

# Kinetic study of the photoactivated hydrosilylation of some $\beta$ -dicarbonyl complexes of trialkylplatinum(IV)

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## Abstract

$\beta$ -dicarbonyl trialkylplatinum(IV) complexes are able to photoactivate efficiently a hydrosilylation reaction. The efficacy as hydrosilylation catalysts of the platinum complexes is inversely correlated to their reducibility. Under irradiation the complexes are decomposed via a triplet excited state and a radical stage into an active hydrosilylation catalyst and finally into less reactive colloidal platinum. The homogeneous character of the hydrosilylation is pointed out. A general kinetic scheme is proposed but the relative reactivities of the hydrosilane olefin and catalyst used lead to a case for which the nature of the first insertion reactive compound is not determinable.

**Keywords:** Hydrosilylation; Platinum Pt(IV) complex catalyst; Radication curing; Photochemistry

## 1. Introduction

The  $\beta$ -dicarbonyl platinum complexes studied (Fig. 1) were first synthesized in 1928 by Menzies [1]. Truter and coworkers [2] have made structural studies on the alkyl and alkoxy  $\beta$ -diketonates **a** and **b**; in the solid state the  $\beta$ -diketone acts as a tridentate ligand, using the carbonyl oxygen atoms and the methylene ( $\gamma$ -carbon) to form bonds. The Pt–C bond between the two dimer moieties is weaker than the Pt–CH<sub>3</sub> bonds but strong enough to resist breaking in the presence of some other chelating agents [3]. The dimeric structure is, at least partially, conserved in non-polar solvents such as hexane or dichloroethane. In the presence of a strong chelating ligand such as 2,2'-bipyridyl, the Pt–O bonds are replaced by Pt–N bonds [3]. However, according to [4], <sup>1</sup>H nuclear magnetic resonance (NMR) of the methine proton and the IR stretching of the carbonyl bonds seem to indicate that the dicarbonyl ligand is in a bidentate configuration in the case of the phenyl-substituted  $\beta$ -diketonate **c**. Obviously the stability of the dimer depends on the dicarbonyl ligand substitution and increases when going from the phenyl to trifluoro, n-octyl, methyl and ethoxy. Some other properties such as cyclic voltammograms and electronic spectra seems to follow the same trend.

In a previous paper [5] the use of the trimethyl ( $\beta$ -dicarbonyl) platinum(IV) complexes represented in Fig. 1 as photohydrosilylation catalysts was described. The efficacy of

these compounds as catalysts in the hydrosilylation reaction were checked by using a model mixture of silicone polymers containing SiH and Si-vinyl parts. The observed reactivity of the complexes as photohydrosilylation catalysts follows the trend **a** > **b** > **d** > **c**. Some of these complexes are as good as other known platinum-based photohydrosilylation catalysts. In order to show more in detail the nature of the processes governing the reactivity of our complexes, their spectroscopic and photochemical properties in neat solvents and in the presence of hydrosilanes and olefins were studied. Finally a kinetic model which described well the observed hydrosilylation rates is proposed.

## 2. Experimental part

Compounds **a-d** (Fig. 1) were prepared with 80–90% isolated yield under a dry nitrogen or argon atmosphere using standard Schlenk techniques; trimethyl platinum iodide tetramere (**A**) is synthesized by treatment of potassium hexachloroplatinate with an excess of CH<sub>3</sub>MgI. The reaction of **A** with metallated acetylacetonate ligands leads to the compounds **a-d** [6] characterized by elemental analysis and NMR. Fourier transform IR (FTIR) and UV–visible spectra were recorded on a Perkin–Elmer 1600 FTIR and a Beckman DU 7400 diode array spectrophotometer respectively. The light

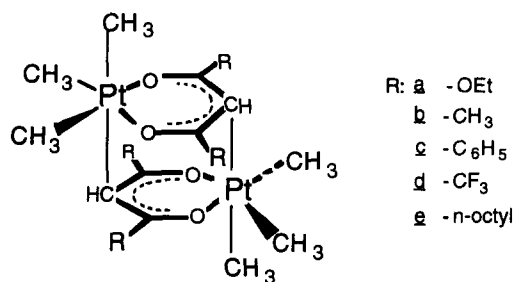


Fig. 1. Dimeric structure of the trimethyl( $\beta$ -dicarbonyl) platinum(IV) complexes.

