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The First Alkene−Platinum−Silyl Complexes: Lifting the Hydrosilation Mechanism Shroud with Long-Lived Precatalytic Intermediates and True Pt Catalysts

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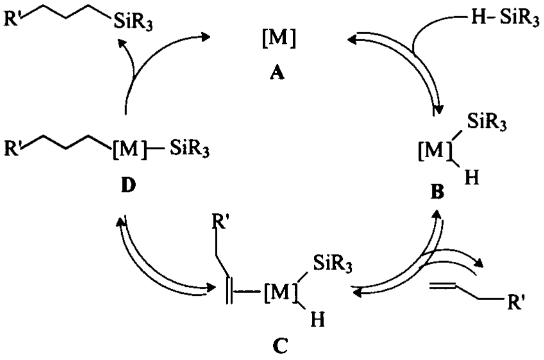
Abstract: The synthesis, characterization, and exploratory chemistry of two classes of alkene−platinum−silyl complexes, which have been postulated as hydrosilation intermediates, are described in this report. The unique dimeric complexes **1**, $[R_3Si(\mu\text{-Cl})(\eta^2\text{-COD})Pt]_2$ {R_3Si = Et_3Si, $MeCl_2Si$, Me_2ClSi, "$(EtO)_3Si$", $PhMe_2Si$, and $(Me_3SiO)Me_2Si$; COD = cycloocta-1,5-diene}, and the bis-silyl complexes **2**, $(\eta^4\text{-COD})Pt(SiR_3)_2$ (R_3Si = Cl_3Si, $MeCl_2Si$, Me_2ClSi, and $PhMe_2Si$), are formed from the sequential reaction of 2 and 4 equiv of the corresponding hydrosilanes, respectively, with $Pt(COD)Cl_2$ in the presence of a small excess of COD. Complexes **1** are stable for many days in solution at room temperature but decompose via slow elimination of chlorosilane. Some of the bis-silyl compounds **2** are stable for extended periods under inert atmosphere and especially below 0 °C, either in the solid state or in solution (in the presence of a small excess of free COD). Complexes **2** display catalytic activity as discrete, molecular, and mononuclear species for hydrosilation and isomerization reactions. Compound **2c** (R_3Si = $MeCl_2Si$) was fully characterized via multinuclear NMR spectroscopy and X-ray crystal structure analysis. The facile H-transfer rather than Si-transfer to bound COD provides experimental support for the sequence of insertive steps in the Chalk−Harrod catalytic cycle, at least for Pt-catalyzed hydrosilation.

Introduction

Platinum-catalyzed hydrosilation is a versatile reaction in organosilicon chemistry and is second only to the Rochow process for its importance to silicon−carbon bond formation in the silicone industry.[1] Since Speier's extensive work with hexachloroplatinic acid as a catalyst for the addition of hydrosilanes to alkenes,[2,3] numerous salts, complexes, and supported forms of platinum have been used to add hydrosilanes to a variety of unsaturated compounds, yet little is known about the nature of the reactive intermediates involved in the catalytic cycle. Some years following Speier's initial reports, Chalk and Harrod proposed a mechanism for the catalytic cycle based on the similarities between transition metal-catalyzed hydrogenation and hydrosilation (Scheme 1).[4]

Scheme 1. Chalk−Harrod Mechanism



The elementary steps of the Chalk−Harrod catalytic cycle consist of the formation of reactive intermediates **B**, **C**, and **D** via oxidative addition, alkene coordination to the metal center, migratory insertion between a metal−element bond, and reductive elimination. The nondescript species **A** is visualized to be the active, catalytic metal complex in its resting state. Of the above four species in this catalytic cycle with platinum, to our knowledge **B** is known only with phosphines as the ancillary ligands on platinum,[5] with the exception of one unique series of compounds containing the aromatic η^5-cyclopentadienyl ligand, and a few more recent examples with nitrogen-based donors.[6] Only a few compounds of the type **D** (again, with phosphines and select alkyl/aryl groups) have been reported in

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(1) (a) Marciniec, B., Ed. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, England, 1992, and the review references therein. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1479. (c) Harrod, J. F.; Chalk, A. J. In *Organic Synthesis Via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; p 673.

(2) Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.

(3) Speier, J. L. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1979; Vol. 17, pp 407−447.

(4) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

(5) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

(6) (a) Boardman, L. D. *Organometallics* **1992**, *11*, 4194. (b) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3748. (c) Fang, X.; Scott, B. L.; Watkin, J. G.; Kubas, G. J. *Organometallics* **2000**, *19*, 4193.

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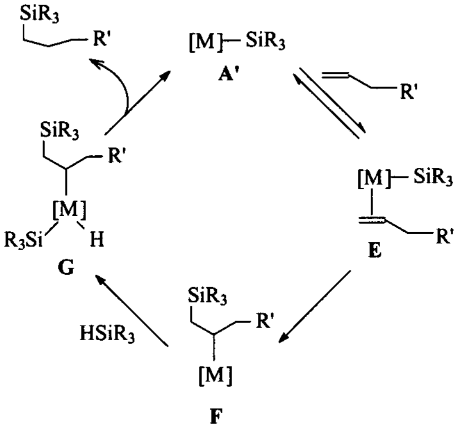
Scheme 2. Modified Chalk−Harrod Mechanism



the context of hydrosilation.[7,8] Species **A** and **C** have never been observed for Pt, although a few examples of **C** are known for the much less active metals Ir and Rh.[5,9,10]

Although the basic aspects of the Chalk−Harrod mechanism still enjoy wide acceptance, a number of phenomena, including an induction period for many precatalysts and the formation of vinylsilanes, are not explained by this mechanism.[11] Scheme 2 describes a catalytic cycle based on silyl transfer to alkene occurring first (**E** to **F**), followed by oxidative addition of silane and reductive elimination of the silylated alkane from **G**. This order of migratory insertion and elimination is the opposite of that proposed in the Chalk−Harrod mechanism and has been suggested by several researchers on the basis of identification of intermediates in hydrosilations catalyzed by metals such as Fe, Co, Rh, and Pd.[1c,12−17] This representation of the modified Chalk−Harrod mechanism implies that a metal−silyl species, **A′**, is the active catalyst. However, the scheme can just as easily be redrawn to accommodate species **A**, **B**, and **C** from the Chalk−Harrod cycle. The main difference between the two mechanisms is in the intermediates **D** and **F** (formed via hydride transfer to alkene or silyl transfer to alkene, respectively). From Scheme 2, the formation of vinylsilane products can be explained via β-hydride transfer to the metal in **F**, followed by vinylsilane decomplexation. It is noteworthy that intermediates of the type **E**, **F**, or **G** have not been reported in the literature for platinum, and vinylsilane formation to any significant extent in Pt-catalyzed alkene hydrosilation is rare. On the contrary, alkene isomerization, a common phenomenon in Pt-catalyzed hydrosilation, can be readily explained from species **D** via β-hydride transfer to the metal followed by isomerized alkene decomplexation. Thus, the modified Chalk−Harrod mechanism is a plausible pathway in hydrosilation catalyzed by metals of lower activity in this reaction, but its applicability to Pt-catalyzed hydrosilation as the primary mechanistic pathway is doubtful, particularly in light of the findings reported here.

Because dark-colored solutions are often observed in Pt-catalyzed hydrosilation and precipitation of black, metallic Pt at the end of the reaction or even during catalysis is a common occurrence, the role of homogeneous catalysis has been unclear. In 1986, Lewis and Lewis proposed[18] that colloidal Pt particles (formed via reduction of Pt complexes with the reactant silane) were a prerequisite for catalytic activity for most platinum complexes, except for clearly homogeneous ones such as $(Ph_3P)_4Pt$. Subsequent studies by Lewis's group[19,20] using Karstedt's catalyst, Pt(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)$_3$, as well as H_2PtCl_6 led to the following conclusions: (1) The vinylsiloxane ligands surrounding platinum in the Karstedt catalyst are hydrosilated away prior to reaction of the substrate alkene. This constitutes the induction period. (2) During the most active stages of hydrosilation, only species containing Pt−C and Pt−Si bonds (but no Pt−Pt bonds) were observed, irrespective of the nature or stoichiometry of the reagents: thus, only mononuclear Pt species were postulated to be catalytic. (3) The platinum end products depended strongly on reagent stoichiometry and alkene coordination strength. With excess strongly coordinating alkene, only species with Pt−C bonds were present. But, for weakly coordinating alkenes (even in excess over SiH) or with excess hydrosilane, only species with Pt−Si and Pt−Pt bonds were observed at the end. These results were also identical when chloroplatinic acid was used as the precatalyst. (4) On the basis of these observations and others reported in the paper, the researchers conclude that mononuclear, homogeneous, and likely structurally identical Pt species are responsible for hydrosilation catalysis using ordinary metal complexes. Further, oxygen acts to break up the Pt−Pt bonded species formed during hydrosilation of weakly coordinating alkenes, such that a constant supply of the catalytic mononuclear compounds can be maintained, and finally, Pt−Pt multinuclear species are likely responsible for olefin isomerization.

Just prior to the publication of the work of Lewis et al. in 1999, a report appeared on the efficient, homogeneous hydrosilation of olefins using Karstedt's catalyst modified with electron-deficient ligands such as naphthoquinones, tetracyanoethylene, fumaronitrile, etc.[21] Not only were all the naphthoquinone-modified catalysts more active than Karstedt's catalyst, but the reactions remained completely homogeneous, whereas darkening of solution color and precipitation of Pt was observed during the course of hydrosilation with Karstedt's catalyst alone. In addition, a significantly higher total turnover was achieved with excess quinone-based ligand present in the system. An even more active catalyst was one where the chelating siloxane ligand was replaced with two norbornene ligands, the third alkene on Pt being a methylnaphthoquinone. Homogeneity and heterogeneity test results showed that reactions with the modified catalysts were clearly homogeneous but hydrosilations with Karstedt's catalyst were apparently homogeneous at the beginning and likely a combination of homogeneous and heterogeneous as the reaction progressed. The report concludes that the electron-deficient ligands help stabilize and solubilize the active

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(7) Ozawa, F.; Hikida, T.; Hayashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2844.
(8) Ozawa, F. *J. Organomet. Chem.* **2000**, *611*, 332.
(9) Carlton, L.; Molapisi, J. J. *J. Organomet. Chem.* **2000**, *609*, 60.
(10) Duczmal, W.; Maciejewska, B.; Sliwinska, E.; Marciniec, B. *Transition Met. Chem.* **1995**, *20*, 162.
(11) For a concise but excellent review of mechanistic studies, see: Chan, D. Ph.D. Thesis, University of York, York, UK, 1999.
(12) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289.
(13) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415.
(14) Bergens, S. H.; Whelan, P. N. *J. Am. Chem. Soc.* **1992**, *114*, 2128.
(15) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90.
(16) Yasue, T. R. *Organometallics* **1996**, *15*, 2098.
(17) LaPointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906.
(18) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.
(19) Lewis, L. N.; Stein, J.; Gao, Y.; Colborn, R. E.; Hutchins, G. *Platinum Metals Rev.* **1997**, *41*, 66.
(20) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 3693.
(21) Steffanut, P.; Osborn, J. A.; DeCian, A.; Fisher, J. *Chem. Eur. J.* **1998**, *4*, 2008.

