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Platinum-Catalyzed Hydrosilylation of Allyl Aryl Ethers: Kinetic Investigation at Moderately High Dilution

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A kinetic investigation of the platinum-catalyzed hydrosilylation of some allyl aryl ethers by dimethylsilyl end groups of a monofunctional model oligomer or of a telechelic poly(dimethylsiloxane) was performed with use of quantitative infrared spectrophotometry. The reactivity of (allyloxy)benzene (1), examined at low initial concentration of reactants in toluene (ca. 10^{-2} equiv·L^{-1}), with dichloro(dicyclopentadiene)platinum(II) as a precursor of the catalyst was found to be different from the reactivity of the allylic groups of methyl 3,5-bis(allyloxy)benzoate (2). The reaction rate can be expressed by $v(1) = k_3[Pt][Si\text{-}H]^2$ in the case of reactions with 1 and by $v(2) = k_4[Pt]^2[Si\text{-}H]^2$ for reactions with 2. In addition to the determination of the values of the phenomenological rate constants deduced from measurements carried out under mild conditions, the obtained results lead us to propose some special features for the effective catalytic process.

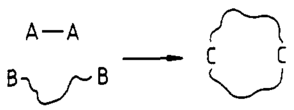
Introduction

In order to choose an elementary coupling process A + B → C to successfully perform a macrocyclization reaction as depicted in Scheme I, it is necessary to consider first the efficiency of the reaction from the point of view of final yield and of chemical selectivity. A second requirement is the need to perform the reaction at a very low concentration in order to induce ring formation, which competes with intermolecular reactions leading to oligomerization. In most cases, good experimental control of the reaction carried out according to the high-dilution principle[1] will ensure the production of significant yields of cyclic products.

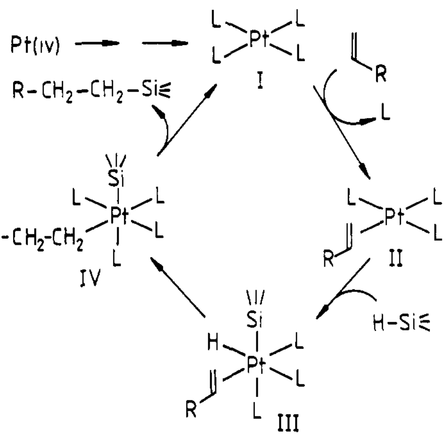
The synthesis of well-defined poly(dimethylsiloxane) (PDMS) macrocycles having a single functional side group is of current interest to us. One reasonable route to such ring-shaped polymers, with an ester side function for example, involves the coupling by hydrosilylation (eq 1) of the two allyloxy groups of resorcylic ester 2 with the two end groups of telechelic PDMS 4.

$$\mathrm{Ar{-}O{-}CH_2{-}CH{=}CH_2 + H{-}Si{\equiv} \longrightarrow Ar{-}O{-}CH_2{-}CH_2{-}CH_2{-}Si{\equiv}} \qquad (1)$$

Scheme I



Scheme II



Due to the limited number of functional groups present in the reactants, the platinum-catalyzed reaction is expected to afford selectively the desired coupling products if performed under standard and mild conditions in the presence of an appropriate catalyst. The relevance of the use of the dilution principle is nevertheless in question after examination of the accepted mechanism of the hydrosilylation of olefins by homogeneous catalysts derived from hexachloroplatinic acid.[2] The catalytic process outlined in Scheme II actually reveals some uncertainties concerning the very structure of intermediates I–IV. A crucial point is the nature of undefined ancillary ligands L, which could be any anionic or neutral species having some affinity for the transition metal. Such a ligand could be one of the following: a chloride ion coming from the platinum salt of oxidation state II or IV used as a precursor, a hydride resulting from the reduction of the platinum precursor by silicon hydride during the induction period, a molecule of coordinating solvent or an olefinic ligand. It is clear that an olefin that reacts with a silicon hydride to give the addition product shows a sufficiently high affinity for the platinum center.

After examination of an elementary model that takes into account the interactions of the metal center, ionic or neutral, with one olefin and some labile ligands of another type—and where the influence on the binding ability of one ligand on other ligands already present on the metal is deliberately neglected for simplicity—it is concluded that, in the presence of an excess of ligands of higher affinity that the olefin, the activity of the catalyst is partly if not totally inhibited. In the presence of species with lower affinity (as can be expected with toluene as the solvent), the olefin may displace more than one weak ligand and occupy several coordination sites. This last possibility would naturally make the high-dilution technique considerably less efficient for inducing ring formation. According to the model of Scheme II, the cyclization would indeed require that, in the key step III → IV, the

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(1) Rossa, L.; Vögtle, F. *Top. Curr. Chem.* **1983**, *113*, 1.

(2) (2) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253–330. Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407–445.

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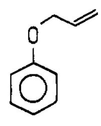
hydrogen atom inserts in the olefinic end of a nonsymmetric polymeric chain connected to the Pt by its dimethylsilyl end group. The maximum ratio of the intramolecular process competing with the intermolecular one in the sphere of the metal complex would then be levelled, at infinite dilution, to the value $^1/_2$ when two olefins are coordinated to the platinum and to $^1/_3$ for a complex with three olefins.

An updated rationalization of the results obtained by numerous authors since the publication of the early qualitative model of Chalk and Harrod[3] is obviously lacking. A kinetic investigation of the Pt-catalyzed hydrosilylation of some allyl aryl ethers was thus undertaken in order to obtain more precise information concerning the reaction mechanism and to check if this reaction can be advantageously used for the preparation of PDMS macrocycles. We now report the results obtained by reacting the Si–H function of dimethylsilyl end-capped silicon compounds with monofunctional model 1 and with diallyl derivative 2.



