Journal of Organometallic Chemistry, 72 (1974) 163—170
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THE CLEAVAGE OF Si—C BONDS BY TRANSITION METAL COMPOUNDS. METHYLATION AND PHENYLATION OF OLEFINS BY ORGANOSILICON COMPOUNDS IN THE PRESENCE OF PALLADIUM SALTS*

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(Received December 4th, 1973)

Summary

Palladium(II) compounds are able to cleave Si—R bonds in various alkyl- and aryl-silanes, and linear and cyclic siloxanes and silazanes at 60-120°. The Group VIII metals and metal compounds $PdCl_2$, H_2PtCl_6, H_2PtCl_6 + $SnCl_2$, $Pt(PPh_3)_3$, $Pt(PPh_3)_4$, Pt/C and Pd catalyse the cleavage of the Si—Me bond in hexamethyldisiloxane at 100-200° to give linear trisiloxane as the main product. This reaction which involves the transfer of methyl or phenyl groups from the Si to the Pd atom, can be used for methylation and phenylation of olefins by organosilicon compounds.

Introduction

Although Si—R (R = Alk, Ar) bonds are extremely thermally stable and unreactive towards oxidation reagents they can be decomposed by various electrophilic and nucleophilic agents. This behaviour of the Si—R bond may be explained by its polarity (the ionic character of the Si—C bond amounts to 12%).

Khvalovski has recently reviewed the reactions of Si—R bond cleavage [3]. Amongst new data not included in the review an interesting paper by De Simone [4] must be mentioned. De Simone noted that such customary PMR standards as tetramethylsilane, 3-trimethylsilylpropionate and sodium 2,2-dimethyl-2-silapentane-5-sulfonate are capable of methylating Hg^{II} salts instantaneously at room temperature. Comparing the reactivities of various mercury salts and taking account of the solvent effect, De Simone has concluded that the mercury salts act as Lewis acids. He also noted that unlike mercury salts, palladium acetate and nitrate were found to leave the Si—Me bond untouched. Other attempts at cleaving the Si—R bond with Group VIII transition metal compounds were

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* For preliminary communications of this work see refs. 1 and 2.

unsuccessful*; for instance phenyl and benzyl radicals were not cleaved from the Si atom even under prolonged reflux with Zeise's salt in alcohol (96 h) [6]. The only exception to this is $FeCl_3$, a strong Lewis acid, which has been shown to be able to cleave alkyl and aryl radicals from a silicon atom [10]. It is noteworthy that Jakubovich and Motzarev [11] have succeeded in inducing the cleavage of the Si—Ar bond with $FeCl_3$ and the transfer of the aryl radical to acetyl chloride (eqns. 1 and 2), which is all the more significant since the Si—Alk

$$Ph_2SiCl_2 + FeCl_3 \rightarrow [PhFeCl_2] + PhSiCl_3 \qquad (1)$$

$$[PhFeCl_2] + MeCOCl \rightarrow PhCOMe + FeCl_3 \qquad (2)$$

and Si—Ar bonds remained uncleaved by transition metal compounds in the widely investigated hydrosilylation and telomerization reactions using organosilanes. The only case where Si—C bond cleavage was observed was in the hydrosilylation of 1-hexane with $(Me_3SiO)_2SiMeH$ at 140° in the presence of H_2PtCl_6 [12] giving $Me_3SiOSiMe_2C_6H_{13}$ as a by-product. The formation of this compound could be accounted for by an intramolecular exchange of methyl and trimethylsiloxy groups.

It is also worth mentioning an exchange of an Si—Me group with halogen in the reaction of organosilicon compounds with $HSiCl_3$ in the presence of H_2PtCl_6, (157°, 24 h) [13]. The platinum compounds also catalyse R—H exchange in silicone hydrides [14].

Results and discussion

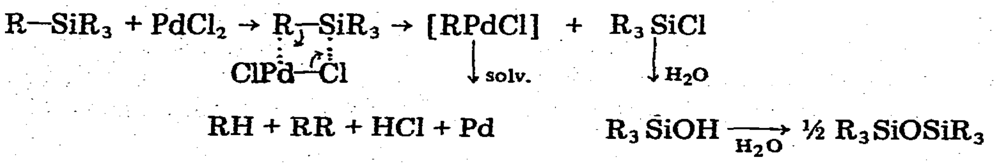
We have observed that Pd^{II} chlorides can cleave the Si—C bonds in organosilicon compounds such as tetraalkyl-, trialkyl-, chloromethyl- and aryltrialkylsilanes and linear and cyclic siloxanes and silazanes. The reactions proceed in various solvents, e.g. tetrahydrofuran, acetonitrile and alcohols at 60-120°. Thus, at 60° tetramethylsilane was demethylated by Pd^{II} salts to give Me_3SiCl, methane and ethane (eqn. 3). Similarly $PdCl_2$ or Li_2PdCl_4 cleave trimethylphenylsilane to form Me_3SiCl, benzene and biphenyl (eqn. 4).

