J. Am. Chem. Soc. 1987, 109, 3586-3595

Silica-Supported Bis(trialkylphosphine)platinum Oxalates. Photogenerated Catalysts for Hydrosilation of Olefins

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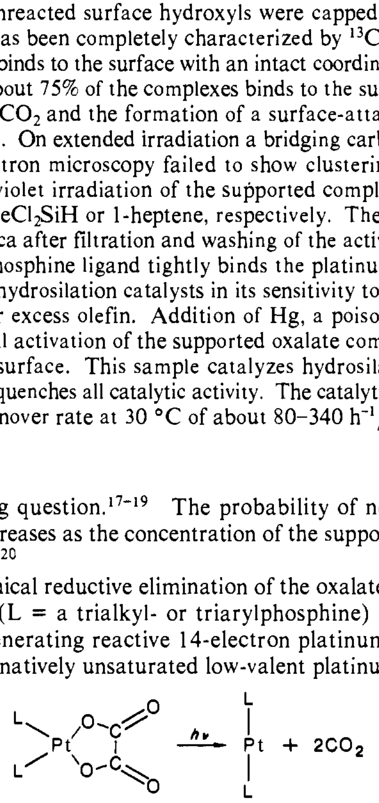
Received October 3, 1986

Abstract: A heterogeneous hydrosilation catalyst has been prepared by linking a photoactive $Pt(C_2O_4)L_2$ complex to silica ($300\ m^2/g$) by using the functionalized ligand $L = (OMe)_3Si(CH_2)_2PEt_2$. Unreacted surface hydroxyls were capped with inert $SiMe_3$ groups in all experiments. The surface-attached oxalate complex has been completely characterized by ^{13}C, ^{31}P, and ^{29}Si CP-MAS solid-state NMR spectroscopies. This shows that the complex binds to the surface with an intact coordination sphere. At maximum loading (5.4×10^{-4} mol of Pt/g) the NMR data suggest about 75% of the complexes binds to the surface with both L. Ultraviolet irradiation results in the loss of the oxalate ligand as CO_2 and the formation of a surface-attached PtL_2 species that can be trapped with CO to yield a supported $PtL_2(CO)_2$ species. On extended irradiation a bridging carbonyl species was observed, in the FTIR spectrum. Scanning and transmission electron microscopy failed to show clustering or polymerization of the complex on the surface down to 20-Å resolution. Ultraviolet irradiation of the supported complex in 1-heptene or $MeCl_2SiH$ generated a catalyst for hydrosilation on addition of $MeCl_2SiH$ or 1-heptene, respectively. The lack of catalytic activity in the filtrate and the retention of catalytic activity in the silica after filtration and washing of the activated catalyst suggest the catalyst is heterogeneous. Apparently the small trialkylphosphine ligand tightly binds the platinum on the surface. The kinetic behavior of the supported catalyst differs from soluble hydrosilation catalysts in its sensitivity toward oxygen, lack of an induction period, and inhibition by coordinating solvents or excess olefin. Addition of Hg, a poison for metallic platinum, to catalysis solutions did not alter the catalytic rate. Thermal activation of the supported oxalate complex (200 °C) appears to produce Pt particles (~20-Å diameter by TEM) on the surface. This sample catalyzes hydrosilation of olefins after a long induction period, and addition of Hg to the catalysis solution quenches all catalytic activity. The catalytically active site for the photoactive catalyst is postulated to be monomeric with a turnover rate at 30 °C of about 80-340 h^{-1}/site.

Immobilized transition metals on insoluble supports have been used to combine the selectivity of homogeneous catalysts with the ease of separation for heterogeneous species. These "third generation" catalysts[1,2] have received much attention,[3-11] and several reviews of the area are available.[1,12,13] In the preparation of supported catalysts a wide variety of support materials have been used including cross-linked polymers,[14,15] silica gel,[4] and high surface area glasses.[16] Inorganic supports possess a rigid structure, which is not hampered by solvent swelling during catalytic reactions. The rigidity of inorganic supports may also stabilize coordinatively unsaturated complexes, which oligomerize on more mobile organic supports. Whether complexes anchored to surfaces distribute uniformly or form small aggregates of molecules remains an interesting question.[17-19] The probability of near neighbor clustering increases as the concentration of the supported complex increases.[5,18,20]

Photochemical reductive elimination of the oxalate ligand from $Pt(C_2O_4)L_2$ (L = a trialkyl- or triarylphosphine) provides one method of generating reactive 14-electron platinum centers (eq 1).[21] Coordinatively unsaturated low-valent platinum phosphine complexes find use in many homogeneous catalytic systems.[21-27] One problem with photochemical generation of PtL_2 fragments for use in catalysis is their tendency to rearrange to PtL_3 or PtL_4 and platinum metal by bimolecular pathways.[21] Photochemical activation of stable surface-confined species allows control of site isolation because the density of active sites depends on the amount of irradiation, a continuously variable parameter.



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Catalytic hydrosilation of olefins with soluble compounds of platinum was first described by Speier et al.,[28-30] and the commercial catalyst (hexachloroplatinic acid) bears his name. Many

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platinum compounds may be used as hydrosilation catalyst precursors.[25,31-33] Variable induction periods and irreproducible kinetics for the known catalysts hinder detailed studies of reaction mechanisms. The abrupt onset of catalysis can pose problems on an industrial scale since hydrosilation is highly exothermic. There have been few reports[34,35] of hydrosilation with surface-anchored metal catalysts. Most previous studies[2,5-10] of phosphine-supported transition-metal complexes employed the easily synthesized arylphosphine anchoring ligands. This may not be the optimum choice for a supporting ligand because arylphosphines are (1) mediocre ligands, which often dissociate from inorganic complexes[36] and lead to catalyst leeching, (2) bulky, hindering access of substrate to the metal center, and (3) susceptible to P–C bond cleavage[37] reactions more readily than alkylphosphine analogues. Thus one study[34] of surface-attached $Pt(PPh_3)_4$ as a hydrosilation catalyst, which provided no test for catalyst heterogeneity, leaves doubt about the heterogeneous nature of the active species.

Small trialkylphosphines are among the most difficult ligands to displace from a metal center and greatly increase the basicity at the metal center. Herein we report to our knowledge the first example of a functionalized triethylphosphine anchoring ligand used to support a metal complex. By placing Pt(II) on the support as a stable bisphosphine oxalate complex, unwanted side reactions, such as phosphine oxidation, can be avoided as evidenced by solid-state (^{13}C and ^{31}P CP-MAS) NMR spectra. Photochemical generation of the reactive Pt centers permits fine control over the degree of site isolation. Unlike homogeneous hydrosilation catalysts that exhibit variable induction periods, the supported catalyst exhibits uniform rate behavior, which permits limited kinetic studies.

Experimental Section

Materials. High-purity *n*-hexane (UV grade) was obtained from Burdick and Jackson and maintained and transferred under nitrogen. The solvents benzene and tetrahydrofuran (Aldrich, Gold Label) were dried over potassium–benzophenone and distilled under nitrogen. 1-Heptene, dichloromethylsilane, and triethoxysilane were distilled under nitrogen. Hexamethyldisilazane (HMDS), 1,7-octadiene, diethylphosphine, and vinyl(trimethoxy)silane were obtained from Aldrich, stored under nitrogen, and used without purification. Triply distilled mercury was used in poisoning experiments. Davison silica gel, grade 62, 60–200 mesh, 140 Å, 300 m^2/g, was dried under vacuum at 300 °C for 3 days and used immediately.

Physical Measurements. IR spectra were recorded with use of a Perkin-Elmer 1320 IR spectrometer or a IBM IR/32 FTIR. Gas chromatographic separations were recorded on an HP5890A instrument using a 10-ft 10% SP-2100 on 100/120 Supelcoport column. Liquid-state Fourier transform NMR spectra were recorded on Nicolet 200 (^{31}P 80.99 MHz, ^{29}Si 39.74 MHz) and GE-300 (^{13}C 75.48 MHz) spectrometers. The notation $\{^1H\}$ denotes broad-band noise decoupling of hydrogen nuclei. Proton and silicon chemical shifts were measured relative to Me_4Si at 0.0 ppm, and ^{31}P chemical shifts were measured relative to the deuterium resonance of the solvent by using the internal frequency lock of the spectrometer so the resonance from a capillary of 85% H_3PO_4 centered in a 10-mm NMR tube containing deuteriated solvent appeared at 0 ppm at 20 °C. The ^{29}Si chemical shift measurements used internal Me_4Si as a standard.

An NT-150 wide-bore instrument was operated at 37.74 MHz for solid-state ^{13}C and at 60.75 MHz for ^{31}P NMR spectroscopy. The solid sample ^{29}Si NMR spectra were measured with use of a NT-200 instrument operating at 39.75 MHz. Magic angle spinning, cross-polarization, and high-power decoupling were employed. Magic angle spinning, MAS, reduces line broadening from chemical shift anisotropy. Cross-polarization, CP, enhances sensitivity and permits more rapid signal averaging. Typical CP contact times were 2 ms for ^{13}C and ^{31}P spectra and 5 ms for ^{29}Si spectra. High-power decoupling reduces the observed line width of the NMR signal.

The scanning electron microscope, SEM, studies were performed[38] on a Cambridge S410 or an Hitachi H500 STEM instrument. With the Cambridge S410 instrument, samples were mounted on a carbon stub and coated with 100 Å of gold/palladium. For the Hitachi H500, specimens were mounted on a 3-mm carbon film substrate and coated with gold/platinum. Transmission electron microscope, TEM, studies were carried out[39] on a STEM JEOL-100CX instrument with a lattice relaxation of 3.4 Å. Specimens were prepared by suspending them in denatured alcohol, transferring them via pipet to a holey carbon grid, filtering, and drying at room temperature.

