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Mechanism of Formation of Platinum(0) Complexes Containing Silicon–Vinyl Ligands

Larry N. Lewis,^{*,†} Robert E. Colborn,^{*,†} Hans Grade,[†] Garold L. Bryant, Jr.,^{†,‡}
Chris A. Sumpter,[†] and Robert A. Scott[§]

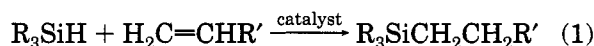
GE Corporate Research and Development Center, Schenectady, New York 12301, and
Center for Metalloenzyme Studies, Chemistry Building, The University of Georgia,
Athens, Georgia 30602-2556

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Reactions are described in detail between H_2PtCl_6 and vinyl–silicon-containing compounds such as 1,3-divinyldimethyltetramethyldisiloxane ($\text{M}^{\text{vi}}\text{M}^{\text{vi}}$) and divinyltrimethylsilane ($(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$). The structures of the platinum and silicon products were examined from these reactions with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ and 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane (D_4^{vi}). The platinum products were all $\text{Pt}(0)$ –olefin complexes. The reaction of chloroplatinic acid with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ gave a mixture of platinum complexes containing $\text{M}^{\text{vi}}\text{D}_x\text{M}^{\text{vi}}$ ligands (**1**; $x = 0$ –11). Some complexes are polynuclear with bridging ligands and no metal–metal bonds, such as $\text{Pt}_2(\text{M}^{\text{vi}}\text{M}^{\text{vi}})_3$ (**2**). The conversion of $\text{Pt}(\text{IV})$ complexes to $\text{Pt}(0)$ species resulted in the net conversion of a silicon–vinyl group to a silicon–oxygen group. The reaction of H_2PtCl_6 with $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$ gave both a $\text{Pt}(0)$ (**4**) and a $\text{Pt}(\text{II})$ (**5**) product. A three-dimensional, X-ray crystal structure of **5** was solved, which showed a doubly chloro bridged platinum dimer with no metal–metal bond of stoichiometry $\text{C}_{18}\text{H}_{38}\text{Cl}_2\text{Pt}_2\text{Si}_3$. The dimer contained a bridging $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$ ligand. Additionally each Pt atom had a chelating $(\text{CH}_3)_2\text{Si}(\eta^2\text{-CH}=\text{CH}_2)(\eta^1\text{-CH}_2\text{CH}_2)$ ligand, resulting from formal protonation of one of the vinyl groups. Crystallographic data: $a = 6.799(3)$ Å, $b = 19.830(8)$ Å, $c = 18.847(10)$ Å, $\beta = 95.43(4)^\circ$; space group $P2_1/c$; $Z = 4$. The structure of **4** was determined by spectroscopic analysis to be a $\text{Pt}(0)$ –olefin complex. The structures of **4** and **5** were further confirmed by preparation of chemical derivatives with $\text{P}(\text{C}_6\text{H}_5)_3$, which formed known platinum phosphine compounds. Compound **4** converted to compound **5** by reaction with HCl . A mechanism for the reaction of $\text{Pt}(\text{IV})$ with silicon–vinyl is presented based on the analysis of platinum, silicon, and gaseous products. Mechanistic experiments included reactions with D_2PtCl_6 and reactions in the presence of added C_2H_4 or C_2D_4 .

Introduction

The hydrosilylation reaction (eq 1) has been the subject of several extensive reviews.^{1–8} The reaction is employed for the synthesis of monomers with Si–C bonds and for forming cross-linked networks by using multifunctional polymers.⁹



The most active catalysts for hydrosilylation are complexes of the platinum-group metals; among these, platinum complexes are the most active.^{10,11} An example of a highly active catalyst is Karstedt's catalyst,¹² this catalyst is typically prepared via the procedure shown in eq 2. Details of such a synthesis were recently

[†] GE Corporate Research and Development Center.
[‡] Present address: Physical & Analytical Chemistry Research, The Upjohn Co., Kalamazoo, MI 49001-0199.

[§] The University of Georgia.

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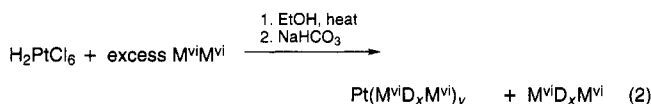
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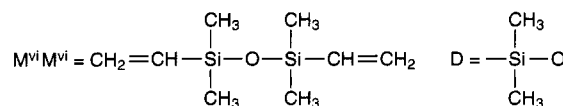
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1
 $x = 0$ –11, $y = 2$ –4
1a: $x = 0$, $y = 2$



described.^{13,14} Lappert and co-workers have recently described some of the chemistry from eq 2, including a

(9) Stein, J.; Lewis, L. N.; Smith, K. A.; Lettko, K. X. *J. Inorg. Organomet. Polym.* **1991**, 1, 325. The use of M, D, T, and Q shorthand has been described in this paper.

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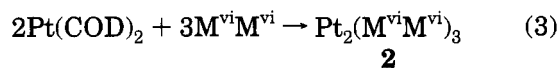
description of the gaseous products¹⁴ and the oligosiloxanes.^{14,15} The structure of the platinum product(s) (1) from eq 2 has been discussed.^{10,16} Willing had previously reported the reaction of H_2PtCl_6 with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$.¹⁷ However, Willing's reaction conditions did not use ethanol or the sodium bicarbonate workup procedure. It is well-known in the synthetic literature for platinum that complexes of the type L_2PtX_2 , where L is an olefin, alkyne, or diene and X is a halogen, may be prepared from alcoholic solutions of H_2PtCl_6 and ligand.^{18,19} The alcohol serves as a reducing agent to give Pt(II) complexes and the corresponding aldehyde. An unusual feature of the procedure of eq 2 is the formation of a Pt(0) compound. Indeed, the dihalides are often replaced by carbonate, e.g., $[\text{PtL}_2(\text{CO}_3)]$, to make the Pt(0) olefin complex from a Pt(II) precursor.²⁰

This article describes our efforts to further identify the products from the reaction in eq 2 and understand their mechanism of formation. The critical question is to resolve the formation of the Pt(0) complexes from the vinyl–siloxane ligands; this is important both from a synthetic perspective and for their role as industrial catalysts. We have used ligands other than $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ in the direct synthesis of Pt(0) olefin complexes from Pt(IV) precursors. A subsequent report will describe the catalytic performance of some of these new platinum complexes.

Results and Discussion

Synthesis and Structure of Pt Complexes with $(\text{CH}_3)_2(\text{CH}_2=\text{CH})\text{SiOSi}(\text{CH}=\text{CH}_2)(\text{CH}_3)_2$. The reaction in eq 2 was originally reported by Karstedt.¹² Earlier, Willing¹⁷ had described the reaction between H_2PtCl_6 and $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ at reflux temperature. Willing's workup procedure involved aqueous extraction of the product until the extractant was neutral, presumably removing residual acid and chloride. Ashby and Modic¹⁶ reported a field desorption mass spectroscopic (FDMS) analysis of two chromatographically separated fractions obtained from eq 2. Their FDMS analysis suggested the empirical formulas $\text{Pt}(\text{M}^{\text{vi}}\text{M}^{\text{vi}})_2$ (**1a**) and $\text{Pt}(\text{M}^{\text{vi}}\text{M}^{\text{vi}})(\text{M}^{\text{vi}}\text{M}^{\text{OH}})$. Lappert defined "solution A" as the combined product mixture from eq 2.¹⁵

The Lappert group¹⁵ reported the dimeric structure of the platinum product $\text{Pt}_2(\text{M}^{\text{vi}}\text{M}^{\text{vi}})_3$ (**2**), obtained from the reaction of $\text{Pt}(\text{COD})_2$ (COD = 1,5-cyclooctadiene) with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ (eq 3). Dimer **2** has no Pt–Pt bond and one bridging $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$, and each Pt atom has a chelating $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ ligand. It is not clear if **2** is a true representative of the platinum species in solution from eq 2. We shall address this question in our experiments described below.



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Many Pt(0) olefin complexes have been prepared and studied as hydrosilylation catalysts.²¹ One recent report described an unusual Pt(0) complex with DBA ligands (DBA = dibenzylideneacetone) and summarized most of the structural data for Pt(0)–olefin complexes.²² These platinum complexes generally are planar and three-coordinate. The four-coordinate, tetrahedral complex $\text{Pt}(\text{COD})_2$ appears to be an exception.²³ Only a few examples exploiting the synthetic methodology of eq 2 to make Pt(0) complexes have appeared.^{14,15,24} One problem is that the reaction of H_2PtCl_6 with most olefins gives Pt(II) compounds.^{25,26} Some limited work using other silicon–vinyl sources has been reported: 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane (D_4^{vi}),^{12,14,27} $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$,^{12,27} $(\text{C}_6\text{H}_5)_2\text{Si}(\text{CH}=\text{CH}_2)_2$,^{12,27} and 1,3-divinyl-1,3-diphenyldimethyldisiloxane.²⁸

Due to the possible role of ethanol in the reduction of Pt(IV), the great majority of the reactions described in this paper were carried out with no ethanol in the presence of excess vinylsilane. In the standard reaction with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ (eq 2), such a process leads to the same Pt species in the same yield with a similar family of oligosiloxanes.

