Organometallic Chemical Vapor Deposition of Platinum. Reaction Kinetics and Vapor Pressures of Precursors[1]

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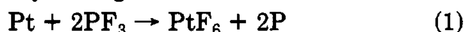
The kinetics of chemical vapor deposition of platinum from cyclopentadienyltrimethylplatinum ($CpPtMe_3$) and (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$) under hydrogen atmosphere have been studied. For deposition on substrates heated to between 90 and 180 °C, the platinum films are essentially pure, containing less than 1.0 atom % carbon and oxygen and no other impurities. The ligands on the organometallic complexes are quantitatively converted into their hydrocarbon analogues: 1 mol of $CpPtMe_3$ produces 3 mol of methane and 1 mol of cyclopentane, and 1 mol of $MeCpPtMe_3$ produces 3 mol of methane and 1 mol of methylcyclopentane. The decomposition reaction is initially very slow and then rapidly accelerates due to autocatalysis by the fresh platinum deposit. The rate of the initial slow decomposition depends on the substrate composition, indicating that this reaction is also heterogeneous. Using $CpPtMe_3$, the activation energy for initiation of deposition (i.e., for the induction period) is 115 ± 10 kJ/mol on glass and 60 ± 15 kJ/mol on Teflon. The heats of sublimation of $CpPtMe_3$ and $MeCpPtMe_3$ are 71.2 ± 2.1 and 71.5 ± 2.1 kJ/mol, respectively. The heat of vaporization of $MeCpPtMe_3$ is 43.6 ± 1.3 kJ/mol. The vapor pressures of $CpPtMe_3$ and $MeCpPtMe_3$ at 23 °C are 0.045 and 0.053 Torr.

Introduction

Organometallic chemical vapor deposition (OMCVD) has become one of the preferred processes for generating thin film devices. Many different materials can be deposited by this technique, including metals, semiconductors, and ceramics.[2-7] Recently, much progress has been made in identifying suitable precursors for chemical vapor deposition of transition-metal films in high purity.[8-12] In particular, several excellent precursors have been identified for the deposition of platinum.

A summary of prior work on the OMCVD of platinum is shown in Table I. Rand was the first to study this process.[13-15] He examined three complexes, Pt(acetylacetonate)$_2$, $Pt(CO)_2Cl_2$, and $Pt(PF_3)_4$. Decomposition of the acetylacetonate complex at 550 °C generated a film containing approximately the same amount of carbon and platinum. In this complex, the Pt–O bonds are of comparable strength to the internal C–C bonds of the ligand, so that the ligand decomposes together with the complex. Deposition using the carbonyl chloride produced wrinkled films which did not adhere to the substrate. In addition, the complex slowly decomposed to $PtCl_2$ while it was held at 125 °C during the experiment. Rand obtained the best results with the trifluorophosphine complex. At 250 °C in 1 atm of hydrogen, adherent and bright films of 100-Å platinum crystallites were obtained. However, the films were contaminated with phosphorus from the ligands. The phosphorus segregated to the platinum/silicon interface (about 1 atom %) and to the outer surface (about 15 atom %).[15] The phosphorus contamination can be rationalized by the strong thermodynamic driving force for oxidation of the platinum by the ligand:



$$Pt + 2PF_3 \rightarrow PtF_6 + 2P \qquad (1)$$

We thought that Rand's results could be improved upon by using all-hydrocarbon complexes of platinum, in particular, $CpPtMe_3$ and $MeCpPtMe_3$, and by depositing the film in the presence of hydrogen.[16-18] The Pt–C bonds in this complex are easily hydrogenated, yielding as the only products platinum metal and volatile hydrocarbons.[19-21] An additional advantage of these source molecules is they are volatile at room temperature. Also, $MeCpPtMe_3$ is a liquid above 30 °C and can be vaporized in a more controlled fashion than a solid source.

