(η^5-Cyclopentadienyl)trialkylplatinum Photohydrosilylation Catalysts. Mechanism of Active Catalyst Formation and Preparation of a Novel Bis(silyl)platinum Hydride

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The use of (η^5-cyclopentadienyl)trialkylplatinum complexes as photohydrosilylation catalysts is described. Photolysis of $CpPtMe_3$ in the presence of a silane leads to the formation of an active hydrosilylation catalyst that evidence suggests is a heterogeneous platinum colloid. The catalyst is poisoned by elemental mercury but is not inhibited by dibenzo[*a,e*]cyclooctatetraene. In the presence of certain reactive silanes such as $HMe_2SiOSiMe_3$ the novel bis(silyl)platinum hydrides $CpPt(SiR_3)_2H$ are formed as isolable species, which are not, however, intermediates on the primary pathway to the active hydrosilylation catalyst. The evidence suggests that the silyl methyl hydride complex $CpPtMe(SiR_3)H$ is the critical intermediate which is partitioned under the reaction conditions between colloidal platinum and $CpPt(SiR_3)_2H$. When they are treated with a second reactive silane, bis(silyl)platinum hydride complexes may undergo facile silane exchange via sequential reductive-elimination/oxidative-addition reactions at platinum to give other bis(silyl)platinum hydrides $CpPt(SiR'_3)_2H$. A mechanism connecting $CpPtMe_3$, $CpPt(SiR_3)_2H$, and colloidal platinum is proposed and discussed.

Introduction

First described by Speier,[1] transition-metal-catalyzed hydrosilylation is a much-studied reaction of considerable industrial importance.[2] The reaction is formally analogous to hydrogenation, and many hydrogenation catalysts also catalyze the hydrosilylation reaction. Hydrosilylation catalysts involving every metal in groups 8–10 have been described, but the most active catalysts are those containing platinum. Although catalysis of this reaction has been intensively studied, the overwhelming bulk of published work to date has dealt with thermally activated systems; relatively few examples of radiation-activated catalysts have been disclosed. Faltynek[3] has described the photochemical generation of the coordinatively unsaturated rhodium complex $ClRh(PPh_3)_2$ from $ClRh(PPh_3)_3$ and the use of this intermediate as a hydrosilylation catalyst. In a similar fashion, irradiation of $(CO)_4CoSiEt_3$ induces loss of CO, and Wrighton[4] has shown that the resulting 16-electron cobalt complex is an active hydrosilylation catalyst. In both of these cases, the formation of the proposed catalytically active species involves a reversible ligand dissociation. In contrast, photolysis of the platinum oxalate $Pt(C_2O_4)(PEt_3)_2$ leads to the irreversible expulsion of the oxalate ligand as 2 equiv of CO_2, and the platinum(0) product has been shown by Trogler[5] and coworkers to readily catalyze the hydrosilylation reaction. Another example of the photochemical destruction of a coordinating ligand has been described by Eckberg;[6] photolysis of certain platinum azo complexes leads to the expulsion of molecular nitrogen and the simultaneous liberation of coordinatively unsaturated platinum.

The mechanisms of transition-metal-catalyzed hydrosilylation reactions, both of the generation of the active catalytic species and of the hydrosilylation itself, have also been subjected to much scrutiny. The traditionally accepted mechanism for hydrosilylation was first described by Chalk and Harrod[7] and is normally depicted involving a homogeneous mononuclear catalyst. Lewis, however, has recently presented compelling evidence that many platinum-catalyzed hydrosilylation processes thought to involve homogeneous catalysts in fact involve heterogeneous platinum colloids as the active catalytic species,[8] and he has proposed a mechanism for the hydrosilylation reaction involving colloidal catalysts.

This paper describes the use of (η^5-cyclopentadienyl)-trialkylplatinum(IV) complexes as photoactivated hydrosilylation catalysts[9,10] and presents evidence that a platinum colloid is the active catalytic species. The preparation of a novel bis(silyl)platinum hydride is described, and a possible mechanism relating $CpPtMe_3$ (Cp = η^5-C_5H_5), the platinum hydride, and the platinum colloid is offered.

Results and Discussion

Exposure of an equimolar mixture of $HMe_2SiOSiMe_3$ and 1-octene containing 10 ppm of platinum as $CpPtMe_3$ to a source of ultraviolet radiation results in the initiation of a very rapid hydrosilylation reaction leading to the formation of $(n\text{-}C_8H_{17})Me_2SiOSiMe_3$ in essentially quantitative yield (eq 1); no reaction was observed after 20 days in a similar mixture held at room temperature in the dark. Once initiated, the reaction continues to proceed in the

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[6] Eckberg, R. P. U.S. Patent No. 4,670,531, 1987.

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

[8] (a) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228. (b) Lewis, L. N.; Lewis, N. *Chem. Mater.* **1989**, *1*, 106. (c) Lewis, L. N.; Uriate, R. J. *Organometallics* **1990**, *9*, 621. (d) Lewis, L. *J. Am. Chem. Soc.* **1990**, *112*, 5998. (e) Lewis, L. N.; Uriarte, R. J.; Lewis, N. *J. Catal.* **1991**, *127*, 67.

[9] Preliminary results were presented at the XXIIIrd Organosilicon Symposium, Midland, MI, April 20–21, 1990.

[10] (a) Drahnak, T. J. U.S. Patent 4,510,094, 1985. (b) Drahnak, T. J. U.S. Patent 4,600,484, 1986.

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$$Me_3SiOSiMe_2H + H_2C{=}CH\text{-}C_6H_{13} \xrightarrow[h\nu]{CpPtMe_3} Me_3SiOSiMe_2(C_8H_{17}) \quad (1)$$

absence of further irradiation. Hence, the hydrosilylation is truly catalytic with respect to the initiating radiation, in contrast to a photoassisted process which can be stopped by terminating the photolysis.[3]

Nature of the Active Catalyst. Catalytic turnover numbers as large as 10000 turnovers per Pt per minute have been measured. As noted by Lewis,[8] this would be an unusually fast reaction for a process catalyzed by a homogeneous species, and presently available evidence suggests that the active catalytic species derived from $CpPtMe_3$ is in fact a heterogeneous platinum colloid.

The use of elemental mercury to selectively amalgamate or physiabsorb heterogeneous metal colloids, with consequent attenuation of catalytic activity, has been described previously as a method of investigating the mechanisms of transition-metal-catalyzed processes.[11] In contrast, exposure to mercury generally has little effect on soluble, molecular catalysts. A series of experiments was carried out to determine the effect of mercury on the active catalyst derived from $CpPtMe_3$ (see Experimental Section). A dilute cyclohexane solution of $CpPtMe_3$ (1.7×10^{-4} M) containing approximately 1500 equiv of both $HMe_2SiOSiMe_2OSiMe_3$ and 1-octene as well as a small drop of mercury was irradiated in order to generate an active hydrosilylation catalyst in the presence of elemental mercury. Subsequent addition of an equimolar mixture of $HMe_2SiOSiMe_2OSiMe_3$ and 1-octene to aliquots of this solution after varying periods of time resulted in hydrosilylation reaction rates that were retarded relative to the rate observed in a control solution that did not contain mercury. This result implicates a heterogeneous component to the reaction and implies the involvement of a platinum colloid. Catalyst deactivation was not a rapid process; 5–24 h was required to reduce catalyst activity to zero. This may reflect the time required to completely convert small amounts of soluble intermediates produced on photolysis of $CpPtMe_3$ to colloidal platinum rather than the time required for colloid amalgamation.