Since it is difficult to obtain rigorously dry chloroplatinic acid, one also needs to consider the possible role of water in the reduction of the platinum species. By analogy to Wacker chemistry, one might propose a scheme to convert the silyl olefin to an aldehyde with concomitant production of HCl. However, in an analysis of the volatile fraction by both NMR spectroscopy and GC/MS, no organic products based on oxygen addition at the olefin are observed. Moreover, smooth reduction of anhydrous PtCl_4 takes place to produce the same distribution of platinum compounds (vide infra). In such a reaction, silyl chlorides are observed as the primary reaction products.

In the present work, NMR analysis of solution A was carried out after first concentrating it in vacuo. The ^1H NMR spectrum of the solution A concentrate showed a 1:1 ratio of free vinyl to Pt-bound vinyl. The bound vinyl protons exhibit a complex multiplet from δ 2.8 to 4.2 significantly upfield from the free vinyl protons. FDMS analysis of the recovered distillate showed mostly oligomers of the formula $\text{M}^{\text{vi}}\text{D}_x\text{M}^{\text{vi}}$ ($x = 0$ –11). The FDMS analysis of solution A concentrate showed that **1**, specifically including **1a**, was present, but no dimer **2** was observed.

In contrast, the FDMS analysis of the product from eq 3, when 6 equiv of $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ was used (relative to Pt), showed that both **2** and **1a** were formed. The ^1H NMR spectrum of the reaction product between $\text{Pt}(\text{COD})_2$ and 6 equiv of $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ is quite different from that of solution A concentrate; the region for the Pt–vinyl protons for

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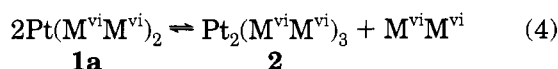
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solution A has many more peaks than the product from $\text{Pt}(\text{COD})_2$. The complex nature of the ^1H NMR spectrum for solution A concentrate suggested that a mixture of platinum species was present. These might include a variety of bridging divinyloligosiloxane ligands.

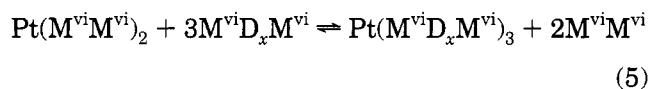
Further spectroscopic analyses were employed to determine the species in the solution A mixture. Typical ^{195}Pt NMR spectra for solution A showed a pair of resonances, as reported by Lappert,¹⁴ at -6148 and -6149 ppm in a 2:1 ratio, respectively. Lappert suggested that these resonances were due to isomers of **2**, i.e., *rac* and *meso* forms. In our experiments, when additional $\text{M}^{\text{vi}}\text{D}_x\text{M}^{\text{vi}}$ oligomers were added to a solution A concentrate, only a single ^{195}Pt NMR signal was observed at -6148 ppm. Thus, another interpretation for the 2:1 set of resonances observed in the solution A concentrate is an equilibrium between complexes of different nuclearity, such as **2** and **1a** (shown in eq 4).

change in nuclearity



FDMS analysis of solution A showed the silicon products were $\text{M}^{\text{vi}}\text{D}_x\text{M}^{\text{vi}}$ ($x = 0-11$). The platinum-containing products in the spectrum were identified on the basis of the characteristic isotope pattern for platinum. Clusters of peaks were separated by 74 amu corresponding to D units ($(\text{CH}_3)_2\text{SiO}_{2/2}$). FDMS also demonstrated the presence of **1a** and other monomeric platinum complexes where the ligands $\text{M}^{\text{vi}}\text{D}_x\text{M}^{\text{vi}}$ varied in composition from $x = 0$ to $x = 5$. However, because we failed to detect **2** by FDMS, yet another equilibrium based on ligand exchange as in eq 5 may be operative.

ligand exchange



In a related experiment, solution A was combined with $\text{MD}^{\text{vi}}\text{M}$. No ^{195}Pt NMR signal was observed when 10 mol equiv was added (based on Pt), presumably due to a broadening based on exchange between different sites; however, when 100 equiv of $\text{MD}^{\text{vi}}\text{M}$ was added, a new resonance was observed at -6155 ppm. New ^{13}C NMR signals were also observed for the mixture containing 100 equiv of $\text{MD}^{\text{vi}}\text{M}$ and 1 equiv of solution A, replacing those observed for solution A. These results confirm replacement of $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ with $\text{MD}^{\text{vi}}\text{M}$ when 100 equiv of the latter was added.

Extended X-ray absorption fine structure (EXAFS) analysis was carried out on a Karstedt's catalyst solution (Figure 1a). The first platinum shell contained carbon, $d_{\text{Pt-C}} = 2.17 \text{ \AA}$, with a Pt-C coordination number of 6. The EXAFS data also showed the absence of a significant amount of chlorine in the coordination sphere around platinum. The second coordination shell contained silicon ($d_{\text{Pt-Si}} = 3.41 \text{ \AA}$) with a Pt-Si coordination number of 3. The near-edge region was consistent in shape and area with $\text{Pt}(0)$ species.²⁹

In summary, the platinum compounds in solution A are best viewed as zerovalent and as a mixture of vinyl-

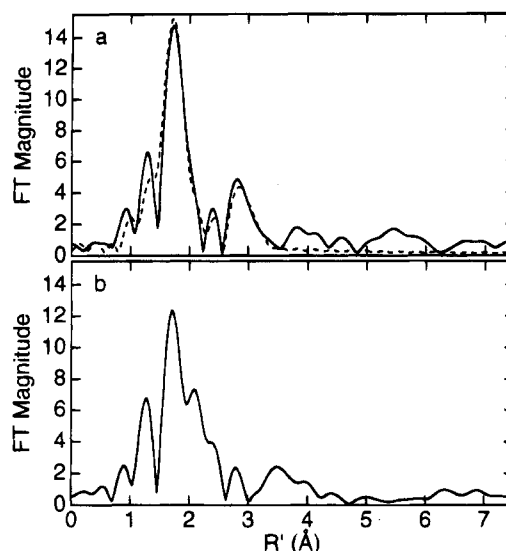


Figure 1. Fourier transforms ($k = 2-13 \text{ \AA}^{-1}$, k^3 weighting) of the Pt EXAFS of **1** (a) and **4** (b). The dashed line in (a) is the Fourier transform of a simulated EXAFS spectrum composed of six Pt-C at 2.17 \AA ($\sigma^2 = 0.0021 \text{ \AA}^2$) and two Pt-Si at 3.40 \AA ($\sigma^2 = 0.0031 \text{ \AA}^2$).

coordinated siloxane species similar to **1** and **2**. The exact composition is undoubtedly a function of the ratio of platinum to ligand and the extent of hydrolysis in the siloxanes.

Analysis of Gaseous Products from Eq 2. The synthesis of **1** (eq 2) was repeated except that D_2PtCl_6 was employed in the reaction with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$. The gaseous products were then analyzed and compared to those observed for the reaction with H_2PtCl_6 . These experiments showed that the main volatile products were ethylene and butadiene, while lesser amounts of products included ethane, butane, hydrogen chloride, and vinyl chloride. The ethylene had substantial $\text{C}_2\text{H}_3\text{D}$, while the ethane had significantly more deuterium, $\text{C}_2\text{H}_x\text{D}_{6-x}$ ($x = 3, 4$ predominated). Butadiene had significant deuterium incorporation as well, but it was not possible to obtain quantitative data about these products. The hydrogen chloride had no detectable deuterium, while the vinyl chloride had small amounts of the monodeuterated species but mostly contained all protio material. Absence of observable DCl by GC/MS could be due to exchange with hydrogen on the walls of the ion source. Finally, butenes were not observed but may have been present though masked by butadiene.

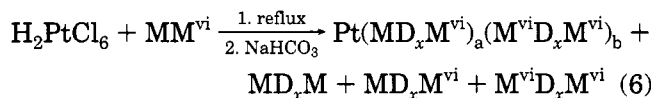
The reaction of eq 2 was rerun except that K_2PtCl_4 was used in place of H_2PtCl_6 . Analysis of the gases from this reaction showed essentially only butadiene was produced with only a trace of ethylene. This result strongly suggests that H_2PtCl_6 provided the hydrogen atom required to form ethylene in the reaction as derived from the Si-vinyl species.

Analysis of Polysiloxane Products from the Reaction of Platinum Halides with Silicon-Vinyl Compounds. Analysis of the polysiloxane products from eq 2 (as discussed above) showed mainly $\text{M}^{\text{vi}}\text{D}_x\text{M}^{\text{vi}}$ oligomers. A lesser series of oligomeric products were observed as high-retention-time shoulders in the GC and GC/MS analyses for each oligomer x of $\text{M}^{\text{vi}}\text{D}_x\text{M}^{\text{vi}}$; these products were identified as $\text{M}^{\text{Et}}\text{D}_x\text{M}^{\text{vi}}$. When $\text{D}_2\text{-PtCl}_6$ was used in place of H_2PtCl_6 in eq 2 as described

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above in the gas analysis section, some deuterium incorporation was noted in the $M^{Et}D_xM^{vi}$ set of oligomers but not in the $M^{vi}D_xM^{vi}$ set. $M^{Et}DM^{vi}$ contained molecules where 79% were all protio, 14% contained one deuterium, and 4% contained two deuterium atoms. For $M^{Et}D_2M^{vi}$, 76% of the molecules were all protio, 16% were monodeuterated, 5% were doubly deuterated, and 3% were triply deuterated.

