# STUDIES ON THE THERMAL ACTIVATION OF IODOTRIMETHYLPLATINUM(IV) TETRAMER: HYDROSILATION CATALYST GENERATION FROM AN INERT PRECURSOR

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#### Summary

Thermal decomposition of catalytically-inert iodotrimethylplatinum(IV) tetramer in the presence of olefin and organosilicon hydride substrates leads to soluble platinum catalysts that actively promote hydrosilation. Characterization of the complexes formed on tetramer decomposition and their relation to the active catalytic species is discussed.

# Introduction

Complexes of the platinum group metals have proven to be efficient homogeneous catalysts for a variety of important alkene addition reactions including hydrogenation [1], hydroformylation [2], and hydrosilation [3]. In the course of our work on metal-promoted hydrosilation, we found that among the stable, well-characterized organometallics of the Group VIII elements, iodotrimethylplatinum(IV) tetramer and closely related molecules occupy a unique position in terms of being non-reactive toward mixtures of unsaturated molecules and organosilicon hydrides at room temperature [4]. In order to gain a better understanding of its unusual room temperature inertness and elevated temperature catalytic activity, we have studied the thermal decomposition of iodotrimethylplatinum(IV) tetramer in the presence of hydrosilation substrates. The present paper describes intermediates observable during tetramer decomposition under catalytic conditions, and delineates a series of reactions that transform the inert precatalyst into potentially more reactive monometallic species. In light of these results, we postulate a mechanism for tetramer-catalyzed hydrosilation.

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## **Results and discussion**

The platinum tetramer was transformed into a potent hydrosilation catalyst above 120  $^{\circ}$ C either by reaction with hydrosilation substrates or by decomposition to smaller homogeneous or heterogeneous aggregates [4]. Our goal in this study was to identify the products formed upon tetramer reaction or decomposition, and to determine which set of new platinum species thus produced is likely to enter into a prolonged catalytic cycle. The key question was: what precatalyst formed from the tetramer is stable and sufficiently durable to account for the high turnover numbers observed in hydrosilation\*?

Tetramer activation can proceed via a variety of mechanisms including simple decomposition to platinum metal and reaction with either organosilicon hydride or alkene substrate before or after declusterization. Our data support the notion that tetramer declusterization in the presence of substrate leads to soluble monoplatinum precatalysts which readily yield active hydrosilation agents.

Thermolysis of the tetramer in dodecane at  $175 \cdot 200$  °C produced nearly quantitative amounts of elemental platinum, ethane and iodomethane. Proton NMR in benzene-d<sub>6</sub> revealed clean loss of the tetramer, gain of the organic products, and no evidence for other methylated platinum species at 150 °C. Even though heterogeneous forms of platinum are known to catalyze hydrosilation [5, 6], we have conclusively ruled out the participation of metallic platinum in tetramer-catalyzed hydrosilation by conducting a variation of the Dunsworth and Nord colloidal catalyst test [7, 8]. The literature claims that heterogeneous dispersions of platinum group metals readily catalyze the hydrogenation of nitrobenzene to aniline, and we have confirmed that hydrogen-saturated dodecane solutions containing equimolar heptamethylcyclotetrasiloxane (HMCTS), pentene-1, nitrobenzene and 1.0 mol.% platinum black form the expected adduct *and* aniline in the course of 3 days:

HMCTS + 
$$(HMCTS)$$
  $\xrightarrow{Pt}$   $(HMCTS)$   $(HMCTS)$   $(1)$ 

Repeating the experiment with an equivalent amount of the tetramer instead of platinum black led to a low concentration of adduct *and no aniline* after 7 days at room temperature\*\*. Since hydrosilation but no hydrogenation was observed in this competitive experiment, we conclude that the tetramer-catalyzed hydrosilation reaction is a truly homogeneous process,

<sup>\*</sup>Turnover numbers are  $10^3 \cdot 10^4$  per mol Pt on the 1-pentene/heptamethylcyclo-tetrasiloxane model system.

<sup>\*\*</sup>Colloidal dispersions of elemental platinum (particles too small to see) readily hydrogenate nitrobenzene to aniline under these conditions as well. See ref. 7.

and that activation schemes leading ultimately to metallic platinum are not viable alternatives for catalyst generation.

Associative activation mechanisms where the tetramer remains intact, coordinates substrate, and behaves like a solubilized metallic platinum fragment are also unlikely. Nucleophilic ligands readily decluster the tetramer under mild conditions [9 - 11] and in our hands at temperatures below its decomposition point, the tetramer was unreactive toward the  $\pi$ -acid ligands carbon monoxide and ethylene. Accordingly, it is unlikely that the tetramer can initiate hydrosilation in an associative manner by coordinating an alkene, or by undergoing Si—H oxidative addition.

