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Functionally substituted derivatives of (η^5-cyclopentadienyl) triisopropoxytitanium and (η^5-cyclopentadienyl) trichlorotitanium

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Abstract

A series of new functionally substituted (η^5-cyclopentadienyl)titanium trichlorides and triisopropoxides are described. (η^5-Pentaphenylcyclopentadienyl)- (**1**)- and (η^5-diphenylphosphinylcyclopentadienyl)titanium triisopropoxide (**2**) have been obtained in good yield from reactions of $(C_5Ph_5)Na$ and $(C_5H_4PPh_2)Li$, respectively, with chlorotitanium triisopropoxide. Treatment of **1** with hydrogen chloride in refluxing toluene forms (η^5-pentaphenylcyclopentadienyl)titanium trichloride (**6**) in quantitative yield. (η^5-N,N-Dimethylaminocyclopentadienyl)titanium trichloride is produced in 54% yield from a reaction between equimolar amounts of $(C_5H_4NMe_2)Li$ and titanium tetrachloride in pentane solution. A reaction between titanium tetrachloride and carbomethoxytrimethylsilylcyclopentadiene, formed from $(C_5H_4CO_2Me)Na$ and $ClSiMe_3$, produces (η^5-carbomethoxycyclopentadienyl)titanium trichloride in 78% yield.

Keywords: Titanium; Alkoxides; Cyclopentadienyl derivatives

1. Introduction

A rather wide variety of functionally substituted titanocene dichlorides and related compounds have been described in the literature. In addition to the well-known methyl and permethyl derivatives, titanocene dichlorides containing diphenylphosphinyl [1,2], dimethylphosphinyl [2], chloro [3], N,N-dimethylamino [4], trifluoromethyl [5], carbomethoxy [6], vinyl [7,8], trimethylsilyl [9,10], phenyl [10–12], benzyl [12] and 2-methoxyethyl [13] substituents have been prepared. Several of these ring-substituted titanocene dichlorides have been investigated as catalysts for the homogeneous polymerization of ethylene and propylene [14].

In contrast, mono-cyclopentadienyl trichloride and trialkoxide derivatives of titanium that contain functional ring substituents are much more limited in number [13,15–18]. We have recently prepared some (η^5-tetramethyl- and (η^5-tetraphenylcyclopentadienyl) titanium triisopropoxide analogs, and have evaluated their catalytic activities for syndioselective styrene polymerization [19]. In an effort to expand substantially this important, useful class of organometallic compounds, we now report on the synthesis and characterization of a series of new functionally substituted (η^5-cyclopentadienyl)titanium triisopropoxides and trichlorides.

2. Results and Discussion

We have recently described the preparation of (η^5-tetramethyl- and (η^5-tetraphenylcyclopentadienyl) titanium triisopropoxides in high yields from reactions of $ClTi(OC_3H_7i)_3$ and $(C_5HMe_4)Li$ or $(C_5HPh_4)Na$ in

