

131.62 (t), 137.62 (d), 148.92 (d), 150.28 (d); IR (KBr plates, cm^{-1}) 3057 (w), 3017 (w), 2970 (s), 1600 (w), 1417 (m), 1255 (s), 1187 (m), 1018 (m), 843 (s); MS, m/e (relative intensity) 209 (M - 15, 1), 169 (31), 141 (14), 86 (10), 85 (100), 83 (9), 73 (32), 59 (78), 58 (11), 55 (14), 43 (25), 31 (11); exact mass calcd for $\text{Si}_2\text{C}_{12}\text{H}_{24}$ 224.1416, found 224.1410.

Product distribution from pyrolysis of (Z)-4 under the same conditions was butadiene (5%), 6 (3%), 7 (17%), 8 (18%), (E)-4 (3%), 5 (26%), and unreacted (Z)-4 (26%). Decomposition of (Z)-4 was 74%, and mass balance was approximately 70%.

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Registry No. 1, 1450-29-9; 2, 108367-02-8; 3, 108367-03-9; (E)-4, 108367-04-0; (Z)-4, 108367-05-1; 5, 108394-64-5; 6, 27549-17-3; 7, 108367-06-2; 8, 108394-65-6; methoxytrimethylsilane, 1825-61-2.

Quaternary Onium Hexachloroplatinates: Novel Hydrosilylation Catalysts

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A number of quaternary ammonium, phosphonium, and arsonium hexachloroplatinates have been synthesized and used as hydrosilylation catalysts. The highest activity was observed for the quaternary hexachloroplatinates with highly lipophilic cations. Phase-transfer agents (onium salt, crown ether) were found to activate K_2PtCl_6 during hydrosilylation by solubilizing the PtCl_6^{2-} ion. It has been shown that polymer-bound quaternary phosphonium hexachloroplatinate is also an effective hydrosilylation catalyst that can be used repeatedly without appreciable loss of activity.

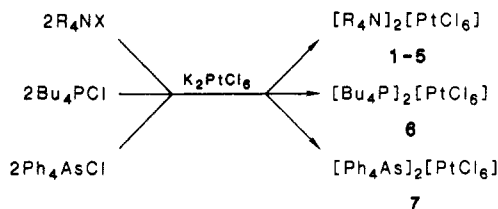
Introduction

Catalytic hydrosilylation most commonly involves the use of Speier's catalyst (hexachloroplatinic acid dissolved in isopropyl alcohol) whose activity is deemed to be due to the PtCl_6^{2-} ion.¹⁻³ However, there have been no reports so far on how the nature of the counterion might affect the activity of the hexachloroplatinate anion.

Herein we describe the preparation of some quaternary ammonium, phosphonium, and arsonium hexachloroplatinates and their activity as catalysts for hydrosilylation.

Results and Discussion

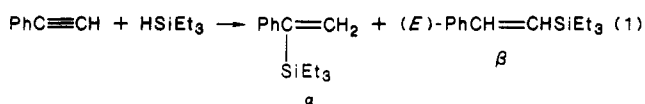
The quaternary bis(onium)hexachloroplatinates 1-7 have been prepared by ion exchange using stoichiometric amounts of K_2PtCl_6 dissolved in water and the corresponding onium halides dissolved in dichloromethane or water.



1, R = Me; 2, R = Bu; 3, R = *n*-C₈H₁₇; 4, R = *n*-C₁₈H₃₇; 5, R₄ = Et₃(PhCH₂); X = Cl, Br, HSO₄

The hexachloroplatinates 1-7 were obtained in 75-95% yield as crystals varying in color from beige to red (Table I). The ¹H NMR spectra of the synthesized platinates (Table II) were essentially the same as those of the starting quaternary onium halides.

The catalytic properties of the onium hexachloroplatinates obtained were examined in the hydrosilylation of phenylacetylene by triethylsilane. In the presence of platinates 1-7, a mixture of two isomers, the α - and β -cis-addition products, are invariably formed (eq 1). Their



formation was confirmed by GC, ¹H NMR, and GC-mass spectrometry studies. The ¹H NMR parameters were consistent with the literature data;⁴ the GC-mass spectra showed molecular ion peaks with m/z 218. The tetraalkylammonium hexachloroplatinates 2, 3, and 4 with bulky lipophilic⁵ cations were the most active among the compounds examined. Phosphonium (6) and arsonium (7) platinates as well as the catalysts 1 and 5 containing a less lipophilic tetraalkylammonium cations⁵ were the least reactive (Table III). β -Addition is predominant in all cases, the ratio of the α - and β -isomers depending on the catalyst cation. The relative content of the α -isomer in the products increases with decreasing net rate of the hydrosilylation (Table III).

