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The formation of ring-substituted titanocene derivatives containing chloro and carbomethoxy substituents

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Abstract

(Carbomethoxycyclopentadienyl)thallium has been prepared in high yield via a new and convenient procedure starting with sodium carbomethoxycyclopentadienide. Reactions of (carbomethoxycyclopentadienyl)thallium with either (η^5-cyclopentadienyl)titanium trichloride or titanium tetrachloride produce carbomethoxytitanocene dichloride or 1,1′-dicarbomethoxytitanocene dichloride, respectively, in good yield. Reductions of these dichlorides in the presence of carbon monoxide have afforded carbomethoxy- and 1,1′-dicarbomethoxytitanocene dicarbonyl. Chloro- and 1,1′-dichloro-titanocene dicarbonyl can likewise be prepared via reductive carbonylation of the respective chloro-substituted titanocene dichlorides.

Introduction

Since its discovery in the early 1950's [1–4], dichlorobis(η^5-cyclopentadienyl)titanium (titanocene dichloride) has played an extremely important role in the development of organotitanium chemistry, including homogeneous Ziegler–Natta catalysis [5–7]. The vast majority of the chemistry associated with this organotitanium compound has involved reactions at the metal center. Early attempts to react titanocene dibromide with acetyl chloride under Friedel–Crafts conditions failed [3]. However, indirect approaches to functionally substituted titanocene dihalides using appropriately substituted metal cyclopentadienides have been successful [8]. In addition to the well-known methyl and permethyl derivatives, titanocene dichlorides containing phenyl [9–11], benzyl [11], trimethylsilyl [10,12], vinyl [13], dimethylamino [14], chloro [15] and trifluoromethyl [16] groups have been prepared in this manner.

Variations of ring substituents in substituted titanocene and zirconocene dihalides are known to have pronounced effects on the steric, electronic and catalytic properties of these systems [16–20]. Such changes might also be expected to influence other reactions at the metal center, such as the rates of substitution of corresponding titanocene dicarbonyls by phosphines [21]. In an effort to expand the area of functionally substituted titanocene compounds, we now report on the synthesis and characterization of a series of mono- and di-carbomethoxy derivatives. These represent the first titanocene compounds that contain oxygen-functional ring substituents. Some analogous titanocene dicarbonyls that contain chloro ring substituents are also described.

Results and discussion

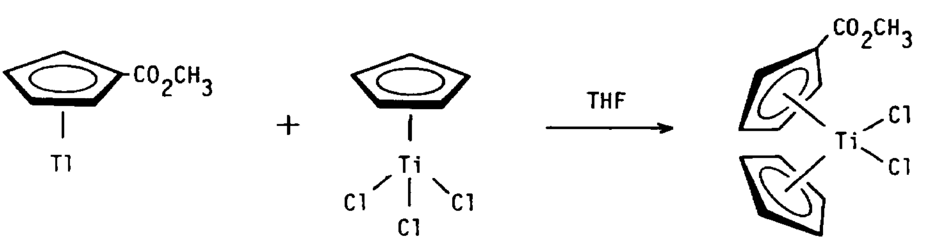
We have previously shown that reactions of sodium carbomethoxycyclopentadienide with a variety of middle and late transition metal halides as well as tin halides provide facile routes to carbomethoxycyclopentadienyl derivatives of these metals [22–24]. Efforts to extend these studies to early transition metals proved less successful. Thus, a reaction between sodium carbomethoxycyclopentadienide and titanium tetrachloride in benzene solution produced an intractable product, whereas a similar reaction with (η^5-cyclopentadienyl)titanium trichloride afforded the expected product carbomethoxytitanocene dichloride (II), but only in 22% yield [25].

In contrast, we and others have demonstrated that reactions of substituted cyclopentadienylthallium reagents bearing phenyl [11], chloro [15], diphenylphosphino [26], and trifluoromethyl [16] substituents with various titanium chlorides lead to the corresponding substituted cyclopentadienyltitanium compounds in very good to excellent yields. It was thus of interest to investigate the possible reactions of (carbomethoxycyclopentadienyl)thallium (I) as an alternate route for the formation of II as well as 1,1′-dicarbomethoxytitanocene dichloride (III).