$$Me_4Si \xrightarrow[H_2O]{Pd^{II}} Me_3SiOSiMe_3 + CH_4 + C_2H_6 \qquad (3)$$

$$Me_3SiPh \xrightarrow[H_2O]{Pd^{II}} Me_3SiOSiMe_3 + PhH + Ph{-}Ph \qquad (4)$$

Scheme 1 is a tentative mechanism for the splitting of silanes by Pd^{II} compounds.

SCHEME 1



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*It has, however, been shown that Pd and Pt complexes may rupture labile Si—C bonds in strained cyclic compounds and take off very labile vinyl, allyl or ethynyl groups from silicon [5-9].

It is possible that the electrophilic Pd^{II} attacks the carbon atom bonded to the silicon atom with simultaneous coordination of the halide anion to silicon*. A nucleophilic transfer of the organic radical from the silicon to the metal atom then takes place via formation of an unstable alkyl- or aryl-palladium derivative, the latter decomposing to a hydrocarbon and metallic Pd.

From this scheme it follows that tetraalkylsilanes would be cleaved by Pd^{II} into chlorosilanes or, after hydrolysis, disiloxanes. We found, however, that disiloxanes themselves react with palladium salts but unlike methylsilanes the reaction occurs under more drastic conditions.

The reaction of hexamethyldisiloxane has been studied in detail. This disiloxane was demethylated by Pd salts both in various polar and nonpolar solvents, and also without any solvent. The main reaction product was octamethyltrisiloxane, methane and ethane also being formed.

Scheme 2 may be proposed for the cleavage of hexamethyldisiloxane by Pd salts.

SCHEME 2

$$Me_3SiOSiMe_3 + PdCl_2 \rightarrow Me_3SiOSiMe_2Cl + [MePdCl]$$

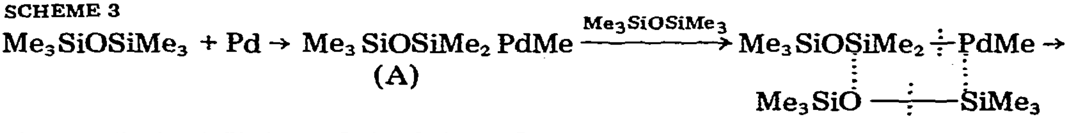
$$Me_3SiOSiMe_3 + Me_3SiOSiMe_2Cl \rightarrow Me_3SiOSiMe_2OSiMe_3 + Me_3SiCl$$

$$[MePdCl] \xrightarrow{\text{Solvent}} CH_4 + C_2H_6 + Pd + HCl$$

The intermediate formation of $Me_3SiOSiMe_2Cl$ was demonstrated by the mass spectrum of the corresponding silanol. An intense peak corresponding to the $M{-}CH_3$ ion (m/e 149) was observed.

As the temperature of demethylation of hexamethyldisiloxane to trisiloxane was increased $PdCl_2$ was found to behave as a catalyst. It is of interest that some platinum and iridium compounds, e.g. H_2PtCl_6, $H_2PtCl_6 + SnCl_2$, $Pt(PPh_3)_4$, $Pt(PPh_3)_3$, as well as the metals themselves (Pd/C, Pd-black) also catalyse this reaction. It may be assumed that insertion of the metal or its coordinatively unsaturated complex into an $Si{-}CH_3$ bond is an important stage of this catalytic process. Intermediate (A) then attacks the disiloxane to form the trisiloxane and free metal, the latter causing repetition of the process (Scheme 3).

