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THE PREPARATION AND PROPERTIES OF SOME σ-ALKYL AND σ-ARYL DERIVATIVES OF TITANIUM

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Summary

Reactions between chlorotriisopropoxytitanium and either methyllithium or pentafluorophenyllithium have produced σ-methyltriisopropoxytitanium and σ-pentafluorophenyltriisopropoxytitanium, respectively. These organotitanium compounds are very sensitive to moisture and are associated in benzene solution. The synthesis and properties of several titanocene derivatives containing two different σ-bonded organic substituents are also described.

In 1952, Herman and Nelson [1] reported the isolation of a relatively stable lithium complex of σ-phenyltriisopropoxytitanium from a reaction between phenyllithium and tetraisopropoxytitanium. The organotitanium compound was freed from the complex by a reaction with titanium tetrachloride. This result represented the first successful isolation of a compound containing a titanium—carbon σ-bond since Cahours [2] first attempted the feat in 1861. σ-Phenyltriisopropoxytitanium (I) formed under these conditions was found to be stable at 10° under a nitrogen atmosphere and melted at 88—90°. Subsequent papers by these workers [3, 4] described reactions of various Grignard reagents with tetraalkoxytitanium derivatives, and although no discrete organometallic compounds were isolated from these reactions, it was shown by indirect methods that σ-bonded organotitanium compounds were indeed present. An improved route to (I) was described by Holloway [5] in 1962, and involved a reaction of halide-free phenyllithium with chlorotriisopropoxytitanium.

It was of interest to us to determine if Holloway's method could be extended for the synthesis of still other alkoxide-stabilized σ-organotitanium compounds of the type $RTi(OR')_3$ *.

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* Clauss [6] has recently described the formation of II by this method, although no elemental analysis or spectral data for the product were given.

TABLE 1

PROTON NMR SPECTRA OF SOME σ-TRIISOPROPOXYTITANIUM COMPOUNDS

Compound		Chemical shift and multiplicity [a]			
		$(C\underline{H}_3)_2CHO$	$(CH_3)_2C\underline{H}O$	σ-R	Solvent
$ClTi(iso\text{-}OC_3H_7)_3$		8.69 d [b]	5.34 m		CCl_4
$C_6H_5Ti(iso\text{-}OC_3H_7)_3$	(I)	8.73 d [b]	5.35 m	2.88 m	$CDCl_3$
$CH_3Ti(iso\text{-}OC_3H_7)_3$	(II)	8.74 d [b]	5.39 m	9.02 s	C_6H_6
$C_6F_5Ti(iso\text{-}OC_3H_7)_3$	(III)	8.77 d [b]	5.60 m		$CDCl_3$

[a] Given in τ (ppm) units; s, singlet; d, doublet; m, multiplet. Spectra were calibrated by imposing side bands of known frequency on TMS with an external audio-oscillator. Estimated accuracy ± 0.02 ppm. The degree of association of the NMR samples is not known; the concentration dependence of the chemical shifts was not investigated. [b] J 6 Hz.

$$RLi + ClTi(iso\text{-}OC_3H_7)_3 \rightarrow R\text{—}Ti(iso\text{-}OC_3H_7)_3 + LiCl$$

$$\begin{array}{l} \text{(I)}\ R = C_6H_5 \\ \text{(II)}\ R = CH_3 \\ \text{(III)}\ R = C_6F_5 \end{array}$$

Reactions of chlorotriisopropoxytitanium with both methyllithium and pentafluorophenyllithium readily afforded the corresponding σ-organotitanium compounds II and III. The pentafluorophenyl derivative III, like I, is a white crystalline solid, while the methyl derivative II is a bright yellow liquid which may be distilled under high vacuum without decomposition. We have observed that II undergoes a color change from yellow to deep blue-green when allowed to stand at room temperature under nitrogen over a period of ca. 12 h. This result may be indicative of a reduction of II to a Ti^{III} species. All the isopropoxy-stabilized compounds I, II and III are very sensitive to moisture and must be manipulated under an atmosphere of dry nitrogen. The methyl compound II, for example, reacts violently with water.