Elemental analyses, performed by Galbraith Laboratories (Knoxville, TN), were used to determine catalyst loadings on silica.

Irradiations. All photochemical experiments used the water-filtered (10-cm path) output of a 200-W Hg-Xe Kratos arc lamp with quartz collimating optics. A fixed irradiation geometry was used in quantitative studies.

Diethyl(2-(trimethoxysilyl)ethyl)phosphine, $(MeO)_3Si(CH_2)_2PEt_2$, L.[40] A slight excess of diethylphosphine (5.0 g, 55 mmol) was added to vinyl(trimethoxy)silane (7.0 mL, 53 mmol) in a quartz Schlenk tube under nitrogen. This mixture was irradiated, with stirring, for 36 h. An IR spectrum of this clear solution showed complete loss of the 1630-cm^{-1} absorption of the vinyl C=C stretch. Excess phosphine was removed under a purge of nitrogen (showing complete loss of the P–H stretch at 2240 cm^{-1} in the IR spectrum). Both GC analysis and the $^{31}P\{^1H\}$ NMR spectrum showed a single product: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −12.6.

8-(Triethoxysilyl)-1-octene, $(EtO)_3Si(CH_2)_6(CHCH_2)$. In an adaptation of the synthesis of $Cl_3Si(CH_2)_6CHCH_2$,[10] an excess of 1,7-octadiene (37.0 mL, 0.25 mol) was added to triethoxysilane (10.0 mL, 0.055 mol) under nitrogen in a 200-mL flask equipped with a stir bar. To this mixture was added 1 mL of a 10% H_2PtCl_6 in EtOH solution. The mixture was stirred and heated to 50 °C for 23 h. Excess reactants and ethanol were removed by vacuum distillation at 2 torr. The product, a clear viscous liquid, distilled (2 torr) at 130 °C: IR (neat) 1632 cm^{-1} (m, C=C); ^1H NMR (C_6H_6) δ 3.65 (q, J = 7 Hz, CH_3CH_2O), 4.76 (d, J = 7 Hz, $C{=}CH_2$), 5.60 (m, $CCH{=}CH_2$); ^{29}Si NMR (C_6D_6) δ −45.7 (s).

Diethyl(8-(triethoxysilyl)octyl)phosphine, $(EtO)_3Si(CH_2)_8PEt_2$, L*.[10] The title complex was prepared by the same photochemical procedure as $(OMe)_3SiCH_2CH_2PEt_2$, using a 35% excess of $HPEt_2$. After photolysis the volatile $HPEt_2$ was removed with an N_2 purge. The product, a clear viscous liquid, was characterized by IR and ^1H NMR spectroscopies (showing complete absence of the C=C double bond and P—H stretches): $^{31}P\{^1H\}$ NMR (C_6D_6) δ −19.8 (s); ^1H NMR (C_6H_6) δ 3.7 (q, J = 7 Hz, CH_3CH_2O).

***trans*-Dichlorobis(dimethyl sulfide)platinum(II), $PtCl_2(SMe_2)_2$.** A modification of the literature method[41] was used to prepare $PtCl_2(SMe_2)_2$. An aqueous solution of K_2PtCl_4 and Me_2S was refluxed for 1 h. The resulting yellow solution was filtered immediately and the water removed by evaporation. Because of the low solubility of $PtCl_2(SMe_2)_2$, it must be Soxhlet extracted from the KCl into benzene. After the benzene is removed the resulting yellow crystalline solid (70% yield) was converted to the oxalate (60% yield) as described previously[21] for the diethyl sulfide analogue.

Bis(diethyl(2-(trimethoxysilyl)ethyl)phosphine)(oxalato)platinum(II), $Pt(C_2O_4)L_2$. An excess of insoluble $Pt(C_2O_4)(SMe_2)_2$ (1.17 g, 2.9 mmol) was suspended in 50 mL of distilled benzene under N_2 and stirred. The silylphosphine, $(OMe)_3SiCH_2CH_2PEt_2$ (0.85 mL, 4.4 mmol), was added slowly, and the mixture was stirred for 5 h. As the phosphines replaced the two labile SMe_2 ligands, the complex went into solution. Unreacted $Pt(C_2O_4)(SMe_2)_2$ (0.32 g, 0.8 mmol) was filtered (Schlenk techniques), and the product was obtained by removing the benzene and SMe_2 under vacuum to yield an insoluble viscous oil: IR (C_6H_6) 1665, 1695 cm^{-1} (C=O); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 7.1 (J_{Pt-P} = 3490 Hz). The compound appeared to be most stable if stored as a concentrated solution in benzene.

Bis(diethyl(8-(triethoxysilyl)octyl)phosphine)(oxalato)platinum(II), $Pt(C_2O_4)L_2$*.[8] This complex was prepared with a procedure similar to that used for the synthesis of $Pt(C_2O_4)L_2$ except that THF must be substituted for benzene as solvent: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 6.0 (J_{Pt-P} =

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3480 Hz); ^1H NMR (C_6D_6) δ 3.75 (q, OCH_2CH_3).

Preparation of the Silica-Supported Platinum Oxalate Complexes, $[SiO_2]L_2Pt(C_2O_4)$. Silica gel, grade 62 (60–200 mesh, 300 m^2/g, 140-Å pore size), was dried under vacuum at 300 °C for 3 days. Then 4.00 g of silica was transferred under N_2 to a 100-mL Schlenk flask equipped with a stir bar. After addition of 35 mL of freshly distilled benzene under N_2, the flask was wrapped with Al foil (to exclude light) and brought to reflux. Addition of $Pt(C_2O_4)L_2$ (1 mmol), dissolved in 40 mL of distilled benzene, via syringe pump at a rate of 2.6 mL/h was followed by a 5-h reflux. At this point 5.0 mL of HMDS (3.6 g, 23 mmol) was added by syringe. Reflux was continued for 4 h, and the suspension was cooled to room temperature. The white functionalized silica was collected by Schlenk filtration, washed 3 times with distilled benzene, dried in vacuo, and stored in the absence of light, under a nitrogen atmosphere: IR (Nujol) 1700, 1678 cm^{-1} (C=O). After irradiation (10 min) of the Nujol IR sample bubbles were evident in the mull, and the IR spectrum showed complete loss of the oxalate group and the appearance of an absorption at 2320 cm^{-1} for evolved CO_2.

$[SiO_2]L_2{}^*Pt(C_2O_4)$. The silica-supported oxalate complex was prepared as for the previous sample, except that freshly distilled THF was substituted for benzene. The product was collected by filtration under N_2, washed with THF (3 × 10 mL), and dried in vacuo: IR (Nujol) 1700, 1665 cm^{-1} (C=O). After irradiation of the Nujol sample, the IR spectrum showed complete loss of the oxalate group, and the CO_2 absorption at 2320 cm^{-1} appeared.

Preparation of the Supported Platinum Carbonyl Complexes. A suspension of $[SiO_2]L_2Pt(C_2O_4)$ (0.30 g, 5.0 × 10^{-4} mol of Pt/g) in 20 mL of distilled benzene was placed in a quartz Schlenk tube and sealed with a septum cap. The vessel was connected to a mineral oil bubbler, and a slow stream of CO was passed through the suspension while stirring and irradiating for several hours. The benzene was removed under a purge of CO leaving the silica slightly discolored to light yellow. The IR spectrum showed incomplete conversion to carbonyl complexes as discussed later.

Preparation of Standards for Hydrosilation. Dichloro(*n*-heptyl)methylsilane, $MeCl_2Si(C_7H_{15})$. To 1-heptene (2.0 mL, 14.2 mmol) and dichloromethylsilane (2.0 mL, 19.2 mmol) in a Schlenk flask under a nitrogen atmosphere was added 1 mL of a 10% ethanolic solution of H_2PtCl_6 by syringe. This mixture was heated to 50 °C with stirring for 2 h, at which point the IR spectrum showed complete loss of the olefinic group at 1630 cm^{-1}. After isolation by vacuum distillation (3 torr at 58–60 °C, lit. value 207.5 °C/750 torr) it was found to be free of reactants by gas chromatography and IR, ^1H, and ^{29}Si NMR spectroscopies: $^{29}Si\{^1H\}$ NMR (C_6D_6) δ 34.4.

Dichloromethyl(*n*-pentyl)silane, $MeCl_2Si(C_7H_{15})$. This complex was prepared following the previous procedure: $^{29}Si\{^1H\}$ NMR (C_6D_6) δ 32.5.

$[SiO_2]L_2Pt(C_2O_4)$ as Hydrosilation Catalyst for the Preparation of $MeCl_2Si$(*n*-heptyl). To $[SiO_2]L_2Pt(C_2O_4)$ (0.10 g, 8.4 × 10^{-5} mol of Pt/g) in a quartz Schlenk tube under N_2 was added $MeCl_2SiH$ (4.0 mL, 38.5 mmol), and the suspension was irradiated with stirring for 1 h. After addition of 1-heptene (5.0 mL, 35.5 mmol) a slightly exothermic reaction was observed initially. After 15 h the IR spectrum showed complete loss of olefin. The silica was removed by filtration under N_2, and the excess $MeCl_2SiH$ was removed under a N_2 purge leaving a single product, by GC analysis, as a clear solution: $^{29}Si\{^1H\}$ NMR (C_6D_6) δ 34.5. The GC retention time and ^{29}Si NMR spectra are the same as those of the authentic sample of $MeCl_2Si$(*n*-heptyl).