SCHEME 3



$$Me_3SiOSiMe_3 + Pd \rightarrow \underset{(A)}{Me_3SiOSiMe_2PdMe} \xrightarrow{Me_3SiOSiMe_3} \begin{array}{ccc} Me_3SiOSiMe_2 & \vdots & PdMe \\ \vdots & & \vdots \\ Me_3SiO & \vdots & SiMe_3 \end{array} \rightarrow$$

$$Me_3SiOSiMe_2OSiMe_3 + [Me_3SiPdMe] \rightarrow Pd + \text{products}$$

Heating hexamethyldisiloxane to 100-200° in the presence of 0.01-1.0% of the catalyst affords up to 20% octamethyltrisiloxane. This reacts with the linear trisiloxane leading to small amounts of a linear tetrasiloxane and other higher polysiloxanes. Demethylation of Me_4Si, Me_3SiPh and other methylsilanes to give $Me_3SiOSiMe_3$ also gave under certain conditions small quantities of $Me_3SiOSiMe_2OSiMe_3$ and higher siloxanes (eqn. 5).

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*Such an attack would be in agreement with the concept of "soft and hard acids and bases".

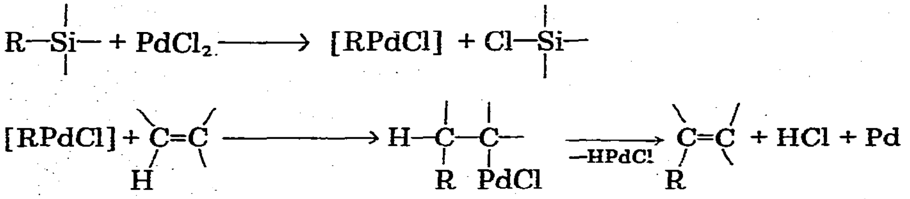
$$\mathrm{Me_3SiR \xrightarrow[H_2O]{-R} Me_3SiOH \xrightarrow[H_2O]{} Me_3SiOSiMe_3 \xrightarrow[H_2O]{-R} Me_3SiOSiMe_2OH \rightarrow} \quad (5)$$

$$\mathrm{\rightarrow Me_3Si(OSiMe_2)_2OSiMe_3 \rightarrow etc. \rightarrow Me_3Si(OSiMe_2)_{\mathit{n}}OSiMe_3}$$

The proposed mechanism for the cleavage of organosilanes by $\mathrm{Pd^{II}}$ salts involves formation of the unstable intermediate σ-organopalladium compounds RPdCl. These Pd compounds would be expected to transfer the alkyl and aryl groups from Si atom to the organic substrates. Indeed, we have found that various organosilicon compounds will methylate and phenylate olefins on heating in the presence of Pd compounds.

The results of methylation of styrene by organosilicon compounds are presented in Table 1. It is evident that the reactivities of the various organosilanes used decrease in the series: $\mathrm{Me_4Si \approx Me_3SiEt > Me_3SiNHSiMe_3 > Me_3SiOSiMe_3 > Me_3SiCH_2Cl > Me_3SiPh > Me_3SiCl}$.

In general electron withdrawing substituents such as Ph, $\mathrm{CH_2Cl}$, NH, O and Cl hinder cleavage of the Si—Me bond. Halogen deactivates the silicon atom to a such extent that chlorosilanes were found to be inert under the conditions used. It is possible that the mechanism of this reaction (eqn. 6) is analogous to the transfer of methyl and aryl groups from e.g. Hg, Sn and Pb atoms to olefins by Pd compounds, as studied in detail by Heck [15]. These data are consistent with the idea of an electrophilic $\mathrm{Pd^{II}}$ attack at the Si—C group carbon atom. Substituents which increase the carbanion mobility of the radical R facilitate the cleavage.



$$\mathrm{R{-}\overset{|}{\underset{|}{Si}}{-} + PdCl_2 \longrightarrow [RPdCl] + Cl{-}\overset{|}{\underset{|}{Si}}{-}}$$

$$\mathrm{[RPdCl] + \underset{H}{C}{=}C{<} \longrightarrow H{-}\underset{R}{C}{-}\underset{PdCl}{C}{-} \xrightarrow[-HPdCl]{} \underset{R}{C}{=}C{<} + HCl + Pd} \quad (6)$$

As is evident from Table 1 the structures of the methylstyrenes obtained depend on the initial organosilicon compounds used. This influence can be ex-

TABLE 1

THE METHYLATION OF STYRENE BY ORGANOSILICON COMPOUNDS

(Solvent: MeCN; temp.: 120°, 10 h, molar ratio $\mathrm{R{-}Si{-}/{>}C{=}C{<}/LiPdCl_3}$ = 1/2/1).