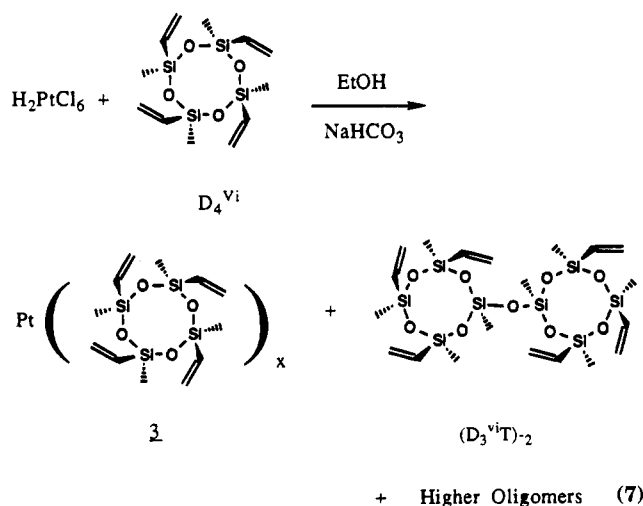
The reaction of eq 2 was repeated except that in one case MM ($(CH_3)_3Si-O-Si(CH_3)_3$) was added to $M^{vi}M^{vi}$ and in another case MM^{vi} was used in place of $M^{vi}M^{vi}$. In both cases the oligomeric mixture of products was the same and was more complicated than in the case of eq 2. The results in eq 6 show the typical



product distribution for the reaction of H_2PtCl_6 with either $M^{vi}M^{vi}$ or MM or of H_2PtCl_6 with MM^{vi} . The results in eq 6 show that each of the siloxane units can exchange with each other, reminiscent of the well-known⁴³ Lewis-acid-catalyzed exchange of siloxy units; in this case the platinum species served as the Lewis acid.

Reactions were carried out with added C_2H_4 or C_2D_4 to probe the effects on the reduction process and oligosiloxane formation. The latter experiment was complementary to the experiments above using D_2PtCl_6 . The effect of ethylene pressure on the oligomer product distribution is shown graphically in Figure 2. Here it is shown that when eq 6 was run under a pressure of C_2H_4 (60 equiv based on Pt), the population of higher oligomers increased vs the case when no ethylene was present. A similar pattern was observed for the reaction of eq 2 run with and without ethylene (Figure 3). When eq 2 was run under pressure of C_2H_4 , analysis of the gases showed C_2H_4 , as well as C_2H_6 , C_4H_6 , and C_4H_8 . The presence of added C_2H_4 led to more saturated products; C_2H_4 was apparently a proton source for the formation of ethane and butene (from butadiene). In the reaction of eq 2 run under ethylene, if the platinum concentration was increased 5-fold, a higher yield of gases (ethane, butadiene, and butene) was noted. Clearly platinum was involved in the formation of these additional gas products. When eq 2 was run under C_2D_4 , no deuterium incorporation was noted in any of the silicon-containing products. Analysis of the gases from the reaction of H_2PtCl_6 with $M^{vi}M^{vi}$ under C_2D_4 showed both C_2D_4 and C_2H_4 with no evidence of H-D exchange; e.g., no $C_2H_4-xD_x$ was observed. Some deuterium incorporation was noted in the hydrogenated gaseous products as $C_2D_{6-x}H_x$ and $C_4D_{8-x}H_x$. Hence, hydrogenated products, e.g., ethyl oligosiloxane, ethane, or butene, may derive hydrogen atoms from the H_2PtCl_6 or ethylene. No deuterium incorporation was noted in any vinyl polysiloxane product. Thus, there is no significant pathway to exchange free ethylene with a vinyl hydride coordinated material.

Synthesis and Structure of Pt Complexes with $[(CH_3)(CH_2=CH)SiO]_4$. Another common ligand for platinum used in polysiloxane applications is $[(CH_3)(CH_2=CH)SiO]_4$, known as D_4^{vi} . H_2PtCl_6 was reacted with D_4^{vi} (eq 7) in a fashion analogous to the reaction in eq 2. The platinum products were assigned as Pt(0)



olefin complexes **3** on the basis of the following analysis. ^{195}Pt NMR spectroscopy showed an envelope 10 ppm wide centered at -6166 ppm consistent with a mixture of Pt(0)-olefin complexes. EXAFS analysis was practically identical with that from the reaction with disiloxane; it showed that the first coordination shell around platinum contained carbon ($d_{Pt-C} = 2.18 \text{ \AA}$) with a Pt-C coordination number of 6. The second coordination shell around platinum contained silicon ($d_{Pt-Si} = 3.40 \text{ \AA}$) with a coordination number of 3. By analogy to the work of Lappert using $M^{vi}M^{vi}$ to give solution A, we call the product solution from eq 7 solution B. Solution B was subjected to vacuum stripping to remove volatile compounds. The 1H NMR spectrum of the solution B concentrate showed broad resonances from 2 to 4 ppm in the region of Pt-vinyl. The ^{13}C NMR spectrum of solution B concentrate also showed resonances characteristic of Pt-vinyl at 54-59 ppm. The NMR spectra for solution B concentrate showed broad envelopes rather than individually resolved peaks, suggestive of a mixture of compounds of related structure.

As shown in eq 2, some of the M^{vi} ($(H_2C=CH)Si-(CH_3)_2O_{1/2}$) functionality was converted to a D ($(CH_3)_2SiO_{2/2}$) group, thus giving rise to the oligomeric product $M^{vi}D_xM^{vi}$. Likewise, in the reaction of eq 7 some of the D^{vi} groups of D_4^{vi} were changed to T ($(CH_3)SiO_{3/2}$) groups. Analysis of the silicon-containing products in solution B concentrate by gas chromatography/mass spectroscopy (GC/MS) and by FDMS showed the presence of two types of products: higher cyclics, D_x^{vi} ($x = 4-6$), and T-containing oligomers, such as $(D_3^{vi}T)_2$ (as shown in eq 7), $D_4^{vi}T-TD_3^{vi}$, and $(D_4^{vi}T)_2$. Thus, with D_4^{vi} if one D^{vi} group transformed into a SiOH and then reacted with an identical molecule eliminating water, $(D_3^{vi}T)_2$ would form.

Reactions with $(CH_3)_2Si(CH=CH_2)_2$. In eq 2, a Pt(IV) starting material is reduced to Pt(0). No Pt(II) intermediate is isolated or observed by ^{195}Pt NMR; the Pt(0) region is roughly upfield of -4000 ppm, while Pt(II) compounds have resonances in the region of -2500 to -4500 ppm (some overlap exists in the literature).^{30,31} When a mixture of H_2PtCl_6 and $M^{vi}M^{vi}$ was stirred and heated to 80 °C for 2 h (with no ethanol or $NaHCO_3$ added), ^{195}Pt NMR analysis showed the Pt(0) resonances and a new broad resonance at -3470 ppm.

(30) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.

(31) Pregosin, P. S. *Annu. Rep. NMR Spectrosc.* **1986**, *17*, 285.

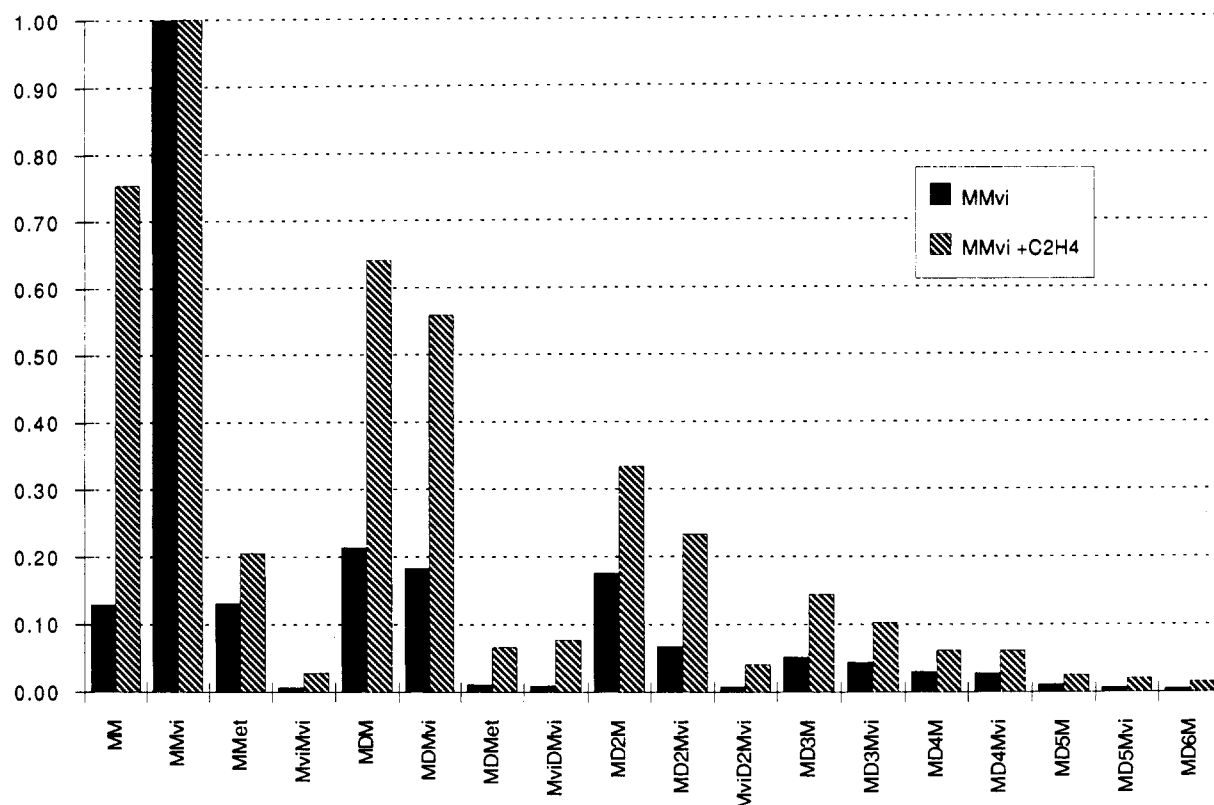


Figure 3. Histogram giving distribution of polysiloxane products from eq 2 run with and without added C_2H_4 pressure.