The currently available synthesis of thallium reagent I involves initial reaction of cyclopentadienylmagnesium bromide with carbon dioxide followed by esterification of the diacid to form the dimethyl ester [27]. Alternatively, carbomethoxycyclopentadiene dimer can be prepared directly in low yield from a reaction between sodium cyclopentadienide and methyl chloroformate [23,28]. The dimeric ester is then thermally cracked under reduced pressure followed by passing the unstable carbomethoxycyclopentadiene directly into an aqueous solution of thallium(I) chloride or thallium(I) acetate [23,27,29]. This route to I is both lengthy and tedious, and in our hands the cracking step often produces variable yields of the desired product.

An alternative and simpler route to thallium reagent I has been developed based on sodium carbomethoxycyclopentadienide, which is readily prepared in excellent yield [22,23]. To a stirred THF solution of the sodium reagent was added a molar excess of water at $-20\,^\circ$C. The solution was stirred for 4 h at this temperature, then combined with an aqueous solution of thallium(I) chloride and potassium hydroxide in a blender. After blending, the resulting white precipitate was filtered, washed and dried to afford I as an air-stable white solid in 83% yield. A ^{1}H NMR spectrum of I in $\text{Me}_2\text{SO-}d_6$ exhibited a pair of triplets for the two sets of non-equivalent ring protons at δ 5.78 and 6.39 ppm, as well as a sharp singlet for the methyl protons at δ 3.58 ppm.

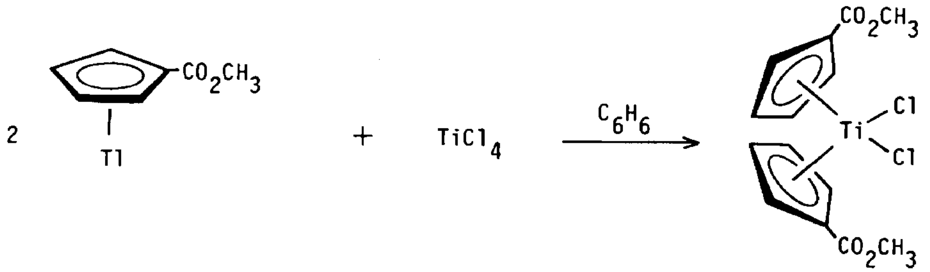
A reaction between equimolar amounts of I and (η^5-cyclopentadienyl)titanium trichloride in THF solution produced II as an air-stable red solid in 57% yield. IR analysis (KBr) gave strong characteristic absorption at 1722 and 1153 cm^{-1} for



I II

C=O and C–O stretching frequencies, respectively. The ^{1}H NMR spectrum of II in $CDCl_3$ exhibited a pair of triplets for the substituted-ring protons at δ 6.65 and 7.14 ppm, a singlet for the unsubstituted cyclopentadienyl ring protons at δ 6.65 ppm, and a singlet for the methyl protons at δ 3.91 ppm.

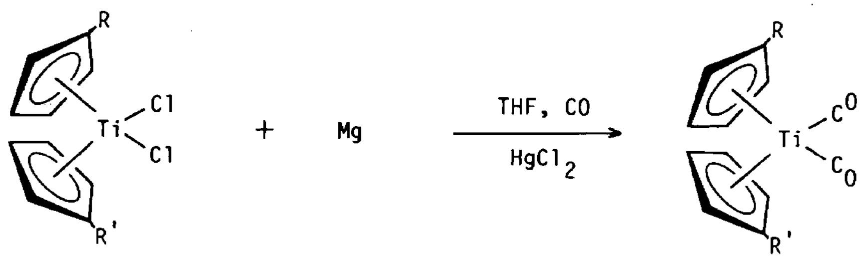
In a similar manner, a reaction between two equivalents of I and titanium tetrachloride in benzene solution afforded a 62% yield of III. This product was also



I III

an air-stable red solid whose IR spectrum (KBr) contained C=O and C–O stretching bands at 1720 and 1158 cm^{-1}, respectively. The ^{1}H NMR spectrum of III exhibited 2 pairs of triplets for the substituted-ring protons at δ 6.58 and 7.20 ppm as well as a singlet for the methyl protons at δ 3.91 ppm. In the ^{1}H NMR spectra of both II and III, the lower field resonances most likely represent the protons adjacent to the electronegative carbomethoxy substituent [H(2,5)], based on unequivocal correlations developed for substituted ferrocenes [30]. In the latter compounds the rings are parallel, however, while in II and III the rings are canted, a feature that could lead to differential shielding effects. Any assignments of triplet resonances in these and related ring-substituted titanocene dichlorides must therefore be regarded as tentative at present.