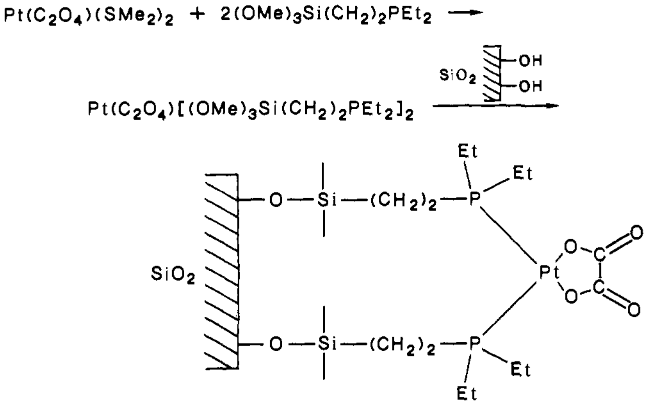
Rate Studies. Catalytic Rate of Formation of $MeCl_2Si$(*n*-heptyl) with *n*-Hexane as Solvent. To $[SiO_2]L_2Pt(C_2O_4)$ (0.10 g, 8.4 × 10^{-5} mol of Pt/g) in a quartz Schlenk flask under N_2, *n*-hexane (4.0 mL) and 1-heptene (1.3 mL, 9.2 mmol) were added via syringe. The suspension was irradiated for 3.5 h, removed from the UV light beam, and maintained at 30.0 °C in a constant-temperature bath. After the addition of 3.7 mL of *n*-hexane and 1.0 mL (9.6 mmol) of $MeCl_2SiH$, aliquots were removed periodically from the suspension by syringe and injected into the gas chromatograph for product analysis.

Catalytic Rate of Formation of $MeCl_2Si$(*n*-heptyl) with an Excess of Silane. The procedure followed that as above, except the silica was irradiated as a suspension in the silane (8.0 mL, 76.9 mmol), the suspension was maintained at 30.0 °C, and 0.5 mL (3.5 mmol) of 1-heptene was added via syringe. Aliquots were removed periodically for GC analysis.

Attempted Mercury Poisoning of the Hydrosilation of 1-Heptene and $MeCl_2SiH$. The catalyst was activated photochemically as a suspension in hexane and 1-heptene. After irradiation the mercury was added via syringe followed by the silane. Kinetics were determined by GC analysis of products and showed no significant differences because of the addition of mercury.

Phosphine Poisoning of the Hydrosilation of 1-Heptene and $MeCl_2SiH$. To $[SiO_2]L_2Pt(C_2O_4)$ (0.10 g, 8.4 × 10^{-5} mol of Pt/g), activated as described above in hexane/1-heptene, was added 0.003 mL (2 × 10^{-5} mol) of PEt_3 via syringe followed by 1.0 mL of $MeCl_2SiH$. The suspension was maintained at 30 °C, and aliquots were removed periodically. After 48 h no product was observable by GC analysis.

Scheme I



Thermal Activation of $[SiO_2]L_2Pt(C_2O_4)$. A sample of $[SiO_2]L_2Pt(C_2O_4)$ (0.10 g, 8.4 × 10^{-5} mol of Pt/g) was placed in a Schlenk tube under N_2 and heated to 200 °C for 5 h. After the silica cooled to room temperature, 7.7 mL of hexane, $MeCl_2SiH$ (1.0 mL, 9.6 mmol), and 1-heptene (1.3 mL, 9.2 mol) were added via syringe, and the suspension was brought to 30 °C in a constant-temperature bath. Aliquots of the solution were removed periodically, and product concentration was determined by GC analysis.

Kinetics of Hydrosilation Using the Soluble Catalyst, $Pt(C_2O_4)(PEt_3)_2$. A sample of $Pt(C_2O_4)(PEt_3)_2$ (0.058 g, 1.1 × 10^{-4} mol) was placed in a quartz Schlenk tube containing a stir bar, capped with a septum stopper, and purged with nitrogen. Acetonitrile (7.7 mL) and 1-heptene (1.3 mL, 9.2 mmol) were added by syringe. The solution was stirred and cooled with an air flow during irradiation for 40 min. The solution turned light yellow and was filtered through a fine frit under nitrogen. To the filtrate was added $MeCl_2SiH$ (1 mL, 9.6 mmol), and the reaction progress was monitored by GC analysis of products.

Results and Discussion

Characterization of the Supported Complex. A stable $Pt(C_2O_4)L_2$ species was covalently linked to a silica support using the functionalized triethylphosphine ligand L = $(OMe)_3Si(CH_2)_2PEt_2$. Two methods, commonly employed to attach metal complexes to silica, differ only in the reaction sequence. One procedure first attaches phosphine groups to the silica through the reaction of $(OMe)_3Si(CH_2)_2PR_2$ with surface hydroxyl groups.[3,4] The metal complex can be attached to phosphinated silica via ligand exchange reactions. We adopted the less common approach of preparing a functionalized metal complex for attachment to silica (Scheme I). This method allows precise control over the metal to ligand ratio in the complex, an advantage when complexes of different metal to ligand ratios can form. Prior coordination of the phosphine ligand to platinum(II) also predicts it against oxidation, a serious concern when phosphine ligands are attached to silica.[42,43]

To prepare a $Pt(C_2O_4)L_2$ complex capable of binding to silica, the labile SMe_2 ligand in $Pt(C_2O_4)(SMe_2)_2$ was replaced with the phosphinated silane L = $(OMe)_3SiCH_2CH_2PEt_2$ (Scheme I). Addition of L to insoluble $Pt(C_2O_4)(SMe_2)_2$ in benzene yielded only the disubstituted platinum phosphine complex as a soluble species. This provides a convenient synthesis of the desired intermediate in high purity since the volatile SMe_2 coproduct is easily removed from $Pt(C_2O_4)L_2$. A synthesis that minimizes impurities is important because the $Pt(C_2O_4)L_2$ complex is a hydrolytically sensitive oil that would be difficult to purify. The $Pt(C_2O_4)L_2$, used as a solution in benzene, shows a ^{31}P NMR spectrum consistent with formation of a *cis*-phosphine oxalate complex of better than 96% purity (i.e., no other phosphorus resonances were detectable). Comparison with the spectrum of the soluble analogue,

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(42) (a) Maciel, G. E. *Science* (*Washington, DC*) **1984**, *226*, 282–288. (b) Oldfield, E.; Kirkpatrick, R. J. *Ibid.* **1985**, *227*, 1537–1544.

(43) Bemi, L.; Clark, H. C.; Davies, J. A.; Fyfe, J. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 438–445.

Table I. Solution and Solid-State ^{13}C NMR Data

compd	^{13}C, δ^{a}
$Pt(C_2O_4)(PEt_3)_2{}^{b}$	166.7 (s), 13.7 (m), 6.9 (m)
L^{c}	50.4 (s), 18.9 (d, J = 14), 18.7 (d, J = 16.4), 9.7 (d, J = 12.9), 4.9 (d, J = 9.7)
$Pt(C_2O_4)L_2{}^{c}$	164.6 (s), 50 (s), 24.0 (m), 7.2 (s), 3.0 (s)
$[SiO_2]L_2Pt(C_2O_4)^{d}$	165.2 (s), 50.9 (s), 16.8 (s), 8.3 (s), 2.3 (s)
$[SiO_2]L_2Pt(C_2O_4)^{e}$	164.8 (s), 50.9 (s), 16.8 (s), 6.65 (s), 0.23 (s)

[a] ^{13}C NMR are in δ relative to Me_4Si, s = singlet, m = multiplet. Solid-state NMR spectra were measured with CP-MAS. J values are in hertz. [b] In acetonitrile solution with a C_6D_6 lock. [c] L = $(OMe)_3Si(CH_2)_2PEt_2$, in C_6D_6. [d] 5.4 × 10^{-4} mol of Pt/g. [e] 1.0 × 10^{-4} mol of Pt/g.

$Pt(C_2O_4)(PEt_3)_2$,[21] shows comparable Pt–P couplings of 3490 vs. 3522 Hz.

Addition of a solution containing $Pt(C_2O_4)L_2$ to dry silica in refluxing benzene gives the supported oxalate complex. Repeated washing with benzene removes unreacted $Pt(C_2O_4)L_2$. The IR spectrum of the functionalized silica, $[SiO_2]L_2Pt(C_2O_4)$, shows oxalate stretches at 1700 and 1678 cm^{-1} as expected for platinum bisphosphine oxalate complexes.[21] On irradiation the oxalate absorptions decrease in intensity. If unreacted OH groups on the silica are capped with hexamethyldisilazane, then generation of CO_2 was observed by IR spectroscopy; otherwise, no evolved CO_2 was seen. Basic sites on the surface may trap CO_2 as carbonate or bicarbonate. It has been noted that capping of excess surface hydroxyl groups minimizes the occurrence of side reactions during the use of supported catalysts in hydrogenation and hydroformylation reactions.[3-5] Bemi et al.[43] found that surface silanol groups are involved in the oxidation of tertiary phosphine and that capping of these groups greatly decreases oxide formation. Drago and Pribich[20] noted that a rhodium catalyst, supported on silica in which the free hydroxyl groups were alkylated by Me_3SiCl, showed less tendency to aggregate. Capping of these hydroxyl groups may prevent the complex from migrating along the surface. For these reasons, all the following studies used silica that was treated with HMDS after the platinum complex was attached. In control experiments we showed that no reaction occurs between HMDS and $Pt(C_2O_4)L_2$.

