Platinum(II) Bis(β-diketonates) as Photoactivated Hydrosilation Catalysts

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Irradiation of platinum(II) bis(β-diketonates) in the presence of hydrosilanes and olefins results in olefin hydrosilation. The initial rate of hydrosilation is dependent upon the choice of β-diketonate ligand, hydrosilane, and olefin. Formation of an active catalyst requires the presence of either triethylsilane or triethylvinylsilane during a brief period of irradiation. Addition of the second reactant results in hydrosilation without further irradiation. Substantial inhibition of hydrosilation is observed when dibenzo[*a,e*]cyclooctatetraene is added following irradiation and prior to addition of the second reactant, but not when mercury is added following irradiation. These results indicate that the active form of the photogenerated catalyst is homogeneous rather than heterogeneous. Correlation of hydrosilation reactivity with the spectroscopic changes which occur during irradiation suggests that the primary photoproduct is not catalytically active and that a secondary photochemical reaction results in the loss of one of the two β-diketonate ligands and the formation of the active catalyst.

Introduction

Thermal and photochemical activation of a large number of platinum compounds has been reported to result in the formation of highly active catalysts for the hydrosilation of olefins.[1–8] Both homogeneous and heterogeneous mechanisms have been proposed for platinum-catalyzed hydrosilation. Coordinatively-unsaturated, low-valent platinum complexes and colloidal platinum, respectively, are presumed to be the catalytically active species in these reactions. Since low-valent platinum complexes are often unstable with respect to the formation of platinum metal, the same catalyst precursor might be expected to form either a homogeneous or heterogeneous catalyst, depending on the reaction conditions. In fact, Lewis and co-workers[3] have suggested platinum colloids are the active catalytic species in many reactions once thought to involve thermally-generated homogeneous catalysts. Boardman[6] has also proposed that a platinum colloid is the active hydrosilation catalyst formed upon irradiation of $CpPtMe_3$ ($Cp = \eta$-C_5H_5). Prignano and Trogler[4b] have photochemically generated a surface-supported immobilized PtL_2 (L = trialkylphosphine) hydrosilation catalyst and found that its behavior differs in several respects from that reported for colloidal platinum catalysts. The immobilized catalyst is inhibited by oxygen and strongly coordinating olefins, but not by mercury, whereas the colloidal platinum catalyst requires the presence of oxygen for optimized activity, is unaffected by coordinating olefins, and is inhibited by mercury.

We report here the results of our investigation of the generation of a highly active hydrosilation catalyst upon irradiation of dilute solutions of several platinum(II) bis(β-diketonates) in the presence of either a hydrosilane or olefin. While both thermal[7] and photochemical[8] generation of hydrosilation catalysts from platinum(II) bis(β-diketonates) has been reported, the nature of the active catalytic species and the mechanism of its formation have not been investigated previously. We find that irradiation initially yields a highly active homogeneous catalyst which is converted either photochemically or thermally to a less active heterogeneous catalyst. Only the less active heterogeneous catalyst is formed thermally. The distinction between homogeneous and heterogeneous mechanisms is based upon absorption spectral data and the the effects of added oxygen, mercury,[9] and a coordinating bis(olefin).[10] A mechanism for the formation of the active homogeneous catalyst is proposed on the basis of these results and our parallel investigation of the primary photochemistry of the platinum(II) bis(β-diketonates) which is described in the preceding paper.[11]

Results

Addition of Triethylsilane and Triethylvinylsilane in the Presence of Platinum(II) Bis(β-diketonates). Irradiation of 0.5 M Et_3SiH, 0.5 M $Et_3Si(vinyl)$, and 5×10^{-4} M $Pt(acac)_2$ (acac = acetylacetonate) in deoxygenated (nitrogen purged) dichloromethane solution at room temperature with Pyrex-filtered light ($\lambda > 300$ nm) results in conversion of the silane reactants to the hydrosilation adduct $Et_3SiCH_2CH_2SiEt_3$. Minor amounts (<2%) of reduced olefin and silylated olefin are also detected by GC-MS. While no reaction is observed in the absence of light, only a short period of irradiation is necessary in order to obtain ca. 85% conversion of reactants to products. A plot of composition vs reaction time for a solution irradiated for 10 min and then monitored by GC is shown in Figure 1.

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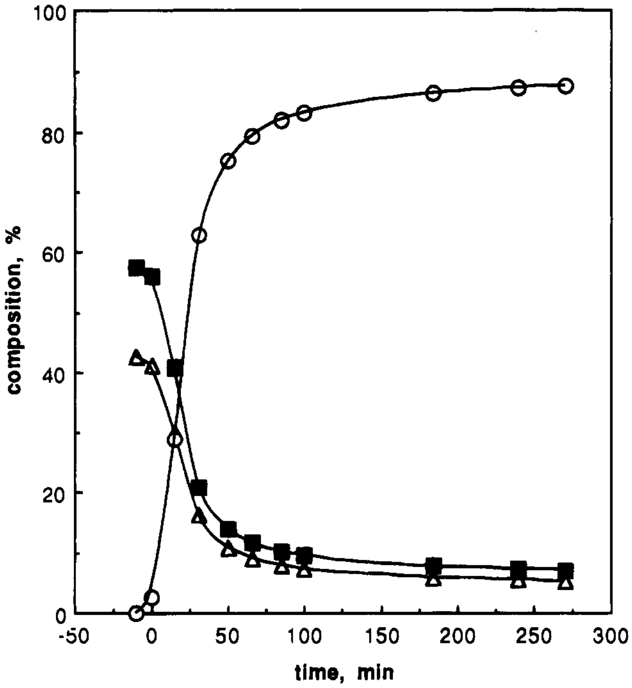


Figure 1. Composition (weight percent) of a deaerated dichloromethane solution containing 5 × 10^{-4} M $Pt(acac)_2$, 0.5 M Et_3SiH (△) and $Et_3Si(vinyl)$ (■), and adduct (○) versus dark reaction time. Negative time corresponds to the period irradiation with Pyrex-filtered light and positive time to dark at room temperature (24 °C).

During the 10 min irradiation period, <5% adduct is formed. Following the termination of irradiation, rapid adduct formation is observed for a period of 30–40 min, followed by slower adduct formation for a period of several hours. Longer irradiation times (20 min, 30 min, or continuous irradiation) do not alter the appearance of Figure 1. In all cases, a period of rapid hydrosilane formation is observed commencing ca. 10 min after irradiation is begun and continuing for 30–40 min. Shorter irradiation times (<3 min) result in slower adduct formation and lower ultimate adduct yields. Similar results are obtained using Pyrex-filtered light or monochromatic 365 nm irradiation.

Both the initial reaction rate and the ultimate yield of adduct are dependent upon the concentration of reactants. A $Pt(acac)_2$ concentration of 5 × 10^{-4} M is sufficient to absorb >99% of the 365 nm irradiation incident upon a 12 mm o.d. Pyrex tube. Increasing the $Pt(acac)_2$ concentration has no effect on the rate or yield of adduct, whereas decreasing the concentration results in diminished rates and yields of adduct. The use of lower concentrations (0.05 M) of Et_3SiH and $Et_3Si(vinyl)$ also results in slower rates and lower yields. The use of higher reactant concentrations was not investigated; however, addition of a second aliquot of Et_3SiH and $Et_3Si(vinyl)$ to a irradiated solution after a 2 h reaction time results in conversion of the added reactants to adduct, albeit with a rate somewhat slower than than for the initial reaction. The ratio of moles of adduct formed per mole of $Pt(acac)_2$ in this reaction is 1.6 × 10^3. The use ethanol in place of dichloromethane as the solvent results in lower adduct yields. Using the reaction conditions in Figure 1, the yield of adduct after 10 min irradiation and 5 h dark reaction time is 30%.

