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Catalysis of Hydrosilylation: Part XXIV. H_2PtCl_6 in Cyclohexanone as Hydrosilylation Catalyst—What is the Active Species in this Catalytic System?

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A cyclohexanone solution of H_2PtCl_6 was examined to find the catalytic species responsible for the hydrosilylation of the olefinic C=C bond. Similarly to other H_2PtCl_6–solvent systems (e.g. Speier's and Karstedt's catalysts), the real catalyst appeared to be colloidal platinum formed *in situ* by stepwise reduction [Pt(IV)→Pt(O)] and dechlorination of the platinum precursor. The role of cyclohexanone seems to be to form sufficiently stable platinum complexes to avoid rapid platinum precipitation and aggregation. The studies of H_2PtCl_6–solvent systems are of practical importance since these compounds are widely used catalyst precursors for hydrosilylation on an industrial scale.

Keywords: Hexachloroplatinic acid/cyclohexanone, hydrosilylation, catalysis, platinum colloid

INTRODUCTION

Although a wide range of catalysts has been tested for hydrosilylation reactions, most research and industrial syntheses are carried out in the presence of platinum complexes[1,2] for which hexachloroplatinic acid hydrate (H_2PtCl_6/aq.) is most commonly used as the initial precursor. In addition to its isopropanol solution (referred to as Speier's catalyst[3]), other alcohols, ketones, esters and ethers have also been used in the preparation of active catalytic species from hexachloroplatinic acid.[1,2]

A generally characteristic feature of the H_2PtCl_6–solvent catalytic system is the induction period which occurs in its presence, being followed by a fast and exothermic hydrosilylation process. It is known that the catalytic activity of H_2PtCl_6 depends on the type of solvent used and the method of preparation of the catalyst solution. Despite the vast number of patents and papers on hydrosilylation reactions applying these catalytic systems, little study has been undertaken regarding the composition of the active catalytic species formed during the activation in solvent molecules and, later, during the initial induction period.

More than 20 years after the discovery of Speier's catalyst, Benkeser and co-workers have shown that it contains the complex $H(C_3H_6)PtCl_3$ and its $(C_3H_6)PtCl_3^-$ anion, which is stable and active in hydrosilylation.[4] However, Lewis and co-workers have recently suggested that Speier's catalyst is colloidal in character in the presence of the hydrosilane.[5] Solutions of chloroplatinic acid in n-octyl alcohol, often referred to as lamoreaux catalysts,[6,7] contain platinum(II) species with lowered Cl/Pt ratios (up to 2–3.5 : 1) and some octyl aldehydes and ethers; however, no more details are known. During the preparation of chloroplatinic acid in tetrahydrofuran (THF) a reduction of platinum(IV) to platinum(II) and platinum(0) species is observed, generating several organic products during the oxidation of THF molecules.[8] Karstedt's catalyst, obtained by treating hexachloroplatinic acid with divinyltetramethyldisiloxane, has been most used in recent years, but was patented 20 years ago.[9] Its crystal structure was determined[10] but, according to Lewis, this catalyst also acts as colloidal platinum formed *in situ* in the presence of the hydrosilane.[11] Additionally, the size and morphology of the colloid prepared reflects its catalytic activity. In view of the above information, some attempts have been made recently to apply platinum(0) complexes as direct catalysts of hydrosilylation, namely $Pt(PPh_3)_4$,[12,13] $Pt(PPh_3)_2(CH_2{=}CH_2)$[14,15] and $Pt(PPh_3)_2$(vinylsiloxane).[10]

Therefore, the aim of this work is to follow activation of another platinum catalyst originating

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from hexachloroplatinic acid, namely H_2PtCl_6–cyclohexanone solution, which, similarly to other H_2PtCl_6-based catalytic systems, is also effective under oxygen conditions and is well-known as an active catalyst in many laboratory and industrial hydrosilylation reactions.[16–20]

EXPERIMENTAL

Materials

Triethoxysilane was obtained by alcoholysis of $HSiCl_3$, according to a standard procedure. 1-Alkenes, allyl compounds, trichlorosilane, $H_2PtCl_6 \cdot /aq$ (9.1%pt) and cyclohexanone were commercial products. The benzene and ethanol were dried by standard procedures.

