

THE SYNTHESIS AND STRUCTURE OF SILICA-SUPPORTED BIS(h^5 -CYCLOPENTADIENYL)DICHLOROTITANIUM(IV) COMPLEXES

Alena REISSOVÁ^a, Zdeněk Bastl^b and Martin ČAPKA^a

^a *Institute of Chemical Process Fundamentals,*

Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchbát and

^b *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,*

Czechoslovak Academy of Sciences, 118 40 Prague 1

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The title complexes have been obtained by functionalization of silica with cyclopentadienylsilanes of the type $R_x(CH_3)_{3-x}Si(CH_2)_n C_5H_5$ ($x = 1-3$, $n = 0, 1, 3$), trimethylsilylation of free surface hydroxyl groups, transformation of the bonded cyclopentadienyl group to the cyclopentadienyl anion, followed by coordination of (h^5 -cyclopentadienyl)trichlorotitanium. The effects of single steps of the above immobilization on texture of the support, the number of free hydroxyl groups, the coverage of the surface by cyclopentadienyl groups and the degree of their utilization in anchoring the titanium complex have been investigated. ESCA study has shown that the above anchoring leads to formation of the silica-supported bis(h^5 -cyclopentadienyl) dichlorotitanium(IV) complex.

In recent years, increasing interest has been shown in immobilized homogeneous catalysts¹. However, as far as hydrogenation reactions are concerned, most studies have been devoted to immobilized rhodium complexes² whereas hydrogenation catalysts based on the cheaper titanium have attracted much less attention (for review see ref.³). Only a few studies^{4,5} on heterogenized cyclopentadienyl complexes bonded to inorganic supports might result from apprehension that free surface hydroxyl groups remaining after functionalization of the support can exert unfavourable effect on catalytic properties of the resulting transition metal complexes. For that reason, in the case of functionalization of silica by cyclopentadienyl ligands followed by anchoring titanium(IV) complex, we have centered on the study of single steps of immobilization, changes in the support texture and the number of free surface hydroxyl groups and on the structure of immobilized complexes.

EXPERIMENTAL

Chemicals. Silica (Kieselgel 100 (Merck), particle size 0.063–0.2 μ m, mean pore diameter 10 nm, surface area 365 m²/g) was dried at 200°C/0.01 Pa for 5 h. Trimethylchlorosilane (Lachema, Kolín) and hexamethyldisilazane were distilled under argon before use. Cyclopentadienyltrichlorosilane⁶, cyclopentadienyl(methyl)dichlorosilane⁷, cyclopentadienyldimethylchlorosilane⁸, (cyclopentadienylmethyl)triethoxysilane⁹, (3-cyclopentadienylpropyl)triethoxysilane⁹, (h^5 -cyclo-

pentadienyl)trichlorotitanium¹⁰, and bis(h⁵-cyclopentadienyl)dichlorotitanium¹¹ were prepared by reported procedures, as indicated.

Cyclopentadienyl-substituted alkoxy silanes were obtained by reaction of the corresponding chlorosilane with anhydrous ethanol in diethyl ether. After the appropriate amount of ethanol had been added, the mixture was refluxed for 2 h and then the present hydrogen chloride was neutralized by 10% sodium ethanolate solution, using phenolphthalein as the indicator. The solids formed were filtered off, the solvent distilled off and the product was obtained by fractional distillation.

Functionalization of Silica

The dried silica was placed in a flask, twofold volume of toluene was added and the mixture was refluxed for 4 h. Then, one half of the solvent was distilled off, the support was washed thrice with toluene, separated by filtration and dried *in vacuo*. Trimethylsilylation of the unreacted hydroxyl groups was made with toluene solution of trimethylchlorosilane and hexamethyldisilazane (1 : 1). Reaction conditions and analysis of functionalized supports are given in Table I.

Immobilization of Titanium Complexes on Silica

The cyclopentadienyl group anchored to the support was transformed into h⁵-cyclopentadienyl anion by adding hexane solution of n-butyllithium in excess to the functionalized silica. Then, a solution of (h⁵-cyclopentadienyl)trichlorotitanium was added, the mixture was shaken, the so prepared heterogenized complex was washed with toluene until discolouration and then it was dried *in vacuo*. Reaction conditions and analyses are given in Table II.