In a complementary fashion, dibenzo[*a*,*e*]cyclooctatetraene (DBCOT) has been used as a selective poison for homogeneous transition-metal-containing catalysts.[11b] The conformational constraints of this molecule make it an excellent chelating ligand for a variety of transition metals but severely limit interactions with metal surfaces. As a consequence, the presence of this ligand should have little effect on the catalytic activity of a heterogeneous platinum colloid. The behavior of the present system supports this argument and is consistent with published results.[11b] A solution of $CpPtMe_3$ in cyclohexane containing approximately 1000 equiv of both $HMe_2SiOSiMe_2OSiMe_3$ and 1-octene and 2 equiv of DBCOT was irradiated. Subsequent addition of $HMe_2SiOSiMe_2OSiMe_3$/1-octene resulted in a reaction rate only slightly reduced relative to that of a control experiment. Apparently, the added ligand is unable to effectively bind any initial homogeneous photoproducts (see below), and the reactions of DBCOT with intermediates produced upon the addition of silane are not competitive with further reactions of these intermediates leading to colloidal platinum. In a second experiment a dilute cyclohexane solution of $CpPtMe_3$ (5.0×10^{-5} M) containing approximately 1000 equiv of both $HMe_2SiOSiMe_2OSiMe_3$ and 1-octene was irradiated in order to generate an active hydrosilylation catalyst. Addition of up to 5 equiv of DBCOT to this solution had no effect on the observed reaction rates following subsequent addition of $HMe_2SiOSiMe_2OSiMe_3$/1-octene, as expected for a heterogeneously catalyzed process.

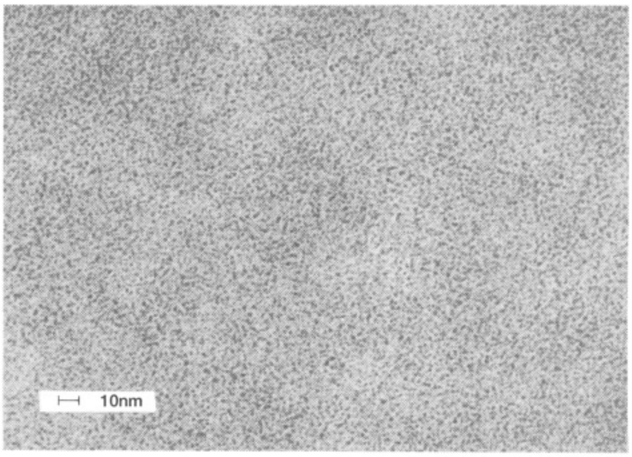

Figure 1. Transmission electron micrograph of the platinum colloid formed upon photolysis of $CpPtMe_3$ in the presence of $HMe_2SiOSiMe_3$ in cyclohexane.

Examination of a photolyzed solution of $CpPtMe_3$ and $HMe_2SiOSiMe_3$ in cyclohexane by transmission electron microscopy (TEM) confirmed the formation of colloidal platinum. The photomicrograph in Figure 1 shows 10–25-Å particles, and the electron diffraction pattern of the colloid could be indexed to crystalline platinum.[12]

Photolysis of $CpPtMe_3$ and Reaction of the Photoproduct with Silanes. The ultraviolet spectrum of $CpPtMe_3$ (Figure 2a) shows λ_{max} at 254 nm ($\epsilon = 10000$) with a shoulder at 285 nm ($\epsilon = 3000$). Irradiation of a 1×10^{-4} M solution of $CpPtMe_3$ in cyclohexane resulted in clean first-order disappearance of the platinum complex. Various derivatives of $CpPtMe_3$ behaved in essentially the same manner, although quite large rate differences were observed, depending on the nature of the ligands involved (Figure 3). Examination of a similarly photolyzed solution of $CpPtMe_3$ in cyclohexane-d_{12} by ^1H NMR failed to show the presence of any soluble reaction products. A value of 4.4×10^{-3} has been reported by Wojcicki[13] for the quantum yield of disappearance of $CpPtMe_3$ in methylcyclohexane at 350 nm, and he has suggested that the photolysis results in homolysis of a Pt–Me bond. The methyl radical was observed by ESR as its nitrosodurene spin-trap adduct, and while the other product of this reaction was not identified, photolysis of a frozen solution of $CpPtMe_3$ in petroleum ether at −196 °C permitted observation by ESR of a broad signal at 2668 G, presumably due to the 17-electron platinum-containing fragment $CpPtMe_2$, in addition to the signal for the methyl radical.[13] We find that recombination of methyl radical with $CpPtMe_2$ after cage escape is apparently not a significant process. The ^{195}Pt chemical shifts of $CpPtMe_3$ and the d_9 isotopomer $CpPt(CD_3)_3$ are −5237 and −5273 ppm, respectively.[14]

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[12] *X-ray Powder Data File*; ASTM Special Technical Publication 48-J; American Society for Testing Materials: Philadelphia, PA, 1960; Card 4-0802.

[13] Hackelberg, O.; Wojcicki, A. *Inorg. Chim. Acta* **1980**, *44*, L63.

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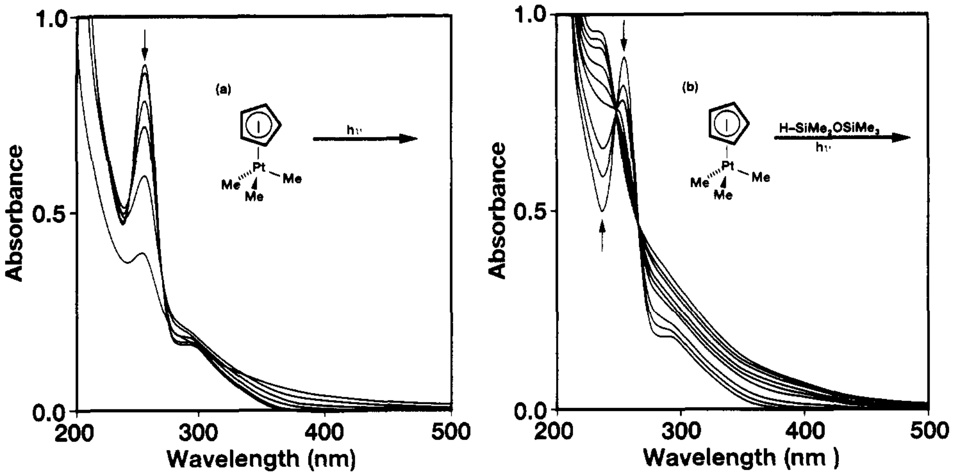


Figure 2. Spectral changes during the photolysis of 1.0×10^{-4} M $CpPtMe_3$ in cyclohexane: (a) in the absence of $HMe_2SiOSiMe_3$; (b) in the presence of 200 equiv of $HMe_2SiOSiMe_3$.

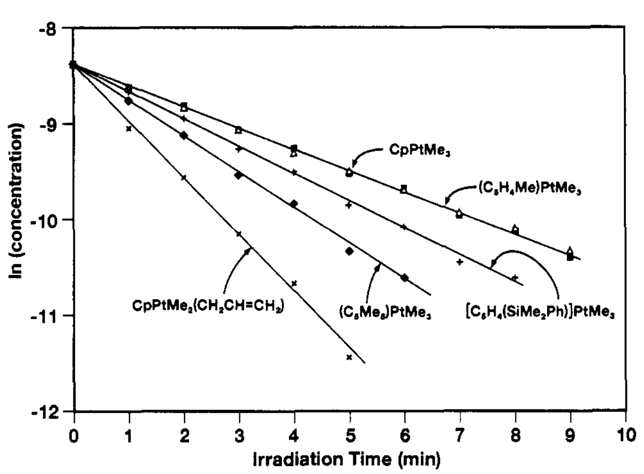


Figure 3. Photodecomposition of $CpPtMe_3$ derivatives in cyclohexane.