Table 1. Experimental Data for the Crystallographic Analysis of 5

empirical formula	$C_{18}H_{38}Cl_2Pt_2Si_3$
color, habit	clear flat needle
a , Å	6.799(3)
b , Å	19.830(8)
c , Å	18.847(10)
β , deg	95.43(4)
V , Å ³	2530(2)
Z	4
$F(000)$	1516
space group	$P2_1/c$
T , K	158
$\lambda(Mo K\alpha)$, Å	0.710 73
ρ (calc), g cm ⁻³	2.103
abs coeff, mm ⁻¹	11.521
diffractometer used	Siemens R3m/V
monochromator	highly oriented graphite cryst
2θ range, deg	3.5–55.0
scan type	Wyckoff
scan speed in ω , deg min ⁻¹	variable; 1.50–14.65
scan range (ω), deg	0.60
std rflns	3 meas every 47 rflns
index ranges	$0 \leq h \leq 8, 0 \leq k \leq 25, -24 \leq l \leq 24$
no. of rflns collected	6475
no. of indep rflns	5806 ($R_{int} = 3.02\%$)
no. of obs rflns	4365 ($F > 6.0\sigma(F)$)
no. of abs cor	face-indexed numerical

Pt–C bond lengths found in **5** between Pt and the C=C groups. While the average distance of 2.16 Å agreed with the similar distance of 2.17 Å in (COD)PtCl₂,³⁵ the spread in the distances (see Table 5) was quite large. This apparent asymmetry in the Pt–vinyl distances may represent some strain in the molecule.

The Pt–Cl distances in **5** average 2.52 Å, slightly longer than in square-planar bridging Pt(II) halides

Table 2. Solution and Refinement Data for 5

syst used	Siemens SHELXTL PLUS (VMS)
soln	direct methods
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
extinction coeff	$\chi = -0.000011(10)$, where $F^* = F[1 + 0.002\chi F^2/(\sin 2\theta)]^{-1/4}$
H atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0012F^2$
no. of param refined	227
final R indices (obs data), %	$R = 3.28, R_w = 4.34$
R indices (all data), %	$R = 4.87, R_w = 4.92$
goodness of fit	1.00
largest and mean Δ/σ	1.127, 0.070
data-to-param ratio	19.2:1
largest diff peak, e Å ⁻³	3.45
largest diff hole, e Å ⁻³	-1.45

such as bis(μ -chloro)dichlorobis(olefin)diplatinum(II) (2.32–2.36 Å)³⁶ or the tetrameric allylchloroplatinum (2.37–2.46 Å).³⁷ The Pt–Cl bonds trans to the σ -carbon averaged 2.505 Å, consistent with a strong trans influence previously observed.^{38,39} The other Pt–Cl bond was 2.54 Å, which was quite long but again consistent with reduced electron density due to the presence of two olefins in the pseudo-equatorial plane, i.e., five versus four-coordination.

The silyl–ethyl linkage was truly saturated, as noted by the C–C bond lengths of 1.519 Å. The Pt–C distances for the silyl–ethyl ligand were 2.06 Å (0.1 Å shorter than the Pt–C distance to the vinyl groups) but were consistent with the former having a true metal–

(36) Bordner, J.; Wertz, D. W. *Inorg. Chem.* **1974**, *13*, 1639–1643.

(37) Raper, G.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1979**, 655.

(38) Whitla, W. A.; Powell, H. M.; Venzani, L. M. *J. Chem. Soc., Chem. Commun.* **1966**, 310–311.

(39) Anderson, G. K.; Cross, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Solomon, T. *J. Organomet. Chem.* **1979**, *170*, 385–397.

(35) Syed, A.; Stevens, E. D.; Cruz, S. G. *Inorg. Chem.* **1984**, *23*, 3674–3674.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for **5**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Pt(1)	8510(1)	-1594(1)	2683(1)	19(1)
Cl(1)	5911(3)	-893(1)	1963(1)	24(1)
Cl(2)	9858(3)	-492(1)	3166(1)	21(1)
Pt(2)	6849(1)	150(1)	2688(1)	18(1)
C(1)	6155(12)	462(4)	3720(4)	27(2)
C(2)	5307(12)	-169(3)	3596(4)	23(2)
Si(1)	6089(3)	-946(1)	4110(1)	22(1)
C(3)	8041(12)	-741(4)	4844(5)	30(2)
C(4)	3859(13)	-1231(4)	4521(5)	31(3)
C(5)	6755(12)	-1705(4)	3586(4)	24(2)
C(6)	8566(12)	-2052(4)	3713(5)	27(2)
C(7)	4392(12)	665(4)	2251(5)	29(2)
C(8)	4230(12)	658(4)	1435(4)	29(2)
Si(2)	6685(3)	877(1)	1117(1)	25(1)
C(9)	6863(14)	1805(4)	959(6)	37(3)
C(10)	7253(15)	408(5)	309(6)	42(3)
C(11)	8527(11)	628(4)	1894(4)	25(2)
C(12)	8697(12)	1001(4)	2519(5)	27(2)
C(13)	7442(16)	-2503(4)	2280(5)	37(3)
C(14)	7195(15)	-2521(5)	1477(6)	40(3)
Si(3)	9320(3)	-2104(1)	1083(1)	24(1)
C(15)	11214(14)	-2704(5)	813(6)	42(3)
C(16)	8329(18)	-1591(5)	302(6)	49(4)
C(17)	10435(11)	-1566(4)	1820(5)	24(2)
C(18)	11457(11)	-1850(4)	2431(5)	28(2)

^a Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond Lengths (\AA) for **5**

Pt(1)–Cl(1)	2.539(2)	Pt(1)–Cl(2)	2.507(2)
Pt(1)–C(5)	2.180(8)	Pt(1)–C(6)	2.139(9)
Pt(1)–C(13)	2.061(8)	Pt(1)–C(17)	2.183(9)
Pt(1)–C(18)	2.163(8)	Cl(1)–Pt(2)	2.527(2)
Cl(2)–Pt(2)	2.504(2)	Pt(2)–C(1)	2.135(9)
Pt(2)–C(2)	2.183(8)	Pt(2)–C(7)	2.062(8)
Pt(2)–C(11)	2.182(8)	Pt(2)–C(12)	2.146(8)
C(1)–C(2)	1.388(11)	C(2)–Si(1)	1.870(8)
Si(1)–C(3)	1.868(8)	Si(1)–C(4)	1.854(9)
Si(1)–C(5)	1.879(8)	C(5)–C(6)	1.411(11)
C(7)–C(8)	1.531(12)	C(8)–Si(2)	1.877(9)
Si(2)–C(9)	1.870(8)	Si(2)–C(10)	1.856(11)
Si(2)–C(11)	1.899(8)	C(11)–C(12)	1.388(12)
C(13)–C(14)	1.507(14)	C(14)–Si(3)	1.878(11)
Si(3)–C(15)	1.860(10)	Si(3)–C(16)	1.862(11)
Si(3)–C(17)	1.856(8)	C(17)–C(18)	1.406(11)

alkyl linkage. Related Pt(II) olefin–alkyl chelating ligands have Pt–C σ bonds of 2.04 and 2.05 \AA .^{40,41}

Solutions of crystals of **5** or mixtures which contained **4** and **5** were analyzed spectroscopically to confirm that the crystal structure of **5** is maintained in solution. In the ^1H NMR of **5**, which also contained the oligomeric products from the reaction in eq 8, namely $\text{M}^{\text{vi}}\text{D}_x\text{M}^{\text{vi}}$, the free vinyl resonance from the oligomeric product appeared from 6.3 to 5.4 ppm. The coordinated vinyl proton peaks occurred from 4.0 to 2.8 ppm. The protons on the methylene group coordinated to Pt were observed at 1.9 ppm ($J_{\text{Pt-H}} = 50$ Hz), while the methylene protons of the ethyl group adjacent to Si were observed at 0.94 ppm. The Si–methyl proton resonances were present from 0.2 to -0.35 ppm.