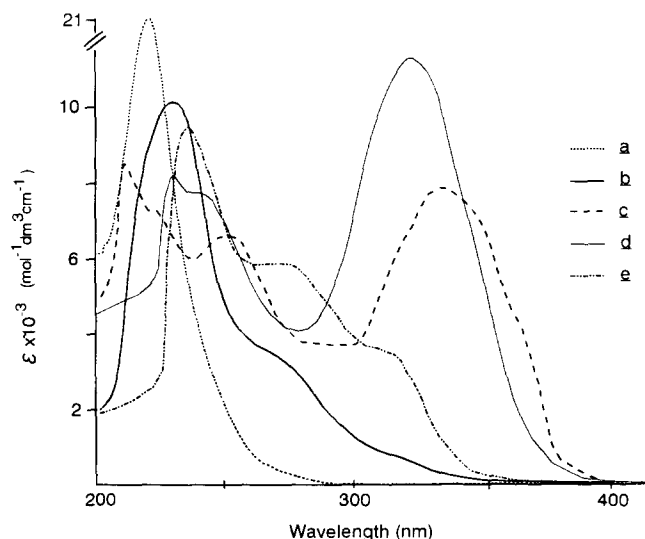


Fig. 2. Absorption spectra of a–e in hexane.

source was an air-cooled HPK125W medium pressure mercury lamp filtered by a water-containing quartz cell and a Pyrex glass plate. Hexane was Aldrich 99+ % UV or high performance liquid chromatography grade.

The solutions were prepared by adding first a known weighed quantity of the olefin to 1.5 ml of a fresh complex–

hexane solution. Just before irradiation the hydrosilane was added and the volume of the solution was adjusted to 3.5 ml. For all experiments the concentration of **b** was  $1 \times 10^{-4}$  mol  $l^{-1}$ . The solutions with known quantities of octene, Si–H parts and complexes were exposed to glass-filtered light ( $\lambda > 300$  nm). During irradiation, small aliquots (about 50  $\mu$ l) of solution were taken with a syringe and put into an IR liquid KBr cell (optical path, 100  $\mu$ m). The disappearance of the vinyl and Si–H moieties was then followed by FTIR spectroscopy using the characteristic stretching vibrations of Si–H (about 2120  $cm^{-1}$ ) and oct-1-ene double bond (1642  $cm^{-1}$ ). The Beer–Lambert law for hexane solutions of oct-1-ene and pentamethyldisiloxane was verified up to concentrations of 2 M and 1.3 M respectively.

### 3. Results and discussion

#### 3.1. Electronic spectra

The electronic spectra of the acetylacetonate complexes in cyclohexane solution are shown in Fig. 2 and the emission characteristics are reported in Table 1. The longest-wavelength absorption part decreases from -phenyl, -CF<sub>3</sub>, -octyl, -CH<sub>3</sub> to -OC<sub>2</sub>H<sub>5</sub> and disappears almost completely for the last. Simultaneously,  $\epsilon$ , the molar extinction coefficient of the UV absorption band near 230–260 nm, increases.

[Me<sub>3</sub>Pt(dibenzoylmethane)]<sub>2</sub> (**c**) exhibits an absorption band at 358 nm whose maximum is shifted to a lower energy with increasing solvent polarity (in dichloromethane,  $\lambda_{max} = 358$  nm) which indicates the charge transfer character of the transition involved.

The UV–visible spectrum of **a** remained nearly the same in hexane and in methanol. Only a small shoulder was observed in the latter case. The initial dimeric structure was conserved. On the contrary, **b** showed a new band at 310 nm

Table 1  
Spectroscopic properties and reduction potential of the complex

Compound	$\sigma_p^+$ <sup>a</sup>	$\lambda_{max}$ (nm)	$\epsilon$ (mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup> )	$E_{1/2}$ <sup>b</sup> (V (SCE))	Gel time <sup>c</sup> (h)
<b>a</b> (-OC <sub>2</sub> H <sub>5</sub> )	-0.81	226	21000	None up to -2.3 V	48
<b>b</b> (-CH <sub>3</sub> )	-0.31	231 268	10230 4270	-0.94	12
<b>c</b> (-phenyl)	-0.18	257 340	6760 7590	-	-
<b>d</b> (-CF <sub>3</sub> )	0.61	240 323	8510 11220	-0.72	7
<b>e</b> (-n-octyl)	-	235 274 310	9550 5890 3550	-1.07	-

<sup>a</sup> Brown resonance parameter [7].

<sup>b</sup> First reduction potential vs a saturated calomel electrode (SCE) measured in acetonitrile with tetrabutylammonium perchlorate as supporting electrolyte.

<sup>c</sup> Gel time at 25 °C of a model mixture of silicone containing the same amount of platinum.