Catalysts

Preparation of H_2PtCl_6 in cyclohexanone solution

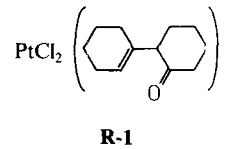
Preparation of M-1 Cyclohexanone (150 cm^3) was added to 7.5 g of H_2PtCl_6/aq. and heated under a condenser at 50 °C for three days. To expel water, anhydrous magnesium sulphate ($MgSO_4$) was added and removed in hydrated form several times; the final catalyst solution was prepared with a platinum concentration of 4.53 mg Pt cm^{-3}.

Preparation of M-2 Cyclohexanone (150 cm^3) was added to 40 g of H_2PtCl_6/aq. and after the addition of 250 cm^3 of dried benzene the mixture was evaporated at room temperature under reduced pressure. After several azeotropic distillations with fresh, dried benzene, the final catalyst solution was prepared with a platinum concentration of 21.20 mg Pt cm^{-3}.

Reaction of M-1 solution with triphenylphosphine PPh_3 (0.1 g) was added to 10 cm^3 of **M-1** solution; a yellowish solid which was precipitated almost immediately at room temperature was collected and washed several times with benzene to yield a white complex, characterized as the well-known $PtCl_2(PPh_3)_2$ [0.084 g, 46% yield; m.p. 300 °C; elemental analysis (%) Pt 24.1, P 8.0, Cl 9.1 (calcd 24.7, 7.8, 8.9, resp.)] with IR spectra identical with that of an authentic complex sample.

Preparation of platinum catalysts with 2-(1-cyclohexenyl)cyclohexanone

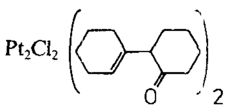
Preparation of R-1 H_2PtCl_6/aq (1 g) was added to 3 cm^3 of 2-(1-cyclohexenyl)cyclohexanone and the mixture was shaken at room temperature for 24 h. After several days the grey solid which had precipitated from the solution was collected, washed several times with chloroform and isolated as a yellow complex, [0.1490 g, 72% yield; m.p. (decomp.) 190–195 °C; elemental analysis (%) C 32.1, H 4.0, Cl 15.5, Pt 43.0 (calcd 32.4, 4.1, 16.0, 43.9, resp.); IR (CsI) (cm^{-1}) 2940, 2860, 1640, 1586, 1440, 1255, 1033, 640, 607, 362, 313; MS [*m/z*, I(%)] 149.1 (100), 178.1 (60.8), 79.1 (57.6), 81.1 (45.4), 91 (45.9), 67 (40.4)].



R-1

This complex was insoluble in typical NMR solvents, except dimethyl sulphoxide (DMSO); however, in this case destruction of the compound was observed and ^1H and ^{13}C NMR spectra were almost identical with those observed for the free ligand i.e. 2-(1-cyclohexenyl)cyclohexanone.

Preparation of R-2 H_2PtCl_6/aq. (1 g) was evaporated with absolute ethanol several times, then 10 cm^3 of 2-(1-cyclohexenyl)cyclohexanone was added to 20 cm^3 of the ethanolic solution of H_2PtCl_6. The solution was heated at 65 °C for 15 min. Anhydrous Na_2CO_3 (4 g) was added to the grey–brown solution and the resulting mixture was heated to 65 °C. Carbon dioxide was evolved from the reaction mixture, the colour of which changed to light orange. After several hours at room temperature a dark solid was precipitated. It was collected, washed with ethanol and isolated as a cream complex, **R-2**



R-2

[0.204 g, 83% yield; m.p. (decomp.) 180–185 °C; elemental analysis (%) C 36.4, H 3.66, Cl 10.9, Pt 47.0; IR (CsI) (cm^{-1}) 2918, 2855, 1674, 1642, 1422, 1383, 1220, 1120, 820, 273, 220; ^1H NMR ($CDCl_3$) {δ(ppm)} 5.46 (CH), 4.06 (CH), 3.00, 2.65, 2.37, 2.12, 1.89, 1.50 (CH_2); ^{13}C NMR ($CDCl_3$) {δ(ppm)} 201.54 (C=O), 123.9, 105.0 (C=C), 20.0–30.0 (C—C).