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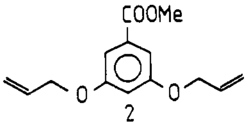
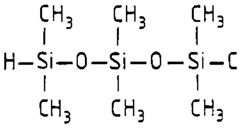


2

Experimental Part

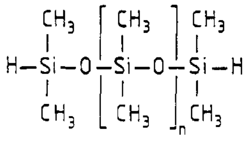
Starting Materials. Aryl Allyl Ethers. (Allyloxy)benzene (1) (Aldrich) was redistilled (bp = 63 °C). Methyl 3,5-bis(allyloxy)benzoate (2) was prepared from α-resorcylic acid[4] and twice recrystallized (mp = 35 °C).

Si–H Terminated Siloxanes. 1,1,1,3,3,5,5-Heptamethyltrisiloxane (3) (Petrarch Systems) was used as received. α,ω-Bis(dimethylsiloxy)poly(dimethylsiloxane) (4) free of the low molecular weight fraction was obtained by acid-catalyzed redistribution of octamethylcyclotetrasiloxane in the presence of tetramethyldisiloxane and subsequent devolatilization at 180 °C under high vacuum.[5] The number-average molecular weight $\bar{M}_n$ determined by IR titration of Si–H end groups was 3300 (see IR measurements). Dichloro(dicyclopentadiene)platinum(II) (5) was prepared from hexachloroplatinic acid (Merck) and cyclopentadiene dimer (Aldrich) according to ref 6 and twice recrystallized from tetrahydrofuran–dichloromethane (1:4, v/v) solutions. 5 was used as a stock solution in dichloromethane, the concentration of which (ca. 6 × 10^{-3} mol·L^{-1}) was checked by ultraviolet (UV) spectrophotometry (ε (232 nm) = 12 500 L·mol^{-1}·cm^{-1}).



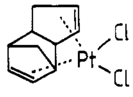
$H-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-CH_3$

3



$H-Si(CH_3)_2-O-[Si(CH_3)_2-O]_n-Si(CH_3)_2-H$

4



5

Solvent. Analytical grade toluene was distilled over sodium benzophenone ketyl complex immediately before use.

Reaction Conditions. Preparative runs were carried out as follows. To a heated mixture of allyl ether 1 (60 mg, 0.45 mmol) and of polymer 4 (750 mg, 0.455 mequiv of Si–H) in toluene (25 mL) was added the Pt salt 5 (0.5 μmol). The reaction was allowed to proceed for 2 h at 60 °C. The crude product, dimethyl phenoxypropyl-terminated PDMS 6, obtained after evaporation of the solvent, gave the following nuclear magnetic resonance (NMR) data recorded on a Bruker AW 300 spectrometer: ^{1}H NMR (CDCl$_3$) δ 0.1 (s, *n* × 6 H), 0.65 (m, 2 H), 1.80 (m, 2 H), 3.90 (t, 3 H, *J* = 7 Hz), 6.85 (m, 3 H), 7.25 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 0.8 (q), 1.0 (q), 14.3 (t), 23.6 (t), 70.5 (t), 114.6 (d), 120.4 (d), 129.4 (d), 159.2 (s).

In a similar procedure, methyl ester 2 (31 mg, 0.125 mmol) and trisiloxane 4 (57 mg, 0.255 mmol) in toluene (25 mL) were reacted in the presence of the Pt salt (0.75 μmol) for 4 h at 30 °C. The crude product, methyl bis-3,5-[[3-(heptamethyltrisiloxanyl)propyl]oxy]benzoate (7) gave the following spectroscopic and analytical data: IR (neat sample; ν, cm^{-1}) 2950 (str), 1725 (str), 1595 (str), 1450 (med), 1260 (str), 1050 (weak), 850 (weak), 800 (weak); ^{1}H NMR (CDCl$_3$) δ 0.10 (m, 42 H), 0.65 (m, 4 H), 1.80 (m, 4 H), 3.85 (s, 3 H), 3.90 (t, 4 H, *J* = 7 Hz), 6.60 (t, 1 H, *J* = 2.4 Hz), 7.10 (d, 2 H, *J* = 2.4 Hz); ^{13}C NMR (CDCl$_3$) δ 0.15 (q), 1.25 (q), 1.8 (q), 14.2 (t), 23.2 (t), 52.0 (t), 70.8 (t), 107.0 (s), 108.1 (d), 131.9 (s), 159.5 (s), 166.6 (s); mass spectrometry, *m*/*e* 692.3 (M$^+$, 7.2%), 221.2 (Me$_3$SiOSiMe$_2$ − OSiMe$_2$, 100%). Anal. Calcd for $C_{28}H_{60}O_8Si_6$ (693.30): C, 48.50; H, 8.72. Found: C, 48.41; H, 8.19.

Kinetic runs were performed on 50-mL solutions of reactants in toluene. The reaction flask was maintained in an essentially dry atmosphere controlled by silica gel water absorbants at the temperature given in the text with variations not exceeding 0.5 °C. The platinum salt solution (10–250 μL) was introduced at the moment considered as the initial time of the reaction, *t*. Samples to be quantitatively analyzed were transferred by means of a syringe into the IR cell at time *t*.

IR measurements were performed with a Perkin-Elmer 1430 spectrophotometer with pure toluene in the reference cell. The path length between the NaCl windows of the two cells was 0.5 mm. Absorption measurements at the wavenumber of the Si–H stretching band (maximum at 2125 cm^{-1} with base line set at 2200 and 2020 cm^{-1}) were standardized with toluene solutions of 3 of concentrations ranging from 1 to 50 mequiv·L^{-1}.