We found that the platinum films grown from $CpPtMe_3$ and $MeCpPtMe_3$ in hydrogen were of exceptional purity.[16] Platinum was the only element detected by X-ray photoelectron spectroscopy and Auger electron spectroscopy after lightly sputtering the film with argon ions. The carbon 1s and oxygen 1s photoelectron peaks were not discernible in the spectra, indicating that less than 1 at. % of these impurities were present. As shown in Table I, this purity is much higher than that obtained with other

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(1) This work is taken in part from the M.S. dissertation of H. Thridandam, UCLA, 1990, and in part from the Ph.D. dissertation of Z. Xue, UCLA, 1989.

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Table I. Summary of Previous Studies of Platinum CVD

source	source temp, °C	deposition temp, °C	carrier gas	impurities (atom)	ref
$Pt(acac)_2$[a]	150	550	vacuum	50% C	Rand[13]
$Pt(PF_3)_4$	125	400	H_2 + CO	5% P	Rand[13]
$Pt(CO)_2Cl_2$	25	250	H_2	<1% C,Cl	Rand[13,15]
$CpPtMe_3$	25	180	H_2	<1% C,O	Chen et al.[16]
$MeCpPtMe_3$	25	120	H_2	<1% C,O	Xue et al.[18]
$PtMe_2(MeNC)_2$	40–120	250	H_2	5% C	Puddephatt[22–24]
$(COD)PtMe_2$[b]	40–120	250	H_2	4% C, 2% O	Puddephatt[22–24]
$(COD)PtMe(\eta^1\text{-}Cp)$	40–120	250	H_2	5% C	Puddephatt[22–24]
(COD)PtMeCl	40–120	250	H_2	9% C, 3% O	Puddephatt[22–24]
CpPtMe(CO)	40–120	250	vacuum	27% C, 2% O	Puddephatt[22–24]
CpPt(allyl)[c]	40–120	250	vacuum	38% C, 2% O	Puddephatt[22–24]
$(acac)PtMe_3$	40–120	250	vacuum	30% C, 4% O	Puddephatt[22–24]

[a] acac = acetylacetonate. [b] COD = cyclooctadiene. [c] Allyl = $\eta^3\text{-}C_3H_5$.

platinum precursors. Films deposited from $CpPtMe_3$ and $MeCpPtMe_3$ were always bright and reflective. Scanning electron micrographs revealed that the films consisted of cube-shaped crystallites between 250 and 1000 Å in diameter. Powder X-ray diffraction patterns of the films contained sharp lines typical of polycrystalline platinum metal. We also measured the sheet resistivities of thick films (>2000 Å) with a four-point probe. The resistivities ranged from 26 to 28 $\mu\Omega$ cm. This is somewhat higher than values of 15–20 $\mu\Omega$ cm observed for sputtered or evaporated platinum films.[13]

Recently, Puddephatt and co-workers[22–24] examined the chemical vapor deposition of platinum from a variety of organometallic complexes in vacuum and in hydrogen. When hydrogen is present, the methyl groups on the platinum complex are hydrogenated to methane. Deposition with hydrogen also reduces the amount of carbon in the films to between 4 and 5%.

The good results achieved using all-hydrocarbon complexes of platinum has prompted us to investigate this system more thoroughly. In this paper, we report on the kinetics of chemical vapor deposition of platinum from $CpPtMe_3$ and $MeCpPtMe_3$ in hydrogen. We also present a thorough analysis of the solid–vapor and liquid–vapor phase equilibria of the complexes.

Experimental Section

The organometallic precursors $CpPtMe_3$ and $MeCpPtMe_3$ were synthesized according to literature methods with some modifications.[25,26] All syntheses were conducted in an inert atmosphere using Schlenk techniques. To a solution of trimethylplatinum iodide in diethyl ether, 1.2 equiv of CpNa or MeCpNa in tetrahydrofuran was added at −77 °C. After slowly warming to 23 °C over 6 h, the volatile components were removed under reduced pressure in the temperature range −20 to 0 °C. The residue was sublimed at 40–50 °C onto a coldfinger at 0 °C, yielding white crystals of $CpPtMe_3$ or $MeCpPtMe_3$. A detailed synthesis procedure is given elsewhere.[18]