No adduct formation is observed after several days when a deaerated dichloromethane solution of 0.5 M Et_3SiH, 0.5 M $Et_3Si(vinyl)$, and 5 × 10^{-4} M $Pt(acac)_2$ is stored in the dark. Hydrosilation does occur, however, when the reactants are heated at 82 °C in deaerated 1,2-dichloroethane solution. A 55% yield of hydrosilation adduct is observed in solution after 5 h of heating, and an 81% yield of adduct is observed after 21 h of heating. The reaction is slowed considerably when Et_3SiH, $Et_3Si(vinyl)$, and $Pt(acac)_2$ are heated in an oxygenated 1,2-dichloroethane solution. Such a solution contains 22% adduct after 5 h of heating and 51% adduct after 24 h of heating. Large black particles also are formed in the aerated solution during the heating period.

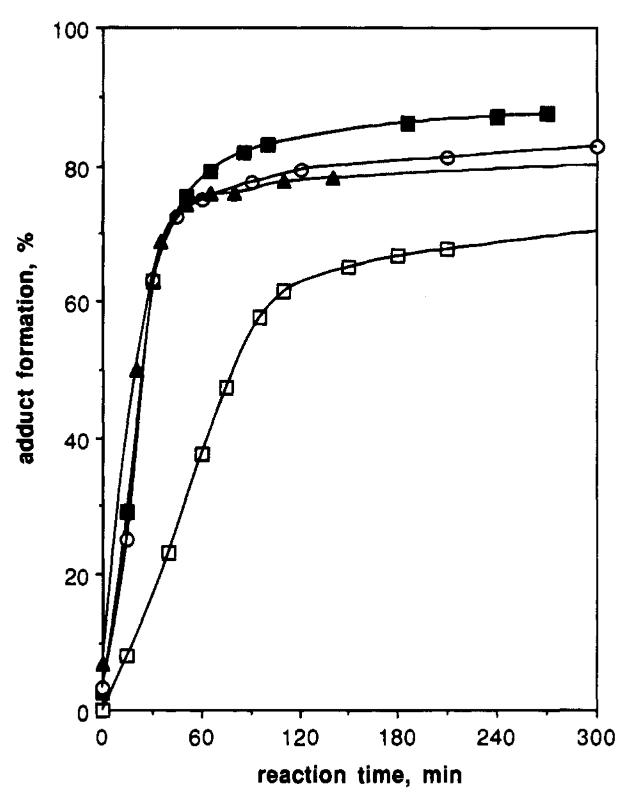


Figure 2. Adduct formation vs dark reaction time for deaerated dichloromethane solutions containing 0.5 M Et_3SiH and $Et_3Si(vinyl)$ after 10 min of Pyrex-filtered irradiation in the presence of 5 × 10^{-4} M $Pt(acac)_2$ (■), $Pt(ba)_2$ (○), $Pt(dbm)_2$ (▲), or $Pt(hfac)_2$ (□).

Irradiation of Et_3SiH and $Et_3Si(vinyl)$ in the presence of several Pt(II) β-diketonates, $Pd(acac)_2$, and $Ni(acac)_2$ has also been investigated. The time dependence of adduct formation using the conditions of Figure 1 with $Pt(acac)_2$, $Pt(ba)_2$ (ba = benzoylacetonoate), $Pt(dbm)_2$ (dbm = dibenzoylmethanate), and $Pt(hfac)_2$ (hfac = hexafluoroacetylacetonate) is shown in Figure 2. The rates of reaction at these concentrations are similar when $Pt(acac)_2$, $Pt(ba)_2$, and $Pt(dbm)_2$ are used, but the rate for $Pt(hfac)_2$ is slower. Irradiation of Et_3SiH and $Et_3Si(vinyl)$ in the presence of $Ni(acac)_2$ or $Pd(acac)_2$ (10^{-4}–10^{-2} M) with Pyrex-filtered light results in formation of Hacac and precipitated metal but fails to produce detectable hydrosilation adduct, even after prolonged irradiation.

Catalyst Formation and Stability. The generation of an active hydrosilation catalyst requires the presence of a Pt β-diketonate and either Et_3SiH or $Et_3Si(vinyl)$ during the 10 min irradiation period. Thus irradiation of 5 × 10^{-3} M $Pt(acac)_2$ and 0.5 M Et_3SiH in deaerated dichloromethane solution followed by the immediate addition of $Et_3Si(vinyl)$ (0.5 M) results in adduct formation with a dark time dependence similar to that shown in Figure 1. Similar results are obtained upon immediate addition of Et_3SiH (0.5 M) to an irradiated solution of 5 × 10^{-3} M $Pt(acac)_2$ and 0.5 M $Et_3Si(vinyl)$. However, irradiation of 5 × 10^{-3} M $Pt(acac)_2$ and 0.05 M Et_3SiH followed by the immediate addition of Et_3SiH (0.45 M) and $Et_3Si(vinyl)$ (0.5 M) results in only 4.1% adduct formation after 4 h dark reaction time and 43% adduct formation after 24 h dark reaction time.

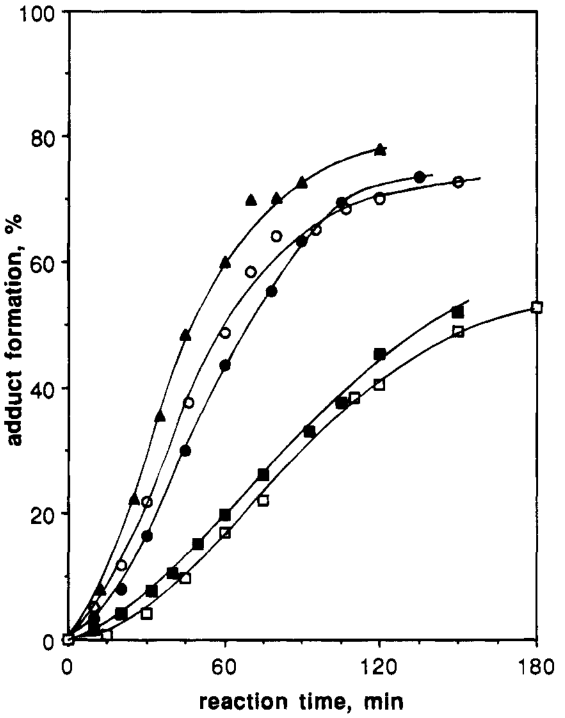


Figure 3. Effect of irradiation time (Pyrex-filtered light) on the formation of adduct (weight percent) from 5 × 10^{-3} M Pt(acac)$_2$ and 0.5 M Et$_3$SiH in deaerated dichloromethane solution. Et$_3$Si(vinyl) (0.5 M) is added to the solution immediately after completion of the designated irradiation time and the solution is then stored in the dark (24 °C): 5 min (■), 10 min (●), 30 min (▲), 2 h (○), 15 h (□).

The activity of the hydrosilation catalyst generated by irradiation of Pt β-diketonates in the presence of Et$_3$SiH is dependent upon both the irradiation time and postirradiation time prior to addition of Et$_3$Si(vinyl). The time dependence of adduct formation for solutions of 5 × 10^{-3} M Pt(acac)$_2$ and 0.5 M Et$_3$SiH irradiated for 5 min to 15 h followed by immediate addition of 0.5 M Et$_3$Si(vinyl) is shown in Figure 3. The initial rate of adduct formation increases with irradiation time, reaches a maximum for 30–60 min irradiation time, and decreases for longer irradiation times. When Et$_3$Si(vinyl) is added to a solution of 0.5 M Et$_3$SiH and 5 × 10^{-4} M Pt(acac)$_2$ immediately following irradiation (10 min, Pyrex-filtered light), 70% conversion to adduct occurs within 2 h of dark reaction time (Figure 4a). When the irradiated solution is kept in the dark for 12 h prior to addition of Et$_3$SiH, the yield of adduct is 10% after 2 h and 25% after 4 h of dark reaction time (Figure 4b).