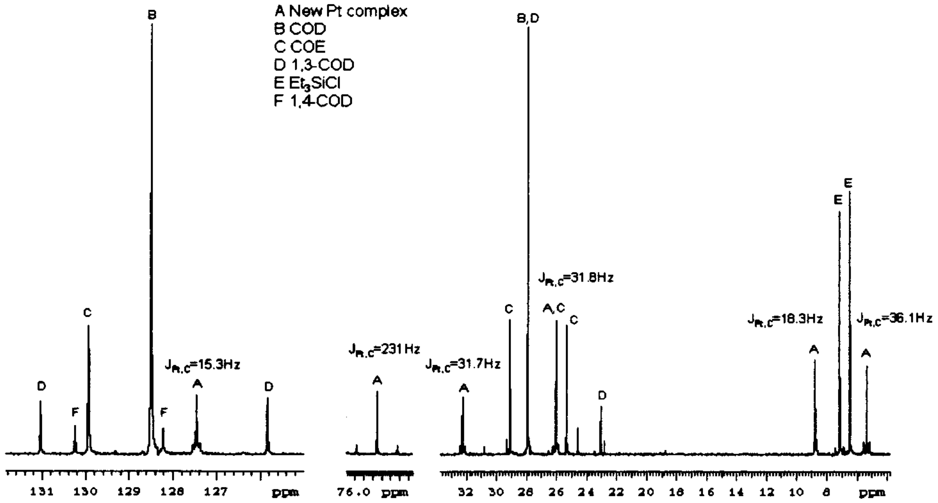

Figure 1. Expanded ^{13}C NMR spectrum of **1a** (reaction mixture) showing Pt-coupled carbons and signals due to other products.

catalytic species, and that monomeric and dimeric (hydrido-bridged) species are likely involved in the catalytic cycle.

Preamble to the Present Work. The observation that the cyclic olefins cyclooctene (COE) and cycloocta-1,5-diene (COD) are highly resistant to hydrosilation even at low concentration levels, but in their presence hydrosilations using platinum precatalysts such as H_2PtCl_6 appeared to remain completely homogeneous on repeated use of the charge of platinum, led us to postulate that these olefins remained coordinated to platinum throughout the hydrosilation cycle. Thus, they could potentially serve as chemical tracers for studying and "trapping" reactive intermediates in Pt-catalyzed hydrosilation. Accordingly, this initial study was designed to investigate stoichiometric reactions of a series of hydrosilanes with simple platinum complexes in the presence of COD in particular. The objective was to attempt to identify and characterize intermediates and reaction products from these interactions via multinuclear NMR spectroscopy. $PtCl_2$ and $Pt(COD)Cl_2$ were used as starting platinum compounds in the presence of COD. A deliberate effort was made to use a relatively high platinum concentration in solution (0.05−0.3 M) for faster analysis and easier observation with NMR spectroscopy.

Results

Reaction of Et_3SiH with $PtCl_2$ (or with $PtCODCl_2$) in the Presence of COD. Since the formation of highly reactive species was anticipated, $CDCl_3$ was used as the solvent for reaction to facilitate NMR analysis of reaction mixtures. A reaction between $PtCl_2$, Et_3SiH, and COD in a 1:1:1 ratio yielded no observable platinum complex. With 2 equiv of silane and 2−6 equiv of COD per platinum, analysis of the reaction mixture within 1−2 h of reaction by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy showed the presence of a Pt−alkene complex, COE, COD, isomerized COD (both 1,4- and 1,3-cyclooctadiene), and Et_3SiCl. Closer analysis of the NMR spectra showed the following interesting and unusual features. In the ^{29}Si NMR spectrum, only two signals were observed—one was determined to be due to Et_3SiCl (against authentic sample), and the other, at 22.9 ppm, showed distinct satellites due to Pt coupling with $^1J_{PtSi} = 1014$ Hz. In the ^{13}C NMR spectrum, two sets of Et_3Si signals were present—one due to Et_3SiCl and a second with Pt coupling to both the CH_3 and CH_2 carbons. Among several signals in the allylic region (due in part to the presence of COD, hydrogenated COD (COE), and isomerized COD), only two showed clear coupling to Pt. Farther downfield, a Pt-coupled signal was present at 74.8 ppm, with $J_{PtC} = 231$ Hz. Since complexation with Pt typically produces significant upfield shifts for olefin carbon signals, the peak at 74.8 ppm was suspected to be due to the binding of COD to Pt. However, examination of the integrals showed that only one C=C of COD was represented by the signal at 74.8 ppm.

Over 1−5 days, the complex gradually decomposed to produce more Et_3SiCl (the sole species in the ^{29}Si NMR spectrum at full decomposition) and a small quantity of $Pt(COD)Cl_2$, together with black metallic Pt. Upon careful, partial removal of volatiles from a fresh reaction mixture, a second Pt-coupled olefin signal could be seen at 127.5 ppm (only about 1 ppm upfield of pure COD) with weak coupling to Pt ($J_{PtC} = 15.3$ Hz), and with a peak integral identical to that for the Pt−olefin peak at 74.8 ppm (Figure 1). Integral comparisons now showed the composition of the Pt complex to consist of one Pt, one COD, and one Et_3Si group per "unit". Taking into account that the complex on decomposition produced Et_3SiCl, it appeared certain that it also contained one Cl per Pt as well. Additionally, the ^{195}Pt NMR spectrum showed only one Pt signal (at −4216 ppm), with the expected ^{29}Si satellites indicating that only one Pt complex was present. This required that both pairs of Pt-coupled alkene carbon signals originate from the same complex. Integration showed that the ratios of the two Pt-coupled alkene groups and the Et_3Si group was 1:1:1, meaning that there was one silyl group and one COD per Pt. Additionally, the COD was unsymmetrically bound to platinum! This is a most unusual bonding mode for COD. In all metal complexes of cycloocta-1,5-diene that we were aware of, the two olefin groups were known to be symmetrically bonded to the metal in an η^4 fashion.[22] However, in this complex, with a nearly imperceptible upfield shift of one alkene signal, it appeared that this alkene group was not directly bonded to Pt and that the coordination mode for COD was η^2 rather than η^4. The most probable structure of this complex, **1a**, as a chloride-bridged dimer, is shown below. It represents the first

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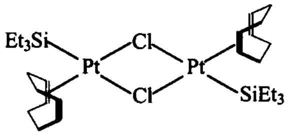
[22] A very recent publication reported the first examples of complexes of COD with η^2 bonding, to our knowledge. Oberbeckmann, N.; Merz, K.; Fischer, R. A. *Organometallics* **2001**, *20*, 3265.



1a

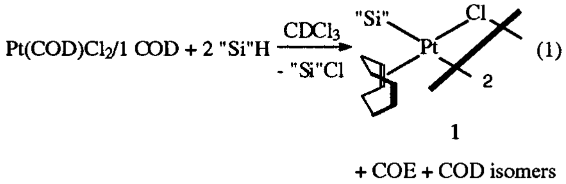
Pt complex ever seen containing a simple alkene−Pt−Si moiety. Though $PtCl_2$ was initially used as the starting platinum compound, $Pt(COD)Cl_2$ was found to be a much better substrate. Not only is this white, crystalline COD complex more soluble in $CDCl_3$, but its reactions were also easier to follow visually and were cleaner, leading to simpler NMR spectra.

Reaction of Other Representative Organosilanes with Pt(COD)Cl$_2$ in the Presence of COD. In accordance with the original plan of examining a full series of tertiary silanes in reactions with Pt compounds, representative members of hydrochlorosilanes, hydroalkoxysilanes, hydroarylsilanes, and hydrosiloxanes were examined. Trichlorosilane failed to react with $Pt(COD)Cl_2$, even under refluxing conditions or at room temperature over several days. Very weak signals for possible Pt−alkene interactions were observable in the ^{13}C NMR spectrum, but not much else could be deduced. However, both Me_2SiHCl and $MeSiHCl_2$ reacted very cleanly in the presence of only 1 mol of excess COD per mole of $Pt(COD)Cl_2$. While dimethylchlorosilane reacted at 55−58 °C, methyldichlorosilane required refluxing at 65−70 °C for 45 min to 1 h for complete reaction. In both cases, the reaction mixture was a white suspension in the beginning but became totally clear and colorless over a 2−5 min period at the reaction temperature. For dimethylchlorosilane, the clear solution then quickly turned yellow to light brown, while for methyldichlorosilane only a permanent light yellow color developed. The solutions were cooled quickly after reaction to room temperature or below using an ice bath. In view of the clean reactions with these two silanes, it is likely that trichlorosilane failed to react with $Pt(COD)Cl_2$, in part because of the silane's low boiling point, but its reaction under pressure was not examined in this study.

^1H, ^{13}C, ^{29}Si, (and ^{195}Pt) NMR spectra of the reaction mixtures from the two methylhydrochlorosilanes showed signal patterns identical to those seen for **1a**. Inequivalent olefin signals and allylic carbon signals appeared in the same regions as for **1a**, again clearly pointing to the preference for η^2-bonding of COD to Pt. Additionally, another set of small olefin and MeSi signals showing coupling to Pt appeared downfield of the corresponding signals for the main dimer compounds in the ^{13}C NMR spectra for both chlorosilane reactions. Single signals (with respective satellites) corresponding to these smaller ^{13}C peaks were also seen in the ^{29}Si and ^{195}Pt NMR spectra (see below).

As NMR analysis showed in each of the above three cases, the initial Pt complex formed contained one monodentate COD, one silyl group, and one Cl per Pt. The question remaining was whether the complex is monomeric or a Cl-bridged dimer. APCI MS was performed on the solution resulting from the reaction of $MeSiHCl_2$ with $Pt(COD)Cl_2$ and 1 equiv of excess COD. The most abundant ion observed in the high mass envelope was 909 Da, which corresponds to the Pt dimer plus three protons. The isotope pattern observed was similar to the calculated pattern. No ion was observed in the mass range of a monomeric Pt complex, but several fragment patterns corresponding to loss of Cl, Cl_2, and COD from the Pt dimer were observed to be among the strongest ions in the mass spectrum. The addition of three protons to a parent ion is unusual, but since NMR had unambiguously established the species around Pt, the APCI MS data clearly showed the Pt complex to be the four-coordinate Cl-bridged Pt dimer.

Reaction of $(EtO)_3SiH$ with $Pt(COD)Cl_2$ occurred at 58−60 °C to produce a light yellow solution which turned brown in a few hours. Although a single Pt-coupled signal among the three observed in the ^{29}Si NMR initially indicated a clean reaction, the presence of $Si(OEt)_4$ as a significant silane redistribution product and several Pt−olefin signals in the ^{13}C NMR spectrum were clear signs of a complex mixture of products (one of which could possibly be the expected dimer). Reactions with $PhMe_2SiH$ and $Me_3SiOSiMe_2H$, however, were very clean. Both the arylsilane and the siloxysilane produced the dimeric platinum compounds with the same NMR spectral patterns as for the two chlorosilanes and triethylsilane. For $PhMe_2SiH$, in addition to the dimer signals, a very small set of secondary Pt-coupled signals as for the chlorosilanes was evident in the ^{13}C NMR spectrum. Equation 1 summarizes the reactions of common classes of silanes with $Pt(COD)Cl_2$, in the presence of an additional equivalent of COD, to yield the dimers **1**. ^{13}C and ^{29}Si NMR chemical shifts for **1** are compiled in Table 1. It is particularly noteworthy that, for all silanes (except triethoxysilane), the Pt complexes **1** formed in an essentially quantitative manner as determined by NMR.



"Si" = Et_3Si **1a**
$MeCl_2Si$ **1c**
Me_2ClSi **1d**
$(EtO)_3Si$ **"1e"**
$PhMe_2Si$ **1f**
Me_3SiOMe_2Si **1g**

The clean formation of structurally identical platinum dimers from a representative range of common silanes strongly suggests that this is a common path taken by platinum−chloride-based precatalysts in their initial reaction with silanes in the presence of alkene. Various aspects of this striking observation leading to the first series of platinum complexes containing simultaneously bound alkene and silyl groups (alkene−Pt−Si) are addressed in the Discussion section.

Brief attempts were made to prepare monoolefin (cyclooctene, COE) as well as norbornadiene (NBD) equivalents of **1**. However, these reactions led to mixtures containing only chlorosilane (indicating unstable intermediates) or produced the COD-based dimer only. A few reactions of $Pt(COD)Ph_2$ (readily soluble in $CDCl_3$) with Et_3SiH were also carried out to quickly examine the effect of using a non-chloride-based starting Pt compound. Reaction was extremely slow under conditions similar to those used for eq 1. Forcing conditions produced mostly decomposition products, although some Pt−olefin signals could be clearly detected.