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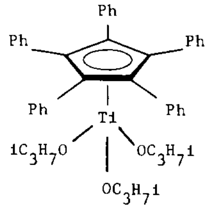
THF solution [19]. In the present study, a related reaction between equimolar amounts of $(C_5Ph_5)Na$ and $ClTi(OC_3H_7i)_3$ has likewise produced the pentaphenylcyclopentadienyl analog (**1**) in 67% yield. In a similar manner, a reaction between $(C_5H_4PPh_2)Li$ and $ClTi(OC_3H_7i)_3$ afforded a diphenylphosphinyl derivative (**2**) in 72% yield. Both compounds were characterized by microanalyses and by their ^1H NMR spectra. The latter contained doublet and heptet resonances for the three isopropoxy groups in the expected ratio of 18 : 3, and the spectrum of **2** also exhibited pseudo-triplet resonances for the ring $H_{2,5}$ and $H_{3,4}$ protons at 6.30 ppm and 6.19 ppm, respectively.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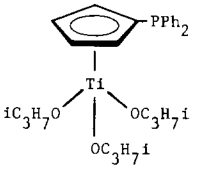
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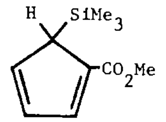
Studies by Jutzi, Clark and their coworkers in 1979/80 demonstrated that an efficient route to $(\eta^5\text{-}C_5H_5)TiCl_3$ and substituted derivatives involved reactions of an appropriate substituted trimethylsilylcyclopentadiene and titanium tetrachloride in a suitable solvent [15,16]. In related studies, we have investigated a reaction between the readily available $(C_5H_4CO_2Me)Na$ [20] and $ClSiMe_3$, which led to carbomethoxytrimethylsilylcyclopentadiene (**3**) in 90% yield. ^1H NMR spectral analysis of the initial reaction product indicated that several isomers were present. Following vacuum distillation to produce an analytical sample, spectral data indicated that **3** was the major isomer present. The ^1H NMR spectrum contained a three-proton multiplet assignable to the olefinic protons between 6.6–6.3 ppm, a singlet for the methyl ester protons at 4.02 ppm, a one-proton singlet for the proton on the saturated ring carbon at 3.80 ppm, and a singlet for the trimethylsilyl protons at 0.37 ppm. The ^{13}C NMR spectrum contained four major peaks in the olefinic region (124, 122, 120, 118 ppm) as well as peaks at 57 ppm and 0.5 ppm for the methyl-ester carbon and the trimethylsilyl carbons, respectively. The IR spectrum of **3** exhibited a moderately strong carbonyl absorption for the ester at 1724 cm^{-1}. A GC-MS analysis of **3** was also performed. The parent ion was not detected, although a major peak assignable to carbomethoxycyclopentadiene (m/e 124) was observed.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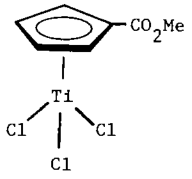
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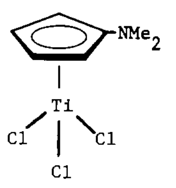
A subsequent reaction between **3** and titanium tetrachloride in pentane solution afforded (η^5-carbomethoxycyclopentadienyl)trichlorotitanium (**4**) in 87% yield after washing the product with pentane and drying. Compound **4** is slightly soluble in hydrocarbons, therefore a minimum amount of pentane was employed. An analytical sample was best prepared by vacuum sublimation. The ^1H NMR spectrum of **4** showed the characteristic A_2B_2 pseudo-triplets for the $H_{2,5}$ and $H_{3,4}$ protons at 7.36 ppm and 7.02 ppm, respectively, whereas the carbomethoxymethyl protons occurred as a sharp singlet at 3.93 ppm.

Although reactions between equimolar amounts of cyclopentadienyllithium reagents and titanium tetrachloride often lead to the corresponding titanocene dichlorides as well as the desired trichlorides, in some instances these reactions can nevertheless be used successfully for the formation of ring-substituted cyclopentadienyltitanium trichlorides [8]. Another example has involved the addition of $(C_5H_4NMe_2)Li$ [21] to titanium tetrachloride in pentane solution, which after extraction and crystallization of the product has produced (η^5-N,N-dimethylaminocyclopentadienyl)trichlorotitanium (**5**) in 54% yield as air-sensitive dark blue crystals. The ^1H NMR spectrum of **5** exhibited A_2B_2 pseudo-triplets for the substituted cyclopentadienyl ring protons as well as a singlet resonance for the N,N-dimethylamino protons at 3.15 ppm.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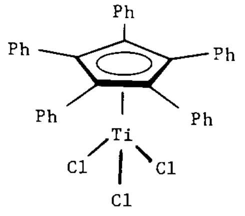
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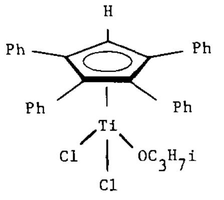
A third-route to ring-substituted cyclopentadienyltitanium trichlorides is based on early studies by Nesmeyanov et al. [22], who found that treatment of cyclopentadienyltitanium trialkoxides with a suitable chlorinating agent such as acetyl chloride generated the parent compound $(\eta^5\text{-}C_5H_5)TiCl_3$. In an extension of this procedure, the triisopropoxide derivative **1** was readily converted to (η^5-pentaphenylcyclopentadienyl)trichlorotitanium (**6**) by heating **1** at reflux in toluene for 1 h while bubbling hydrogen chloride through the solution. An almost immediate color change from yellow to purple was observed, and subsequent extraction of the product and drying produced **6** in quantitative yield.