In a manner analogous to that developed for the synthesis of titanocene dicarbonyl [31,32], both II and III could be reductively carbonylated to form the corresponding substituted titanocene dicarbonyls. Thus, a reaction between II and magnesium metal in THF under a carbon monoxide atmosphere gave carbomethoxytitanocene dicarbonyl (IV) in 26% yield, whereas use of aluminum filings as the reducing agent increased the yield of IV to 54%. The IR spectrum of IV in C_6D_6 contained strong absorptions for terminal and organic carbonyl groups at 1984, 1912 and 1725 cm^{-1}. The ^{1}H NMR spectrum of IV in C_6D_6 exhibited triplet resonances for the substituted ring protons at δ 3.64 and 4.86 ppm, a singlet resonance at δ 3.95 ppm for the unsubstituted cyclopentadienyl ring protons, and a methyl proton singlet at δ 2.83 ppm.



II R = CO_2CH_3; R' = H

III R, R' = CO_2CH_3

VI R = Cl; R' = H

VII R, R' = Cl

IV R = CO_2CH_3; R' = H

V R, R' = CO_2CH_3

VIII R = Cl; R' = H

IX R, R' = Cl

A similar reduction of III in THF solution using magnesium metal under a carbon monoxide atmosphere produced 1,1′-dicarbomethoxytitanocene dichloride (V) in 77% yield. The IR spectrum of V in C_6D_6 contained strong carbonyl absorptions at 1998, 1933 and 1715 cm^{-1}. The ^1H NMR spectrum of V in this solvent exhibited triplet resonances for the substituted ring protons at δ 3.63 and 4.88 ppm as well as a methyl proton resonance at δ 2.79 ppm.

It is noteworthy that the ring protons in the dicarbonyls IV and V all exhibit similar shielding effects relative to the respective protons in the dihalides II and III. An analogous upfield shift of ring protons is observed in the ^1H NMR spectrum of titanocene dicarbonyl relative to titanocene dichloride.

Since both chlorotitanocene dichloride (VI) and 1,1′-dichlorotitanocene dichloride (VII) were available [15], it was of interest to determine if they could likewise be reductively carbonylated to their respective dicarbonyls without interference of the ring chloro substituents. Using the general procedure developed for the carbomethoxy analogs IV and V, VII was converted into 1,1′-dichlorotitanocene dicarbonyl (IX) in 67% yield. In addition to carbonyl bands in the IR spectrum (hexane) of IX at 1985 and 1912 cm^{-1}, the ^1H NMR spectrum exhibited triplet resonances for the substituted ring protons at δ 4.42 and 4.78 ppm. The observance of triplet resonances for IX is of interest, since the ^1H NMR spectra of both VI and VII under similar conditions showed the substituted ring protons as singlets [15].

An analogous reduction of VI afforded chlorotitanocene dicarbonyl (VIII) in 71% yield. Although a ^1H NMR spectrum of VIII was not obtained, its IR spectrum (hexane) contained strong carbonyl bands at 1998 and 1979 cm^{-1}, and it was characterized by a satisfactory elemental analysis.

Studies to examine the chemistry and possible catalytic properties of these functionally substituted titanocene dichlorides are in progress in our laboratory.

Experimental

General

All operations were carried out under an argon atmosphere using standard Schlenk or vacuum line techniques except where specified. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and phosphorus pentoxide. All glassware except where specified was ovendried, evacuated and flushed with argon, and cooled under argon. Tetrahydrofuran (THF) was predried over sodium wire and distilled under argon from sodium-benzophenone ketyl. Benzene, hexane and dichloromethane were dried and distilled from calcium hydride. ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer, while IR spectra were recorded on a Perkin–Elmer 1310 or a Beckman IR-10 spectrometer. Melting points were obtained in sealed capillaries under argon and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

Purified titanium tetrachloride was used as commercially available from Fisher Scientific Co., whereas thallium(I) chloride was used as obtained from Alfa Products, Morton-Thiokol, Inc. $(C_5H_5)TiCl_3$ [33], $(C_5H_5)(C_5H_4Cl)TiCl_2$ [15], $(C_5H_4Cl)_2TiCl_2$ [15] and $(C_5H_4CO_2CH_3)Na$ [23] were prepared by literature methods. Neutral grade CAMAG alumina was deactivated with degassed water (5%) under argon before use.