Photolysis of a 1:1 mixture of these two complexes in cyclohexane and examination of the resultant solution by ^{195}Pt NMR showed only the resonances at −5237 and −5273 ppm, each at 30% of the integrated intensity recorded before irradiation; signals at −5249 and −5261 ppm corresponding to the crossover products $CpPtMe_2(CD_3)$ and $CpPtMe(CD_3)_2$ were not observed.[15] This result does not, of course, exclude efficient recombination of $CpPtMe_2$ and methyl radical in the solvent cage, which could account for the low quantum yield for disappearance of $CpPtMe_3$ reported by Wojcicki.[13]

Wojcicki also reported that thermolysis of photolyzed solutions of $CpPtMe_3$ lead to the precipitation of metallic platinum.[13] The cyclopentadienyl ligand is apparently lost as methylcyclopentadiene in this process. In Figure 2a, the increased absorption observed at longer wavelengths beyond 350 nm is consistent with the formation of colloidal metal.[16]

When a 1×10^{-4} M solution of $CpPtMe_3$ containing 200 equiv of $HMe_2SiOSiMe_3$ was irradiated, disappearance of $CpPtMe_3$ in the ultraviolet spectrum was accompanied by the appearance of a new band with λ_{max} at 238 nm; clean isosbestic points were seen at 248 and 265 nm (Figure 2b).

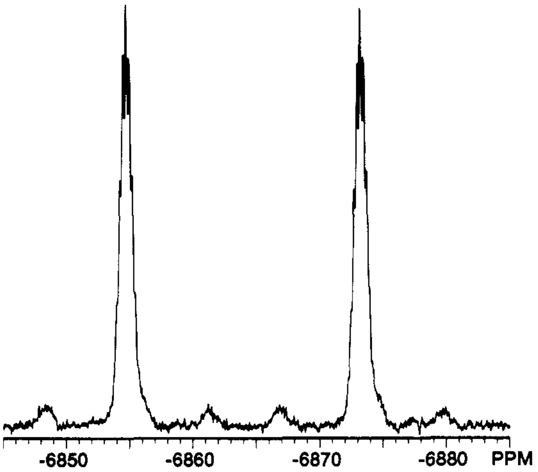
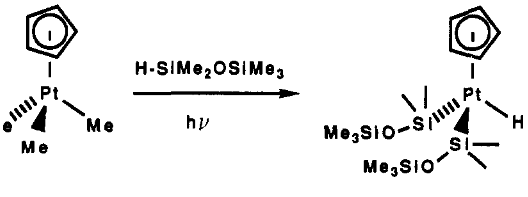


Figure 4. ^{195}Pt NMR spectrum of $CpPt(SiMe_2OSiMe_3)_2H$ in $CDCl_3$.

No intermediates could be observed by ^1H NMR. Again, as in the photolysis of $CpPtMe_3$ in the absence of $HMe_2SiOSiMe_3$, increased absorption at longer wavelengths suggested the formation of colloidal platinum. The product, identified as the novel bis(silyl)platinum hydride $CpPt(SiMe_2OSiMe_3)_2H$ (**1a**), was readily isolated in 80% yield (based on consumed $CpPtMe_3$) from a photolyzed solution of $CpPtMe_3$ in HMe_2SiOMe_3 by flash chromatography on silica of the residue after concentration (eq 2). The ^1H NMR spectrum of **1a** shows the hydride



(2)

1a

proton as a 1:4:1 triplet at −16.94 ppm; the outer two lines are ^{195}Pt satellites ($^1J_{Pt-H}$ = 1577 Hz). A band in the infrared spectrum of **1a** at 2275 cm^{-1} corresponds to the Pt–H stretch. The methyl groups attached to the silicons bonded directly to platinum are diastereotopic and appear in the ^1H spectrum at 0.52 and 0.53 ppm ($^3J_{Pt-H}$ = 21 and 20 Hz, respectively) and in the ^{13}C spectrum at 13.06 and 13.57 ppm ($^2J_{Pt-C}$ = 111 and 104 Hz, respectively). The ^{29}Si NMR spectrum shows signals at 0.95 ($^1J_{Pt-Si}$ = 1100 Hz) and 5.78 ppm for the α- and β-silicons, respectively.

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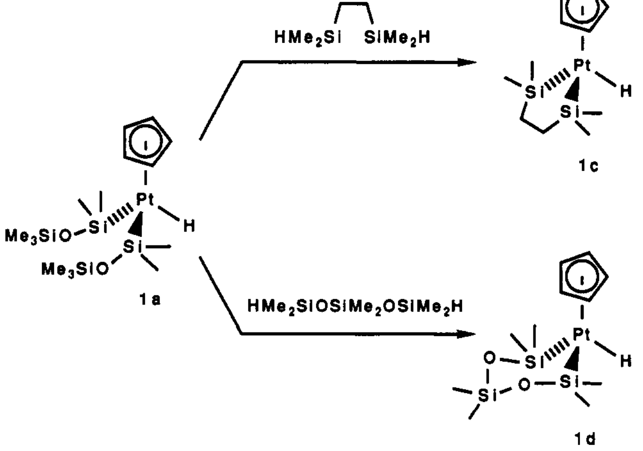
[15] For an example of the use of ^{195}Pt NMR to follow the exchange of methyl groups at platinum, see: Baxter, S. M.; Ferguson, G. S.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4231.

[16] (a) Vogler, A.; Quett, C.; Kinkely, H. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1486. (b) Klassen, R. B.; Baum, T. H. *Organometallics* **1989**, *8*, 2477.

The ^{195}Pt NMR spectrum of **1a** (Figure 4) is particularly diagnostic, showing a 1577-Hz doublet at −6863 ppm due to coupling of the ^{195}Pt nucleus with the hydride proton, and ^{29}Si satellites ($^1J_{\text{Pt-Si}}$ = 1100 Hz) can be seen at the 8% level symmetrically located about each resonance of the doublet. Each resonance of the doublet is further split into a multiplet due to coupling with the α-methyl protons of the silyl ligands ($^3J_{\text{Pt-H}}$ = 21 Hz).

Silylplatinum complexes are well-known,[17] and several derivatives have been reported that contain both silyl and hydride ligands;[18] however, to our knowledge **1a** is the first mononuclear complex of its type not incorporating at least one phosphine ligand. Complexes of this type are of particular interest as postulated intermediates in the platinum-catalyzed hydrosilylation reaction. Preliminary results indicate that **1a** is a surprisingly stable molecule. The complex undergoes extensive decomposition at room temperature on exposure to air to a mixture of various siloxanes, cyclopentadiene, and platinum, but it can be stored for weeks under argon at −20 °C with minimal discoloration. Heating at 70 °C or photolysis of a cyclohexane solution of **1a** for 3 h yields a dark solution containing approximately 90% of the original charge of **1a** by ^{1}H NMR; the dark color is indicative of the formation of metallic platinum. The same experiments in the presence of added $HMe_2SiOSiMe_3$ (10 equiv) resulted in no discoloration of the solutions or loss of **1a**, suggesting reductive elimination of $HMe_2SiOSiMe_3$ from platinum as a possible first step in the decomposition pathway.