Platinum films were deposited from $CpPtMe_3$ or $MeCpPtMe_3$ in the apparatus shown in Figure 1. It consisted entirely of glass tubes and Teflon valves and fittings. Prior to each experiment, the apparatus was disassembled, and all parts downstream of the source holder were cleaned as follows. The parts were rinsed for 5 min each in pentane, acetone, and deionized water, soaked overnight in aqua regia, rinsed in tap water, washed with Liquinox detergent, and rinsed for 5 min each in deionized water and methanol. The parts were then dried at 150 °C under 10 Torr (1 Torr = 133 N/m²). The deposition section of the apparatus consisted of $^1/_4$-in. glass or Teflon tubes with 4-mm inside diameters. The glass tubes were cleaned along with the rest of the apparatus, but the Teflon tubes were used as received from Alltech. After removing the parts from the vacuum oven, the apparatus was reassembled and purged with 10 cm³/min helium and 10 cm³/min hydrogen for 1 h. The heater was held at the deposition temperature during the purge. The hydrogen and helium were supplied by Liquid Air Corp. and were 99.995% pure. They were purified further by passing the gas through 13X molecular sieve traps immersed in dry ice.

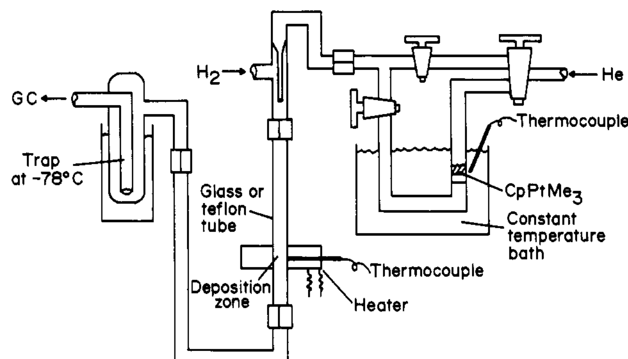

Figure 1. Schematic of the apparatus for chemical vapor deposition of platinum.

Deposition was begun by directing the helium flow over the organometallic source. The source was held at 14.0 ± 0.1 °C. The helium became saturated with the organometallic compound and then passed downstream where it was mixed with hydrogen and fed to the reactor. The length of the deposition zone was close to that of the heater width of 1 cm. The temperature of the wall in the deposition zone was varied between 25 and 180 °C. The effluent from the reactor was passed through a trap at −78 °C to remove any unreacted organometallic compound. The hydrocarbon product distribution in the effluent exiting the trap was analyzed on-line with an HP 5880A gas chromatograph, using a Haysep Q column (Alltech) at 225 °C and a flame ionization detector. Samples were injected every 2 min. The gas chromatograph was calibrated for methane, ethane, propane, butane, hexane, cyclopentane, and methylcyclopentane. Products from the reaction were positively identified by GC-MS. Occasionally the contents of the trap were analyzed by ¹H NMR on a Bruker AF200.

For the vapor pressure measurements, the experimental procedure was modified as follows. The flows of hydrogen and helium were set at 7 cm³/min. Deposition was carried out at 180 °C on a glass tube that was already covered with a platinum film. This ensured that all the organometallic compound fed to the reactor decomposed, so that the amount of hydrocarbons detected by the gas chromatograph was directly proportional to the amount of the compound vaporized into the helium. The heats of sublimation of $CpPtMe_3$ and $MeCpPtMe_3$ were measured at temperatures between −15.0 and 25.0 °C, and the heat of vaporization of $MeCpPtMe_3$ was measured at temperatures between 31.0 and 46.0 °C. During these latter measurements, the flow lines to the reactor were heated to 61 °C.