The ^{13}C spectrum of **5** showed the CH of the coordinated vinyl (determined from a separate APT experiment) at 81.39 ppm ($J_{\text{Pt-C}} = 150$ Hz) and the CH_2 resonance at 70.30 ppm ($J_{\text{Pt-C}} = 120$ Hz). In the upfield

Table 5. Bond Angles (deg) for **5**

Cl(1)–Pt(1)–Cl(2)	85.9(1)	Cl(1)–Pt(1)–C(5)	93.9(2)
Cl(2)–Pt(1)–C(5)	90.7(2)	Cl(1)–Pt(1)–C(6)	132.0(2)
Cl(2)–Pt(1)–C(6)	93.8(2)	C(5)–Pt(1)–C(6)	38.1(3)
Cl(1)–Pt(1)–C(13)	94.5(3)	Cl(2)–Pt(1)–C(13)	179.1(3)
C(5)–Pt(1)–C(13)	90.0(3)	C(6)–Pt(1)–C(13)	86.5(3)
Cl(1)–Pt(1)–C(17)	91.3(2)	Cl(2)–Pt(1)–C(17)	91.3(2)
C(5)–Pt(1)–C(17)	174.5(3)	C(6)–Pt(1)–C(17)	136.6(3)
C(13)–Pt(1)–C(17)	87.9(3)	Cl(1)–Pt(1)–C(18)	128.6(2)
Cl(2)–Pt(1)–C(18)	88.3(2)	C(5)–Pt(1)–C(18)	137.3(3)
C(6)–Pt(1)–C(18)	99.4(3)	C(13)–Pt(1)–C(18)	90.9(4)
C(17)–Pt(1)–C(18)	37.7(3)	Pt(1)–Cl(1)–Pt(2)	91.8(1)
Pt(1)–Cl(2)–Pt(2)	93.1(1)	Cl(1)–Pt(2)–Cl(2)	86.2(1)
Cl(1)–Pt(2)–C(1)	131.5(2)	Cl(2)–Pt(2)–C(1)	93.6(2)
Cl(1)–Pt(2)–C(2)	94.1(2)	Cl(2)–Pt(2)–C(2)	90.4(2)
C(1)–Pt(2)–C(2)	37.5(3)	Cl(1)–Pt(2)–C(7)	92.0(2)
Cl(2)–Pt(2)–C(7)	177.5(3)	C(1)–Pt(2)–C(7)	88.9(3)
C(2)–Pt(2)–C(7)	91.5(3)	Cl(1)–Pt(2)–C(11)	96.1(2)
Cl(2)–Pt(2)–C(11)	90.3(2)	C(1)–Pt(2)–C(11)	132.4(3)
C(2)–Pt(2)–C(11)	169.9(3)	C(7)–Pt(2)–C(11)	88.1(3)
Cl(1)–Pt(2)–C(12)	133.2(2)	Cl(2)–Pt(2)–C(12)	89.1(2)
C(1)–Pt(2)–C(12)	95.2(3)	C(2)–Pt(2)–C(12)	132.5(3)
C(7)–Pt(2)–C(12)	90.9(3)	C(11)–Pt(2)–C(12)	37.4(3)
Pt(2)–C(1)–C(2)	73.2(5)	Pt(2)–C(2)–C(1)	69.4(5)
Pt(2)–C(2)–Si(1)	120.7(4)	C(1)–C(2)–Si(1)	124.2(6)
C(2)–Si(1)–C(3)	110.6(4)	C(2)–Si(1)–C(4)	105.3(4)
C(3)–Si(1)–C(4)	108.0(4)	C(2)–Si(1)–C(5)	117.3(4)
C(3)–Si(1)–C(5)	111.9(4)	C(4)–Si(1)–C(5)	102.9(4)
Pt(1)–C(5)–Si(1)	120.5(4)	Pt(1)–C(5)–C(6)	69.4(5)
Si(1)–C(5)–C(6)	123.5(6)	Pt(1)–C(6)–C(5)	72.5(5)
Pt(2)–C(7)–C(8)	112.0(6)	C(7)–C(8)–Si(2)	109.7(5)
C(8)–Si(2)–C(9)	110.6(4)	C(8)–Si(2)–C(10)	114.0(4)
C(9)–Si(2)–C(10)	109.9(5)	C(8)–Si(2)–C(11)	103.6(4)
C(9)–Si(2)–C(11)	109.3(4)	C(10)–Si(2)–C(11)	109.2(4)
Pt(2)–C(11)–Si(2)	107.0(4)	Pt(2)–C(11)–C(12)	69.9(5)
Si(2)–C(11)–C(12)	120.8(6)	Pt(2)–C(12)–C(11)	72.7(5)
Pt(1)–C(13)–C(14)	113.1(6)	C(13)–C(14)–Si(3)	111.7(7)
C(14)–Si(3)–C(15)	113.9(4)	C(14)–Si(3)–C(16)	108.6(5)
C(15)–Si(3)–C(16)	110.0(5)	C(14)–Si(3)–C(17)	103.4(4)
C(15)–Si(3)–C(17)	109.2(4)	C(16)–Si(3)–C(17)	111.7(4)
Pt(1)–C(17)–Si(3)	108.2(4)	Pt(1)–C(17)–C(18)	70.3(5)
Si(3)–C(17)–C(18)	121.2(6)	Pt(1)–C(18)–C(17)	71.9(5)

Table 6. ^{195}Pt NMR Shifts

	reacn	eq	^{195}Pt NMR shift, ppm
$\text{H}_2\text{PtCl}_6 + \text{M}^{\text{vi}}\text{M}^{\text{vi}}$ (soln A)	2	-6148, -6149	
soln A + excess $\text{M}^{\text{vi}}\text{DM}^{\text{vi}}$	4	-6148	
soln A + excess $\text{MD}^{\text{vi}}\text{M}$		-6155	
$\text{H}_2\text{PtCl}_6 + \text{M}^{\text{vi}}\text{M}^{\text{vi}}$, no NaHCO_3	2	-6148, -6149, -3470	
$\text{H}_2\text{PtCl}_6 + [(\text{CH}_3)(\text{CH}_2=\text{CH})\text{SiO}]_4$	7	-6166	
$\text{H}_2\text{PtCl}_6 + (\text{CH}_3)_2\text{Si}(\text{CH}_2=\text{CH})_2$	8	-6152, -3603	

region of the ^{13}C NMR spectrum of **5**, the silyl–ethyl resonances were observed at 11.17 and 9 ppm. The broadness of the latter peak suggested that it was the resonance associated with the CH_2 bound to Pt. The silyl–methyl resonances appeared from 1.3 to -3.1 ppm.

Crystals of **5** had a sharp decomposition point at 37 $^\circ\text{C}$. The C,H analysis for **5** was low by over 50% vs the calculated expected value. The error in the elemental analysis suggested incomplete combustion in the analysis. Platinum analysis was performed at the GE research center, where much time and effort was devoted to ensuring complete dissolution of the analyte. Platinum bis(acetylacetonate) was employed as an organic-soluble Pt standard. For **5** the calculated percentage of Pt was 48.8% and the measured value was 49.8%.

Attempts were made to analyze **5** via FDMS. The FDMS spectrum for crystals of **5** (Figure 6) showed an isotope pattern whose relative intensities matched a computer-generated model for $\text{C}_{12}\text{H}_{28}\text{Cl}_2\text{Pt}_2\text{Si}_2$. The mass spectrum is consistent with loss of $(\text{CH}_3)_2\text{Si}$ –

(40) Panattoni, C.; Bombieri, G.; Forsellini, E.; Crociani, B. *J. Chem. Soc., Chem. Commun.* **1969**, 187.

(41) Pedone, C.; Benedetti, E. *J. Organomet. Chem.* **1971**, 31, 403–414.

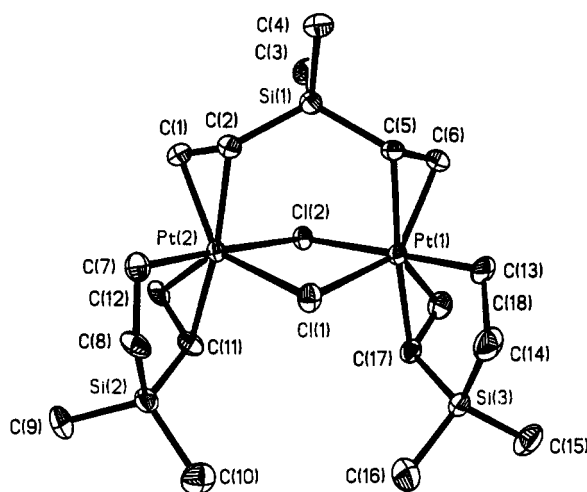


Figure 4. Thermal ellipsoid plot for **5**.

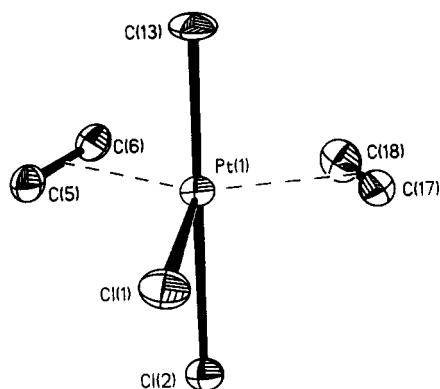


Figure 5. Coordination environment for Pt(1) in **5** emphasizing the TBP geometry at platinum. X(1A) = centroid between C(17) and C(18) and X(1B) = centroid between C(5) and C(6). Pt–Cl(1) = 2.540 Å, Pt–Cl(2) = 2.508 Å, Pt–C(13) = 2.061 Å, Pt–X(1A) = 2.056 Å, Pt–X(1B) = 2.041 Å. C(13)–Pt–Cl(2) = 179°, X(1A)–Pt–X(1B) = 137.2°, X(1A)–Pt–Cl(1) = 109.9°, X(1B)–Pt–Cl(1) = 112.8°.