Silane Exchange. The reversibility of silane oxidative addition to the platinum center implies that one silyl ligand can be readily exchanged for another.[19,20] Indeed, **1a** is a convenient starting material for the preparation of other bis(silyl)platinum hydrides. Attempted preparation of the homologous complex $CpPt[(SiMe_2O)_2SiMe_3]_2H$ (**1b**) using the same method employed for the preparation of **1a** by photolysis of a solution of $CpPtMe_3$ in $HMe_2SiOSiMe_2OSiMe_3$ gave an approximately 2:1 mixture of **1b** and a second hydride complex. The ^{1}H NMR spectrum of the mixture showed two signals in the Pt–H region at −16.87 ($J_{\text{Pt-H}}$ = 1574 Hz; **1b**) and −16.79 ($J_{\text{Pt-H}}$ = 1574 Hz) ppm. Photolysis of $CpPtMe_3$ in siloxane hydrides leads to extensive siloxane redistribution (see below), and the second complex may be a mixed bis(silyl) derivative such as $CpPt[(SiMe_2O)_2SiMe_3][(SiMe_2O)_3SiMe_3]H$. However, simply stirring **1a** with 10 equiv of $HMe_2SiOSiMe_2OSiMe_3$ overnight cleanly provided **1b** in approximately 75% isolated yield after chromatography. In an analogous fashion, exchange of 1,2-bis(dimethylsilyl)ethane and $HMe_2SiOSiMe_2OSiMe_2H$ for $HMe_2SiOSiMe_3$ afforded the platinacycles **1c** and **1d** in 77% and 86% isolated yields, respectively (eq 3). These exchange reactions presumably proceed by way of initial reductive elimination of $HMe_2SiOSiMe_3$ from **1a** followed by oxidative addition of the exchanging silane. Repetition of these two steps (in the case of a difunctional silane such as 1,2-bis(dimethylsilyl)ethane the second oxidative addition is intramolecular) would provide the exchanged product.



(3)

Relative Reactivities of $CpPtMe_3$ and 1a. The relative efficiencies of $CpPtMe_3$ and the bis(silyl)platinum hydride **1a** as hydrosilylation catalyst precursors were compared. Equimolar mixtures of 1-octene and $HMe_2SiOSiMe_2OSiMe_3$ in cyclohexane containing 0.01 mol % of either $CpPtMe_3$ or **1a** were irradiated with a source of ultraviolet radiation. An analogous pair of reaction mixtures was allowed to stand in the dark, and the progress of the hydrosilylation reactions was monitored by GLC (Figure 5). No reaction was observed in the dark mixture containing $CpPtMe_3$ (see above) after 40 h. However, in the dark reaction mixture containing **1a**, after an induction period of several hours (only 3% reaction after 2 h), a 76% conversion to product was recorded after 13 h; reaction was essentially complete (96%) after 40 h. The induction period probably corresponds to the time required for thermal decomposition of **1a** to provide sufficient platinum(0) in the form of colloidal platinum to efficiently catalyze the reaction. In marked contrast, reaction was 72% complete after only 30 min in the photolyzed solution containing $CpPtMe_3$, whereas only 17% reaction was observed in the photolyzed solution containing **1a**. If only one pathway from $CpPtMe_3$ to the active hydrosilylation catalyst is operative, and **1a** is an intermediate on that pathway, the reactivity of **1a** upon irradiation should be at least as great as that of $CpPtMe_3$. The significantly lower activity of **1a** implies that another pathway is primarily responsible for formation of the active catalyst.[21] The irradiated reaction of **1a** is, however, faster than the dark reaction of this complex. Part of this acceleration may be due to some heating of the sample from the radiation source; however, minor participation of a pathway to the active catalyst involving **1a** has not been rigorously excluded.

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(17) For a review of transition-metal silyl derivatives, see: Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1415.

(18) (a) Eaborn, C.; Pidcock, A.; Ratcliff, B. *J. Organomet. Chem.* **1974**, *66*, 23. (b) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1975**, 2212. (c) Green, M.; Howard, J. A. K.; Proud, J.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1976**, 671. (d) Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murry, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 659. (e) Powell, J.; Sawyer, J. F.; Shiralian, M. *Organometallics* **1989**, *8*, 577. (f) Müller, C.; Schubert, U. *J. Organomet. Chem.* **1991**, *405*, C1.

(19) For examples of silyl group exchange at other metals, see: (a) Haszeldine, R. N.; Malkin, L. S.; Parish, R. V. *J. Organomet. Chem.* **1979**, *182*, 323. (b) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1984**, *111*, 8043. (c) Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995. (d) Ruiz, J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1986**, 862. (e) Ruiz, J.; Bentz, P. O.; Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2709. (f) Fernândez, M. J.; Esteruelas, M. A.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1987**, *6*, 1751. (g) Knorr, M.; Müller, J.; Schubert, U. *Chem. Ber.* **1987**, *120*, 879. (h) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757.

(20) Since these results were initially communicated,[9] a second example of silyl group exchange at platinum has been reported: Schubert, U.; Müller, C. *J. Organomet. Chem.* **1991**, *418*, C6.

(21) For a discussion of the role of analogous silylrhodium hydride complexes in rhodium-catalyzed hydrosilylation reactions, see: Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90.

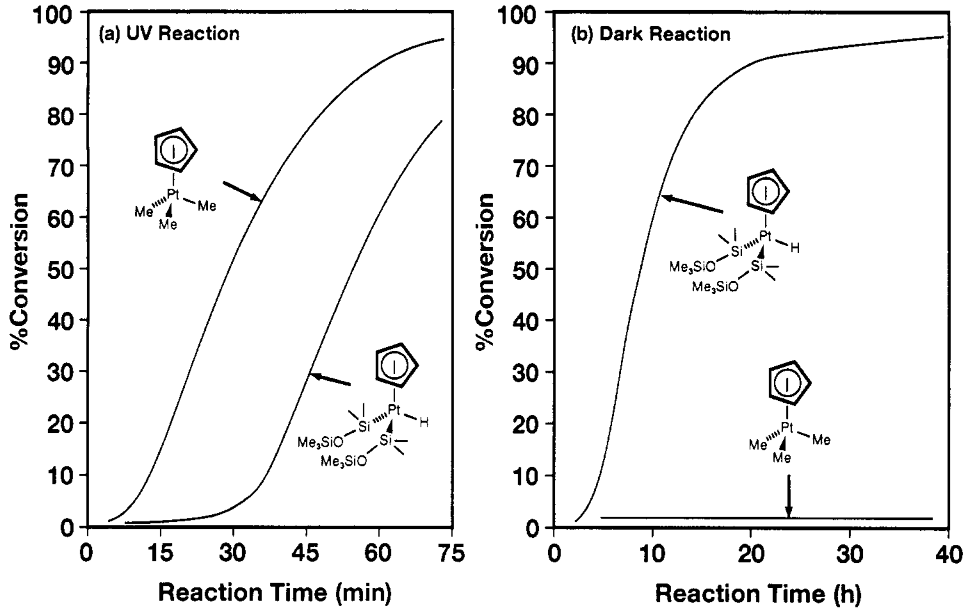
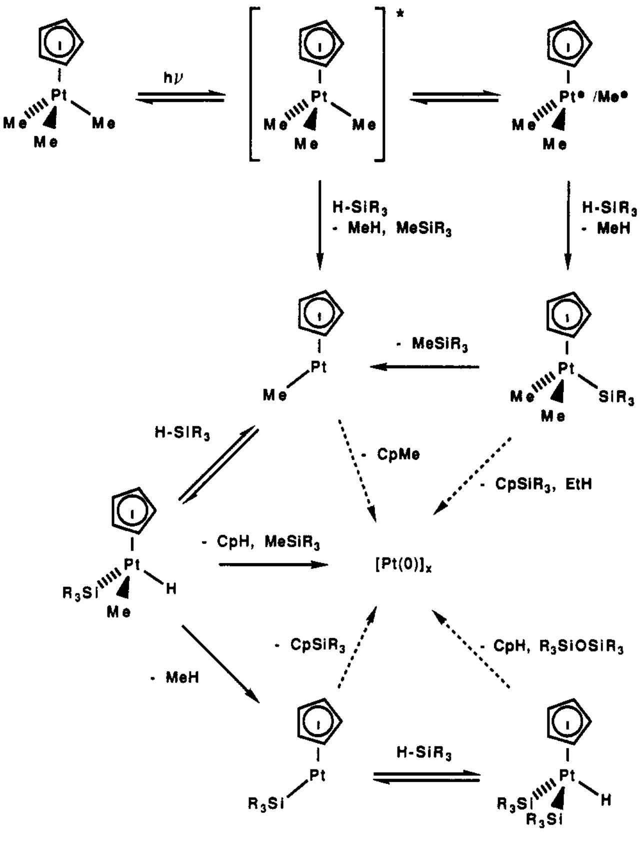