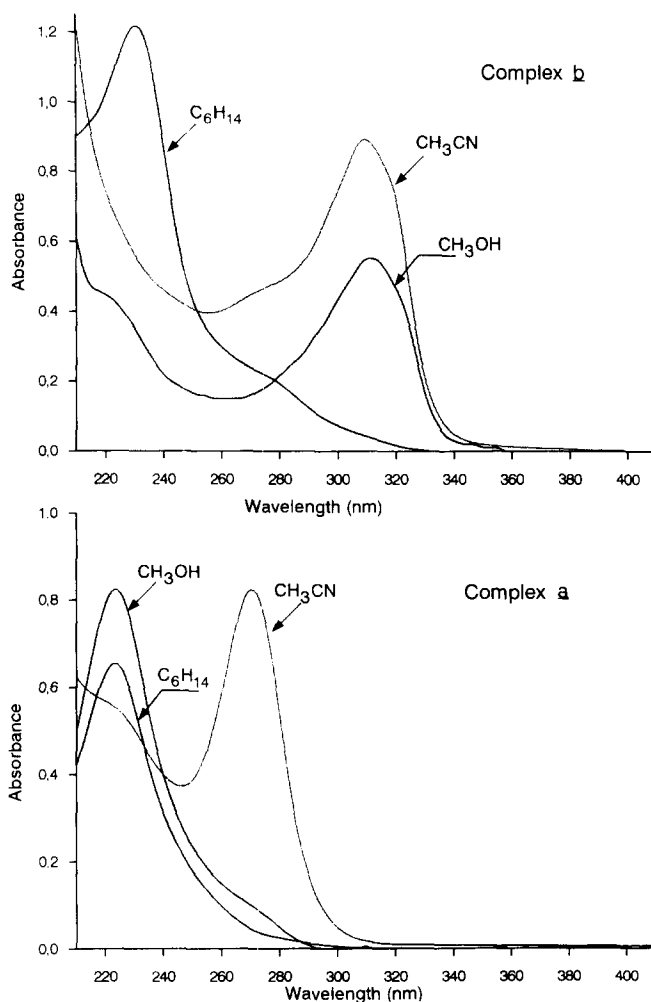


Fig. 3. Solvent effect on the absorption spectra of **a** and **b**.

in methanol which indicated the loss of the dimeric structure and therefore the lower stability of the acetylacetonate complex (Fig. 3). Moreover, in benzene as solvent a shoulder at 310 nm was evidenced for **b** but not for **a**. In acetonitrile, both **a** and **b** showed new absorption spectra with an absorption maximum at 272 and 309 nm respectively (Fig. 3).

### 3.2. Photolysis

Under irradiation with non-filtered UV light the photolysis ends with the formation of colloidal platinum which appears as a continuous broad absorption from 200 to 800 nm before aggregation. In non-polar solvents, photolysis of **a** and **b** can be separated into four stages. The evolution of the UV absorption spectra of **a** in hexane under irradiation with non-filtered UV light is presented in Fig. 4. The first step shows a first-order disappearance of the UV absorption band with simultaneous growth of new products. Interestingly, for irradiation up to about 1 min a partial reversibility is observed when the solution is placed in the dark. Photolysis of alkyl-platinum complexes such as  $\text{CpPtMe}_3$  results in homolysis of a Pt–Me bond [8]. Therefore recombination of the methyl radical after cage escape can explain the observed reversibil-

ity at the beginning of the photolysis. Moreover the first photoproducts undergo in the dark a thermal decomposition which did not lead to colloids as observed under irradiation.

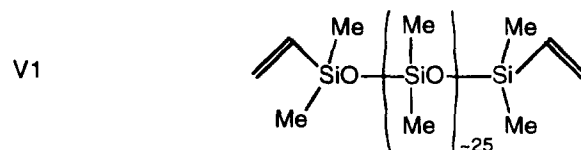
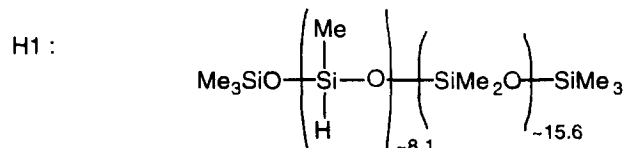
The characteristic absorption of colloidal particles appears under our conditions after irradiation for from 8 min to about 25 min where aggregation and decreases in the absorption occur. While, in hexane, aggregation occurs after about 25 min, this colloidal solution is stable for several hours in acetonitrile.

In hydroxylic solvents, such as glycol and methanol, the irradiation of solutions containing **b** leads to the disappearance of the first absorption band near 300 and 310 nm respectively and the appearance of a band at 275 nm (Fig. 5) which can be assigned to a monodentate ligand configuration or to the free protonated ligand pentane-2,4-dione whose absorption maxima in hexane is 272 nm. The lowest allowed  $\pi$ – $\pi^*$  transition of free acetylacetonate anion ( $\text{acac}^-$ ) would be observable at lower energies [9].

With glass-filtered light a time of several hours is necessary in order to observe the production of colloids. The use of triplet sensitizers such as benzophenone or thioxanthone in argon- or nitrogen-flushed solutions can greatly accelerate the formation of colloids which occurs then in the same range of time as with non-filtered light.

