

HYDROSILYLATION CATALYSED BY TRANSITION METAL COMPLEXES COORDINATELY BOUND TO INORGANIC SUPPORTS*

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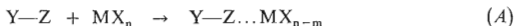
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A series of Rh, Pd, and Pt complexes was prepared whose tert-phosphine, tert-amine, cyano or pyridine ligands are bonded directly or through alkylene chain to inorganic supports. The complexes were tested as catalysts for hydrosilylation of several alkenes and of 1,3-butadiene by trichloro-, triethyl-, and triethoxysilane. In comparison with similar soluble complexes, supported catalysts were more selective and some could be reused. In several cases their effectiveness was greater than that of the soluble catalysts. The factors influencing the activity of supported catalysts are discussed.

In recent years the attempt has been made to combine the advantages of homogeneous and heterogeneous catalysis¹, mostly by using catalysts which comprised a transition metal complex bound to an organic support substituted with functional groups acting as ligands. Such supported catalysts were used with success in hydrogenation^{2,3}, hydroformylation⁴, and hydrosilylation^{5,6}. Because of the lower thermal stability and lesser inertness toward solvents of organic polymers, the successful attempt has been made to replace organic supports by inorganic material, such as silica containing phosphine groups⁷. Silica was also employed in preparing polymerisation catalysts from allyl complexes of transition metals⁸⁻¹⁰.

In continuation of our study on supported transition metal complexes as hydrosilylation catalysts¹¹, in this work we were concerned with the scope and limitations of the use of transition metal complexes bound to inorganic materials. With this aim we investigated (a) the applicability of several inorganic materials as supports, (b) the effect of the ligands bound to the supports on the catalytic activity of supported complexes, compared to the activity of similar soluble hydrosilylation catalysts, and (c) the mode of their action and the possibility of their recycling.

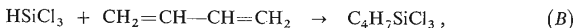
For this purpose we prepared a series of supported transition metal complexes by the following way



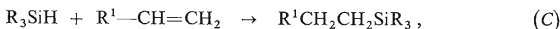
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- Y = γ -alumina, silica, molecular sieve, and glass,
 Z = $-\text{P}(\text{C}_6\text{H}_5)_2$, $\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$, $-\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{CN}$,
 $\equiv\text{Si}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$, $\equiv\text{Si}(\text{CH}_2)_3\text{CN}$, and $\equiv\text{Si}(\text{CH}_2)_2\text{C}_5\text{H}_4\text{N}$,
 MX_n = PdCl_2 , RhCl_3 , and H_2PtCl_6 ,

and compared their catalytic activity with that of related soluble complexes using the reactions



and



where $\text{R} = \text{C}_2\text{H}_5$, $\text{C}_2\text{H}_5\text{O}$, and Cl , and $\text{R}^1 = n\text{-C}_4\text{H}_9$, $n\text{-C}_5\text{H}_{11}$.

EXPERIMENTAL

Compounds Used

RhCl_3 (Fluka A. G.), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, and PdCl_2 (Kovohutě Works, Vestec) were commercial products as indicated. $[(\text{C}_6\text{H}_5)_3\text{P}_3]\text{RhCl}$ was prepared by the literature procedure¹². The supports, γ -alumina, KSK silica gel, and Nalsit 4A molecular sieve, were supplied by Lachema Works (Brno). 1-Hexene, 1-heptene, 1-decene, vinyl ethyl ether, styrene (stabilised with 2,6-di-tert-octylpyrocatechol) and 1,3-butadiene used without further purification, were dried over Nalsit 4A molecular sieve. Trichlorosilane was of inland provenience. Diphenylphosphine¹³, allyldimethylamine¹⁴, triethoxysilane¹⁵, triethylsilane¹⁵, 3-cyanopropyltrichlorosilane¹⁶, 3-cyanopropyltriethoxysilane¹⁷, methyl(3-cyanopropyl)diethoxysilane¹⁷, 3-(dimethylamino)propyltriethoxysilane^{18,19}, 2-(4-pyridyl)ethyltrichlorosilane²⁰, 1-hexyltriethoxysilane²¹, 1-heptyltriethoxysilane²¹, 1-decyltrichlorosilane²⁰, 1-decyltriethoxysilane²², 1-decyltriethylsilane²⁰, *cis*-2-butenyltrichlorosilane²³, and 2-ethoxyethyltriethoxysilane²⁴ were prepared by literature procedures as indicated. 2-Ethoxyethyltriethylsilane was obtained by ethylation²⁵ of the trichlorosilyl derivative²⁴ by ethylmagnesium bromide. 1-Phenylethyltriethoxysilane and 2-phenylethyltriethoxysilane were prepared by esterification of corresponding trichlorosilyl derivatives²⁶ with ethanol²⁷. 2-Hexyltriethylsilane was prepared by the reaction of 2-hexylmagnesium bromide with triethylchlorosilane. The 2-bromohexane used was obtained by reduction²⁸ of 2-hexanone to 2-hexanol, followed by its reaction with hydrogen bromide²⁹.