Determination of Concentration of Free Surface Hydroxyl Groups

The direct determination of surface hydroxyl group concentrations was made by the reaction of active hydrogen with zinc tetrahydrofuranate¹². The released methane was detected gas chro-

TABLE I
Synthesis of functionalized silica

Designation	Silica, g	Cyclopentadieny silane (g)	Analysis, %	
			C	H
00	—	none	0.03	0.61
01/Cl	60	C ₅ H ₅ Si(CH ₃) ₂ Cl (20)	3.27	1.05
01	123	C ₅ H ₅ Si(CH ₃) ₂ OC ₂ H ₅ (25)	4.07	1.05
02/Cl	53	C ₅ H ₅ Si(CH ₃)Cl ₂ (10)	2.68	0.88
02	124	C ₅ H ₅ Si(CH ₃)(OC ₂ H ₅) ₂ (25)	4.71	1.07
03/Cl	42	C ₅ H ₅ SiCl ₃ (6)	2.12	0.78
03	124	C ₅ H ₅ Si(OC ₂ H ₅) ₃ (25)	4.71	1.07
13	128	C ₅ H ₅ CH ₂ Si(OC ₂ H ₅) ₃ (32)	4.48	1.12
33	155	C ₅ H ₅ (CH ₂) ₃ Si(OC ₂ H ₅) ₃ (52)	6.45	1.37

matographically (a thermal conductivity detector connected to an integrator). The determination was made with the use of a microreactor for very fine materials¹³.

Determination of Porosity and Specific Surface Area of the Support

Determination was made on Micrometrics Autopore 9 200 instrument. Data obtained by mercury porosimetry were treated in the usual way, assuming the tubular shape of pores. The following characteristics of the support were calculated: porosity, specific surface area, mean pore diameter, and pore distribution.

Spectroscopic Measurements

IR spectra of functionalized supports were recorded on Specord 75 IR (Zeiss Jena, G.D.R.) instrument in the 4 000–400 cm^{-1} region. ESCA spectra were recorded on ESCA 3 Mk II (VG Scientific, U.K.) spectrometer using ALK excitation line. Because of large grain size, the samples were grounded and laid on double-sided adhesive tape.

RESULTS AND DISCUSSION

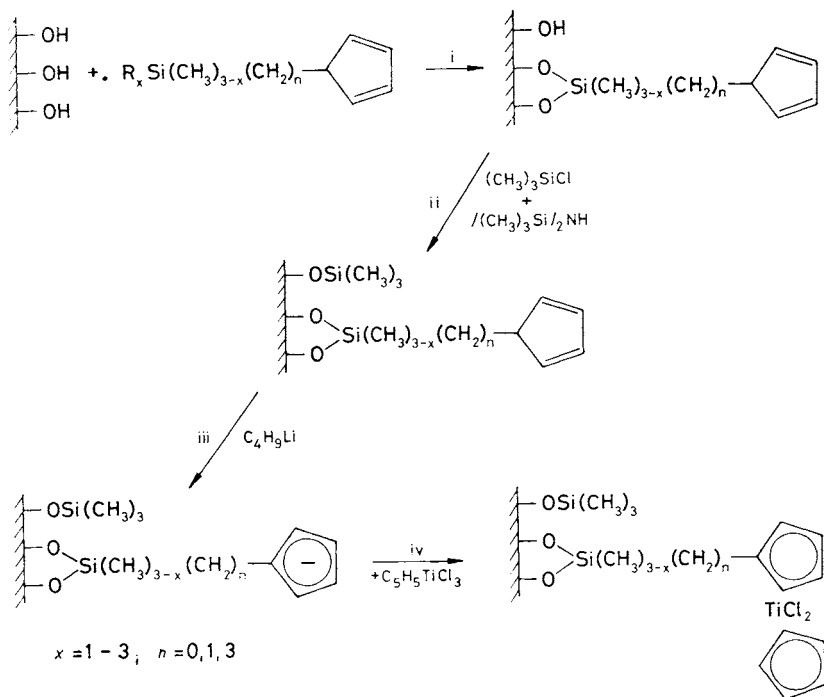
For heterogenizing h^5 -cyclopentadienyltitanium complexes, we have chosen successive formation of the complex on the support (Scheme 1), *i.e.* functionalization of silica by organosilicon reagent (*i*), trimethylsilylation of free surface hydroxyl groups (*ii*), transformation of the cyclopentadienyl group to the cyclopentadienyl anion (*iii*), and coordination of the titanium complex (*iv*). In the case of inorganic supports, this procedure of immobilization has not yet been applied. Therefore, we