### 3.3. The photohydrosilylation reaction

The practical photoinitiating hydrosilylation activity of **a–d** was checked using a mixture of two industrial silicone polymers (Rhône-Poulenc) containing Si–H (H1) and Si–vinyl fragments (V1):



A silicone polymers mixture with excess of Si–H parts (molar ratio of Si–H to Si–vinyl, 1.7) and containing 250–300 ppm platinum equivalent was prepared. Under irradiation with UV light a rapid hydrosilylation reaction was observed accompanied by the gelation of the mixture. In the dark the mixture remains liquid for several hours but a slow hydrosilylation occurs, which means that a hydrosilylation catalyst can be formed without light. The nature of this thermal hydrosilylation catalyst can be the same as in the photoactivated hydrosilylation; only the greater rate of formation of this active species is then responsible for the higher cure speed under irradiation. If this is not the case the photochemically

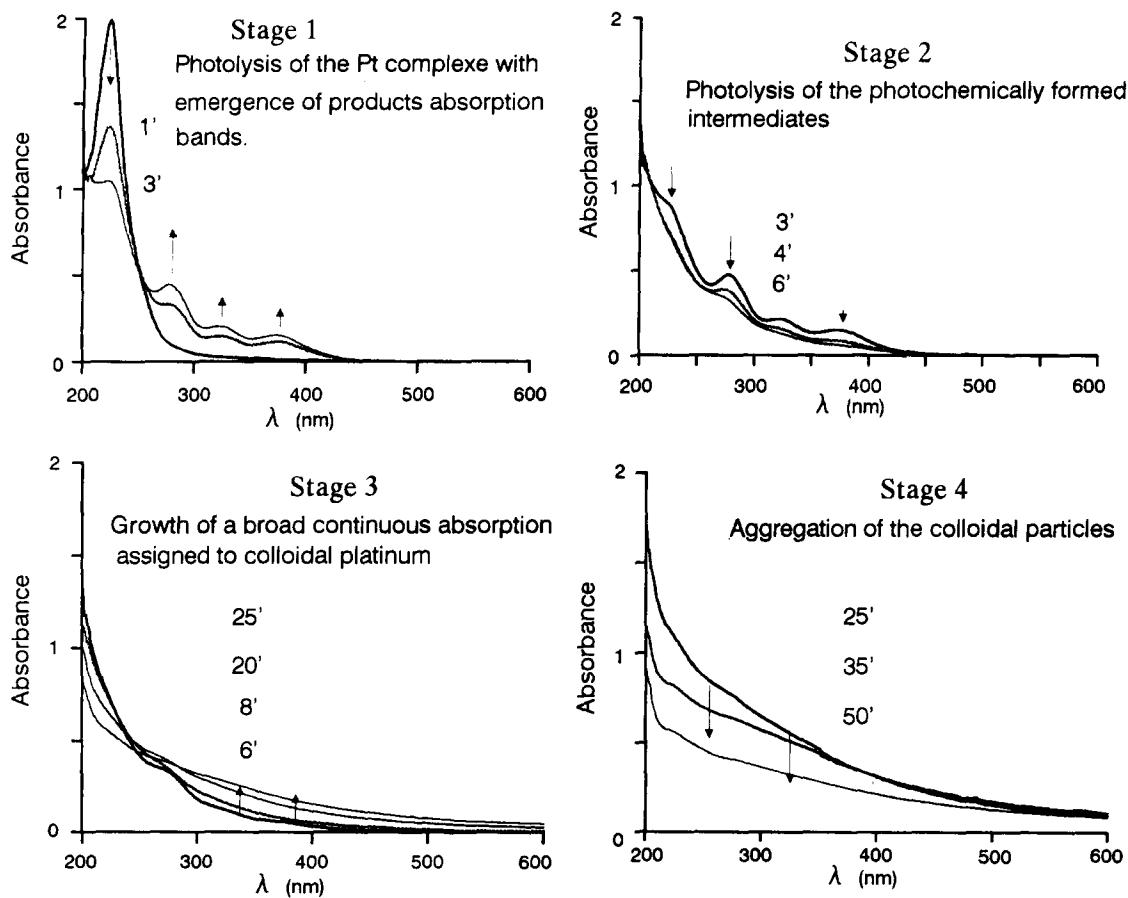


Fig. 4. UV-visible spectral changes during the photolysis of a with non-filtered UV light.

formed compound must be far more active than the thermally formed compound.

In the dark, the addition of a small amount of oct-1-ene (about 0.04 M) in a hexane solution of **b** ( $c = 1 \times 10^{-4}$  M) results in the emergence of an absorption band at 270 nm which is maximum after about 3 h at room temperature. If larger quantities of olefins were added (about 0.5 M) a second small band is observed at 309 nm which then decreases as long as the 270 nm band increases. After irradiation with glass-filtered light for only a few minutes the same 270 nm

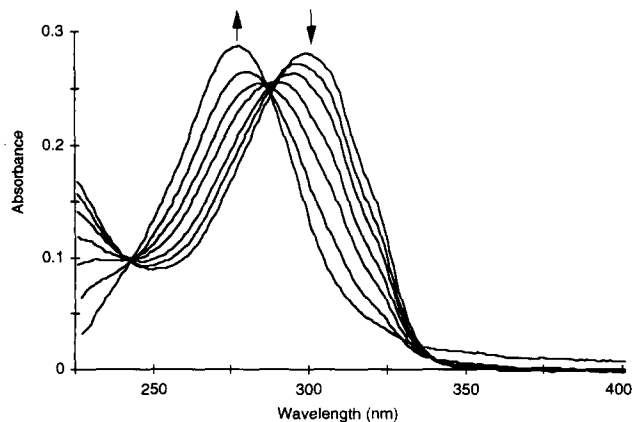


Fig. 5. Spectral changes during photolysis of **b** in glycol with non-filtered UV light.

absorption band appeared and raise to its maximum. This observation corresponds probably to the break-up of the dimer into the monomer. Under glass-filtered light, colloid formation is not observed after irradiation for 6 h but, if the glass filter is removed, greyish colloids are formed within 1 min. The same stable product between the complex and the olefin seems to be formed but the rate of formation is enhanced by light. If the solution containing the thermally formed species between complex and olefin is added to a polymerizable mixture and exposed to glass-filtered light, no influence on the hydrosilylation rate nor dark reaction rate is observed compared with the use of the crude complex **b** stock solution without previous addition of olefin.