A less active hydrosilation catalyst can be formed by irradiation of a Pt β-diketonate in the absence of hydrosilane or olefin. Addition of Et$_3$SiH and Et$_3$Si(vinyl) (0.5 M) to a solution of 5 × 10^{-3} M Pt(acac)$_2$ immediately after 10 min irradiation results in 25% adduct formation after 5 h dark reaction time. Similarly, irradiation of a dichloromethane solution of 5 × 10^{-4} M Pt(ba)$_2$ with Pyrex-filtered light for 3 h followed by addition of Et$_3$SiH and Et$_3$Si(vinyl) results in 25% adduct formation after 5 h dark reaction time. Irradiation for 18 h results in the formation of a black precipitate. Addition of Et$_3$SiH and Et$_3$Si(vinyl) at this point results in the formation of 34% adduct after 5 h dark reaction time.

Inhibition by Oxygen, Mercury, and Dibenzocyclooctatetraene. The presence of oxygen during either the irradiation or postirradiation period inhibits adduct formation. Using the reaction conditions in Figure 1, the yield of adduct after 5 h dark reaction is reduced from 85% to 15% when the solution is not deoxygenated by nitrogen purging prior to irradiation and to 4% when the solution is purged with air or oxygen for 1 min prior to irradiation. Purging with oxygen for 1 min after the 10 min irradiation period results in an adduct yield of 14% after 5 h. Continuous irradiation of oxygenated solutions does not result in an increase in the yield of adduct.

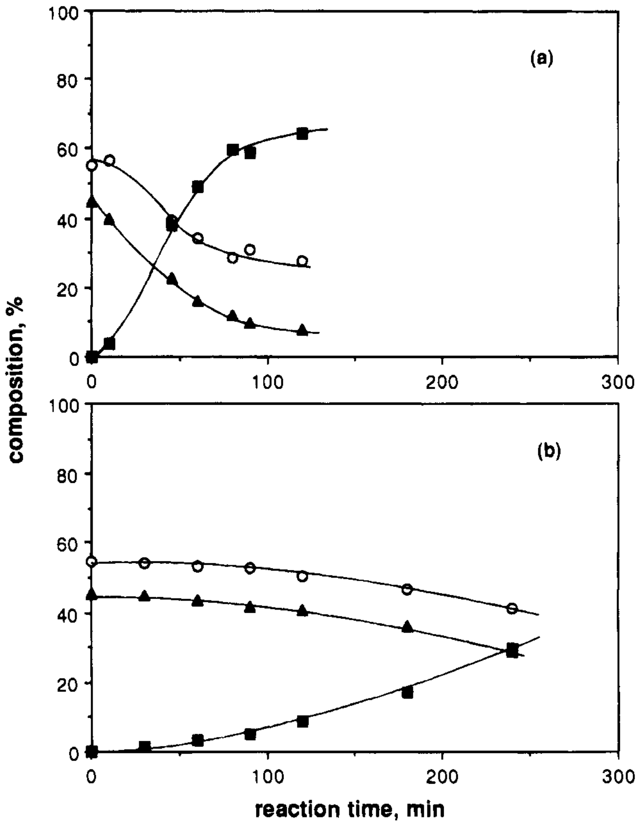


Figure 4. Composition (weight percent) of reactants and adduct (■) of a deaerated dichloromethane solution containing 5 × 10^{-4} M Pt(acac)$_2$ and 0.5 M Et$_3$SiH (▲) versus dark reaction time following irradiation (λ ≥ 300 nm; 10 min): (a) 0.5 M Et$_3$Si(vinyl) (○) added immediately after irradiation period; (b) 0.5 M Et$_3$Si(vinyl) (○) added 12 h after irradiation period.

Both added mercury and dibenzo[*a,e*]cyclooctatetraene (DBCOT) partially inhibit adduct formation. The time dependence of adduct formation for a deaerated dichloromethane solution of 5 × 10^{-4} M Pt(acac)$_2$ and 0.5 M Et$_3$SiH to which a small drop of mercury was added prior to irradiation and 0.5 M Et$_3$Si(vinyl) added immediately after irradiation is shown in Figure 5a. In comparison to the results obtained in the absence of mercury (Figure 4a), both the initial rate and the final yield of adduct are approximately half as large. When mercury is added after irradiation and the solution stirred for 12 h prior to addition of 0.5 M Et$_3$Si(vinyl), only 2% adduct is formed after 5 h reaction time (Figure 5b). Comparison with the results obtained under similar conditions in the absence of mercury (Figure 5a) reveals a 10-fold decrease in adduct formation. Results similar to those shown in parts a and b of Figure 5 are obtained when mercury is added after irradiation and the solution stirred for 10 min and 12 h, respectively, prior to addition of Et$_3$Si(vinyl). Irradiation of 5 × 10^{-4} M Pt(acac)$_2$ and 0.5 M Et$_3$SiH in deaerated dichloromethane solution followed by sequential addition of 1.5 × 10^{-3} M DBCOT and 0.5 M Et$_3$Si(vinyl) results in only 10% adduct formation after 5 h reaction time compared to 70% adduct formation in the absence of DBCOT (Figure 4a). Similar results are obtained when the delay time between additions of DBCOT and Et$_3$Si(vinyl) is several minutes or several hours.

Hydrosilane and Olefin Dependence. The photoinitiated hydrosilation of Et$_3$Si(vinyl) with several hydrosilanes and of

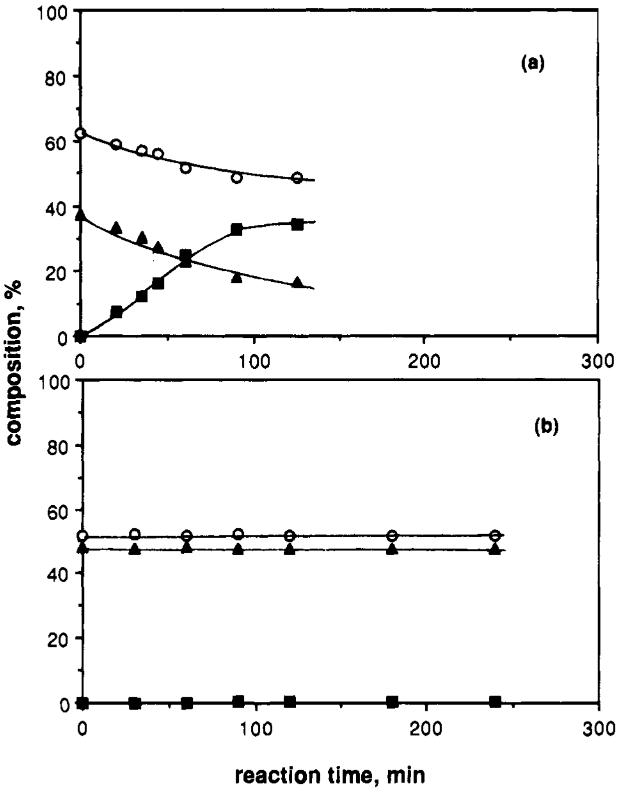


Figure 5. Effect of mercury on the conversion (weight percent) of reactants Et_3SiH (○) and $Et_3Si(vinyl)$ (▲) to adduct (■) in deaerated dichloromethane solution vs dark reaction time following irradiation ($\lambda \geq 300$ nm; 10 min) of 0.5 M Et_3SiH in the presence of 5×10^{-4} M $Pt(acac)_2$ and one drop of added mercury: (a) 0.5 M $Et_3Si(vinyl)$ added immediately after irradiation period; (b) 0.5 M $Et_3Si(vinyl)$ added 12 h after irradiation period.