Table 1 Catalytic activity of H_2PtCl_6 catalysts

Catalyst	Conditions $[{\equiv}SiH]:[C{=}C]:[cat.]$	Yield of product (%)			
		1 h	2 h	6 h	15 h
$Cl_3SiH + CH_2{=}CHCH_2Cl \xrightarrow{\text{reflux}} Cl_3Si(CH_2)_3Cl$					
H_2PtCl_6 (isopropanol)		1	4	—	—
H_2PtCl_6 (cyclohexanone)	$1:1:5\times10^{-6}$	55	75	—	—
H_2PtCl_6 (isopropanol)	$1:1:10^{-4}$	10	30	—	—
$(EtO)_3SiH + CH_2{=}CHCH_2NH_2 \xrightarrow{\text{reflux}} (EtO)_3SiC_3H_6NH_2$					
H_2PtCl_6 (isopropanol)		0	2	4	—
H_2PtCl_6 (cyclohexanone)	$1:1:10^{-4}$	3	6	16	—
$Cl_3SiH + CH_2{=}CH(CH_2)_5CH_3 \xrightarrow{\text{glass ampoule}} Cl_3Si(CH_2)_7CH_3$					
H_2PtCl_6 (isopropanol)		—	—	84(8)[a]	78(14)
H_2PtCl_6 (cyclohexanone)	$1:1:10^{-3}$; room temp.	—	—	87(2)	90(2)

[a] Yield of by-products in parentheses.

Catalytic tests

Hydrosilylation experiments were carried out in sealed glass ampoules (under air) or under reflux. The reaction mixtures were kept at room temperature or were warmed to reflux temperature and then analysed by gas–liquid chromatography (GLC). Substrate ratios and reaction conditions are described in the tables.

Homogeneity tests

Hydrosilylation reactions were carried out in Supelco vials. In the case of triethoxysilane addition to decene-1, Si–H bond conversion (measured by the GLC method) was checked after 20–60 min. Mercury(0) was added at the start and/or during the course of the reaction. In the second test, the catalyst solution **M-1** was activated at room temperature with one of the substrates (silane or vinylsilane) in the presence of mercury for 18 h and then the resulting mixture was subjected to the hydrosilylation reaction.

Equipment and analytical measurements

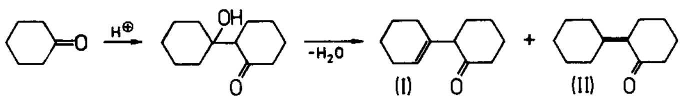
^1H and ^{13}C NMR spectra were recorded on an FX909 JEOL spectrometer. GLC was performed on Chrom 5 apparatus with a 2 m steel column filled with 10% SE-30 on Chromosorb P. Infrared spectra were recorded on a Perkin–Elmer model 180 spectrophotometer. Mass spectra were recorded on a JMSD 100 spectrometer and an electron-microscopic investigation of the catalyst solution was performed using a transmission electron microscope (JEOL JEM-7A).

Elemental analyses were performed using a Beckman analyser and platinum was determined spectrophotometrically (at λ 403 nm) after reaction of the sample with aqua regia and complexation in $SnCl_2$ solution by a standard procedure.

RESULTS AND DISCUSSION

A cyclohexanone solution of chloroplatinic acid has been used as a catalyst in the hydrosilylation of some olefins, showing higher activity and selectivity than Speier's catalyst (Table 1). Therefore, we have focused our interest on this catalytic system and have tried to explain the role of the cyclohexanone molecule in the activation of hexachloroplatinic acid.

Two dark-brown catalyst solutions, **M-1** and **M-2**, were prepared (for details, see the Experimental section). According to the first preparation procedure a solution of H_2PtCl_6 was heated at 50 °C in a large excess of cyclohexanone and desiccated with $MgSO_4$; in the latter, benzene



Scheme 1

was used for azeotropic distillation/evaporation of the excess water (at room temperature and reduced pressure). GLC analysis of both solutions showed a low concentration of cyclohexanone and the appearance of new peaks originated from the products of cyclohexanone aldol-type condensation (Scheme 1).