The addition of an Si-H-containing compound, such as H1 or pentamethyl siloxane, results in reduction of the complex with the disappearance of the UV absorption band and emergence of the 270 nm peak and finally appearance of brownish colloidal platinum. If this solution is added to a polymerizable mixture, the dark reaction rate is enhanced and the induction time slightly reduced.

Obviously, the addition of vinyl or Si-H-containing compounds in solution of the  $\beta$ -dicarbonyl complex **b** leads first to a ligand exchange reaction and can be followed by increases in the absorption band near 270 nm, which is probably due to a monodentate acac ligand configuration or to free acetylacetonate. If the vinyl-substituted complex has no

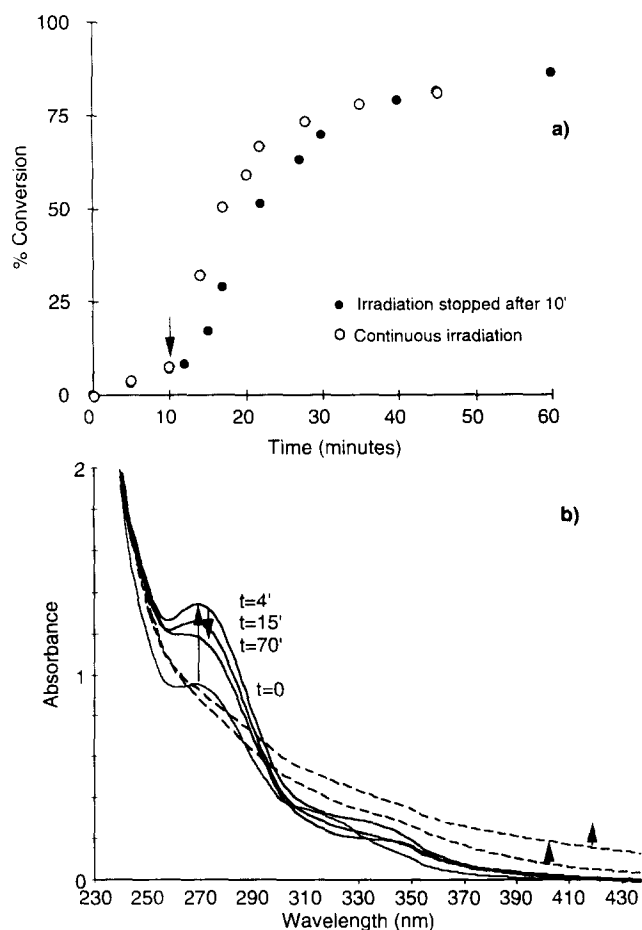


Fig. 6. (a) Disappearance of Si-H vs. time:  $\circ$ , continuous irradiation with a HPK125W lamp using the emission lines with wavelengths greater than 300 nm;  $\bullet$ , dark reaction after 10 min exposure to glass-filtered light. (b) UV-visible spectral changes (—) during the photohydrosilylation at  $t=0$ , 15 and 70 min and characteristic UV-visible absorption (---) of colloidal platinum observed 5 and 10 min after removing the glass filter ( $[\text{SiH}]_0 = 0.9 \text{ mol l}^{-1}$ ;  $[\text{oct-1-ene}]_0 = 1.13 \text{ mol l}^{-1}$ ; photoinitiator **b**; 200 ppm platinum equivalent; hexane as solvent).

significant influence on the photohydrosilylation or thermal hydrosilylation rate, reaction of an Si-H-containing compound leads to the formation of products which enhance the dark reaction. This more important effect of SiH on the thermal reaction is confirmed by the fact that the gel time of the polymerizable mixture containing both Si-vinyl and SiH parts depends on the reducibility of the platinum complex used (Table 1). The first reduction peak potentials reported in Table 1 show that the reducibility of the complexes decreases and their thermal stability by hydride attack of an Si-H silicone increases in the following order:  $\mathbf{c}, \mathbf{d} < \mathbf{b} < \mathbf{a}$ . The hydride affinity is reduced by electron donor groups at the carbonyl carbon atom of the  $\pi$  ligand. Consequently a silicone mixture in the presence of **a** as photoinitiator is thermally much more stable than in the presence of **d**.