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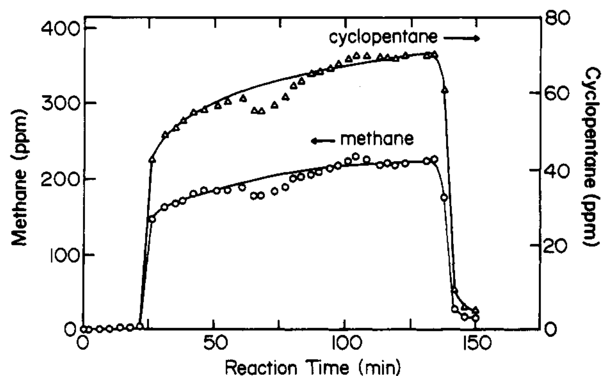


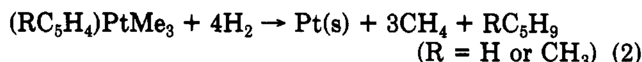
Figure 2. Dependence of the methane and cyclopentane product concentrations on reaction time for deposition on glass at 95 °C.

Table II. Induction Times for $CpPtMe_3$ Decomposition on Different Reactor Surfaces

reactor	reaction temp, °C	induction time, min
platinum film	25	0
glass calcined at 300 °C	25	0
glass etched in HF	90	0
glass washed and dried	90	29
Teflon, as received	90	20
Teflon dried at 150 °C	90	47

Results

Deposition Kinetics. Chemical vapor deposition of platinum from the hydrocarbon complexes in hydrogen produces only two gaseous products. These are methane and cyclopentane from $CpPtMe_3$ and methane and methylcyclopentane from $MeCpPtMe_3$. The ratio of methane to the cyclic hydrocarbon is close to 3, as is expected for complete hydrogenation of the ligands to saturated hydrocarbons:



$$(RC_5H_4)PtMe_3 + 4H_2 \rightarrow Pt(s) + 3CH_4 + RC_5H_9 \quad (R = H \text{ or } CH_3) \quad (2)$$

Shown in Figure 2 is the dependence of the methane and cyclopentane concentrations on time for decomposition of $CpPtMe_3$ on glass at 95 °C. During the first 12 min of reaction, no hydrocarbon products are detected, and no platinum deposit is visible on the glass. At 14 min, the methane and cyclopentane concentrations suddenly increase from near zero to a value coincident with complete decomposition of the complex. Further reaction produces a bright and reflective film of platinum on the hot glass walls. Analysis of the coldtrap contents by ^1H NMR reveals that undecomposed $CpPtMe_3$ accumulates during the first 14 min of reaction. Thereafter, no significant amount of organoplatinum compounds condense into the trap. The existence of an induction period of slow reaction followed by a rapid acceleration of the rate is characteristic of an autocatalytic reaction.

The length of the induction period depends on the composition of the reactor walls and the reaction temperature. Shown in Table II are the lengths of the induction period for deposition on a platinum film, on glass, and on Teflon. No induction time is observed at 25 °C on the platinum film, confirming that it catalyzes the rapid decomposition of the organometallic complex. The induction time on the glass varies over a wide range depending on the method of cleaning the tube prior to deposition. The induction times are 0 min at 25 °C on glass calcined in air at 300 °C, 0 min at 90 °C on glass etched in hydrofluoric acid, washed in deionized water, and dried in vacuum at 150 °C, and 29 min at 90 °C on glass washed and dried as described in the Experimental Section. On

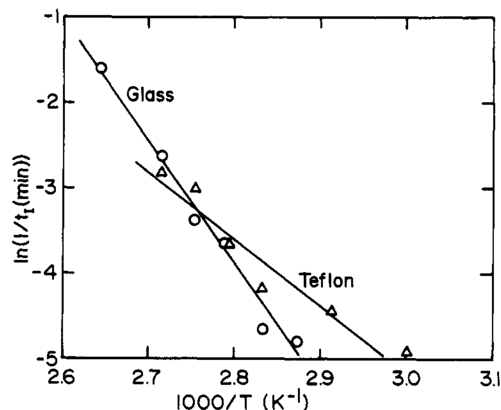


Figure 3. Dependence on the induction time on reaction temperature for deposition on washed and dried glass and on Teflon used as received.

the Teflon used as received, the induction period is 20 min at 90 °C. Drying the Teflon in flowing helium at 150 °C increases this time from 20 to 47 min at 90 °C. The strong dependence of the induction time on the composition of the reactor walls suggest that the reaction occurring during the initial stage of growth is heterogeneous.

