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Metal Colloid Morphology and Catalytic Activity: Further Proof of the Intermediacy of Colloids in the Platinum-Catalyzed Hydrosilylation Reaction

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Transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM) were used to analyze the platinum colloids formed during hydrosilylation reactions. Reaction solutions were analyzed for the addition of Et_3SiH to either *n*-hexene or neohexene catalyzed by bis{1,3-divinyl,1,1,3,3-tetramethyldisiloxane}Pt^0 (Karstedt's catalyst) and this analysis showed dramatic differences between the morphology of the Pt colloid formed in each case. The neohexene reaction, which gave 62% conversion to products in 1 h, contained polycrystalline, 2.5-nm-diameter Pt particles, whereas the *n*-hexene reaction only went to 10% conversion in 1 h and contained 1- to 1.5-nm Pt particles. The reaction of Et_3SiH with styrene gave results similar to those with neohexene.

INTRODUCTION

We recently described the synthesis and structure of platinum group metal colloids prepared from the direct reaction of metal halides and R_3SiH compounds (*1*). This work in turn was inspired by our previous work which suggested that colloidal platinum was a key intermediate in platinum-catalyzed hydrosilylation (*2*):

$$R_3SiH + CH_2{=}CHR' \xrightarrow[\text{catalyst}]{} R_3SiCH_2CH_2R'. \quad (1)$$

Because the hydrosilylation reaction is catalyzed by colloids, the morphology of the colloid then has an effect on the selectivity and rate of the reaction.

This report describes our observations which further support the intermediacy of colloids in the hydrosilylation reaction. It has been well established that curious and unexplained color changes occur during hydrosilylation (*3*). We confirm here that these color changes are directly related to the changes that occur in the colloid structure and that these structure changes affect catalyst activity.

METHODS

General

Reactions were carried out in air. Relative rate experiments were carried out in virgin glass vials. Reagents were measured using syringes and needles; each reagent had its own syringe and needle. This was especially important in the addition of catalysts, because we found that contaminated syringes or needles can affect catalysis. ^{13}C and ^{29}Si NMR spectra were recorded on a Varian XL 300 NMR spectrometer at 75.43 and 59.3 MHz, respectively. Gas chromatography was performed using a HP Model 5890 gas chromatograph employing a 6-ft, 3% OV 101 column, and a thermal conductivity detector. The TEM analyses were performed on a Hitachi H-600-1 operated at 100 kV and equipped with an EEG Ortec Si(Li) energy-dispersive X-ray detector. Elemental analyses for elements having atomic numbers greater than that of Na were obtained from

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X-rays generated using a focused electron probe approximately 10 nm in diameter. The HREM was performed on a Philips EM 430 instrument operated at 300 kV.

Et_3SiH Reactions

The olefins were purified by distillation after passing down an Al_2O_3, activity I column. A standard peroxide test strip test (1 ppm sensitivity) gave negative readings for the purified olefins. In a typical run (Eq. (2); see Results and Discussion), neohexene (1.38 ml, 10.8 mmol) was combined with a xylene solution of the Karstedt catalyst (2.7 μl, 0.7 μmol) and decane (internal standard, 0.2 ml, 1.03 mmol). Addition of Et_3SiH (1.72 ml, 10.8 mmol) at room temperature initiated the reaction; a yellow color formed after 1 h. The reaction with *n*-hexene (Eq. (3)) in place of neohexene was also carried out. These reactions were monitored by GC and analyzed by ^{13}C and ^{29}Si NMR analysis. After 1 h, the neohexene had gone to 62% conversion whereas the *n*-hexene was only 10% complete.

NMR Data for the Product of Eq. (2)

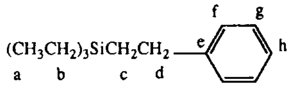
$(CH_3CH_2)_3)SiCH_2CH_2C(CH_3)_3$ (Eq. (2))
a b c df e

^{13}C: 37.76 **(d)**, 31.04 **(f)**, 28.73 **(e)**, 7.38 **(b)**, 5.02 **(c)** and 3.18 **(a)**; ^{29}Si: 7.58, single isomer.

Reaction with Styrene, Eq. (4)

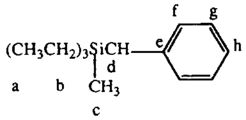
Styrene was substituted for neohexene as in Eq. (2).

Equation (4), β-isomer.