Figure 5. Comparison of $CpPtMe_3$ and $CpPt(SiMe_2OSiMe_3)_2H$ (**1a**) as active catalyst precursors for the reaction between 1-octene and $HMe_2SiOSiMe_3$: (a) under irradiation; (b) in the dark.

Mechanism of Colloid Formation. A proposed mechanism connecting $CpPtMe_3$, the bis(silyl)platinum hydride **1a**, and colloidal platinum is offered in Scheme I. Each of the suggested intermediates is depicted as a mononuclear complex with the cyclopentadienyl ligand coordinated in an η^5 mode, although this is by no means certain, in particular for coordinatively unsaturated species such as CpPtMe. Presently available evidence (see below) suggests that a silane may intercept either the electronically excited complex produced on photolysis of $CpPtMe_3$ or the intimate radical pair $[CpPtMe_2/Me]$ derived from this excited state to yield 1 equiv of methane, 1 equiv of a methylsiloxane such as $Me_3SiOSiMe_3$, and the coordinatively unsaturated platinum(II) intermediate CpPtMe. The silyl dimethyl complex $CpPtMe_2(SiMe_2OSiMe_3)$ may or may not be an intermediate in this process. Alternatively, in the presence of a suitable hydrogen donor such as a silane, the 17-electron species $CpPtMe_2$ might be expected to abstract a hydrogen atom to yield the hydride complex $CpPtMe_2H$, which after reductive elimination of methane leads to the same intermediate, CpPtMe. In either event, oxidative addition of $HMe_2SiOSiMe_3$ to CpPtMe, reductive elimination of methane, and finally, oxidative addition of a second equivalent of $HMe_2SiOSiMe_3$ provides a reasonable mechanism for the formation of the bis(silyl)platinum hydride **1a**.

Scheme I



Formation of colloidal platinum could conceivably take place by wholesale reductive elimination of ligands from any one or more of at least five species (Scheme I). Analysis of photolyzed solutions of $CpPtMe_3$ in $HMe_2SiOSiMe_3$ by GC–MS revealed a complex mixture of products. The primary processes appear to be platinum-catalyzed hydrolysis of silane by adventitious moisture and siloxane redistribution.[22] Formation of disilanes such as $Me_3SiOSiMe_2–SiMe_2OSiMe_3$ by dehydrogenative coupling[23] was not observed. Conspicuous by their absence in the product mixture were methylcyclopentadiene and any cyclopentadienylsiloxanes, ruling out the platinum(II) intermediates CpPtMe and $CpPt(SiMe_2OSiMe_3)$ as well as the possible platinum(IV) intermediate $CpPtMe_2(SiMe_2OSiMe_3)$ as direct colloid precursors. Also absent was a significant amount of ethane; analysis of the gases above the reaction mixture showed a methane:ethane ratio of approximately 10 000:1.

GC–MS analysis of the reaction mixtures did, however, detect approximately 1 equiv of cyclopentadiene with respect to platinum not accounted for by either **1a** or unreacted $CpPtMe_3$ in the reaction mixtures. In analogous fashion, the corresponding reaction of $(MeCp)PtMe_3$ permitted the observation of methylcyclopentadiene but

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[22] (a) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213. (b) Gustavson, W. A.; Epstein, P. S.; Curtis, M. D. *J. Organomet. Chem.* **1982**, *238*, 87. (c) Bell, L. G.; Gustavson, W. A.; Thanedar, S.; Curtis, M. D. *Organometallics* **1983**, *2*, 740. (d) Curtis, M. D. *J. Polym. Sci.* **1983**, *70*, 107.

[23] Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.

only traces of dimethylcyclopentadiene and cyclopentadiene. Although cyclopentadiene and various siloxanes are expected and observed among the decomposition products of **1a** by GC–MS, the relative reactivities of $CpPtMe_3$ and **1a** as hydrosilylation catalyst precursors (see above) preclude **1a** as the primary precursor of the active catalyst. Therefore, it appears that $CpPtMe(SiMe_2OSiMe_3)H$ is the critical intermediate, which in the presence of a silane is partitioned between **1a** and colloidal platinum.

In addition to cyclopentadiene, formation of a platinum colloid from $CpPtMe(SiMe_2OSiMe_3)H$ also requires production of 1 equiv of an $Si–CH_3$-containing species. For example, in the presence of the silane $HMe_2SiOSiMe_3$, the formation of 1 equiv of $Me_3SiOSiMe_3$ is expected. As a result of the hydrolysis and redistribution reactions mentioned above, photolyzed solutions of $CpPtMe_3$ in $HMe_2SiOSiMe_3$ contain a large number of different methylsiloxanes, including the expected $Me_3SiOSiMe_3$. However, substitution of the d_9 isotopomer $CpPt(CD_3)_3$ for $CpPtMe_3$ allows the ultimate fate of the methyl groups attached to platinum to be determined. GLC analysis of a photolyzed solution of $CpPt(CD_3)_3$ in $HMe_2SiOSiMe_3$ showed a complex mixture with a strong peak for $Me_3SiOSiMe_3$. Mass spectral analysis of this component showed a peak at 147 amu at 14% relative abundance corresponding to loss of a methyl group from the molecular ion as well as a base peak at 150 amu corresponding presumably to the d_3 isotopomer $Me_3SiOSiMe_2(CD_3)$.[24] Significant $(M - 15 + 3)^+$ peaks were also observed for the $Me_3SiOSiMe_2OSiMe_3$ and $Me_3SiO(SiMe_2O)_2SiMe_3$ also formed in the reaction.

In a separate experiment, photolysis of a solution of 0.127 mmol of $CpPt(CD_3)_3$ in $HMe_2SiOSiMe_2OSiMe_3$ for 1 h led to the formation by ^1H NMR of 0.074 mmol of the hydride **1b** with 0.029 mmol of $CpPt(CD_3)_3$ remaining unconsumed; 0.024 mmol of platinum was unaccounted for by either **1b** or $CpPt(CD_3)_3$ and was presumably in the form of possibly colloidal platinum metal. The total amount of deuterated siloxanes produced was 0.107 mmol, approximately equal to 1 equiv/equiv of **1b** formed plus 2 equiv/equiv of platinum not accounted for by unreacted $CpPt(CD_3)_3$ and **1b** (0.122 mmol). This result supports the overall mechanism outlined in Scheme I, including the initial reaction of silane with either $[CpPtMe_3]^*$ or $[CpPtMe_2/Me]$. The alternative hydrogen abstraction route would require production of only 1 equiv of CD_3–siloxane/equiv of platinum colloid (0.024 mmol), much less than the experimentally observed value.