Reaction 1 was also carried out in the presence of hexachloroplatinic acid and potassium hexachloroplatinate. The latter practically fails to catalyze the process; the activity of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ is equal to that of the most active tetraalkylammonium hexachloroplatinates (Table III). The hygroscopicity of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ causes some difficulties in its handling, but the nonhygroscopic quaternary onium platinates are easy to store and handle.

The hydrosilylation of phenylacetylene in the presence of one of the most active platinum catalysts, $[\text{Bu}_4\text{N}]_2[\text{PtCl}_6]$, was performed by various silanes. Table IV sum-

(1) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *J. Organomet. Chem. Libr.* 1977, 5, 1.

(2) Speier, J. L. *Adv. Organomet. Chem.* 1979, 17, 407.

(3) Marciñiec, B., Ed. *Hydrosilylowanie*; Państwowe Wydawnictwo naukowe: Warszawa, 1981.

(4) Pukhnarevich, V. B.; Sushchinskaya, S. P.; Pestunovich, V. A.; Voronov, M. G. *Zh. Obshch. Khim.* 1973, 43, 1283.

(5) Dehmlow, E. V. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 493.

Table I. Synthesis of Bis(onium) Hexachloroplatinates

bis(onium) hexachloroplatinate	starting onium compd	method of synthesis ^a	yield, %	color
[Me ₄ N] ₂ [PtCl ₆] (1)	[Me ₄ N]Br	A	75	red
[Bu ₄ N] ₂ [PtCl ₆] (2)	[Bu ₄ N]HSO ₄	B	90	orange
[(<i>n</i> -C ₈ H ₁₇) ₄ N] ₂ [PtCl ₆] (3)	[(<i>n</i> -C ₈ H ₁₇) ₄ N]Br	B	95	bright orange
[(<i>n</i> -C ₁₈ H ₃₇) ₄ N] ₂ [PtCl ₆] (4)	[(<i>n</i> -C ₁₈ H ₃₇) ₄ N]Br	B	85	beige
[Et ₃ (PhCH ₂)N] ₂ [PtCl ₆] (5)	[Et ₃ (PhCH ₂)N]Cl	C	90	orange
[Bu ₄ P] ₂ [PtCl ₆] (6)	[Bu ₄ P]Cl	B	90	orange
[Ph ₄ As] ₂ [PtCl ₆] (7)	[Ph ₄ As]Cl·H ₂ O	C	95	orange
[⊖-CH ₂ PBu ₃] ₂ [PtCl ₆] (8)	[⊖-CH ₂ PBu ₃]Cl (0.78 mmol of Cl ⁻ /g)	D	100	orange

^a See Experimental Section.

Table II. Analytical and Spectral Data for Bis(onium) Hexachloroplatinates

compd	elemental anal. (found/calcd)			¹ H NMR (90 MHz, Me ₄ Si)		solvent
	C	H	N	chem shift (ppm)		
1	17.41/17.27	4.19/4.32	4.77/5.03	3.11 (s, CH ₃)		Me ₂ SO- <i>d</i> ₆
2	43.01/43.05	8.30/8.07	2.93/3.14	0.98 (m, 24 H, CH ₃), 1.3-1.9 (m, 32 H, CH ₂), 3.2-3.6 (m, 16 H, CH ₂ N)		CDCl ₃
3	56.95/57.31	10.49/10.22	1.94/2.09	0.89 (m, 24 H, CH ₃), 1.31 (m, 96 H, CH ₂), 3.29 (b s, 16 H, CH ₂ N)		CDCl ₃
4	70.21/70.14	12.73/12.01	1.04/1.14	0.87 (m, 24 H, CH ₃), 1.1-1.6 (m, 256 H, CH ₂), 3.29 (b s, 16 H, CH ₂ N)		CDCl ₃
5	39.26/39.38	5.66/5.55	3.44/3.53	1.30 (t, 18 H, <i>J</i> = 7 Hz, CH ₃ CH ₂), 3.16 (q, 12 H, <i>J</i> = 7 Hz, CH ₃ CH ₂ N), 4.66 (s, 4 H, PhCH ₂ N), 7.49 (s, 10 H, Ph)		Me ₂ SO- <i>d</i> ₆
6	41.74/41.47	7.79/7.77		0.94 (m, 24 H, CH ₃), 1.3-1.8 (m, 32 H, CH ₂), 2.2-2.6 (m, 16 H, CH ₂ N)		CDCl ₃
7	49.15/49.06	3.52/3.41		7.6-8.1 (m, Ph)		Me ₂ SO- <i>d</i> ₆