Results and Discussion

Reaction Conditions and Reaction Products. In order to avoid the ill-defined first steps leading to complex I (Scheme II) when a Pt(IV) compound such as hexachloroplatinic acid is the source of Pt catalyst, we have used for this study the Pt(II) derivative 5. This complex can be easily obtained with high purity, and it shows very good storage stability in the crystalline state as well as in diluted dichloromethane solutions, which give identical UV spectra over a period of several months. Since our final goal will lead us to perform the coupling reaction at low concentrations of reactants, the model study was carried out with a unusually low starting concentration of Si–H functions (ca. 10^{-2} equiv·L^{-1}). The good selectivity of the hydrosilylation reaction was checked under these conditions. The spectroscopic and analytical data for the crude products obtained from the reaction between 1 and polymer 4 or between ester 2 and trisiloxane 3 with 0.1–0.3 mol % of Pt derivative at moderate temperature (30–60 °C) (see the Experimental Part) support a single reaction process with high conversion. No significant trace of unreacted or isomerized olefin was detected in NMR spectra while the signals corresponding to the new trimethylenic link supported the selective addition of the silicon to the unsubstituted olefinic carbon of the allyloxy groups. The reaction written in eq 1 was thus considered as the only process leading to the concomitant consumption of one allyloxy and one Si–H group, the conversion of the latter being monitored by quantitative IR measurements.

Kinetics of the Reaction of Allyl Ether 1 with Model Trisiloxane 3. The variations of the molar fraction of unreacted Si–H end groups, $\alpha = [\text{Si–H}]_t/[\text{Si–H}]_0$, obtained with the most simple system using stoichiometric amounts of monofunctional compounds 1 and 3 reacted

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[3] Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

[4] Coqueret, X.; Wegner, G. *Makromol. Chem.*, in press.

[5] Coqueret, X.; Mercier, R.; Lablache-Combier, A.; Loucheux, C. *Eur. Polym. J.* **1988**, *24*, 639.

[6] Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 47.

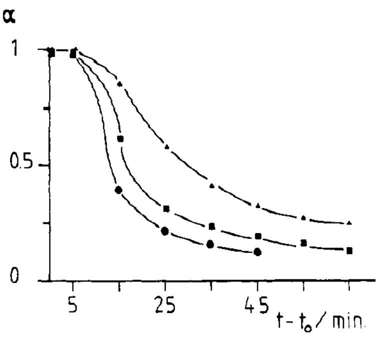

Figure 1. Reaction of 1 with 3. Plot of the decrease of α against reaction time. Conditions: $[\mathrm{Si{-}H}]_0 = 11.0$ mequiv·L^{-1}; $[\mathrm{C{=}C}]_0 = 10.8$ mequiv·L^{-1}; [Pt] = 1.35 (▲), 2.70 (■), 3.05 (●) μequiv·L^{-1}; $T = 25$ °C.

Table I. Second-Order Rate Constants, k_2, of the Reaction of 1 with 3 at 25 °C (Reactions Conditions as Given for Figure 1)

10^6[Pt]/equiv·L^{-1}	1.35	2.70	3.05
k_2/L·equiv^{-1}·min^{-1}	5.0	9.6	15.1

at 25 °C gave the curves of Figure 1. At this temperature, a rather long induction period of 5–10 min is observed, the reaction starting then with a rapid rate to give conversions of 75% or higher in the next 60 min. The experimental data were treated according to the standard procedure[7] assuming that the reaction rate can be expressed by

$$v = -\mathrm{d}[\mathrm{Si{-}H}]/\mathrm{d}t = -\mathrm{d}[\mathrm{C{=}C}]/\mathrm{d}t = k_n[\mathrm{Si{-}H}]^a[\mathrm{C{=}C}]^b \tag{2}$$

where $n = a + b$ is the overall reaction order.

Using the dimensionless variable α defined earlier, eq 2 can be rewritten as

$$-\mathrm{d}\alpha/\mathrm{d}t = k_n[\mathrm{Si{-}H}]_0^{\,n-1}\alpha^a(\alpha + f - 1)^b \tag{3}$$

where f is the ratio of the initial concentrations of reactants $[\mathrm{C{=}C}]_0/[\mathrm{Si{-}H}]_0$. Under stoichiometric conditions ($f = 1$), eq 3 becomes

$$-\mathrm{d}\alpha/\mathrm{d}t = k_n[\mathrm{Si{-}H}]_0^{\,n-1}\alpha^n \tag{4}$$

whose integrated form

$$F_n(\alpha) = \int \alpha^{-n}\,\mathrm{d}\alpha \tag{5}$$

can allow the determination of n by the graphical method. Among the possible corresponding integral functions tested for the first integer values of n, only those of second order

$$F_2(\alpha) = \alpha^{-1} - 1 \tag{6}$$

show an acceptable linear dependence upon time (Figure 2), suggesting that $n = 2$. The values of the second-order rate constants, k_2, deduced from the slopes, $k_{\mathrm{obs}} = k_2[\mathrm{Si{-}H}]_0$, of the three curves indicate a probable first-order dependence on the concentration of platinum salt (Table I).

A more accurate determination of kinetic parameters nevertheless requires a shorter length for the induction period in order to extend the useful part of the curves. The transient phenomenon is most probably the consequence of a slow process controlling the emergence of the active catalytic species. Its origin may well be found in the slow dissociation of parent salt 5 permitting an exchange of ligands. A slight thermal activation by an increase in temperature of 5 °C is sufficient to reduce the induction phenomenon to a period shorter than 5 min, allowing a better interpretation of the experimental results. The plots of Figure 3 obtained under stoichiometric conditions at 30 °C allow an unambiguous discrimination to be made between possible integer orders. $F_2(\alpha)$ indeed gives a straight line until 85% conversion.