Table 1. ^{13}C and ^{29}Si NMR Shifts of the Indicated Signal (in ppm) and Pt Coupling Constants (in Hz) for the Pt Dimer Series **1**

	^{13}C						^{29}Si
Pt dimer	C=C(1), J_{PtC}	C=C(2), J_{PtC}	allyl(1), J_{PtC}	allyl(2), J_{PtC}	Me, J_{PtC}	SiCH$_2$, J_{PtC}	silyl, J_{PtSi}
1a	127.5, 15.3	74.8, 230.7	32.3, 31.7	26.1, 31.1	8.8, 18.3	5.4, 36.0	22.9, 1014
1c	126.7, <1	86.2, 200.2	32.0, 24.9	26.8, 21.2	10.6, 88.9		18.2, 1791
1d	126.4, none	82.7, 218.1	31.9, 27.8	26.6, 27.1	7.0, 62.2		31.2, 1329
“**1e**”	83.6, 260[a]	80.7, 253[a]	34.6, 35	24.2, 52			−23.5, 2659
1f	127.0, 12.8	77.3, 230.2	32.0, 30.4	26.2, 29.3	0.1, 37.7		1.4, 1053
1g	127.0, 15	77.8, 235.6	31.3, 31.8	26.4, 31.8	5.2, 66.2	1.56, <1[b]	8.2, 1151

[a] Several Pt−alkene resonances were observed in the ^{13}C spectrum. Peak assignments for “**1e**” are tentative. [b] SiCH$_3$.

Reactivity of Bridged Platinum Dimers toward Additional Silane. Observation of the formation of structurally identical Pt dimers from a range of silanes immediately raised the question of whether these compounds were just initial intermediates or actual catalytic species. To address this, interaction of these dimers with additional silane (and alkene) needed to be examined. Early probing of interaction of **1a** with excess Et$_3$SiH had indicated complete decomposition of the dimer (the likely reason that Lewis and co-workers and other researchers before them did not observe compounds of type **1** in their studies with Pt(COD)Cl$_2$ and silanes). However, the second set of apparently paired Pt−alkene and Pt−Si*Me* signals observed in the ^{13}C NMR spectra during dimer formation with MeSiHCl$_2$, Me$_2$SiHCl, and PhMe$_2$SiH raised the question of whether these signals were due to precursors of **1c**, **1d**, and **1f**, respectively, or whether they were due to subsequent reaction products.

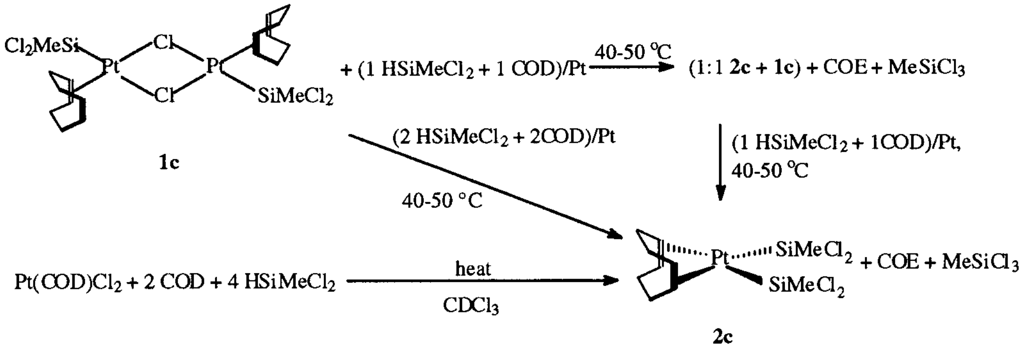
To simplify NMR spectral analysis of products, dimer **1f** was chosen first for interaction with additional silane to minimize reactive Si−Cl bonds in the system. A measured aliquot of **1f** in CDCl$_3$ was transferred to a 16 mm Si-free NMR tube at −70 °C. One equivalent of cold PhMe$_2$SiH (per Pt) was added, and the tube was shaken on a vortex mixer and quickly inserted into the NMR probe, which was precooled to −65 °C. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were acquired. These spectra all showed the presence of PhMe$_2$SiH and **1f** in 1:1 ratio. Upon raising the temperature to −50 °C, clear evidence of reaction was observed. Comparisons with the ^{13}C and ^{29}Si NMR spectra from the preparation of **1f** showed that about half of **1f** had been converted to the new Pt complex **2f** with concomitant loss of 1 equiv of PhMe$_2$SiCl. Although the ^{13}C NMR spectrum was rather crowded due to the presence of many signals from remaining **1f** and byproducts from its synthesis, new Pt-coupled olefin (δ 110.4 ppm) and Si*Me$_2$* signals due to **2f** were now prominent. The new signals exactly corresponded to those seen during the preparation of **1f**. The ratio between these signals was roughly 1:1, suggesting a normally (η^4) bound COD and two PhMe$_2$Si groups on Pt. The ^{29}Si NMR spectrum showed only three signals—due to PhMe$_2$SiCl, **1f**, and a new signal with much larger platinum coupling to silicon (J_{PtSi} = 1532 Hz) than in **1f** itself (J_{PtSi} = 1053 Hz). Further structural characterization via NMR of **2f** was difficult due to the complexity of the ^{13}C NMR spectrum and onset of decomposition above ca. −30 °C.

Much clearer structural insight on this new type of platinum complex was obtained when the reaction was repeated with MeSiHCl$_2$. One equivalent of MeSiHCl$_2$ (per Pt) was added to a CDCl$_3$ solution of **1c** (prepared as in eq 1) in an NMR tube in the spectrometer probe at −60 °C. The temperature was then raised in 20−30 °C steps. No reaction was apparent until 40−45 °C, when, as with PhMe$_2$SiH and **1f**, a growing set of new Pt−olefin and Pt−SiMeCl$_2$ signals was observed in the ^{13}C NMR spectrum. These new signals appeared at chemical shifts identical to those seen in the preparation of **1c** above. The formation of compound **2c**, with ^{13}C NMR spectral signal and integration patterns identical to those of **2f**, was further confirmed from the ^{29}Si NMR spectrum, where a new signal with larger Pt−Si coupling (J_{PtSi} = 2110 Hz) than in **1c** (J_{PtSi} = 1791 Hz) was prominent. Since only about half of **1c** had reacted with 1 equiv of silane, accompanied by the formation of an equivalent of MeSiCl$_3$, it was apparent that an additional equivalent of MeSiHCl$_2$ would likely convert **1c** completely to **2c**. This was confirmed experimentally, with a second equivalent of silane reacting to transform the remaining **1c** to **2c**. Further, a separate experiment showed that when 2 equiv of MeSiHCl$_2$ per Pt were added at one time, **1c** was completely converted to **2c**. Even more significantly, Pt(COD)Cl$_2$ could be converted completely, in a near quantitative fashion, to **2c** via reaction directly with 4 equiv of MeSiHCl$_2$, in the presence of 2−3 equiv of excess COD. The excess COD is needed because COD is lost due to both hydrogenation and isomerization reactions. The significant implications of these last two processes with COD are discussed later. The synthesis of the bis-silylplatinum (bs-Pt) species **2c** via various but equivalent paths is summarized in Scheme 3.

The clean synthesis of **2c** and the ability to remove most byproducts and solvent yielded excellent NMR spectra. From the ^{13}C NMR spectrum of **2c**, it was now clear that this new Pt complex contained only symmetrically (η^4) bound COD (as evidenced by a single olefin carbon signal with weak Pt−alkene coupling at 117.4 ppm and a single allylic carbon signal) and two SiMeCl$_2$ groups per Pt. Further, since only Si coupling and no hydride coupling to the single ^{195}Pt signal (−4577 ppm, J_{PtSi} = 2110 Hz) was observed and no Pt−hydride signal was discernible in the ^{1}H NMR spectrum, any oxidatively added Si−Pt−H-type complex could be ruled out. Figure 2 shows the ^{29}Si and ^{13}C NMR spectra for **2c**. Chemical shifts and coupling constants are tabulated in Table 2. While molecular ions for **2c** could not be directly observed via mass spectrometry despite several attempts using TOFSIMS as well as APCI MS techniques, single-crystal X-ray structure analysis showed that the structure of this compound is, indeed, that of the expected “square-planar” Pt(II) complex (see Discussion section).

Although a direct attempt was not made in this study to specifically prepare the Me$_2$ClSi− analogue **2d**, its formation during the preparation of the corresponding dimer **1d** is readily apparent from the small but identical signal patterns in the ^{13}C, ^{29}Si, and ^{195}Pt spectra for **1d**, as mentioned in the previous section (see Tables 2 and 3 for spectral data on **2d**). Platinum complex **2b**, based on −SiCl$_3$ groups on platinum, and which was not readily accessible via the above route, was prepared via a different procedure, as discussed below. It should be

Scheme 3. Formation of **2c** via Equivalent Routes



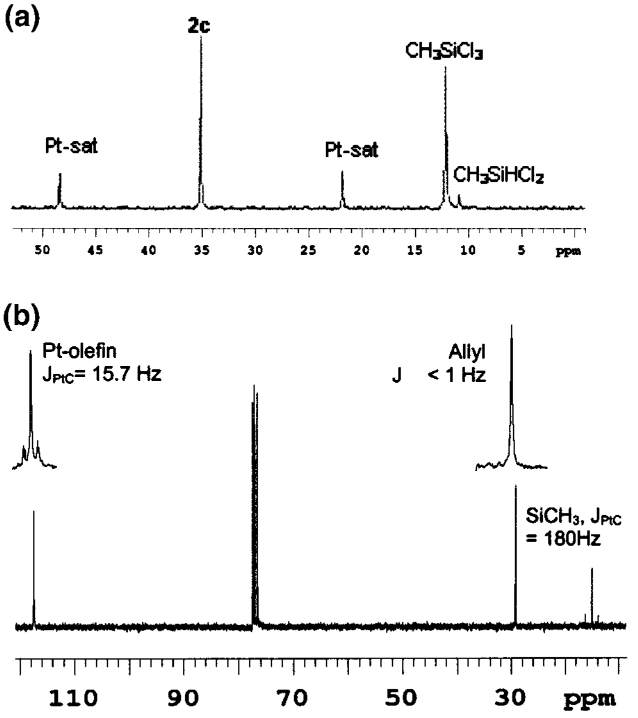


Figure 2. (a) ^{29}Si NMR spectrum of **2c** (crude). (b) ^{13}C NMR spectrum of **2c** (recrystallized).

Table 2. ^{13}C and ^{29}Si NMR Shifts of the Indicated Signal (in ppm) and Pt Coupling Constants (in Hz) for Bis-silylplatinum (bs-Pt) Complex Series **2**

	^{13}C			^{29}Si
bs-Pt	vinyl, J_{PtC}	allyl, J_{PtC}	SiMe, J_{PtC}	silyl, J_{PtSi}
2c	117.4, 15.7	29.1, <1	15.0, 180	35.0, 2110
2d	114.7, <1	buried	10.2, 137.2	39.9, 1694
2f	110.4, <1	28.9, <1	3.8, 95.1	−2.9, 1532

pointed out at this juncture that the compound identified as “**1e**” (via ^{29}Si NMR) in eq 1 could possibly be the bis-silyl-Pt−COD complex “**2e**” instead, since the coupling constant for the Si−Pt interaction is fairly large ($J_{\mathrm{Pt-Si}}$ = 2659 Hz for “**1e**”) compared to the values for the other dimers **1**.

The scarcity of ^{195}Pt NMR data (and even ^{29}Si NMR data) on Pt−Si complexes has been a handicap in understanding structure−property relationships in this area.[5] Thus, in this study, ^{195}Pt NMR spectra were acquired for both the Pt dimer and bs-Pt series where possible, and stacked plots of expanded spectra are presented in Figure 3. For the dimers, the spectra are arranged to reflect an apparent effect of silyl substituents on Pt chemical shift (Table 3). The fortuitous appearance of signals for both **1** and **2** in the same chemical shift window greatly facilitated their identification. A normal electronic effect of silicon substituents on the trend in ^{195}Pt chemical shifts for the dimers **1** is apparent, but what seems to be the opposite effect in **2** cannot be confirmed without data on more members of the bis-silyl complexes.

Table 3. ^{195}Pt NMR Shifts for Pt Dimer Series **1** and the bs-Pt Series **2**

Pt dimer	ppm	bs-Pt	ppm
1a	−4212		
1c	−4042	**2c**	−4573
1d	−4134	**2d**	−4558
“**1e**”	−4126[a]		
1f	−4193		
1g	−4168		

[a] Identification of “**1e**” is tentative.