Elemental analysis of the functionalized silica showed the presence of Pt and P in ratios of 1:1.9 to 1:2.1, close to the expected 1:2 ratio. This implies that the bis(phosphine)platinum moiety remains intact during loading onto silica. A typical loading for the catalytic studies was about 8.4 × 10^{-5} mol of Pt/g, which corresponds to 1 Pt/620 Å^2. The heaviest loaded samples that could be prepared contained 5.4 × 10^{-4} mol of Pt/g, which correspond to 1 Pt/100 Å^2. Inorganic supports are known to have an upper loading limit of 1–2 mequiv of monofunctional groups per gram of matrix.[13d] To determine monolayer coverage we reacted the dried silica with excess HMDS to replace all surface hydroxyl groups by $OSi(CH_3)_3$. Elemental analysis (C, H) of this sample gave one active site (surface OH) per 34 Å^2. This is in good agreement with one surface hydroxyl group per 43 Å^2 as proposed by Drago and Pribich.[20] Our catalytic samples thus contain below a monolayer coverage. The heavier loaded samples approach a monolayer coverage, and, as is evident in the solid-state NMR experiments to be discussed, not all the OMe groups on the silylated phosphine have reacted with surface hydroxyl groups.

The supported complex has been examined by electron microscopy. In the scanning mode we see no observable differences between untreated and treated silica (at loadings of 8.4 × 10^{-5} and 5.4 × 10^{-4} mol of Pt/g) at 40 000 X. From this we conclude there is not gross puddling of substrate down to 200-Å resolution. However, the several hours of stirring required to attach the oxalate complex to the silica decreases the size of the silica particles to about 30% that of untreated silica, as seen in SEM photographs. A TEM study also showed no observable clumping of $[SiO_2]L_2Pt(C_2O_4)$ at 160 000 X or 20-Å resolution. A catalyst, activated thermally by heating to 200 °C, did show distinct particles at this magnification of about 20-Å size. The color change of this sample from white to grey and the kinetics of catalysis observed with this sample (vide infra) suggest decomposition of the supported complex to a Pt colloid on silica. Thus thermolysis of the supported oxalate may permit synthesis of highly dispersed platinum metal on silica.

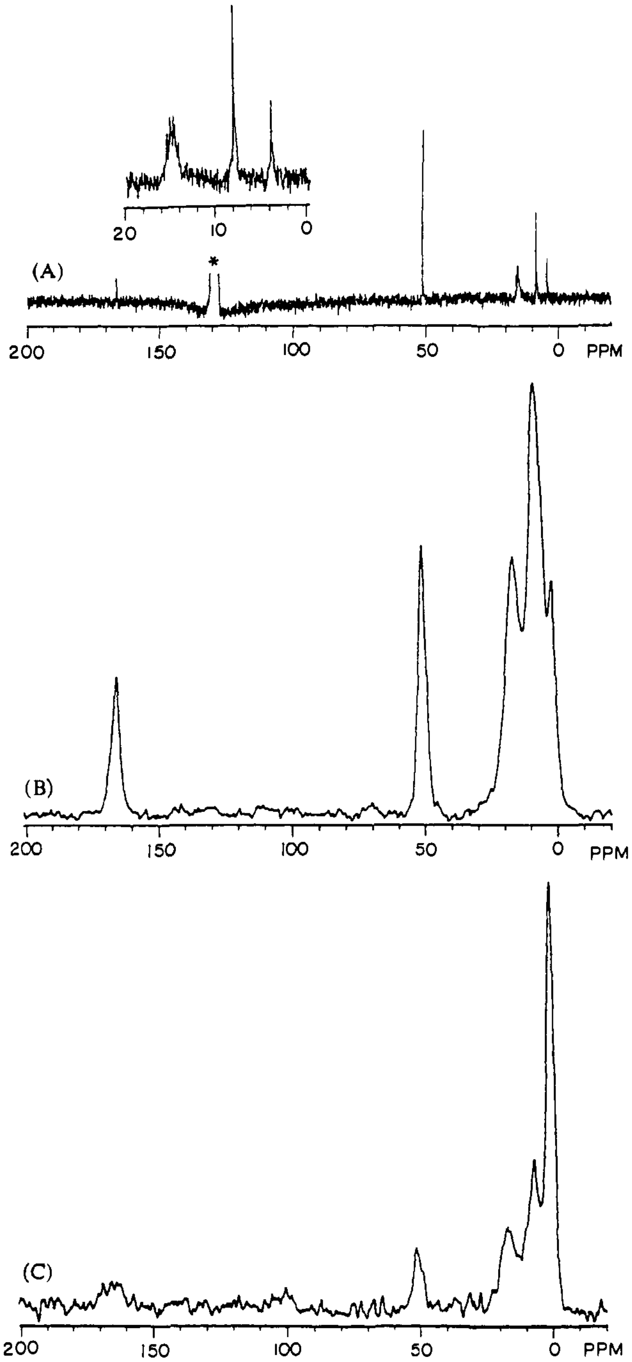

Figure 1. (A) Liquid-state ^{13}C NMR spectrum of $Pt(C_2O_4)[(OMe)_3Si(CH_2)_2PEt_2]_2$ in C_6D_6. The asterisk denotes the solvent C_6H_6/C_6D_6 resonance. (B) Solid-state CP-MAS ^{13}C NMR spectrum of the silica-supported $[SiO_2]L_2Pt(C_2O_4)$ at 5.4 × 10^{-4} mol of Pt/g. (C) Solid-state CP-MAS ^{13}C NMR spectrum of the silica-supported complex at 1.0 × 10^{-4} mol of Pt/g.

Solid-State NMR Studies. A powerful technique for study of soluble platinum phosphine complexes has been NMR spectroscopy. The recent development of high-power decoupling, cross-polarization (CP), and magic angle spinning (MAS) techniques permits NMR studies of dilute nuclei to be performed on solid samples.[7,42-45] We applied CP-MAS NMR to the molecular

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(44) (a) Fyfe, C. A.; Clark, H. C.; Davies, J. A.; Hayes, P. J.; Wasylishen, R. E. *J. Am Chem. Soc.* **1983**, *105*, 6577–6584. (b) Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Hayes, P. J.; Wasylishen, R. E. *Organometallics* **1983**, *2*, 177–180.

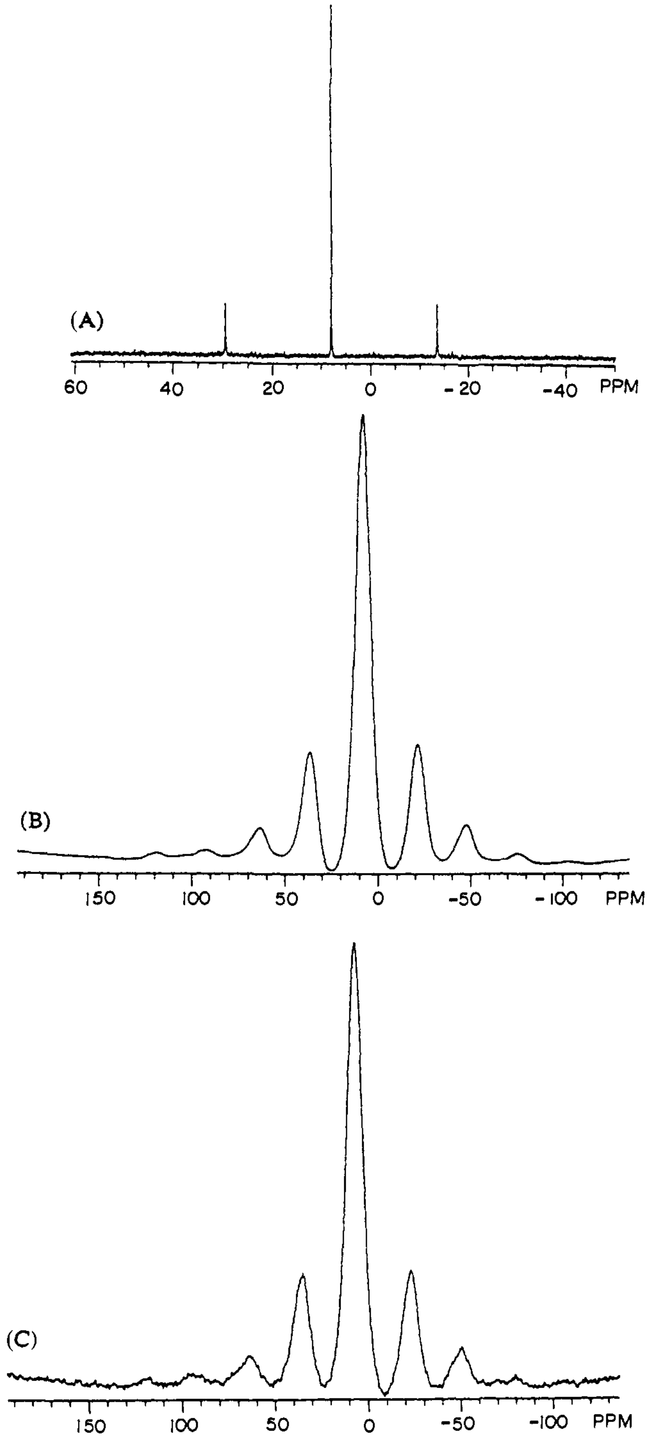

Figure 2. (A) Liquid-state ^{31}P NMR spectrum of $Pt(C_2O_4)[(OMe)_3Si(CH_2)_2PEt_2]_2$ in C_6D_6 solution. Note the ppm scale difference from the solid-state spectra below. (B) Solid-state CP-MAS ^{31}P NMR spectrum of the silica-supported complex $[SiO_2]L_2Pt(C_2O_4)$ at 5.4×10^{-4} mol of Pt/g. (C) Solid-state CP-MAS ^{31}P NMR spectrum of the silica-supported complex at 1.0×10^{-4} mol of Pt/g.

characterization of the surface-confined platinum bisphosphine oxalate complex. Tables I and II and Figures 1–3 contain a summary of the ^{13}C, ^{31}P, and ^{29}Si NMR data for both the surface-attached molecules and for their soluble analogues. Although the line widths in the solid state are appreciably larger than those obtained in solution, it has been shown in other studies[42-44] that the chemical shifts as well as coupling constants are comparable and may be used in structural assignments.