Supports Containing Functional Groups

Support A. To 85 g of silica and 150 ml of benzene were dropwise added 15 g of vinyltrichlorosilane with stirring which was continued for another 1 h, then the support was separated by filtration, washed successively with 100 ml-portions of benzene, ethanol, saturated aqueous sodium carbonate solution, and with ethanol, which was removed by distillation. Then 300 ml of benzene, 13 g of diphenylphosphine, and 5 ml of 0.1M benzene solution of phenyllithium were added to the reaction mixture. The mixture was refluxed for 10 h, the support was filtered off, washed successively with three 200 ml-portions of benzene and two 100 ml-portions of ethanol.

Support B. To 79 g of Nalsit 4A molecular sieve (dried by heating to 350°C for 6 h under the pressure of 1 Torr) was added dropwise a solution of 111 g of PBr_3 in 110 ml of n-hexane and the mixture was refluxed for 6 h, the support was filtered and washed twice with 200 ml of n-hexane. Then it was reacted with 500 ml of 1M ether solution of phenylmagnesium bromide, removed from the reaction mixture by filtration with suction, washed twice with 100 ml of diethyl ether and twice with 200 ml of hexane and dried *in vacuo* (0.69% P).

Support C. A mixture of 15 g of γ -alumina, 20 g of vinyltrichlorosilane, and 50 ml of benzene was kept under mild reflux for a period of 12 h. The support, separated by filtration, was then washed successively with 100 ml of hexane, 100 ml of ethanol, a mixture of 100 ml of ethanol and 5 ml of pyridine, 100 ml of 10% sodium carbonate solution, and finally with two 100 ml- portions of ethanol. To the support dried under vacuum were added 80 ml of benzene and 5.4 g of diphenylphosphine and the mixture was refluxed for 2 h. Then 1 ml of 1M benzene solution of phenyllithium was added and the refluxing was continued for another 8 h. The so treated support was washed thrice with 100 ml of benzene and dried *in vacuo* (3.4% Si, 1.1% P).

Supports D—M. The reaction components in the amounts recorded in Table I were heated at 80°C for 8 h. In the case of trichlorosilyl derivatives, the half volume of benzene was removed by distillation, the support was then separated by filtration with suction, washed with 100 ml of benzene, 100 ml of ethanol, 50 ml of 5% sodium carbonate solution, 100 ml of water, twice with 100 ml of ethanol and dried *in vacuo*. When the alkoxyxilanes were used, the solvent was removed by distillation and the reaction vessel containing the support was heated to 150°C for 3 h. The support was then washed twice with 100 ml of benzene and dried *in vacuo*.

Supported Catalysts

Transition metal compounds were reacted with the supports containing functional groups in an appropriate solvent under the conditions recorded in Table II. The so prepared catalysts were separated by filtration with suction and washed with the following solvents. Catalysts *I, IV—VI, X, XIII, and XIV* with ethanol, catalyst *II* with ethanol and hexane, catalysts *III, VII—IX, XI, XII, and XV* with ethanol and benzene, catalysts *XVI—XIX* with isopropanol and chloroform, catalysts *XX and XXI* with isopropanol and benzene, and catalyst *XXII* with benzene and ethanol. All were then dried *in vacuo*. The surface areas of the dry catalysts were determined by the method reported by Kljačko-Gurvič³⁰. The content of transition metals in the prepared catalysts was determined by the methods worked out in the Analytical Department of this Institute³¹.

