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Organometallics, **1990**, 9 (3), 621-625• DOI: 10.1021/om00117a015 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Hydrosilylation Catalyzed by Metal Colloids: A Relative Activity Study

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Received June 12, 1989

The relative activities of the platinum group metal colloids were measured for the hydrosilylation reaction between (vinyl)$SiMe_3$ (VTMS) and $(hexyl)_3SiH$ or $(EtO)_3SiH$. The relative activities of the colloids were the same as those reported in the literature for molecular complexes Pt > Rh > Ru = Ir ≫ Os. The synthesis of Me(decyl)Si$(octyl)_2$ (silahydrocarbon) is discussed, and the relative activities of Pt and Rh for this reaction were compared. Rh was more active than Pt in the synthesis of silahydrocarbon from 1-octene and Me(decyl)SiH_2. It was also found that aeration was critical for these reactions, consistent with the fact that hydrosilylation is cocatalyzed by O_2. It was discovered in the silahydrocarbon synthesis that dihydride inhibited Pt-catalyzed hydrosilylation but had no effect on Rh. This effect was further demonstrated with model reactions that showed that, in contradiction to the literature, the relative rate of addition to olefins for $R_{3-x}SiH_x$ addition catalyzed by Pt is $R_3SiH > R_2SiH_2$. For Rh the relative rates were $R_2SiH_2 > R_3SiH$; these relative rates were thus opposite those for Pt. The addition of $RSiH_3$ to olefins was also investigated. We conclude that R_2SiH_2 and $RSiH_3$ poison Pt toward catalysis while no poisoning occurs for Rh.

Introduction

In 1986, strong evidence was reported to support the intermediacy of metal colloids in platinum-catalyzed hydrosilylation reactions.[1] Since this report, several workers have considered metal colloids as possible intermediates in this reaction.[2-5] We recently reported an improved synthesis and structure of platinum group metal colloids from the direct reaction of metal halide salts and SiH compounds.[6] It is believed that many ostensibly homogeneous platinum group metal catalyzed hydrosilylation reactions go through colloidal intermediates. Therefore, the activity of the colloids as hydrosilylation catalysts has broad implications for many of the hydrosilylation reactions regardless of which starting species is used as the catalyst.

In this paper, we describe the relative activities of the platinum group metals as catalysts. It is accepted lore that platinum is the most active metal for SiH addition to terminal olefins.[7-10] However, we have found one case where rhodium is more active than platinum and where there appears to be an inconsistency in the literature with regard to the relative activity between dihydrides, R_2SiH_2, and monohydrides, R_3SiH, in hydrosilylation reactions.

Results and Discussion

Relative Activities of Metal Colloids. In all of our studies and in the countless reports of others, the general trend in relative activities for platinum group metal catalysts for hydrosilylation was Pt > Rh > Ir = Ru > Os, Pd. We compared the activities for the metal colloids, prepared according to eq 1,[6] where the solid metal chlorides

$$Me_2(EtO)SiH \text{ (excess)} + MCl_x + D_4^{vi} \rightarrow H_2 + \text{Si products} + M_{colloid} \quad (1)$$

M =

(a) Pt (no D_4^{vi}), (b) Rh, (c) Ru, (d) Ir, (e) Os, (f) Pd

were added directly to the liquid SiH compound in the presence of $[Me(vinyl)SiO]_4$ (D_4^{vi}). The addition of D_4^{vi} served as a colloid stabilizer that prevented bulk metal formation; the D_4^{vi} was a hydrogen acceptor. Platinum was an exceptional case in that bulk metal formation did not occur in the absence of D_4^{vi}.