Table III. Product Yields (%)^a in the Reaction between PhC≡CH and HSiEt₃ in the presence of Various Platinum Catalysts (the Molar Ratio of PhC≡CH:HSiEt₃:Catalyst = 1:1:0.001) at 80 °C

cat.	isomer	time, h					
		1	1.5	2	2.5	3	4
[Me ₄ N] ₂ [PtCl ₆] (1)	α	8	30	48			
	β	18	48	52			
[Bu ₄ N] ₂ [PtCl ₆] (2)	α	30					
	β	70					
[(<i>n</i> -C ₈ H ₁₇) ₄ N] ₂ [PtCl ₆] (3)	α	23					
	β	77					
[(<i>n</i> -C ₁₈ H ₃₇) ₄ N] ₂ [PtCl ₆] (4)	α	22					
	β	78					
[Et ₃ (PhCH ₂)N] ₂ [PtCl ₆] (5)	α	6	7	23	31	38	42
	β	9	11	30	49	55	55
[Bu ₄ P] ₂ [PtCl ₆] (6)	α	23	24	25	26	26	26
	β	63	65	67	67	67	67
[Ph ₄ As] ₂ [PtCl ₆] (7)	α	3	11	32	33	35	35
	β	5	14	50	54	54	54
[⊖-CH ₂ PBu ₃] ₂ [PtCl ₆] (8)	α	33	34 (33, ^b 35°)	34	34		
	β	52	61 (63, ^b 62°)	61	61		
H ₂ PtCl ₆ ·6H ₂ O	α	30					
	β	70					
K ₂ PtCl ₆	α	2	
	β	2	

^a GC data. ^b Upon second use of the recycled catalyst. ^c Upon third use of the recycled catalyst.Table IV. Hydrosilylation of Phenylacetylene by Various Silanes in the Presence of Catalyst [Bu₄N]₂[PtCl₆] (the Molar Ratio of PhC≡CH:Silane:Catalyst = 1:1:0.001)

silane	reactn temp, °C	reactn time, h	products	M ⁺ , <i>m/z</i>	yield, % (GC, ¹ H NMR)
HSiEt ₃ (I)	80	1	H ₂ C=C(Ph)SiEt ₃	218	30
			(<i>E</i>)-PhCH=CHSiEt ₃	218	70
HSiCl ₃ (II)	80	1.5	H ₂ C=C(Ph)SiCl ₃	236 ^a	2
			(<i>E</i>)-PhCH=CHSiCl ₃	236 ^a	98
HSiCl ₂ Me (III)	80	1.5	H ₂ C=C(Ph)SiCl ₂ Me	216 ^a	2
			(<i>E</i>)-PhCH=CHSiCl ₂ Me	216 ^a	98
HSiClMe ₂ (IV)	80	1.5	H ₂ C=C(Ph)SiClMe ₂	196 ^a	5
			(<i>E</i>)-PhCH=CHSiClMe ₂	196 ^a	95
HSiMe ₃ (V)	80	3	H ₂ C=C(Ph)SiMe ₃	176	60
			(<i>E</i>)-PhCH=CHSiMe ₃	176	40
HSiMe ₂ Ph (VI)	120	1	H ₂ C=C(Ph)SiMe ₂ Ph	238	28
			(<i>E</i>)-PhCH=CHSiMe ₂ Ph	238	72
HSiMePh ₂ (VII)	120	1	H ₂ C=C(Ph)SiMePh ₂	300	22
			(<i>E</i>)-PhCH=CHSiMePh ₂	300	78
HSiPh ₃ (VIII)	140	3	H ₂ C=C(Ph)SiPh ₃	362	5
			(<i>E</i>)-PhCH=CHSiPh ₃	362	95

^a Molecular ion peaks are indicated for the ³⁵Cl isotope.