Table II. Solution and Solid-State ^{31}P and ^{29}Si NMR Spectral Data

compd	^{31}P, δ	J_{Pt-P}, Hz	^{29}Si, δ^a
$Pt(C_2O_4)(PEt_3)_2{}^b$	7.1	3522	
L^c	-12.9		-42.5
$Pt(C_2O_4)L_2{}^c$	7.1	3490	-43
$[SiO_2]L_2Pt(C_2O_4)^d$	7.2	3520 ± 20	-44, -52, -60, -67

[a] ^{31}P NMR chemical shifts are in δ relative to 85% H_3PO_4; ^{29}Si NMR chemical shifts are in δ relative to Me_4Si. Solid-state NMR spectra were measured with CP-MAS. [b] In acetonitrile with a C_6D_6 lock. [c] $L = (OMe)_3Si(CH_2)_2PEt_2$, in C_6D_6. [d] 5.4×10^{-4} mol of Pt/g.

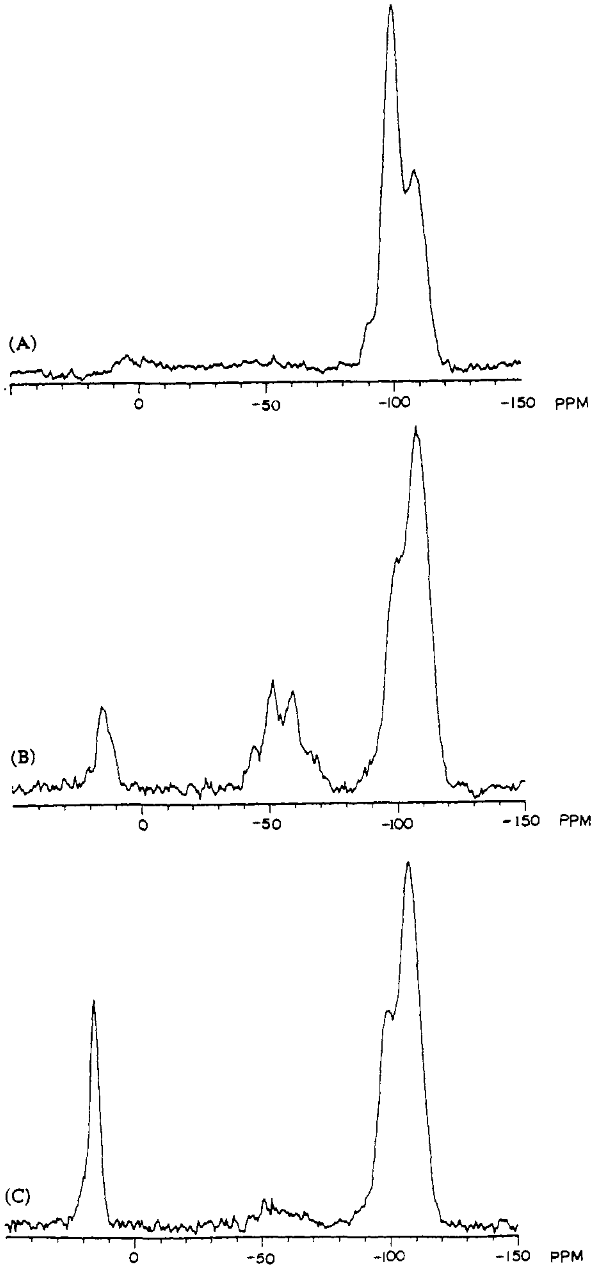

Figure 3. (A) Solid-state CP-MAS ^{29}Si NMR spectrum of bulk silica. (B) Solid-state CP-MAS ^{29}Si NMR spectrum of the silica-supported $[SiO_2]L_2Pt(C_2O_4)$ at 5.4×10^{-4} mol of Pt/g. (C) Solid-state CP-MAS ^{29}Si NMR spectrum of the silica-supported complex at 1.0×10^{-4} mol of Pt/g.

The information derived from the ^{13}C NMR spectra allows a comparison of both the surface-confined and solution oxalate complexes as well as a comparison of low and high loadings of the platinum oxalate on silica (Figure 1). The surface-confined species shows five different types of carbons. Comparison with other complexes and the free ligand allows for an unambiguous assignment of the resonances. The resonance of 165 ppm, at-

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(45) (a) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 3767–3776; (b) **1983**, *105*, 1848–1851; (c) **1983**, *105*, 1487–1493; (d) **1981**, *103*, 4263–4265; (e) **1980**, *102*, 7606–7607.

tributed to the oxalate carbons, confirms that the oxalate complex remains intact after attachment of the species to the support. The carbon of the OMe group appears at 51 ppm, and the carbons adjacent to phosphorus are at 16.8 ppm. For the heavier loaded sample the terminal carbon of the PEt_2 moiety appears at δ 8.3 along with the carbons adjacent to silicon at δ 2.3. For the lighter loaded sample both resonances shift slightly up field to δ 6.7 and 0.23, respectively. The observation of the OMe carbons shows that complete trans esterification of the Si–OMe bonds to surface hydroxyls does not occur during the synthetic procedure, and the relative intensity of the other carbon signals shows that a large fraction of the Si–OMe bonds are intact in the $[SiO_2]L_2(C_2O_4)Pt$ complex. A similar observation was made by Liu et al.[7], who used a similar procedure to attach ruthenium carbonyl species to silica. The line widths of the attached oxalate complex are too broad to observe long-range coupling to phosphorus. Apparently, the methylene groups attached to silicon as part of the ligand, L, and the Si–Me groups from the trimethylsilyl cap of surface Si–OH groups overlap at ~2.3 ppm because of their similar chemical shifts. For the heavily loaded sample all resonances from the organometallic complex are large and easily observable. In the lightly loaded sample the most intense peak (Figure 1) results from carbons of the $OSi(CH_3)_3$ capping groups on the surface.

The ^{31}P NMR spectra are also consistent with clean attachment of the $Pt(C_2O_4)L_2$ species according to Scheme I. Comparison with the solution NMR spectrum shows a remarkable similarity (see Figure 2), with a resonance at δ 7.1 for the solution species, 7.2 for the heavily loaded sample, and 5.7 for the lower loaded sample. The coupling in the solid state, $J_{Pt-P} \approx 3500 \pm 20$ Hz is consistent with *cis*-phosphines (e.g., 3490 Hz for $Pt(C_2O_4)L_2$ in solution). The solid-state NMR spectrum shows no detectable free phosphine ligands (~–20 ppm) and no phosphine oxide formation (~49 ppm) on the silica. From this we conclude that no appreciable decomposition occurs during the synthetic procedure as this invariably leads to formation of phosphine oxides. Loss of oxalate would also be expected to yield other platinum bis(phosphine) complexes containing the more stable trans structure.

The ^{29}Si solid-state NMR spectrum of the surface-attached oxalate species (Figure 3) could only be obtained for the heavier loaded sample. The ^{29}Si–^{1}H cross-polarization limits detection to those silicon atoms that are near protons; hence only atoms at or near the surface are seen. The spectrum may be assigned through comparison with literature studies and solution spectra. The region –90 through –110 ppm arises from silica (Figure 3A), and these resonances have been assigned previously by Sindorf and Maciel.[45] The most intense peak in this region of our spectra (Figure 3B and 3C), at –109 ppm, corresponds to $\mathit{Si}(OSi)_4$, a silicon with no hydroxyl groups attached. The only other peak seen is a shoulder at –100 ppm, attributable to $(HO)\mathit{Si}(OSi)_3$. No resonance is seen at –91 ppm, where $(HO)_2\mathit{Si}(OSi)_2$ is expected. In untreated bulk silica (Figure 3A) the –100 ppm resonance dominates the spectrum. These results show that few hydroxyl groups remain on the silica surface after functionalization and capping. The resonance at 14.8 ppm arises from $O\mathit{Si}(CH_3)_3$ groups used to cap unreacted hydroxyls on the silica surface. The functionalization of the surface with $Pt(C_2O_4)[PEt_2CH_2CH_2Si(OMe)_3]_2$ is seen in the region –40 to –60 ppm. The resonance at –44 ppm is assigned to unreacted $CH_2\mathit{Si}(OMe)_3$ by comparison with solution studies that show the soluble complex exhibits a single resonance at –43 ppm. The next two upfield resonances at –52 and –60 ppm are assigned as $CH_2\mathit{Si}(OMe)_2(O)$ and $CH_2\mathit{Si}(OMe)(O)_2$, for complexes with one and two bonds to a surface oxygen per phosphine ligand, respectively. A small shoulder at –67 ppm may correspond to the triply bound $CH_2Si(O)_3$ where all three methoxy groups per phosphine ligand have reacted with surface hydroxyls. It should be noted that the samples for NMR analysis are more heavily loaded with platinum complex than those used in the catalytic studies. With loading approaching a monolayer it is expected that not all the methoxy groups would react. Nonetheless, the small amount of $CH_2Si(OMe)_3$ groups observed, even at high loadings, is evidence that the platinum complex is covalently attached to silica and not adsorbed. The small $CH_2Si(OMe)_3$ peak can be attributed to complexes where only one of two L groups per platinum links to the surface.