Further support for this scheme was provided by methane quantification experiments. Photolysis of 0.310 mmol of $CpPtMe_3$ in $HMe_2SiOSiMe_2SiMe_3$ for 1 h led to the formation, as indicated by ^1H NMR, of 0.105 mmol of **1b**, with 0.152 mmol of $CpPtMe_3$ unchanged and the remaining 0.053 mmol of platinum presumably in the form of colloidal platinum. GLC analysis of the gases above the reaction mixture indicated the formation of 0.232 mmol of methane, approximately equal to 2 equiv/equiv of **1b** formed plus 1 equiv/equiv of platinum not accounted for by unreacted $CpPtMe_3$ and **1b** (0.263 mmol), i.e., per equivalent of colloidal platinum. Here, the alternative mechanism demands formation of 3 equiv of methane/equiv of **1b** plus 2 equiv/equiv of platinum colloid (0.421 mmol), significantly more than that observed.

When the photolysis of $CpPtMe_3$ was carried out in cyclohexane-d_{12} in the presence of varying amounts of $HMe_2SiOSiMe_3$, the extent of conversion of $CpPtMe_3$ into the hydride complex **1a** depended on the silane concentration. For example, in the presence of 4 equiv of $HMe_2SiOSiMe_3$ after 15-min irradiation, ^1H NMR analysis indicated 78% of $CpPtMe_3$ and 5% of **1a**. In the presence of 13 equiv of $HMe_2SiOSiMe_3$, 63% of $CpPtMe_3$ and 18% of **1a** were observed and, in the presence of 62 equiv, 38% of $CpPtMe_3$ and 53% of **1a**. Platinum not accounted for by unreacted $CpPtMe_3$ or **1a** was presumably converted to colloidal platinum. Photolysis of $CpPtMe_3$ must initially produce the excited-state complex $[CpPtMe_3]^*$. In the absence of an intervening external reactant, this excited-state complex can either relax back to the ground state or undergo homolysis of a Pt–Me bond to give rise to the intimate radical pair $[CpPtMe_2/Me]$. The latter may in turn undergo internal return to starting material or go on to a solvent-separated radical pair before undergoing further chemistry. Since recombination of the separated radicals was shown by ^{195}Pt NMR not to occur (see above), and no other products are observed, the effect of silane concentration also implies attack of this reagent on either the excited state $[CpPtMe_3]^*$ or intimate pair $[CpPtMe_2/Me]$. If the silane instead reacted with the free radical $CpPtMe_2$, the degree of conversion of $CpPtMe_3$ to products would be expected to be independent of silane concentration since the rate of reaction with $HMe_2SiOSiMe_3$ would be limited by the rate of production of $CpPtMe_2$.

Conclusions

Photolysis of $CpPtMe_3$ or its derivatives in the presence of a silane leads to the formation of an active hydrosilylation catalyst, currently believed to be a platinum colloid. In the presence of certain reactive silanes, bis(silyl)platinum hydrides are formed as isolable species, which are not, however, intermediates on the primary pathway to catalytically active colloids. The evidence implicates the silyl methyl hydride complex $CpPtMe(SiR_3)H$ as the critical intermediate which is partitioned under the reaction conditions between colloidal platinum and a bis(silyl)platinum hydride such as **1a**. Oxidative addition/reductive elimination of silanes at platinum is facile and can be utilized preparatively in the synthesis of other bis(silyl)platinum hydrides.

Experimental Section

General Methods. Infrared spectra were recorded on a Mattson 4020 Galaxy FT-IR spectrophotometer. NMR spectra were recorded on a Varian XL-400 NMR spectrometer operating at 400 MHz for ^1H, and chemical shifts are reported relative to tetramethylsilane for ^1H, ^{13}C, and ^{29}Si and aqueous H_2PtCl_6 for ^{195}Pt. UV–visible spectra were recorded on an IBM 9430 UV–visible spectrophotometer. Routine gas–liquid chromatographic (GLC) analyses were performed on a Hewlett-Packard 5890 chromatograph equipped with an HP-1 methyl silicone gum column (10 m × 0.53 mm × 2.65 μm film thickness). Chromatograms were recorded on a Hewlett-Packard 3392A integrator. Gas chromatography–mass spectrometry experiments were carried out on Hewlett-Packard 5995 (for electron impact experiments) and 5988 (for chemical ionization experiments) GC–MS (quadrupole) instruments equipped with J&W DB-1 capillary columns (30 m × 0.53 mm × 1.5 μm film thickness). Methane quantification experiments were carried out on a Hewlett-Packard 5890 gas chromatograph with cryogenic cooling capability equipped with a J&W DB-5 capillary column (30 m × 0.53 mm × 1.5 μm film thickness) and a flame ionization detector.

All manipulations involving organometallic compounds were carried out under an atmosphere of argon using standard techniques.[25] Irradiations were carried out either in a light box

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[24] Electron impact mass spectra of methyl siloxanes usually do not show molecular ions due to facile loss of a methyl group from these species. For example, see: Moore, J. A. In *The Analytical Chemistry of Silicones*; Smith, A. L., Ed.; Wiley: New York, 1991; p 451.

equipped with six 15-W Sylvania Black Light Blue (F15T8/BLB) lamps, each with a maximum output at 365 nm, or with a Sylvania Sunlamp (047, 275W RSM). $CpPtMe_3$ and its derivatives were prepared as described previously.[14] Dibenzo[*a,e*]cyclooctatetraene was prepared by the method of Griffin.[26] All other materials were purchased from appropriate sources and used as received.

Preparation of $CpPt(SiMe_2OSiMe_3)_2H$ (1a). A solution of $CpPtMe_3$ (1.04 g, 3.4 mmol) in $HMe_2SiOSiMe_3$ (5.0 g, 34 mmol) in a quartz tube was irradiated for 5 h in the light box. The resulting yellow-green solution was concentrated under reduced pressure, and the dark residue was resolved by flash chromatography (silica, hexanes),[27] returning 0.44 g of $CpPtMe_3$ (42%) and providing 0.87 g of **1a** (80% based on consumed $CpPtMe_3$) as a slightly yellowish oil, homogeneous by TLC: IR (neat) 2260 cm^{-1}; ^1H NMR ($CDCl_3$) δ −16.94 (s, J_{Pt-H} = 1577 Hz, 1 H), 0.11 (s, 18 H), 0.52 (s, J_{Pt-H} = 21 Hz, 6 H), 0.53 (s, J_{Pt-H} = 20 Hz, 6 H), 5.69 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 2.18 (6 C), 13.06 (J_{Pt-C} = 111 Hz, 2 C), 13.57 (J_{Pt-C} = 104 Hz, 2 C), 95.01 (J_{Pt-C} = 18 Hz, 5 C); ^{29}Si NMR ($CDCl_3$) δ 0.95 (J_{Pt-Si} = 1100 Hz, 2 Si), 5.78 (2 Si); ^{195}Pt NMR ($CDCl_3$) δ −6863 ($^1J_{Pt-H}$ = 1577 Hz, $^3J_{Pt-H}$ = 21 Hz, J_{Pt-Si} = 1100 Hz). Exact mass: calcd for $C_{15}H_{36}O_2{}^{194}PtSi_2$ 554.1440, found 554.1414.