Hydrosilylations

All experiments were carried out in sealed glass ampoules under argon, using degassed reaction components. The conditions are given in Tables III—IV. Alkene and silicon hydride were used in equimolar amounts (4—40 mmol each) and catalysts were weighed in such amounts which ensured the same concentration of a given metal in all experiments with both polymer and corresponding soluble model catalysts. The following molar ratios of alkene to metal were used: alkene: Pt = 1 : 2 × 10⁻⁵, alkene: Rh = 1 : 1 × 10⁻⁴, and alkene: Pd = 1 : 5 × 10⁻⁵. The products were isolated and their structure was confirmed by IR and NMR spectroscopy and by comparing their GLC retention times with those of authentic samples prepared independently (see Compounds Used).

The composition of reaction mixtures was determined by gas-liquid chromatography under following conditions: chlorosilyl derivatives were analysed on a chromatograph equipped with thermal conductivity detector, using 3 m-column filled with 16% Trifluoropropyl Methyl Silicone

TABLE I

Supports with Functional Groups

The synthesis was carried out in 70–100 ml of benzene at 80°C over a period of 8 h, propylamine was added after 4 h.

Support	Inorganic material, (g)	Silicon derivative, (g)	Propylamine, g
D ^a	γ -alumina (10)	$(\text{H}_3\text{C})_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$	(3.2) 2.5
E	glass (6.5)	$(\text{H}_3\text{C})_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$	(3.0) 1.5
F ^b	γ -alumina (10)	$\text{NC}(\text{CH}_2)_2(\text{CH}_3)\text{Si}(\text{OC}_2\text{H}_5)_2$	(4.7) 2.7
G ^c	γ -alumina (4.3)	$\text{NC}_5\text{H}_4(\text{CH}_2)_2\text{SiCl}_3$	(3.0) —
H	silica (15)	$\text{NC}(\text{CH}_2)_3\text{SiCl}_3$	(9.0) —
I	silica (15)	$\text{NC}(\text{CH}_2)_3\text{SiCl}_3$	(4.5) —
J	silica (15)	$\text{NC}(\text{CH}_2)_3\text{SiCl}_3$	(1.0) —
K	silica (10)	$\text{NC}(\text{CH}_2)_3\text{SiCl}_3$	(0.19) —
L	silica (10)	$\text{NC}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$	(1.0) 0.5
M	silica (15)	$\text{NC}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$	(0.5) 0.5

The supports contained ^a 1.4% N, ^b 2.9% N, ^c 2.2% N.

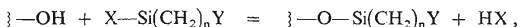
FS 1 (Pye, London) on Chromosorb W and nitrogen as carrier gas, alkyl- and alkoxy-silyl derivatives were analysed on Chrom III instrument (flame ionisation detector, produced by Laboratorní přístroje, Prague), using 1.6 m-column filled with 10% Silicone Elastomer E 301 on Chromaton and hydrogen as carrier gas. The yields of reaction products were determined from GLC peak areas in the usual way.

RESULTS AND DISCUSSION

Synthesis of Supported Catalysts

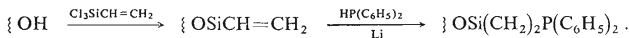
In preparing the catalysts we used inorganic supports containing functional groups ($-\text{CN}$, $-\text{N}(\text{CH}_3)_2$, $-\text{C}_5\text{H}_4\text{N}$, and $-\text{P}(\text{C}_6\text{H}_5)_3$) bonded to the inorganic material either directly or through an $-\text{O}-\text{Si}(\text{CH}_2)_n$ -chain. Three different ways were employed to introduce above functional groups, each utilizing the reactivity of surface hydroxyl groups of inorganic oxide support. 1) The support was reacted with phosphorus tribromide to give surface oxyphosphorus bromide which was subsequently converted to phenyl derivative by phenylmagnesium bromide (support B, see Experimental). This treatment led to substantial decrease in surface area of the support which resulted in relatively small surface area of catalysts prepared from it (catalysts II and XI). 2) Inorganic oxide supports were treated with alkoxy- or chlorosilanes containing suitable organofunctional groups. The Si—OR or Si—Cl groups of these

compounds readily react with surface hydroxyl groups of the supports under formation of thermally stable support... O—Si linkages:



X = C₂H₅O, Cl; Y = functional group; n ≠ 0.