In the model reaction of eq 2, run at ambient temperature and monitored by gas chromatography (GC), we

$$(n\text{-}C_6H_{13})_3SiH + (CH_2{=}CH)SiMe_3 \xrightarrow[\text{catalyst}]{} (n\text{-}C_6H_{13})_3SiCH_2CH_2SiMe_3 \quad (2)$$

found for both 25 ppm metal and 100 ppm metal that the order of activity was indeed Pt > Rh, with almost negligible activity for Ru, Ir and Os. The model reaction was carried out by adding the appropriate amount of metal colloid solution to a mixture of trihexylsilane, vinyltrimethylsilane (VTMS), and an internal standard. Addition of the metal colloid initiated the hydrosilylation reaction, which was then monitored by GC. After 10 h, the Pt-catalyzed reaction had reached 68% conversion, whereas the Rh-catalyzed reaction was 38% complete. After 80 h, the Pt and Rh reactions had reached nearly 100% conversion, whereas the Ir reaction was about 6% complete and the Ru and Os about 2% complete. The Pd colloid showed no activity at all. In the case of Pd, immediate deposition of black solid (presumably Pd metal) occurred, and no evidence of organic (soluble silicon containing) product formation was observed. VTMS was chosen for the model study because this olefin will not undergo bond isomerization. In reactions where an unblocked β position exists (such as 1-hexene), double-bond migration (isomerization) can occur to form the olefin with an internal double bond. Thus to avoid formation of the internal double bond, which was unreactive toward addition of hydrosilanes in this study, the vinylsilane was employed where possible.

Catalyst activities were also compared with a more reactive SiH compound, $(EtO)_3SiH$, being used in place of $(C_6H_{13})_3SiH$ (eq 3). This allowed us to compare the ac-

$$(EtO)_3SiH + (CH_2{=}CH)SiMe_3 \xrightarrow[\text{catalyst}]{} (EtO)_3SiCH_2CH_2SiMe_3 \quad (3)$$

[†] GE Silicones, Waterford, NY 12188.

(1) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.
(2) Onopchenko, A.; Sabourin, E. T. *J. Org. Chem.* **1987**, *52*, 4118.
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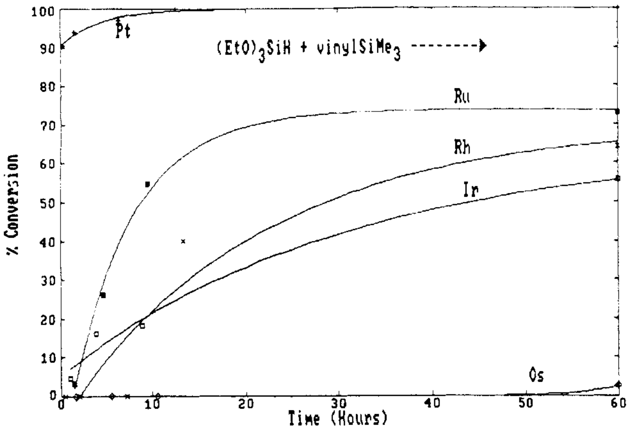

Figure 1. Relative rates of conversion of starting materials: $(EtO)_3SiH$ + (vinyl)$SiMe_3$ to product $(EtO)_3SiCH_2CH_2SiMe_3$ (eq 3), catalyzed by Pt, Rh, Ru, Ir, Os colloid catalysts. Reaction run at ambient temperature, followed by GC, decane employed as an internal standard. Moles of internal standard: moles of substrate/moles of catalyst 30000/1. Lines were drawn through data points with a monotonic power function fit: $Y = bX^c + a$. For Pt, $a = 110$, $b = 16$, $c = -0.13$; Rh, $a = -11.3$, $b = -10$, $c = 0.5$; ir, $a = -1.7$, $b = 7.4$, $c = 0.5$; Ru, $a = 110$, $b = 122$, $c = -0.3$; Os, least-squares fit.

tivities of the metal colloids in a similar environment but with a hydride of much different electronic character. Figure 1 illustrates the activities of each colloid, with the platinum catalyst being the most active, and rhodium, iridium, and ruthenium having roughly equivalent activities. Note that compared to the activities for eq 2, rhodium is less active and iridium and ruthenium are more active in eq 3.