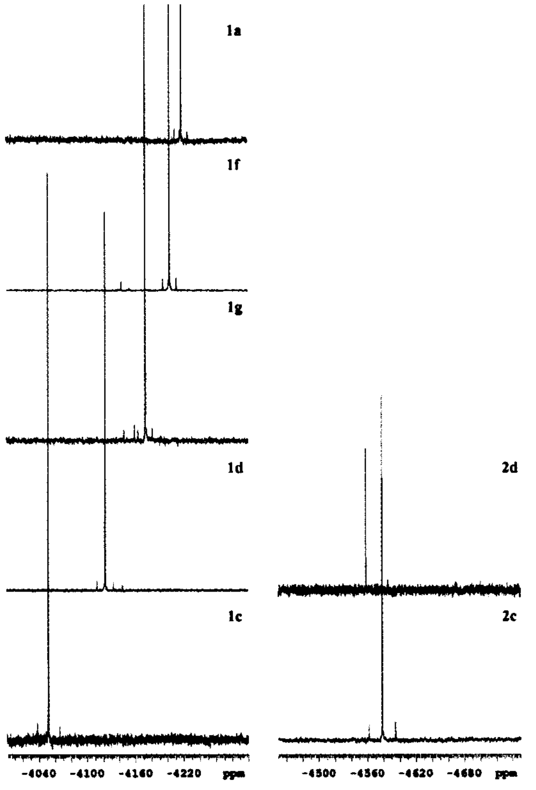


Figure 3. Stacked plots of ^{195}Pt NMR spectra of the Pt dimer series **1** and the bis(silyl)Pt series **2**.

Are Complexes 2 Catalytic? Reactions with Silane and Alkene. As with the dimers **1**, the question of whether complexes **2** were catalytic in nature was addressed in light of this study's focus to identify and characterize reactive intermediates in Pt-catalyzed hydrosilation. Since a deliberate strategy was to examine reactions at stoichiometric levels of Pt using concentrations readily detectable via NMR, a reaction between 1-hexene and $MeSiHCl_2$ was examined in the presence of 0.5 equiv of **2c** as prepared in solution from $Pt(COD)Cl_2$ and $MeSiHCl_2$. The alkene was added at −30 °C to an NMR tube containing freshly prepared **2c**. This precipitated some of the **2c**. No interaction of 1-hexene alone with the Pt complex was observed up to 25 °C. The NMR tube was cooled to −65 °C, and 1 equiv of $MeSiHCl_2$ was added. Upon raising the temperature in ca. 30 °C steps, a slow reaction began at 35 °C and was complete in about 3 h at 50 °C. At this point, the NMR tube contained only *n*-hexylmethyldichlorosilane and **2c**, in addition to the byproducts already present from the synthesis of **2c** (eq 2). It is likely that the excess olefin byproducts present

$$\mathbf{2c} + 2\ \text{hexene-1} \xrightarrow[50\ °\text{C}]{2\ \text{MeSiHCl}_2} 2\ n\text{-hexylMeSiCl}_2 + \mathbf{2c} \quad (2)$$

slowed the hydrosilation reaction by effectively competing with 1-hexene for Pt complexation. No unreacted 1-hexene or any of its isomerization products was observed, nor was any decomposition of **2c** detected. This provided the first clue that **2c** was likely a true catalyst by definition, i.e., *a species facilitating transformation of the reactants to product but not exhibiting structural change itself at the end*. Given the observed susceptibility of compounds **2** to undergo further interaction with silane (that leads to rapid decomposition at elevated temperatures) in the absence of hydrosilatable alkenes, it is unlikely that all of the **2c** initially present would have survived in the presence of silane if **2c** were not playing a true catalytic role in the conversion of 1-hexene to *n*-hexylsilane.

To dispel the possibility that a catalytic amount of another Pt complex, rather than **2c**, was responsible for the observed catalysis, an aliquot of the above reaction mixture containing 50 μmol of **2c** per mole of alkene was used to catalyze the hydrosilation of 1-hexene (0.1 mol) with $MeSiHCl_2$ in a flask under nitrogen at ca. 60 °C. The reaction was complete at the end of silane addition (no reflux of unreacted silane). NMR analysis of the light yellow solution showed complete conversion of 1-hexene to *n*-hexylmethyldichlorosilane with no trace of 1-hexene or any isomerized product (eq 3). The solution

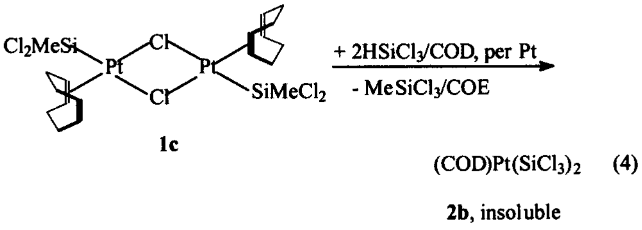
$$\text{hexene-1} + \text{MeSiHCl}_2 \xrightarrow{\substack{50\ \mu\text{mol of } \mathbf{2c} \\ \text{(aliquot from eq 2} \\ \text{product mixture)} \\ 60\ °\text{C}}} n\text{-hexylMeSiCl}_2 \quad (3)$$

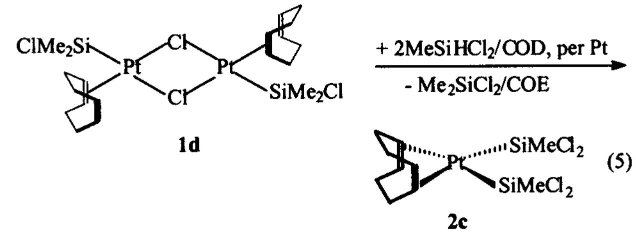
remained yellow, with no Pt precipitation observable for several weeks, unlike the brown solutions and platinum precipitation within a day that is typically observed with common catalysts such as H_2PtCl_6.

Since a homogeneous Pt complex can be readily detected even at close to 1% level by NMR (depending on ligand NMR characteristics), it is clear that the above aliquot containing 50 μmol of **2c** would contain less than about 0.5 μmol of another homogeneous Pt complex (no other homogeneous Pt species was evident by NMR in the stoichiometric reaction). At this low level, catalysis of the 1-hexene hydrosilation by such a second species would be expected to be quite slow, unlike the fast rate of reaction that was actually observed. Thus, the bis(silyl)platinum complex, **2c**, is a true, active hydrosilation catalyst (in its resting state).

The catalytic nature of **2c** was further corroborated by the observation that with excess COD (but no hydrosilatable alkene) in the system, addition of 1 equiv of $MeSiHCl_2$ and storage of the mixture at room temperature for 5 days caused extensive isomerization of COD to essentially all 1,3-cyclooctadiene with some hydrogenation to cyclooctene. Only a very small loss of **2c** and $MeSiHCl_2$ was observed. Upon heating this mixture at 50 °C for 15 h, the silane was consumed via what appears to be hydrosilation of 1,3-cyclooctadiene, but again little loss of **2c** was noted.

Silyl-Exchange Reactions with 1c and 1d. Observations on the relative stabilities of the complexes within the series **1** and **2** were indicative of higher strength of the Pt−Si bond in those complexes with greater electronegativity of the substituents (and the number of such substituents) on silicon. As expected, when dimers **1c** and **1d** were allowed to react with $HSiCl_3$ and $MeSiHCl_2$ (2 equiv per Pt), respectively (eqs 4 and 5), the predominant (>90%) bis-silyl-Pt complex formed was the one containing the more electronegative silyl group. Although **2b** is highly insoluble in common, nonreactive solvents (which thwarted purification and elemental microanalysis), its weak NMR signals (in $CDCl_3$ or $C_2D_2Cl_4$) followed the patterns for **2c**, **2d**, and **2f**, so that combined with NMR signal of byproducts (>90% $MeSiCl_3$, <10% $SiCl_4$, all $HSiCl_3$ and **1c** consumed), its identity was not in question. Despite its initial insolubility in the reaction medium, **2b** readily catalyzes hydrosilation reactions, just like **2c**. For example, at 60 μmol of Pt, **2b** acts as a fast catalyst for the hydrosilation of styrene with $MeSiHCl_2$. Interestingly, the ratio of internal to terminal hydrosilation products is much higher (58:42) than seen with the usual homogeneous Pt precatalysts, and this ratio is unchanged on using the original hydrosilation product mixture as heel for a second run.





Discussion

I. Alkene−Pt−Si Dimeric Complexes 1. The series of dimeric Pt complexes, **1**, has provided a first clear glimpse of a class of platinum compounds that contain a π-bonded simple alkene and silyl groups simultaneously bound to platinum. Hence, several aspects of their synthesis, characterization, and structural characteristics are discussed below.

A. Formation of 1. The likely reason complexes of the type **1** were not detected in earlier studies[4,18,23,24] with Pt−COD complexes is a combination of two reaction condition factors: the lack of sequential and controlled addition of equivalents of silane and the presence of excess COD. Excess silane (often used in catalyst preparation) beyond the precise equivalents per Pt necessary to form **1** and **2** quickly leads to the decomposition of **2**, especially at elevated temperatures.

Several observations in connection with the formation of complexes **1** call for comment. Although essentially all the reactions with $PtCl_2$ and $Pt(COD)Cl_2$ were carried out in $CDCl_3$, a few reactions with Et_3SiH were performed in refluxing toluene. These clearly showed the presence of **1a** in the product mixture, albeit in very small amount due to the rapid decomposition of **1a** at the elevated temperature used. Thus, the formation of **1** as a common reactive intermediate is likely not dependent on a strong solvent effect, provided the solvent does not possess coordinating characteristics.

As was commonly observed in this study, hydrogenation of COD to COE, and even to some cyclooctane, has been reported by Lewis and Lewis for silane reactions with $Pt(COD)Cl_2$.[18] Hydrogenation of styrene to ethylbenzene in $(styrene)_2PtCl_2$ by 2 equiv of Et_3SiH/Pt, producing 2 equiv of Et_3SiCl and the complex $(styrene)_3Pt$ in the presence of excess styrene, has been reported by Caseri and Pregosin.[23] Thus, it is apparent that complexes of Pt(2+) containing chloride and alkene ligands or added alkene undergo this general reaction of alkene hydrogenation and reductive elimination of chlorosilane to produce Pt(0) species stabilized by complexation with suitable alkene. In this study, however, COD presents a special situation where the hydrogenated COD (COE) can be very rapidly displaced by the much stronger chelating COD present in solution. Without excess COD present, only some dimer is observed, with significant precipitation of metallic Pt. However, the hydrogenation of COD during the formation of **1** is not efficient (often 30% or less, the rest of the hydrogen escaping as gaseous H_2). Though the exact sequence of steps and intermediates is not yet clear, it is likely that via some sort of steric−electronic stabilization, COD provides an opportunity for the dimeric Pt(2+) complexes **1** to form and remain relatively stable to chlorosilane elimination. It might be noted in this connection that we are aware of only a small number of other examples of stable platinum complexes containing a silyl group and chloride simultaneously bound to platinum (Si−Pt−Cl), and these contain phosphines as auxiliary ligands but no alkene.[5,25,26] Another intriguing aspect of the reaction between $Pt(COD)Cl_2$ and the silanes that were examined is the long induction period (particularly for the chlorohydridosilanes) before any visible reaction. Yet once the reaction started, essentially all of the $Pt(COD)Cl_2$ reacted within 1−3 min. It is possible that, at least for chloride-based platinum precatalysts, this represents part of the induction period before the formation of the active catalyst.