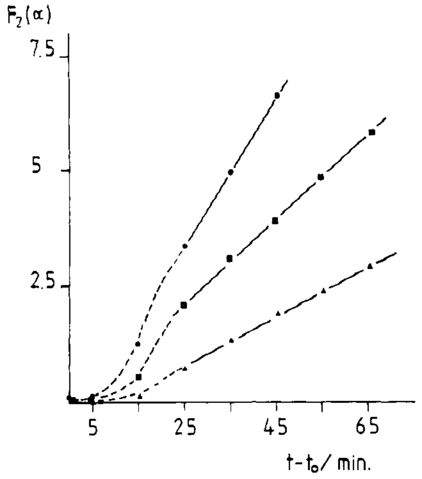

Figure 2. Reaction of 1 with 3. Plot of the variations of integrated relation $F_2(\alpha)$ against reaction time. Conditions: $[\mathrm{Si{-}H}]_0 = 11.0$ mequiv·L^{-1}; $[\mathrm{C{=}C}]_0 = 10.8$ mequiv·L^{-1}; [Pt] = 1.35 (▲), 2.70 (■), 3.05 (●) μequiv·L^{-1}; $T = 25$ °C.

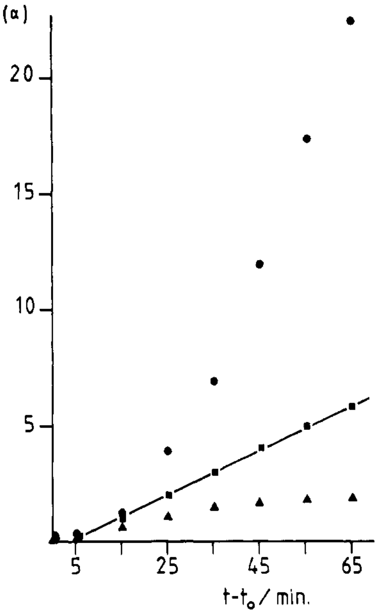

Figure 3. Reaction of 1 with 3. Plot of the time dependence of integrated relation $F_n(\alpha)$ for $n = 1$ (▲), 2 (■), or 3 (●). Conditions: $[\mathrm{Si{-}H}]_0 = 10.3$ mequiv·L^{-1}; $[\mathrm{C{=}C}]_0 = 10.0$ mequiv·L^{-1}; [Pt] = 2 μequiv·L^{-1}; $T = 30$ °C.

Considering now an overall reaction order $n = 2$ as the sum of integer partial orders, the linearity must be observed for the integral form given by eq 4 if $a = 2$.

$$F_2(\alpha) = \frac{1}{f-1}\ln\frac{\alpha + f - 1}{\alpha f} \qquad a = b = 1 \tag{7}$$

$$F_2(\alpha) = \frac{1}{\alpha + f - 1} - \frac{1}{f} \qquad b = 2 \tag{8}$$

The corresponding curves obtained from experiments carried out with a 2-fold excess of olefin 1 ($f = 2$) are plotted in Figure 4, which shows that the rate is second-order dependent on the Si–H concentration. The influence of the amount of platinum salt introduced was finally

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[7] Bamford, C. H.; Tipper, C. F. *Comprehensive Chemical Kinetics*; Elsevier: Amsterdam, 1969.

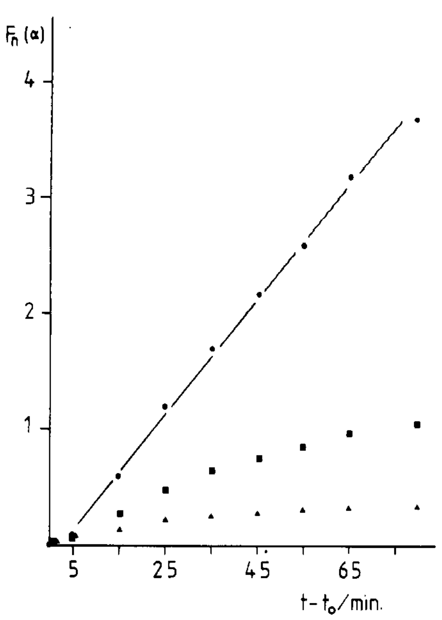

Figure 4. Reaction of 1 with 3. Plot of the time dependence of $F_2(\alpha)$ for different partial reaction orders of $a = 2$ (●), $a = b = 1$ (■), and $b = 2$ (▲). Conditions: $[\text{Si-H}]_0 = 10.25$ mequiv·L^{-1}; $[\text{C}{=}\text{C}]_0 = 20.3$ mequiv·L^{-1}; [Pt] = 1.1 μequiv·L^{-1}; T = 28 °C.