TABLE II
Synthesis of immobilized titanium(IV) complexes

Designation	Modified silica ^a (g)	Butyllithium mmol	Ti complex ^b mmol	Ti content mmol g ⁻¹
00-Ti	00 (19)	0	4	0.04
01/Cl-Ti	01/Cl (11)	26	3.5	0.15
01-Ti	01 (16)	40	5.1	0.16
01/Cl-Ti	02/Cl (9)	15	1.6	0.13
02-Ti	02 (10)	20	3.2	0.20
03/Cl-Ti	03/Cl (7)	20	2.1	0.12
03-Ti	03 (10)	25	3.2	0.26
13-Ti	13 (10)	17	3.2	0.23
33-Ti	33 (10)	25	3.2	0.2

^a For designation see Table I. ^b (h^5 -Cyclopentadienyl)trichlorotitanium.

have studied single steps of immobilization and verified the structure of the anchored complex.



SCHEME 1

The dried silica was modified with organosilicon compounds of the type $R_x(CH_3)_{3-x}Si(CH_2)_nC_5H_5$ (R = ethoxy or chloro group, $n = 0, 1, 3$ and $x = 1$ to 3; in support designation the first and second numeral denotes n and x , respectively). The reactivity of the support to chloro- and alkoxy-silanes was compared and the recent success in preparing triethoxysilylalkylcyclopentadienes⁹ made it possible to use – in addition to functionalizing agents containing cyclopentadiene–silicon bond – the silanes containing methylene or propylene spacer between silicon and cyclopentadienyl group.

The results presented in Table III show that with ethoxysilanes the higher coverage of support surface by cyclopentadienyl groups can be obtained than with chlorosilanes. This rather surprising finding (chlorosilanes undergo hydrolysis at much faster rate compared to alkoxy-silanes) can be explained by the strong adsorption of the hydrogen chloride formed by hydrolysis of chlorosilanes on the support surface, which decreases the accessibility of other molecules of the functionalizing

agent. This assumption is supported also by a significant colour change which is characteristic of the reaction of silica with the chlorosilanes and by the fact that when the support is modified with chlorosilanes the essentially same coverage of the surface by cyclopentadienyl groups (0.35 ± 0.02 mmol/g) is obtained, irrespective of the structure of the modifying agent. This seems to indicate that in all the cases, the adsorption of hydrogen chloride saturates the same number of active sites.

By contrast to it, on functionalizing silica with the ethoxysilanes, the number of surface cyclopentadienyl groups increases with increasing functionality (*i.e.* with the number of ethoxy groups in the molecule — *cf.* samples 01, 02, and 03), attaining maximum value for triethoxysilanes. Furthermore, this value is not sub-

TABLE III

Functionalized supports prepared by the reaction of silica (support 00) with the silanes $R_x(CH_3)_{3-x}Si(CH_2)_n C_5H_5$

Support	Surface group	R	C_5H_5 concn. mmol g ⁻¹	OH group concn. ^a mmol g ⁻¹	
				A	B
00	—OH	—	—	2.25	
01/Cl	$\begin{array}{c} CH_3 \\ \\ -O-Si-C_5H_5 \end{array}$	Cl	0.37	1.64	0.80
01	$\begin{array}{c} CH_3 \\ \\ -O-Si-C_5H_5 \end{array}$	OC ₂ H ₅	0.41	1.42	0.86
02/Cl	$\begin{array}{c} CH_3 \\ \\ -O-Si-C_5H_5 \end{array}$	Cl	0.35	1.67	0.83
02	$\begin{array}{c} CH_3 \\ \\ -O-Si-C_5H_5 \end{array}$	OC ₂ H ₅	0.57	1.38	0.74
03/Cl	$\begin{array}{c} CH_3 \\ \\ -O-Si-C_5H_5 \end{array}$	Cl	0.33	1.7	0.88
03	$\begin{array}{c} CH_3 \\ \\ -O-Si-C_5H_5 \end{array}$	OC ₂ H ₅	0.63	1.27	0.61
13	$\begin{array}{c} CH_3 \\ \\ -O-Si-CH_2-C_5H_5 \end{array}$	OC ₂ H ₅	0.61	1.22	0.54
33	$\begin{array}{c} CH_3 \\ \\ -O-Si-(CH_2)_3-C_5H_5 \end{array}$	OC ₂ H ₅	0.66	1.32	0.65

^a A = after reaction with the organosilicon reagent, B = after additional trimethylsilylation by the trimethylchlorosilane + hexamethyldisilazane (1 : 1) mixture.

stantially affected by the spacer between silicon and cyclopentadienyl group (*cf.* samples 03, 13, and 33).