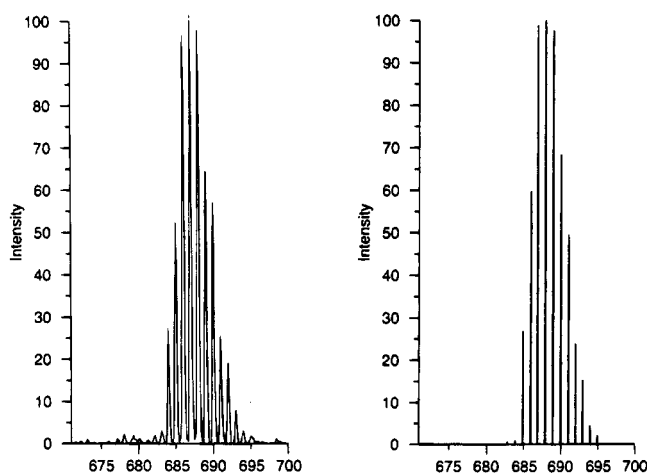


Figure 6. Field desorption mass spectrum of **5** (left) and modeled spectrum for $C_{12}H_{27}Cl_2Pt_2Si_2$ (right; this fragment corresponds to **5** with loss of the bridging ligand $(CH_3)_2Si(CH=CH_2)_2$).

$(CH=CH_2)_2$ from the parent molecule **5**, followed by protonation. Note the proposed assignment for the observed pattern is composed of contributions due to two platinum atoms and two chlorine atoms and therefore is likely to be a correct match. GC/MS analysis of the

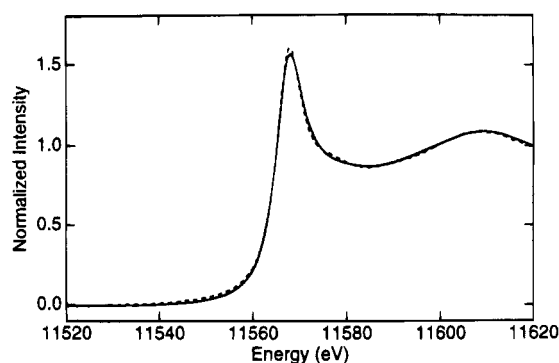


Figure 7. Pt K X-ray absorption edge spectra for **1** (—) and **4** (---).

products from eq 8 showed that $M^{vi}M^{vi}$ and higher oligomers of $M^{vi}D_xM^{vi}$ ($x > 0$) were formed as well.

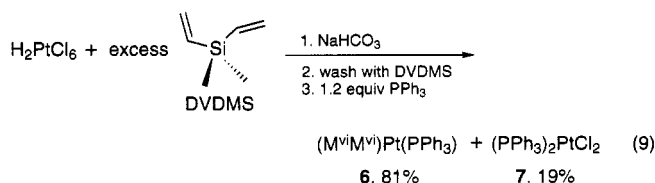
Structure of 4. In the proton NMR spectrum of **4**, the silyl–ethyl resonances of **5** are absent. Moreover, no resonances are observed for free vinyl protons when the sample was subjected to vacuum stripping for 3 days. It was never possible in the synthesis of Karstedt's catalyst to completely remove all of the free vinyl due to the higher molecular weight of the $M^{vi}D_xM^{vi}$ formed in the preparation of **1**. However, the volatility of the vinyl-stopped oligosiloxane formed in eq 8 was sufficiently high for it to be completely removed under vacuum (0.01 mmHg). Samples of **4** did not crystallize from solution at $-15^\circ C$ for over 6 months.

The ^{13}C NMR spectrum of **4** shows coordinated vinyl at nearly the same resonance as the bound vinyl of **1**, consistent with a Pt(0) complex. As in the 1H spectrum, the resonances due to the vinyl and silyl–ethyl groups of **5** were absent. These spectra demonstrated that no **5** was present when excess $NaHCO_3$ was employed in the reaction of eq 8.

A solution of **4** was added to CH_2Cl_2 and stirred vigorously with 0.1 M $HCl(aq)$ for 1 h. The CH_2Cl_2 layer was separated from the aqueous layer, and then the CH_2Cl_2 was removed in vacuo to leave an oil. The oil was placed in a freezer compartment of a refrigerator (ca. $-15^\circ C$), and crystals of **5** formed within 4 days. These results can be summarized by the lower portion of eq 8. The spectroscopically observed yield described above for **5** was 10%, while the recovered yield of the crystals was 1–2%.

EXAFS and X-ray absorption near edge spectroscopy (XANES) analyses were carried out on solutions of **4**. The XANES analysis clearly showed that the platinum oxidation state of **4** was identical with that of **1** (Figure 7). As shown in Figure 1b, the EXAFS of **4** was far more complicated than that of **1** but appeared to contain Pt–C in the first coordination sphere and Pt–Si in the second coordination sphere.

The mixture obtained from eq 8 was reacted with 1.2 equiv of $P(C_6H_5)_3$ to derivatize the platinum products and learn more about the structure of **4** (eq 9). Lappert's



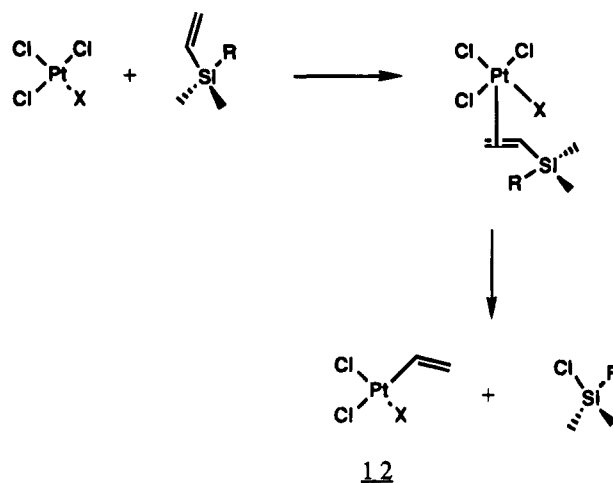
group carried out similar experiments with phosphines and solution A, which generated analogs of complex **6**.¹⁴ The product ratios from eq 9 were determined by ³¹P NMR integration and confirmed by isolated yields. The presence of compounds **6**⁴² and **7** was determined by ³¹P NMR spectroscopy. Both **6** and **7** were isolated as crystalline products; **7** crystallized first, and large crystals of **6** were then obtained by slow evaporation of the filtrate. The identity of **6** was confirmed by ¹H and ¹³C NMR and FDMS.⁴² ¹H and ¹³C NMR analysis of **7** showed phenyl resonances, shifted from those of free triphenylphosphine. The NMR data for **6** showed resonances for the bound vinyl of M^{vi}M^{vi}; these resonances were absent in the NMR of **7**. Compound **7** was further identified by FDMS analysis, which showed a molecular ion centered at 790 amu.

All known Pt(0) olefin compounds are three- or four-coordinate. It seems likely that **4** is a Pt(0) complex with three or four olefin ligands in the coordination sphere of platinum derived from some combination of (CH₃)₂Si(CH=CH₂)₂ and M^{vi}M^{vi}, e.g. Pt₂(M^{vi}M^{vi})_x((CH₃)₂Si(CH=CH₂)₂)_y (x and/or y = 2).

We suggest that **5** (the Pt(II) complex) is NOT an intermediate in the formation of **4** (the Pt(0) complex) from H₂PtCl₆ and (CH₃)₂Si(CH=CH₂)₂, although one might argue that hydrolysis of **5** occurs to give a bound silanol, eliminating ethylene and HCl, which were both observed during decomposition of **5**. Rapid condensation of the silanols would lead to formation of the Si—O—Si bond. However, when anhydrous PtCl₄ was reacted with (CH₃)₂Si(CH=CH₂)₂ under anhydrous conditions,¹⁹⁵Pt NMR analysis showed only Pt(0) was present (no Pt(II) signal was observed). Analysis of the silicon-containing products by ²⁹Si NMR showed that, besides unreacted (CH₃)₂Si(CH=CH₂)₂, the major product was (CH₃)₂Si(CH=CH₂)Cl. After exposure to air, analysis by GC/MS confirmed the presence of (CH₃)₂Si(CH=CH₂)Cl and the formation of M^{vi}M^{vi} (M^{vi}M^{vi} was present in only trace amounts before exposure to air). Thus, silicon—vinyl reacted with Pt—Cl to give Si—Cl and Pt—vinyl (vide infra). Therefore, we conclude that the more likely scenario is that **5** results from the reaction of **4** with HCl generated by the hydrolysis of silyl chloride species.

Mechanism of Formation of Pt(0) Complexes with Si—Vinyl Reducing Agents. The most important step in the chemistry described here is the reduction of platinum by silicon—vinyl. Under anhydrous conditions, silicon—chloride products were formed directly from reaction of silicon—vinyl with platinum chloride. Formation of the silicon—chloride bond constitutes a thermodynamic driving force. This piece of the chemistry is shown in Scheme 1, where X can be Cl, H, or D. Scheme 1 explains the formation of the silicon products. There is ample precedent for such a transformation, particularly in palladium and platinum systems.^{44–47} Fitch and co-workers have noted the relative instability of dichloro—Pt(II) vinylsilane com-

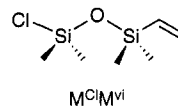
Scheme 1



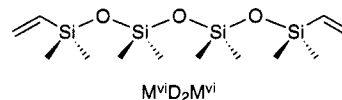
plexes relative to the Pt(0) species.^{48,49} Hydrolysis of the chlorosilane produced in Scheme 1 gives the observed siloxane products. The reactions in Scheme 2 show the hydrolysis, condensation, and equilibration reactions that account for the methyl- and vinyl-containing siloxane products.