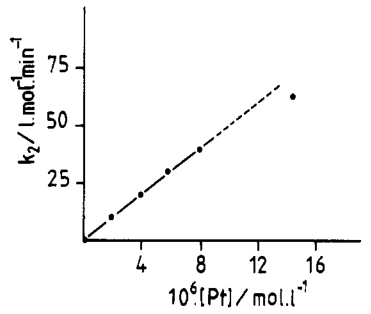

Figure 5. Reaction of 1 with 3. Variations of the second-order rate constant with the concentration in Pt salt. Conditions: $[\text{Si-H}]_0 = 10.3$ mequiv·L^{-1}; $[\text{C}{=}\text{C}]_0 = 10.0$ mequiv·L^{-1}; $T = 30$ °C.

examined under stoichiometric conditions, and the first-order dependence of k_2 upon [Pt] is exemplified by the results given in Figure 5. The phenomenological reaction rate can thus be expressed by eq 9, which applies to the given experimental conditions.

$$v = k_3[\text{Pt}][\text{Si-H}]^2 \qquad k_3 = 5 \times 10^6\ \text{L}^2\cdot\text{equiv}^{-2}\cdot\text{min}^{-1} \quad (9)$$

Kinetics of the Reaction of Resorcylic Ester 2 with Trisiloxane 3. A similar series of experiments was performed at 30 °C with diallylic compound 2. Under stoichiometric conditions, the plot of the integrated relations $F_n(\alpha)$ as a function of the reaction time (Figure 6) for the first integer values of n showed that an overall order $a + b = 2$ was obeyed by this system up to more than 80% conversion. The good linearity of $F_2(\alpha)$ suggests that if a chelate effect increases the stability of a complex between a Pt center and the starting bis(allyloxy) compound 2, it has no significant kinetic influence on the hydrosilylation process. The reactivity of the second allyloxy group indeed seems to be unchanged after hydrosilylation of the first unsaturation. Under nonstoichiometric conditions, with $f = 1$, the reaction rate was found to be independent of the olefin concentration (Figure 7), thus giving consistency to the preceding observation. An unexpected result is the influence of the Pt salt concentration on the second-order rate constant, k_2, measured for a series of experiments performed under stoichiometric conditions at 30 °C. Over a wide range of concentration (Figure 8), k_2 showed a linear

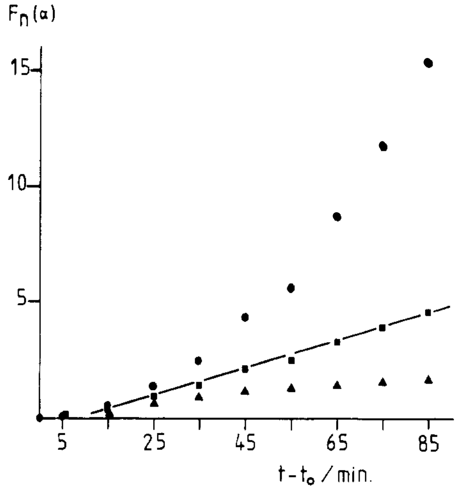

Figure 6. Reaction of 2 with 3. Plot of the time dependence of integrated relation $F_n(\alpha)$ for $n = 1$ (▲), 2 (■), or 3 (●). Conditions: $[\text{Si-H}]_0 = 10.2$ mequiv·L^{-1}; $[\text{C}{=}\text{C}]_0 = 10.0$ mequiv·L^{-1}; [Pt] = 15.6 μequiv·L^{-1}; $T = 30$ °C.

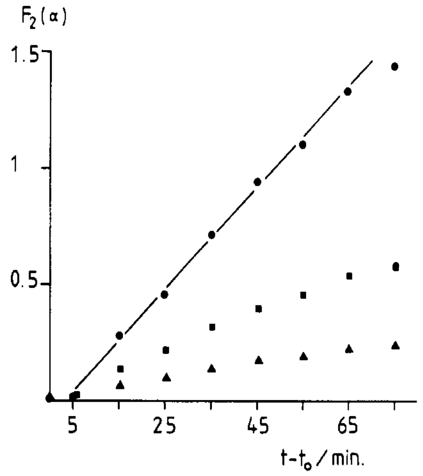

Figure 7. Reaction of 2 with 3. Plot of the time dependence of $F_2(\alpha)$ for different partial reaction orders $a = 2$ (●), $a = b = 1$ (■), and $b = 1$ (▲). Conditions: $[\text{Si-H}]_0 = 10.2$ mequiv·L^{-1}; $[\text{C}{=}\text{C}]_0 = 19.7$ mequiv·L^{-1}; [Pt] = 9.2 μequiv·L^{-1}; $T = 30$ °C.

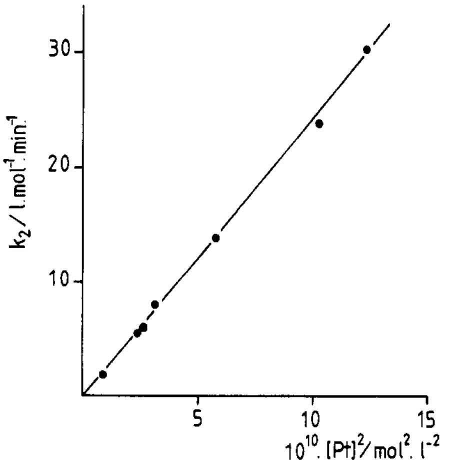

Figure 8. Reaction of 2 with 3. Plot of the variations of k_2 against the square of the concentration in Pt salt. Conditions: $[\text{Si-H}]_0 = 10.3$ mequiv·L^{-1}; $[\text{C}{=}\text{C}]_0 = 10.0$ mequiv·L^{-1}; $T = 30$ °C.

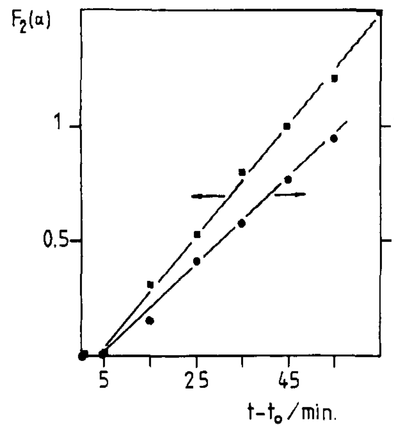

Figure 9. Reaction of 2 with 4. Plot of the time dependence of integrated relation $F_2(\alpha)$. Conditions: [Pt] = 8.0 (■), 23.0 (●) μequiv·L^{-1}; $[\text{Si-H}]_0$ = 10.8 mequiv·L^{-1}; $[\text{C=C}]_0$ = 10.1 mequiv·L^{-1}; T = 30 °C.