Remaining options for tetramer activation include dissociative pathways involving thermal tetramer fragmentation and interception of unsaturated Pt moieties by substrate molecules, or a pathway involving gross reduction of the entire  $Pt_4I_4$  core by organosilicon hydride at elevated temperatures. These possibilities are illustrated in the schemes 1 - 3.

 $[Pt(CH_3)_3I]_4 \xrightarrow{\Delta} 4 Pt(CH_3)_3I$ 



Scheme 1: Fragmentation  $\rightarrow$  coordination.

Scheme 3 is intrinsically the most interesting possibility because it proceeds through a series of unknown organoplatinum complexes (hexamethyldiplatinum has been reported [12], but later work indicates its probable non-existence [13, 14]) and it satisfies the notion that initiation of catalyst activity involves organosilicon hydride reduction of platinum to an oxidation state lower than (IV).

At the heart of Scheme 2 is the assumption that the fragmented tetramer forms stable hydrides via oxidative addition of organosilicon



Hydrosilation

Scheme 2: Fragmentation  $\rightarrow$  oxidative addition.



Hydrosilation

Scheme 3: Tetramer core reduction.

hydride. The platinum(VI) species shown in Scheme 2 is a highly unlikely intermediate, and we feel that reductive elimination of ethane or iodomethane would precede the addition of the silane as illustrated. If the thermal decomposition of tetramer occurs according to Scheme 2, the proton NMR should exhibit new Pt-CH<sub>3</sub> resonances (triplets of 1:4:1 intensity with J(Pt-H) = 40 - 90 Hz as well as a high field Pt-H ( $\tau > 10$ ) signal. In fact, experiments carried out in benzene-d<sub>6</sub> with stoichiometric amounts of tetramer and a variety of organosilicon hydrides (trichlorosilane, dimethylphenylsilane, triethylsilane, triphenylsilane, heptamethylcyclotetrasiloxane) in sealed NMR tubes revealed that at 180 °C the only new products are methane, the appropriate iodosilane, and metallic platinum, implying that reduction of coordinated ligands is more important than Si-H oxidative addition in the reaction of  $R_3SiH$  with the tetramer. Since elemental platinum itself is not the ultimate catalyst in the tetramer system (vide supra), we conclude that the fragmentation-oxidative addition scheme cannot transform the tetramer into a suitable precatalyst.

Similarly, reduction of the tetramer core prior to fragmentation, Scheme 3, would lead to unique methylplatinum resonances in the NMR. At temperatures up to 120 °C in benzene- $d_6$ , we observed no interaction between stoichiometric amounts of either triphenylsilane or heptamethylcyclotetrasilane and the tetramer. As noted above, when the temperature was increased to 180 °C, reduction of coordinated methyl groups and formation of elemental platinum resulted. It follows that the fragmentationcoordination route, Scheme 1, best describes the conversion of the tetramer into the required homogeneous catalyst precursor.

Thermolysis of the tetramer with excess 1,5-cyclooctadiene yields a homogeneous solution containing the platinum(II) organometallics shown in eqn. (2), supporting Scheme 1:

 $[Pt(CH_3)_3I]_4 + \bigcup_{(COD)} \xrightarrow{175^\circ} CH_3 + I CH_3$ (2)

Furthermore, reaction of stoichiometric amounts of cis-(COD)Pt(CH<sub>3</sub>)Cl with alkyl or aryl silicon hydrides at 175 °C led to quantitative production of R<sub>3</sub>SiX, where X is either the chloride or methyl group originating on platinum:

<sup>\*</sup>The appearance of triplets due to  $^{195}$ Pt—<sup>1</sup>H coupling in Pt—CH<sub>3</sub> complexes is observed at room temperature in *all* known examples of this type except Li<sub>2</sub>[Pt(CH<sub>3</sub>)<sub>6</sub>] [15]. The latter ill-characterized compound exhibits a broad singlet upfield from TMS which splits into the expected triplet at -10 °C and also (inexplicably) at elevated temperature (50 °C).