(Carbomethoxycyclopentadienyl)thallium (I)

A 250-ml 3-necked, round-bottom flask equipped with a pressure-equalizing addition funnel and magnetic stirring bar was flushed with argon. Sodium carbomethoxycyclopentadienide (7.71 g, 52.7 mmol) and 100 ml of THF were combined in the flask and a mercury overpressure valve was attached. The stirred solution was cooled to −20 °C and 2.0 ml (0.11 mol) of degassed distilled water was added dropwise. The solution was stirred for 4 h at −20 °C during which time the color changed from clear to yellow to light brown. The solution was then added in air to a 900-ml blender that contained 12.01 g (50.1 mmol) of thallium(I) chloride, 28.09 g (0.50 mol) of potassium hydroxide and 200 ml of distilled water. The mixture was blended at moderate to high speed for 4 min, producing a white precipitate. The solid was filtered, washed with 2 × 25 ml of water, 2 × 20 ml of diethyl ether, 10 ml of absolute ethanol, and dried in vacuo to yield 13.85 g (85%) of (carbomethoxycyclopentadienyl)thallium as a white powder, m.p. 136–139 °C (lit. m.p. 140–142 °C [27], m.p. 136–140 °C [23]).

(η^5-Methoxycarbonylcyclopentadienyl)(η^5-cyclopentadienyl)dichlorotitanium (Carbomethoxytitanocene dichloride) (II)

A 300-ml 3-necked, round-bottom flask equipped with a pressure-equalizing addition funnel and magnetic stirring bar was flushed with argon. (Carbomethoxycyclopentadienyl)thallium (4.96 g, 15.1 mmol) and 100 ml of THF were added and a mercury overpressure valve was attached. To the stirred solution, $(C_5H_5)TiCl_3$ (3.31 g, 15.1 mmol) in 75 ml of THF was added dropwise over a 30 min period. The reaction mixture was stirred for 20 h at room temperature, filtered through a glass frit and the solvent evaporated in vacuo, producing a dark red solid. The latter was placed in a Soxhlet extractor under an argon atmosphere and extracted initially with 100 ml of hexane to remove impurities and starting material. The solid was then extracted with 100 ml of dichloromethane, yielding a deep red solution. Removal of the solvent gave 2.66 g (57%) of carbomethoxytitanocene dichloride as an air-stable red solid, m.p. 191–193 °C (dec). An analytical sample was obtained by vacuum sublimation of a portion of the product at 135–140 °C/10^{-3} torr. (Found: C, 47.23; H, 3.82. $C_{12}H_{12}Cl_2O_2Ti$ calcd.: C, 46.94; H, 3.94%).

Bis(η^5-methoxycarbonylcyclopentadienyl)dichlorotitanium (1,1′-Dicarbomethoxytitanocene dichloride)

Into a 500-ml 3-necked round-bottom flask flushed with argon was added 6.38 g (19.4 mmol) of (carbomethoxycyclopentadienyl)thallium and 200 ml of benzene. The reaction vessel was equipped with a magnetic stirring bar and connected to a mercury overpressure valve. Titanium tetrachloride (1.84 g, 1.35 ml, 9.70 mmol) was added to the stirred solution via a syringe, and stirring was continued for 24 h at room temperature. The solvent was removed in vacuo to afford a brown solid. Under an argon atmosphere, the solid was placed in a Soxhlet extractor and extracted initially with 100 ml of hexane to remove impurities. Extraction was continued with 100 ml of dichloromethane, producing a bright red solution. The solvent was removed in vacuo to yield 2.19 g (62%) of 1,1′-dicarbomethoxytitanocene dichloride as an air-stable, light red solid, m.p. 193–194 °C (dec). An analytical sample was prepared by recrystallization of the product from dichloromethane/hexane at −20 °C. (Found: C, 45.81; H, 3.76; Cl, 19.96. $C_{14}H_{14}Cl_2O_4Ti$ calcd.: C, 46.06; H, 3.86; Cl, 19.42%).