A method for formation of ethylene and butadiene and for further reduction of platinum is shown in Scheme 3. Note that when the platinum source was D₂PtCl₆, then **8** reacted with DCl to form PtCl₄ and C₂H₃D. Compound **8** can also react with more vinylsiloxane to make the divinyl compound **9**. Note that if X = H or D, formation of Si—Cl was always observed and that formation of Si—H (or Si—D) was never observed nor were any products based on addition of Si—H to vinyl observed. Again, the chlorosilane product reacts as shown in Scheme 2. Compound **13** may react via a reductive-elimination path to give butadiene and the Pt(II) product. Recall that when K₂PtCl₄ was used in place of H₂PtCl₆, butadiene was the main gaseous product and ethylene was only formed when H₂PtCl₆ was the platinum source.

The molecular weight of the M^{vi}D_xM^{vi} oligomers was higher when H₂PtCl₆ was reacted with M^{vi}M^{vi} in the presence of added ethylene than when no ethylene was added. M^{vi}M^{vi} can take part in one of two reactions. If M^{vi}M^{vi} reacts with platinum as shown in Scheme 1, then



forms, which then reacts as in scheme 2 to form



Alternatively, M^{vi}M^{vi} can react with M^{vi}D₂M^{vi} (or any other oligomer) in the Lewis-acid-catalyzed equilibration reaction of Scheme 2 to form 2 equiv of M^{vi}DM^{vi}. When

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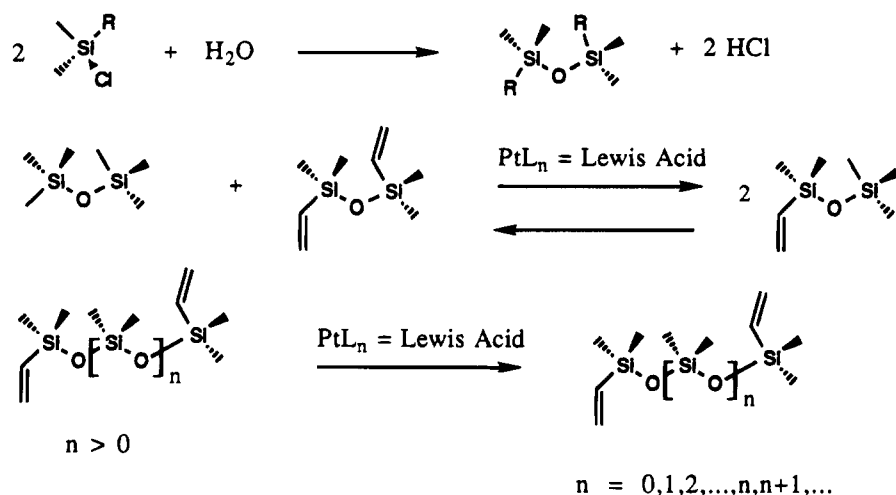
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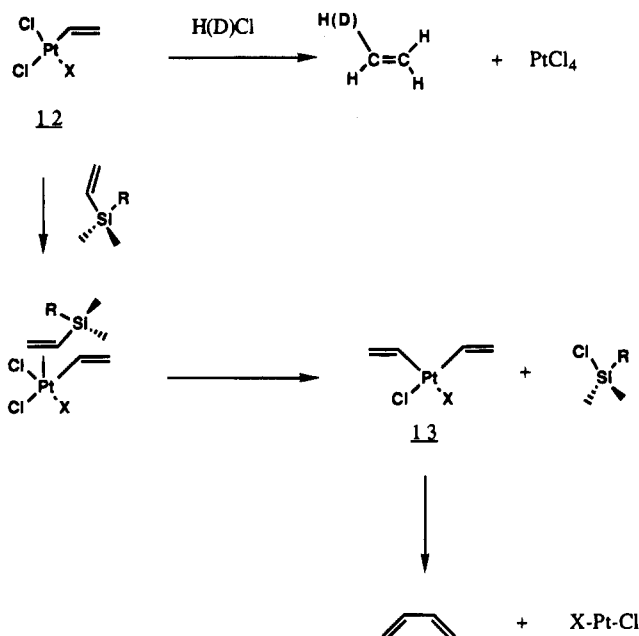
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Scheme 2



Scheme 3



M^{vi}M^{vi} was reacted with H₂PtCl₆ in the presence of ethylene, the reaction of silicon-vinyl with platinum was inhibited because silicon-vinyl must compete with ethylene for coordination sites on platinum. Thus, the M^{vi}M^{vi} equilibration reaction with higher oligomers was more likely when ethylene was present. The equilibration reaction must consume M^{vi}M^{vi} at a faster rate than did the reaction in Scheme 1. The histograms in Figures 2 and 3 may simply show that M^{vi}M^{vi} was more rapidly consumed when ethylene was present than when ethylene was absent.

The other observed products are explained by the following observations. Equation 2 gave mostly ethylene and butadiene gaseous products with lesser amounts of ethane, butenes, and butane. The main polysiloxane products were M^{vi}D_xM^{vi} oligomers with lesser amounts of M^{vi}D_xM^{Et}. The hydrogen source which converted the unsaturated olefins to the observed saturated species was from the hydrogen atoms of chloroplatinic acid and from ethylene. When D₂PtCl₆ was reacted with M^{vi}M^{vi}, the observed ethylene contained C₂H₃D. This result suggested that the deuterium of D₂PtCl₆ would react with the vinyl ligand. Indeed, the HCl observed at the

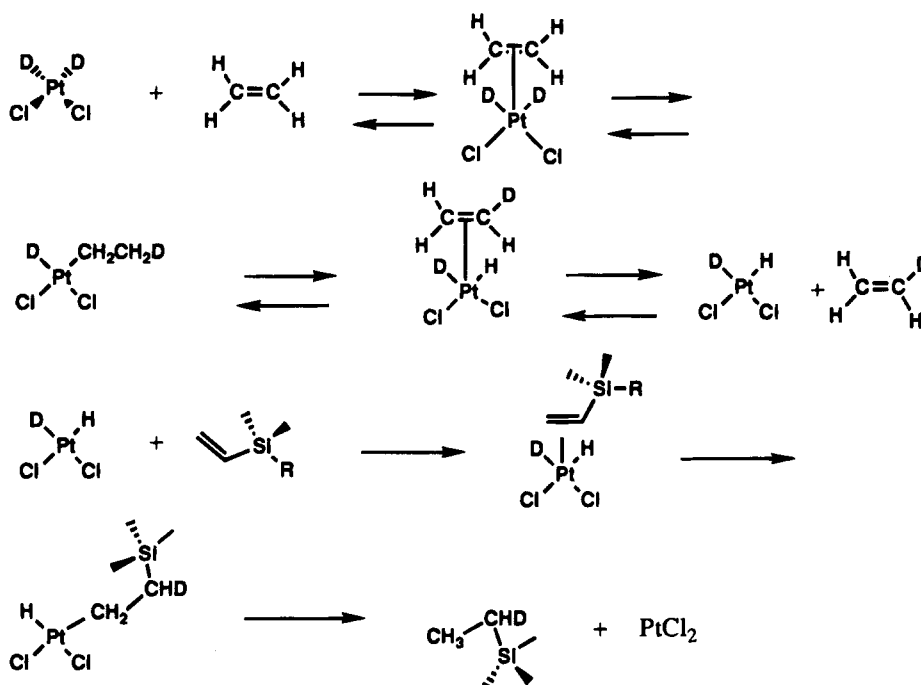
end of the reaction contains only protio material, because the gas is generated ultimately by the reaction between water and silyl chloride (also, DCl is difficult to detect because of exchange as discussed above). When D₂PtCl₆ was reacted with M^{vi}M^{vi}, deuterium was observed in the M^{vi}D_xM^{Et} oligomers as well as in the gaseous products ethane and butenes. The products derived from hydrogenation of unsaturated groups were formed in very low yield relative to ethylene, butadiene, and the vinyl-polysiloxane products. The reactions in Scheme 4, which attempt to explain these results, must have occurred with low efficiency. In summary, there is a pathway to exchange hydrogen atoms from vinyl to ethyl on ligands, but there does not seem to be a reversible shuttle from olefin to vinyl.

When C₂D₄ was present during the reaction of H₂-PtCl₆ with M^{vi}M^{vi}, GC/MS analysis of the ethylene product showed only C₂H₄ and C₂D₄. This result confirms that the steps that occurred in Scheme 4 happen to a very small extent. The presumed mixed ethylene, e.g. C₂D₃H, was present in small quantities compared to C₂H₄ and C₂D₄. Deuterated ethyl-silicon, ethane, etc. were observed because these products were only formed from the exchange processes shown in the schemes.