^{13}C: 145.47 **(e)**, 128.61 **(g)**, 127.58 **(f)**, 125.35 **(h)**, 29.96 **(d)**, 7.33 **(a)**, 3.43 **(c)**, 3.17 **(b)**, ^{29}Si: 6.93.

Equation (4), α isomer.



^{13}C: 144.8 **(e)**, 127.73 **(g)**, 126.2 **(f)**, 125.7 **(h)**, 6.7 **(c)**, 14.0 **(d)**, 7.3 **(a)**, 3.2 **(b)**; ^{29}Si: 7.4.

*Effect of Hg on Na_2PtCl_6/*IPA Catalyst

One milliliter of a 1 : 1 Et_3SiH : vinyl$SiMe_3$ (Eq. (5)), 10% decane internal standard stock solution was used to compare the activity of the metal solutions. Na_2PtCl_6 (0.14 g, 0.25 mmol) was dissolved in 25 ml *i*-PrOH. Reactions were initiated by addition of 10 μl (0.1 μmol) of the Pt catalyst solution. Additionally, the reaction was run where 1 drop of Hg was present. The reactions were all run at ambient temperature. All these reactions were rerun at 80°C by submersion of the reaction vials into a heated oil bath.

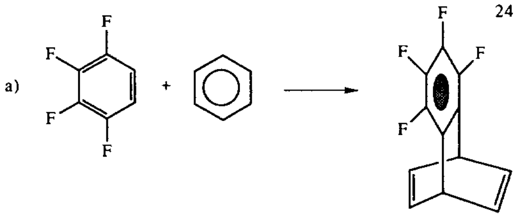
Product of Eq. (5)

$(CH_3CH_2)_3SiCH_2CH_2Si(CH_3)_3$
a b c d e

^1H ($CDCl_3$) 0.95 (t, 9Hz, **a**), 0.55 (m, **b**), 0.42 (m, **c** + **d**), 0.02 (s, **e**); ^{13}C ($CDCl_3$) 9.08 (**c**), 7.88 (**b**), 3.34 (**a** + **d**), −1.91 (**e**).

Synthesis of DBCOT

A three-step procedure was followed. *n*-BuLi (2.35 *M* in hexane, 35 ml) was added dropwise overnight to a stirred benzene solution (100 ml) of pentafluorobenzene (10.36 g, 61.7 mmol) at 0°C under N_2. The solvents were removed *in vacuo* to give a yellow oil and colorless crystals. The crystals were separated by sublimation (mp 65–8°C), 1.0 g, 7% yield. ^1H NMR ($CDCl_3$): δ6.92 (t, J_{HH} = 5 Hz, olefin), δ5.30 (q, J_{HH}, J_{HF} = 5-Hz bridgehead).



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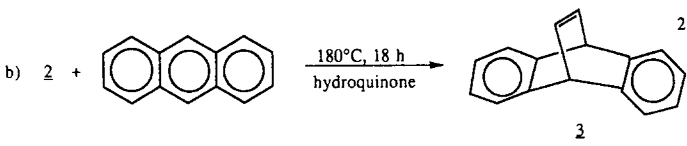

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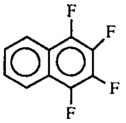
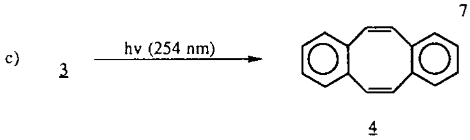
Compound **2** (0.275 g, 1.22 mmol), anthracene (0.211 g, 1.19 mmol), and hydroquinone (0.011 g, 0.097 mmol) were placed in a 1-ml ampoule, which was then sealed under N_2 and placed in a 180°C oven for 12 h. Sublimation of the solids at 50°C, 0.3 mm resulted in isolation of



(^{1}H NMR δ8.37 (hydroquinone), δ8.00 (4 line m, 3 Hz), δ7.41 (4 line m, 3 Hz)). The unsublimed material (0.22 g) had ^{1}H NMR consistent with **3**: δ7.07 (m), δ4.07 (s), δ2.20 (s).



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Compound **3** (0.22 g) was dissolved in THF (30 ml) and placed in a quartz tube and then the solution was irradiated with a medium pressure mercury lamp (Hanovia) for 24 h. After irradiation, the solution was reduced in volume under vacuum and then subjected to column chromatography (20 × 2 cm silica gel–hexane). The product **4** was obtained by elution with 20% CH_2Cl_2/80% hexane, yield—65 mg (mp 195–200°C). ^{1}H NMR (CD_2Cl_2) δ7.13 (m), 5.03 (m).