This principle is widely used to chemically link organosilicon coupling agents with inorganic solids³² and was employed also by Allum⁷ in preparing a phosphorus containing silica. It is noteworthy that the so formed bond between the silicon compound and the support is liable to hydrolysis. In the case of silica the activation energy of this process was reported³² to be 23.6 kcal/mol. The silanol formed is then bonded to the surface only via hydrogen bridge. As found, this bonding is however still by about one order of magnitude stronger than mere adsorption. For that reason the use of alkoxysilanes and nonaqueous media is more advantageous. This procedure was employed in preparing supports D—F, L, and M (Table I). In several cases we introduced functional groups also by means of appropriate chlorosilanes, with the aim to examine how a weaker bonding with inorganic surface reflects in the performing of supported catalysts (supports G—K, Table I; these contain organosilicon compound, probably polysiloxane, hydrogen-bonded due to hydrolysis occurring during removal of formed hydrogen chloride by washing with aqueous solutions). Surface areas of the supports prepared in the above ways were found to be lower than those of primary supports, more so when the supports were reacted with chlorosilanes. When compared with method 1, surface area decrease was here smaller. 3) Phosphorus-containing supports were prepared also in such a way that inorganic oxide support was first reacted with chlorosilane containing alkenyl group and so pre-treated material was then subjected to the lithium catalysed reaction with diphenylphosphine³³ (supports A and C, see Experimental). The procedure can be schematically depicted as follows:



As to surface area decrease this procedure was more favourable than method 1, which manifested itself in the catalytic activity and service life of some catalysts based on them (catalysts I, X, and XII, see later).

Synthesis of the catalysts was realized by coordination of transition metal compounds to functional groups of the supports. Conditions used are recorded in Table II, together with probable mode of linking. From the inspection of the table it becomes immediately clear that during preparation a part of fixed silicon compound is abstracted from the support (compare *e.g.* phosphorus content in catalyst VIII with support C) the dissolving being greater at elevated temperatures (see catalysts VII

and VIII). This is accompanied by certain "reformation" of the surface lost during preparing support containing functional groups (catalysts VII and VIII, and III and IV). In the case of rhodium and palladium compounds the use of elevated temperature increased metal content in catalysts, unfortunately mainly due to the formation of catalytically inactive metals (catalysts III and VII); such reduction has not occurred, however, during preparation of platinum catalysts (X and XI).

Activity of Supported Hydrosilylation Catalysts

Rhodium catalysts. From the results recorded in Table III it follows that in the addition to alkenes the activity of the catalysts decreases (with one exception) in dependence on the silicon hydride used in the order $\text{HSi}(\text{OC}_2\text{H}_5)_3 > \text{HSi}(\text{C}_2\text{H}_5)_3 > \text{HSiCl}_3$. This is not unexpected as similar situation was already observed both with some soluble rhodium complexes³⁴ and with rhodium compounds bound to organic polymers^{5,6} and was ascribed to differences in stability of respective silylrhodium complexes transiently formed in the course of the reaction (for detailed discussion see ref.³⁵). Several of the catalysts tested were comparable in activity to the soluble rhodium complexes used as reference catalysts (catalysts I, IV, and V). The very low activity of catalysts II and III is obviously due to the fact that the higher temperature and longer reaction time used in their preparation led to reduction of rhodium compound to catalytically inactive metallic rhodium. The reason of unexpectedly high effectiveness of catalyst VI in the addition of trichlorosilane to 1-heptene is unclear. It cannot be accounted for by eventual interaction of trichlorosilane with tert-amine groups of the support³⁶, since catalyst V does not act in similar way. While the reactions of alkenes with triethoxysilane and trichlorosilane lead to expected 1-silyl-substituted alkenes, 1-hexene + triethylsilane reaction catalysed by soluble rhodium catalysts gave along with terminal product also its nonterminal isomer, 2-triethylsilylheptane. This is of interest, since so far the formation of the latter compound was observed only under rather unusual conditions¹¹ (large excess of the olefin with respect to the silane). Moreover, the fact that the latter isomer is not formed in the reaction catalysed by supported catalysts I, IV and V illustrates the change of selectivity by coordination of metal compound to the support, which at the same time has some consequences in regard to the mode of the action of such catalysts. In general, supported catalyst may be assumed to act in three different ways: 1) The reaction takes place on the surface of supported catalyst, *i.e.* catalytically active species formed is bonded to the support during whole process. 2) Catalytically active species or its precursor is abstracted from support to solution, this process being reversible. Catalyst then acts as homogeneous one³⁷. 3) Similarly to 2) the reaction proper takes place in solution, the abstraction being however irreversible. Cases 1) and 2) can be experimentally distinguished only with difficulty. Notwithstanding, as to practical performance of catalysts, in both cases conditions are formed for

TABLE II

The Preparation and Properties of Supported Catalysts

Unless otherwise stated, the reaction conditions were 25°C and 24 h. The procedure see Experimental.