Organosilicon compound	Yield of methylstyrene (%)	Isomer content (%)	
		β-Methylstyrene	α-Methylstyrene
$\mathrm{(CH_3)_4Si}$	66	98.5	1.5
$\mathrm{(CH_3)_3SiC_2H_5}$	66	89.5	10.5
$\mathrm{(CH_3)_3SiC_6H_5}$ [a]	8	100	0
$\mathrm{(CH_3)_3SiCH_2Cl}$	32	100	0
$\mathrm{(CH_3)_3SiNHSi(CH_3)_3}$	52	89	11
$\mathrm{(CH_3)_3SiOSi(CH_3)_3}$	34	ca. 100	traces
$\mathrm{(CH_3)_3SiCl}$	0		

[a] For this compound competitive styrene phenylation reaction (see text) is also taking place.

TABLE 2

SOLVENT EFFECT ON THE STYRENE METHYLATION BY Me_4Si

(Molar ratio: $Me_4Si/Styrene/LiPdX_n$ = 1/2/1, temp.: 120°, 10 h)

Solvent	Yield of methylstyrenes (%)	Isomer content (%)	
		β-Methylstyrene	α-Methylstyrene
MeCOOH	0		
MeOH	19	100	0
THF	64.8	91.5	8.5
MeCN	66	98.5	1.5

plained by the formation of a MePdCl intermediate complex with the organosilicon compound.

Table 2 shows how the methylation of styrene by tetramethylsilane is affected by solvents. Solvent activity is shown to decrease in the series: MeCN ⩾ THF > MeOH > MeCOOH. The ratio of α- and β-methylstyrenes is also affected by the solvent used, the maximum content of α-isomer being attained in THF.

Experimental results show that olefins are phenylated more readily than they are methylated. Thus, the reaction of Me_3SiPh with styrene in THF (120°, 10 h) produces 94% *trans*-stilbene and none of the methylation product. Under the same conditions but in MeCN, 65% *trans*-stilbene and 8% methylstyrenes were obtained. In the reaction of Me_3SiPh with cyclohexene only phenylation is observed.

The experimental data are presented in Table 3, from which it is evident that considerable phenylation occurs even at 60°. At 120° *trans*-stilbene is formed quantitatively.

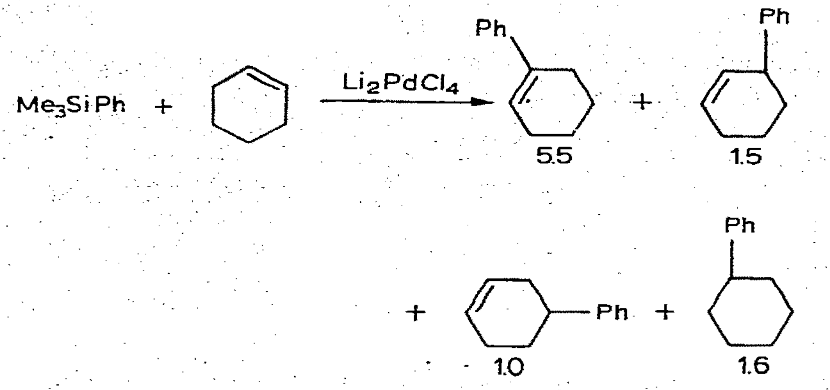
trans-Stilbene is the only product in the reaction of Me_3SiPh with styrene. However, in the reaction of Me_3SiPh with cyclohexene (80°, THF) 3- and 4-phenylcyclohexenes are formed in addition to the main product, 1-phenylcyclohexene, in the proportions indicated in eqn. 7.

TABLE 3

PHENYLATION OF OLEFINS BY Me_3SiPh

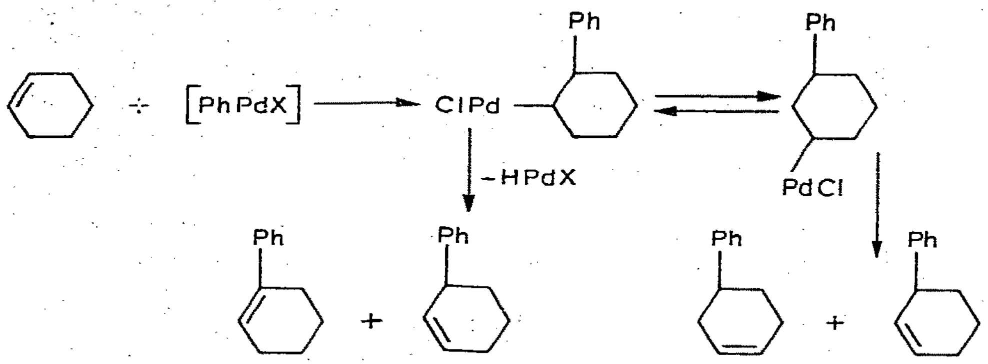
(Molar ratio $R{-}\overset{|}{\underset{|}{Si}}{-}/\,{>}C{=}C{<}\,/Li_nPdCl_m$ 1/2/1)