Preparation of $CpPt(SiMe_2OSiMe_2OSiMe_3)_2H$ (1b). A solution of **1a** (176 mg, 0.32 mmol) in $HMe_2SiOSiMe_2OSiMe_3$ (0.81 g, 3.6 mmol) was prepared and allowed to stand at room temperature overnight. The mixture was concentrated, and the crude product was purified by flash chromatography (silica, hexanes) to afford 137 mg (61%) of **1b** as a slightly yellowish oil: ^1H NMR ($CDCl_3$) δ −16.88 (s, J_{Pt-H} = 1573 Hz, 1 H), 0.02 (s, 18 H), 0.09 (s, 12 H), 0.50 (s, J_{Pt-H} = 22 Hz, 6 H), 0.52 (s, J_{Pt-H} = 20 Hz, 6 H), 5.67 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 1.58 (4 C), 1.79 (6 C), 12.88 (J_{Pt-C} = 112 Hz, 2 C), 13.29 (J_{Pt-H} = 102 Hz, 2 C), 95.02 (J_{Pt-C} = 17 Hz, 5 C); ^{29}Si NMR ($CDCl_3$) δ −22.51 (2 Si), 1.03 (J_{Pt-Si} = 1100 Hz, 2 Si), 7.22 (2 Si); ^{195}Pt NMR ($CDCl_3$) δ −6863 (J_{Pt-H} = 1573 Hz, J_{Pt-Si} = 1100 Hz).

Preparation of Platinacycle 1c. A solution of **1a** (103 mg, 0.19 mmol) in 1,2-bis(dimethylsilyl)ethane (0.73 g, 5.0 mmol) was prepared and allowed to stand at room temperature overnight. The reaction mixture was concentrated, and the crude product was purified by flash chromatography (silica, hexanes) to give 58 mg (77%) of the platinacycle **1c** as a colorless solid: ^1H NMR ($CDCl_3$) δ −17.74 (s, J_{Pt-H} = 1547 Hz, 1 H), 0.43 (s, J_{Pt-H} = 29.3 Hz, 6 H), 0.46 (s, J_{Pt-H} = 19.3 Hz, 6 H), 0.55–0.67 (m, 2 H), 0.67–0.83 (m, 2 H), 5.63 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 7.27 (J_{Pt-C} = 39 Hz, 2 C), 9.19 (J_{Pt-C} = 70 Hz, 2 C), 16.96 (J_{Pt-C} = 126 Hz, 2 C), 93.45 (5 C); ^{29}Si NMR ($CDCl_3$) δ 26.01 (J_{Pt-Si} = 935 Hz, 2 Si); ^{195}Pt NMR ($CDCl_3$) δ −7160 (J_{Pt-H} = 1551 Hz, J_{Pt-Si} = 935 Hz). Exact mass: calcd for $C_{11}H_{22}{}^{194}PtSi_2$ 404.0888, found 404.0910.

Preparation of Platinacycle 1d. A solution of **1a** (194 mg, 0.35 mmol) in $HMe_2SiOSiMe_2OSiMe_2H$ (0.75 g, 3.6 mmol) was prepared, and after 30 min at room temperature, reaction was judged by TLC to be complete. The reaction mixture was concentrated, and the crude product was purified by flash chromatography (silica, 98:2 hexanes–ethyl acetate) to give 141 mg (86%) of the platinacycle **1d** as a colorless solid: ^1H NMR ($CDCl_3$) δ −17.14 (s, J_{Pt-H} = 1589 Hz, 1 H), 0.03 (s, 3 H), 0.05 (s, 3 H), 0.50 (s, J_{Pt-H} = 17.4 Hz, 6 H), 0.56 (J_{Pt-H} = 14.6 Hz, 6 H), 5.67 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 0.77, 1.32, 12.17 (J_{Pt-C} = 91 Hz, 2 C), 14.22 (J_{Pt-C} = 82 Hz, 2 C), 94.23 (5 C); ^{29}Si NMR ($CDCl_3$) δ −8.90, 3.41 (J_{Pt-Si} = 1045 Hz, 2 Si); ^{195}Pt NMR ($CDCl_3$) δ −6860 (J_{Pt-H} = 1588 Hz, J_{Pt-Si} = 1042 Hz). Exact mass: for $C_{11}H_{24}O_2{}^{194}PtSi_3$ 466.0712, found 466.0731.

Relative Reactivities of $CpPtMe_3$ and 1a. A stock solution was prepared by combining 1.57 g of undecane (as an internal GLC standard, 10.0 mmol), 2.25 g of 1-octene (20.0 mmol), and 4.46 g of $HMe_2SiOSiMe_2OSiMe_3$ (20.0 mmol). Dilution of 5.4 mg of $CpPtMe_3$ and 11.5 mg of **1a** to 10.00 mL with cyclohexane provided 1.8×10^{-3} and 2.1×10^{-3} M solutions of these complexes, respectively. A mixture of 15 g of cyclohexane, 3.50 g of the stock solution, and 0.58 mL of the solution of $CpPtMe_3$ (0.012 mol % Pt) was prepared and divided into two equal portions. One portion was maintained in the dark at room temperature, and the second portion was irradiated in the light box. In the same fashion, a mixture of 15 g of cyclohexane, 3.50 g of the stock solution, and 0.50 mL of the solution of **1a** (0.012 mol % Pt) was prepared and treated in the same way. Progress of the four reactions was monitored by GLC with the results plotted in Figure 4.

Photolysis of $CpPtMe_3$ in $HMe_2SiOSiMe_2OSiMe_3$. GC–MS Analysis of the Products. A mixture of 141.3 mg (0.463 mmol) of $CpPtMe_3$, 490.2 mg (2.203 mmol) of $HMe_2SiOSiMe_2OSiMe_3$, and 26.6 mg (0.289 mmol) of toluene (as an internal GLC and NMR standard) was prepared in a 30-mL Schlenk tube. An approximately 200-mg sample of the mixture was separated and diluted with $CDCl_3$ for initial ^1H NMR and GLC analysis. The tube was fitted with a stopcock and joint designed to be married directly into the inlet port of the gas chromatograph, and the remaining 440.6 mg (0.310 mmol of Pt) was photolyzed in the light box for 1 h. Analysis of the gases above the reaction mixture by GLC indicated the formation of 0.232 mmol of methane. The tube was opened, and analysis of the reaction mixture by ^1H NMR indicated the presence of 0.105 mmol of the hydride **1b** and 0.152 mmol of unreacted $CpPtMe_3$; 0.053 mmol of the 0.310 mmol of $CpPtMe_3$ originally photolyzed was unaccounted for by ^1H NMR. GLC analysis of the solution indicated the formation of 0.043 mol of cyclopentadiene.

A mixture of 60.0 mg (0.191 mmol) of $CpPt(CD_3)_3$, 204 mg (0.92 mmol) of $HMe_2SiOSiMe_2OSiMe_3$, and 5.7 mg (0.062 mmol) of toluene was prepared in a 2-mL glass vial. An approximately 90-mg sample of the mixture was separated and diluted with $CDCl_3$ for initial ^1H NMR and GLC analysis. The remaining 180 mg (0.127 mmol of Pt) was photolyzed in the light box for 1 h. The vial was opened, and analysis of the reaction mixture by ^1H NMR indicated the presence of 0.074 mmol of the hydride **1b** and 0.029 mmol of unreacted $CpPt(CD_3)_3$; 0.024 mmol of the 0.127 mmol of $CpPt(CD_3)_3$ originally photolyzed was unaccounted for by ^1H NMR. GLC analysis of the solution indicated the formation of 0.027 mmol of cyclopentadiene. Analysis of the solution by GC–MS indicated the incorporation of 0.107 mmol of CD_3 groups into siloxanes such as $Me_3SiOSiMe_2OSiMe_3$.