Table V. Hydrosilylation of Phenylacetylene by Triethylsilane in the Presence of K_2PtCl_6 and Phase-Transfer Agents^a

cat.	total yield of α - and β -adducts ^b (%) at different reaction times, h									
	none ^c			CCl_4 ^c				<i>o</i> - $Cl_2C_6H_4$ ^c		
	1	2	3	1	3	4	6	2	4	6
K_2PtCl_6	4	5	4
K_2PtCl_6 + $[Bu_4N]HSO_4$ (1:2)	20	45	70	18	31	40	55	35	65	76
K_2PtCl_6 + 18-crown-6 (1:2)	8	32	65							
$[Bu_4N]_2[PtCl_6]$ (2)	100			51	65	84	100	45	75	90

^a Molar ratio of $PhC\equiv CH:HSiEt_3:PtCl_6^{2-} = 1:1:0.001$; 80 °C. ^b GC data. ^c Solvent 50% (v).

marizes the temperatures and reaction times that provide 100% conversion of the starting compounds. The product yields (GC data) were quantitative. Two isomers, the α - and β -trans-adducts, were formed in all cases according to GC, ¹H NMR, GC-mass, and mass spectrometry evidence. The hydrosilylation of phenylacetylene by all the chlorine-containing silanes (II-IV) and by triphenylsilane occurs almost exclusively via β -addition (95-98%). As in the case of triethylsilane, the reaction with methylphenylsilanes VI and VII yields predominantly the β -trans-product (70-78%), whereas in the reaction of phenylacetylene with $HSiMe_3$ α -addition seems to predominate (Table IV). Hence it can be concluded that the systems containing the hexachloroplatinate anion and a fairly lipophilic onium cation actively promote hydrosilylation.

So far, we have been discussing results obtained for the hydrosilylations in the presence of previously synthesized individual onium platinates. On the other hand, the lipophilic quaternary onium salts are known to act as phase-transfer agents for various anions and are capable of solubilizing them in a nonpolar medium.⁶⁻⁹ Therefore, it is reasonable to assume that active catalysts can be synthesized under hydrosilylation conditions using a mixture of K_2PtCl_6 (virtually devoid of catalytic activity) and some onium salt with a lipophilic cation and a hydrophilic, readily exchangeable anion. This salt appears to promote the transfer of $PtCl_6^{2-}$ anions from solid K_2PtCl_6 to liquid organic reactants.

In order to test this assumption, reaction 1 was carried out in the presence of catalytic amounts of K_2PtCl_6 and $[Bu_4N]HSO_4$ (1:2). The catalytic activity of this system was superior to that of K_2PtCl_6 being used alone (Table V) which is indicative of catalyst formation in situ. However, the system is less active, if we compare it with freshly prepared platinates 2, possibly due to insufficient solubility of $[Bu_4N]HSO_4$ in the reaction mixture. To overcome this problem, hydrosilylation (eq 1) was carried out in a reaction mixture diluted with carbon tetrachloride and *o*-dichlorobenzene (50% v) which are capable of dissolving $[Bu_4N]HSO_4$.⁸ In fact, the use of solvents resulted in catalytic properties of the K_2PtCl_6 + $[Bu_4N]HSO_4$ system (1:2) close in effectiveness to those of preformed $[Bu_4N]_2[PtCl_6]$ (Table V), especially when *o*- $Cl_2C_6H_4$ was present.⁸

We have also examined the efficiency of 18-crown-6 as a phase-transfer agent for solubilization of K_2PtCl_6 , the catalyst being formed during hydrosilylation. Like the onium salt, the crown ether was found to activate K_2PtCl_6 for hydrosilylation (Table V), although product yields in

its presence were somewhat lower than in the case of $[Bu_4N]HSO_4$.

Hence, the above experiments serve to support the usefulness of mixtures of K_2PtCl_6 with phase-transfer agents as catalysts without prior preparation of the corresponding hexachloroplatinates (although the latter possess a somewhat higher activity).