B. Structural Aspects of 1. The unique structural feature of compounds **1**, with η^2-bonded COD, is rather intriguing, although their similarity to Zeise's dimer-type complexes is apparent. First, all of the clearly identified members of the series appear to be rather stable to monomer formation. ^{13}C NMR signals, particularly for the Pt−alkene and allylic carbons, remain sharp over a wide temperature range (from −65 to 55 °C for **1c**), maintaining constant J_{PtC} coupling. This is indicative of the absence of both rapid olefin exchange and monomer−dimer equilibrium. The rather small or nonexistent coupling of the nonbonded olefin of COD to Pt and the insignificant upfield shift of these carbons (relative to free COD) are suggestive of interaction through σ bonds with platinum rather than a weak π-interaction, although the latter cannot be completely ruled out from the available data. Since several bis(alkene)$PtCl_2$ complexes are known in their monomeric form, the question arises as to why complexes **1** would be dimeric. It is highly probable that the answer lies in the well-known, relatively strong trans-influence of silicon. The C═C of COD that would be trans to the silyl group in a monomeric complex would experience a significant bond-weakening effect in its interaction with Pt. As a result, the complex might be expected to prefer bridging chloride σ-coordination to satisfy preferred four-coordinate geometry. The dimer−monomer equilibrium that has been reported for $(styrene)_2PtCl_2$ by Pregosin et al.[23,27] is disfavored for **1** due to the trans-influence of silicon. Again, because of this trans-influence, it might be expected that dimeric complexes **1** would prefer a trans geometry for the silyl and η^2-COD ligands across the two Pt centers. This would ensure that the two bridging chloride ligands are equivalently bonded to the two Pt nuclei. However, this aspect of the structure is less certain without support from direct crystal structure evidence. Because the salient NMR chemical shifts for all the complexes **1** follow an identical pattern, the structural aspects of these complexes are also expected to be identical. Additionally, perhaps the strongest indirect support for the structural features of **1** is evident in a report by Pregosin and co-workers, where the preparation (via different chemistry) of a series of anionic Pt complexes containing various mono-olefin, chloride, and stannyl groups on Pt is described.[28] These anionic stannyl−Pt−alkene complexes are direct equivalents of Zeise's salt and can also be visualized as anionic monomeric analogues of **1**. Indeed, one might anticipate that such anionic and monomeric complexes can be made from **1** via appropriate transformations or directly from Na_2PtCl_4.

C. Decomposition Pathway. Although byproducts from the synthesis of several of the complexes can be partially removed, and the solids left behind are stable for timely NMR analysis, the slow but continuous elimination of chlorosilane from **1** hampered our ability to purify and maintain these complexes for crystal structure or elemental microanalysis. The most visibly noticeable change as **1** decomposes is the steady formation of black, "metallic platinum". The major pathway for decomposition is unquestionably via loss of chlorosilane, as evidenced from NMR. However, for all members of the series, a small amount of the starting preparative complex, $Pt(COD)Cl_2$, is also produced. Monitoring the preparation and decomposition of **1** via ^{13}C NMR showed the total disappearance of the Pt−vinyl signal due to $Pt(COD)Cl_2$ upon completion of the preparative reaction, followed by gradual reappearance and growth of this signal over time (2−15 days) as the signals due to **1** diminished. The formation of $Pt(COD)Cl_2$ as a decomposition product of **1**

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(23) Caseri, W.; Pregosin, P. S. *Organometallics* **1988**, *7*, 1373.
(24) Caseri, W.; Pregosin, P. S. *J. Organomet. Chem.* **1988**, *356*, 259.
(25) Brost, R. D.; Bruce, G. C.; Joslin, F. L.; Stobart, S. R. *Organometallics* **1997**, *16*, 5669.
(26) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1997**, *16*, 4696.
(27) Albinati, A.; Caseri, W.; Pregosin, P. S. *Organometallics* **1987**, *6*, 788.
(28) Albinati, A.; Pregosin, P. S.; Rüegger, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 78.

requires that an accounting for the silyl groups be made. Disilane formation, an obvious pathway to account for the silicon, was not detected in any of the decomposition reactions, nor was any other soluble silicon compound identifiable via NMR. Therefore, the only logical explanation is the formation of insoluble Pt−Si species together with the metallic platinum. It is tempting to speculate whether such Pt−Si species might not retain the ability to be resurrected to active catalytic species in the presence of silane and alkene. This mode of silyl loss is consistent with Lewis's observation via EXAFS of Pt−Si bonds (together with Pt−Pt bonds) at the end of hydrosilation with excess silane[20] and might explain why hydrosilation mixtures that show visible precipitation of "Pt" can still be used to catalyze further hydrosilation at appreciable rates.

D. Mechanistic Implications. Perhaps the most scientifically useful aspect of the ability to synthesize relatively stable complexes of the type **1** lies in unraveling the structural, compositional, orientatational, and other critical characteristics of the hydrosilation catalytic pathway. This is an important primary step toward building a foundation for structure−activity relationships in hydrosilation catalysis. The observation during the synthesis of **1** that COD is readily hydrogenated and isomerized by hydrosilanes but that the silyl group on Pt does not transfer preferentially or even competitively to the alkene bound to Pt suggests that hydride transfer to alkene is facile and is kinetically favored in a competitive mode, at least for Pt-catalyzed hydrosilation. This directly reinforces the Chalk−Harrod mechanism. In this context, it should be mentioned that the strong resistance of COD and COE to hydrosilation can now clearly be seen to be due to the inability of the silyl group to transfer to either the alkene or the alkyl group formed via hydride transfer. Early reports in the literature of COD hydrosilation using Pt as catalyst under ordinary conditions are clearly questionable. In fact, it is likely (from NMR observations) that not COD but its isomerization product 1,3-cyclooctadiene undergoes slow hydrosilation (likely in the 1,4 fashion of conjugated dienes), as has been suggested by Yamamoto and Kumada.[29] The origin of the resistance of COD and COE to hydrosilation is most probably steric in nature, as is believed to be the case for most internal olefins.

II. True Hydrosilation Catalytic Species, (COD)Pt(SiR_3)$_2$, 2. Although the true catalysts **2** are remarkably simple in compositional and structural characteristics, because of their intrinsic importance to hydrosilation, aspects related to their formation, structural features, stability, catalytic behavior, and implications to catalysis necessitate further analysis and discussion.

A. Formation of 2 from 1. Two observations on the synthesis of **1** and **2** reported in the Results section are very insightful. First, during the synthesis of **1c**, **1d**, and **1f**, formation of 5−10% **2c**, **2d**, and **2f**, respectively, was typically detected by NMR. This suggests that the species **2** are preferential products in the sequential and consecutive reaction of chloride-based platinum precatalysts with silane, even when there is a stoichiometric deficiency of silane in the medium. This was further corroborated by a second observation (made during reaction of silane with **1**) that adding only 1 equiv of silane per Pt consumes one-half of the dimer **1** to yield a 1:1 mixture of **1** and **2**. Thus, the intermediate formed from reaction of silane with **1** must be much more reactive toward silane than **1** itself. Otherwise, the intermediate species, or its decomposition products, would likely have been detected. It is very pertinent to note here that, in a recent study with cationic phenanthroline−Pd complexes, Brookhart et al. reported on just such behavior upon reaction of the Pd precatalysts with 1 or 2 equiv of silane per Pd.[17] Indeed, these researchers reported the detection and characterization of not only Pd−silyl species that are true hydrosilation catalysts, but also bis-silyl-Pd complexes containing a hydride moiety. In the present case with platinum, no hydride resonance was observed even at temperatures as low as −65 °C. This is almost certainly due to the fact that the hydride was quickly consumed via hydrogenation of COD, unlike in the Pd complexes containing phenanthroline as the ancillary ligand. The lack of an available group for hydride transfer trapped the hydride from the second equivalent of silane in the Pd compounds. This suggests that Pt−H-containing species also bearing alkene and silyl ligands might be accessible via use of alkenes that are sterically resistant to hydrogenation, provided oxidative addition of the silane to Pt is possible. Just such an opportunity may possibly be presented by the sterically demanding derivative of COD, dibenzo[*a*,*e*]cyclooctatetraene (DCT).[30]

B. Bonding and Structure. The bonding in **2** is expected to be much like bonding in complexes of the general formula *cis*-(alkene)$_2$PtX_2, where X is a halide or other anionic ligand. Thus, structural features of **2** and Pt(COD)Cl_2 would be similar, except that a weaker coordination of COD to Pt in **2** would be anticipated on the basis of the strong trans-influence of the silyl groups in a square-planar geometry. This weaker binding of COD to Pt in **2** is, indeed, evidenced by a significant downfield shift of the Pt−olefin signal in the ^{13}C NMR spectrum relative to Pt(COD)Cl_2 (110−118 ppm for **2** compared to 100 ppm for the chloride complex). In a formal sense, the oxidation state of Pt in **2** is (+2), since the compound can be viewed as formed from the oxidative addition of a disilane to a coordinatively unsaturated (COD)Pt(0). Figure 4a and b represent two different ORTEP views of the crystal structure for **2c**. Some pertinent crystal data are summarized in Table 4.

From the crystal structure for **2c**, a nearly square-planar geometry around platinum is obvious, if one visualizes the centroids of the two olefinic bonds of COD to be part of the square plane. Of particular note is the longer (by about 0.17 Å) Pt−C bonds in **2c** compared with those in Pt(COD)Cl_2.[31] This lengthening of the Pt−C π-bonds (which are nearly symmetrical) may be attributed to the trans-influence of silicon and correlates well with the Pt−olefin chemical shifts and Pt−C coupling in the ^{13}C NMR spectra for these two complexes. Another point to note is the existence of packing disorder in the crystal with respect to one Cl and the methyl group at each silicon. The Cl and Me groups above and below the Si−Pt−Si plane alternate in up and down positions with 50% probability at each silicon, but only chloride groups [Cl(3) and Cl(3)′] are observed in the "in-plane" positions at each silicon. The effect of the differences in bonding mode of COD (in **2**) and of 1,1,3,3-tetramethyl-divinyldisiloxane (in Karstedt's catalyst) with platinum is clearly borne out by the inability of the chelating disiloxane to displace COD from **2c**, even at a 2:1 concentration advantage in favor of the disiloxane. Yet, it was found that the

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[29] Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1968**, *13*, 131.

[30] Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.

[31] Ashfaquzzaman, S.; Stevens, E. D.; Cruz, S. G. *Inorg. Chem.* **1984**, *23*, 3673.

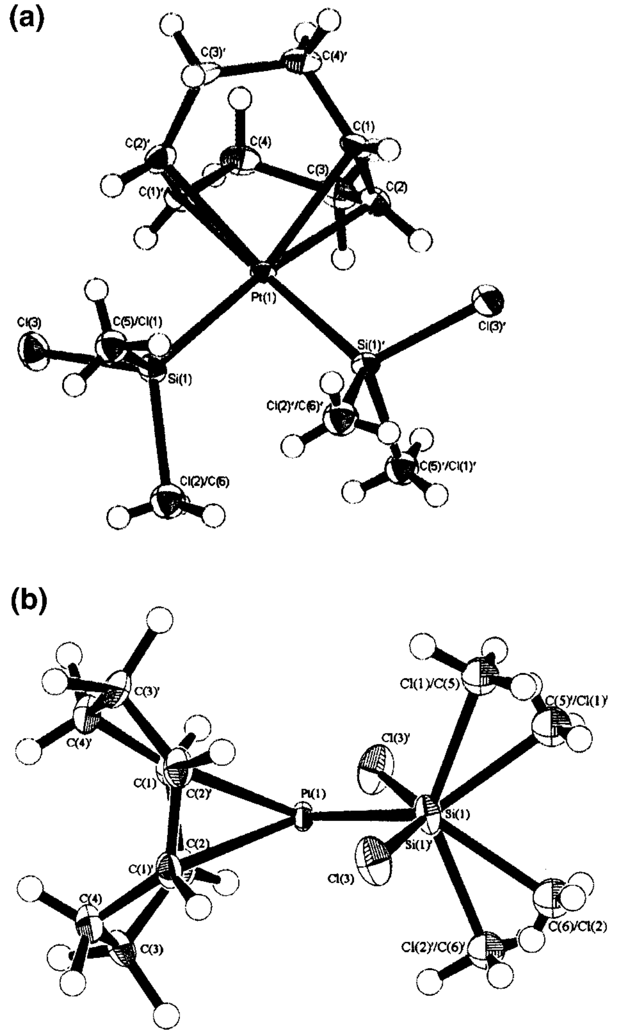

Figure 4. (a) "Bird's-eye" ORTEP view of the X-ray crystal structure of **2c** showing that Cl(3)/Cl(3)′ locations are fixed, while the positions of Cl(1)/Cl(1)′ and Cl(2)/Cl(2)′ with respect to the Si−Pt−Si plane are up and down with 50% probability at the two silicon atoms. Hydrogen atoms have been shown at idealized positions to help visualize the potential for steric interactions between Si−Me groups and bound COD. (b) ORTEP side-view of the X-ray crystal structure of **2c** showing an essentially square-planar geometry for ligand bonding around platinum, with the two C═C centroids as part of the square plane.