Photolysis of $CpPtMe_3$ in $HMe_2SiOSiMe_3$. Effect of $HMe_2SiOSiMe_3$ Concentration on the Rate of Formation of 1a. A solution of 20 mg (0.066 mmol) of $CpPtMe_3$ in 2.5 mL of C_6D_{12} was prepared and divided into four equal portions in 5-mm NMR tubes. To these solutions were added 3.8 mg (1.6 equiv), 9.3 mg (3.9 equiv), 30.6 mg (12.9 equiv), and 168.1 mg (62 equiv) of $HMe_2SiOSiMe_3$, respectively. The samples were irradiated in the light box for 15 min and examined by ^1H NMR: sample 1, 78% of the original charge of $CpPtMe_3$ and 7% of the theoretical yield of **1a**; sample 2, 78% of $CpPtMe_3$ and 5% of **1a**; sample 3, 63% of $CpPtMe_3$ and 18% of **1a**; sample 4, 38% of $CpPtMe_3$ and 53% of **1a**. The samples were irradiated for an additional 15 min and again examined by ^1H NMR: sample 1, 67% of $CpPtMe_3$ and 3% of **1a**; sample 2, 71% of $CpPtMe_3$ and 15% of **1a**; sample 3, 24% of $CpPtMe_3$ and 49% of **1a**; sample 4, 0% of $CpPtMe_3$ and 85% of **1a**.

Inhibition by Elemental Mercury of the Active Hydrosilylation Catalyst Formed from $CpPtMe_3$. A stock solution was prepared by combining 2.39 g of undecane (as an internal GLC standard, 15.3 mmol), 3.36 g of 1-octene (30.0 mmol), 6.68 g of $HMe_2SiOSiMe_2OSiMe_3$ (30.1 mmol), and sufficient cyclohexane to provide a volume of 30.0 mL. Dilution of 4.4 mg of $CpPtMe_3$ to 10.00 mL with cyclohexane provided a 1.44×10^{-3} M catalyst solution. To each of two 10-mL glass vials were added 2.0 mL of cyclohexane, 0.23 mL of the catalyst solution, and 0.5 mL of the stock solution, and the mixtures were labeled A (control) and B. Both mixtures were irradiated with a sunlamp for 60 s, and within approximately 1 h, reaction was 80–90% complete in each case by GLC. After 1 h following the irradiation, a small drop of mercury was added to mixture B. After an additional 1 h, each mixture was divided into two equal portions, A into A′ and A″ and B into B′ and B″; the drop of mercury was left with the still stirred B″. To A′ and B′ was added 2.0 mL of the stock solution (additions were staggered by 15 min to allow for GLC analysis), and the progress of the reactions was monitored by GLC. After 6 h following the irradiation (5 h following the addition of mercury), the mercury was separated from B″, 2.0 mL of the stock

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[25] Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

[26] Griffin, C. E.; Peters, J. A. *J. Org. Chem.* **1963**, *28*, 1715.

[27] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2933.

Table I. Inhibition of Colloidal Platinum by Mercury

mixture	yield (%) of $(n\text{-}C_8H_{17})Me_2SiOSiMe_2OSiMe_3$ at times after addition of stock soln					
	0.0 h[a]	1.0 h	3.0 h	7.5 h	24 h	48 h
A′	12	25	74			
B′	11	40	78			
A″	10	22			85	88
B″	9	12			48	73
C′	3	9		64	77	86
D′	3	4		11	22	55
C″	3	11		38	78	80
D″	2	3		3	3	3

[a] $(n\text{-}C_8H_{17})Me_2SiOSiMe_2OSiMe_3$ present at 0.0 h is derived from stock solution present initially to precipitate formation of active catalyst.

Table II. Effect of Dibenzo[*a*,*e*]cyclooctatetraene on Catalyst Activity

mixture	amt of DBCOT, equiv	yield (%) of $(n\text{-}C_8H_{17})Me_2SiOSiMe_2OSiMe_3$ at times after addition of stock soln			
		0 min[a]	20 min	40 min	60 min
A		5	35	73	80
B	0.5	5	48	72	81
C	1.0	5	49	67	75
D	2.0	5	55	72	79
E	5.0	5	38	59	71

[a] $(n\text{-}C_8H_{17})Me_2SiOSiMe_2OSiMe_3$ present at 0 min is derived from stock solution present initially to precipitate formation of active catalyst.

solution was added to A″ and B″ (additions were staggered by 15 min to allow for GLC analysis), and the progress of the reactions was again monitored by GLC. Results are recorded in Table I.

The experiment was repeated essentially as described above, but a longer period of time for catalyst amalgamation was allowed. To each of two 10-mL glass vials were added 2.0 mL of cyclohexane, 0.24 mL of the catalyst solution, and 0.1 mL of the stock solution, and the mixtures were labeled C (control) and D. Both mixtures were irradiated with a sunlamp for 60 s. After 30 min following the irradiation, a small drop of mercury was added to mixture D. After 5 h each mixture was divided into two equal portions, C into C′ and C″ and D into D′ and D″; the drop of mercury was left with the still stirred D″. To C′ and D′ was added 2.0 mL of the stock solution (additions were staggered by 15 min to allow for GLC analysis), and the progress of the reactions was monitored by GLC. After approximately 24 h following the irradiation, the mercury was separated from D″, 2.0 mL of the stock solution was added to C″ and D″ (additions were staggered by 15 min to allow for GLC analysis), and the progress of the reactions was again monitored by GLC in the same manner as before. Results are recorded in Table I.

Effect of Dibenzo[*a*,*e*]cyclooctatetraene on the Active Catalyst Formed from $CpPtMe_3$. A stock solution was prepared by combining 1.56 g of undecane (as an internal GLC standard, 10.0 mmol), 2.81 g of 1-octene (25.0 mmol), 5.56 g of $HMe_2SiOSiMe_2OSiMe_3$ (25.0 mmol), and sufficient cyclohexane to provide a volume of 25.0 mL. Dilution of 5.5 mg of $CpPtMe_3$ to 10.00 mL with cyclohexane provided a 1.80×10^{-3} M catalyst solution. Dilution of 3.3 mg of dibenzo[*a*,*e*]cyclooctatetraene (DBCOT) to 10.00 mL provided a 1.62×10^{-3} M inhibitor solution. To 15.0 mL of cyclohexane was added 0.42 mL of the catalyst solution and 0.8 mL of the stock solution. A 3.5-mL aliquot was separated, and the UV spectrum between 200 and 400 nm was recorded. The remaining solution was irradiated with a sunlamp for 60 s, and a second 3.5-mL aliquot was analyzed by UV spectrophotometry. Comparison of the two spectra indicated disappearance of 84% of the initial charge of $CpPtMe_3$. Three 2.0-mL aliquots were separated and labeled A (control), B, and C. To samples B and C were added 31 μL (0.5 equiv of DBCOT with respect to total platinum) and 62 μL (1.0 equiv of DBCOT) of the inhibitor solution, respectively, and all three samples were allowed to stand in the dark. After 120, 200, and 280 min, respectively, 4.0 mL of the stock solution was added to each of samples A, B, and C, and the progress of the reactions was monitored by GLC. The experiment was repeated using 2.0 and 5.0 equiv of DBCOT (samples D and E). Results are recorded in Table II.

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