Et_3SiH with several terminal olefins has been investigated. The time dependence of adduct formation under the conditions of Figure 1 for the reactions of $Et_3Si(vinyl)$ with Bu_3SiH, i-Pr_3SiH, Ph_3SiH, $(EtO)_3SiH$, and $MeCl_2SiH$ is shown in Figure 6. Adduct formation is observed with all of the hydrosilanes except i-Pr_3SiH. In comparison to the Et_3SiH reaction, the reactions with $(EtO)_3SiH$ and $MeCl_2SiH$ display greater yields of adduct formation during the 10 min irradiation period, faster initial rates, and larger adduct yields. The initial reaction rate for Bu_3SiH is somewhat slower than that of Et_3SiH, but the adduct yields are similar after several hours. The yield of adduct is distinctly lower using Ph_3SiH; however, the initial reaction rate appears to be similar to that of Et_3SiH.

The time dependence of adduct formation under the conditions of Figure 1 for the reactions of Et_3SiH with $(EtO)_3Si(vinyl)$, $Cl_3Si(vinyl)$, butyl methacrylate, styrene, and 1-hexene in the presence of either $Pt(acac)_2$ or $Pt(ba)_2$ is shown in Figure 7. The reactions of both $(EtO)_3Si(vinyl)$ and $Cl_3Si(vinyl)$ display periods of slow adduct formation after irradiation, followed by more rapid adduct formation. The adduct yield for $(EtO)_3Si(vinyl)$ after several hours is similar to that for $Et_3Si(vinyl)$, while that for $Cl_3Si(vinyl)$ is lower. Slow formation of adduct is observed with butyl methacrylate; however the yield of adduct continues to increase after 5 h. Rapid initial adduct formation is observed for both styrene and 1-hexene, but the conversions to adduct after 5 h are <50% for styrene and <10% for 1-hexene.

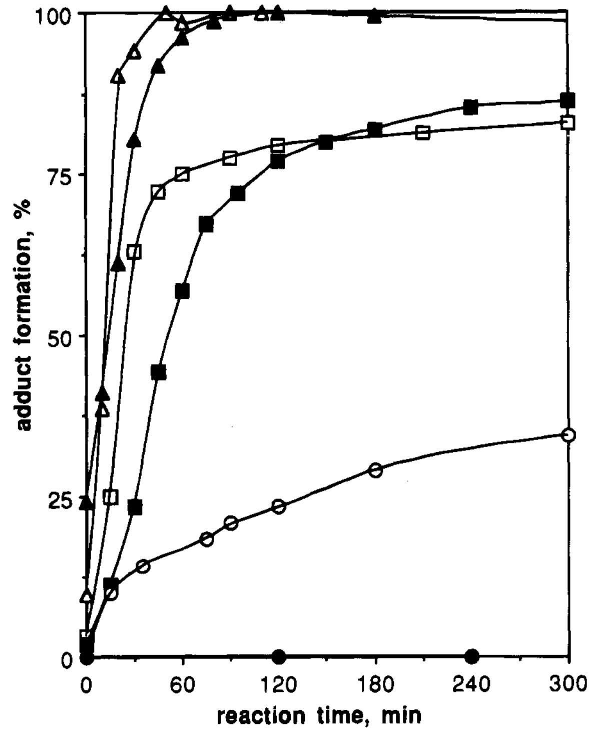


Figure 6. Effect of hydrosilane (0.5 M) on adduct formation (weight percent) with 0.5 M $Et_3Si(vinyl)$ in the presence of 5×10^{-4} M $Pt(ba)_2$ in deaerated dichloromethane solution after 10 min of Pyrex-filtered irradiation: $(EtO)_3SiH$ (△), $MeCl_2SiH$ (▲), Et_3SiH (□), Bu_3SiH (■), Ph_3SiH (○), i-Pr_3SiH (●).

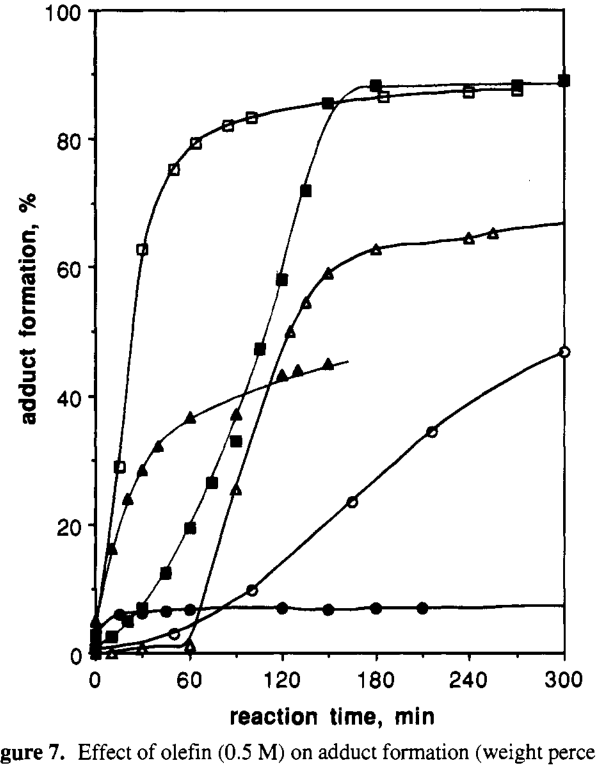
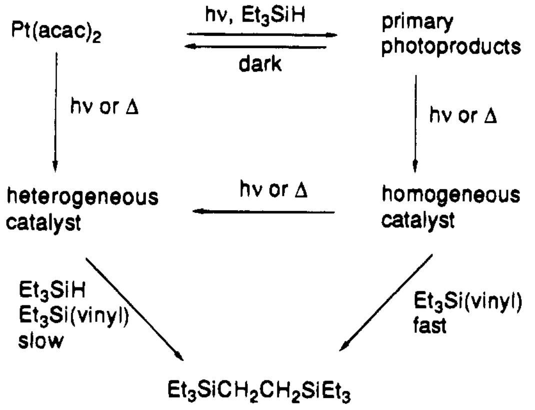


Figure 7. Effect of olefin (0.5 M) on adduct formation (weight percent) with 0.5 M Et_3SiH in the presence of 5×10^{-4} M $Pt(ba)_2$ [or 5×10^{-4} M $Pt(acac)_2$ where indicated by an asterisk] in deaerated dichloromethane solution after 10 min of Pyrex-filtered irradiation: $Et_3Si(vinyl)$ (□), $(EtO)_3Si(vinyl)$* (■), $Cl_3Si(vinyl)$ (△), styrene (▲), butyl methacrylate* (○), 1-hexene (●).

