Catalytic activity of bis(dialkylamino)carbenium salts in hydrosilylation reactions

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Bis(dialkylamino)carbenium salts $\{[(Me_2N)_2CCl]^+\}_2MCl_4{}^{2-}$ (M = Ni, Pd) and $\{[Me_2NC(X)NR_2]^+\}_2PtCl_6{}^{2-}$ (R = Me, All; X = H, Cl, Me) are efficient catalysts for hydrosilylation of allyl phenyl ether, triallylamine, allyl chloride, allylamine, and 1-octene with various hydrosilanes. The catalytic activity is dependent on the salt composition and the nature of the metal M, the saturated compound, and the hydrosilane used. The catalysts used are usually insoluble in the reaction mixture, active, and stable. In some cases, carbenium salts are more selective than Speier's catalyst. Novel catalysts, silica-immobilized dialkylaminocarbenium salts, have been prepared. The kinetics of the reaction have been considered.

Key words: unsaturated compounds, hydrosilanes; hydrosilylation, catalysis by bis(dialkylamino)carbenium salts, kinetics.

The earlier synthesized[1,2] bis(dialkylamino)carbenium salts $\{[(Me_2N)_2CCl]^+\}_2MCl_n{}^{2-}$ and $\{[Me_2NC(X)NR_2]^+\}_2PtCl_6{}^{2-}$ have been studied as catalysts for hydrosilylation of various unsaturated compounds. We studied the addition of trichlorosilane to allyl phenyl ether in the presence of chlorobis(dimethylamino)carbenium salts $\{[(Me_2N)_2CCl]^+\}_2MCl_n{}^{2-}$ (Table 1).

$$CH_2{=}CHCH_2OPh + HSiCl_3 \xrightarrow{Cat} \underset{\mathbf{1}}{Cl_3Si(CH_2)_3OPh} + \underset{\mathbf{2}}{Cl_3SiCH(Me)CH_2OPh}$$

The data presented in Table 1 demonstrate that the catalytic activity of chlorobis(dimethylamino)carbenium salts depends substantially on the nature of the metal-containing anion and decreases in the following order: $PtCl_6{}^{2-} \gg NiCl_4{}^{2-} > PdCl_4{}^{2-} > CoCl_4{}^{2-} > CuCl_4{}^{2-} > GeCl_4{}^{2-} > MnCl_4{}^{2-}$.

Table 1. Hydrosilylation of allyl phenyl ether by trichlorosilane in the presence of $\{[(Me_2N)_2CCl]^+\}_2MCl_n{}^{2-}$ salts (glass tubes, 100 °C, 3 h, [M] = $8.3 \cdot 10^{-3}$ mol per 1 mol of olefin, method *A*)

MCl_n	Conversion (%)	1/(1 + 2)
$PtCl_6$	90.8	1.00
$NiCl_4$	47.1	0.74
$PdCl_4$	12.8	0.72
$CuCl_4$	3.5	0.82
$CoCl_4$	4.6	0.60
$GeCl_4$	1.7	0.73
$MnCl_4$	0.5	1.00
$SnCl_4$	0	—

The effect of the nature of the hydrosilane has been studied using the hydrosilylation of allyl phenyl ether, 1-hexene, and triallylamine in the presence of $\{[(Me_2N)_2CCl]^+\}_2PtCl_6{}^{2-}$ salt as examples (Table 2). It has been established that the decrease in activity in the following order, $Me_2PhSiH > MePh_2SiH > (EtO)_3SiH > MeCl_2SiH > Me_2ClSiH > Et_3SiH > Cl_3SiH > MePhClSiH$, does not correlate with Taft's inductive