Treatment of a pentane solution of (η^5-tetraphenylcyclopentadienyl)triisopropoxytitanium [19] with hydrogen chloride at reflux for 1.5 h surprisingly resulted in cleavage of only two isopropoxy substituents, and (η^5-tetraphenylcyclopentadienyl)dichloroisopropoxytitanium (**7**) was obtained in 76% yield.



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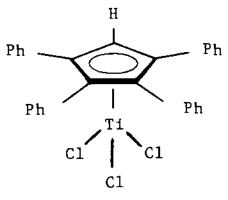

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Further chlorination of **7** by means of thionyl chloride, however, gave the desired product (η^5-tetraphenylcyclopentadienyl)trichlorotitanium (**8**) in quantitative yield. It is interesting to note that the unique cyclopentadienyl proton resonance for (η^5-C_5HPh_4)Ti(OC_3H_7i)$_3$ occurs as a singlet at 6.72 ppm, whereas this same resonance is shifted over 1 ppm downfield to 7.82 ppm in the spectrum of **8**, because of the strong deshielding effects of the three chloro substituents.

3. Experimental Section

All operations were carried out under an argon atmosphere using Schlenk techniques, or under nitrogen using glove box techniques. The argon was deoxygenated by passage through a heated copper (BTS) column and dried with phosphorus pentoxide and molecular sieves. Pentane, hexane and toluene were distilled under argon from sodium-potassium alloy. Tetrahydrofuran (THF) and diethyl ether were pre-dried over sodium wire. THF was predistilled from sodium wire, and both solvents were distilled under argon from sodium-potassium alloy. Methylene chloride was distilled under argon from calcium hydride. (C_5Ph_5)Na [23], ($C_5H_4PPh_2$)Li [24], ($C_5H_4CO_2Me$)Na [20], ($C_5H_4NMe_2$)Li [21], and (C_5HPh_4)Ti(OC_3H_7i)$_3$ [19] were prepared by literature procedures. Hydrogen chloride was generated by adding concentrated sulfuric acid to sodium chloride under an argon atmosphere. Chlorotitanium triisopropoxide, chlorotrimethylsilane, and titanium tetrachloride were purchased from Aldrich Chemical Co. Infrared spectra were recorded on either Perkin-Elmer 1310 IR or 1600 FTIR spectrometers. NMR spectra were recorded on a Hitachi HT-1200 or a Varian XL300 spectrometer. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

3.1. *(η^5-Pentaphenylcyclopentadienyl)triisopropoxytitanium (1)*

Pentaphenylcyclopentadienylsodium (1.77 g, 3.78 mmol) and chlorotitanium triisopropoxide (0.99 g, 3.78 mmol) were added to separate 100 ml round-bottom Schlenk flasks in a glove box. Both solids were dissolved in a minimum amount of THF and then placed in an ice-salt bath for 15 min. The solution of the sodium salt was slowly transferred via a cannula with stirring into the titanium solution, and allowed to react at a cold temperature for 3 h. The reaction mixture was then allowed to warm to room temperature. THF was removed in vacuo and the resulting purple solid was extracted under argon in a Soxhlet apparatus with hexane overnight. The hexane was removed in vacuo resulting in 1.70 g (67%) of **1**. An analytical sample was obtained by recrystallization from hexane at −20°C overnight, producing yellow needles, mp 219–221°C. Anal. Found: C, 78.56; H, 6.80. $C_{44}H_{46}O_3Ti$ Calc.: C, 78.79; H, 6.91%. ^1H NMR ($CDCl_3$): δ 7.09 (25H, br s, Ph); 4.65 (3H, h, C–H); 1.11 (18H, d, CH_3).