As noted, the onium platinates 1-7 can be used to catalyze hydrosilylation (Tables III and IV). However, they are soluble in the reaction medium and cannot be readily separated from reaction products. The regeneration and repeated use of platinum catalysts would be desirable.

The general method for obtaining catalytic systems for repeated utilization involves heterogenization of soluble catalysts,¹⁰⁻¹³ including hydrosilylation catalysts,¹⁴ by binding them onto a polymer surface. In most cases, these systems are represented by neutral transition-metal complexes with polymeric ligands. Much less known are the heterogeneous catalysts in which the metal complex ion is bound to a polymer that functions as a counterion. A pertinent example can be provided by citing the work of Reikhsfeld and collaborators,¹⁵ who reported heterogenization of $PtCl_6^{2-}$ on the anion exchange resin AV-17-8 containing $-N^+Me_3$ groups. However, polymers of this type are thermally unstable (maximum working temperature 50 °C¹⁶) and show little swelling in nonpolar organic media,¹⁷ which limits the scope of their application.

Therefore, it appears worthwhile to use polymers with more thermally stable and lipophilic quaternary onium groups for the heterogenization of $PtCl_6^{2-}$ ions. A well-known phase-transfer catalyst, the polymer-supported benzyltri-*n*-butylphosphonium chloride purchased from Fluka ($\text{C}_6\text{H}_4\text{CH}_2\text{P}^+\text{Bu}_3\text{Cl}^-$, the commercial name "tributylmethylphosphonium chloride polymer bound"), meets these requirements. It is prepared via quaternization of tributylphosphine by its reaction with chloromethylated styrene-divinylbenzene copolymer (Merrifield resin).^{18,19} The reaction of the above polymer (while undergoing swelling in dichloromethane) with a saturated aqueous solution of K_2PtCl_6 involves ion exchange, affording polymer-bound phosphonium hexachloroplatinate (8) in quantitative yield (Table I).

(10) Bailar, J. C. *Catal. Rev.—Sci. Eng.* 1974, 10, 17.

(11) Allum, K. G.; Hancock, R. D.; Howell, I. V.; Pitkethly, R. C.; Robinson, J. J. *Organomet. Chem.* 1975, 87, 189.

(12) Lisichkin, G. V.; Yuffa, A. Ya. *Heterogeneous Metal-Complex Catalysts*; Khimiya: Moscow, 1981 (in Russian).

(13) Manecke, G.; Storek, W. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 657.

(14) Čapka, M.; Svoboda, P.; Kraus, M.; Heflejš, J. *Chem. Ind. (London)* 1972, 650.

(15) Nikitin, A. V.; Reikhsfeld, V. O. *Zh. Obshch. Khim.* 1985, 55, 2079 and references therein.

(16) Lurie, A. A. *Chromatographic Materials*; Khimiya: Moscow, 1978 (in Russian).

(17) Regen, S. L. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 421.

(18) Cinquini, M.; Colonna, S.; Molinari, H.; Montanari, F.; Tundo, P. *J. Chem. Soc., Chem. Commun.* 1976, 394.

(19) Molinari, H.; Montanari, F.; Quici, S.; Tundo, P. *J. Am. Chem. Soc.* 1979, 101, 3920.

(6) Weber, W.; Gokel, G. *Phase Transfer Catalysis in Organic Synthesis*; Springer Verlag: Berlin, 1977.

(7) Starks, C. M.; Liotta, C. *Phase Transfer Catalysis. Principles and Technique*; Academic: New York, 1978.

(8) Keller, W. E. *Compendium of Phase-Transfer Reactions and Related Synthetic Methods*; Fluka AG: Buchs, 1979.

(9) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*; Verlag Chemie: Weinheim, 1980.

The hydrosilylation of phenylacetylene by triethylsilane (reaction 1) was carried out in the presence of polymeric platinate **8** demonstrating that the catalytic activity of the latter is similar to that observed for tetrabutylphosphonium hexachloroplatinate (Table III).

The possibility of repeated utilization of the polymer-bound catalyst **8** was also explored. After cessation of reaction 1, the catalyst was separated from the reaction mixture by filtration to be further used with fresh reactants. Upon recycling its catalytic activity remained virtually unaltered, yielding hydrosilylation products within limits of error in the same amounts as previously obtained (Table III). Similarly, catalyst **8** used for the third time running showed identical activity (Table III).