Before irradiation, the addition of a mixture containing both pentamethylsiloxane and octene lead to the observation of two absorption maxima at 272 and 315 nm. During the first 4 min of irradiation with glass-filtered light, which cor-

respond approximately to the observed induction time in the hydrosilylation process, the absorption band at 272 nm increases whereas the second maximum is shifted to 335 nm. In a second stage the absorption bands of this primary photoproduct(s) decreases. After exposure for 15 min the period in which the hydrosilylation rate was maximum is achieved; however, the characteristic absorption of colloidal platinum is not observed (Fig. 6). Even after irradiation for 70 min, when the hydrosilylation reaction is completed (more than 90% conversion), no colloids are observed. The disappearance of the reactive compounds follows a nice 1:1 molar ratio even during the induction time.

If the glass filter is then removed, and the solution irradiated with 254 nm light, colloidal platinum is formed after a few minutes (Fig. 6(b)). Therefore colloidal platinum cannot be the active heterogeneous hydrosilylation catalyst in our system.

Moreover, if after 10 min exposure to glass-filtered light, and hence at the end of the induction period, the irradiation is stopped, the hydrosilylation reaction occurs in the dark with only a small rate decrease (Fig. 6(a)). This observation shows that hydrosilylation occurs via a photoactivated homogeneous process. As expected for an essentially photoactivated process, while the induction time decreases with increasing light intensity, the hydrosilylation rate is only slightly increased.

In the presence of sensitizers such as benzophenone or Michler's ketone the hydrosilylation reaction rate is increased and the induction time shortened (Fig. 7). The hydrosilylation reaction is almost completely inhibited by 2,2'-dimethoxy-2-phenylacetophenone (DMPA) and a radical trap such as phenothiazine but not if DMPA is added at the end of the induction period after about 8 min irradiation. A reaction step involving radicals plays a key role in the

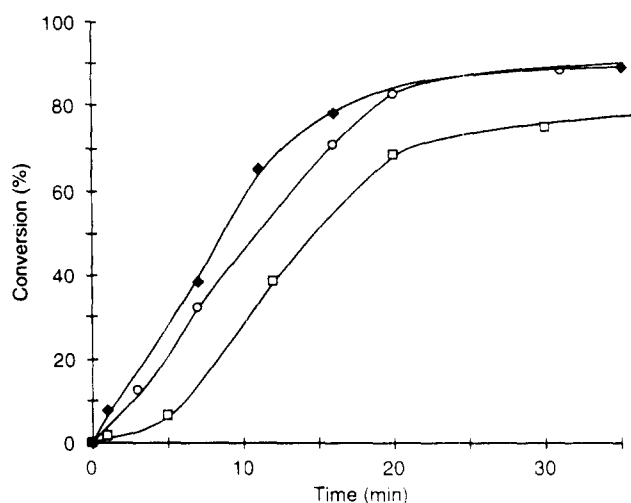
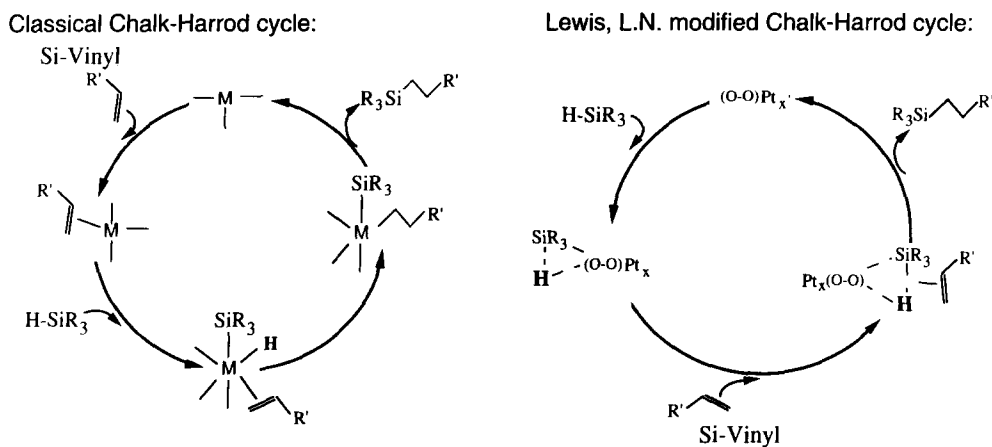


Fig. 7. Hydrosilylation sensitized with Michler's ketone under irradiation with 366nm light:  $\square$ , without sensitizer;  $\circ$ , with Michler's ketone in air-saturated solvent;  $\blacklozenge$ , with sensitizer in argon-flushed hexane ( $[\text{octene}] = 1.8 \text{ mol l}^{-1}$ ; hydrosilane H1 containing about 1.25 g of SiH parts in 100 g of oil;  $[\text{SiH}] \approx 1.8 \text{ M}$ ; catalyst **b**; 400 ppm platinum equivalent).



Scheme 1.

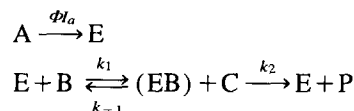
formation of the active catalyst and not in the hydrosilylation reaction.