The silanes of the higher functionality can interact not only with the surface but also with each other to form the Si—O—Si bond. Therefore, the results of elemental analysis have also been used to estimate the extent of the substitution of the alkoxy groups in cyclopentadienyltriethoxysilanes (in this case, the substitution of one, two or three ethoxy groups is possible theoretically). For each of the mentioned possibilities, theoretical C : H ratios were calculated and compared with experimental results. The best agreement was obtained for the substitution of three ethoxy groups which takes place either by the surface reaction or by mutual interaction of two molecules of the reagent.

The presence of cyclopentadienyl group on support surface was proved by comparison of IR spectra of the starting silica and the modified support, the latter showing the distinct increase in the 2950 cm^{-1} band assigned to saturated C—H bonds. The bands above 3000 cm^{-1} corresponding to the cyclopentadiene ring are weak and are overlapped with the O—H band of the silica.

From data presented in Table III it becomes evident that even at relatively high degree of coverage of the surface by cyclopentadienyl groups, the predominant portion (approximately two thirds) of surface hydroxyl groups remains unreacted (likely from steric reasons). As the free hydroxyl groups would interfere in the subsequent transformation of cyclopentadienyl groups to the corresponding anions, the modified silica was further trimethylsilylated by the less sterically demanding and more effective trimethylsilylation agents, *i.e.* by a mixture of trimethylchlorosilane and hexamethyldisilazane (reaction(ii)), after which reaction the number of surface hydroxyl groups decreased to one third up to one fourth of the original value. We have not succeeded in decreasing further this value. Therefore, the reducing agent was used in excess in the reaction (iii) (Scheme 1).

The so prepared surface cyclopentadienyl anion was then used to coordinate (h^5 -cyclopentadienyl)trichlorotitanium, giving the heterogenized analogue of titanocene (reaction (iv)). The amount of the immobilized titanium complex is given in Table II. It is seen that the titanium complex is not essentially bonded to free hydroxyl groups, *i.e.* by the interaction observed by Skupinski^{14,15}, as only very small amount (0.04 mmol/g) of the complex is found to reside on the unmodified support. On the other hand, the amount of the complex immobilized on the silicas modified with cyclopentadienyl groups is roughly proportional to the number of anchoring ligands on the support. This holds for both chlorosilanes and ethoxysilanes. Comparison of data given in Tables II and III shows that the cyclopentadienyl groups are coordinately utilized from 40, 37, and 40 percent for supports 01/Cl, 02/Cl, and 03/Cl, respectively, providing that one molecule of the titanium complex is bonded to one surface cyclopentadienyl group. In the case of the supports 01, 02, and 03 this utilization degree is 39, 35, and 41 percent. If the inaccuracy of analyses

and possible nonhomogeneity of individual samples are taken into account, the dependence of the amount of anchored titanium on the number of anchoring ligands can be considered quite obvious. Surprisingly, the degree of utilization of cyclopentadienyl groups decreases, however, with the longer spacer between cyclopentadienyl group and support surface (41, 37, and 32% for the supports 03, 13, and 33), which may be due to the fact that the cyclopentadienyl anion bonded to the longer and more mobile spacer can interact easier with the surface, prior to its interaction with the titanium complex.

The fact that titanium is bonded to the surface in the form of bis(h^5 -cyclopentadienyl)dichlorotitanium complexes was confirmed by ESCA spectroscopy. The

TABLE IV
Core-level binding (eV) for titanium complexes (accuracy ± 0.2 eV)

Complex	Line			
	Cl(2p)	C(1s)	Si(2p) ^a	O(1s)
$(C_5H_5)_2TiCl_2$	198.8	285.0	—	532.7
$\begin{array}{l} O-Si(CH_2)_3C_5H_4TiCl_2(C_5H_5) \\ O-SiCH_2C_5H_4TiCl_2(C_5H_5) \end{array}$	199.1	284.8	103.4	532.8
	199.1	284.7	103.4	532.6

^a Used as internal standard for static charge referencing.

