs of ring protons (observed as two multiplets) and the two protons of both equivalent benzyl methylene groups (observed as two doublets with $J_{\text{H-H}} = 9.5$ Hz) non-equivalent. This behaviour was also confirmed by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum which shows four carbon-bearing resonances. All attempts made to obtain complex **7** on a preparative scale by the addition of a stoichiometric amount of water to its toluene or THF solutions followed by stirring for 4 h, led to mixtures containing **7** as the major component together with other oxo compounds, which could not be separated. For this reason complex **7** could not be identified by elemental analysis.

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 methods. $\text{C}_5\text{H}_5\text{SiMe}_3$ [16], $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2$ [17], and $\text{LiN}(\text{SiMe}_3)_2$ were prepared according to the literature procedures. *n*-BuLi, $^t\text{BuNH}_2$, SiMeCl_3 , SiCl_4 and TiCl_4 (Aldrich) were obtained commercially. NEt_3 (Merck) was distilled and stored over molecular sieves. NMR spectra were recorded at 25°C in C_6D_6 on Varian Unity FT-300 and 500 MHz instruments. (^1H and ^{13}C chemical shifts were referenced to Me_4Si , δ 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-(trimethylsilyl)cyclopentadiene (I)

Methyltrichlorosilane (6.27 ml, 53.42 mmol) was added at once to a suspension of $\text{Li}[\text{C}_5\text{H}_4(\text{SiMe}_3)]$ (7.7 g, 53.42 mmol) in 200 ml of hexane at -20°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 **1** as a pale yellow liquid (11.3 g, 45.0 mmol, 84% yield). ^1H NMR (300 MHz): δ 0.04 (s, 9H, SiMe_3), 0.13 (s, 3H, SiMeCl_2), 6.42 (m, 2H, C_5H_4), 6.60 (m, 2H, C_5H_4) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz): δ -1.7 (s, SiMe_3), 1.6 (s, SiMeCl_2), 59.1 [s, $\text{C}_{ipso}(\text{C}_5\text{H}_4)$], 133.0 , 133.7 [s, $\text{C}_2\text{-C}_5(\text{C}_5\text{H}_4)$].

3.3. Synthesis of [[dichloro(methyl)silyl]- η^5 -cyclopentadienyl] trichloro titanium (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°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°C to give **2** as a yellow microcrystalline solid (4.27 g, 12.85 mmol, 75% yield). ^1H NMR (300 MHz): δ 0.70 (s, 3H, SiMeCl_2), 5.94 (m, 2H, C_5H_4), 6.47 (m, 2H, C_5H_4) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz): δ 5.1 (s, SiMeCl_2), 87.0 [s, $\text{C}_{ipso}(\text{C}_5\text{H}_4)$], 125.3, 127.9 [s, $\text{C}_2\text{-C}_5(\text{C}_5\text{H}_4)$] ppm. Anal. Found: C, 21.80; H, 2.29%. $\text{C}_6\text{H}_7\text{Cl}_5\text{SiTi}$ Calc.: C, 21.65; H, 2.10%.

3.4. Synthesis of [*[(dichloro(methyl)silyl)]- η^5 -cyclopentadienyl]* dichloro bis(trimethylsilyl)amido titanium (IV) (3)

Solid lithium amide $\text{LiN}(\text{SiMe}_3)_2$ (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 and was cooled to -30°C to give orange crystals which were characterised as **3** (0.59 g, 1.29 mmol, 83% yield). ^1H NMR (300 MHz): δ 0.22 (s, 18H, $\text{N}(\text{SiMe}_3)_2$), 0.99 (s, 3H, SiMeCl_2), 6.13 (m, 2H, C_5H_4), 6.70 (m, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz): δ 5.4 (s, $\text{N}(\text{SiMe}_3)_2$), 6.6 (s, SiMeCl_2), 118.6 [s, $\text{C}_2\text{--C}_5$ (C_5H_4)], (C_{ipso} and another $\text{C}_2\text{--C}_5$ not observed). Anal. Found: C, 31.81; H, 5.48; N, 2.51%. $\text{C}_{12}\text{H}_{25}\text{Cl}_4\text{Si}_3\text{NTi}$ Calc.: C, 31.56; H, 5.48; N, 3.00%.