3.2. *(η^5-Diphenylphosphinylcyclopentadienyl)triisopropoxytitanium (2)*

Diphenylphosphinylcyclopentadienyllithium (5.18 g, 20.3 mmol) and chlorotitanium triisopropoxide (5.30 g, 20.3 mmol) were added to separate 200 ml round-bottom Schlenk flasks in a glove box. Both solids were dissolved in a minimum amount of diethyl ether and then placed in an ice-salt bath for 15 min. The solution of the lithium salt was slowly cannulated with stirring into the titanium solution, and allowed to react at a cold temperature for 3 h. The reaction mixture was then allowed to warm to room temperature. Diethyl ether was removed in vacuo and the resulting yellow-brown oil was extracted by stirring with hexane overnight. The hexane solution was filtered through a plug of 10% deactivated silica gel and Celite on a Schlenk frit. The hexane was removed in vacuo yielding 6.95 g (72%) of **2** as a yellow air-sensitive oil. Anal. Found: C, 65.69; H, 7.35. $C_{26}H_{35}O_3Pti$ Calc.: C, 65.82; H, 7.44%. ^1H NMR ($CDCl_3$): δ 7.20 (10H, m, Ph); 6.30 (2H, t, $H_{2,5}$); 6.19 (2H, t, $H_{3,4}$); 4.42 (3H, h, C–H); 1.07 (18H, d, CH_3). ^{31}P NMR (THF): δ −19.6.

3.3. *Carbomethoxytrimethylsilylcyclopentadiene (3)*

Carbomethoxycyclopentadienylsodium (10.11 g, 69.2 mmol) was added to a 300 ml round-bottom Schlenk flask in a glove box. The tan solid was suspended in 150 ml of pentane under argon, then chlorotrimethylsilane (8.75 ml, 69.2 mmol) was added via a syringe. The reaction mixture was stirred overnight at room temperature. The mixture of pink solid and yellow solution was filtered through. Celite on a Schlenk frit, then washed three times with 10 ml portions of pentane. The pentane was removed in vacuo, resulting in 12.2 g (90%) of a yellow-orange oil. An analytical sample was obtained by vacuum distilling the product twice at 60°C 0.5 mm Hg^{-1}. Anal. Found: C, 60.88; H, 8.29. $C_{10}H_{16}O_2Si$ Calc.: C, 61.18; H, 8.21%. ^{1}H NMR ($CDCl_3$): δ 6.7–6.3 (3H, m, olefinic-H); 4.02 (3H, s, OCH_3); 3.80 (1H, d, sat.-H); 0.37 (9H, s, Si–CH_3). ^{13}C NMR ($CDCl_3$): δ 124, 122, 120, 118, 57, 0.5. IR (hexane): 1724 (m), 1711 (sh) cm^{-1}.

3.4. (η^5-Carbomethoxycyclopentadienyl)trichlorotitanium (4)

Titanium tetrachloride (1.10 ml, 10.0 mmol) was added to an argon-purged, 100 ml Schlenk flask equipped with a pressure-equalizing addition funnel. Pentane (15 ml) was added to the flask, which was then placed in a dry ice/acetone bath for 15 min. Carbomethoxytrimethylsilylcyclopentadiene (1.90 g, 7.24 mmol) was added to the addition funnel, followed by 30 ml of pentane. The resulting solution was added dropwise to the flask with stirring over 15 min. The cold bath was then removed and the reaction mixture allowed to warm to room temperature. The mixture was stirred at room temperature for 30 min, and then filtered using a Schlenk frit. The orange solid was washed three times with 10 ml portions of pentane. The solid was dried in vacuo to give 2.1 g (78%) of **4**. An analytical sample was obtained by Soxhlet extraction of the product with hexane followed by vacuum sublimation at 70°C 0.01 mm Hg^{-1}. Anal. Found: C, 30.32; H, 2.49. $C_7H_7Cl_3O_2Ti$ Calc.: C, 30.31; H, 2.54%. ^{1}H NMR ($CDCl_3$): δ 7.36 (2H, t, $H_{2,5}$); 7.02 (2H, t, $H_{3,4}$); 3.93 (3H, s, CH_3).