Table 2. Hydrosilylation of unsaturated compounds in the presence of $\{[(Me_2N)_2CCl]^+\}_2PtCl_6{}^{2-}$ salt (70 °C, [Pt] = $9 \cdot 10^{-5}$ mol per 1 mol of olefin, method *B*) with various R and R′

$$RCH_2CH{=}CH_2 + HSiR'_3 \longrightarrow R(CH_2)_3SiR'_3$$

R'_3	R = PhO		R = Pr		R = All_2N*	
	t /h	Yield (%)	*t* /h	Yield (%)	*t* /h	Yield (%)
Me_2Ph	0.7	89.4	2	78.4	5	71.4
$MePh_2$	0.7	78.6	2	52.4	5	52.3
$MeCl_2$	3.0	71.4				
Me_2Cl	3.0	66.5				
Cl_3	3.0	51.3	6	37.4		
$(OEt)_3$	0.7	72.4	3	45.4	13	56.5
Et_3	3.0	67.5	6	48.7	13	36.4
PhMeCl	4.0	19.4	6	18.6		

* *T* = 110 °C.

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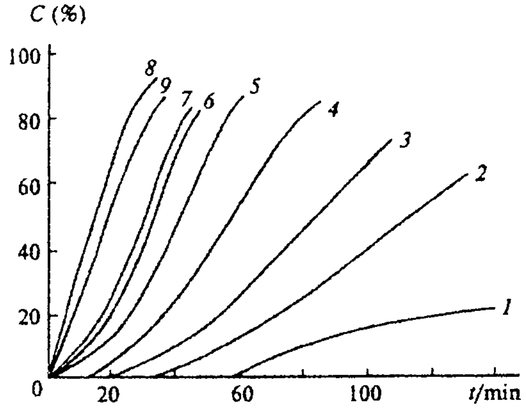


Fig. 1. Kinetic curves of the hydrosilylation (procedures *C—E*) of allyl phenyl ether by triethoxysilane in the presence of chlorobis(dimethylamino)carbenium) hexachloroplatinate(IV): olefin/silane = 1 : 1, *T*/°C = 50 (*1—4*), 60 (*5*), 70 (*6—9*); [Pt]/olefin (mol/mol) = $1 \cdot 10^{-5}$ (*1*), $2 \cdot 10^{-5}$ (*2*), $4 \cdot 10^{-5}$ (*3*), $8 \cdot 10^{-5}$ (*4—9*); the catalyst was treated with allyl phenyl ether (*7*), with triethoxysilane (*8*), with additives of Me_2PhSiH (*9*).

σ*-constants of substituents.[3] Probably the different activities of the studied olefins in the hydrosilylation reaction is due to the effect of substituents on the electron density of the double bond, the polarity of the medium, and the possible additional interaction of functional groups of the substrate with the silane and the catalyst.

The kinetic studies of the addition of triethoxysilane to allyl phenyl ether in the presence of $\{[(Me_2N)_2CCl]^+\}_2PtCl_6^{2-}$ salt (Fig. 1) have demonstrated that in all cases, the reaction proceeds with an induction period, during which formation of a catalytically active complex occurs. When the catalyst is reused, the reaction proceeds with no induction period. Silane exerts a crucial effect on the formation of the active complex. If the carbenium salt is pre-treated with triethoxysilane for 25 min at 70 °C there is no induction period in the reaction. The nature of allyl phenyl ether has a negligible effect on the duration of the induction period. The use of dimethylphenylsilane (which is more reactive than triethoxysilane) as an additive significantly cuts the induction period, but does not affect the rate of the addition of triethoxysilane to allyl phenyl ether. In the second part of the kinetic curves, in the conversion region from 15 to 75%, the rate of hydrosilylation is approximated by an equation for a zero-order reaction, where the step limiting the whole process may be either transformation of the transition complex or desorption of the reaction products from the catalyst surface. The same pattern is observed[4,5] in hydrosilylation carried out on anion exchangers with the counter-ion $PtCl_6^{2-}$. If consumption of the catalyst decreases to $1 \cdot 10^{-5}$ mol per 1 mol of olefin, the reaction order changes from 0 to 1.