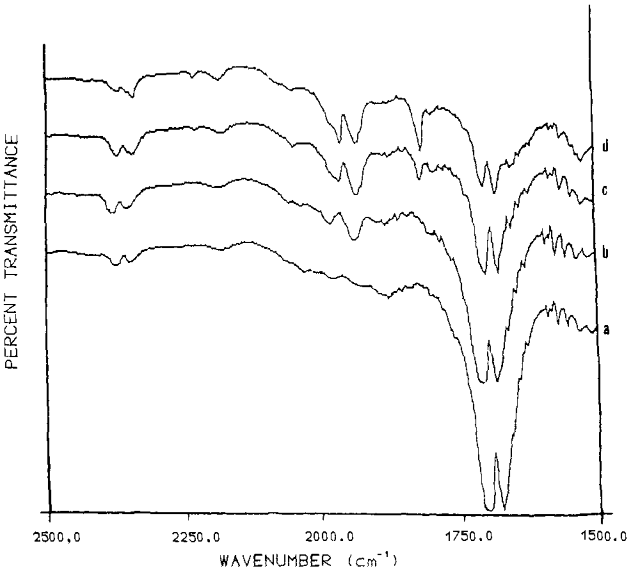

Figure 4. Changes in the FTIR spectra of the supported oxalate complex (5.0×10^{-4} mol of Pt/g) after UV irradiation of a suspension in C_6H_6 under a CO atmosphere. Periods of irradiation of (a) 2, (b) 4, (c) 6, and (d) 9.5 h show the time at which samples were withdrawn and pressed between CaF_2 plates for spectral analysis.

Both the ^{13}C and ^{29}Si solid-state NMR spectra of the heavily loaded samples suggest that about half of the Si–OMe groups have reacted with the silica or with Si–OH groups formed if any $Si(OMe)_3$ groups underwent hydrolysis. Therefore on average there are three Si–O–Si linkages between a platinum center and the surface. From the ^{29}Si NMR study it appears that for the silylphosphine ligands about 40% have two Si–O–Si linkages and another 40% have one Si–O–Si bond to the surface. About 15% of the ligands have not reacted, and the remaining 5% may have three Si–O–Si linkages to the surface. From this we conclude that most platinum centers, >75%, have both ligands covalently attached to the surface with one or two Si–O–Si linkages. The remaining platinum oxalate complexes are attached to the silica by only one ligand with one, two, or three bonds to the surface. An alternative that is difficult to distinguish would be hydrolysis and inter- and intramolecular linking of $Si(OMe)_3$ groups on the phosphine ligands. The SEM and TEM photographs did not show evidence for puddling from polymerization on the surface. Care was taken to exclude water during the synthesis to avoid undesirable hydrolysis side reactions. Although the electron micrographs did not show gross polymerization, it is possible that some could occur and remain undetected in these experiments.

Photochemistry of the Supported Complex. Irradiation of $Pt(C_2O_4)(PEt_3)_2$ in solution under a CO atmosphere yields $Pt(CO)_2(PEt_3)_2$. To see whether a similar reaction occurs on the surface, a benzene suspension (note C_6H_6 was found[21] to stabilize $Pt(PEt_3)_2$ in solution and minimize formation of side products) of $[SiO_2]L_2Pt(C_2O_4)$ was irradiated under a CO atmosphere. The IR spectra (Figure 4) show a dependence on the amount of irradiation (IR bands appear broader for derivatized silica in a Nujol mull as compared to molecular species in solution). At short irradiation times only absorptions at 1921 and 1963 cm^{-1} appeared for terminal carbonyls. These are about 10 cm^{-1} lower than those reported by Chini and Longoni for the soluble analogue $Pt(CO)_2(PEt_3)_2$: 1931 and 1973 cm^{-1}.[46] This contrasts with work of Wrighton et al.[7] with silica-supported ruthenium carbonyl complexes in which surface-confined systems had absorptions shifted about 10 cm^{-1} to higher energy than those in solution. At longer irradiation times an absorption (1810 cm^{-1}) in the bridging carbonyl region appeared before complete loss of oxalate. These

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(46) Chini, P.; Longoni, G. *J. Chem. Soc. A* **1970**, 1542–1546.

Table III. Hydrosilation Reactions (30 °C) Catalyzed[a] by $[SiO_2]L_2Pt(C_2O_4)$

silane	olefin	product	hours of reaction	yield,[a] %
$MeCl_2SiH$[b]	1-heptene	$MeCl_2Si$(*n*-heptyl)	5	95
$(EtO)_3SiH$[b]	1-heptene	$(OEt)_3Si$(*n*-heptyl)	24	50
Et_3SiH[b]	1-heptene	Et_3Si(*n*-heptyl)	24	15
Ph_3SiH[b]	1-heptene	nr[e]	48	0
$MeCl_2SiH$[c]	1-pentene	$MeCl_2Si$(*n*-pentyl)	48	>90
$MeCl_2SiH$[c]	*trans*-2-pentene	$MeCl_2Si$(*n*-pentyl)	48	>90
$MeCl_2SiH$[d]	1-heptene	$MeCl_2Si$(*n*-heptyl)	2	45

[a] The catalyst was generated by UV irradiation for 45 min in olefin/hexane. [b] [Silane] = 1.0 and [1-heptene] = 1.0 M, 0.1 g of $[SiO_2]L_2Pt(C_2O_4)$ (8.4×10^{-5} mol of Pt/g), in hexane. [c] [Silane] = 5.6 and [1-pentene] = 3.7 M, 0.1 g of $[SiO_2]L_2Pt(C_2O_4)$ (1.1×10^{-4} mol of Pt/g). [d] Catalyst is $[SiO_2]L^*_2Pt(C_2O_4)$, [silane] = 1.0 and [1-heptene] = 1.0 M, 0.1 g of $[SiO_2]L^*_2Pt(C_2O_4)$ (3.3×10^{-5} mol ofPt/g). [e] No reaction.

IR data suggest that platinum colloid is not forming during photolysis. While studies of carbon monoxide on transition-metal colloids often include a band in the 1810–1870-cm^{-1} region it is characteristically weak and broad and shifts to higher frequency as CO coverage increases.[47,48] Furthermore, the most intense absorption associated with CO adsorbed on platinum colloids appears[48] at 2045 cm^{-1}. Our IR spectra show no absorptions from bound CO above 2000 cm^{-1}.

The bridged carbonyl product was observed at a high complex loading, 5.0×10^{-4} mol of Pt/g and at a long irradiation time. High loadings are expected to allow some site–site interactions.[5,17-19] The above behavior can be explained by initial formation of isolated PtL_2 sites, which react with CO to give the terminal carbonyl product. Further irradiation results in loss of the oxalate ligand from nearby (formerly inert) platinum complexes, allowing for interaction between platinum centers and formation of a bridging carbonyl species. It is also possible that Pt–P bond breaking could occur on extended photolysis. The photochemical technique permits the generation of isolated Pt(0) sites at low photochemical conversions even when the surface is heavily loaded with platinum complexes.

Catalytic Hydrosilation Study. The $[SiO_2]L_2Pt(C_2O_4)$ species catalyzes hydrosilation of olefins (Table III) after UV irradiation. Hydrosilation products were identified by comparison of their ^{29}Si NMR chemical shifts and GC retention times to those of authentic samples prepared with Speier's catalyst. The supported catalyst can be generated by irradiation of the supported Pt oxalate complex as a suspension in either reactant. Addition of the second reactant, in the absence of UV light and at room temperature, yields a single hydrosilation product. Irradiation (about 30 min) in silane yields a more active catalyst than for samples irradiated in olefin solvent. In both reactions there was found to be incomplete loss of oxalate by IR analysis of the catalyst. The difference in rates with activating solvent may be attributed to the UV absorbing nature of the substrates, with the more transparent $MeCl_2SiH$ allowing more of the oxalate to be converted to catalyst.

The reaction can be conducted in noncoordinating solvents such as hexane or cyclohexane by irradiation of the supported oxalate complex in solvent that contains a small amount of one reactant. The second reactant was added after photolysis. Irradiation in hexane solvent that contained no reactants yields a catalyst with reduced activity after addition of the olefin and silane. Coordinating solvents such as benzene, THF, and acetonitrile completely inhibit catalysis as does admission of oxygen. The latter behavior offers an interesting contrast to Speier's catalyst and other conventional platinum hydrosilation catalysts that are oxygen promoted[33b] and often used in the presence of coordinating alcohol solvents. The oxygen sensitivity of the supported complex may arise from oxygen sensitivity of the alkylphosphine ligands at the active site. Addition of an excess of free phosphine, PEt_3, to a suspension of the activated heterogeneous catalyst also completely inhibits the hydrosilation reaction. This probably results from formation of a stable inactive tris- or tetrakisphosphine complex on the support.

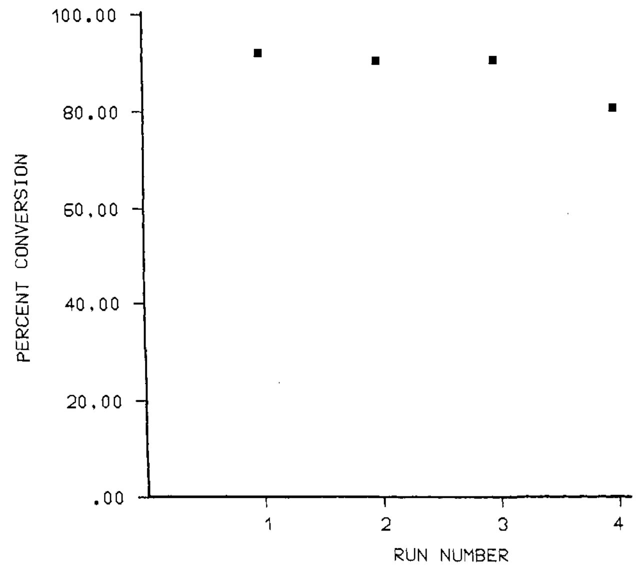

Figure 5. Variation in catalytic activity with repeated use for 0.10 g of silica at 8.4×10^{-5} mol of Pt/g. The substrate consisted of 77 mmol of $MeCl_2SiH$ and 3.9 mmol of 1-heptene for each run. The catalyst was generated in $MeCl_2SiH$ with 60 min of UV irradiation. Percent conversion is for 1-heptene to $MeCl_2Si$(*n*-heptyl) after 24 h of reaction.