3.5. Synthesis of [*[(η^1 -*tert*-butylamido)(chloro)(methyl)silyl]- η^5 -cyclopentadienyl]*] dichlorotitanium (IV) (4)

Solid lithium amide LiNH^tBu (0.20 g, 2.52 mmol) and NEt_3 (0.35 ml, 2.52 mmol) were added at once to a previously cooled (-30°C) solution of **2** (0.84 g, 2.52 mmol) in 75 ml of toluene. The reaction mixture was slowly warmed to room temperature and was stirred overnight. The precipitate which formed was filtered through Celite and volatiles were removed from the filtrate to yield an orange solid. Recrystallisation from toluene–hexane solutions gave **4** as a microcrystalline solid (0.56 g, 1.69 mmol, 68% yield). ^1H NMR (300 MHz): δ 0.42 (s, 3H, SiMeCl), 1.44 (s, 9H, N^tBu), 5.81 (m, 1H, C_5H_4), 6.31 (m, 1H, C_5H_4), 6.37 (m, 1H, C_5H_4), 6.46 (m, 1H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz): δ 2.8 (s, SiMeCl_2), 32.0 [s, $\text{C}(\text{CH}_3)_3$], 82.2 (s, CMe_3), 124.2, 125.2, 126.6, 127.0 [s, $\text{C}_2\text{--C}_5$ (C_5H_4)], (C_{ipso} not observed) ppm. Anal. Found: C, 35.80; H, 4.94; N, 3.57%. $\text{C}_{10}\text{H}_{16}\text{Cl}_3\text{SiNTi}$ Calc.: C, 36.11; H, 4.81; N, 4.21%.

3.6. Synthesis of [*[(dichloro(methyl)silyl)]- η^5 -cyclopentadienyl]*] tribenzyl titanium (IV) (5)

A solution of $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2(\text{THF})_2$ (1.58 g, 4.5 mmol) in 30 ml of toluene was added dropwise to a stirring solution of **2** (1 g, 3 mmol) in 40 ml of hexane at -20°C . The reaction mixture was stirred for 2 h at low temperature and a further 10 h at 20°C to ensure completion of the reaction. The toluene solution was filtered through Celite and the filtrate was concentrated under vacuum to ca. 30 ml. Cooling to -30°C yielded red crystals of the title compound **5** (0.84 g, 1.68 mmol, 52% yield). ^1H NMR (300 MHz): δ 0.50 (s, 3H, SiMeCl_2), 3.0 (s, 6H, CH_2Ph), 5.62 (m, 2H, C_5H_4),

6.12 (m, 2H, C_5H_4), 6.80–7.06 (m, 15H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz): δ 6.4 (s, SiMeCl_2), 95.4 (s, CH_2Ph), 121.6, 121.7 [s, $\text{C}_2\text{--C}_5$ (C_5H_4)], (C_{ipso} C_5H_4 not observed), 123.6, 127.4, 129.0 [s, $\text{C}_2\text{--C}_6$ (C_6H_5)], 147.9 [s, C_{ipso} (C_6H_5)]. Anal. Found: C, 64.85; H, 5.73%. $\text{C}_{27}\text{H}_{28}\text{Cl}_2\text{SiTi}$ Calc.: C, 64.94; H, 5.65.

3.7. Synthesis of [*[(dichloro(methyl)silyl)]- η^5 -cyclopentadienyl]*] (μ -oxo)dichlorotitanium (IV) (6)

A solution of **2** (1.40 g, 4.0 mmol) in 30 ml of toluene was treated with deoxygenated H_2O (72 μl , 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). ^1H NMR (300 MHz): δ 0.07 (s, 3H, SiMeCl), 5.88 (m, 1H, C_5H_4), 6.43 (m, 1H, C_5H_4), 6.63 (m, 1H, C_5H_4), 6.84 (m, 1H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz): δ -2.9 (s, SiMeCl_2), 124.0, 125.5, 127.5, 127.8 [s, $\text{C}_2\text{--C}_5$ (C_5H_4)], (C_{ipso} C_5H_4 not observed). Anal. Found: C, 25.33; H, 2.85%. $\text{C}_{12}\text{H}_{14}\text{Cl}_6\text{O}_2\text{Si}_2\text{Ti}_2$ Calc.: C, 25.97; H, 2.52%.

3.8. Hydrolysis of [*[(dichloro(methyl)silyl)]- η^5 -cyclopentadienyl]*] tribenzyl titanium (IV)

A solution of **5** (0.05 g, 0.1 mmol) in C_6D_6 in a NMR tube was treated with deoxygenated D_2O (1.8 μl , 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. ^1H NMR (500 MHz): δ 0.57 (s, 3H, SiMeCl), 2.64 (s, 2H, CH_2Ph), 3.59 (s, 2H, CH_2Ph), 5.97 (m, 2H, C_5H_4), 6.00 (m, 2H, C_5H_4), 6.84–7.13 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz): δ 5.2 (s, SiMeCl), δ 100.0 [s, CH_2Ph], δ 123.1, 123.4, 124.1, 124.3 [s $\text{C}_2\text{--C}_5$ (C_5H_4)], (C_{ipso} C_5H_4 not observed), δ 127.3, 127.7, 129.0 [s, $\text{C}_2\text{--C}_5$ (C_6H_5)], δ 124.5 [s, C_{ipso} C_6H_5].

Acknowledgements

We are grateful to the DGICYT (Project PB-92-0178-C) and CAM (I + D 0034/94) for financial support. B.R. acknowledges Universidad de Alcalá de Henares for support provided (Project 042/95).

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