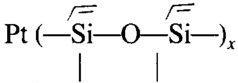
Effect of DBCOT on Pt-Catalyzed Hydrosilylation

A stock solution of DBCOT (0.017 g, 0.083 mmol) in xylene (5 ml) was prepared. A control reaction was run in which Me_3Si (0.2 ml, 1.38 mmol), Karstedt catalyst (1 μl of a 5% Pt solution), decane (0.05 ml), and xylene (30 μl) were combined, and then $(Me_3SiO)_2Si(H)CH_3$ (0.4 ml, 1.46 mmol) was added. An exothermic reaction occurred; GC analysis showed >90% conversion in 10 min. The effect of DBCOT was measured by combining Me_3Si (0.2 ml, 1.38 mmol), Karstedt catalyst (1 μl of a 5% Pt solution, 0.26 μmol), decane (0.05 ml), and the DBCOT stock solution (30 μl, 0.5 μmol). Addition of $(Me_3SiO)_2Si(H)CH_3$ (0.4 ml, 1.46 mmol) resulted in an exothermic reaction; GC analysis showed >90% conversion in 10 min.

In a second set of experiments, a control catalyst was prepared by combining Karstedt catalyst (10 μl) with xylene (300 μl). A second catalyst solution was prepared by combining Karstedt catalyst (10 μl, 2.6 μmol) with the DBCOT stock solution (300 μl, 5 μmol). The relative activities of these two catalyst solutions were compared using the reaction of $(Me_3SiO)_2Si(H)CH_3$ with Me^3Si (test reaction of Eq. (6). GC analysis showed there was no inhibition from DBCOT.

RESULTS AND DISCUSSION

The catalytic activity and structure of the Karstedt's platinum catalyst (*4*) has been described by us (*2*) and others (*5*).



$$\mathrm{Pt}\,(\text{—}\mathrm{Si}\text{—}\mathrm{O}\text{—}\mathrm{Si}\text{—})_x$$

Karstedt Pt catalyst

We showed that the key step in reactions catalyzed by this complex was the formation of colloidal platinum; thus Karstedt's catalyst is an excellent source of stable colloid precursor. A general description of a hydrosilylation reaction catalyzed by Karstedt's catalyst involved addition of an SiH-containing compound to a mixture of olefin and catalyst. After an induction period, the reaction proceeded with formation of a yellow to brown color. Onset to formation of the yellow color closely matched the onset to formation of the colloid and the point at which most of the reaction occurred (*2*).

In the present work, we observed that reactions between Et_3SiH and a number of olefins, all catalyzed by Karstedt's catalyst, went at different rates and produced different color reaction mixtures. For example, the addition of Et_3SiH to a mixture of either *n*-hexene and Karstedt's catalyst or 3,3′-dimethyl-1-butene (neohexene) and Karstedt's catalyst gave different results. The progress of the reactions, if any, was monitored by gas chromatography and the mixtures were then analyzed by ^{13}C and ^{29}Si NMR spectroscopy. It was found that for neohexene the expected addition product, **1**, formed,

$$CH_2{=}CHC(CH_3)_3 + Et_3SiH \xrightarrow[\text{Karstedt}]{1\,h} \qquad (2)$$

$$Et_3SiCH_2CH_2C(CH_3)_3$$

1

62%,

but that slower conversion to the *n*-hexene addition product, **2**, occurred:

$$CH_2{=}CH(CH_2)_3CH_3 + Et_3SiH \xrightarrow[\text{Karstedt}]{1\,h} \qquad (3)$$

$$Et_3Si(CH_2)_5CH_3$$

2

10%.

Both reactions were run at ambient temperature.

Examination of the reaction solutions from Eqs. (2) and (3) by transmission electron microscopy (TEM) showed that the morphologies of the platinum colloids in the solutions were quite different. As shown in Fig. 1, the yellow solution from Eq. (2) had clusters of particles whose individual diameter was about 2.5 nm. A dark field image was generated using a portion of the diffraction ring. Some of the particles "light up" in this mode, consistent with polycrystalline regions. X-ray spectra of the regions, in which there were heavy particle concentrations, showed the presence of Pt and Si, whereas areas devoid of particles showed mostly Si with little or no Pt present; note that Si was always present when we found Pt.