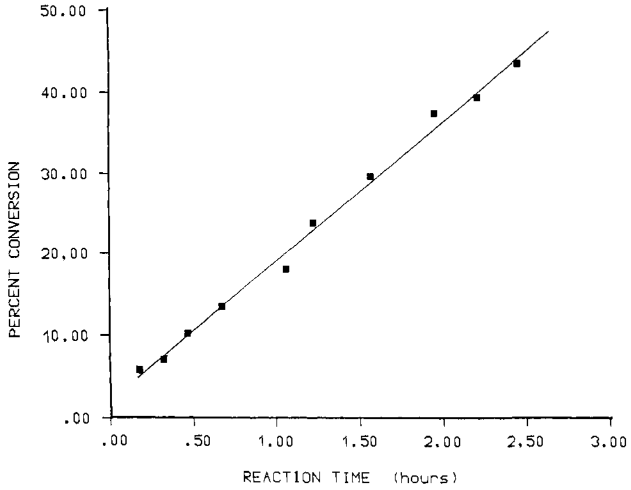

Figure 6. Percent conversion of 1-heptene to $MeCl_2Si$(*n*-heptyl) after 30 min of UV irradiation of 0.10 g silica with 8.4×10^{-5} mol of Pt/g, 77 mmol of $MeCl_2SiH$, and 3.9 mmol of 1-heptene at 30 °C.

The catalyst can be removed from the reaction mixture by filtration under N_2 or by removing the filtrate with a cannula and then washing the silica with either of the reactants. If the activated catalyst was removed from a hydrosilation mixture by filtration and washed with the same reactant, then neither the filtrate nor the combined filtrate and washings show catalytic activity. The recovered silica, even after washing with either reactant, showed little decrease in catalytic activity during the first four runs (Figure 5), ranging from 93% conversion in 24 h to 80% conversion for the fourth run. These observations suggest that the catalyst binds tightly to silica. The small decrease in activity with reuse may arise from the extreme oxygen sensitivity of the catalyst.

To test for the behavior of a metallic platinum catalyst, platinum colloid formation on silica was induced by heating the bound

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(47) Gasser, R. P. H. *An Inroduction to Chemisorption and Catalysis by Metals*; Claredon: Oxford, 1985.

(48) (a) Lin, K. C.; Witt, J. D.; Hammaker, R. M. *J. Chem. Phys.* **1971**, *55*, 1148–1151. (b) Blyholder, G.; Sheets, R. *J. Phys. Chem.* **1979**, *74*, 4335–4338. (c) Garland, C. W.; Lord, R. C.; Troiano, P. F. *Ibid.* **1965**, *69*, 1188–1192. (d) Hanmaker, R. M.; Francis, S. A.; Eischans, R. P. *Spectrochim. Acta.* **1965**, *21*, 1295–1308.

Table IV. Hydrosilation of 1- and 2-Pentenes and $MeCl_2SiH$ with Various Catalysts

catalyst	mol of olefin / mol of catalyst	hours of reaction	reaction temp, °C	yield, %	ref
olefin = 1-pentene					
none		17	100	0	28
OsO_4	600	17	100	0	28
$PdCl_2{\cdot}2H_2O$	400	17	100	0	28
3% Pd/C	1600	8	160	4	28
K_2PtCl_4	400	17	100	100	28
Pt-black	800	6	100	92	28
$H_2PtCl_6{\cdot}6H_2O$	10^6	0.5	200	93	28
0.06% Pt/C	10^5	1.25	100	84	28
$[SiO_2]L_2Pt(C_2O_4)$	1850	24	30	>90	*a*
olefin = 2-pentene					
$H_2PtCl_6{\cdot}6H_2O$	2×10^4	0.5	100	89	28
0.06% Pt/C	10^6	7	100	0	28
1% Pt/C	1000	20	100	56	28
K_2PtCl_4	1600	20	100	65	28
$[SiO_2]L_2Pt(C_2O_4)$	1850	24	30	>90	*a*

[a] This work.

Table V. Addition of Triethoxysilane to Olefins Catalyzed by Silica-Supported Transition-Metal Complexes

olefin	catalyst	mol of olefin / mol of catalyst	hours of reaction	temp, °C	yield, %	ref
1-hexene	Pt	100	2	80	96	55
1-hexene	Rh	100	2	80	61	55
1-hexene	Pd	100	2	80	41	55
1-hexene	Rh	2940	5	100	88	54
1-heptene	Rh	2940	5	100	86	54
1-octene	Rh	2940	5	100	89	54
1-heptene	$[SiO_2]L_2Pt(C_2O_4)$	160	24	30	50	*b*
1-hexene	Rh	*a*	2	80	92	35
trans-2-heptene	Rh	*a*	2	80	5	35

[a] Olefin:catalyst ratio not given. [b] This work.

oxalate complex to over 200 °C under nitrogen. At this point the silica showed an obvious color change from white to light grey, and colloidal (~20 Å) platinum could be observed on the surface by transmission electron microscopy. The rate of catalysis observed differs from those catalysts produced by ultraviolet irradiation. Activation by irradiation yields catalysts that show a linear formation of product with time and no induction period (Figure 6). The colloidal Pt-supported catalyst showed reactivity typical of conventional platinum hydrosilation catalysts in which there is a long induction period followed by a rapid reaction. Further evidence that the active platinum species produced on irradiation is not colloidal comes from results of a mercury poisoning study. Mercury(0) has been used as a selective poison for catalysis with bulk platinum metal, and it has been shown not to effect homogeneously catalyzed reactions.[49] As a test for platinum metal catalysis we added triply distilled mercury to a suspension of the supported catalyst after irradiation but before addition of the silane. The presence of mercury did not effect the rate of catalysis when the second substrate was added. However, when mercury was added to the platinum colloid on silica no hydrosilation product was observed after 72 h. This shows Hg does not act by occluding the pores of the support, and the catalytic activity of supported Pt metal differs from that of the photoactivated supported catalyst.

Kinetics for catalysis with the soluble analogue $Pt(C_2O_4)(PEt_3)_2$, after irradiation in acetonitrile solution containing 1-heptene and adding $MeCl_2SiH$, led to a long induction period followed by a rapid reaction (Figure 7). Thus surface attachment has a profound effect on catalytic behavior in this system. Since reactions between Pt(0) phosphine complexes and silanes can yield cluster products,[50] which may be catalytically inactive, isolation of these sites on the surface may result in the different reactivity observed for the supported complex.

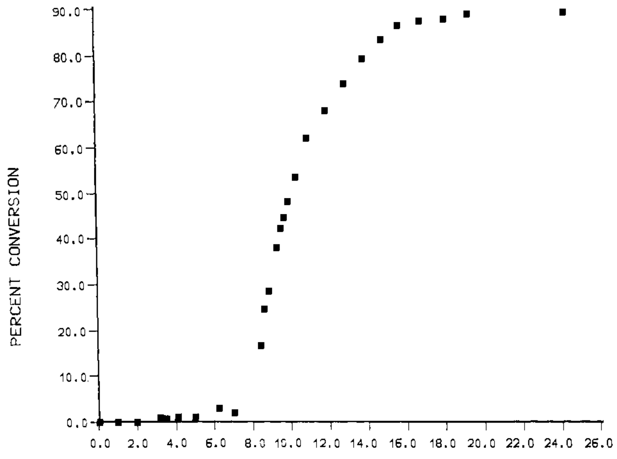

Figure 7. Plot for the rate of addition of $MeCl_2SiH$ to 1-heptene in acetonitrile solvent at 30 °C with the soluble complex $Pt(C_2O_4)(PEt_3)_2$ as catalyst after UV irradiation for 40 min for [Pt] = 0.011, $[MeCl_2SiH]$ = 0.96, and [1-heptene] = 0.92 M.

The rate of hydrosilation decreases in the order $MeCl_2SiH > (OEt)_3SiH > Et_3SiH$ for the supported photocatalyst. This parallels results found for many soluble and supported platinum metal catalysts.[51] Electronegative groups on silicon promote hydrosilation. With Speier's catalysts, $(OEt)_3SiH$ was found to add to linear olefins much slower than Cl_3SiH.[25] The efficacy of hydrosilation for the heterogenized catalyst compares favorably to many soluble platinum metal catalysts (Tables IV and V) even though it operates at lower temperatures. As with most hydro-

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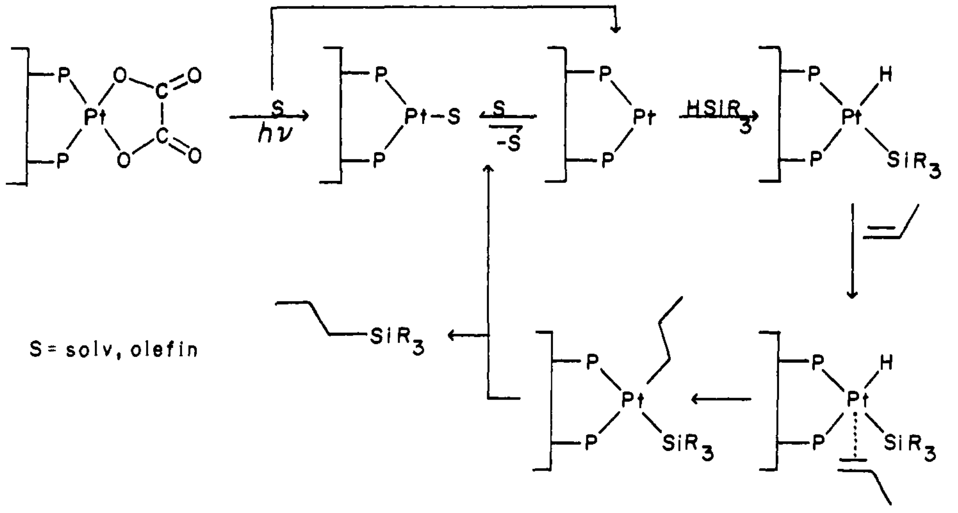
Scheme II



silation catalysts, the internal olefin 2-pentene gave only the isomerized terminal product, $MeCl_2Si$(*n*-pentyl). The conversion of 1- and 2-pentene was seen to be clean and efficient at moderate temperatures.