When either electron-rich or relatively electron-defficient SiH compounds are used, these results qualitatively demonstrated that the colloid solutions of the platinum group metals had the same relative activity as previously found when molecular compounds were employed as catalysts.

Hydrosilylation with R_2SiH_2. Recently several workers described the preparation of Me(decyl)Si(octyl)$_2$, so-called silahydrocarbon, which is of interest as a wide-temperature use hydraulic fluid. Silahydrocarbon was first prepared via Grignard reaction,[11,12] and the synthesis of silahydrocarbon has also been reported via hydrosilylation by addition of Me(decyl)SiH_2 to 2 equiv of 1-octene[13-16] (eq 4). When a Pt catalyst was employed, variable results

$$\text{Me(decyl)SiH}_2 + 2[\text{1-octene}] \xrightarrow[\text{catalyst}]{80\ ^\circ\text{C}} \text{Me(decyl)Si(octyl)}_2 \quad (4)$$

silahydrocarbon

were obtained; yield to final product often required hours to weeks to complete. When Me(decyl)SiH_2 was added to 1-octene in the presence of Karstedt Pt catalyst,[17] the reaction seemed to stall, giving mostly Me(decyl)Si(H)(octyl). High yields of silahydrocarbon were observed only after continuous bubbling of an oxygen–nitrogen gas mixture from the start and only after the dihydride was mostly converted to the monohydride (vide infra).

Table I. Relative Percent Conversion after 1 h

	Me(decyl)SiH_2	Me(decyl)Si(H)(octyl)	Me(decyl)Si(octyl)$_2$
Rh	0	0	99.8
Pt	35.1	58.7	6.2

Table II. Percent Conversion for R_3SiH + (vinyl)$SiMe_3$

R	time, h	Pt	Rh
octyl	3.5	48	39
hexyl	6.5	94	5[a]

[a] After the reaction mixture was heated to 70 °C for 1 h, the reaction was 98% complete.

Previous workers[14,15] employed Wilkinson's catalyst, $ClRh(PPh_3)_3$, in place of platinum for the reaction of eq 4 and obtained high conversion rates. Given our data above that showed that colloids and molecular compounds will give similar reactivity, we carried out the reaction of eq 4 by addition of solid $RhCl_3$ to 1-octene at 80 °C with rapid stirring, followed by slow addition of Me(decyl)SiH_2. Analysis of the reaction by GC showed that immediate conversion to silahydrocarbon product occurred without formation of the monohydride intermediate, Me(decyl)Si(H)(octyl). The relative activity of Pt vs Rh is shown in Table I.

During the course of the reaction we noted that the solid suspension of the $RhCl_3$ "dissolved" and the solution took on a maroon color. The sequence of events described for silahydrocarbon synthesis was similar to the method of preparation of Rh colloid, wherein solid $RhCl_3$ was added to an SiH-containing compound.[6] When independently produced Rh colloid was employed as the catalyst in place of the $RhCl_3$, identical results were obtained. Addition of the Me(decyl)SiH_2 to the 1-octene/Rh colloid mixture at 80 °C gave immediate formation of silahydrocarbon. We propose that the maroon color formed in the reaction catalyzed by $RhCl_3$ was indicative of colloid formation and that this colloid was the active catalyst in all instances.

Two additional problems occurred in the synthesis of silahydrocarbon via eq 4. It was noted that for both Pt and Rh catalysts, large-scale reactions often failed to go to completion even after prolonged heating. We found that intentionally aerating the solution eliminated this problem and drove the reactions to completion. The need for catalytic amounts of air in hydrosilylation has been known for some time but to date has not been explained.[2,9] A second problem related to the reactions catalyzed by Rh.[15] When exactly 2 equiv of 1-octene was employed in the reaction, the conversion to silahydrocarbon was often less than 100%. Analysis of the recovered unreacted octene from the reaction revealed that isomerization to *cis*-2-octene had occurred. Hydrosilylation of internal olefins under our conditions did not occur. Thus low conversion was caused by the competing bond isomerization reaction, which converted 1-octene to the unreactive internal olefin.