Experimental Section

General Considerations. All operations were carried out in air with standard reagents unless otherwise noted. ¹H and ¹³C NMR spectra were recorded on a GE QE-300 instrument at 300.15 and 75.48 MHz, respectively. Additional ¹³C, ²⁹Si, and ¹⁹⁵Pt NMR spectra were recorded on a GE GN-Omega 500 NMR instrument at 125.8, 76.77, and 107.512 MHz, respectively. ²⁹Si NMR spectra were all recorded with 1% Cr(acac)₃ relaxation reagent and employed gated decoupling. In order to record ¹⁹⁵Pt NMR spectra where peaks were separated by more than 2000 ppm, the transmitter offset had to be moved and the probe retuned. GC measurements were made with a Hewlett-Packard Model 5890 instrument coupled to a Model 3393 integrator and Model 7673A auto sampler and using a 6-ft, 3% OV-101 column with a thermal conductivity detector. GC/MS analysis was carried out using a JEOL SX 102 high-resolution, double-focusing magnetic sector instrument; for liquid samples a 30 m DB 5 capillary column was employed, and for gas samples a 10 ft Supelco Fluorocol 1/8 in. packed column was used. FDMS measurements were made using a JEOL Model HX 110 instrument. Platinum analyses were

Scheme 4

**Table 7. PtL_{III} EXAFS Data Collection and Reduction for Platinum Samples**

SR facility	SSRL
beam line	7-3
monochromator cryst	Si[220]
energy resolution, eV	~1
detection method	fluorescence
detector type	13-element solid state array ^a
scan length, min	21
scans in average	12
temp, K	10
energy std	Pt foil (inflection)
energy calibration, eV	11563
E_0 , eV	11580
pre edge bkgd energy range	11240–11725 (2)
eV (polynomial order)	
spline bkgd energy range	11580–11725 (2),
eV (polynomial order)	11725–11948 (3),
	11948–12250 (3)

^a Maintained by NIH Biotechnology Research Resource at SSRL.⁵⁴

performed by ICP (inductively coupled plasma) by digesting the samples in refluxing aqua regia, after which aqueous NaOH was added to dissolve the polysiloxane portion. $\text{Pt}(\text{acac})_2$ was used as a spike standard. $\text{Pt}(\text{COD})_2$ ^{50,51} and $\text{Cl}_2\text{-Pt}(\text{PPh}_3)_2$ ⁵² were made by literature methods.

EXAFS Analysis. X-ray absorption spectroscopic data collection was performed at Stanford Synchrotron Radiation Laboratory (SSRL). Data reduction was performed using XFPACK software developed as described.⁵³ Details of the data collection and reduction are summarized in Table 7. On beam line X10C at NSLS, the beam was also focused horizontally and vertically downstream of the monochromator and the vertical beam position was stabilized by feedback control of the mirror tilt angle using an in-hutch beam position monitor.

Curve-fitting analyses of the EXAFS data used scattering functions calculated by the FEFF program (v3.25).⁵⁴ In all

FEFF calculations, the amplitude reduction factor was set to 0.9, the Debye–Waller factor (σ^2) was set to zero, the coordination numbers for central and scattering atoms were left as 1, and the muffin-tin potential overlap was set to 1.0 (no overlap). All other parameters were defaulted to values recommended by the FEFF authors.⁵⁴ The resulting FEFF scattering parameters were ported to XFPACK and used in curve-fitting optimizations that varied only absorber–scatterer distance (R_{as}) and Debye–Waller factor (σ_{as}^2). Tests of such FEFF parameters on a series of model compounds determined that a ΔE_0 of +10 eV was required (i.e., 10 eV must be added to the calculated phase functions) to match these parameters to our arbitrary selection of $E_0 = 11\,580$ eV used in extracting the experimental EXAFS. These tests also confirmed that the FEFF parameters yield bond distance to an accuracy better than ± 0.02 Å.

Chloroplatinic Acid + Vinyl–Polysiloxanes. The reaction of H_2PtCl_6 with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ has been described.¹⁴ A representative reaction of H_2PtCl_6 with a vinyl–polysiloxane is given here. H_2PtCl_6 (1 g, 2.0 mmol) was combined with pentamethylvinylidisiloxane, MM^{vi} (20 g, 115 mmol), and heated to 80 °C with stirring for 2 h. At this point NaHCO_3 (1.3 g, 15.4 mmol) was added and gas evolution was noted. The solution was then stirred an additional 1 h at ambient temperature and then filtered and washed with 0.7 g of MM^{vi} to give 18.2 g of a maroon solution, 1.68% Pt by weight. If a lower amount of MM^{vi} was used (9.4 g), then the resultant solution was 0.07% Pt by weight; i.e., most of the platinum is filtered off as insoluble material.

$\text{Pt}(\text{COD})_2 + \text{M}^{\text{vi}}\text{M}^{\text{vi}}$. $\text{Pt}(\text{COD})_2$ (0.0074 g, 0.018 mmol) was dissolved in C_6D_6 (0.5 mL) in an NMR tube, and then $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ (0.0197 g, 0.106 mmol) was added. The NMR data are discussed in the text.

Reaction of H_2PtCl_6 with $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$. (a) $\text{H}_2\text{-PtCl}_6$ (1 g, 2 mmol) was combined with $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$ (15 g, 134 mmol) and heated at 85 °C with stirring for 2.5 h. NaHCO_3 (0.35 g, 4.1 mmol) was then added, and this mixture was stirred an additional 1 h at ambient temperature. This solution was filtered and the filtrate washed with $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$ (2 g) to give 11.1 g of a yellow solution, 3.37% Pt by weight. This solution was stored in a freezer (–15 °C) in

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the dark, and white crystals of **5** formed after about 2 weeks. A 0.025 g amount of white crystals was obtained: 3% isolated yield based on H_2PtCl_6 ; mp. 37°C dec. The crystals were stored in the freezer in the dark and were used for the single-crystal X-ray and FDMS analyses.

(b) The reaction was carried out as in (a) except that 8 equiv of NaHCO_3 (1.4 g) was used. A yellow solution, 9.8 g, 3.78% Pt by weight, was obtained.

(c) The reaction was carried out as in (a) except that ethanol (2 mL) was added initially. A yellow solution, 9.6 g, 3.93% Pt by weight, was obtained. No crystals formed using methods b or c.

Reaction of H_2PtCl_6 with $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$ in the Presence of PPh_3 . H_2PtCl_6 (1 g) and $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$ (15 g, 134 mmol) were combined and heated as described in method a above to give a yellow solution. Then 11.32 g (1.96 mmol of Pt) of this yellow solution was combined with PPh_3 (0.64 g, 2.4 mmol) dissolved in CH_2Cl_2 (10 mL). White crystals were initially obtained, which precipitated. These were collected by filtration and washed with hexane and then dried in vacuo. The yield was 0.3 g (0.38 mmol) of **7** (19%). The ^1H NMR spectrum and FDMS agreed with those obtained for $(\text{PPh}_3)_2\text{PtCl}_2$ made according to a literature procedure.⁵² The residual mother liquor was allowed to sit several days, from which crystals of **6** deposited, 1 g, 1.5 mmol, 81% yield.

Reaction of D_2PtCl_6 with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$. H_2PtCl_6 (2 g) was dissolved in D_2O (10 mL) and then heated in an oven at 100°C until a dry free-flowing solid was obtained, which was assumed to be mostly D_2PtCl_6 . D_2PtCl_6 (1 g, 2 mmol) and $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ (25 g, 0.13 mol) were heated at ca. 120°C for 7 h. The polysiloxane product from this reaction was then analyzed by GC/MS.

Reaction of H_2PtCl_6 with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ and MM. H_2PtCl_6 (1 g, 2 mmol) was combined with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ (10 g, 53.8 mmol) and MM (4.3 g, 26.5 mmol) and then heated at 70°C for 90 min. Some insoluble black solid formed. NaHCO_3 (1 g) was added, and the mixture was stirred an additional 30 min. The mixture was then filtered, and a yellow liquid was obtained (1.64% Pt).

Reaction of H_2PtCl_6 with $\text{M}^{\text{vi}}\text{M}$. H_2PtCl_6 (1 g, 2 mmol) was combined with $\text{M}^{\text{vi}}\text{M}$ (9.4 g, 54 mmol) and then heated for 90 min at 70°C to give a maroon solution. NaHCO_3 (1 g)

was added, and the solution was stirred an additional 30 min. The solution was filtered to give a pale yellow solution (690 ppm of Pt).

Reaction of H_2PtCl_6 with $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ under an Ethylene Atmosphere. Reactions were carried out with either C_2H_4 or C_2D_4 ; a representative experiment is described. A 90 mL Fischer–Porter thick-walled glass bottle, equipped with a magnetic stirbar, was charged with H_2PtCl_6 (0.5 g, 1.2 mmol) and $\text{M}^{\text{vi}}\text{M}^{\text{vi}}$ (5 g, 26.9 mmol). The bottle was then subjected to three cycles of degassing and readdition of N_2 ; the last step left the bottle under reduced pressure. C_2H_4 (54 psig, 13.5 mmol) was added to the evacuated, degassed bottle, and the contents were stirred while the pressure was monitored to ensure no leak was present in the system. The tube was then heated behind a protective shield to 70°C for 17 h. After the system was cooled to ambient temperature, the pressure in the bottle exceeded 100 psig, indicating that gas was produced in the reaction. The gases were collected by condensing with dry ice and then analyzed by GC/MS. The solution remaining had a dark precipitate.

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Supplementary Material Available: Figures giving additional NMR spectra for the compounds discussed in this paper (8 pages). Ordering information is given on any current masthead page.

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