Catalyst	Support, (g) metal compound ^a , (g)	Solvent, ml	Probable mode of linking	Metal, % surface ^b , m ² /g
<i>I</i> ^c	A (43) Rh (3-0)	EtOH (200)	silica...OSi(CH ₂) ₂ P(C ₆ H ₅) ₂ ...RhL _x	0-23 219
<i>II</i> ^d	B (26) Rh (1-5)	EtOH (150)	zeolite...OP(C ₆ H ₅) ₂ ...RhL _x	0-09 ^e 8
<i>III</i> ^f	C (2-2) Rh (0-7)	EtOH (25)	alumina...OSi(CH ₂) ₂ P(C ₆ H ₅) ₂ ...RhL _x	8-7 ^g 75
<i>IV</i>	C (1-0) Rh (0-3)	EtOH (10) + + PhH (10)	alumina...OSi(CH ₂) ₂ P(C ₆ H ₅) ₂ ...RhL _x	1-35 ^h 70
<i>V</i>	D (2-9) Rh (0-3)	EtOH (40)	alumina...OSi(CH ₂) ₃ N(CH ₃) ₂ ...RhL _x	2-67 ⁱ 56
<i>VI</i>	E (8-5) Rh (1-0)	EtOH (500) + + (CH ₂) ₄ O (100)	glass...OSi(CH ₂) ₃ N(CH ₃) ₂ ...RhL _x	0-005 ^j 6
<i>VII</i> ^f	C (2-1) Pd (0-8)	EtOH (25) + + PhH (20)	alumina...OSi(CH ₂) ₂ P(C ₆ H ₅) ₂ ...PdL _x	3-08 ^k 125
<i>VIII</i>	C (0-9) Pd (0-4)	EtOH (10) + + PhH (10)	alumina...OSi(CH ₂) ₂ P(C ₆ H ₅) ₂ ...PdL _x	1-13 ^l 94
<i>IX</i>	F (2-0) Pd (0-6)	EtOH (20) + + PhH (20)	alumina...OSi(CH ₃)(CH ₂) ₃ CN...PFL _x	1-65 113
<i>X</i> ^d	A (43) Pt (3-4)	EtOH (200)	silica...OSi(CH ₂) ₂ P(C ₆ H ₅) ₂ ...PdL _x	0-35 127
<i>XI</i> ^d	B (5-9) Pt (0-5)	EtOH (35) EtOH (35)	zeolite...OP(C ₆ H ₅) ₂ ...PtL _x	0-95 ^m 5
<i>XII</i>	C (2-0) Pt (1-0)	EtOH (25) + + PhH (20)	alumina...OSi(CH ₂) ₂ P(C ₆ H ₅) ₂ ...PtL _x	2-20 ⁿ 76

XIII	D (2-9) Pt (1-0)	EtOH (40)	alumina... OSi(CH ₂) ₃ N(CH ₃) ₂ ...PtL _x	3-32 ^a 42
XIV	E (9-5) Pt (0-4)	EtOH (50)	glass... OSi(CH ₂) ₃ N(CH ₃) ₂ ...PtL _x	0-007 ^P 6
XV	G (1-9) Pt (0-4)	EtOH (50)	alumina... OSi(CH ₂) ₂ C ₅ H ₄ N...PtL _x	1-26 ^d 83
XVI	H (15) Pt (0-6)	i-PrOH (2) + + PhH (50)	silica... OSi(CH ₂) ₃ CN...PtL _x	0-10 134
XVII	I (15) Pt (0-3)	i-PrOH (2) + + PhH (50)	silica... OSi(CH ₂) ₃ CN...PtL _x	0-09 131
XVIII	J (15) Pt (0-2)	i-PrOH (2) + + PhH (50)	silica... OSi(CH ₂) ₃ CN...PtL _x	0-16 136
XIX	K (10) Pt (0-1)	i-PrOH (1) + + PhH (40)	silica... OSi(CH ₂) ₃ CN...PtL _x	0-37 204
XX	L (10) Pt (0-2)	i-PrOH (2) + + PhH (50)	silica... OSi(CH ₂) ₃ CN...PtL _x	0-36 155
XXI	M (15) Pt (0-2)	i-PrOH (2) + + PhH (50)	silica... OSi(CH ₂) ₃ CN...PtL _x	0-15 215
XXII	silica (7) Pt (0-1)	i-PrOH (1) + + PhH (50)	adsorbed Pt compound	0-09 202