Discussion

Homogeneous and Heterogeneous Catalysis. As previously reported by Oxman and Boardman,[8] irradiation of several platinum(II) bis(β-diketonates) at 25 °C in the presence of a hydrosilane and terminal olefin results in hydrosilation of the olefin. No hydrosilation is observed when the hydrosilane and olefin are irradiated or heated at 82 °C in the absence of a

Scheme 1



platinum(II) bis(β-diketonate). In the absence of light, solutions containing platinum(II) bis(β-diketonates), hydrosilane, and olefin are stable indefinitely at 25 °C but undergo slow adduct formation upon heating at 82 °C. Rapid hydrosilation is observed when a dichloromethane solution containing 5×10^{-4} M $Pt(acac)_2$, 0.5 M Et_3SiH, and 0.5 M $Et_3Si(vinyl)$ is either irradiated continuously or irradiated for a short period of time (ca. 10 min) and then placed in the dark (Figure 1). Rapid hydrosilation is also observed when either Et_3SiH or $Et_3Si(vinyl)$ is present during the 10 min irradiation period and the other reactant added after termination of irradiation (Figure 4a). Slow hydrosilation is observed when neither Et_3SiH nor $Et_3Si(vinyl)$ is present during the irradiation period and both are added after termination of irradiation.

Correlation of the results of hydrosilation formation and the spectral changes which accompany irradiation of $Pt(acac)_2$ in the presence of Et_3SiH or $Et_3Si(vinyl)$ indicate that the 10 min irradiation time required to generate the active hydrosilation catalyst corresponds to the time required for essentially complete disappearance of the long-wavelength UV absorption band of 5×10^{-4} M $Pt(acac)_2$ and for the formation and destruction of a primary photoproduct detected by both UV and ^1H NMR spectroscopy.[11] However, the complete photodecomposition of $Pt(acac)_2$ to liberate both ligands and form colloidal platinum does not occur during this brief irradiation period. These observations lead us to postulate that short periods of irradiation result in the formation of a homogeneous hydrosilation catalyst which is slowly converted to a less active heterogeneous catalyst similar to that formed upon thermal decomposition of $Pt(acac)_2$ (Scheme 1).

Evidence supporting the postulated formation of a homogeneous catalyst which is converted to a less active heterogeneous catalyst is provided by the effects of added mercury and dibenzo[*a,e*]cyclooctatetraene (DBCOT). The use of mercury as a selective inhibitor of heterogeneous vs homogeneous platinum-catalyzed hydrosilation has been proposed by Whitesides et al.[9] Evidently, amalgamation of bulk platinum metal renders the heterogeneous catalyst inactive while having little effect upon homogeneous platinum hydrosilation catalysts. Boardman[6] observed that the colloidal platinum hydrosilation catalyst formed upon irradiation of $CpPtMe_3$ is inhibited by added mercury. Prignano and Trogler[4b] observed that mercury inhibits hydrosilation catalyzed by silica-supported colloidal platinum but not by surface-immobilized, monomeric, coordinatively-unsaturated platinum. We find that the hydrosilation catalyst generated by brief irradiation of 5×10^{-4} M $Pt(acac)_2$ and 0.5 M Et_3SiH in the presence of mercury is only slightly less active than the catalyst generated in the absence of mercury (Figures 4a and 5a). When similar solutions are stirred in the dark overnight prior to addition of $Et_3Si(vinyl)$, the low catalytic activity observed in the absence of mercury is almost completely inhibited by mercury (Figures 4b and 5b). Such extensive inhibition suggests that the only catalyst present under 12 h after termination of irradiation is colloidal platinum.

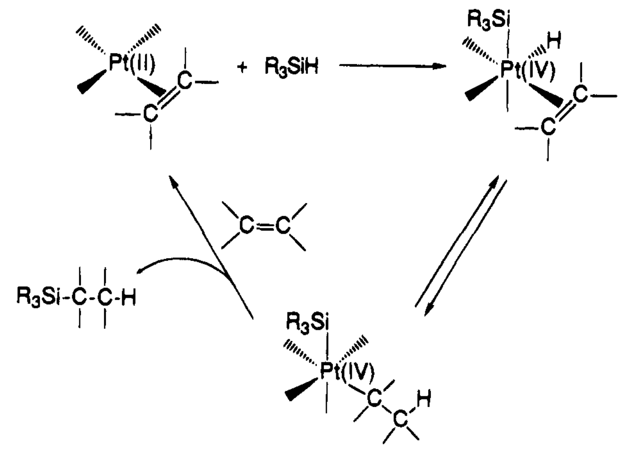
A complementary test for homogeneous vs heterogeneous platinum-catalyzed hydrosilation is provided by the use of DBCOT. Anton and Crabtree[10] have reported that DBCOT coordinates strongly to coordinatively-unsaturated platinum, rendering it unreactive as a hydrosilation catalyst. Prignano and Trogler[4b] observed that their silica-supported homogeneous hydrosilation catalyst is inhibited by 1,7-octadiene. We find that the hydrosilation catalyst generated by brief irradiation of 5×10^{-4} M $Pt(acac)_2$ and 0.5 M Et_3SiH prior to addition of $Et_3Si(vinyl)$ is partially inhibited when DBCOT is added to the irradiated solution prior to the addition of $Et_3Si(vinyl)$. The initial period (ca. 100 min) of rapid hydrosilation is almost completely inhibited while the slow hydrosilation observed at longer reaction times is uninhibited. Boardman[6] observed that the colloidal platinum catalyst formed upon irradiation of $CpPtMe_3$ is not inhibited by added DBCOT.

Homogeneous and heterogeneous platinum hydrosilation catalysts are also reported to show different responses to the presence of oxygen. While Harrod and Chalk[2b] found that the presence of oxygen was required for the occurrence of hydrosilation using platinum(II) catalysts, they offered no explanation for the function of oxygen. Lewis[3d] has suggested that the presence of oxygen is essential both to generate colloidal platinum of high catalytic activity and to prevent its irreversible agglomeration into less active macroscopic metal particles. Prignano and Trogler[4b] have observed that oxygen completely inhibits hydrosilation by their surface-immobilized monomeric coordinatively-unsaturated platinum catalyst. We find that oxygen saturation prior to brief irradiation of a solution containing 5×10^{-4} M $Pt(acac)_2$, 0.5 M Et_3SiH, and 0.5 M $Et_3Si(vinyl)$ results in nearly total inhibition of photoinitiated hydrosilation. Oxygen saturation following the irradiation period results in only partial inhibition, similar to that observed for DBCOT. The initial period of rapid hydrosilation is more strongly inhibited than is the slow phase of hydrosilation. Introduction of oxygen after the initial period of rapid hydrosilation also has no effect on the slower phase of hydrosilation.

Oxygen inhibition of hydrosilation might result from either oxygen quenching of the primary photoprocess or reaction of the photogenerated catalyst or catalyst precursor with oxygen. Prignano and Trogler[4b] have suggested that the oxygen sensitivity of their supported catalyst may result from reaction of oxygen with alkylphosphine ligands at the active site. While oxygen is observed to inhibit the photodecomposition of $Ni(acac)_2$ and $Pd(acac)_2$, this is not the case for $Pt(acac)_2$. Oxygen has little effect on either the rate of disappearance of the long wavelength absorption band of $Pt(acac)_2$ or the rate of formation of the primary photoproduct.[11]

In summary, the results of inhibition studies using mercury, DBCOT, and oxygen support the proposal that irradiation of $Pt(acac)_2$ in the presence of either Et_3SiH or $Et_3Si(vinyl)$ results in the formation of a highly reactive homogeneous hydrosilation catalyst that is slowly converted to a less active heterogeneous catalyst (Scheme 1). A less active heterogeneous catalyst is also formed upon irradiation of $Pt(acac)_2$ in the absence of Et_3SiH or $Et_3Si(vinyl)$ and upon thermal decomposition of $Pt(acac)_2$ in the presence or absence of Et_3SiH and $Et_3Si(vinyl)$. A measure of the activity of the photogenerated homogeneous catalyst is provided by comparison of our results with those reported by Lewis and Lewis[3a] for the colloidal platinum catalyst obtained upon reaction of $Pt^0(COD)_2$ (COD = 1,5-cycloocta-

