The Preparation of Some Triorganosiloxy Derivatives of Bis-cyclopentadienyltitanium Dichloride

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(Received May 13, 1968)

Very little researches have been made on the organosiloxytitanium compounds with cyclopentadienyl groups attached to the titanium atom. The preparation of triphenylsiloxy-bis-cyclopentadienyltitanium chloride[1] and bis-triphenylsiloxy-bis-cyclopentadienyltitanium[1] from the reaction of bis-cyclopentadienyltitanium dichloride with sodium triphenylsilanolate are the only examples reported in the literature.

We wish to report on the preparation of some triorganosiloxy derivatives of bis-cyclopentadienyltitanium dichloride from the reaction of bis-cyclopentadienyltitanium dichloride with the corresponding triorganosilanols in the presence of triethylamine as a hydrogen chloride acceptor

1) J. G. Noltes and G. J. M. Van der Kerk, *Rec. Trav. Chim.*, **81**, 39 (1962).

according to the following schemes:

$$Cp_2TiCl_2 + R_3SiOH + Et_3N \rightarrow R_3SiOTi(Cl)Cp_2 + Et_3N\text{-}HCl \text{ and}$$

$$Cp_2TiCl_2 + 2R_3SiOH + 2Et_3N \rightarrow (R_3SiO)_2TiCp_2 + 2Et_3N\text{-}HCl$$

Most of the products obtained were colored crystalline substances. They are bis-triphenylsiloxy-bis-cyclopentadienyltitanium, bis-diphenylmethylsiloxy-bis-cyclopentadienyltitanium, diphenylmethylsiloxy-bis-cyclopentadienyltitanium chloride, bis - dimethylphenylsiloxy - bis - cyclopentadienyltitanium, dimethylphenylsiloxy-bis-cyclopentadienyltitanium chloride and diphenylbutylsiloxy-bis-cyclopentadienyltitanium chloride, the last five being new compounds. All products were well-defined and characterized by their IR spectra. As for crystalline substances, the X-ray powder patterns were also determined for their rapid identification.

Experimental

Triorganochlorosilanes. Triphenylchlorosilane (mp 98—99°C) was isolated from the high boiling residue[2] of the direct synthesis of phenylchlorosilanes. Diphenylmethylchlorosilane (bp 128—130°C/3 mmHg), dimethylphenylchlorosilane (bp 55—56°C/5 mmHg), diphenylbutylchlorosilane (bp 153—155°C/4 mmHg) were prepared by a Grignard route.[3]

Triorganosilanols. Triphenylsilanol (mp 150—151°C), diphenylmethylsilanol (bp 132—133°C/1.5 mmHg), dimethylphenylsilanol (bp 73.5—74.5°C/5 mmHg) and diphenylbutylsilanol (bp 157—158°C/1.5 mmHg) were prepared by the method[4] reported previously.

Bis-cyclopentadienyltitanium Dichloride. The reaction of cyclopentadienylsodium with titanium tetrachloride in tetrahydrofuran gave bis-cyclopentadienyltitanium dichloride, mp 288—290°C (lit.[5] mp 289—291°C), as bright-red acicular crystals with a yield of 33—35%.

The Preparation of Bis-diphenylmethylsiloxy-bis-cyclopentadienyltitanium and Diphenylmethylsiloxy-bis-cyclopentadienyltitanium Chloride. Typical procedures will be described in detail, using the preparations of mono- and di-diphenylmethylsiloxy derivatives of bis-cyclopentadienyltitanium dichloride as examples. A mixture of bis-cyclopentadienyltitanium dichloride (5 g, 0.02 mol), diphenylmethylsilanol (10.1 g, 0.047 mol) and triethylamine (5 g, 0.05 mol) gave a deep red solution when dissolved in 250 ml of tetrahydrofuran. The red solution gradually turned yellowish when refluxed with gentle stirring, and triethylamine hydrochloride precipitates. After it was refluxed for 25 hr, the hydrochloride was filtered off and the filtrate was concentrated under reduced pressure, leaving a brown viscous liquid from which a brown semi-solid separated on addition of cold *n*-hexane.

Extraction of the brown mass with hot *n*-hexane for 30 hr gave a deep yellow solution from which, on cooling in an ice-bath, 1 g (11.7%) of diphenylmethylsiloxy-bis-cyclopentadienyltitanium chloride was obtained as red acicular crystals melting at 160—161.5°C. After filtration of the red crystals, the yellow filtrate was evaporated, giving 5 g (41.3%) of pale yellow platelets.

The extraction residue was a brown solid which proved to be a mixture of unreacted bis-cyclopentadienyltitanium dichloride and its cleavage products.

Further purification of the platelets was effected by recrystallization from *n*-hexane, giving pure bis-diphenylmethylsiloxy-bis-cyclopentadienyltitanium melting at 113.5—114.5°C.

$Ph_2MeSiOTi(Cl)Cp_2$: Found: Si, 6.49; Ti, 11.29; C, 65.00; H, 5.43; Cl, 8.35% (determined by combustion method); mol wt (determined ebullioscopically in benzene), 424. Calcd for $C_{23}H_{23}OSiTiCl$: Si, 6.58; Ti, 11.22; C, 64.71; H, 5.43; Cl, 8.31%; mol wt, 426.9.

$(Ph_2MeSiO)_2TiCp_2$: Found: Si, 9.15; Ti, 8.16; C, 71.85; H, 5.90%; mol wt, 616. Calcd for $C_{36}H_{36}O_2Si_2Ti$; Si, 9.29; Ti, 7.92; C, 71.50; H, 6.00%; mol wt, 604.8.