We endeavored to learn the origin of the differences in activity between platinum and rhodium in the rate of formation of silahydrocarbon. We considered the possibility that the sterically bulky nature of the SiH reactants in eq 4, especially the intermediate product Me(decyl)Si(H)(octyl), led to the low yields. Following the Pt-catalyzed reaction by GC, it was noted that the rate of sila-

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(12) Gschwender, L. J.; Anderson, D. R.; Chen, G. J. USAF Internal Report AFWAL-TR-81-4163, Dec. 1981.

(13) Onopchenko, A.; Sabourin, E. T., U.S. Patent 4,578,497, 1986.

(14) Onopchenko, A.; Sabourin, E. T. U.S. Patent 4,572,791, 1986.

(15) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389.

(16) Tamborski, C.; Snyder, C. E. U.S. Patent 4,367,343.

(17) The catalyst referred to as Karstedt catalyst is bis(divinyltetramethyldisiloxane)platinum(0). As described earlier by us,[1] this catalyst formed a colloid during the hydrosilylation reaction and therefore acted as a colloid precursor whose reactivity could be directly compared to the colloids used in this study. (a) Karstedt, B. D., U.S. Patent 3,775,452, 1973. (b) Ashby, B. A.; Modic, F. J. U.S. Patent 4,288,345, 1981. (c) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F., *Organometallics* **1987**, *6*, 191.

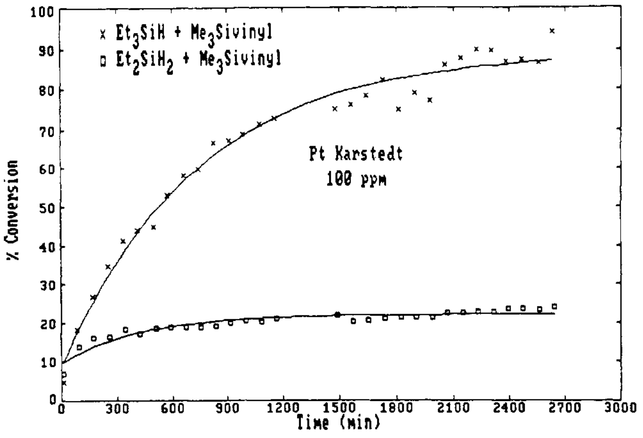

Figure 2. Relative rates of addition of Et_3SiH or Et_2SiH_2 to excess (vinyl)$SiMe_3$ catalyzed by Pt Karstedt catalyst, run at ambient temperature. Lines were drawn through data points with a monotonic power function fit: $Y = bX^c + a$. For ×, $a = 30.6$, $b = 17.1$, $c = 0.25$; for □, $a = 74$, $b = -76.1$, $c = -0.05$.

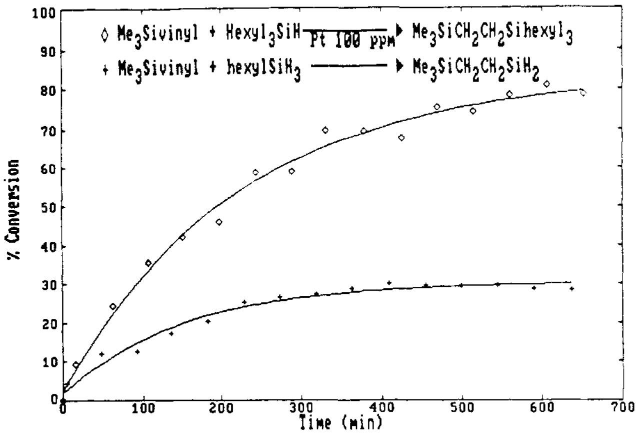

Figure 3. Relative rates of addition of (hexyl)$_3$SiH and (hexyl)SiH_3 to excess vinyltrimethylsilane catalyzed by platinum colloid run at ambient temperature. Lines were drawn through data points with a monotonic power function fit: $Y = bX^c + a$. For +, $a = -0.75$, $b = 3.44$, $c = 0.35$; for ◇, $a = -5.9$, $b = 6.7$, $c = 0.4$.