Water accelerates the initial rate of $CpPtMe_3$ decomposition in hydrogen. The induction times on the washed and dried glass and the Teflon drop significantly when the molecular-sieve traps in the gas supply lines become saturated with water. To avoid this problem, the traps were regenerated about once every 2 weeks.

The induction period is the time required to build up enough *catalytic* platinum to cause rapid acceleration of the deposition rate. A mass balance on the deposited platinum is

$$d[Pt(s)]/dt = r_d = A \exp(-E_a/RT) P_{Pt}{}^m P_{H_2}{}^n \quad (3)$$

where [Pt(s)] is the concentration of adsorbed platinum, r_d is the deposition rate, A is the preexponential factor, E_a is the apparent activation energy, P_{Pt} and P_{H_2} are the partial pressures of $CpPtMe_3$ and H_2, m and n are the reaction orders, R is the gas law constant (8.314 J/mol K), and T is the temperature. The partial pressures of $CpPtMe_3$ and H_2 remain constant throughout the induction period, because only a small percentage of the organometallic complex decomposes in the reactor. In this case, the mass balance simplifies to

$$d[Pt(s)]/dt = a_0 \exp(-E_a/RT) \quad (4)$$

where a_0 is a constant. Equation 4 states that initially the adsorbed platinum accumulates at a constant rate. It assumes that not many of the sites for $CpPtMe_3$ decomposition on the reactor walls are consumed prior to autocatalysis. Integration of eq 4 from time 0 to the end of the induction period gives

$$[Pt]_I = a_0 \exp(-E_a/RT) t_I \quad (5)$$

Here, $[Pt]_I$ is the concentration of adsorbed platinum required for autocatalysis, and t_I is the induction time. Equation 5 may be rearranged to

$$\ln (1/t_I) = -E_a/RT + \ln a_0 \quad (6)$$

A plot of $\ln (1/t_I)$ versus $1/T$ should yield a straight line with a slope equal to $-E_a/R$. These plots are shown in Figure 3 for $CpPtMe_3$ decomposition on glass and on Teflon. The activation energies obtained from the slopes are 115 ± 10 and 60 ± 15 kJ/mol, respectively. Good reproducibility was obtained from one set of runs to the

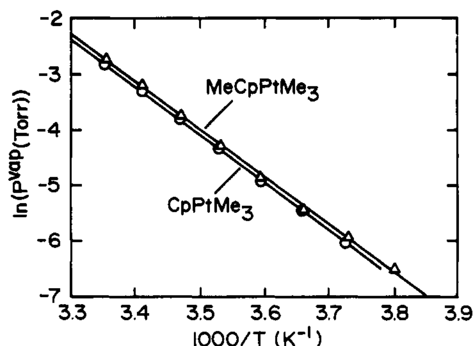


Figure 4. Dependence of the vapor pressures on temperature for sublimation of solid $CpPtMe_3$ and solid $MeCpPtMe_3$.

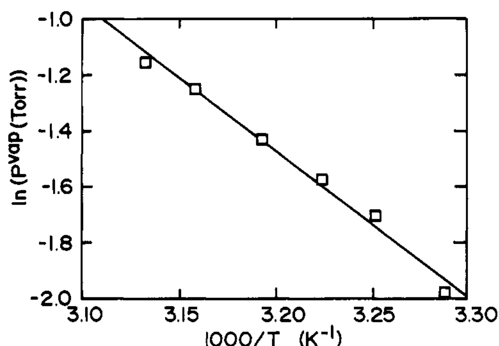


Figure 5. Dependence of the vapor pressure on temperature for vaporization of liquid $MeCpPtMe_3$.

next, provided the apparatus was carefully cleaned as described in the Experimental Section.