Two mechanisms for the platinum-catalyzed hydrosilylation reaction are generally proposed: the classical Chalk-Harrod cycle which involves olefin addition to the metal center followed by oxidative addition of the hydrosilane [10] and the more recent proposals of Lewis [11] where the addition by Si-H precedes the nucleophilic attack of the olefin (Scheme 1). The latter mechanism explains more easily the observed electronic substituent effects on  $R_3SiH$  and on the olefin. In addition, compelling evidence of the presence of colloidal platinum as the active metal intermediates was given by Lewis [12] and Boardman [13]. The well-known induction period and the formation of the characteristic yellow color in this reaction were directly linked to the formation of the colloid [12]. However, the proposed mechanisms are based on experimental observations, but only kinetic studies designed to establish the rate-determining step of the hydrosilylation reaction can distinguish between the two proposals.

Moreover, it was seen previously that, in our experimental conditions, colloidal platinum appears only after the hydrosilylation reaction had finished. The question of the real active catalyst in the platinum photohydrosilylation process remains open.

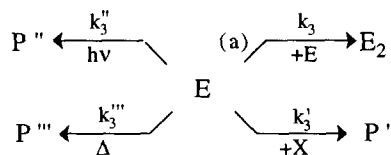
In order to answer this question and to elucidate the mechanistic and kinetic behavior of our system the photohydrosilylation reaction was followed by IR spectroscopy and UV-visible spectroscopy in solution.

The following reaction scheme can be proposed (Scheme 2). Whatever the nature of the active species E, cluster or platinum complex, it is photochemically generated from A with an overall quantum yield  $\Phi$  and a rate  $\Phi \cdot (I_a)^n$ , with  $I_a$  the incident light intensity and  $n$  the photochemical order. E reacts with B to form an intermediate EB. The hydrosilylation reaction occurs by addition of C and results in the formation of the hydrosilylation product P and regeneration of E.



Scheme 2.

B and C can be either the hydrosilane or the olefin. E can follow several ways of deactivation such as aggregation (a), chemical reaction (+X), photolysis ( $h\nu$ ) (Scheme 3).



Scheme 3.

If more than one deactivation pathway is effective, the expression of  $v_E$ , the rate of disappearance of E, can be quite difficult to establish. If only one deactivation pathway is rate determining,  $v_E$  can be simply expressed as a function of  $k_3$ .

Under stationary state conditions and with the knowledge that the rate of disappearance of B and C are the same, the following expression of the reaction rates is obtained:

$$\frac{(x + [C]) d[C]}{[C]([B]_0 - [C]_0 + [C])} = \frac{(x + [C]) d[B]}{[B]([C]_0 - [B]_0 + [B])} = -k_1 f(k_3) dt \quad (1)$$

with  $x = k_{-1}/k_2$ ;  $[B]_0$  and  $[C]_0$  are the initial concentrations of B and C.

Three cases must be considered.

(i) For  $x \ll [C]$ , the rate expression reduces to a first-order kinetic:

$$\ln \left( \frac{[B]}{[B]_0} \right) = -k_1 f(k_3) t \quad (2)$$

Interestingly the observed rate of hydrosilylation must then be independent of the initial concentration of C, the second insertion compound.

(ii) For  $x \gg [C]$  a pseudo-second-order expression is obtained:

$$\ln\left(\frac{[B][C]_0}{[B]_0[C]}\right) = -\frac{k_1}{x}f(k_3)([C]_0 - [B]_0)t \quad (3)$$

which in the particular case of equimolar concentrations of B and C reduces to

$$\frac{1}{[C]_0} - \frac{1}{[C]} = -\frac{k_1}{x}f(k_3)t \quad (4)$$

(iii) If  $x \neq [C]$ , the rate expression is

$$\left[ (x + [C]_0 - [B]_0) \ln\left(\frac{[B]}{[B]_0}\right) + x \ln\left(\frac{[C]_0}{[C]}\right) \right] = -k_1 f(k_3)([C]_0 - [B]_0)t \quad (5)$$

As for the case (ii),  $x \gg [C]$ , the rate expression depends on the concentrations of the two reactants. The results of the kinetic treatment for some experiments are given in Fig. 8.

Obviously the hydrosilylation is not pseudo-first order; the observed rate constant after the induction period depends on both the olefin and the Si-H initial concentrations. After an induction period and establishment of the steady-state regime the representation of Eqs. (3) and (5) vs. time gives good linear correlations. However, the linear correlation is better at the beginning of the reaction if an  $x$  value between