The solution from Eq. (3) was examined by TEM (Fig. 2). As shown in this figure, large clumps composed of ca. 1-nm particles were present. These clumps were analyzed by X-ray spectroscopy and this analysis showed the presence of Pt and Si. The presence of crystalline regions in the colloid formed in Eq. (3) was confirmed by a dark field TEM image of this material.

Further analysis of the solutions from Eqs. (2) and (3) was made by high-resolution electron microscopy (HREM). As shown in the inset to Fig. 1, the colloid formed from Eq. (2) contained 2.2- to 2.8-nm particles observed at much lower magnification which were indeed crystalline. The particles exhibited fringes which corresponded to the spacing of the (111) planes in platinum (*1*). The electron diffraction pattern obtained from this sample indexed to crystalline platinum. The HREM analysis of the solution from Eq. (3) gave a similar result. As shown in the inset to Fig. 2, there were 1.5- to 2.0-nm particles present which were also crystalline and which displayed the fringes of the (111) planes. The key difference between the colloids formed from these two reactions was the degree of agglomeration; large agglomerated clumps containing smaller size particles from Eq. (3) vs the Pt with a lesser degree of agglomeration but composed of larger individual particles from Eq. (2).

Formation of crystalline Pt was not limited to this one neohexene example. Addition of Et_3SiH to a mixture of styrene and Karstedt's catalyst caused immediate yellow color formation. Analysis of the products from the styrene reaction by ^{13}C (proton decoupled and off-resonance decoupled) and ^{29}Si NMR showed that complete conversion to the two likely products from the reaction