Table 4. Basic Crystal Data for Complex **2c**

empirical formula	$C_{10}H_{18}Cl_4Si_2Pt$
formula weight	531.33
crystal color, habit	colorless, cut block
crystal dimensions	$0.56 \times 0.31 \times 0.15$ mm^3
crystal system	orthorhombic
lattice type	primitive
lattice parameters	$a = 8.260(2)$ Å
	$b = 16.961(3)$ Å
	$c = 11.406(2)$ Å
	$V = 1597.9(4)$ Å^3
space group	*Pbcn* (No. 60)
Z value	4
D_{calc}	2.208 g/cm^3
F_{000}	1008.00
GOF indicator	2.40
μ(Mo Kα)	95.41 cm^{-1}

divinyldisiloxane was readily hydrosilated in the presence of **2c** without any decomposition or loss of **2c**. This, of course, has important implications in understanding the platinum orbitals that are used in precatalysts of various oxidation states and in hydrosilation catalytic intermediates generated from these precatalysts. The trans-influence of silyl groups may be of paramount importance in these areas.

C. Stability of 2: Effect of Silicon Substituents. Complex **2c** is relatively quite stable in solution over periods of months (at −20 °C) in the presence of some excess free COD, which imparted the stability needed during shipping so that its crystal structure could be determined. The trichlorosilyl-based complex **2b** appears to have much higher stability to spontaneous decomposition in an inert atmosphere, as no degradation of the white solid was observed on storage in a flask at room temperature for a year. Part of this stability may be attributed to the high insolubility of **2b** but perhaps partly also to a smaller overall trans-influence of silyl groups with more electronegative substituents. Conversely, the weakening of Pt−COD π-bonding may be expected with increasing electron-donating substituents on silicon. This effect is probably reflected in the lower stabilities for **2** with more methyl (or ethyl) substituents on silicon. Thus, the triethylsilyl-based **2a** was not observed in this work, at least at room temperature, although this may also in part be due to steric effects of the Et_3Si group. Higher bond strength for the Pt−Si bond and weaker trans-influence of the corresponding silyl group with electronegative substituents have been predicted by Sakaki et al., and most of our observations related to stability and reactivity of the alkene−Pt−silyl complexes are in line with these predictions.[32] Although a thorough understanding of the effects of silicon substituents on catalytic aspects of transition metal behavior is lacking, it appears that studies are beginning to address the subject of structure−property relationship in reactions of catalytically active transition metal complexes with silanes.[33]

D. Catalytic Behavior: Proposed Activation and Catalytic Cycle. The singular characteristic of **2** that is of the highest interest for understanding structural aspects of reactive intermediates in Pt-catalyzed hydrosilation is the true catalytic nature of this series of silyl-Pt−COD complexes. In addition to preliminary demonstration of the catalytic nature of **2c**, it was also shown that hydrosilations, such as that of styrene by $MeSiHCl_2$, are catalyzed by **2b** which, though initially insoluble even at the catalytic level, dissolves in the reaction medium either upon raising the temperature or upon reaction with the silane. The reaction mixture remains homogeneous and light yellow essentially throughout the course of the hydrosilation. Interestingly, for **2b** in particular, precipitation of the off-white catalyst after consumption of all alkene was observed. This is in line with the high insolubility of this complex. An important question that arises with respect to the ability of compounds **2** to behave as true hydrosilation catalysts is whether these complexes with two silyl groups on Pt are capable of accommodating a third silyl group on Pt via oxidative addition of SiH to **2**. Indirect but very strong evidence for this ability is provided by the known anionic complexes of Pt containing η^4-bound COD and three trichlorostannyl groups, such as $[Ph_4As]^+[(COD)Pt(SnCl_3)_3]^-$.[28] If platinum can accommodate three stannyl groups and an η^4-bound COD, then the simultaneous bonding of three silyl groups (smaller than equivalent stannyl groups) and an η^4-coordinated COD on platinum can be readily visualized. Thus, a much clearer catalytic cycle for hydrosilation

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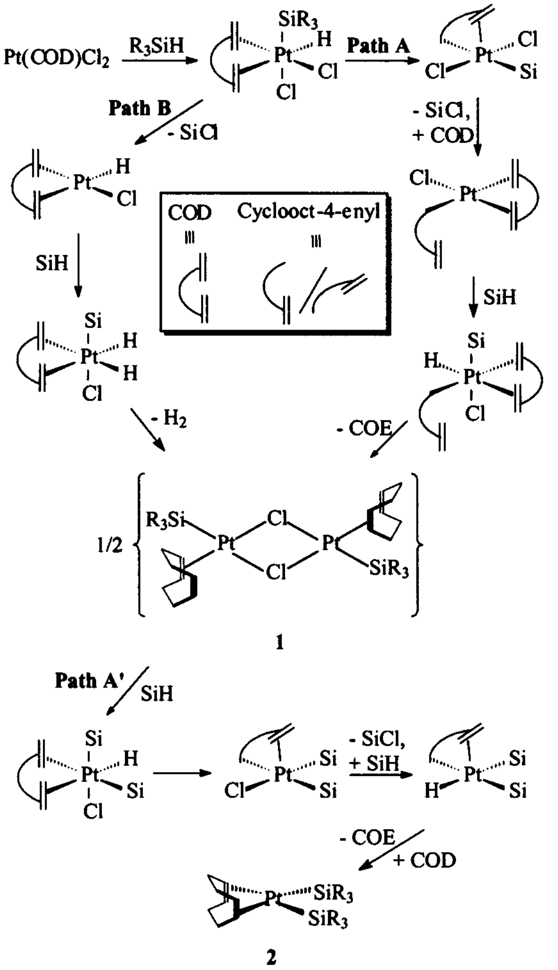
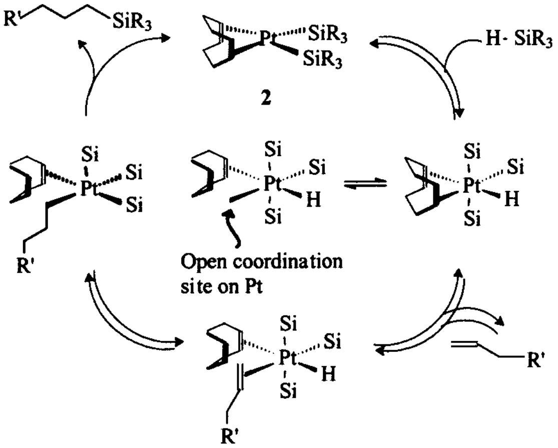
(32) Sakaki, S.; Mizoe, N.; Sugimoto, M. *Organometallics* **1998**, *17*, 2510.
(33) Lemke, F. R.; Galat, K. J.; Youngs, W. J. *Organometallics* **1999**, *18*, 1419.



Scheme 4. Formation of Catalytic Species **2** from Starting Precatalyst: The “Induction Period”



Scheme 5. Chalk−Harrod Mechanism with Bis(silyl)Pt(COD), **2**, as a True Catalyst

with chloride-based Pt(2+) precatalysts containing COD or another non-hydrosilatable ligand may now be proposed (Schemes 4 and 5). These proposed catalytic schemes not only are consistent with the results of this work but also take into account various observations reported by the groups of Lewis,[20] Brookhart,[17] Osborn,[21] and Pregosin.[23,24] The same catalytic cycle with only minor modifications may well be generally applicable to common Pt(2+) precatalysts containing other halide or various oxo species as anionic ligands that are also capable of bridging coordination. Whether a dimeric intermediate with bridging ligands is formed may depend on the nature of the other ligands at the coordination sites occupied by COD.

Scheme 4 depicts possible pathways for the formation of **1** and **2** from Pt(COD)Cl$_2$ and 4 equiv of silane in the presence of excess COD. For the formation of **1**, both pathways A and B seem probable, although B may be favored since inefficient hydrogenation of COD to COE and the visible loss of a good amount of hydrogen gas is observed. For the formation of **2** from **1**, however, a pathway similar to A′ may be preferred, since during this part of the activation process hydrogenation of COD to COE is very efficient and suggests that dihydrido-Pt species are likely not present. The pentacoordinate Pt(4+) reactive intermediates are visualized on the basis that Jennings and co-workers have reported a similar Pt(4+) metallacycle compound where a bicyclic cyclooctene-derived moiety is both σ- and π-bonded to platinum.[34,35] However, in this work, with additional alkene/diene present in the system, it is possible that the pentacoordinate intermediates depicted are actually hexacoordinate Pt(IV) species.

Comparison of Chalk and Harrod’s original proposed mechanism (Scheme 1) with the structurally much-clarified version that we propose (Scheme 5) by simply substituting **2** for [**M**] shows that ours is also fully compatible with the tenets of fundamental transitional metal chemistry, namely, oxidative addition, dynamic metal−ligand equilibrium, insertion into metal−ligand bond, and reductive elimination. The visualization of the η^2-COD complex ↔ η^4-COD complex rapid equilibrium (especially with *trans*-silyl groups) is supported by Ozawa and co-workers’ findings of the inhibitory effect of added phosphine in hydrosilations catalyzed by bis(phosphine)platinum complexes, where the prior dissociation of a phosphine ligand from Pt is a prerequisite for migratory insertion.[7,8,36] In fact, such an inhibitory effect is often observed when COD is in excess for hydrosilations catalyzed by Pt−COD complexes.

The delineation of the Chalk−Harrod mechanism that the use of COD has permitted now allows consideration of the possibility that the hydrosilation of many alkenes using initial Pt(II) and Pt(IV) complexes may actually proceed via catalytic cycles containing bis-silyl-Pt catalytic species. However, it also appears from the work of Pregosin et al. with (styrene)$_3$Pt, Lewis and co-workers’ recent report using Karstedt’s catalyst, and the results of Osborn’s group with electron-deficient-alkene-modified Karstedt’s catalyst that tris(alkene)Pt(0) complexes [and likely other Pt(0) complexes] do not require a complex series of activation steps (since a reductive elimination to remove species such as chlorosilanes is not necessary). Thus, catalytic cycles based on these types of complexes may involve intermediates with only one or two silyl groups on platinum at any point in the catalytic cycle. Nevertheless, it may be reasonably inferred at this point in the evolution of Pt-catalyzed hydrosilation understanding that Pt(0) ↔ Pt(II) or Pt(II) ↔ Pt(IV) transitions could equally efficiently effect hydrosilation catalytic cycles. The nature of the auxiliary ligands present in the system might determine the (resting) oxidation state of the active catalyst species. This flexibility in oxidation states for catalytic behavior likely partially rationalizes why a myriad of platinum compounds are such versatile hydrosilation precatalysts.

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(34) Parsons, E. J.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 1793.
(35) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241.
(36) Ozawa, F.; Kamite, J. *Organometallics* **1998**, *17*, 5630.