 $(R = CH_3 \text{ or } C_6H_5; X = CH_3 \text{ or } Cl)$ 

The bracketed platinum(II)-hydride in eqn. (3) has not been characterized except in a more thermally stable model system (vide infra), but the excellent silicon mass-balance observed here suggests that the final soluble organoplatinum products from tetramer decomposition are metallohydrides. Of great significance in linking the results in eqns. (2) and (3) to the actual catalytic situation is the fact that an experiment employing 1.0 mol.% cis-(COD)Pt(CH<sub>3</sub>)I in equimolar triphenylvinylsilane and methyldiphenylsilane yielded iodomethyldiphenylsilane and dimethyldiphenylsilane along with the expected hydrosilation product:



Observation of methyl and iodosilanes among the products in the catalytic reaction strongly suggested that the activation sequence initiated as in Scheme 1 is operable for the tetramer. The exact nature of the bracketed complex formed during the key reaction shown in eqn. (3) remains in doubt, but we favor its formulation as a platinum(II) hydride on the basis of platinum(II)-phosphine chemistry discussed below:

Tertiary phosphine ligands are electronically equivalent to alkenes, and there are many examples in the literature illustrating the one-to-one correspondence between phosphine and alkene complexes of the same metal [16]. By the reactions shown in eqns. (5) [9] and (6) [17], we have prepared the *trans* isomer of iodomethylbis(triethylphosphino)platinum(II), which is the electronic equivalent of the COD-platinum reactant in eqn. (3).

$$[Pt(CH_3)_3I]_4 + 8PR_3 \xrightarrow{25 \ ^{\circ}C} 4fac - Pt(CH_3)_3(PR_3)_2I$$
(5)

$$fac-Pt(CH_3)_3(PR_3)_2I \xrightarrow{\Delta} trans-Pt(PR_3)_2(CH_3)I$$
(6)  
(R = C\_2H\_5)

The reaction is clean and the product identity is unambiguous by field desorption mass spectrometry and Pt-P coupling constant magnitude [18].\* At 175 °C in benzene-d<sub>6</sub>, this platinum(II) model complex reacts smoothly with dimethylphenylsilane, yielding chiefly the trans isomer of hydrido-(iodo)bis(triethylphosphino)platinum(II) and trimethylphenylsilane along hydridomethylbis(triethylphosphino)platinum(II) with traces of and dihydrobis(triethylphosphino)platinum(II). The experiment illustrates that platinum(II) hydrides are readily formed from organosilicon hydrides and halo(alkyl)platinum(II) complexes, supporting the as-of-yet uncharacterized chemistry in eqn. (3). We note that the products formed between organosilicon hydrides and platinum(II) phosphine compounds are dependent upon the electronegative groups on platinum, eqns. (7) (this work), (8) [19], and (9) [20].

$$trans-Pt(PR_3)_2(CH_3)I + R_3SiH \xrightarrow{\Delta} trans-HPt(PR_3)_2I$$
(7)

$$cis-Pt(PR_3)_2Cl_2 + R_3SiH \xrightarrow{\Delta} trans-HPt(PR_3)_2Cl$$
 (8)

$$cis-Pt(PR_3)_2(CH_3)_2 + R_3SiH \xrightarrow{\Delta} cis-HPt(PR_3)_2SiR_3$$
 (9)

The fact that all three examples transfer hydride to the metal center underscores the generality of this reaction, however.

In summary, we have demonstrated that the hydrosilation catalyst generated from iodotrimethylplatinum(IV) tetramer thermolysis is homogeneous in nature, and that only one of the obvious decomposition mechanisms considered leads to truly homogeneous metallic products. Other activation mechanisms, including those involving paramagnetic metal centers abstracting hydrogen from  $R_3SiH$  cannot be ruled out completely, nor can the possibility that spectroscopically non-detectable precatalysts are paramount to success. Our experiments have clearly shown, however, that processes leading to eqn. (3) are indeed in operation, even though the postulated platinum hydride has not been characterized except in a phosphine model system.

Schemes 4 and 5 illustrate logical catalyst generation and recyclability diagrams based on these studies.

### Experimental

# General

Silicon-containing reagents were obtained from Silar Labs, Inc. or Petrarch Systems, Inc. and used without further purification. Platinum

<sup>\*&</sup>lt;sup>31</sup>P chemical shifts in ref. 17 have reversed signs, but the same absolute values as our observed shifts.



Scheme 4

complexes were synthesized via literature procedures cited in the text, or as discussed below. Reagent grade chemicals were purchased from appropriate commercial sources (Aldrich Chemical Co., Eastman Kodak, Wiley Chemicals, Strem Chemicals, Inc.)