Olefin	Solvent	Pd compound	Temperature (°C)	Time (h)	Product	Yield(%)
Styrene	THF	Li_2PdCl_4	60	6	Stilbene	17
Styrene	MeOH	Li_2PdCl_4	60	6	Stilbene	12
Styrene	MeOH + H_2O	Li_2PdCl_4	60	6	Stilbene	19
Styrene	THF	Li_2PdCl_4	120	10	Stilbene	94
Styrene	MeCN	$LiPdCl_3$	120	10	Stilbene	65
Styrene	MeOH	Li_2PdCl_4	120	10	Stilbene	47
Styrene	THF	Pd	120	10	Stilbene	0
Styrene	MeCOOH	$Pd(OCOCH_3)_2$	120	10		0
Cyclohexene	THF	Li_2PdCl_4	120	10	Phenylcyclohexane	35
Cyclohexene	MeCN	$LiPdCl_3$	120	10	1-Phenylcyclohexene	23
Cyclohexene	MeOH	Li_2PdCl_4	120	10	Phenylcyclohexane Diphenyl	38 15



(7)

Specially designed experiments revealed the possibility of the main reaction product, 1-phenylcyclohexene, isomerising under these conditions. Therefore it is likely that the formation of 3- and in particular 4-phenylcyclohexenes is due to the rearrangement of an intermediate Pd compound (eqn. 8).



(8)

Phenylcyclohexane (Table 3) was the only product of the phenylation of cyclohexene with $(CH_3)_3SiPh$ in THF at 120°. This result may be explained by hydride ion transfer from the solvent.

The phenylation of cyclohexene with $(CH_3)_3SiPh$ in methanol at 120° gives phenylcyclohexane and diphenyl (1/2) both of which are the disproportionation products of 1-phenylcyclohexene formed initially.

Experimental

The mass-spectra were recorded at 70 eV on a Varian-Mat CH-8 chromato-mass-spectrometer. Typical procedures for cleavage of the organosilicon compounds and alkylation (arylation) reactions of the olefins in the presence of palladium compounds are described below.

(a). Cleavage of the Si—C bond by transition metal compounds

(i). A mixture of 0.88 g (10 mmole) of tetramethylsilane and 8 ml of a 0.25 *M* solution of Li_2PdCl_4 in THF was heated in a sealed tube for 9 h at 60°. GLC analysis of the volatile fraction (after hydrolysis) gave 0.029 g of hexa-

methyldisiloxane, yield 3.6/9*. After 10 h at 80° 0.22 g (27/68) hexamethyldisiloxane was obtained. Methane and ethane were shown to be present in the gaseous fraction by means of GLC and mass-spectrometry.

(ii). 0.28 g (1.9 mmol) of Me_3SiPh and 5 ml of a 0.2 *M* solution of $LiPdCl_3$ in CH_3CN were heated in a sealed tube for 10 h at 80°. The volatile fraction (after hydrolysis) contained 0.033 g of hexamethyldisiloxane (yield 22/40) along with benzene and diphenyl.

(iii). 0.15 g (1 mmol) of Me_3SiPh and 4 ml of a 0.25 *M* solution of Li_2PdCl_4 in THF were heated in a sealed tube for 6 h at 100°. 3 ml of water was added and the reaction mixture was extracted repeatedly with pentane. The pentane extracts were dried over $MgSO_4$. After removal of the solvent the mixture was analyzed by GLC and mass-spectrometry. The analysis gave hexamethyldisiloxane, benzene, diphenyl and the highest siloxanes as the products. Chromato-mass-spectrometry (CMS) showed that the mixture contained $Me(Me_2SiO)_2SiMe_3$, $Me(Me_2SiO)_3SiMe_3$, $Me_3SiOSiMe_2OH$ and $Me_2PhSiOSiMe_3$ in the ratio 2.5/2.1/1.1/1.

(iv). 0.36 g (0.22 mmol) of hexamethyldisiloxane and 0.08 ml of a 0.25 *M* solution of Li_2PdCl_4 in THF were heated in a sealed tube for 10 h at 120°. GLC and CMS analysis of the volatile fraction indicated 0.028 g (11/595) of octamethyltrisiloxane.