All of the attempts to modify above procedure, using dioxane, toluene and xylene as reaction media and using pyridine, aniline, *N,N*-dimethylaniline as hydrogenchloride acceptors, proved to be less satisfactory than the combination of tetrahydrofuran and triethylamine because of the complexity of the procedure and the lower yield of the aimed products.

The reaction of bis-cyclopentadienyltitanium dichloride with equimolar diphenylmethylsilanol gave diphenylmethylsiloxy-bis-cyclopentadienyltitanium chloride with reproducible yields of 60—65%, and bis-diphenylmethylsiloxy-bis-cyclopentadienyltitanium was obtained in the yield of less than 5%.

Other Triorganosiloxy Derivatives. Bis-triphenylsiloxy-bis-cyclopentadienyltitanium, white platelets melting at 199—200°C (lit.[1] mp 208—210°C); bis-phenyldimethylsiloxy-bis-cyclopentadienyltitanium, a deep red low melting solid; phenyldimethylsiloxy-bis-cyclopentadienyltitanium chloride, a carmine red solid melting at 56°C; diphenylbutylsiloxy-bis-cyclopentadienyltitanium chloride, an orange yellow crystalline mass melting at 97—99°C. These were all obtained by procedures similar to those used for diphenylmethylsiloxy derivatives.

$(Ph_3SiO)_2TiCp_2$: Found: Si, 7.86; Ti, 6.45; C, 76.3; H, 5.58%; mol wt, 739. Calcd for $C_{46}H_{40}O_2Si_2Ti$: Si, 7.71; Ti, 6.57; C, 75.80; H, 5.53%; mol wt, 728.9.

$Ph_2BuSiOTi(Cl)Cp_2$: Found: Si, 5.76; Ti, 10.09; C, 66.80; H, 6.37; Cl, 7.73%; mol wt, 457. Calcd for $C_{26}H_{29}OSiTiCl$; Si, 5.99; Ti, 10.21; C, 66.59; H, 6.23; Cl, 7.56%; mol wt, 469.0.

$(Me_2PhSiO)_2TiCp_2$: Found: Si, 11.81; Ti, 10.05; C, 65.60; H, 6.75%; mol wt, 461. Calcd for $C_{26}H_{32}O_2Si_2Ti$: Si, 11.69; Ti 9.97; C, 64.98; H, 6.71%; mol wt, 480.6.

$Me_2PhSiOTi(Cl)Cp_2$: Found: Si, 7.81; Ti, 13.30; C, 59.25; H, 5.79; Cl, 9.90% mol wt, 355. Calcd for: $C_{18}H_{21}OSiTiCl$: Si, 7.70; Ti, 13.13; C, 59.26; H, 5.80; Cl, 9.72%; mol wt, 364.8.

2) T. Takiguchi and M. Abe, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 679 (1965).
3) T. Takiguchi and M. Abe, *ibid.*, **66**, 625 (1963).
4) T. Takiguchi, *J. Am. Chem. Soc.*, **81**, 2359 (1959).
5) G. Wilkinson and J. M. Birmingham, *ibid.*, **76**, 4281 (1954).

All products thus obtained were readily soluble in tetrahydrofuran, toluene, benzene, chloroform and acetone, partly soluble in boiling *n*-hexane and sparingly soluble in cyclohexane, ether and carbon tetrachloride.

IR Absorption Spectra and X-Ray Powder Patterns. As for the IR absorption spectra, the absorption bands due to the Ti-O-Si bonding were observed at 915 cm^{-1} with $(R_3SiO)_2TiCp_2$ type derivatives and at 950 cm^{-1} with $R_3SiOTi(Cl)Cp_2$ type derivatives as a sharp and strong peak in agreement with the previous descriptions[1].

The X-ray powder diffraction was observed for crystalline products by using the Cu$K\alpha$ radiation filtered by Ni as follows.

$(Ph_3SiO)_2TiCp_2$:

d,kX:	2.99	3.48	3.59	3.74	4.08	4.64	4.87	5.13	5.28
	5.95	6.50	6.70	7.55	9.86	13.15			
I/I_0:	0.23	0.18	0.21	0.25	0.35	0.65	0.90	1.00	0.20
	0.24	0.20	0.26	0.44	0.55	0.25			

$Ph_2BuSiOTi(Cl)Cp_2$:

d,kX:	4.00	4.54	4.64	4.89	5.29	5.80	7.25	7.38	8.30
	9.79								
I/I_0:	0.55	0.58	0.47	0.54	0.54	0.71	0.56	1.00	0.71
	0.40								

$(Ph_2MeSiO)_2TiCp_2$:

d,kX:	4.15	4.61	4.76	5.50	6.11	6.92	10.07
I/I_0:	0.37	0.32	0.20	1.00	0.23	0.22	0.34

$Ph_2MeSiOTi(Cl)Cp_2$:

d,kX:	3.89	4.00	4.57	5.04	5.19	5.46	5.78	6.01	6.90
	7.89	9.40	12.06						
I/I_0:	0.39	0.52	1.00	0.24	0.48	0.33	0.41	0.38	0.29
	0.73	0.23	0.32						

The authors are grateful to the Shin-etsu Chem. Ind. Co. for the supply of chlorosilanes, to the Hitachi Chem. Works Co. for the supply of dicyclopentadiene and to Dr. S. Nakatani of the National Institute of Science and Technology, Tokyo, for his kind co-operation in the elementary analyses of the products reported herein.