hydrocarbon from monohydride intermediate was slow until all of the Me(decyl)SiH_2 was consumed, and then the second step proceeded rapidly. These results strongly suggest that the dihydride was inhibiting the platinum catalyst for the second addition reaction. To substantiate this idea, we compared the relative rates of reaction between R_3SiH (R = hexyl or octyl) and VTMS catalyzed by either Pt or Rh. As shown in the Table II, the platinum colloid catalyst was a more active catalyst for the addition of the bulky silanes to the olefin.

According to the literature, the relative rate of activity for the platinum-catalyzed addition of a single olefin to $R_{3-x}SiH_x$ is $RSiH_3 > R_2SiH_2 > R_3SiH$.[18,19] We compared the relative rate of addition to VTMS for Et_3SiH and Et_2SiH_2, where the VTMS was present in excess, and we monitored disappearance of starting material. As shown in Figure 2, the addition of 1 equiv of Et_3SiH occurred at a faster rate than the addition of 1 equiv of Et_2SiH_2 (eqs 5 and 6, respectively). Note that in a manner analogous

$$Et_3SiH + 10[(vinyl)SiMe_3] \xrightarrow[\text{catalyst}]{} Et_3SiCH_2CH_2SiMe_3 \quad (5)$$

$$Et_2SiH_2 + 10[(vinyl)SiMe_3] \xrightarrow[\text{catalyst}]{} Et_2(H)SiCH_2CH_2SiMe_3 \quad (6)$$

to the silahydrocarbon synthesis, essentially no diaddition product, $Et_2Si[CH_2CH_2SiMe_3]_2$, was formed. The result in Figure 2 specifically contradicted the literature results.[18,19] To further demonstrate the effect of $R_{3-x}SiH_x$ addition rates to olefins where $x > 2$, we compared the relative rates of addition to VTMS for (hexyl)$_3$SiH and (hexyl)SiH_3 (eqs 7 and 8, respectively). As shown in

$$(hexyl)_3SiH + 10[(vinyl)SiMe_3] \xrightarrow[\text{catalyst}]{} (hexyl)_3SiCH_2CH_2SiMe_3 \quad (7)$$

$$(hexyl)SiH_3 + 10[(vinyl)SiMe_3] \xrightarrow[\text{catalyst}]{} (hexyl)(H)_2SiCH_2CH_2SiMe_3 \quad (8)$$

Figure 3, the rate of addition of the first equivalent of trihexylsilane went at a faster rate than the addition of the first equivalent of hexylsilane. Again, note that just as in the case of Et_3SiH vs Et_2SiH_2 subsequent reaction of (hexyl)(H)$_2$SiCH$_2$CH$_2$SiMe$_3$ with more VTMS was negligible.[20]

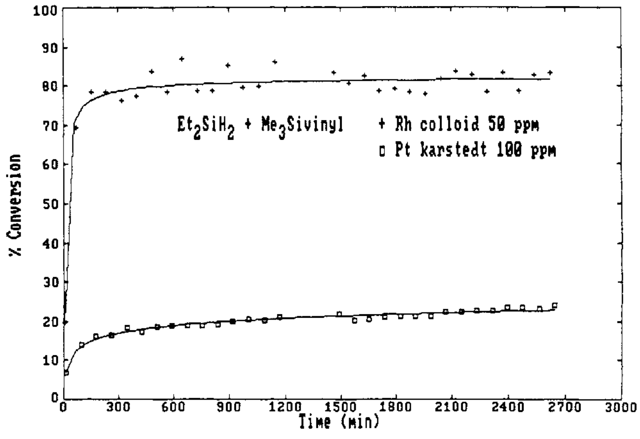

Figure 4. Relative rate of reaction of eq 6, Et_2SiH_2 + (vinyl)-$SiMe_3$; rates of reaction of 50 ppm Rh colloid compared to 100 ppm Pt Karstedt catalyst, run at ambient temperature. Lines were drawn through data points with a monotonic power function fit: $Y = bX^c + a$. For +, $a = 82.8$, $b = -151.6$, $c = -0.63$; for □, see Figure 2.