Dicarbonyl(η^5-methoxycarbonylcyclopentadienyl)(η^5-cyclopentadienyl)titanium (Carbomethoxytitanocene dicarbonyl (IV)

Method A. A 300-ml Schlenk flask was flushed with argon, and carbomethoxytitanocene dichloride (1.34 g, 4.36 mmol), magnesium turnings (0.318 g, 13.1 mmol) and 100 ml of THF were added. The flask was equipped with a magnetic stirrer and connected to a mercury overpressure valve. The system was purged under a moderate flow of carbon monoxide for 5 min, mercuric chloride (0.59 g, 2.18 mmol) was added, and the reaction mixture was then allowed to stir at room temperature for 24 h under a slight flow of carbon monoxide. The solvent was removed in vacuo and the residue was extracted with benzene and filtered through an alumina plug (2.5 × 4 cm). Evaporation of the solvent gave a deep maroon oil which was extracted with a minimum amount of pentane, concentrated and cooled to −20 °C. The cold mother liquor was removed via a cannula and the residue was dried under high vacuum to give 0.40 g (31%) of carbomethoxytitanocene dicarbonyl. An analytical sample was obtained by sublimation of a portion of the product at 70–90 °C/10^{-3} torr, MS m/e 292 (M^+). (Found: C, 57.28; H, 4.18. $C_{14}H_{12}O_4Ti$ calcd.: C, 57.56; H, 4.14%).

Method B. A similar reaction was conducted employing aluminum filings instead of magnesium turnings. The resulting brown solid was placed on a drypacked alumina column. Elution with pentane removed a very small amount of titanocene dicarbonyl. Subsequent elution with 1/1 benzene/diethyl ether removed a red-brown band, which when collected and the solvent removed afforded carbomethoxytitanocene dicarbonyl in 54% yield.

Dicarbonylbis(η^5-methoxycarbonylcyclopentadienyl)titanium (1,1′-Dicarbomethoxytitanocene dicarbonyl) (V)

The reaction procedure was analogous to that described for carbomethoxytitanocene dicarbonyl (Method A), employing 1.55 g (4.25 mmol) of 1,1′-dicarbomethoxytitanocene dichloride, 0.31 g (12.9 mmol) of magnesium turnings, 100 ml of THF and 0.58 g (2.14 mmol) of mercuric chloride. After stirring for 24 h under a positive flow of carbon monoxide, workup as described in Method A afforded 1.14 g (77%) of 1,1′-dicarbomethoxytitanocene dicarbonyl as an air-sensitive maroon solid, m.p. 160–162°C (dec). (Found: C, 54.50; H, 3.92. $C_{16}H_{14}O_6Ti$ calcd.: C, 54.88; H, 4.03%).

Dicarbonyl(η^5-chlorocyclopentadienyl)(η^5-cyclopentadienyl)titanium (Chlorotitanocene dicarbonyl) (VIII)

Following Method A described for the synthesis of carbomethoxytitanocene dicarbonyl, a reaction was conducted using chlorotitanocene dichloride (0.89 g, 3.11 mmol), magnesium turnings (0.16 g, 6.6 mmol), 75 ml of THF and mercuric chloride (0.36 g, 1.33 mmol). After stirring for 18 h under a positive flow of carbon monoxide, workup as described in Method A yielded 0.60 g (71%) of chlorotitanocene dicarbonyl as an air-sensitive maroon solid. An analytical sample was obtained by crystallization from hexane at −20°C. (Found: C, 52.90; H, 3.59. $C_{12}H_9ClO_2Ti$ calcd.: C, 53.66; H, 3.38%).

Dicarbonylbis(η^5-chlorocyclopentadienyl)titanium (1,1′-Dichlorotitanocene dicarbonyl) (IX)

The reaction procedure was analogous to that described in Method A for carbomethoxytitanocene dichloride, employing 1.33 g (4.19 mmol) of 1,1′-dichlorotitanocene dichloride, 0.34 g (14.0 mmol) of magnesium turnings, 100 ml of THF and 0.76 g (2.8 mmol) of mercuric chloride. The reaction mixture was stirred under a positive flow of carbon monoxide for 18 h. Following workup as described in Method A, 0.84 g (67%) of 1,1′-dichlorotitanocene dicarbonyl was obtained as an air-sensitive maroon solid. An analytical sample was obtained by crystallization from hexane at −20°C, m.p. 57–59°C (dec). (Found: C, 47.04; H, 2.95. $C_{12}H_8Cl_2O_2Ti$ calcd.: C, 47.57; H, 2.66%).

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