Nuclear magnetic resonance spectra were recorded on either a Varian EM 390 (<sup>1</sup>H, 90 MHz) or a Varian XL 200 (<sup>31</sup>P, 81 MHz) instrument. Mass spectroscopy data were obtained by field desorption, atom bombardment, electron impact, or GC/MS techniques employing Varian MAT 731 or Varian MAT 311A instruments. Gas chromatographic analyses were run on a Varian 3700 unit equipped with flame ionization and thermal conductivity detectors, using either 1/8 in stainless steel or 1/4 in glass columns (4 m) packed with 10% OV-101 on Chromosorb W-HP (80 - 100 mesh). Compounds sensitive to oxygen or moisture were routinely handled either using Schlenk techniques under prepurified nitrogen (Ace-Burlitch Inert Atmosphere System) or in a Vacuum Atmospheres Drybox (recirculating argon atmosphere).

## Hydrosilation catalysis

Stock solutions (25.00 ml) containing 0.407 M heptamethylcyclotetrasiloxane (HMCTS) and 0.365 M pentene-1 in decane were treated with 0.001 g of iodotrimethylplatinum(IV) tetramer (0.03 mol.% Pt). Aliquots of 3.00 ml were transferred to 16 mm constricted test tubes and sealed *in vacuo*. The



Scheme 5

samples were heated to 180 °C and monitored until all starting materials were converted to HMCTS-pentane adduct (7 h) as determined by GLC. Turnover rate = mol adduct/mol Pt/min = 8. Turnover number = mol adduct/mol Pt =  $3 \times 10^3$ .

#### Tetramer synthesis

The method of Baldwin and Kaska [21] routinely yielded 60 - 80% of tetramer. Typically, 10.0 g (20.6 mmol) of  $K_2PtCl_6$  were treated with excess (400 mmol)  $CH_3MgI$  in 50/50 (v/v) diethyl ether/benzene and allowed to stir overnight. Workup via the literature procedure gave 4 - 5 g of tan  $Pt_4I_4(CH_3)_{12}$  identified by <sup>1</sup>H NMR (8.13  $\tau$ , J(Pt-H) = 78 Hz in benzene-d<sub>6</sub>) and field desorption mass spectroscopy (in  $CH_2Cl_2$ : found = 1464, calc. = 1464). The platinum methylation reaction is highly sensitive toward reactant stoichiometry and solvent composition [22], and preliminary evidence indicates that it does *not* proceed via simple halide displacement by nucleophilic alkylating reagents [23].

#### Thermal decomposition of tetramer

Four 16 mm diameter test tubes were each charged with 0.10 g (0.068 mmol) of platinum tetramer and constricted for sealing. Each tube was treated with 2.00 ml of an n-heptane/dodecane solution (10% heptane for GLC internal standard), degassed via 4 freeze-pump-thaw cycles, and sealed *in vacuo*. The samples thus prepared were held at 175 °C for 1, 5, and 16 h, and then analyzed for ethane and iodomethane production. After 1 h there were no detectable volatile products, but 5 h and 16 h of heating yielded quantities of ethane and iodomethane at 18% and 64% conversion, respectively. The 5 h data point showed equimolar production of both products, while after 16 h there was roughly twice the amount of iodomethane as ethane, most likely a consequence of low solubility and high volatility of ethane. Elemental platinum was obtained as the other product in 95% yield (0.06 g) from the 16 h reaction.

A 5 mm diameter NMR tube was sealed in vacuo following introduction of 2 ml of a saturated solution of tetramer in benzene- $d_6$ . Progress of the reaction was monitored once an hour for 6 h at 150 °C. At this point all of the tetramer had been converted to elemental platinum, ethane, and iodomethane.

### Proof of homogeneous hydrosilation

In a 25.00 ml volumetric flask, 1.00 ml each of pentene-1 (9.12 mmol), heptamethylcyclotetrasiloxane (3.39 mmol), nitrobenzene (9.78 mmol), and n-heptane (internal standard for GLC analysis) were diluted to the mark with hydrogen-saturated dodecane. Two 25 ml round-bottom flasks were flushed with hydrogen and separately charged with 0.006 g of platinum black and 0.01 g platinum tetramer (equimolar in platinum and 1 mol.% of limiting reagent). Aliquots of the stock reactant solution (10.00 ml) were then added to the flask, and the solutions were stirred under hydrogen. After 72 h at room temperature, the platinum black-catalyzed mixture was completely free of heptamethylcyclotetrasiloxane, and GLC analysis indicated the presence of pentene-heptamethylcyclotetrasiloxane adduct and aniline. With the platinum tetramer catalyst, no discernible reaction occurred in 72 h, but after 168 h a trace of adduct was found in the aniline-free solution.