The relative rates of the reactions in eqs 5 and 6 catalyzed by rhodium were also measured. It was found that the relative rate of addition was opposite that found for platinum. In the Rh-catalyzed reaction, the rate of addition to VTMS was $Et_2SiH_2 > Et_3SiH$ and (hexyl)SiH_3 > (hexyl)$_3$SiH. For example, in reactions catalyzed by rhodium (100 ppm) of eqs 5 and 6, the starting hydride, Et_2SiH_2, was nearly completely consumed at ambient temperature in about 2 h (eq 6), whereas essentially no Et_3SiH was consumed (eq 5) after 50 h at ambient temperature.

The relative activities of Pt and Rh catalysts for the reactions in eqs 5–8 suggest the following general trend: for Pt-catalyzed reactions, the relative rate of addition to olefins is $R_3SiH > R_2SiH_2 > RSiH_3$, whereas for Rh-catalyzed reactions the trend is opposite that for Pt, $RSiH_3 > R_2SiH_2 > R_3SiH$. The silahydrocarbon synthetic results described above were consistent with these trends. In a relative rate study between Pt and Rh catalysts in the

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[18] Reikhsfel'd, V. O.; Koroleva, G. N. *Zh. Obshch. Khim.* **1966**, *36*, 1474.

[19] Koroleva, G. N.; Reikhsfel'd, V. O. *Zh. Obshch. Khim.* **1967**, *37*, 2768.

[20] These results also differ from those reported in ref 15. However, they ran their reactions at elevated temperatures and employed different catalysts. We do not known the reason for the differences in our results.

Table III

metal colloid	% metal (by anal.)	metal colloid	% metal (by anal.)
Pt	1.03	Ir	0.072
Rh	0.19	Ru	0.39
		Os	0.13

addition reaction of eq 6, it was found that 50 ppm Rh colloid was more active than 100 ppm of the Pt Karstedt catalyst (Figure 4). It should be noted that the Pt Karstedt catalyst was only marginally less active in this reaction than the Pt colloid catalyst.[17]

The origin of the variations in reactivity with the different silanes will be discussed in more detail in a subsequent paper about the mechanism of hydrosilylation.[21] We propose that di- and trihydrides act as catalyst poisons toward Pt while they do not act as poisons toward Rh. Thus for R_3SiH additions to olefins, the activity of Pt > Rh, but with di- and trihydrides, the activity of Rh appears higher due to the inhibition by these hydrides on Pt.

Experimental Section

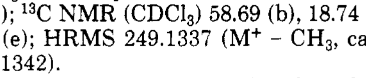
General Procedures. Reactions were carried out in air unless otherwise specified. Silicon starting materials were obtained from Petrarch Systems and used without further purification. ^1H NMR spectra were recorded on a Varian EM 390 NMR (90 MHz) or a GE QE-300 (300.15 MHz) spectrometer. ^{29}Si NMR spectra were recorded on a Varian XL 300 NMR spectrometer at 59.3 MHz. ^{13}C NMR spectra were recorded either on the Varian XL 300 (75.43 MHz) or on the GE QC-300 (75.48 MHz) instruments. Gas chromatography was performed using a HP 5830A gas chromatograph employing a 6-ft 3% OV 101 column, FID detector. GCMS analysis was performed using a Varian MAT 311A instrument.