The apparent molecular weight of II determined osmometrically in benzene solution is 362. This result indicates molecular association, since the molecular weight of the monomer is 240. It is well-known that other alkoxide derivatives of titanium are associated in solution [7]. Further, Giannini and Zucchini [8] have reported the molecular weight of di-σ-benzyldiethoxytitanium as being 590 (monomer 320). It thus appears that σ-bonded alkoxy derivatives of titanium are also associated in solution. This may be a contributing factor to the enhanced thermal stabilities of these compounds, since it is known that the relative thermal stabilities of σ-bonded organic derivatives of titanium can be increased by coordination with donor-type ligands [9, 10].

The proton NMR spectra of these alkoxide-stabilized σ-organotitanium compounds are summarized in Table 1, and are consistent with the proposed structures.

Titanocene dichloride (IV) has proven to be an excellent starting material for the synthesis of a variety of σ-bonded derivatives of titanium [11]. We have found that reactions of either di-π-cyclopentadienyl-σ-methyltitanium chloride (V) or the corresponding σ-phenyl analog VI with pentafluorophenyllithium in ethyl ether solution afford the corresponding disubstituted products VII and VIII.

TABLE 2

PROTON NMR SPECTRA OF SOME σ-ORGANOTITANOCENE DERIVATIVES

Compound		Chemical shift and multiplicity [a]	
		π-C_5H_5	σ-R
$(\pi\text{-}C_5H_5)_2TiCl_2$	(IV)	3.43 s	
$(\pi\text{-}C_5H_5)_2Ti(CH_3)Cl$	(V)	3.75 s	9.20 s
$(\pi\text{-}C_5H_5)_2Ti(C_6H_5)Cl$	(VI)	3.68 s	3.15 m
$(\pi\text{-}C_5H_5)_2Ti(CH_3)C_6F_5$	(VII)	3.75 s	9.39 t [b]
$(\pi\text{-}C_5H_5)_2Ti(C_6H_5)C_6F_5$	(VIII)	3.73 s	3.11 m

[a] Given in τ (ppm) units; s, singlet; t, triplet; m, multiplet. Spectra were calibrated by imposing side bands of known frequency on TMS with an external audio-oscillator. Estimated accuracy ± 0.02 ppm. [b] J 4 Hz.

$$\begin{array}{ll}(\pi\text{-}C_5H_5)_2Ti(R)Cl + C_6F_5Li \rightarrow & (\pi\text{-}C_5H_5)_2Ti(R)C_6F_5 + LiCl \\ \text{(V)}\ \ R = CH_3 & \text{(VII)}\ \ R = CH_3 \\ \text{(VI)}\ R = C_6H_5 & \text{(VIII)}\ R = C_6H_5 \\ & \text{(IX)}\ \ \ R = C_6F_5\end{array}$$

These compounds represent rare examples in organotransition metal chemistry of two different organic substituents σ-bonded to the same metal.

It is well-known that di-π-cyclopentadienyldi-σ-pentafluorophenyltitanium (IX) [12] exhibits appreciable enhanced stability compared to the corresponding dimethyl [13, 14] and diphenyl [15, 16] derivatives. When analytically pure samples of V—VIII were sealed in vacuo in capillaries and heated in an oil bath maintained at 50°, the σ-methyl derivatives V and VII showed little or no discoloration over a period of two days, and the melting points of the samples after this period were essentially undepressed. In contrast, the σ-phenyl analogs VI and VIII decomposed completely in less than ten hours under these conditions. In our studies, therefore, σ-phenyl derivatives of titanocene appear to be less stable thermally than their corresponding σ-methyl counterparts. More quantitative thermal stability studies are clearly desirable and are in progress.

The proton NMR spectra of these titanocene derivatives are in agreement with the assigned structures, and are summarized in Table 2.