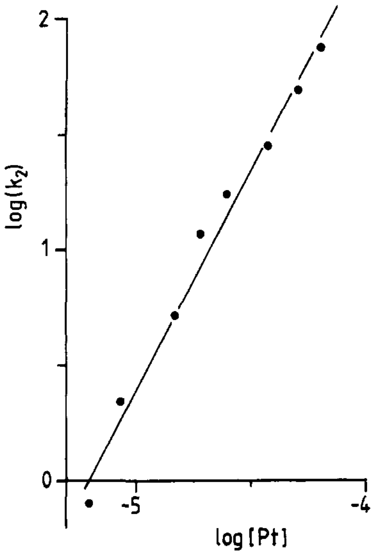

Figure 10. Reaction of 2 with 4. Log–log plot of the variations of k_2 (L·equiv^{-1}·min^{-1}) with the concentration in Pt salt (equiv·L^{-1}). Conditions: $[\text{Si-H}]_0$ = 10.8 mequiv·L^{-1}; $[\text{C=C}]_0$ = 10.1 mequiv·L^{-1}; T = 30 °C.

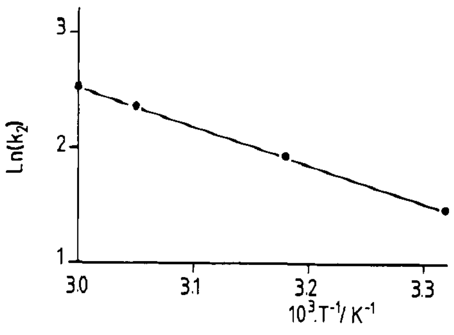

Figure 11. Reaction of 2 with 4. Arrhenius plot of the variations of the second-order rate constant, k_2, with the temperature. Conditions: $[\text{Si-H}]_0$ = 10.8 mequiv·L^{-1}; $[\text{C=C}]_0$ = 10.1 mequiv·L^{-1}; [Pt] = 9.2 μequiv·L^{-1}.

variation with the square of [Pt], the reaction rate being given by

$$v = k_4[\text{Pt}]^2[\text{Si-H}]^2 \qquad k_4 = 2.4 \times 10^{10}\ \text{L}^3\cdot\text{equiv}^{-3}\cdot\text{min}^{-1} \tag{10}$$

Kinetics of the Reaction of Resorcylic Ester 2 with Telechelic PDMS 4. The main kinetic features coming from the results reported in the preceding section were observed for the reaction of ester 2 with telechelic polymer 4 as well. The linearity of the integrated relation $F_2(\alpha)$ is shown on the plots of Figure 9. Due to the relatively short length of the polymer chains of 4, a kinetic effect due to the possible intramolecular nature of the second hydrosilylation[2] could have been observed if the rate-determining step had involved a bimolecular collisional complex between the end groups of a nonsymmetrical chain. This was obviously not the case, the high molecularity of the process implying more complex equilibria as indicated by the kinetic results. The linear dependence of k_2 with $[\text{Pt}]^2$ is again supported by the slope of the log–log curve of Figure 10, whose value is actually close to 1.88. Finally, the effect of the temperature on the rate of reactions carried out at stoichiometry was examined. The Arrhenius plot of Figure 11 yields an apparent activation energy of low value $E^* = 29\ 10^3$ J·mol^{-1} for a concentration in Pt salt of 10^{-4} mol·L^{-1}.

Discussion. The kinetic features observed with 1 as a reference compound and those obtained with the more functional ester 2 enable a mechanistic outline to be proposed for the hydrosilylation of the allyl ethers by hydrosiloxanes under dilute conditions. The first point to be discussed is the homogeneous nature of the catalysis. It was recently suggested that the active species is Pt(0) free of ligand resulting from the reduction of Pt(II) or Pt(IV) salts or from the degradation of Pt(0) diolefin complexes in the presence of Si–H functions.[8] The reported work is in fact essentially based on the characterization and the study of platinum colloids obtained by reacting Pt derivatives with a 6–60-fold excess of silane in the absence of olefin and in dichloromethane, a solvent having poor coordinating aptitude. In our study, the stable homogeneous complex 5 was introduced in reaction mixtures rich in ligand, $10^2 < [\text{C=C}]_0/[\text{Pt}] < 10^5$. An aromatic solvent was used, and the reaction temperature was kept deliberately low. We indeed observe the characteristic darkening of the solution, indicating the formation of a platinum colloid, but only at a long time after the reaction is considered to be complete. This phenomenon, described in the earliest papers on this subject,[3] is observed when concentration or temperature effects reduce the stability of Pt olefin complexes. The formation of colloidal platinum in the late stage of the reaction is thus clearly not sufficient to rule out the hypothesis of homogeneous catalysis, which might now receive some kinetic evidence. A second major question relates to the degree of oxidation of the active catalyst in the steps preceding the oxidative addition of the hydrosilane to the complex. Isolated complexes of Pt(0) such as Pt(COD)_2[9,10] (COD = 1,5-cyclooctatetradiene) are known to be very efficient catalysts for the hydrosilylation of olefins.[11] It has been shown also that $\text{Pt(PhCH=CH}_2)_3$ is generated in styrene by reacting $\text{Pt}^{\text{II}}\text{Cl}_2\text{(COD)}$, a complex similar to 5, with 2 equiv of triethylsilane.[12] A styrene solution of this new complex is active for the hydrosilylation of styrene by Et_3SiH. Applying Scheme II to this example, complexes II and III are identical and should be rewritten Pt^0L_3 (L = styrene molecule). The subsequent steps leading to hydrosilylation products could take place as described in Scheme II. The