Relative Metal Colloid Activities. Metal colloids were made according to our published procedure[6] (Table III). For the reaction of eq 2, a stock solution was prepared: $(hexyl)_3SiH$ (9.5 mL, 26.9 mmol), $(vinyl)SiMe_3$ (3.9 mL, 26.9 mmol), decane (0.8 mL, 4.1 mmol); decane was used as an internal standard. For each metal, the appropriate amount of colloid solution was added to 2 mL of the stock solution. Runs as shown in Figure 1 always showed the same relative rates; absolute conversion varied from run to run by about 5%. For example, for Pt, 0.1 g (5.1 μmol of Pt) of the colloid solution was added to initiate the reaction. Then for all the other metals 5.1 μmol of metal was added. Analysis of the reaction catalyzed by Pt by GCMS showed the single expected reaction product:

$$\underset{a}{CH_3}\underset{b}{CH_2}\underset{c}{CH_2}\underset{d}{CH_2}\underset{e}{CH_2}\underset{f}{CH_2})_3Si\underset{g}{CH_2}\underset{h}{CH_2}Si\underset{i}{(CH_3)_3}$$

$(hexyl)_3SiCH_2CH_2SiMe_3$: ^1H NMR ($CDCl_3$) δ 1.31 (br m, b–e), 0.91 (t, 3 Hz, a), 0.54 (CM,[22] f), 0.40 (m, g + h), 0.03 (s, i); ^{13}C NMR ($CDCl_3$) δ 34.17, 32.13, 24.43 and 23.20 (b–e), 14.60 (f), 12.22 (a), 9.20 (g), 4.75 (h), −1.83 (i); HRMS 384.3627 (M^+, calcd for $C_{23}H_{52}{}^{28}Si_2$ 384.3607).

For the reaction in eq 3, a stock solution was made: $(EtO)_3SiH$ (5 mL, 26.9 mmol), $(vinyl)SiMe_3$ (3.9 mL), and 0.8 mL of decane:



$$(\underset{a}{CH_3}\underset{b}{CH_2}O)_3Si\underset{c}{CH_2}\underset{d}{CH_2}Si\underset{e}{(CH_3)_3}$$

^1H NMR ($CDCl_3$) δ 3.84 (q, 7 Hz, b), 1.23 (t, 7 Hz, a), 0.53 (s, c + d), −0.01 (s, e); ^{13}C NMR ($CDCl_3$) 58.69 (b), 18.74 (a), 8.15 (c), 3.05 (d), −1.93 (e); HRMS 249.1337 ($M^+ - CH_3$, calcd for $C_{10}H_{25}O_3{}^{28}Si_2$ 249.1342).

Silahydrocarbon. A sample of pure silahydrocarbon, prepared via Grignard reaction[11,12] between $MeSiCl_3$ and 2 equiv of (octyl)MgBr and 1 equiv of (decyl)MgBr and then purified by distillation, was received from Wright Patterson Air Force base; ^1H NMR ($CDCl_3$) δ 1.33 (s, br), 0.90 (m), 0.50 (br m), −0.06 (s); ^{13}C NMR ($CDCl_3$) δ 33.87, 31.99, 29.71, 29.32, 23.03, 22.69, 14.08, 13.85; GCMS showed that four compounds were present, namely, $Me(decyl)_3Si$, $Me(decyl)_2Si(octyl)$, $Me(decyl)Si(octyl)_2$, and $MeSi(octyl)_3$; MS, *m/e* for $Me(decyl)Si(octyl)_2$ 395 ($M^+ - CH_3$), 297 (90%, $M^+ - C_8H_{17}$), 269 (100%, $M^+ - C_{10}H_{21}$).

Preparation via Hydrosilylation. Preparation of $Me(decyl)SiCl_2$. To a 1-L, four-neck flask equipped with a condenser, magnetic stirrer, gas dispersion tube, and thermometer were added 100 mL of hexane, 0.28 g of Lamoreaux platinum catalyst[23] (3% platinum by weight in octanol), and 1-decene (112 g, 0.789 mol). The solution was heated to 45 °C, and a 99%/1% N_2/O_2 gas mixture was purged through the solution. The silane, $Me(H)SiCl_2$ (ca. 95 g, slight molar excess) was slowly added to the stirring solution over 45 min. After about 1 mL of the silane was added, an exotherm was noted. The maximum temperature of 87 °C was reached when half of the silane had been added. One hour after addition was complete, analysis by GC showed 99% conversion to $Me(decyl)SiCl_2$.