A last but very important point about the hydrosilation catalytic cycle with discrete molecular precatalysts is the question of whether the catalysis is homogeneous or heterogeneous. The reports of the groups of Pregosin, Lewis, and Osborn, when taken together, point toward a fully homogeneous catalytic cycle. Now, the work documented in this report, describing the identification and characterization of soluble reactive intermediates and true catalysts, clearly provides direct evidence that the catalytic process is, indeed, homogeneous with molecular Pt compounds, as long as Pt-stabilizing and -solubilizing ligands are present in the reaction medium. Employing a fairly reliable method reported by Crabtree and Anton,[37] where the bulky dibenzo[*a*,*e*]cyclooctatetraene (DBCOT or dct) is used to bind with and sterically block various metal complexes, Osborn showed that their Karstedt-based catalyst systems are significantly retarded by DBCOT but not by mercury, which is a known poison for heterogeneous catalysts.[21,38] Such tests on Karstedt's catalyst seem to suggest both homogeneous and heterogeneous reactions, and we are currently investigating hydrosilations with this precatalyst in the presence of COD. Some interesting and surprising results are emerging, which will be reported in future publications. Nevertheless, in line with the suggestions of the groups of Osborn and Lewis in their recent publications, we conclude that, with molecular Pt compounds, the catalytic process is completely homogeneous as long as the Pt can be kept soluble using stabilizing ligands. On isomerization of alkenes, it is clear from this study that mononuclear complexes can isomerize alkenes: multinuclear species do not need to be invoked for isomerization, contrary to Lewis and co-workers' suggestion.[20] However, the findings of the present study concur with Lewis's group's conclusion that one cause of deactivation of homogeneous Pt hydrosilation catalytic species is very likely the formation of metal−metal bonded aggregates in the absence of stabilizing alkenes or other ligands, or in the presence of excess hydrosilane.[20]

Concluding Remarks

This study was undertaken with the objective of elucidating structural and chemical aspects of the hydrosilation catalytic cycle with homogeneous platinum complexes. Employing a strategy of using "non-hydrosilatable" COD as an ancillary but tracer ligand on Pt, two related series of the first complexes containing alkene and silyl groups simultaneously bound to platinum were identified and unambiguously characterized. The dimeric compounds **1** are semistable, precatalytic intermediates formed initially from the reaction of hydridosilanes with $PtCl_2$ or $Pt(COD)Cl_2$ in the presence of additional COD. The nature of COD bonding to Pt in these complexes is unique, but the complexes themselves are analogous to well-known compounds such as Zeise's dimer. The second series of compounds, **2**, formed from **1** via further reaction with silane, were shown to be the first truly catalytic species observed in Pt-catalyzed hydrosilation studies. The relatively high stability exhibited by **1** and **2** is truly remarkable, considering that such complexes have never been observed, even as transitory species. Identification and characterization of complexes **1** and **2** provide direct experimental evidence for the various mechanistic postulations of the catalytic cycle that visualize simultaneous bonding of alkene and silyl groups to the Pt center. Further, the reactivities shown by **1** and **2**, including the lack of any facile interaction between **2** and 1-hexene, styrene, or vinylsiloxane in the absence of silane, together with the reported difficulty of silyl group transfer to ordinary alkenes in other silylplatinum complexes,[26] support the sequence of hydride and silyl transfer visualized in the Chalk−Harrod mechanism. It also appears that the trans-influence of silicon in metal−silyl complexes may play an important role in transition-metal-catalyzed hydrosilation.

The identification of species **1** and **2** and implications of their further utility raise the prospects of additional chemical investigations with these and similar Pt complexes and other starting Pt compounds. It is hoped that this modest beginning in molecular catalytic species identification and structure−property relationship development will invite further studies that lead to better understanding of catalyst behavior and improved reaction control in hydrosilation reactions.

Experimental Section

General. Starting Materials. The following chemicals and solvents were obtained from internal or commercial sources and used without further purification unless otherwise noted. Sigma-Aldrich Chemical: triethylsilane, phenyldimethylsilane, triethoxysilane, COD, COE, 1,3-cyclooctadiene, chlorotriethylsilane, 1-hexene, styrene, *n*-hexane, anhydrous chloroform (amylene stabilized), anhydrous toluene. Dow Corning Corp.: trichlorosilane, methyldichlorosilane, dimethylchlorosilane. Gelest, Inc.: pentamethyldisiloxane. Johnson Matthey Co.: $Pt(COD)Cl_2$, $Pt(COD)Ph_2$. PGP: $PtCl_2$. Isotec, Inc.: $CDCl_3$ (99.8% deuterated), stored over 4 Å molecular sieves from Fisher Scientific. No special effort was made to purify or dry reagents, except to use $CDCl_3$ that was stored over molecular sieves and dry glassware to avoid reaction with surface moisture.

General NMR Spectroscopic Analysis Conditions. ^{13}C and ^{29}Si NMR spectra were generally run on a MercuryVx 400 MHz spectrometer equipped with a 16 mm Si-free Nalorac PulseTune probe and Varian SMS autosample changer. Samples were run in homemade Si-free NMR tubes previously described.[39] ^{1}H and ^{195}Pt spectra were acquired on a MercuryVx 300 MHz spectrometer equipped with a Varian 5 mm switchable ^{1}H/BB PFG probe. ^{13}C, ^{29}Si, and ^{195}Pt spectra were acquired with 90° pulses and Waltz decoupling during the acquisition period only. Relaxation delays of 30, 60, and 4 s were utilized for quantitation, respectively. For ^{1}H spectra, 90° pulses and 15 s relaxation delays were used. All samples were prepared and run in $CDCl_3$, which was used as an internal reference for ^{1}H and ^{13}C spectra at 7.25 and 77.0 ppm, respectively. ^{29}Si spectra were externally referenced to tetramethylsilane at 0 ppm. ^{195}Pt spectra were externally referenced to H_2PtCl_6 at 0 ppm. Spectra were run at room temperature unless otherwise indicated.

General MS Acquisition Conditions. Atmospheric pressure chemical ionization (APCI) MS studies were carried out on a PE Sciex triple-quadrupole API 350 mass spectrometer operating at unit mass resolving power across the entire mass range (30−4500 Da). The APCI source housing was operated at ambient pressure and temperature of 23 °C. The APCI sprayer tube temperature was critically optimized such that solvent evaporation of the sprayed liquid solution could take place efficiently with minimal thermal decomposition of the protonated analytes. Sprayer tube temperatures over the range of 75−200 °C were evaluated. The optimum sprayer tube temperature was found to be 100−110 °C. A 150 ppm (wt/vol) solution of the Pt sample was prepared in molecular-sieve-dried $CHCl_3$ (Fisher HPLC grade). The $CHCl_3$ solutions containing the analytes were directly infused into the APCI ion source

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(37) Crabtree, R. H.; Anton, D. R. *Organometallics* **1983**, *2*, 855.

(38) Whitesides, G. M.; Hackett, M.; Brainard, R.; Lavalleye, J.-P. P.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

(39) Taylor, R. B.; Parbhoo, B.; Fillmore, D. M. In *The Analytical Chemistry of Silicones*; Smith, A. L., Ed.; John Wiley & Sons: New York, 1991.

at a constant flow rate of 30 μL/min using a Harvard Apparatus (model 22) syringe pump, whereby solvent vaporization preceded ionization of the analytes. APCI MS experiments were performed in the positive-ion mode. The nebulizing current applied to the nebulizing needle within the ion source was set to 1.5 μA, and the chemical ionization gas used was 99.9997% pure CH_4 gas mixed with ambient air (present within the ion source). The observed protonated molecular ions within the APCI mass spectra are formed by low-translational-energy ion−molecule reactions that occur in the chemical ionization plasma region of the ion source. The protonated molecular ions formed in these studies were subsequently mass analyzed by the PE Sciex API 350 mass spectrometer and detected utilizing a channeltron detector operating at a voltage of 1800 V (gain $\approx 10^5$), whereby 10 individual mass spectra were signal-averaged to provide a single summed mass spectrum.

General Reaction Conditions for the Synthesis of 1 and 2. [R_3Si-(μ-Cl)(η^2-COD)Pt]$_2$, (1). Typically, Pt(COD)Cl_2 (0.005 mol, 1.87 g) was weighed out into an oven-dried, three-necked, 100 mL round-bottom flask, equipped with an egg-shaped Teflon-coated stirring bar. The flask was fitted with a dropping funnel, a water condenser topped with a gas inlet, and a 10 mL separatory funnel stoppered with a rubber septum (for cannulating the reaction mixture directly into NMR tubes). All joints were connected using Teflon sleeves. The flask containing Pt(COD)Cl_2 was evacuated for 10−15 min at room temperature and 1−2 mmHg. The flask was then backfilled with dry nitrogen. Cycloocta-1,5-diene (cod or COD, 0.005−0.010 mol) was added to the flask through the septum on the dropping funnel, using a syringe. Deuteriochloroform (10 mL) was then added through the dropping funnel to wash down the COD. The respective silane (0.0102 mol, 2% excess) was transferred via syringe to the dropping funnel and diluted with $CDCl_3$ (5 mL). The flask was heated using a water or silicone oil bath to the temperature range (45−75 °C) used for the various silanes, and the silane was added dropwise, usually over 10−20 min to the stirring slurry of Pt(COD)Cl_2, and the mixture heated until all Pt(COD)Cl_2 reacted (typically, in a rapid exotherm), to yield a yellow-to-brown solution. (Fairly steady bubbling of hydrogen at the oil bubbler connected to the flask via the gas inlet was always observed throughout the silane addition process.) A slight positive pressure of nitrogen was maintained in the flask. The transparent reaction mixture was maintained at the reaction temperature for 2−5 min following disappearance of all suspended Pt(COD)Cl_2 and then quickly cooled to room temperature or below, using an ice bath under the flask. For NMR analysis, an 18-gauge stainless steel cannula was used to transfer the solution in the flask to oven-dried 16 mm (Si-free) and 5 mm glass NMR tubes stoppered with rubber septa. Usually, NMR analysis showed nearly quantitative conversion of Pt(COD)Cl_2 to **1**. As needed for further low-temperature reactions or analysis, the NMR tubes were kept in dry ice/IPA baths, and the reaction mixture (cooled to −78 °C) was transferred cold to the NMR tubes.

For the attempts to isolate several **1**, the flask was connected to a dry ice/IPA trap, and volatiles were slowly removed under reduced pressure at temperatures no higher than about 40−45 °C. The solids obtained with **1a**, **1c**, **1d**, and **1f** were always contaminated with some black metallic platinum and residual high-boiling COD, COE, byproduct chlorosilane, or small quantities of **2** (**2c** and **2d**, respectively, in the case of $MeSiHCl_2$ and Me_2SiHCl).

Reaction Conditions for Individual 1. [Et_3Si(μ-Cl)(η^2-COD)Pt]$_2$ (1a). The silane was added over 20 min at 45−47 °C. Following about 90% silane addition, a fast exotherm was noted, and the reaction mixture quickly became transparent yellow over 1−2 min, and then turned light brown. ^{1}H NMR ($CDCl_3$): δ 5.89 (m, 2H, J_{Pt-H} = 26 Hz, olefin), 4.68 (m, 2H, J_{Pt-H} = 77 Hz, Pt−olefin), 1.0 (m, 9H, CH_3), 0.77 (m, 6H, CH_2).

[Cl_2MeSi(μ-Cl)(η^2-COD)Pt]$_2$ (1c). The suspension of Pt(COD)Cl_2 was heated to 60−65 °C, and the silane was added over 10 min (alternatively, the silane can be added all at once at room temperature, followed by heating). The bath temperature was raised to 70−75 °C, and the mixture became clear and light yellow over 3−5 min following reflux for 40−50 min. After reflux was maintained for an additional 5 min, the flask was quickly cooled to room temperature with an ice bath. (Prolonged heating beyond 5−10 min at temperatures above 55 °C leads to slow decomposition of **1c**, rendering a gray, metallic color to the reaction mixture.) ^{1}H NMR ($CDCl_3$, 40C): δ 6.02 (m, 2H, J_{Pt-H} = 28 Hz, olefin), 4.86 (m, 2H, J_{Pt-H} = 71 Hz, Pt−olefin).

[ClMe_2Si(μ-Cl)(η^2-COD)Pt]$_2$ (1d). The silane was added over 10−20 min at room temperature. The bath was heated to 55−58 °C. The mixture became transparent deep yellow at this temperature and was cooled to room temperature after being maintained at 58 °C for 5−8 min following reaction of all Pt(COD)Cl_2. ^{1}H NMR ($CDCl_3$): δ 5.91 (m, 2H, J_{Pt-H} = 26 Hz, olefin), 4.68 (m, 2H, J_{Pt-H} = 75 Hz, Pt−olefin).