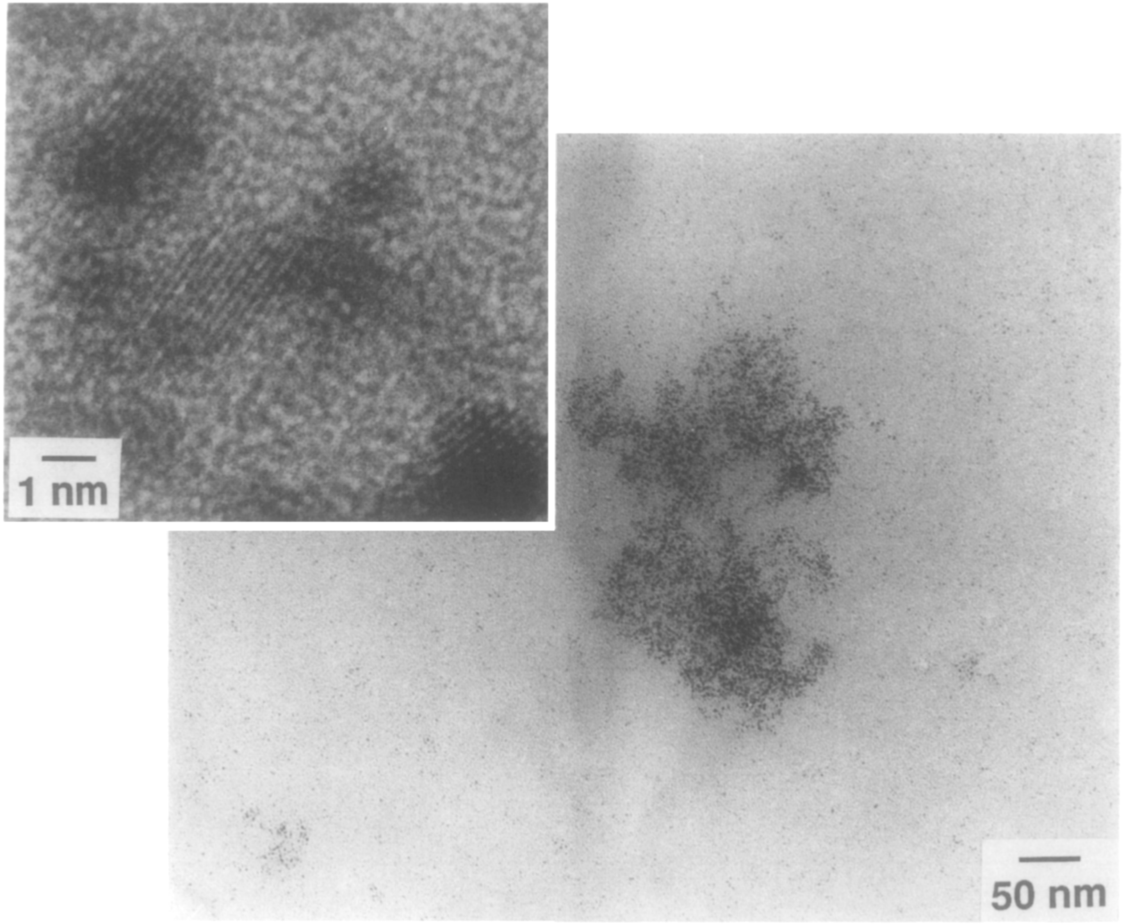


FIG. 1. TEM image of the reaction solution from Eq. (2), Et_3SiH + neohexene catalyzed by Karstedt Pt catalyst. Insert shows HREM image. Note the fringes which correspond to the (111) planes in crystalline Pt.

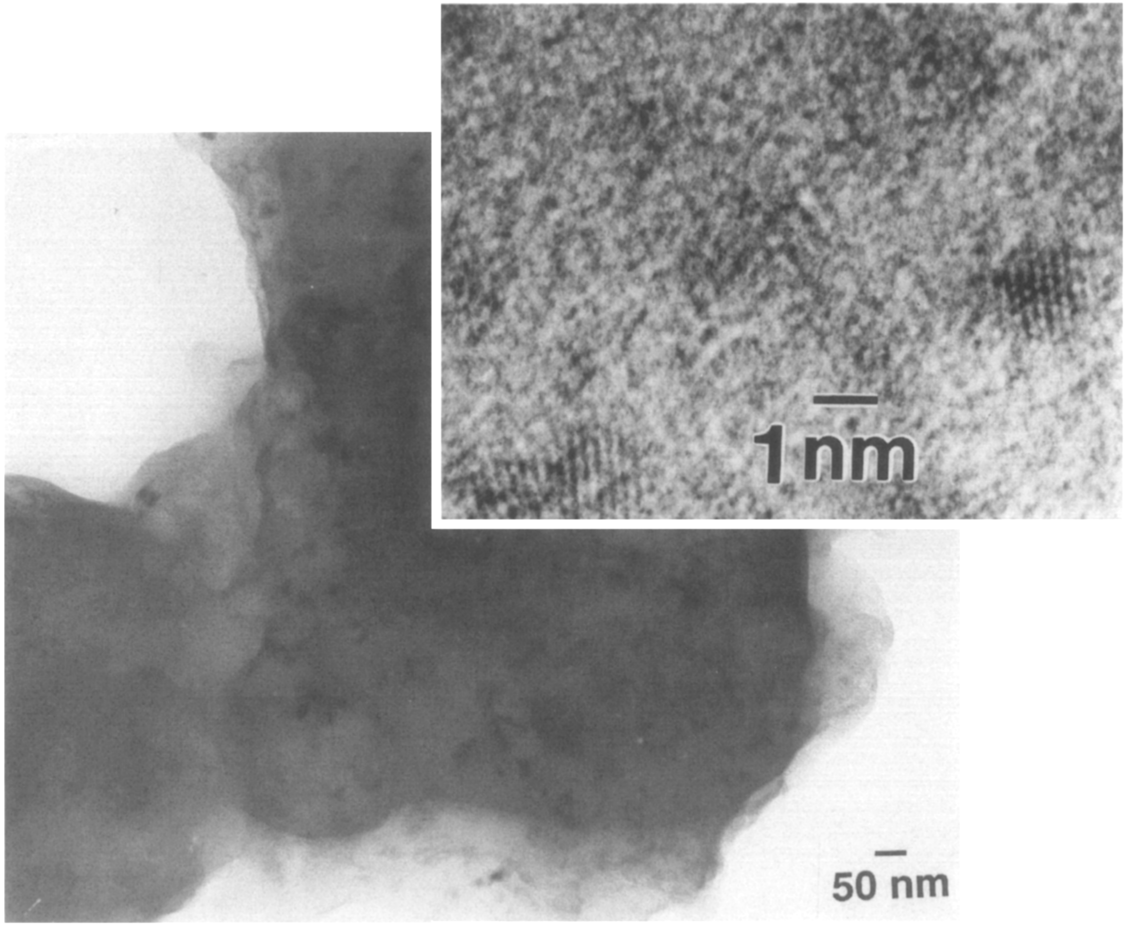


FIG. 2. TEM image of the reaction solution from Eq. (3), Et_3SiH + *n*-hexene catalyzed by Karstedt Pt catalyst. Inset shows HREM image.

$$CH_2{=}CHPh + Et_3SiH \xrightarrow[\text{Karstedt}]{} \underset{\substack{86\% \\ \mathbf{3a}}}{Et_3SiCH_2CH_2Ph} + \underset{\substack{14\% \\ \mathbf{3b}}}{Et_3SiCH(CH_3)Ph} \quad (4)$$

occurred (β product (86%), **3a,** and the α product (14%), **3b**) after 17 h. Analysis of the reaction solution from Eq. (4) by TEM showed that colloids similar to those of Fig. 1 were present in the solution from Eq. (2).