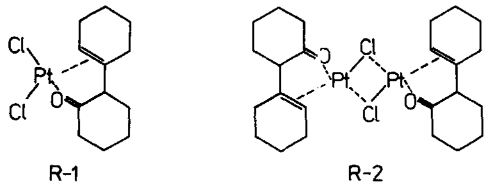
2-(1-Cyclohexenyl)-cyclohexanone (**I**/**II** = 9/1) was easily distilled under vacuum from the reaction mixture and fully characterized [b.p. 122 °C/ 10 mm Hg; ^{1}H NMR (C_6D_6) {δ(ppm)} 2.80 (CH_2), 5.42 (CH); ^{13}C NMR (C_6D_6) {δ(ppm)} 211.0 (C═O), 135.9, 123.6 (C═C), 22.5–31.9 (C—C); IR (CsI) (cm^{-1}) 2930, 1710, 1620, 1450, 1330, 1310, 1200, 1130, 1060].

Both catalyst solutions (**M-1** and **M-2**) reacted vigorously with hydrosilanes with evolution of hydrogen indicating oxidative addition of the silicon hydride to the metal complex followed by reductive elimination of molecular hydrogen. After PPh_3 addition to the catalyst solutions, $PtCl_2(PPh_3)_2$ was produced and precipitated (for its isolation and characterization, see the Experimental section), supporting the idea of Pt(IV)–Pt(II) reduction during the preparation of the catalyst. Addition of sodium carbonate (Na_2CO_3) or sodium hydrogencarbonate ($NaHCO_3$) is followed by the precipitation of sodium chloride and formation of a platinum complex with its Cl/Pt ratio lower than the initial one. The activation process of various chloroplatinic acid solutions is usually considered as tantamount to a lowering of the Cl/Pt ratio to 1 or less, practically independently of the nature of the activator (solvent). On the other hand, a low ratio has caused faster-than-usual deposition of a platinum-black mirror on the laboratory glass surface. The stability of the **M-1** solution was not very high; after a certain time, even at room temperature, a deposition of platinum black was observed, contrary to observations with the **M-2** solution. However, in the latter case some cream-coloured solid precipitated. The fact that directly evolved metallic platinum is practically inactive in hydrosilylation reactions suggests that the tendency generally observed in all these systems, i.e. quick and incidental platinum precipitation (caused also by some organic impurities and particularly by higher temperature), may become a source of considerable practical hazard for the whole process. Although there is a possibility of applying a temperature of 100 °C during the H_2PtCl_6 reaction with cyclohexanone,[20] room-temperature activation (e.g. the **M-2** procedure) seems to be the simplest method to avoid platinum precipitation.

Table 2 Catalytic activity of platinum precursors in the addition of triethoxysilane to decene-1[a]

	Reaction time (min)		
Catalytic system	10	30	70
M-1	20	78	78
M-2	20	76	76
R-1	0	0	0
R-2	39	70	86

[a] 60 °C, air, glass ampoules; [≡SiH] : [C═C] : [cat.] = $1:1:10^{-4}$. The activity is expressed as ≡SiH conversion (%), determined by GLC.


R-1 R-2

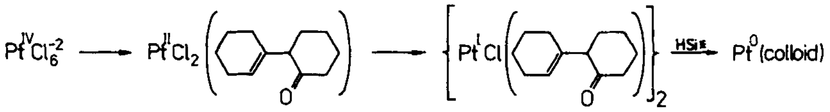
Scheme 2

To examine the system under study, we have isolated 2-(1-cyclohexenyl)cyclohexanone and have prepared a platinum complex with the above organic ligand (**R-1**) starting from H_2PtCl_6/aq.

Table 3 Results of the mercury homogeneity test in the hydrosilylation of the C═C bond[a]

	≡SiH conversion (%)	
Catalytic system	20 min	60 min
$(EtO)_3SiH + CH_3(CH_2)_7CH{=}CH_2$, 30 °C, N_2		
H_2PtCl_6/cyclohexanone (**M-1**)	60	80
M-1 + Hg	28	42
M-1 + $HSi(OEt)_3$[b]	75	90
M-1 + $HSi(OEt)_3$[b] + Hg	Trace	Trace
M-1 + $HSi(OEt)_3$[b] + Hg	50[c]	50
$(EtO)_3SiH + (EtO)_3SiCH{=}CH_2$, 60 °C, air		
H_2PtCl_6/cyclohexanone (**M-1**)	100	—
M-1 + $HSi(OEt)_3$ + Hg (activation at room temp., 18 h)[d]	Trace	8[f]
(**M-1**) + $CH_2{=}CHSi(OEt)_3$ + Hg (activation at room temp., 18 h)[e]	0	0[f]