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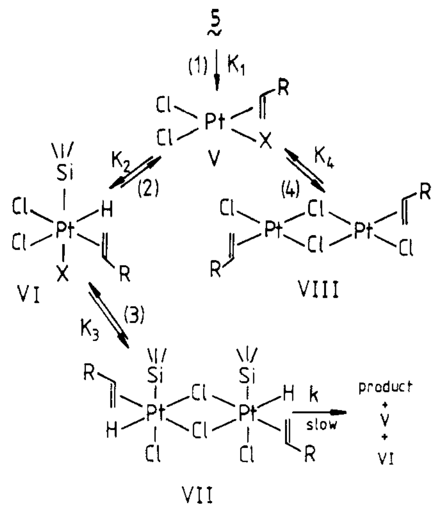
systems we have studied are nevertheless different from this one on the following points: (i) The source of Si–H in our case is a dimethylsiloxane known to have a reactivity contrasting from those of alkyl-, aryl-, or halosilanes.[13] (ii) The olefins are allylic ethers whose oxygen can significantly change the coordination properties of the π-ligand. (iii) The reaction was carried out with a normally high $[C{=}C]_0/[Pt]$ ratio but a rather low absolute concentration in olefin. The starting point of our interpretation arises from the unexpected rate laws observed for both systems **1** or **2** with hydrosiloxanes, and particularly from eq 10, which clearly suggests the existence of dinuclear Pt species as intermediates. The formation of dinuclear complexes requires σ-bonding ligands, such as halides,[14] hydrides,[15] or phosphides,[16] which can give rise to stable planar-bridged structures. The two former types of ligands are known to exist or to be readily available in the reaction mixture, but hydride anion is not believed to act as a bridging ligand in a species containing two octahedral Pt complexes. On the contrary, our hypothesis of a dimeric complex of Pt(IV) with bridging chlorides and one, two, or three σ-ligands in the coordination sphere is substantiated by several examples of stable or intermediate structures in Pt(IV) chemistry.[17] Moreover, the kinetic argument for the existence of a dinuclear key intermediate is strongly reminiscent of a situation reported for the hydrogenation of olefins with $Rh^{I}Cl(PPh_3)_3$ as a homogeneous catalyst.[18] A dimerization equilibrium was proposed to account for some unexpected effect of the rhodium concentration on the hydrogenation rate, and a dimeric complex $[Rh^{III}(\mu\text{-}Cl)H_2(PPh_3)]_2$ with σ-ligands on each metal center was isolated and characterized. This d^6 dinuclear complex has many of the features of the Pt(IV) intermediate we propose in the following mechanism.

We believe that the hydrosilylation products of **1** and **2** are obtained from the same type of dinuclear Pt(IV) intermediate and that the difference in rate law arises from a chelate effect possible with the trifunctional compound **2**. We have already mentioned the absence of change in reactivity during hydrosilylation of **2**. A determining effect on the mechanism of an internal Pt diolefin complex is therefore very improbable. On the other hand, the symmetry of ester **2** and the affinity of carbonyl and carboxylic groups for the metallic center allow a second chelating interaction when at least one allyl function can coordinate.[19]

The two reasonable hypotheses of the dinuclear Pt complexes and of the olefin–carboxylate chelate effect in intermediates containing ester **2** or one of its derivative as a ligand allow the formulation of the mechanism depicted in Scheme III. The rearrangement from a π-olefin to a σ-alkyl complex by transfer of hydrogen as shown in step III → IV of Scheme II, but in the coordination sphere of only one platinum of complex VII, is considered the rate-determining step of the process. The preceding reversible steps, (equilibrium 16) **5** → V and (equilibrium 17) V → VI, are formally written in Scheme II. The difference in the dependence of rate laws upon the concentration of platinum salt can be explained by assuming an additional equilibrium (equilibrium 19) between V and dinuclear complex VIII as observed for styrene complexes of Pt(II).[12] Under standard concentration conditions, the molar fraction of dimer VIII at equilibrium is certainly strongly affected by the nature of the coordinating olefin. A chelate effect in complex V is indeed possible only with **2** as a bidentate ligand. Elementary computations show that with the same molar ratios $[C{=}C]_0/[Pt]_0$, an increase of the overall dilution has a strong additional effect shifting the equilibrium (equilibrium 19) toward the formation of the dimeric species with **1** as a simple ligand and to the mononuclear complex with (allyloxy)benzoate ester **2**. The kinetic consequences of this situation are developed below.

Scheme III[a]



[a] Equilibrium 16: in the presence of olefin **1** or **2**. If **1**, then X = $RCH{=}CH_2$ = **1**; if **2**, X = carboxylate of ester **2** coordinating by one of the allylic groups. Equilibrium 17: reversible addition of the Si–H function. Equilibrium 18: reversible dimerization of VI with elimination of two ligands of X. Equilibrium 19: reversible dimerization of V with elimination of two ligands X. The stereochemistry of dimers VII and VIII as depicted in this scheme is arbitrary.