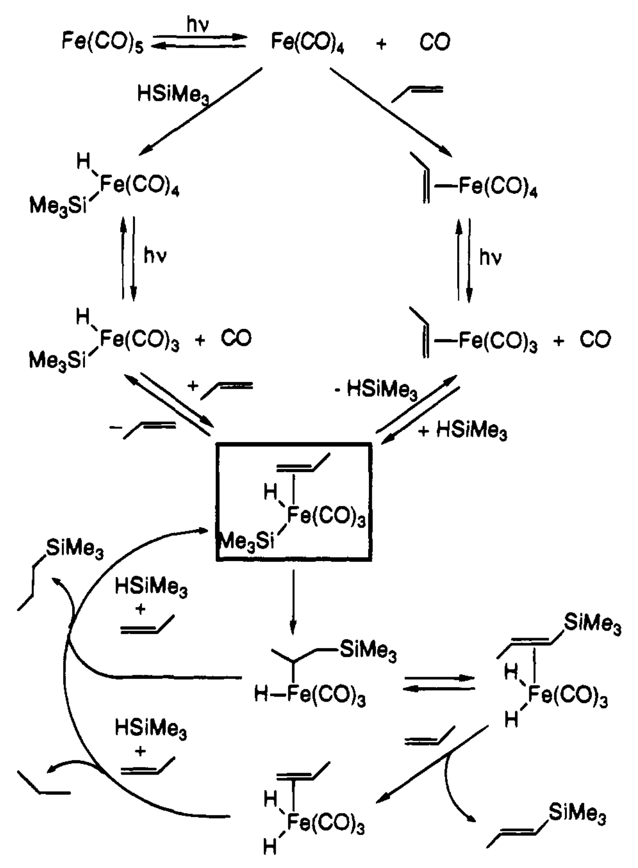
Scheme 2



diene) with $(EtO)_3SiH$ and $Me_3Si(vinyl)$ at 25 °C. They observe complete reaction (10^6 turnovers) within 15 min following a brief induction period. Similar turnover numbers were reported by Boardman[6] for the colloidal platinum catalyst formed upon irradiation of $CpPtMe_3$. We observe essentially complete reaction (10^3 turnovers) of Et_3SiH with $Et_3Si(vinyl)$ within 30 min following a brief irradiation period (10 min, Figure 1). With the more reactive $(EtO)_3SiH$, reaction is complete within 15 min (Figure 6). While we have not attempted to optimize turnover numbers for the photogenerated homogeneous catalyst, we anticipate that they will be comparable to those of the most active heterogeneous hydrosilation catalysts. In contrast, the heterogeneous catalyst formed from $Pt(acac)_2$ is clearly much less active than the colloidal catalysts investigated by Lewis and co-workers.[3a] This may reflect the macroscopic nature of the platinum particles generated upon thermal or photochemical decomposition of $Pt(acac)_2$ in either the absence or the presence of oxygen.

Nature of the Homogeneous Catalyst. The Chalk–Harrod mechanism for platinum-catalyzed homogeneous hydrosilation (Scheme 2) involves oxidative addition of a hydrosilane to a square-planar platinum(II)–olefin complex to form an octahedral platinum(IV) complex.[2] A hydride shift followed by reductive elimination yields the hydrosilation adduct and coordination of another olefin regenerates the homogeneous catalyst. A variation on mechanism was proposed by Schroeder and Wrighton[12] for photoinduced hydrosilation using $Fe(CO)_5$ as the catalyst precursor (Scheme 3). Irradiation of $Fe(CO)_5$ results in loss of CO and the formation of $Fe(CO)_4$ which can react with a hydrosilane to yield a metal silyl hydride or with an olefin to form a metal–olefin complex. Neither complex was found to be a hydrosilation catalyst. However, absorption of a second photon by either complex and loss of a second CO results in the formation of the active catalyst $(H)(R_3Si)Fe(CO)_3$(olefin). The first step of the "hydrosilation cycle", the lower cycle of Scheme 3, is the insertion of the olefin into the metal–silyl bond (i.e., silyl migration). Immediate reductive elimination of the alkylsilane (the hydrosilation adduct) followed by reaction with additional olefin and hydrosilane molecules results in the regeneration of the catalyst.

Scheme 3



Trogler and co-workers[4] have proposed that photochemical reductive elimination of the oxalate ligand from $Pt(C_2O_4)L_2$ (L = trialkyl- or triarylphosphonium) yields a low-valent platinum complex, PtL_2, which can form olefin and hydrosilane complexes and catalyze olefin hydrosilation. The tendency to form platinum metal limits the usefulness of such complexes as homogeneous catalysts; however, immobilization on a silica support provides a moderately active hydrosilation catalyst. Since oxalate photodecarboxylation is irreversible, the photogenerated catalyst retains its activity after irradiation is stopped. The Schroeder–Wrighton mechanism also involves a photogenerated catalyst. However, the photochemical reactions in the photogeneration cycle (Scheme 3; upper cycle) which result in CO elimination are reversible. Therefore, even though the production of alkylsilane products occurs thermally, continuous irradiation is needed in order for the hydrosilation cycle (Scheme 3; lower cycle) to continue.

The Schroeder–Wrighton mechanism can be simply adapted as shown in Scheme 4 to account for the results of our investigation of the photochemical behavior of the platinum(II) bis(β-diketonates) in the presence of hydrosilanes or olefins and their behavior as hyrosilation catalysts. Irradiation of $Pt(acac)_2$ results initially in reversible Pt–O homolysis to yield a coordinatively-unsaturated intermediate which can be trapped by high concentrations (>0.1 M) of hydrosilane or olefin to form a primary photoproduct (P_1 or P_1').[11] While the primary photoproducts obtained in the presence of hydrosilanes and olefins have not been isolated and characterized, their ultraviolet and ^1H NMR spectra are indicative of the formation of a hydrosilane or olefin complex with one chelating and one monodentate acac ligand. The mode of metal–ligand bonding in P_1 and P_1' is presumably square planar η^2 for the olefin[13] and either square planar agostic (η^2)[14] or square pyramidal[15] for the hydrosilane. When irradiation is terminated after the conversion of $Pt(acac)_2$ to either primary product and then the

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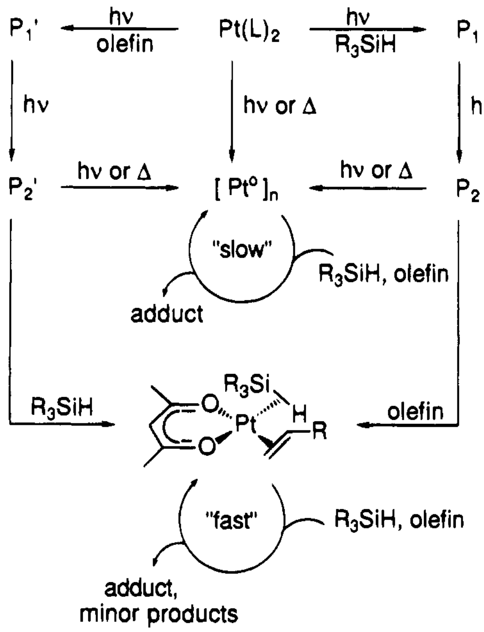
Scheme 4



complementary reactant added, no hydrosilation is observed and the primary products revert slowly to $Pt(acac)_2$ upon standing in the dark. Thus the primary products are not active hydrosilation catalysts. However, continued irradiation results in complete loss of one acac ligand and the formation of the active homogeneous hydrosilation catalyst. Loss of acac yields a secondary photoproduct (P_2 or P_2'), presumably a coordinatively-unsaturated mono-acac complex capable of coordinating either two hydrosilanes or two olefins. Upon introduction of the complementary reactant, either secondary photoproduct can undergo ligand exchange and catalyze hydrosilation.