^a Rh = RhCl₃ · 3 H₂O, Pd = PdCl₂ (used as 40% aqueous solution), Pt = H₂PtCl₆ · 6 H₂O. ^b The surface areas of primary supports: silica 231 m²/g, zeolite 48 m²/g, γ-alumina 130 m²/g, and glass 7 m²/g. ^c 78°C, 1 h. ^d 78°C, 6 h. ^e 0-05% Cl. ^f 78°C, 8 h. ^g 0-08% P. ^h 0-4% P. ⁱ 1-12% N, 3-26% Cl. ^j 0-05% N. ^k 0-06% P. ^l 0-6% P. ^m 0-5% P, 0-45% Cl. ⁿ 0-11% P. ^o 1-22% N, 3-78% Cl. ^p 0-03% N, less than 0-01% Cl. ^q 1-98% N, 5-25% Cl.

TABLE III
Yields (%) of Corresponding 1-Alkylsilanes Obtained by Hydrosilylation (80°C, 2 h) Catalysed by Rhodium Compounds
Reactants in equimolar amounts, the Rh: R₃SiH molar ratio 1 × 10⁻⁴

Catalyst	1-Heptene + + HSiCl ₃		1-Hexene +		Vinyl ethyl ether +	
	(C ₂ H ₅) ₃ SiH	(C ₂ H ₅ O) ₃ SiH	(C ₂ H ₅) ₃ SiH	(C ₂ H ₅ O) ₃ SiH	(C ₂ H ₅) ₃ SiH	(C ₂ H ₅ O) ₃ SiH
RhCl ₃ ^a	traces	62 (8) ^b		86	31	85
RhCl(PPH ₃) ₃	traces	49 (2) ^b		96	19	92
I	8	35		77-73 ^c , 71 ^d , 34 ^e	21-13 ^c	67-43 ^c
II	traces	traces		3	3	5
III	traces	traces		3	--	traces
IV	10	25		99-40 ^c , 3 ^d	9	34
V	6	44-18 ^c		91-59 ^c , 8 ^d	16-4 ^c	31-13 ^c
VI	47	traces		32-7 ^c	--	15

^a 0.01M solution in ethanol. ^b 0.01M solution in benzene. ^c Once used catalyst. ^d Twice used catalyst. ^e Thrice used catalyst.

TABLE IV

Yields (%) of Alkylsilanes Obtained by Hydrosilylation Catalysed by Platinum Compounds

The reaction was carried out at 80°C over a period of 2 h. The reactants were used in equimolar amounts, the Pt : R₃SiH molar ratio was 2 × 10⁻⁵.

Catalyst	1-Decene +		Styrene +	
	HSiCl ₃	(C ₂ H ₅ O) ₃ SiH	HSiCl ₃ (A/B) ^a	(C ₂ H ₅ O) ₃ SiH(C/D) ^b
H ₂ PtCl ₆	77	40	56/27	42/6
X	71·31 ^d	26·3	89/9, 49/0 ^d , 35/0 ^c	7/1
XI	64·13 ^d	5	50/4, 40/0 ^d , 16/0 ^c	0/0
XII	74·10 ^d	14·2 ^d	85/4, 65/2 ^c , 13/0 ^c	14/1, 3/0 ^d
XIII	44·16 ^d	10	49/0, 20/0 ^d , 9/0 ^c	14/5, 5/2 ^d
XIV	42·22 ^d	2	12/0	traces
XV	6·3 ^c	0	2/0	traces
XVI	35	4	7/0	5/1
XVII	22	3	2/0	traces
XVIII	70·43 ^d	3	20/0, 14/0 ^c	4/1
XIX	85·52 ^d	7	64·4, 24·1 ^d , 15·1 ^c	13/1, 4/0 ^d
XX	47	20·5 ^d	50/0, 39/0 ^d , 8/0 ^c	traces
XXI	27	7	31/0	traces
XXII	74	8	69/29, 17/3 ^d	6/0

^a A 2-Trichlorosilyl-1-phenylethane, B 1-trichlorosilyl-1-phenylethane. ^b C 2-Triethoxysilyl-1-phenylethane, D 1-triethoxysilyl-1-phenylethane. ^c 0·01M solution in 2-propanol. ^d The yield obtained with once used catalyst. ^e Twice used catalyst.