In contrast to results found for soluble platinum hydrosilation catalysts, our heterogenized species is completely inhibited by coordinating substrates, such as styrene, ether solvents, excess olefin, and diolefins like 1,7-octadiene. While prior treatment with silane is detrimental to most homogeneous platinum catalysts we found that our species worked best when generated in pure silane. There is no induction period seen with the heterogenized platinum catalyst, again in contrast to conventional hydrosilation catalysts. Finally oxygen, which is required to activate many homogeneous platinum hydrosilation catalysts, poisons the supported catalyst.

Results of Rate Study. Rates of catalytic hydrosilation were measured under pseudo-first-order conditions in excess silane with catalyst produced by irradiation of the supported complex in excess $MeCl_2SiH$. The suspension was removed from ultraviolet light, the 1-heptene added, and the reaction mixture maintained at 30 °C. Conversion of 1-heptene to $MeCl_2Si$(*n*-heptyl) was monitored by GC analysis. A plot of percent conversion vs. reaction time (Figure 6) shows that the rate is independent of olefin concentration at low olefin concentration. Repeating the experiment with a 10-fold excess of the olefin greatly inhibited the reaction. Allowing for the initial rate to be zero order in olefin at low olefin concentration, a study with both reduced $MeCl_2SiH$, 1.0 M, and low 1-heptene, 1.0 M, concentrations in *n*-hexane shows that disappearance of silane is first order (Figure 8).

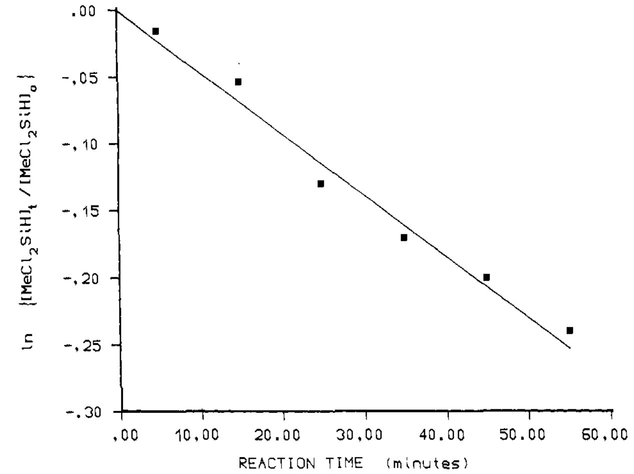


Figure 8. First-order plot of silane loss during the catalytic reaction between $MeCl_2SiH$ and 1-heptene after 210 min of irradiation, to activate the supported catalyst, 0.10 g of silica, with 8.4×10^{-5} mol of Pt/g; [1-heptene] = 1.0 and [$MeCl_2SiH$] = 1.9 M.

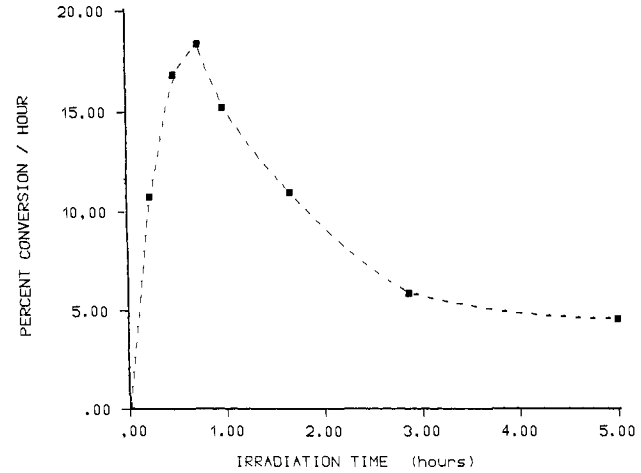


Figure 9. Dependence of supported catalyst activity on the time of irradiation for activation. The percent conversion after 1 h is plotted for various irradiation times containing 0.10 g of silica with 8.4×10^{-5} mol of Pt/g, 77 mmol of $MeCl_2SiH$, and 3.9 mmol of 1-heptene at 30 °C; [1-heptene] = 1.0 M.

Although each batch of catalyst gave internally consistent rates, they differed from batch to batch. This probably results from differences in platinum oxalate loadings that ranged from 2.0×10^{-5} to 5.4×10^{-4} mol of platinum/g of supported silica. The rates for 8.4×10^{-5} mol of platinum/g of silica were found most convenient for kinetic studies. Because of the variability in rates from batch to batch and in irradiation methods, the same sample and irradiation geometry were used in each comparative study. One cannot compare rates from different series. For reproducible results with the same catalyst batch, it must be stored under a dry inert atmosphere. This requirement results from the ready adsorption of water by the silica support. Water inhibits photochemical fragmentation of the oxalate ligand from platinum bisphosphine oxalate complexes[52] and reacts with PtL_2 species.[23]

Hydrosilation of 1-heptene by $MeCl_2SiH$ was also catalyzed by $[SiO_2]L_2{*}Pt(C_2O_4)$. Catalysis with this complex having a longer eight-carbon chain to silica support was found to be similar (Table III) to that of $[SiO_2]L_2Pt(C_2O_4)$ with its short chain. The reaction proceeded with no induction period. The catalyst could be activated by irradiation in excess silane, and the rate did not depend on olefin at low concentrations. Excess olefin again inhibits the reaction. Catalysis could also be conducted in noncoordinating solvents such as hexane. Thus, the possibility that the short-chain

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ligand, L, dictates a cis geometry important for catalysis does not seem necessary.

Rates of 1-heptene conversion also depend on irradiation times. When the catalyst was generated by photolysis in excess $MeCl_2SiH$ before addition of 1-heptene the rate of hydrosilation increased with irradiation time for up to 45 min. After this the rate decreased on increased irradiation and approached 5% conversion/h (Figure 9). This behavior parallels the study of CO binding discussed earlier. At 45 min of irradiation to generate the catalyst there was still unreacted oxalate on the silica surface as seen by FTIR spectroscopy. Assuming a monomeric active species there must be a maximum of isolated active sites after 45 min. Continued irradiation increases the chance of activating nearby platinum oxalates, which allows interaction between active sites and a decrease in catalytic activity. Secondary photolytic decomposition of catalyst may also occur. Catalytically inactive dimers have been shown to form from platinum bisphosphine species during certain catalytic reactions.[26,53] By IR spectroscopy most of the oxalate appears to have been photolyzed after 3 h of irrdiation, and little decrease in activity occurs with continued photolysis. This behavior prevents us from determining turnovers per active site since we are unable to determine the number of sites. The maximum net activity (after 45 min of irradiation) is 85 turnovers/h at 30 °C. Since about 25% of the oxalate has been photolyzed, this gives about 340 turnovers/h as the estimated turnover number per irradiated site. We also used the poison PEt_3 to titrate batches of active catalyst to see how many equivalents quenched the catalytic rate. If one assumes that each PEt_3 quenches one site, we obtain a rate of 80 turnovers/h. If more than one PEt_3 is bound per site or if inactive sites bind PEt_3, then this value should be increased proportionally. The similar magnitude of the two rough estimates for the activity per site suggests that an appreciable fraction of photogenerated PtL_2 yields catalytically active sites. A mechanism consistent with, though not fully substantiated by these experimental data, is shown in Scheme II. An important requirement suggested by the lack of activity in coordinating solvents and the inhibition with excess olefin is generation of a coordinatively unsaturated species before silane oxidatively adds. This differs from the mechanism proposed for conventional hydrosilation catalysts where olefin addition precedes silane oxidative addition.

Conclusions

These results show that platinum(II) oxalate can be supported on silica via a trialkylphosphine chain without ligand oxidation. The use of trialkylphosphine anchoring ligands with PEt_2 instead of PPh_2 groups gives a more stable complex, and no leaching of the platinum was observed under catalytic conditions. The catalyst precursor is thermally stable to 180 °C and can be stored for months in the absence of moisture yet can be activated at ambient temperatures by ultraviolet irradiation. Irradiation time controls the amount of catalyst formed on the surface. Short irradiation times provide site-isolated centers that are surrounded by inactive complexes.

Rate studies using this catalyst for the hydrosilation of olefins show kinetics different from that expected from either colloidal platinum or for a soluble platinum species. The rate law appears to be independent of olefin at low olefin concentration and first order in silane. An excess of olefin or any coordinating substrate or solvent inhibits the reaction. This suggests the "olefin path"[56] seen in some hydrosilation catalyst systems is not important here. Because the catalytic rate maximizes and then decreases with increasing irradiation time, this may imply that isolated platinum centers are formed at shorter irradiation intervals or that secondary photolysis occurs. The induction period observed with conventional hydrosilation catalysts may lead to a violent exothermic catalytic reaction because the reactions are usually conducted without solvent and at higher initiation (80–150 °C) temperatures. Thus the uniform kinetics exhibited by the supported catalyst at 30 °C offers an advantage beyond that of catalyst separation for the heterogenized catalyst.

Acknowledgment. This research was supported by the U.S. Army Research Office under Contract DAAG29-85-K-0263. We thank Johnson Matthey, Inc., for a loan of K_2PtCl_4 under their University Metal Loan Program. Solid-state NMR spectra were performed by the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. CHE-8208821. We thank Prof. G. E. Maciel and Drs. James S. Frye and Chuck Bronnimann at CSU for helpful discussions.

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