The proposed mechanism for $Pt(acac)_2$ photoinitiated hydrosilation (Scheme 4) differs from the Schroeder–Wrighton mechanism (Scheme 3) only in the irreversible loss of one acac ligand in the second photochemical step. Thus the catalyst formed from $Pt(acac)_2$ does not revert to starting material in the dark. In the presence of excess hydrosilane or olefin, the catalyst generated from $Pt(acac)_2$ retains its activity for several hours at room temperature and is only slowly converted to colloidal Pt(0) at room temperature. Heating of $Pt(acac)_2$ also results in its decomposition and the formation of colloidal Pt(0), but not the formation of a reactive homogeneous catalyst. It seems likely that thermal decomposition, like photolysis, involves sequential loss of the two acac ligands; however the coordinatively unsaturated Pt mono-acac complex may be unstable under thermolysis conditions (82 °C) even in the presence of excess hydrosilane or olefin.

Metal, Ligand, Hydrosilane, and Olefin Dependence. Irradiation of $Pt(acac)_2$ in the presence of Et_3SiH and $Et_3Si(vinyl)$ results in hydrosilation (Figure 2) whereas irradiation of $Ni(acac)_2$ or $Pd(acac)_2$ under the same conditions does not. This difference is consistent with the much larger quantum yields for conversion of $Pt(acac)_2$ to primary photoproducts in the presence of hydrosilanes or olefins.[11] $Ni(acac)_2$,[15] $Pd(acac)_2$,[16] and $Pt(acac)_2$[7] have been reported to serve as catalyst precursors for thermal hydrosilation. The thermal reaction (120 °C) of the more reactive hydrosilane $(EtO)_3SiH$ with $Me_3Si(vinyl)$ in the presence of $Ni(acac)_2$ is reported to yield mainly the product of dehydrogenative silation and only traces of the normal hydrosilation product.[15b] Hydrosilation of acetylene with $MeCl_2SiH$ is reported to occur upon heating (80 °C) in the presence of $Pd(acac)_2$, but no reaction occurs with the less reactive Et_3SiH.[16] The common failure of Pd(II) complexes to form homogeneous hydrosilation catalysts was noted by Harrod and Chalk[2b] and attributed to their facile reduction to Pd(0) in the presence of hydrosilanes. Hagiwara et al.[17] have found that the hydrosilation catalytic activity of group 10(II) isocyanide complexes decreases in the order Pt > Ni ≫ Pd. The nonreactivity of the Pd complex was attributed to its rapid decomposition. Paonessa et al.[4a] also report that $PdL_2(olefin)$ complexes (L = trialkylphosphine) are less stable than their Pt analogs.[4a] Our failure to detect primary photoproducts upon irradiation of $Pd(acac)_2$ in the presence of hydrosilanes or olefins[11] is consistent with these reports.

Similar rates of hydrosilation are observed upon irradiation of $Pt(acac)_2$, $Pt(ba)_2$, or $Pt(dbm)_2$ in the presence of Et_3SiH and $Et_3Si(vinyl)$ using Pyrex-filtered light, whereas $Pt(hfac)_2$ is a less active catalyst precursor (Figure 2). The 10 min irradiation time is sufficient to consume essentially all of the catalyst precursor; thus the differences in efficiency of light absorption or primary photoreaction reported in the preceding paper[11] should not influence the observed rates of hydrosilation. The slower rate for $Pt(hfac)_2$ could result from slower turnover or shorter catalyst lifetime.

Both electronic and steric effects are known to influence the reactivity of the hydrosilane in platinum-catalyzed hydrosilation of olefins; electron-withdrawing substituents increase reactivity and bulky substituents decrease reactivity.[1b,3d] Our results for the hydrosilation of $Et_3Si(vinyl)$ using $Pt(ba)_2$ as the catalyst precursor (Figure 6) are in accord with these trends. The trends observed in initial rates for the series $MeCl_2SiH > (EtO)_3SiH > Et_3SiH$ and for the series $Et_3SiH > n\text{-}Bu_3SiH \gg i\text{-}Pr_3SiH$ are similar to those reported for both homogeneous and colloidal platinum catalysts. The trend for the electron-withdrawing substituents correlates inversely with the stability of the primary photoproducts ($Et_3SiH > (EtO)_3SiH > MeCl_2SiH$) as reported in the preceding paper.[11] This observation suggests that rapid turnover in the hydrosilation process may require the formation of a relatively unstable, η^2-coordinated, platinum hydrosilane.[13a]

Platinum-catalyzed hydrosilation is also known to be sensitive to olefin substitution.[1b,3d,18] A pronounced steric dependence is indicated by the failure of internal olefins to undergo hydrosilation. Electron-withdrawing halogen and alkoxy substituents decrease the rate of ethylene hydrosilation, and electron-donating aromatic substituents increase the rate of styrene hydrosilation. Our results for olefin hydrosilation using Et_3SiH and $Pt(ba)_2$ as the catalyst precursor (Figure 7) are in accord with these trends. Rapid initial hydrosilation and high conversion to adduct are observed only in the case of $Et_3Si(vinyl)$. Relatively rapid initial rates but lower conversions are observed for styrene and 1-hexene, while slow initial hydrosilation followed by an increase in rate is observed for $(EtO)_3Si(vinyl)$, $Cl_3Si(vinyl)$, and butyl methacrylate. The primary photoproduct

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formed upon irradiation of $Pt(ba)_2$ with 1-hexene is much more stable than that formed with Et_3Si(vinyl). Thus rapid turnover may require the formation of a relatively unstable platinum–olefin complex. Formation of a stable platinum–olefin complex with the chelating diolefin DBCOT results in inhibition of the homogeneous hydrosilation catalyst. Prignano and Trogler[4b] have also observed that their silica-supported homogeneous hydrosilation catalyst is inhibited by excess 1-heptene and by more strongly coordinating olefins such as styrene and 1,7-octadiene. Since the initially formed homogeneous hydrosilation catalyst is slowly converted to colloidal platinum, the increase in rate observed for several hydrosilanes (Figure 7) might reflect greater reactivity of these hydrosilanes with heterogeneous vs homogeneous catalysts.

Experimental Section

General Methods. Sources and purification of materials and solvents have previously been described.[11] Irradiations were conducted with a Rayonet reactor equipped with 254 or 420 nm lamps or with a Hanovia 450 W medium-pressure mercury lamp in a water-cooled Pyrex lamp well ($\lambda \geq 300$ nm). Reaction solutions were analyzed on a Varian 3700 flame ionization gas chromatograph with a 6 ft × $^1/_8$ in. column containing 3% SP 2100 on Supelcoport. Mass spectra were recorded on a Hewlett-Packard 5986 GC/MS.

In the reactions described below, excess solvent and volatile reactant were added to the initial reaction mixtures to compensate for evaporation which takes place during gas-bubbling procedures (e.g., 0.6 M TES concentrations initially prepared instead of 0.5 M). Deaerated solutions were prepared by bubbling the solutions with dry nitrogen for 10–15 min, and oxygenated solutions were prepared by bubbling the mixtures with oxygen for 30–60 s to subsequently reach the appropriate metal(II) β-diketonate and reactant concentrations. Aerated solutions were prepared without using excesses of the solvent and volatile reactants and the ambient air was not removed. Reactions were typically carried out in 5 mL Pyrex test tubes fit with white rubber stoppers.