Experimental

Titanocene dichloride and bromopentafluorobenzene were purchased from the Arapahoe Chemical Co. and the Pierce Chemical Co., respectively, and were used without further purification. Chlorotriisopropoxytitanium, b.p. 71°/0.025 mm (lit. [5] b.p. 130°/0.1 mm) was prepared in 85% yield from a reaction between tetraisopropoxytitanium and acetyl chloride in anhydrous benzene, essentially according to the method of Holloway [5]. Di-π-cyclopentadienyl-σ-methyltitanium chloride (V) and di-π-cyclopentadienyl-σ-phenyltitanium chloride (VI) were prepared from titanocene dichloride and the appropriate Grignard reagent via a modification of the literature procedures [17, 18]. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Di-π-cyclopentadienyl-σ-methyltitanium chloride (V) and di-π-cyclopentadienyl-σ-phenyltitanium chloride (VI)

Titanocene dichloride (5.0 g, 20.1 mmol), anhydrous ethyl ether (200 ml) and a magnetic stirring bar were placed in a 250 ml, 3-necked flask fitted with an addition funnel, a nitrogen inlet and a nitrogen outlet connected to a mercury check valve. With rapid stirring under nitrogen, 20.1 mmol of methylmagnesium chloride in tetrahydrofuran was added over a period of 45 min at room temperature, and the reaction mixture was stirred at this temperature for an additional 2 h. The mixture was filtered and the solvent concentrated to a small volume to produce 2.98 g (65%) of orange-red crystals. Di-π-cyclopentadienyl-σ-methyltitanium chloride (m.p. 168—169° (lit. [14] m.p. 168—170° dec.)) was produced by recrystallization of the crude product under nitrogen from boiling ethyl ether.

By a procedure analogous to that described above, di-π-cyclopentadienyl-σ-phenyltitanium chloride (3.7 g, 63%) was prepared in ethyl ether (200 ml) from titanocene dichloride (5.00 g, 20.1 mmol) and 20.1 mmol of phenylmagnesium chloride in tetrahydrofuran solution. An analytical sample was prepared by recrystallization from boiling pentane, filtration, and cooling to produce orange platelets, m.p. 120—121° (lit. [18] m.p. 121° dec.). This latter operation can be carried out in air if done rapidly. (Found: C, 65.97; H, 5.31; Cl, 12.43; Ti, 16.71. $C_{16}H_{15}ClTi$ calcd.: C, 66.11; H, 5.20; Cl, 12.20; Ti, 16.48%.)

σ-Methyltriisopropoxytitanium (II)

A 50 ml, 3-necked flask was fitted with an addition funnel, a nitrogen inlet, and a nitrogen outlet connected to a mercury check valve. Chlorotriisopropoxytitanium (2.06 g, 7.89 mmol), anhydrous ethyl ether (25 ml), and a magnetic stirring bar were added to the flask under nitrogen and the contents were cooled to —35°. Methyllithium (3.8 ml, 7.89 mmol) in ethyl ether was added from the addition funnel over a period of 30 min while maintaining the temperature between —35 and —40°. The reaction mixture was then allowed to warm to 0° and stirring was continued for an additional h. The reaction mixture was filtered under nitrogen and the solvent removed under reduced pressure. The residue, which consisted of a pale yellow oil and a white solid, was placed in a vacuum system and distilled from trap to trap. The temperature of the three traps was maintained at 0°. In this way, 1.31 g (69%) of pure σ-methyltriisopropoxytitanium was obtained as a bright yellow liquid, b.p. 35—40°/0.018 mm. (Found: C, 49.75; H, 10.02; O, 19.76; mol. wt. (osmometric in benzene) 357, 367. $C_{10}H_{24}O_3Ti$ calcd.: C, 50.00; H, 10.07; O, 19.98%; mol. wt. 240.)