TABLE V
Texture data for modified silicas

Surface group ^a	Surface area $m^2 g^{-1}$	Pore volume $cm^3 g^{-1}$	Mean pore radius, nm
$ OH$	468	2.189	3.5
$\begin{array}{l} O-Si-C_5H_5 \\ OH \end{array}$ (i)	433	2.045	3.4
$\begin{array}{l} O-Si-C_5H_5 \\ O-Si(CH_3)_3 \end{array}$ (ii)	448	2.045	3.3
$\begin{array}{l} O-Si-C_5H_4Ti(Cl_2)C_5H_5 \\ O-Si(CH_3)_3 \end{array}$ (iv)	358	1.628	2.8

^a Silica surface, steps (i), (ii), and (iv) see Scheme 1.

measurements were made with the homogeneous $(C_5H_5)_2TiCl_2$ and its heterogenized analogues. It can be stated that the binding energies of titanium $2p_{3/2}$ electrons for all the samples differ from each other only within experimental errors ($E_B = 457.5$ eV) and correspond to titanium in the oxidation state between +2 and +3. This formal oxidation state agrees with the assumption that only chloride anions withdraw electrons from titanium, while – similarly as in ferrocene – the back donation of electrons from the ligand to the central atom is very important in the case of h^5 -cyclopentadienyl ligands. Data on the core-level binding energies measured are presented in Table IV.

As the other binding energies for crystalline $(C_5H_5)_2TiCl_2$ differ only slightly from those for heterogenized analogues, the structure of titanium complex on silica surface can be considered as very similar to the structure of the pure crystalline bis(h^5 -cyclopentadienyl)dichlorotitanium. Therefore, free surface hydroxyl groups apparently do not enter the coordination sphere of titanium and will not thus affect the catalytic activity of the complex.

With respect to the use of anchored titanium complexes as catalysts, not only the structure of the anchored complex but also its accessibility is important. Therefore, we have examined whether after steps (i) to (iv) (Scheme 1) the texture of the support remains preserved to the extent which ensures the access of the reactants to the catalytic site. After each step, the surface area of the support, the total pore volume and the mean pore radius were determined.

As shown by the results presented in Table V and in Fig. 1, the first two steps (i.e. anchoring of the cyclopentadienyl group and trimethylsilylation of free hydroxyl groups) do not affect the texture of the support. The differences found are within

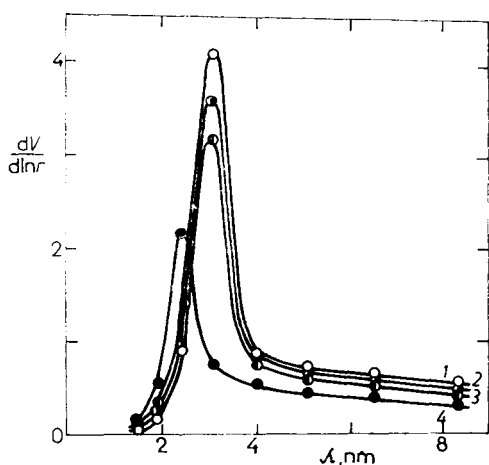


FIG. 1

Changes in pore distribution during immobilization; 1 unmodified silica, 2 after introduction of cyclopentadienyl groups (step (i), Scheme 1), 3 after additional trimethylsilylation of OH groups (step (ii)), 4 after coordination of the titanium complex (step (iv))

experimental errors (± 10 percent). On the other hand, the immobilization of the relatively bulky metal complex affects the texture, as it is seen from Fig. 1, the maximum for pore radius 3 nm decreases and shifts to the region of the smaller radii. However, data show that even after heterogenization, most pores are available for the catalytic process.

Summarizing, by the successive formation depicted in Scheme 1, bis(h^5 -cyclopentadienyl)dichlorotitanium complexes can be prepared which represent the heterogenized form of titanocene. These complexes remain chemically bonded to the support *via* h^5 -cyclopentadienyl bond. In the course of immobilization, the texture of the support does not change significantly and the pores are available for the catalytic process.

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