Table 3. Kinetic parameters of the hydrosilylation of allyl phenyl ether by triethoxysilane in the presence of $\{[Me_2NC(X)NR_2]^+\}_2PtCl_6^{2-}$ salts at 50 °C ([Pt] = $8 \cdot 10^{-5}$ mol per 1 mol of olefin, method *C*)

$Me_2NC(X)NR_2$	Induction period/min	$k \cdot 10^3$ /mol L^{-1} min^{-1}
$(Me_2N)_2CCl$	40	5.44
$(MeN_2)_2COMe$	20	6.46
$(Me_2N)_2CH$	27	7.14
$Me_2NC(H)NAll_2$	30	7.48

The reaction has a fractional order (0.5) with respect to the catalyst. The kinetic parameters of the hydrosilylation of allyl phenyl ether by triethoxysilane in the presence of $\{[Me_2NC(X)NR_2]^+\}_2PtCl_6^{2-}$ salts (Table 3) allowed us to obtain the order of decreasing activity, which depends on the nature of cation: $[Me_2NC(H)NAll_2]^+ > [(Me_2N)_2CH]^+ > [(Me_2N)_2COMe]^+ \gg [(Me_2N)_2CCl]^+$.

The dependence of the hydrosilylation rate on the nature of the cation suggests that dialkylaminocarbenium ions are not merely an inactive matrix but are involved in the formation of the catalytically active complex in which the outer sphere ligands are of great importance. The data obtained are not consistent with the commonly accepted mechanism of hydrosilylation proposed by A. Chalk and J. Harrod,[6] according to which hydrosilylation occurs *via* intracomplex transformations of the Pt-coordinated hydrosilane and olefin (with the latter being coordinated by a π-type bond). The facts accumulated in recent years make it possible to consider several possible modifications of the Chalk—Harrod mechanism (they will be considered in the next article). We believe that the data obtained in this study confirm the previously proposed mechanism[7] that assumes the possibility of hydrosilylation without coordination of the olefin by platinum *via* a π-type bond.

In the course of hydrosilylation, the salt form of the catalyst is retained: there is a strong ν(C$\overset{...}{=}$N) band in the IR spectrum of the reaction mixture, which is typical of carbenium salts. The process apparently occurs on the surface and no Pt complex is liberated into the solution and there is no reduction of the catalyst to colloid Pt as is usually observed for the Speier catalyst. The platinum content in the reaction mixture is $3.1 \cdot 10^{-9}$ mol per 1 mol of olefin (according to the emission analysis data). Repeated use of the catalyst slightly affects the yield of the product. The addition of triethoxysilane to allyl phenyl ether in eight successive experiments (using the same catalyst) occurs in 85.4—89.9% yields; in the case of 1-octene dispersion is somewhat higher, the yields are 78.3—84.3% (Table 4).

The data on hydrosilylation of triallylamine with triethoxysilane presented in Table 5 demonstrate that the activity and selectivity of dialkylaminocarbenium hexachloroplatinates are higher than those of the Speier's catalyst.

Table 4. Hydrosilylation of unsaturated compounds in the presence of carbenium salts ([Pt] = 8 · 10^{-5} mol per 1 mol of olefin, method *F*)

$$RCH{=}CH_2 + (EtO)_3SiH \longrightarrow (EtO)_3Si(CH_2)_2R$$

Catalyst	R	*T* /°C	*t* /h	Yield (%)	
				in 1 synthesis	in 8—10 syntheses
$\{[(Me_2N)_2CCl]^+\}_2PtCl_6{}^{2-}$	$PhOCH_2$	100	2	89.9	85.4—89.0
$\{[(Me_2N)_2COMe]^+\}_2PtCl_6{}^{2-}$	$PhOCH_2$	100	2	89.4	85.5—89.9
	C_6H_{13}	115	2	86.3	78.5—84.3
⫽—$OC^+(MeN_2)_2(PtCl_6{}^{2-})_{0.5}$	$PhOCH_2$	70	1	89.6	88.0—90.0
	C_6H_{13}	100	2	88.4	78.9—86.4
	C_6H_{13}*	100	1	92.4	90.4—93.1

*Hydrosilylation by dimethylphenylsilanes.