σ-Pentafluorophenyltriisopropoxytitanium (III)

A 250 ml, 3-necked flask was fitted with a nitrogen inlet, a nitrogen outlet connected to a mercury check valve and a jacketed addition funnel. Chlorotriisopropoxytitanium (4.08 g, 15.7 mmol), anhydrous ethyl ether (200 ml) and a magnetic stirring bar were placed in the flask and the contents were cooled to 0°. Pentafluorophenyllithium was prepared by the slow addition (ca. 20 min) of n-butyllithium (7.28 ml, 15.7 mmol) to bromopentafluorobenzene (3.87 g, 15.7 mmol) in ethyl ether (25 ml) at —78°. The lithium reagent was subsequently transferred to the jacketed addition funnel which had been previously cooled to —78°, and was added over a period of 30 min to the stirred etheral solution of chlorotriisopropoxytitanium at 0°. The reaction was stirred at 0° for an additional 2 h. The reaction mixture was then filtered and the solvent was removed under reduced pressure. The residue was washed with 15 ml of pentane in small portions and dried under vacuum at room temperature to produce 1.03 g (17%) of white crystals, m.p. 133—135°. An analytical sample was prepared by recrystallization from pentane and drying under vacuum at room temperature. (Found: C, 46.20; H, 5.50; O, 12.20. $C_{15}H_{21}F_5O_3Ti$ calcd.: C, 45.93; H, 5.40; O, 12.24%.)

Di-π-cyclopentadienyl-σ-methyl-σ-pentafluorophenyltitanium (VII)

Pentafluorophenyllithium was prepared under nitrogen in 25 ml of anhydrous ethyl ether at —78°, as previously described, from bromopentafluorobenzene (3.15 g, 12.7 mmol) and a hexane solution of n-butyllithium (5.7 ml, 12.7 mmol). The lithium reagent was transferred to a jacketed addition funnel which had been previously cooled to —78°, and was added under nitrogen over a period of 30 min to a rapidly stirred etheral solution (60 ml) of di-π-cyclopentadienyl-σ-methyltitanium chloride (2.92 g, 12.7 mmol) maintained at 0°. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature over a period of 2.5 h. The reaction mixture was filtered under nitrogen and the solvent was removed under reduced pressure, yielding 2.92 g (64%) of crude product. The protective atmosphere of nitrogen was discontinued at this point, and the crude product was recrystallized twice from anhydrous ethyl ether to produce an analytically pure sample, m.p. 172.5—173.5°. (Found: C, 56.74; H, 3.57; F, 26.17; Ti, 13.28. $C_{17}H_{13}F_5Ti$ calcd.: C, 56.69; H, 3.61; F, 26.38; Ti, 13.30%.)

Di-π-cyclopentadienyl-σ-phenyl-σ-pentafluorophenyltitanium (VIII)

Pentafluorophenyllithium was prepared under nitrogen in ethyl ether (7 ml) at —78° from bromopentafluorobenzene (2.47 g, 10.0 mmol) and a hexane solution of n-butyllithium (4.13 ml, 10.0 mmol). The lithium reagent was transferred to a jacketed addition funnel maintained at —78° and was added to a rapidly stirred etheral solution (60 ml) of di-π-cyclopentadienyl-σ-phenyltitanium chloride (2.91 g, 10.0 mmol) which had previously been cooled to —78° under nitrogen. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature over a period of 2 h. The mixture was filtered under nitrogen and the solvent was removed under reduced pressure. The red-orange residue was taken up in a minimum amount of anhydrous benzene and chromatographed on a Fluorisil column. A red band was eluted with anhydrous ethyl ether. Evaporation of the solvent under reduced pressure produced a red oil which crystallized when treated with a small amount of ethyl ether. The orange crystals were filtered rapidly in air and dried under vacuum at room temperature to produce 0.50 g (12%) of analytically pure product, m.p. 115—117°. (Found: C, 62.76; H, 3.84; F, 22.38; Ti, 11.41. $C_{22}H_{15}F_5Ti$ calcd.: C, 62.58; H, 3.58; F, 22.50; Ti, 11.34%.)

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