Experimental Section

^1H NMR spectra were recorded with a Bruker WH-90/DS spectrometer (90 MHz). Mass spectra were registered on a Kratos MS-25 GC/MS instrument (70 eV) and AEI MS-50 mass spectrometer (70 eV). GC measurements were carried out with a Chrom-4 instrument fitted with a flame-ionization detector using a 1.2 m \times 3 mm glass column packed with 5% OV-17/Chromosorb W-HP (80–100 mesh). Helium (60 cm³/min) was used as carrier gas; the temperature of analyses was varied over a 120–200 °C range depending on reaction mixture composition. Potassium hexachloroplatinate, quaternary onium salts, 18-crown-6, and hydrosilanes (Fluka) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Reakhim) were applied without further purification. Phenylacetylene was redistilled in vacuo prior to use.

Synthesis of Quaternary Onium Hexachloroplatinates (Table I). Method A. To a solution of 0.25 mmol of K_2PtCl_6 in 20 mL of H_2O was added a solution of the onium salt ($[\text{Me}_4\text{N}]\text{Br}$, 0.5 mmol) in 10 mL of H_2O . The mixture was stirred for 1 h at 80 °C and evaporated to dryness. The dry residue was recrystallized from water.

Method B. To a yellow solution of 0.25 mmol of K_2PtCl_6 in 20 mL of H_2O was added a colorless solution of 0.5 mmol of the onium salt ($[\text{Bu}_4\text{N}]\text{HSO}_4$, $[(n\text{-C}_8\text{H}_{17})_4\text{N}]\text{Br}$, $[(n\text{-C}_{18}\text{H}_{37})_4\text{N}]\text{Br}$, or $[\text{Bu}_4\text{P}]\text{Cl}$) in 100 mL of dichloromethane, and the resulting two-phase system was stirred at room temperature. Thereby the organic layer was gradually assumed a yellowish orange color. The stirring was continued to complete decoloration of the aqueous layer (3–5 h). The organic layer was separated and dried over anhydrous MgSO_4 . The solvent was distilled to leave the corresponding products.

Method C. A solution of onium salt ($[\text{Et}_3(\text{PhCH}_2)\text{N}]\text{Cl}$ or $[\text{Ph}_4\text{As}]\text{Cl} \cdot \text{H}_2\text{O}$ (0.5 mmol) in 20 mL of dichloromethane was added to 0.25 mmol of K_2PtCl_6 in 20 mL of H_2O . The two-phase system obtained was stirred for 2–3 h at room temperature until a precipitate ceased to be formed and both phases had become colorless. The residue was removed by filtration and washed successively with water, ethanol, and dichloromethane to yield the corresponding products.

Method D. Polymer-supported benzyltri-*n*-butylphosphonium chloride ($\text{C}_6\text{H}_4\text{CH}_2\text{P}^+\text{Bu}_3\text{Cl}^-$, the commercial name (Fluka) "tributylmethylphosphonium chloride polymer bound" (0.5 g, 0.78

mmol of Cl^-/g), was stirred for 0.5 h in dichloromethane (20 mL) to achieve swelling. A solution of 0.2 mmol of K_2PtCl_6 in 20 mL of H_2O was added to the mixture followed by stirring for 5 h at room temperature. Thereby the solution became colorless, and the polymer particles became orange in color. The resulting product was filtered and washed successively with water and ethanol to give the polymer-bound hexachloroplatinate **8**.

Hydrosilylation of Phenylacetylene in the Presence of Quaternary Onium Hexachloroplatinates 1–8, K_2PtCl_6 , and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (General Procedure). The reaction was carried out in 5-mL Pierce "reacti-vials" by stirring a mixture of the silane (1 mmol), the catalyst (0.001 mmol), and phenylacetylene (1 mmol) at 80–140 °C. The reaction course was monitored by GC and GC-MS (see Tables III and IV). After completion of the reaction, the resulting products were assigned by ^1H NMR spectroscopy and their ratio determined. The reactions of phenylacetylene and silanes I–VI and VIII (Table IV) yield products whose mass and ^1H NMR spectra are compatible with those reported.^{4,20,21} Addition products of HSiMePh_2 and $\text{PhC}\equiv\text{CH}$ are known from the literature,²² but their ^1H NMR spectra have not been described. The ^1H NMR spectral parameters for α -(methylphenylsilyl)styrene [δ 0.44 (s, 3 H, SiMe), 5.38 and 5.93 (each d and each 1 H, $J = 3$ Hz, $=\text{CH}_2$), 7.13 (m, 15 H, Ph)] and for β -*trans*-(methylphenylsilyl)styrene [δ 0.51 (s, 3 H, SiMe), 6.53 and 6.76 (each d and each 1 H, $J = 19$ Hz, *trans*- $\text{CH}=\text{CH}$ -), 7.13 (m, 15 H, Ph)] confirm the above structures.