Consider first the hydrosilylation of **2**. The corresponding reaction rate, $\upsilon(2)$, is given by eq 11 (where C is the concentration of the species indicated) and the mass balance applied to platinum is given by eq 12.

$$\upsilon(2) = kC(\mathrm{VII}) = kK_{18}C^2(\mathrm{VI}) = k(K_{17})^2K_{18}C^2(\mathrm{V})[\mathrm{Si{-}H}]^2 \tag{11}$$

$$[\mathrm{Pt}] = C(\mathbf{5}) + C(\mathrm{V}) + C(\mathrm{VI}) + 2C(\mathrm{VII}) + 2C(\mathrm{VIII}) \tag{12}$$

The amount of platinum engaged in **5** as well as in intermediate species VI and VII can be neglected with respect to stable species V and VIII. Because of the chelate effect in V, equilibrium 19 is inoperative and $C(\mathrm{V}) \approx [\mathrm{Pt}]$. Equation 11 thus becomes

$$\upsilon(2) = k(K_{17})^2K_{18}[\mathrm{Pt}]^2[\mathrm{Si{-}H}]^2 \tag{13}$$

When the reaction is performed with **1**, the reaction rate is then given by

$$\upsilon(1) = kC(\mathrm{VII}) = kK_{18}C^2(\mathrm{VI})C^{-2}(1) = k(K_{17})^2K_{18}C^2(\mathrm{V})[\mathrm{Si{-}H}]^2C^{-2}(1) \tag{14}$$

The concentration of complex V is controlled by equilibrium 19, $C^2(\mathrm{V}) = K^{-1}{}_{19}C(\mathrm{VIII})C^{-2}(1)$, and $C(\mathrm{VIII}) \approx [\mathrm{Pt}]/2$. Equation 14 becomes

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$$v(1) = k\frac{(K_{17})^2}{2K_{19}}K_{18}[\mathrm{Pt}][\mathrm{Si{-}H}]^2 \qquad (15)$$

Conclusion

The results of the kinetic study of the Pt-catalyzed hydrosilylation of allyl aryl ethers 1 and 2 provide expressions for the corresponding rate laws as functions of the concentration of silane and of the platinum salt. The unusual conditions of high dilution, which are probably essential to obtain the observed results, appear to be an interesting tool for mechanistic studies in coordination chemistry. The change in apparent order in platinum depending on the nature of the olefin was clearly unexpected but leads us to propose a mechanism involving a dinuclear homogeneous catalyst. Our interpretation contrasts with recent findings concerning the hydrosilylation of monoolefins. The nature of the reactants as well as the reaction conditions are so different that alternative pathways are not in opposition. With regard to the merit of the hydrosilylation of 2 for the preparation of monofunctional macrocycles, one can conclude that the reaction shows good selectivity at moderately high dilution. The control of the reaction in more diluted media will now be made much easier by the knowledge of rate laws and constants. Moreover, the proposed intermediates VI and VII have only one resorcylic derivative as a ligand; ester 2 can therefore be regarded as a suitable substrate to take advantage of the dilution principle.

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Single-Crystal Neutron Diffraction Study of $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$, a Model for One Type of Chemisorbed Ethylene

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The molecular structure of $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$ (1) has been determined by single-crystal neutron diffraction in order to establish the hybridization at the carbon atoms of the bridging ethylene. The final values for the lattice constants are a = 7.308 (2) Å, b = 13.448 (3) Å, c = 13.482 (4) Å, β = 101.25 (2)°, and V = 1299.5 (3) Å^3; the space group ($P2_1/c$) and value of Z (4) are known from an earlier X-ray study.[1] The results show that the ethylene carbons have almost completely rehybridized to sp^3. The C–C bond length in 1 (1.5225 (26) Å) is comparable to that in ethane and that of ethylene chemisorbed on Pt(111)—suggesting that the ethylene ligand in 1 is a good structural model for ethylene chemisorbed on Pt(111). The Os_2C_2 ring of 1 is distorted further away from planarity than the Os_4 ring of $Os_4(CO)_{16}$ or the C_4 ring of cyclobutane.

Introduction

The unique structural aspects of $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$ (1) were apparent from the X-ray diffraction study carried out by some of us shortly after its preparation in 1982.[1] Whereas countless structures were known in which an ethylene ligand was coordinated to a single transition metal, 1 contained an ethylene which bridged two metals to form a four-membered ring. Just as conventional ethylene complexes suggested one way (Figure 1a) in which ethylene could be chemisorbed onto a metal surface, the diosmacyclobutane ring in 1 resembled the di-σ-bonded arrangement (Figure 1b) that had been proposed[2] as another way in which ethylene could be chemisorbed. The latter analogy has since found practical use: 1 has proven to be an excellent vibrational model for di-σ-bonded ethylene chemisorbed on Pt(111) at low temperatures.[3]

A few reports of dimetallacyclobutanes had appeared before ours on 1. In 1972 Carty, Palenik, and co-workers had reported a diiron adduct of maleic anhydride;[4a] in 1977 Green, Stone, and co-workers had reported a dipalladium adduct of C_2F_4;[4b] in 1981 Theopold and Bergman had reported an unstable dicobalt adduct of benzocyclobutadiene.[4c] However, only the first of these dimetallacyclobutanes had been characterized by X-ray crystallography, and none had contained ethylene itself. Soon after we prepared 1, studies in our laboratory, in the laboratory of Prof. Josef Takats at the University of Alberta,[5] and elsewhere[6] revealed that 1 was the parent compound for an extensive series of substituted diosmacyclobutanes (e.g., $(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHCO_2Me)Os_2(CO)_8$ (2)[5a,c,d] and $(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHC_6H_{13})Os_2(CO)_8$[6b]) and diosmacyclobutenes (e.g.,

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