Preparation and Some Properties of Triorganosiloxy Derivatives of Cyclopentadienyl Titanium

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Several triorganosiloxy derivatives of cyclopentadienyl titanium were synthesized by the reactions of dicyclopentadienyl titanium dichloride or cyclopentadienyltitanium trichloride with triorganosilanols or their sodium salts. The products obtained include π-$Cp_2TiClOSiMe_3$, π-$CpTi(OSiMe_3)_3$, π-$CpTi(OSiMe_2Ph)_3$, π-$CpTi(OSiPh_2Me)_3$, π-$CpTi(OSiPh_3)_3$, π-$CpTi(OSiPh_3)_2Cl$ and π-$CpTi(OSiPh_3)Cl_2$. Some correlations were found to exist between the substituents on silicon atoms and cyclopentadienyl ring protons in NMR spectra and the Ti–O–Si bond absorptions in IR spectra. The chemical stabilities of the Ti–O–Si bonding in the products were dependent on the nature of the organic groups attached to the silicon atoms. The chemical resistance of the products against hydrolytic cleavage was regularly increased with successive replacement of methyl groups by phenyl groups.

In succession to our previous paper[1] dealing with preparation of some siloxy derivatives of cyclopentadienyl titanium, several new compounds in the series listed in Table 1 were obtained by analogous procedures. Most products were crystalline masses with moderate stability.

The NMR spectral investigations of the derivatives indicated that there are some correlations between the proton chemical shifts of cyclopentadienyl ring protons and the nature of the substituents on silicon.

The products generally reacted both with gaseous hydrogen chloride and with acetyl chloride, leaving the cyclopentadienyl groups intact and substituting the chlorine atoms for the siloxy groups, thus yielding partially triorganosiloxy-substituted cyclopentadienyltitanium chlorides.

The hydrolysis of the products was investigated by examining the relative intensities of the absorption bands due to the Si–O–Ti bond. It was found that the hydrolytic stability increased with successive replacement of methyl groups on silicon by phenyl groups.

No indication of any formation of ferrocene was obtained from the reaction between iron(II) chloride and the products.

Experimental

Triorganosilanols: Trimethylsilanol, bp, 98—99 °C, n_D^{20}, 1.3890, was prepared by hydrolysis of trimethylfluorosilane with 2 M-NaOH. Dimethylphenylsilanol, diphenylmethylsilanol, and triphenylsilanol were prepared by the method[2] reported previously.

Triorganosiloxy Derivatives of Cyclopentadienyl Titanium: A tetrahydrofuran (THF) solution of a silanol was added dropwise to a THF solution containing a theoretical amount of dicyclopentadienyltitanium dichloride or cyclopentadienyltitanium trichloride at room temperature under stirring and nitrogen atmosphere for about 30 min. At this point a THF solution of triethylamine (20% excess) was added to the mixture, which was stirred for another 10 hr. The precipitated triethylamine hydrochloride was then filtered off, and the filtrate was concentrated to give the triorganosiloxy derivative as a crude product. Purification either by distillation or by recrystallization from *n*-hexane gave the pure samples listed in Tables 1 and 2.

Reactivities: Some reactions of compounds I—VIII with gaseous hydrogen chloride, acetyl chloride, aqueous solution of sodium hydroxide, and ferrous chloride were investigated by means of NMR and IR spectral measurements.

Reaction with Gaseous Hydrogen Chloride: Dry hydrogen chlo-

TABLE 1. PHYSICAL PROPERTIES AND ELEMENTAL ANALYSIS OF PRODUCTS

	Compound	Mp (°C) bp (°C/mmHg)	Y%	Analytical data (%) Found (Calcd) C	H	Si	Ti	Mol wt Found (Calcd)
I	π-$Cp_2TiCl(OSiMe_3)$	104—105	40	51.85 (51.59)	6.34 (6.33)	9.1 (9.2)	16.9 (15.9)	318 (313)
II	π-$Cp_2TiCl(OSiMe_2Ph)$[a]	97—98.5						
III	π-$Cp_2TiCl(OSiPh_2Me)$[a]	160—161.5						
IV	π-$Cp_2TiCl(OSiPh_3)$	199.5—200.5	40	69.39 (69.00)	5.46 (5.16)	6.0 (5.8)	9.3 (9.8)	500 (489)
V	π-$CpTi(OSiMe_3)_3$	(71/0.15)	40	43.73 (44.42)	8.96 (8.43)	21.3 (22.0)	13.7 (12.6)	368 (380)
VI	π-$CpTi(OSiMe_2Ph)_3$	[b]	30	61.81 (60.77)	6.25 (6.88)	16.0 (17.1)	9.5 (8.6)	593 (557)
VII	π-$CpTi(OSiPh_2Me)_3$	114—115	60	69.85 (70.19)	6.05 (5.89)	10.7 (11.1)	6.3 (6.4)	728 (752)
VIII	π-$CpTi(OSiPh_3)_3$	204.5—205.2	70	75.08 (75.45)	5.69 (5.37)	9.4 (9.9)	5.5 (5.0)	955 (939)

a) Cited from our previous paper[1] b) Undistillable liquid

Table 2. NMR and IR spectral data

	NMR (τ, 6% in $CDCl_3$)		IR (cm^{-1}, 2 mmol% in CS_2)	
	Cp	Me	Ti–O–Si	=CH(π-Cp)
I	3.71	9.92	939	807
II	3.74	9.66	940	808
III	3.76	9.38	945	810
IV	3.76		951	814
V	3.70	9.94	908	803
VI	3.81	9.71	910	810
VII	3.94	9.47	910	810
VIII	4.03		915	816