Hydrosilylation of Phenylacetylene in the Presence of K_2PtCl_6 and Phase-Transfer Agents. The reactions were carried out in 5-mL Pierce "reacti-vials" by adding triethylsilane (1 mmol), K_2PtCl_6 (0.001 mmol), a phase-transfer agent ($[\text{Bu}_4\text{N}]\text{HSO}_4$ or 18-crown-6, 0.002 mmol), and phenylacetylene (1 mmol). When solvents were used in the reaction, their volume amounted to 0.26 mL. The reaction mixture was stirred at 80 °C under GC control (see Table V).

Registry No. 1, 18129-76-5; 2, 18129-78-7; 3, 16905-80-9; 4, 108007-47-2; 5, 107985-53-5; 6, 108007-48-3; 7, 17992-23-3; I, 617-86-7; II, 10025-78-2; III, 75-54-7; IV, 1066-35-9; V, 993-07-7; VI, 766-77-8; VII, 776-76-1; VIII, 789-25-3; $[\text{Me}_4\text{N}]\text{Br}$, 64-20-0; $[\text{Bu}_4\text{N}]\text{HSO}_4$, 32503-27-8; $[(n\text{-C}_8\text{H}_{17})_4\text{N}]\text{Br}$, 14866-33-2; $[(n\text{-C}_{18}\text{H}_{37})_4\text{N}]\text{Br}$, 63462-99-7; $[\text{Et}_3(\text{PhCH}_2)\text{N}]\text{Cl}$, 56-37-1; $[\text{Bu}_4\text{P}]\text{Cl}$, 2304-30-5; $[\text{Ph}_4\text{As}]\text{Cl}$, 507-28-8; $\text{H}_2\text{C}=\text{C}(\text{Ph})\text{SiEt}_3$, 42478-41-1; (*E*)- $\text{PhCH}=\text{CHSiEt}_3$, 21209-32-5; (*E*)- $\text{PhCH}=\text{CHSiCl}_3$, 3412-59-7; (*E*)- $\text{PhCH}=\text{CHSiCl}_2\text{Me}$, 17902-47-5; $\text{H}_2\text{C}=\text{C}(\text{Ph})\text{SiClMe}_2$, 67416-43-7; (*E*)- $\text{PhCH}=\text{CHSiClMe}_2$, 61518-55-6; $\text{H}_2\text{C}=\text{C}(\text{Ph})\text{SiMe}_3$, 1923-01-9; (*E*)- $\text{PhCH}=\text{CHSiMe}_3$, 19372-00-0; $\text{H}_2\text{C}=\text{CH}=\text{CHSiMe}_2\text{Ph}$, 63935-90-0; (*E*)- $\text{PhCH}=\text{CHSiMe}_2\text{Ph}$, 64788-85-8; $\text{H}_2\text{C}=\text{C}(\text{Ph})\text{SiMePh}_2$, 101823-45-4; (*E*)- $\text{PhCH}=\text{CHSiMePh}_2$, 101823-44-3; $\text{H}_2\text{C}=\text{C}(\text{Ph})\text{SiPh}_3$, 804-83-1; (*E*)- $\text{PhCH}=\text{CHSiPh}_3$, 33105-34-9; H_2PtCl_6 , 16941-12-1; K_2PtCl_6 , 16921-30-5; phenylacetylene, 536-74-3.

(20) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tripsis, C. A. *J. Chem. Soc., Dalton Trans.* 1977, 1525.

(21) Brook, A. G.; Duff, J. M.; Reynolds, W. F. *J. Organomet. Chem.* 1976, 121, 293.

(22) Lukevics, E.; Sturkovich, R. A.; Pudova, O. A. *J. Organomet. Chem.* 1985, 292, 151.