A referee suggested that the differences in reactivity between the *n*-hexene and neohexene were caused by the presence of peroxide normally found in *n*-alkenes. The reactions of Eqs. (2) and (3) were rerun in the presence of ca. 100 ppm *t*-butyl hydroperoxide. There was no effect on rate of reaction due to the peroxide.

Colloids are key intermediates in the metal-catalyzed hydrosilylation reaction. It is common to assume "homogeneous catalysis" either when molecular metal complexes are observed spectroscopically or when bulk metal precipitation causes reduction of catalytic activity (*6, 7*). These observations still do not rule out catalysis via colloids. The earliest catalysts for the hydrosilylation reaction were simple metal halide salts in alcohols (*8*), which we have since shown to contain colloids (*2*). We further confirmed the intermediacy of a heterogeneous component by carrying out the Hg test (*9, 10*). The Hg test has been described as a test for the presence of colloidal catalysts; Hg selectively alloys with the heterogeneous, bulk metal-like materials but is unreactive toward truly homogeneous catalysts. The reaction

$$H_2C{=}CHSi(Me)_3 + Et_3SiH \xrightarrow[\text{catalyst}]{} Et_3SiCH_2CH_2SiMe_3 \quad (5)$$

was employed to test the catalytic activity of Pt chloride/*i*-PrOH mixtures with and without Hg. The Pt catalytic solution was composed of a 0.01 *M* solution of Na_2PtCl_6 in *i*-PrOH. As shown in the table below, the Pt/*i*-PrOH catalyst lost most of its activity in the presence of Hg. These results were consistent with heterogeneous catalysts in these latter reactions.

	% Conversion in Eq. (5)	
	3.5 h 80°C	22 h 25°C
Pt/*i*-PrOH	100	40
Pt/*i*-PrOH + Hg	11	5

Further confirmation of the heterogeneous nature of the hydrosilylation came from measuring the effect of a poison selective for homogeneous catalysts. Anton and Crabtree (*10b*) describe the use of dibenzo[*a, e*]cyclooctatetraene (DBCOT) as a test for heterogeneity in catalysis from soluble plantinum group metal complexes. DBCOT, due to its three-dimensional structure, is likely to strongly chelate to low-valent molecular complexes of the platinum group, but should have negligible binding to a metal surface. Thus, the DBCOT test compliments the use of Hg because it will poison homogeneous reactions but not heterogeneous reactions of which colloids are but one class.

The hydrosilylation reaction

$$(Me_3SiO)_2Si(H)Me + H_2C{=}CHSi(Me)_3 \xrightarrow{\text{Karstedt}} (Me_3SiO)_2Si(Me)(CH_2CH_2SiMe_3) \quad (6)$$

was used as a probe for whether the selective homogeneous poison DBCOT had any effect on the reaction. In one experiment a xylene solution of DBCOT was combined with $H_2C{=}CHSi(Me)_3$ and Karstedt catalyst, and the reaction was initiated with addition of $(Me_3SiO)_2Si(H)Me$. An exothermic reaction was noted and GC analysis confirmed that >90% conversion to product occurred with or without DBCOT present. In a second experiment the activity of a stock xylene catalyst solution which contained both Karstedt catalyst and DBCOT was compared to the activity of a xylene solution of Karstedt catalyst without DBCOT in the reaction of Eq. (6). No inhibition by DBCOT was noted. These results and those with Hg further confirm the existence of catalysis by a heterogeneous platinum species.

SUMMARY AND CONCLUSIONS

We have provided additional evidence for our original proposal that metal colloids play a key role in metal-catalyzed hydrosilylation. Strong evidence which linked the color to the presence of the colloid and the size/morphology of the colloid was presented. More critical was the observation that these size and morphology differences reflected catalytic activity. Further, small differences in one of the reagents, *n*-hexene vs neohexene, led to the dramatic differences in the structure of the colloid products.

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