Table 5. Hydrosilylation of triallylamine by triethoxysilane in the presence of X_2PtCl_6 at 110 °C ([Pt] = 8 · 10^{-5} mol per 1 mol of olefin, $All_3N/HSi(OEt)_3$ = 1 : 1, method *B*)

X	*t* /h	Yield (%)	4/3	5/3	6/3	*k* · 10^3 [b] /min^{-1}
H	20	35.5	0.3	0.7	0.18	0.85
$(Me_2N)_2CH$	5	50	0.01	0.18	0.01	8.5
$Me_2NC(H)NAll_2$	5	59	0.01	0.15	0.02	9.2
$(Me_2N)_2COMe$	9	57	0.01	0.15	0.02	6.5
$(Me_2N)_2CCl$	13	57	0.01	0.16	0.06	4.8

[a] The yield given is based on silane.
[b] The constant was calculated by the first order equation.

$$All_3N + HSi(OEt)_3 \xrightarrow{Cat} \underset{\mathbf{3}}{All_2N(CH_2)_3Si(OEt)_3} +$$
$$+ \underset{\mathbf{4}}{All_2NCH_2CH(Me)Si(OEt)_3} + \underset{\mathbf{5}}{AllN[(CH_2)_3Si(OEt)_3]_2} +$$
$$+ \underset{\mathbf{6}}{N[(CH_2)_3Si(OEt)_3]_3}$$

The synthesized catalysts were used for hydrosilylation of other unsaturated compounds (Table 6).

Dialkylaminocarbenium hexachloroplatinates possess a number of advantages. However, like all heterogeneous catalysts, they have one disadvantage: they catalyze hydrosilylation only in the outer layer, whereas the major portion of the reactive centers are in the bulk of the crystal. Therefore, hexachloroplatinates fixed on inorganic supports may be more efficient catalysts from a practical standpoint.

Table 6. Hydrosilylation of unsaturated compounds in the presence of $\{[(Me_2N)_2CCl]^+\}_2PtCl_6{}^{2-}$ salt ([Pt] = 8 · 10^{-5} mol per 1 mol of olefin, method *B*)

$$RCH{=}CH_2 + HSiR'_3 \longrightarrow R(CH_2)_3SiR'_3 + RCH(Me)SiR'_3$$

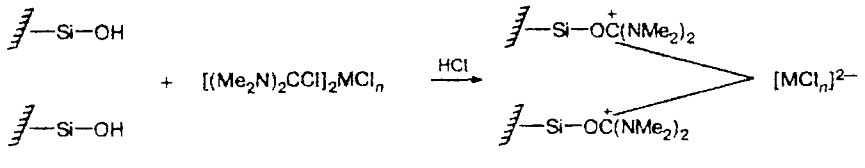
R	R'_3	*t*/h	*T*/°C	Yield of adducts* (%)
$ClCH_2$	$MeCl_2$	10	80	74.3
Pr_2NCH_2	$(OEt)_3$	14	110	64.3
H_2NCH_2	$(OEt)_3$	26	120	72.0
$PrOCH_2$	Me_2Ph	1	100	72.4
$PrOCH_2$	Et_3	1	100	61.4

* The total yield is reported.

Like reactions with alcohols,[2] metal-containing dialkylaminochlorocarbenium salts react with the surface hydroxyl groups of silica gel and are quantitatively immobilized on the support (Scheme 1).

Immobilization of the salts either on porous glass or on silica gel increases their catalytic activity by several orders of magnitude. For example, treatment of silica gel with chlorobis(dimethylamino)carbenium hexachloroplatinate(IV) increases the specific surface (S_{sp}) from 0.01 to 2470 m^2 per 1 g of salt (if the salt powder is mechanically ground in an agate mortar, S_{sp} = 0.89 m^2 g^{-1}).