Vapor Pressures of the Organometallic Complexes. Shown in Figure 4 are the dependencies of the vapor pressures on temperature for the sublimation of $CpPtMe_3$ and $MeCpPtMe_3$. The Clausius–Clapeyron equations derived from these data are

solid $CpPtMe_3$:

$$\ln (P^{vap}(\text{Torr})) = 25.9 - 8.59 \times 10^3/(T(\text{K})) \quad (7)$$

solid $MeCpPtMe_3$:

$$\ln (P^{vap}(\text{Torr})) = 26.1 - 8.60 \times 10^3/(T(\text{K})) \quad (8)$$

The heats of sublimation obtained from eqs 7 and 8 are 71.2 ± 2.1 kJ/mol for $CpPtMe_3$ and 71.5 ± 2.1 kJ/mol for $MeCpPtMe_3$. The error limits are the estimated experimental uncertainty in the measurement. At 23 °C, the vapor pressures of $CpPtMe_3$ and $MeCpPtMe_3$, calculated from the equations, are 0.045 and 0.053 Torr, respectively. These values are in excellent agreement with the vapor pressures measured by the gas-saturation method.[18] This latter measurement gave values of 0.044 and 0.053 Torr for $CpPtMe_3$ and $MeCpPtMe_3$ at 23 °C. The vapor pressure data reveal that the methyl substituent on the cyclopentadienyl ring has no effect on the heat of sublimation of the organometallic complex. However, it does raise the vapor pressure by about 20% at a fixed temperature.

Shown in Figure 5 is the dependence of the vapor pressure on temperature for vaporization of $MeCpPtMe_3$. The Clausius–Clapeyron relationship derived from these data is

liquid $MeCpPtMe_3$:

$$\ln (P^{vap}(\text{Torr})) = 15.3 - 5.24 \times 10^3/(T(\text{K})) \quad (9)$$

The heat of vaporization is 43.6 ± 1.3 kJ/mol for $MeCpPtMe_3$. At 35 °C, the vapor pressure of $MeCpPtMe_3$ is 0.182 Torr. Egger[27] measured the vapor pressure of

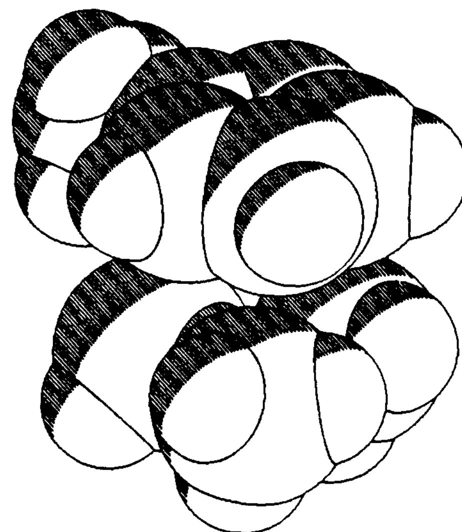


Figure 6. Space-filling model of $MeCpPtMe_3$.

$CpPtMe_3$ above its melting point of 108.5 °C using the isoteniscope technique. He obtained a heat of vaporization of 48.6 ± 2.7 kJ/mol. This value is in fairly good agreement with the heat of vaporization of $MeCpPtMe_3$ measured here, considering the different methods used to obtain the data.

Discussion

Organometallic chemical vapor deposition of platinum from $CpPtMe_3$ and $MeCpPtMe_3$ in hydrogen exhibits autocatalytic behavior. The initially deposited platinum becomes a catalyst for further rapid decomposition of the organometallic complex. Decomposition is so fast on the platinum film that the deposition rate at 25 °C is limited by the feed rate of the metal source to the reactor. Deposition proceeds by the quantitative hydrogenation of $CpPtMe_3$ and $MeCpPtMe_3$ on the film surface to platinum metal, methane, and cyclopentane or methylcyclopentane. Due to the high selectivity for hydrogenation of the ligands to hydrocarbons, the platinum films obtained by this route are essentially free of impurities.

Whitesides and co-workers[19-21] have studied the hydrogenation of (diolefin)dialkylplatinum(II) complexes $[(Ol)_2PtR_2]$ over platinum black in *n*-heptane solvent. Our results are consistent with the findings of their study. Platinum black catalyzes the rapid conversion of the organoplatinum compound into platinum metal and alkanes. At 25 °C, the decomposition rate is limited by the transport of $(Ol)_2PtR_2$ to the catalyst surface. A reaction rate limiting regime is obtained by lowering the temperature to −20 °C. The proposed reaction mechanism is the adsorption of $(Ol)_2PtR_2$ onto the platinum surface via the Pt atom of the complex, followed by conversion of the organic ligands into adsorbed alkyls, and hydrogenation of the alkyls to alkanes. One of these latter two steps appears to be rate determining.