reuse of such catalysts. It can be further expected that the different mode of the action 1) and 2) might in some cases result in differences in selectivity of the catalysts. If, on the other hand, over-all yields of the products obtained on reusing the catalysts exceed the yield achieved with corresponding soluble compound used in the same concentration, according to our opinion, it is reasonable to assume that the coordinated compound is not irreversibly abstracted from support (case 3). In fact, such a situation arises in the addition of triethoxysilane to hexene catalysed by *I*, *IV*, and *V*, and, less distinctly, also in the reaction of vinyl ethyl ether catalysed by *I*. This, along with change of selectivity mentioned above seems to indicate that at least in some cases the catalysts do act as described in paragraph 1).

Palladium catalysts. In contrast to the earlier report³⁸, it has recently been shown^{23,39,40} that some soluble Pd(II) complexes are effective catalysts for hydrosilylation of alkenes and alkadienes. With the aim to examine the action of supported palladium complexes *VII*–*IX*, we compared their activity with that of the soluble compounds, $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ and $\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$, for the addition of trichlorosilane to 1,3-butadiene (50°C, 55 min; the 1,3- C_4H_6 : HSiCl_3 molar ratio 2 : 1, the Pd: HSiCl_3 molar ratio $5 \cdot 10^{-5}$, the solvent benzene used in 1 : 2 vol. ratio with respect to HSiCl_3). Practically quantitative yields of 1-trichlorosilyl-*cis*-2-butene (based on trichlorosilane) were obtained with all the catalysts employed, except the palladium phosphine complex (46% yield; 63% yield after 70 min). This shows that supported palladium-phosphine catalysts *VII* and *VIII* are even slightly more effective than their soluble analogues. However, in no case could these catalysts be reused. The inactivation of once used catalysts is here at least in part due to the abstraction of metal component from the support, which was indicated by blackening of liquid phase during the reaction as a result of reduction of dissolved palladium compound to metallic palladium (*cf.*²³). It should be noted that similar situation was also observed with analogous palladium complexes fixed to organic polymers in the addition of trimethylsilanol to 1,3-butadiene⁴¹.

Platinum catalysts. The results summarized in Table IV show that in the hydrosilylation of 1-decene supported catalysts behave similarly as chloroplatinic acid in that their activity decreases in dependence on the structure of silicon hydride in the expected²¹ order $\text{HSiCl}_3 > \text{HSi}(\text{OC}_2\text{H}_5)_3 > (\text{C}_2\text{H}_5)_3\text{SiH}$. As a rule, the higher yields of reaction products were obtained with the use of platinum-phosphine catalysts (*X*–*XII*) than with platinum-amine ones (*XIII*, *XIV*). The reason of relatively high activity of catalyst *XIV* in the addition of trichlorosilane to 1-decene, relative to the activity of catalyst *XIII* is unclear. In this connection it is worthy of note that rhodium catalyst *VI* bonded to the same support was also surprisingly effective in similar reaction (see p. 159). Platinum catalyst containing metallic component bonded to pyridyl ligand (*XV*) turned out to be little active, even though similar soluble platinum complex was reported to be effective hydrosilylation catalyst⁴².

In case of supported platinum catalysts containing cyano groups (*XVI–XIX*), their activity increases with decreasing concentration of 3-cyanopropyltrichlorosilane used in preparation of the supports (supports H–K, Table I). The results obtained in hydrosilylation of styrene are also of interest. With chloroplatinic acid as catalyst the reaction proceeds under formation of a mixture of both possible isomers, 1-trichlorosilyl-1-phenylethane (α -adduct) and 2-trichlorosilyl-1-phenylethane (β -adduct). We have recently found²⁶ that by the addition of triphenylphosphine, dimethylbenzylamine, or pyridine, the selectivity of the reaction can be increased to such a degree that the β -adduct is formed as a sole reaction product. The results recorded in Table V show that nearly all supported catalysts (excepting *XXII* in which chloroplatinic acid is only adsorbed on the support) significantly increase the yield of the β -adduct. From the reasons discussed earlier in this work (see p. 159) this fact seems to indicate that catalytic process proceeds on the surface of the catalysts. As to the addition of triethoxysilane this effect is difficult to estimate, since already with chloroplatinic acid the addition proceeds with comparatively high selectivity (the β - to α -adduct ratio is here 7 : 1).

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