3.5. (η^5-N,N-Dimethylaminocyclopentadienyl)trichlorotitanium (5)

A solution of 1.23 ml (11.2 mmol) of titanium tetrachloride in 20 ml of pentane was cooled to 0°C and 20 ml of THF was added via a syringe over a period of 5 min. To the stirred yellow suspension was slowly added via a cannula a solution of 1.17 g (10.2 mmol) of N,N-dimethylaminocyclopentadienyllithium in 30 ml of THF, which was maintained at −30°C. The brown reaction mixture was stirred overnight at room temperature. The volatiles were removed in vacuo and the remaining dark-brown residue was extracted with methylene chloride in a Soxhlet apparatus for 30 h. The dark-blue extract was filtered through Celite, concentrated, and cooled to −20°C to yield 1.44 g (54%) of **5** as dark-blue crystals. Anal. Found: C, 32.30; H, 4.04; N, 5.01. $C_7H_{10}Cl_3NTi$ Calc.: C, 32.04; H, 3.84; N, 5.34%. ^{1}H NMR ($CDCl_3$): δ 6.62 (2H, t, $H_{2,5}$); 6.15 (2H, t, $H_{3,4}$); 3.15 (6H, s, NMe_2).

3.6. (η^5-Pentaphenylcyclopentadienyl)trichlorotitanium (6)

(η^5-Pentaphenylcyclopentadienyl)triisopropoxytitanium (0.50 g, 0.75 mmol) was weighed into an argon-purged 100 ml round-bottom flask equipped with a gas inlet, condenser, and bubbling-tube adapter. The yellow solid was dissolved in 40 ml of toluene and the solution was heated at reflux for 1 h while hydrogen chloride was introduced via the bubbling tube. The color changed from yellow to purple within 5 min. After cooling to room temperature, the toluene was removed in vacuo and the product was washed three times with 10 ml portions of pentane. Subsequent drying of the product led to a quantitative yield (0.46 g) of **6** as an air-stable purple solid, mp 245°C. An analytical sample was obtained by recrystalization from toluene at −20°C. Anal. Found: C, 69.78; H, 4.40. $C_{35}H_{25}Cl_3Ti$ Calc.: C, 70.08; H, 4.20%. ^{1}H NMR ($CDCl_3$): δ 7.20 (25H, m, Ph).

3.7. (η^5-Tetraphenylcyclopentadienyl)dichloroisopropoxytitanium (7)

(η^5-Tetraphenylcyclopentadienyl)triisoproxytitanium (3.87 g, 6.51 mmol) was weighed into an argon-purged 250 ml three-neck flask equipped with a gas inlet, condenser, and a gas bubbler tube. The yellow solid was dissolved in 200 ml of hexane and then heated at reflux while hydrogen chloride was introduced via the bubbling tube. The color changed from yellow to dark red within 5 min. After 1.5 h, heating and stirring were stopped, the flask was wrapped in aluminum foil, and a slow stream of argon was allowed to pass over the reaction mixture overnight. The mother liquor was then decanted and the solid was dried in vacuo, producing 2.67 g (76%) of **7** as air-stable red crystals. Anal. Found: C, 70.10; H, 5.40. $C_{32}H_{28}Cl_2OTi$ Calc.: C, 70.22; H, 5.16%. ^{1}H NMR ($CDCl_3$): δ 7.25 (21H, m, aromatic); 4.50 (1H, h, C–H); 1.10 (6H, d, CH_3).

3.8. (η^5-Tetraphenylcyclopentadienyl)trichlorotitanium (8)

(η^5-Tetraphenylcyclopentadienyl)dichloroisopropoxytitanium (0.25 g, 0.46 mmol) was weighed into an argon-purged 100 ml round-bottom Schlenk flask. Thionyl chloride (10 ml) was added to the solid, and the dark-red solution was stirred overnight. The thionyl chloride was removed in vacuo and the product was washed three times with 10 ml portions of pentane. Subsequent drying resulted in a quantitative yield (0.24 g) of **8** as a dark-red solid. An analytical sample was obtained by recrystallization from 250 ml of hot hexane and then storage in a −20°C freezer overnight. Anal. Found: C, 66.09; H, 4.32. $C_{29}H_{21}Cl_3Ti$ Calc.: C, 66.50; H, 4.04%. ^1H NMR ($CDCl_3$): δ 7.82 (1H, s, C_5H); 7.30 (20H, m, Ph).

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