Shown in Figure 6 is the space-filling model of $MeCpPtMe_3$. This model is obtained using the atom positions derived from the crystal structure.[18] The three methyl ligands are at the bottom of the picture, and the methylcyclopentadienyl ring is at the top. In this configuration, it is difficult to see how the platinum atom of the complex can bond to a metal surface. Maybe the η^5-MeCp ring dislocates to lower hapticity, exposing the platinum atom for bonding to the surface. Alternatively,

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the complex may coordinate to a surface platinum atom through the cyclopentadienyl ligand. This latter structure is analogous to the bridging metallocenes formed in triple-decker sandwich complexes.[28] Following attachment of the cyclopentadienyl ligand, the $PtMe_3$ group would move to the surface through intermediates of lower hapticity. One of these early steps involving the breaking of Pt–Cp bonds and the making of $Pt-Pt_s$ bonds may be rate determining. Further studies are needed to resolve these issues.

The strong effect of the reactor composition on the length of the induction period suggests that the reaction occurring during this initial stage of chemical vapor deposition is heterogeneous. The apparent activation energies for $CpPtMe_3$ decomposition on glass and on Teflon are 115 ± 10 and 60 ± 15 kJ/mol, respectively. These values are much lower than the apparent activation energy of 163 ± 21 kJ/mol for homogeneous decomposition of the organoplatinum complex.[27] Furthermore, homogeneous decomposition of $CpPtMe_3$ produces methane and ethane as major hydrocarbon products, consistent with the rate-limiting homolysis of the platinum–methyl bonds. No hydrocarbons other than methane and cyclopentane were observed at any time during our deposition experiments.

The initial heterogeneous decomposition of $CpPtMe_3$ may proceed by electrophilic attack of the organometallic complex by surface hydroxyl groups on the glass and Teflon surfaces. Yermakov[29] has shown that η^3-allyl compounds of platinum, $Pt(\eta^3\text{-}C_3H_5)_2$, react with isolated hydroxyls on silica to form adsorbed organometallic platinum and propylene. A mild treatment in hydrogen converts the adsorbed species to platinum particles and regenerates the hydroxyls:

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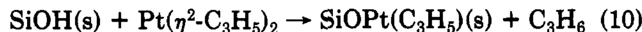

$$SiOH(s) + Pt(\eta^2\text{-}C_3H_5)_2 \rightarrow SiOPt(C_3H_5)(s) + C_3H_6 \quad (10)$$

$$SiOPt(C_3H_5)(s) + H_2 \rightarrow SiOH(s) + Pt(s) + C_3H_8 \quad (11)$$

The participation of hydroxyl groups in the initial decomposition of $CpPtMe_3$ on glass and Teflon is supported by the finding that water substantially decreases the induction times for autocatalysis.

An important issue to resolve in future work is the nature of the adsorbed platinum which catalyzes the rapid hydrogenation of $CpPtMe_3$ and $MeCpPtMe_3$. Is this platinum an isolated atom on the glass or Teflon surface, or is it a small ensemble of platinum atoms? If the latter is true, then the induction period may be the time required for diffusion and agglomeration of the isolated platinum atoms into platinum clusters of a minimum size required for catalysis.

This study has important implications for the chemical vapor deposition of platinum and possibly other transition metals as well. First, it is essential to activate the substrate surface prior to growth to achieve good adherence and a uniform initial coverage of the metal. Chemical treatments of the substrate can either facilitate or inhibit deposition. This concept may be used to deposit metal films on selected areas of a substrate. Second, the reaction rate during the growth of thick, continuous films will be extremely fast. In this case, the deposition rate will be controlled either by the feed rate of $CpPtMe_3$ to the reactor or by mass transfer of $CpPtMe_3$ through the boundary layer to the film surface.

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