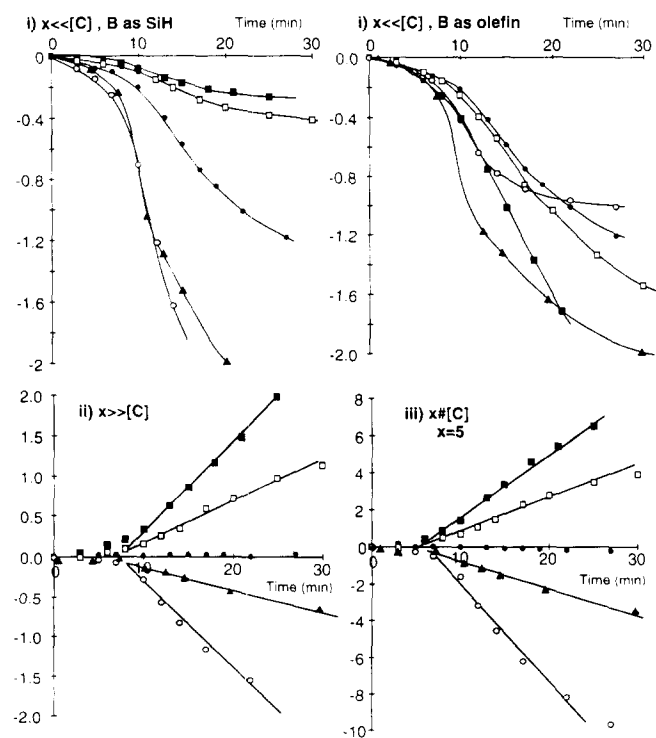


Fig. 8. Examples of kinetic treatments for the three cases considered for  $x$ .

Table 2

Results of the kinetic analysis represented in Fig. 9 where the olefine is oct-1-ene and the hydrosilane is pentamethylsiloxane ( $[b] = 1 \times 10^{-4} \text{ mol}^{-1}$ )

[SiH] ( $\text{mol dm}^{-3}$ )	[olefine] ( $\text{mol dm}^{-3}$ )	$\Delta = [\text{SiH}]_0 - [ ]_0$ ( $\text{mol dm}^{-3}$ )	$p(5)$
1	1.78	-0.78	-1.22
1	1.48	-0.48	-0.725
0.73	1.06	-0.33	-0.615
1.73	1.88	-0.15	-0.198
1	1.02	-0.02	-0.003
1	1	0	0
1.09	1.01	0.08	0.079
1	0.64	0.36	0.374
1	0.66	0.34	0.325
1.38	0.96	0.42	0.537

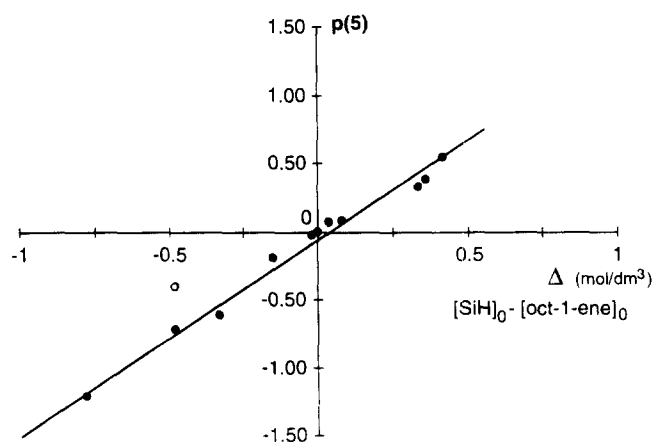


Fig. 9. Representation of  $p(5) = f(\Delta)$  with  $p(5)$  the slope of the straight line obtained by the plot of Eq. (5) vs. time.

2 and 5 is taken into consideration. The limiting step in our system (SiH: pentamethoxydisiloxane, olefin: oct-1-ene, **b** in hexane) seems to be the formation of the first intermediates EB. Further calculations are given by taking in Eq. (5) the hydrosilane as B, the first coordinant.

As expected, a linear relation between the slope  $p(5)$  of the linear part in Fig. 8(iii) and  $\Delta = [\text{SiH}]_0 - [\text{olefine}]_0$  is observed (Table 2 and Fig. 9).

Unfortunately, calculations which take alternatively C as the olefin and the hydrosilane gave the same results within experimental errors. It is not possible to distinguish between the two possibilities for the nature of C or B.

#### 4. Conclusion

The complexes studied are able to photoactivate efficiently a hydrosilylation reaction. In the presence of hydrosilane these compounds are reduced with the formation in the ultimate stage of colloidal platinum. The efficacy as hydrosily-

lation catalysts of the platinum complexes is inversely correlated to their reducibility. Under irradiation the complexes are decomposed via a triplet excited state and a radical stage into an active hydrosilylation catalyst and finally into less reactive colloidal platinum. The homogeneous character of the hydrosilylation is pointed out. The presence of growing colloidal particles as end products supports the hypothesis of cluster precursors as the possible active homogeneous catalysts. After this work was completed, Lewis and Salvi [14] reported for bis( $\beta$ -diketonates) platinum(II) the homogeneous character of the hydrosilylation reaction.

For the system studied, the proposed kinetic scheme applies very well but the relative reactivities of the hydrosilane, olefin and catalyst used lead to a case for which the effective hydrosilylation mechanism is not determinable. Moreover a kinetic study with other olefin-hydrosilane pairs and Pt(IV)-based catalysts is under way in order to show the influence of the nature of the reactants on the effective hydrosilylation mechanism.

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