"[(EtO)$_3$Si(μ-Cl)(η^2-COD)Pt]$_2$" ("1e"). The silane was added over 10 min at room temperature. The bath temperature was raised slowly, and at 62 °C the mixture became transparent light yellow. The solution was cooled to room temperature and became light brown in 2−3 h (NMR analysis was performed on the yellow solution). ^{1}H NMR ($CDCl_3$): δ 6.12 (m, 2H, J_{Pt-H} = 32 Hz, olefin), 4.84 (m, 2H, J_{Pt-H} = 86 Hz, Pt−olefin), 4.74 (m, 2H, J_{Pt-H} = 100 Hz, Pt−olefin).

[PhMe_2Si(μ-Cl)(η^2-COD)Pt]$_2$ (1f). The silane was added over 10 min at room temperature (or at 45 °C). Upon heating, the mixture became transparent yellow and then quickly turned brown at 50−52 °C. After 1−2 min at 50−52 °C, the mixture was quickly cooled to room temperature. ^{1}H NMR ($CDCl_3$): δ 7.7−7.3 (m, 5H, Ph), 5.95 (m, 2H, J_{Pt-H} = 25 Hz, olefin), 4.07 (m, 2H, J_{Pt-H} = 75 Hz, Pt−olefin), 0.60 (s, 3H, J_{Pt-H} = 17.4 Hz, CH_3).

[Me_3SiOMe_2Si(μ-Cl)(η^2-COD)Pt]$_2$ (1g). The siloxyhydride was added over 10 min at 45−50 °C (the mixture started to clear rapidly beyond 60−70% silane addition). The reaction mixture was cooled to room temperature quickly, immediately following completion of silane addition. NMR analysis showed that even though all Pt(COD)Cl_2 was consumed, nearly 60% of **1g** had already decomposed. ^{1}H NMR ($CDCl_3$): δ 5.86 (m, 2H, J_{Pt-H} = 24 Hz, olefin), 4.39 (m, 2H, J_{Pt-H} = 80 Hz, Pt−olefin).

Synthesis of 2. As reported in the Results section, only **2c** (the most stable of the soluble complexes **2** that have been observed in this study) was prepared in separate experiments for the purpose of isolation, purification, and full characterization. The others, **2d** and **2f**, were generated and identified in situ. The insoluble complex **2b** was prepared via a different route, as described below.

Preparation, Isolation, and Purification of (η^4-COD)Pt(SiMeCl_2)$_2$. A 100 mL, three-neck 14/20 round-bottom flask, equipped with Teflon sleeves, water condenser, dropping funnel, and Teflon stirring bar, was charged with Pt(COD)Cl_2 (0.015 mol, 5.61 g) and evacuated for 10 min at 1−2 mmHg. After backfill with dry nitrogen, COD (5.5 mL, 0.045 mol) and sieves-dried $CDCl_3$ (10 mL) were added to the flask via syringe. $MeSiHCl_2$ (6.6 mL, 0.0612 mol) was transferred to the dropping funnel and diluted with 5 mL of $CDCl_3$. The flask was heated with water or silicone fluid bath to 60−65 °C, and the silane was added over 10 min to the stirring slurry in the flask. The funnel was rinsed with 2 mL of $CDCl_3$. The mixture was heated at 72−75 °C until it became completely transparent and clear (30−45 min). The bath temperature was then quickly dropped to 48−50 °C and the mixture heated at this temperature for 2−3 h, midway through which a white precipitate of the product formed (depending on concentration in $CDCl_3$). The mixture was stirred overnight at 30−32 °C. Complete conversion to product was then achieved (as evidenced from NMR analysis). ^{1}H NMR ($CDCl_3$): δ 6.16 (m, 4H, J_{Pt-H} = 35 Hz, Pt−olefin), 2.75 (m, 4H, CH_2), 2.4 (m, 4H, CH_2), 1.11 (s, J_{Pt-H} = 20.8 Hz, CH_3).

Purification of **2c** was accomplished by adding anhydrous hexanes (30 mL) to the flask and stirring the mixture at −78 °C for 1 h to facilitate complete precipitation of the product, followed by cold (medium porosity glass frit) filtration under nitrogen and washing with three 12−15 mL portions of dry hexanes. The microcrystalline solid on the filter was dried directly on the frit under vacuum and transferred back to the original flask. Yield of crude product: 94−95%. If desired, the crude solid may be further purified via dissolution in $CDCl_3$ (30 mL, heating to 30−35 °C) containing added COD at 1−1.5 mol of COD/mol of Pt, a second filtration, and washing with 5−10 mL of $CDCl_3$, followed by recrystallization via storage in a freezer at −20 °C to yield colorless crystals of pure $Pt(COD)(SiMeCl_2)_2$. Several 1−2 mm size crystals, together with mother liquor containing excess COD, were transferred to a clean, oven-dried 8 mm diameter glass ampule inside a glovebag under nitrogen atmosphere. The ampule was attached by using Tygon tubing to a small separatory funnel with a Teflon stopcock and stoppered with a rubber septum, removed from the glovebag, attached to a vacuum line, and flame-sealed after a single freeze−thaw cycle using liquid nitrogen. It was then shipped for single-crystal X-ray structure analysis of **2c**.

Note: Chloroform containing ethanol or even amylenes as stabilizer will cause decomposition of **2c**. However, amylene-stabilized $CHCl_3$ may be used for recrystallization, provided at least one COD per Pt is added to the chloroform. It may also be possible to use amylene-stabilized chloroform for the synthesis, but excess COD imparts significant stability and "shelf life" to solutions of **2c**.

Hydrosilation of 1-Hexene with $MeSiHCl_2$ in the Presence of 0.5 Equiv of 2c. A solution of **2c** containing 0.005 mol of complex in 18 mL of $CDCl_3$ was prepared, and an aliquot containing 0.0014 mol of complex (and byproducts cyclooctene, $MeSiCl_3$ and excess COD) was cannulated to a Si-free Teflon NMR tube. 1-Hexene (350 μL, 0.0028 mol) was added, followed by $MeSiHCl_2$ (302 μL, 0.0029 mol), and the mixture was heated in the NMR probe at 50 °C. NMR analysis after about 4 h indicated complete hydrosilylation of the 1-hexene to *n*-hexylmethyldichlorosilane, with no isomerization of 1-hexene and, more importantly, no measurable loss of **2c** to any reaction with the substrates or the product.

Hydrosilation of 1-Hexene with $MeSiHCl_2$ in the Presence of a Catalytic Level of 2c. A 100 mL, three-neck flask equipped with a Teflon stirring bar, addition funnel, and water condenser was purged with nitrogen and charged with 1-hexene (12.5 mL, 0.10 mol). $MeSiHCl_2$ (ca. 11.0 mL, 0.102 mol) was transferred to the additional funnel. An aliquot of the above "stoichiometric" reaction mixture containing 50 μmol of Pt with respect to 1-hexene was added to the 1-hexene in the flask using a microliter syringe. The flask was heated to 60 °C and the silane added over 20 min. The hydrosilylation reaction began within a few minutes and was essentially over at the end of the silane addition, as evidenced by the lack of any refluxing of unreacted silane (bp 41 °C) in the flask. The light yellow solution was heated for another 30 min, following which NMR analysis showed complete hydrosilylation, with no trace of residual 1-hexene or 2-hexene (isomerization).

Silyl-Exchange Reactions To Prepare 2b and 2c from 1c and 1d, Respectively. 2b from 1c. 1c (0.005 mol Pt) was prepared in solution as described above (except that the water condenser was topped with a dry ice condenser for the setup, and a 4:1 molar ratio of COD:Pt was used). To the stirred solution of **1c** maintained at 45 °C was added $HSiCl_3$ (0.0102 mol, 1.0 mL) from the dropping funnel over 2 min. Within 2 min after addition of $HSiCl_3$, a white solid fell out of solution. The mixture was stirred overnight at 40 °C. NMR analysis of the supernatant liquid showed very weak ^{13}C and ^{29}Si signals attributable to **2b**, but $MeSiCl_3$ and $SiCl_4$ were formed in the ratio of 10−12:1, with no $HSiCl_3$ remaining. The essentially complete consumption of $HSiCl_3$ and **1c** and the highly selective formation of $MeSiCl_3$ provided strong evidence for the preferential formation of **2b**. Thus, **2b**, which cannot be made via direct reaction of $HSiCl_3$ with $Pt(COD)Cl_2$, due to the extremely slow first step to form **1b**, can be made in very high yield via the indirect silyl-exchange reaction. Most of the solvent and byproducts were cannulated out, and the rest was removed under vacuum at 45 °C. The crude off-white **2b** was stored in a flask (stoppered using Teflon sleeves and then wrapped with Parafilm at the necks) at room temperature and showed no visible sign of decomposition in 12 months. Attempts were made to obtain solid-state NMR data on a sample of **2b**, but it failed to tune well, an explanation for which is not apparent.

2c from 1d. 1d (0.005 mol Pt) was prepared in solution as described above (a 4:1 ratio of COD:Pt was used, and 30−45 min heating at 60 °C was required for complete reaction of $Pt(COD)Cl_2$). To the stirred solution of **1d** at 50 °C was added $MeSiHCl_2$ (0.0102 mol, 1.1 mL) from the dropping funnel over 10 min. The mixture was heated at 45−48 °C for 2 h and at 40 °C for 1 h. The solution was light yellow. NMR analysis showed the predominant formation of **2c**, with the ratio of Me_2SiCl_2:$MeSiCl_3$ being >10:1. Even the 5−10% **2d** originally present with **1d** had reacted with $MeSiHCl_2$ to yield **2c**.

Hydrosilation of Styrene with $MeSiHCl_2$ Using 2b as Catalyst. Using glassware as with hydrosilation of 1-hexene, platinum complex **2b** (0.007 g, 60 μmol of white powder) was transferred to the flask under nitrogen, followed by styrene (0.2 mol, 22.9 mL). $MeSiHCl_2$ (0.204 mol, 21.9 mL) was transferred to the addition funnel via syringe. The flask was warmed to 50 °C (the catalyst appeared to dissolve at ca. 30 °C in styrene), and the silane was added over about 25 min. Reaction was almost instantaneous, producing a mild exotherm to 54 °C, and was over by the completion of silane addition. A sample for NMR analysis was withdrawn and showed (by ^1H, ^{13}C, and ^{29}Si NMR) clean hydrosilation of styrene to produce internal and terminal adduct in the ratio ca. 58:42. No residual styrene was detected, but the excess silane used was clearly identified in the product mixture. To the heel from this first reaction was added a second charge of styrene (0.1 mol, 11 mL), and this was again hydrosilated with $MeSiHCl_2$ (0.102 mol, 11 mL). This second hydrosilation was over in 10 min (addition time for silane), again producing a mild exotherm. NMR analysis of this second product mixture showed complete hydrosilation with approximately the same ratio (58:42) of internal to terminal adducts.

X-ray Crystal Structure Analysis for 2c. A colorless cut from a block crystal of $C_{10}H_{18}Cl_4Si_2Pt$ (see purification of **2c**, above) having approximate dimensions of 0.56 × 0.31 × 0.15 mm^3 was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a SMART-1000 CCD area detector with graphite-monochromated Mo Kα radiation. The data were collected at a temperature of -120 ± 1 °C to a maximum 2θ value of 56.5°. Data were collected in 0.30° oscillations with 10.0 s exposures. The crystal-to-detector distance was 50.00 mm. The detector swing angle was 28.00°.

The structure was solved by direct methods and expanded using Fourier techniques. The disordered chlorine and carbon atoms were refined isotropically, while the remaining non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the disordered methyl group were included in fixed positions from the difference Fourier map, while the remaining hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 1637 observed reflections and 95 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of

$$R1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.024$$

$$wR2 = [\sum(w(F_o^{\,2} - F_c^{\,2})^2)/\sum w(F_o^{\,2})^2]^{1/2} = 0.049$$

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Supporting Information Available: ^{1}H NMR spectra for **1a**,**c**,**f**,**g** and **2c**; stacked plots of ^{13}C and ^{29}Si NMR spectra for all **1** identified in the study; APCI MS of reaction mixture from the preparation of **1c**, containing **1c** as the predominant platinum complex; and all information for X-ray crystallographic analysis of **2c**, including tables of bond distances and bond angles (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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