Scheme 1



M = Co^{II}, Mn^{II}, Ni^{II} (*n* = 4), Pt^{IV} (*n* = 6)

The synthesized immobilized catalyst exhibits high activity and stability when it is reused. For instance, in the hydrosilylation of allyl phenyl ether with triethoxysilane carried out on an immobilized catalyst ⫽$-OC^{+}(NMe_2)_2(PtCl_6^{2-})_{0.5}$ the yield of γ-phenoxypropyl(triethoxy)silane remains at 88—90% in 10 successive experiments with the same catalyst (1 h, 70 °C, $[Pt] = 8 \cdot 10^{-6}$ mol per 1 mol of olefin).

In the case of immobilized catalysts, it is possible to change their activity by varying the quantity of $PtCl_6^{2-}$ anions fixed on the surface of the inorganic support. In addition to this, immobilized catalysts should be much more stable with respect to reduction $Pt^{IV} \rightarrow Pt^{0}$, than dialkylaminocarbenium hexachloroplatinates, because one of the planes of the intermediate active complex is protected from silane attack by the matrix.

Experimental

The syntheses were carried out under dry argon; salts with specific surface S_{sp} = 0.893 to 901 $m^2\ g^{-1}$ were used

GLC analysis was carried out on a Tsvet-100 chromatograph (katharometer as detector, a 1500×1 mm column, 15% E-301 on Chromaton, evaporator temperature 400 °C, column temperature 50 to 300 °C, rate of temperature programming 20 deg per min, helium as gas-carrier (60 mL min^{-1})).

Hydrosilylation of unsaturated compounds. *A.* An equimolar mixture of unsaturated compound and hydrosilane was heated in a tube and analyzed by GLC.

B. A mixture of unsaturated compound, hydrosilane, and carbenium salt was controlled thermostatically with vigorous stirring (1000 rpm). Sampling was made at specific intervals and the samples were analyzed by GLC.

C. A catalyst was placed in a four-necked flask fitted with a stirrer, a reflux condenser, a thermometer, and a bubbler under argon. The flask was evacuated and refilled with argon. A mixture of triethoxysilane (6.6 g, 40 mmol) and allyl phenyl ether (5.4 g, 40 mmol) preliminarily heated to a particular temperature was transferred to the flask, while the rate of stirrer rotation was increased smoothly to 1000 rpm; the resulting mixture was controlled thermostatically at a given temperature. At specific intervals the samples were taken and analyzed by GLC. Relative standard deviation was *ca.* 2% for chromatograms calculated by an integrator.

D. Hydrosilylation was carried out by a procedure similar to procedure *C*, but in this case first one of the components was added to a catalyst and the mixture was kept for 25 min at 70 °C, then the second component heated to the same temperature was added.

E. The reaction was carried out by a procedure similar to procedure *C*, but dimethylphenylsilane (0.02 g, 0.15 mmol) was added to a mixture of allyl phenyl ether and triethoxysilane.

F. Studies of the catalytic activity of the salts insoluble in the reaction mixture and immobilized in the course of repeated syntheses were carried out according to procedure *B* at 50 °C; allyl phenyl ether (5.4 g, 40 mmol), triethoxysilane (6.6 g, 40 mmol), and chlorobis(dimethylamino)carbenium hexachloroplatinate(IV) ($3.2 \cdot 10^{-6}$ mol) were used. The reaction mixture was decanted, new portions of the reagents were added to the catalyst washed with hexane (2×2 mL), and the synthesis was repeated.

Preparation of the immobilized catalyst. *A.* Dichloromethane (5 mL) and chlorobis(dimethylamino)carbenium hexachloroplatinate(IV) (13 mg) were added to 0.3 g of porous glass dried at 200—250 °C for 2.5 h. The resulting mixture was refluxed at 40 °C until it was decolorized completely (for 4—5 h), and for an additional 1 h, until the reaction was completed. The dichloromethane was decanted. The reaction product was washed with dichloromethane (2×3 mL) *in vacuo* until its weight became constant (0.313 g). The obtained rose-colored catalyst contained 1.2% Pt; the specific surface was 2470 $m^2 \cdot g^{-1}$.

B. The reaction was carried out by a procedure similar to procedure *A*, but in this case triethylamine was added (0.02 mL), and the reaction mixture was refluxed for 4 h. The prepared catalyst contained 1.2% Pt.

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