(v). 1.62 g (10 mmol) of hexamethyldisiloxane and 0.12 g (0.1 mmol) of $(PPh_3)_4Pt$ were heated in a sealed tube at 200° for 11 h. Methane was detected in the gaseous phase. The solid was separated and 0.16 g of octamethyltrisiloxane (13.6/680) along with small quantity of decamethyltetrasiloxane and the highest cyclic and linear polysiloxanes were identified.

(vi). Hexamethyldisiloxane (1.62 g, 10 mmol) and $PdCl_2$ (0.017 g, 0.1 mmol) when heated to 200° for 12 h gave 0.021 g of an oligomer (18/900). Hexamethyldisiloxane (1.62 g, 10 mmol) and Pt/C (5%, 0.34 g, 0.1 mmol) when heated to 200° for 10 h gave 0.095 g of octamethyltrisiloxane, yield 8/400. With H_2PtCl_6 as catalyst, yields were 0.2/200 (100°, 6 h), 0.8/700 (200°, 6 h).

(b). Methylation and phenylation of cyclohexene

(i). A mixture of trimethylsilane (0.15 g, 1 mmol), cyclohexene (0.16 g, 2 mmol) and 5 ml of a 0.2 *M* solution of Li_2PdCl_4 in THF was heated in a sealed tube for 6 h at 80°. After treatment with water the reaction mixture was extracted repeatedly with pentane. The pentane solution was dried over $MgSO_4$, the solvent evaporated and the residue analysed by GLC and CMS. The solution contained 1-phenylcyclohexene, 3- and 4-phenylcyclohexenes and phenylcyclohexane in the ratio 5.5/1.1/1/1.6. $Me_3SiOSiMe_2Ph$ and hexamethyldisiloxane were also detected. The mixture was hydrogenated over Raney nickel to give phenylcyclohexane and $Me_3SiOSiMe_2Ph$.

(ii). 1-Phenylcyclohexene (0.158 g, 1 mmol) and 5 ml of a 0.2 *M* solution of Li_2PdCl_4 in THF were heated in a sealed tube at 80° for 6 h. CMS analysis showed only 1-phenylcyclohexene to be present.

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*Here and elsewhere the yields refer to the starting organosilicon compound (first value) and the palladium compound (second value) and are expressed as a percentage.

(iii). Me_3SiPh (0.15 g, 1 mmol), cyclohexene (0.16 g, 2 mmol) and 5 ml of a 0.2 *M* solution of Li_2PdCl_4 in THF were heated for 10 h at 120° to give 0.056 g of phenylcyclohexane (35/35).

(iv). Me_3SiPh (0.15 g, 1 mmol), cyclohexene (0.16 g, 2 mmol) and 5 ml of a 0.2 *M* solution of $LiPdCl_3$ in MeCN were heated in a sealed tube for 10 h at 120°. The mixture was treated with water, extracted with pentane, and the solvent was evaporated. GLC analysis gave 0.04 g of 1-phenylcyclohexene, yield 23/23.

(v). Me_3SiPh (0.15 g, 1 mmol), cyclohexene (0.16 g, 2 mmol) and 5 ml of a 0.2 *M* solution of Li_2PdCl_4 in CH_3OH were heated in a sealed tube for 10 h at 120°. The mixture was treated with water, extracted with pentane, dried and the solvent evaporated. GLC analysis gave 0.06 g of phenylcyclohexane (38/38) and 0.06 g of diphenyl (15/15).

(vi). Heating 1-phenylcyclohexene (0.3 g, 2 mmol) and 5 ml of a 0.2 *M* solution of Li_2PdCl_4 in methanol at 120° for 10 h led to complete conversion to a mixture of phenylcyclohexane (1.2 mmol) and diphenyl (0.8 mmol).

(c). Phenylation and methylation of styrene

(i). A mixture of Me_3SiPh (0.15 g, 1 mmol), styrene (0.2 g, 2 mmol) and 5 ml of a 0.2 *M* solution of $LiPdCl_3$ in CH_3CN were heated in a sealed tube for 10 h at 120°. The mixture was treated with water and extracted repeatedly with pentane. The pentane solution was purified by passing through a column containing Al_2O_3. After drying and evaporation of the solvent the products were analyzed by GLC and mass spectrometry. Benzene, hexadisiloxane, diphenyl, 0.01 g of β-methylstyrene (8/8), and 0.086 g of *trans*-stilbene (45/45) were determined. *trans*-Stilbene was isolated and identified additionally by its UV spectrum; λ 308 nm in EtOH.

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