# Tetramer/ $\pi$ -acid interaction

A solution of 0.50 g tetramer in 40 ml of toluene which was previously saturated with carbon monoxide or ethylene was stirred at room temperature under an atmosphere of reactant gas for 16 h. Unreacted tetramer was reclaimed in each case, and no changes were observed in the IR or NMR spectra. Four hours of refluxing a second tetramer sample in toluene under a CO purge led to no new organoplatinum species observed by IR or NMR, and less than 10% decomposition of the starting material.

# Tetramer reduction studies

Samples in sealed NMR tubes containing the platinum tetramer and 5fold excess of organosilicon hydrides (see text) in benzene- $d_6$  were heated for 16 h in a 175 - 180 °C oven. Reduction to elemental platinum, methane, and ISiR<sub>3</sub> was observed in every case; no new platinum-methyl signals were evident. Silyl complexes were identified as  $R_3SiOSiR_3$  ( $R_3 = Me_2Ph$ ,  $Et_3$ ,  $Ph_3$ ) by GC/MS.

#### Characterization of diolefinplatinum(II) intermediates

Two 16 mm diameter test tubes were charged with 2.0 ml of a 0.01 M solution of the tetramer in benzene. One sample was diluted with an additional 1.0 ml of 1,5-cyclooctadiene. The tubes were sealed *in vacuo* and pyrolyzed for 4 h at 180 - 200 °C. The diene-free sample contained no soluble products detectable by field desorption mass spectroscopy, while the second sample remained homogeneous and exhibited parent ions for the products in eqn. (2).

## $Diolefinplatinum(II)-R_3SiH$ interactions

Dimethyl( $\eta^4$ -1,5-cyclooctadienyl)platinum(II) was prepared by the method of Clark and Manzer [24] in 39% yield. Chloromethyl( $\eta^4$ -1,5-cyclooctadienyl)platinum(II) was quantitatively generated (M.W. by field desorption MS = 352) from 0.0623 g of the dimethyl complex (0.19 mmol) and 37% HCl<sub>(aq)</sub> (20  $\mu$ l, 0.019 mmol) in THF. The dimethyl complex (0.15 mmol) was treated with 1.5 equivalent of diphenylmethylsilane (46  $\mu$ l) in benzene-d<sub>6</sub>, and sealed in an NMR tube *in vacuo*. After 4 h at 175 °C, the proton NMR showed resonances for free 1,5-cyclooctadiene [ $\delta$  = 5.64 (4H),  $\delta$  = 2.24 (8H)] and diphenyldimethylsilane ( $\delta$  = 1.00). The identity of the organosilane was confirmed by GC/MS (M-15 = 197 amu). In a parallel experiment with 0.062 g (0.19 mmol) of the chloromethyl complex and an equivalent of diphenylmethylsilane (38  $\mu$ l) in benzene-d<sub>6</sub>, the products observed by proton NMR and GC/MS were 1,3-dimethyl-1,1,3,3-tetraphenyl-disiloxane and 1,5-cyclooctadiene.

#### Platinum-phosphine model compounds

Platinum tetramer (0.043 g, 0.12 mmol Pt) was treated with triethylphosphine (34  $\mu$ l, 0.24 mmol) in 10 ml benzene-d<sub>6</sub> in the drybox. After an hour of room temperature stirring, the <sup>31</sup>P NMR showed the expected resonance for *fac*-Pt(CH<sub>3</sub>)<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>I ( $\delta$  = -36.6 ppm, *J*(Pt-P) = 1138 Hz). The 10 mm diameter NMR tube was then sealed *in vacuo* and held at 80 °C for 2 h, after which <sup>31</sup>P NMR confirmed complete conversion to *trans*-Pt(CH<sub>3</sub>)I(PEt<sub>3</sub>)<sub>2</sub> ( $\delta$  = 11.4 ppm, *J*(Pt-P) = 2732 Hz). Resealing the sample in another 10 mm NMR tube with 36  $\mu$ l (0.24 mmol) PhMe<sub>2</sub>SiH and heating at 175 - 180 °C for 16 h yielded mainly *trans*-HPtI(PEt<sub>3</sub>)<sub>2</sub> (<sup>31</sup>P NMR:  $\delta$  = 20.2 ppm, *J*(Pt-P) = 2650 Hz. <sup>1</sup>H NMR:  $\delta$  = -12.7 ppm, *J*(P-H) = 13 Hz. Field desorption mass spectroscopy: found = 558, calc. = 558). Traces of HPt(CH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub> and H<sub>2</sub>Pt(PEt<sub>3</sub>)<sub>2</sub> were also detected in the field desorption spectrum.

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