[a] [≡SiH] : [C═C] : [Pt] = $1:1:10^{-5}$.
[b] Silane added to catalyst solution prior to the hydrosilylation (see text).
[c] Hg added 10 min after the start of the reaction.
[d] Then $CH_2{=}CHSi(OEt)_3$ added.
[e] Then $HSi(OEt)_3$ added.
[f] After 180 min.



Scheme 3

Ethanol was used as both desiccant and solvent for the organic ligand. On the basis of the experimental data the formulation **R-1** was proposed. Similar ligands are known to produce analogous platinum complexes, which are relatively stable (and catalytically active in hydrosilylation reactions) of general formula $PtCl_2R_n$ and $[RPtCl_2]_n$, where R is mesityl oxide,[21] butanone[21] or acac.[22]

Modification of the above procedure by using additionally Na_2CO_3 to diminish the Cl/Pt ratio allowed preparation of the **R-2** complex, characterized as the dimer (see above). The same solid precipitated from **M-2** solution after several days. **R-1** was insoluble in the hydrosilane $[(EtO)_3SiH]$ even at 40–60 °C, contrary to **R-2**, reacting easily with the above silane with evolution of hydrogen.

The catalytic activity of the prepared solutions and complexes was checked in the test hydrosilylation reaction of $(EtO)_3SiH$ with decene-1 (Table 2).

The **R-2** catalyst was the most effective and, surprisingly, its induction period when compared with those of **M-1** and **M-2** was substantially shortened. The inactivity of the **R-1** complex in this reaction may be due to a very strong interaction between the C=O group and the metal centre (ν_{CO} shift up to 124 cm^{-1} against free ligand) increasing the stability of this complex. In the dimeric **R-2** this interaction is weaker (ν_{CO} shift equal to 36 cm^{-1}) (see Scheme 2).

But what is the actual catalyst in this system? It is generally known that mercury selectively alloys with heterogeneous bulk metal-like materials but is unreactive toward truly homogeneous catalysts. Recently, Lewis employed the mercury test to demonstrate that platinum in H_2PtCl_6/isopropanol (Speier's catalyst) had colloidal intermediates[23] and loses most of its reactivity in the presence of mercury.

Our examination of the reaction mixtures containing the **M-1** catalytic system by transmission electron microscopy confirmed the presence of large platinum aggregates 30–300 nm in diameter. Additionally we have confirmed the intermediacy of a heterogeneous component by carrying out the mercury test: the results are presented in Table 3.

Addition of mercury practically halved the activity of the **M-1** solution; however, in the case of the initial hydrosilane activation of the precursor solution, the addition of mercury stopped the progress of the reaction. It is worth mentioning that triethoxysilane, sealed at 120 °C (12 h) in air in a glass ampoule with the **M-1** solution, undergoes 95% conversion (GLC), mainly towards $Si(OEt)_4$, higher siloxanes and gaseous products (H_2, HCl, SiH_4?). H_2PtCl_6-based catalysts are often activated by addition of hydrosilanes,[24–27] leading to the reduction of platinum(IV) to platinum(II) and platinum(0) species and lowering the Cl/Pt ratio by the elimination of chlorosilane. These processes occur practically independently of the solution composition. Similarly, in the presence of cyclohexanone a stepwise reduction of platinum may be proposed, leading eventually, after introduction of the hydrosilane, to highly active platinum(0) colloids according to Scheme 3.

Thus, the role of cyclohexanone is the formation of platinum complexes stable enough under oxygen conditions (to avoid undesirable rapid platinum precipitation and aggregation) with its condensation product, cyclohexenylcyclohexanone. These are the precursors of the real platinum colloidal catalyst, generated *in situ*, analogously to the case of Karstedt's complex,[11] in the presence of the hydrosilane as a substrate of the reaction mixture. Since there is strong evidence for the catalytic activity improving with decreasing diameter of the colloidal particles,[5] a more detailed study on the size and morphology of the colloids is under way.

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