Thermal Hydrosilation Reactions. Deaerated, aerated, and oxygenated 1,2-dichloroethane solutions (2 mL volumes) of 0.5 M TES and 0.5 M TEVS were heated in the presence or absence of 5×10^{-3} M $Pt(acac)_2$ at 82 °C in 5 mL Pyrex test tubes sealed with Ace threaded stoppers. Reactions were monitored by gas chromatography.

Photochemical Hydrosilation Reactions. The photocatalyzed hydrosilation reactions were carried out using one of the following three methods. For Method A, "$dT = 0$" is the moment when irradiation is terminated (i.e., $h\nu T = 10$ min). For methods B and C, "$dT = 0$" is the moment when the missing reactant (i.e., olefin or hydrosilane, respectively) is added to the irradiated solution.

Method A (Normal Conditions). Deaerated dichloromethane solutions of 0.5 M hydrosilane, 0.5 M olefin, and 5×10^{-4} M $Pt(L)_2$ were irradiated for 10 min using Pyrex-filtered light ($\lambda \geq 300$ nm). After irradiation was terminated, the reaction mixture was placed in the dark at room temperature (23–25 °C) and the thermal hydrosilation reaction was monitored by gas chromatography.

Method B [Generation of Catalyst from $Pt(L)_2$ and Hydrosilane]. Deaerated dichloromethane solutions of 0.5 M hydrosilane and 5×10^{-4} M $Pt(L)_2$ were irradiated for 10 min using Pyrex-filtered light ($\lambda \geq 300$ nm). After irradiation was terminated, 1 equiv of olefin (i.e., 0.5 M) was introduced, and the reaction mixture was placed in the dark at room temperature (23–25 °C). The thermal hydrosilation reaction was monitored by gas chromatography.

Method C [Generation of Catalyst from $Pt(L)_2$ and Olefin]. Deaerated dichloromethane solutions of 0.5 M olefin and 5×10^{-4} M $Pt(L)_2$ were irradiated for 10 min using Pyrex-filtered light ($\lambda \geq 300$ nm). After irradiation was terminated, 1 equiv of hydrosilane (i.e., 0.5 M) was introduced, and the reaction mixture was placed in the dark at room temperature (23–25 °C). The thermal hydrosilation reaction was monitored by gas chromatography.

Mercury Inhibition Studies. Deaerated dichloromethane solutions of 0.5 M Et_3SiH and 5×10^{-4} M $Pt(acac)_2$ or 5×10^{-4} M $Pt(ba)_2$ were irradiated ($\lambda \geq 300$ nm; 10 min) and stirred in the presence or absence of mercury (1 drop). Et_3Si(vinyl) (0.5 M) was added either at once or on the following day, and the thermal hydrosilation reaction was monitored by gas chromatography.

DBCOT Inhibition Studies. Four deaerated dichloromethane solutions of 0.5 M Et_3SiH and 5×10^{-4} M $Pt(ba)_2$ were irradiated for 10 min using Pyrex-filtered light. To each of two solutions (the control solutions) was added Et_3Si(vinyl) (0.5 M) either at once or after 1 h of stirring the irradiated mixtures. Thermal hydrosilation reactions were then monitored by gas chromatography. To each of the other two solutions (the test solutions) was immediately added DBCOT (1.5×10^{-3} M) with stirring, followed by the addition of Et_3Si(vinyl) (0.5 M) either at once or after 1 h of stirring the irradiated DBCOT-containing mixtures. Thermal hydrosilation reactions were then monitored by gas chromatography.

Hydrosilane Adduct GC/MS Data (*m/z*). $Et_3SiCH_2CH_2SiEt_3$ from Et_3SiH and Et_3Si(vinyl): 260 (5%, M + 2), 259 (13%, M + 1), 258 (40%, M^+), 229 (75%), 201 (31%), 173 (6%), 115 (100%), 87 (42%), 59 (19%); $Et_3SiCH{=}CHSiEt_3$, 256 (21%, M^+), 227 (68%), 199 (42%), 140 (28%), 115 (100%), 87 (50%), 59 (29%); Et_4Si, 144 (15%, M^+), 115 (100%), 87 (100%), 59 (30%). **$(EtO)_3SiCH_2CH_2SiEt_3$ from (EtO)SiH and Et_3Si(vinyl):** 277 (100%, M − 29), 249 (34%), 221 (31%), 203 (93%), 193 (39%), 175 (41%), 159 (58%), 87 (23%); Et_4Si, 144 (13%, M^+), 115 (94%), 87 (100%), 59 (33%). **$(Cl)_2(CH_3)SiCH_2CH_2SiEt_3$ from $MeCl_2SiH$ and Et_3Si(vinyl):** 241 (6%, M − 15), 227 (100%, M − 29), 199 (18%), 115 (37%), 87 (48%), 73 (13%), 59 (25%); Et_4Si, 144 (13%, M^+), 115 (92%), 87 (100%), 59 (42%). **$Bu_3SiCH_2CH_2SiEt_3$ from Bu_3SiH and Et_3Si(vinyl):** 342 (40%, M^+), 313 (13%), 285 (50%), 257 (38%), 229 (80%), 199 (51%), 171 (44%), 143 (100%), 115 (38%), 87 (46%), 73 (13%), 59 (42%); Et_4Si, 144 (7%, M^+), 115 (90%), 87 (100%), 59 (35%). **$Ph_3SiCH_2CH_2SiEt_3$ from Ph_3SiH and Et_3Si(vinyl):** 402 (6%, M^+), 373 (72%), 259 (100%), 207 (42%), 181 (15%), 105 (7%), 87 (8%), 59 (6%); Et_4Si, 144 (10%, M^+), 115 (95%), 87 (100%), 59 (42%). **$Et_3SiCH_2CH_2Si(OEt)_3$ from Et_3SiH and $(EtO)_3Si$(vinyl):** 291 (2%, M − 15), 277 (100%, M − 29), 229 (20%), 203 (60%), 159 (33%), 115 (45%), 87 (36%), 59 (25%); $CH_3CH_2Si(OEt)_3$, 192 (2%, M^+), 163 (100%), 147 (22%), 119 (30%). **$Et_3SiCH_2CH_2SiCl_3$ from Et_3SiH and Cl_3Si(vinyl):** 249 (100%, M − 29), 221 (20%), 115 (47%), 87 (53%), 59 (29%). **$Et_3SiCH_2CH_2Ph$ from Et_3SiH and styrene:** 220 (1%, M^+), 191 (100%), 163 (37%), 135 (15%), 115 (12%), 87 (61%), 59 (33%); $Et_3SiCH{=}CHPh$, 218 (28%, M^+), 189 (100%), 161 (56%), 133 (27%), 105 (14%), 87 (6%), 59 (13%); CH_3CH_2Ph, 106 (40%, M^+), 91 (100%), 77 (11%), 65 (11%), 51 (12%). **$Et_3SiCH_2CH(CH_3)CO_2(CH_2)_3CH_3$ from Et_3SiH and butyl methacrylate:** 258 (3%, M^+), 115 (40%), 87 (37%), 73 (32%), 59 (26%), 57 (20%). **$Et_3SiCH_2CH_2(CH_2)_3CH_3$ from Et_3SiH and 1-hexene:** 200 (1%, M^+), 171 (86%), 143 (28%), 115 (30%), 101 (18%), 87 (100%), 73 (5%), 59 (39%).

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