Table 3. Reaction of the compounds with gaseous hydrogen chloride

Sample	Product	NMR (τ)	Ratio[a]
I—IV	π-Cp_2TiCl_2	3.40	100
V	π-$CpTiCl_3$	2.95	100
VI	π-$CpTiCl_3$	2.95	100
VII	π-$CpTi(OSiPh_2Me)Cl_2$[b]	3.45	80
VIII	π-$CpTi(OSiPh_3)_2Cl$	3.84	80
	π-$CpTi(OSiPh_3)Cl_2$	3.51	11

a) Ratio of ring proton converted from the original compounds to the products. b) Not fully identified.

ride was introduced for 2 hr into a boiling solution of 0.2 mmol of a sample in 100 ml of benzene, and volatile materials were removed by evaporation *in vacuo*. The solid residue was then dissolved in $CDCl_3$ and studied spectroscopically. The results are listed in Table 3.

The two partially substituted products from VIII were prepared independently by the following reaction:

$$CpTiCl_3 + 2Ph_3SiONa \xrightarrow[PhCH_3]{} CpTi(OSiPh_3)_2Cl + CpTi(OSiPh_3)Cl_2$$

The product obtained are as follows; the numerals represent respectively mp (°C), yield (%), C%, H%, Cl%, Si%, Ti% [Calcd], NMR (π-Cp, τ in $CDCl_3$) and IR (TiOSi, cm^{-1} in CS_2):

$CpTi(OSiPh_3)_2Cl$: 168—170, 50, 71.15 [70.56], 5.45[5.04], 5.6[5.1], 7.7[8.0], 7.2[6.9], 3.83, 904.

$CpTi(OSiPh_3)Cl_2$: 118—119, 10, 59.88[60.01], 4.50[4.28], 14.7[15.6], 5.9[6.1], 10.6[10.2], 3.50, 938.

On NMR spectra of π-$CpTi(OSiMe_{3-n}Ph_n)_3$ in Table 2 and π-$CpTi(OSiPh_3)_nCl_{3-n}$, it is shown that an increase of the number of phenyl groups leads to a shift of the cyclopentadienyl signal toward high field. This is believed to be due mainly to the diamagnetic anisotropy from phenyl groups and to the electron accepting properties of chlorine atoms. These results are in line with the observations of Beachell and Butter, who reported a detailed study of NMR spectra of titanocene sandwich compounds.[3]

Reaction with Acetyl Chloride: To a solution of 0.1 mmol of a sample in $CDCl_3$ was added 0.1 mmol (for I—IV) or 0.42 mmol (for V—VIII) of acetyl chloride and the mixture was heated at 45 °C for 2 hr. It was then submitted to NMR spectral investigations. The results are shown in Table 4.

Hydrolysis with Aqueous Sodium Hydroxide Solution: A solution of 0.2 mmol of a sample in 8 ml of THF was divided into four portions A, B, C, and D. The last three samples (B, C, and D) were treated with the reagents shown below in order to learn their stabilities towards hydrolytic cleavage.

Table 4. Reaction of the compounds with acetyl chloride

Sample	AcCl ($\times$0.1 mmol)	Product	NMR (τ)	Ratio (%)[a]
I	1.4	π-Cp_2TiCl_2	3.40	100
II	1.4	π-Cp_2TiCl_2	3.40	90
III	1.4	π-Cp_2TiCl_2	3.40	41
IV	1.4	π-Cp_2TiCl_2	3.40	39
V	4.2	π-$CpTi(OSiMe_3)Cl_2$[b]	3.25	90
VI	4.2	π-$CpTi(OSiMe_2Ph)Cl_2$[b]	3.38	90
VII	4.2	π-$CpTi(OSiPh_2Me)_2Cl$[b]	3.75	72
VIII	4.2	π-$CpTi(OSiPh_3)_2Cl$	3.81	46

a), b) The same as in Table 3.

Run	Reagent	Temp.
B	0.1 M-NaOH	r.t.
C	H_2O	70°C
D	0.1 M-NaOH	70°C

After 2 hr, each solution was evaporated *in vacuo* and the residue was dissolved in 2 ml of carbon disulfide to give a sample for IR spectral investigations. The intensities of the Ti–O–Si bond absorption of each sample relative to the intensity of the original sample A are shown in Table 5.

Table 5. Reaction of the compounds with water and aqueous sodium hydroxide solution

Sample	Reagent (μl)	Absorption intensity ratio in IR on TiOSi (A=100)	
I[a]	20	60(B)	15(C,D)
II[a]	20	90(B)	30(C,D)
III[a]	50	65(B)	30(C,D)
	[20]	[100(B)]	[35(C,D)]
IV[a]	50	80(B)	35(C,D)
V	20	35(B)	15(C,D)
VI	20	75(B)	35(C) 25(D)
VII	50	100(B.C)	90(D)
	[20]	[100(B.C)]	[95(D)]
VIII	50	100(B.C.D)	

a) When these samples were treated, besides the absorption band at about 945 cm^{-1}, a band centered at 920 cm^{-1} due to disproportionation appeared; its intensity was I>II>III>IV and in the order of D>C>B with respect to the treatment conditions. NMR spectra investigations indicated formation of π-Cp_2TiCl_2, particularly in run C.

Attempted reaction with Iron(II) Chloride: Attempted reactions of compounds I—VIII with iron(II) chloride prepared from iron(III) trichloride and iron powder in THF did not lead to any formation of ferrocene; this seems to be attributed both to the rather unionic property of the cyclopentadienyltitanium bond and to the steric effect of the triorganiosiloxy groups.

References

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