Preparation of $Me(decyl)SiH_2$. $Me(decyl)SiCl_2$ (10 g, 26.7 mmol) was dissolved in 50 mL of toluene. Vitride dihydride reducing agent ($NaAlH_2(OCH_2CH_2OCH_3)_2$, 70% in toluene, from Hexcel, 7.7 g, 26.7 mmol) was added via a dropping funnel under N_2 at ambient temperature. The solution was stirred for 1 h, at which point GC analysis showed complete conversion to product. The reaction mixture was slowly added to 100 mL of 6 N HCl. The H_2O layer was washed with toluene, and then all the toluene extracts were combined and extracted with water. The product was recovered by first distilling at ambient pressure to remove ca. 80% of the toluene and then the pressure was reduced to 20 mmHg and the distillation carried out through a 10-in. Vigreaux column. The product was collected at 75 °C; recovered yield 4.2 g (22.6 mmol), 84.5%; ^1H NMR ($CDCl_3$) δ 3.60 (sextet), 1.23 (br), 0.80/0.6 (m), 0.06 (t); ^{13}C NMR ($CDCl_3$) δ(CH_2) 32.82, 31.86, 29.61, 25.17, 22.66, 14.01, 10.44, δ (decyl CH_3) 29.33, δ($SiCH_3$) −8.66; GCMS, *m/e* 186 (5%, M^+), 185 (23%, $M^+ - H$) 171 (30%, $M^+ - Me$), 127 (80%), 113 (80%), 99 (83%), 85 (100%).

Preparation of $Me(decyl)Si(octyl)_2$. Pt Reaction. In a 500-mL flask equipped with an air inlet and a reflux condenser was added 1-octene (95.5 g, 0.85 mol) and Pt Karstedt catalyst (0.13 mL of a 5% Pt solution in xylene, 0.038 mmol of Pt). The 1-octene solution was heated to 85 °C with a stream of air blowing through the solution. $Me(decyl)SiH_2$ (40 g, 0.215 mol) was slowly added to the 1-octene/Pt solution. After 2 h, GC analysis showed 35% unreacted $Me(decyl)SiH_2$, 59% Me(decyl)Si(H)(octyl) (vide infra), and 6% silahydrocarbon. The unreacted octene was removed under reduced pressure on a rotary evaporator. Me(decyl)Si(H)(octyl): ^1H NMR ($CDCl_3$) δ 3.75 (m, SiH), 2.07 (m), 1.68 (br s), 1.31 (large s), 0.86 (m), 0.55 (br), 0.02 (m, $SiCH_3$); GCMS, *m/e* 298 (5%, M^+), 297 (13%, $M^+ - H$), 199 (100%), 171 (100%).

Rh Reaction. The preparation of silahydrocarbon was repeated except that Rh colloid was used in place of Pt Karstedt. The Rh colloid was made by addition of $RhCl_3$ to $(EtO)_3SiH$ as described.[6] The Rh colloid solution was 0.16% Rh by weight; 0.6 mL of the solution was added to the 1-octene, which delivered 9 μmol of Rh. Analysis of the Rh-catalyzed reaction by GC showed that after 1 h, >99% conversion to $Me(decyl)Si(octyl)_2$ had occurred. After the reaction was complete, octenes were removed by distillation. Analysis of the recovered octene from the reaction by ^1H NMR showed that conversion to *cis*-2-octene had occurred by comparison to the NMR of an authentic sample. Note that the silahydrocarbon made this way differed from the Air Force sample in that none of the following were present: $Me(decyl)_3Si$ $Me(decyl)_2Si(octyl)$, and $MeSi(octyl)_3$. Anal. Calcd for $C_{27}H_{58}Si$: C, 79.07; H, 14.23; Si, 6.84. Found: C, 78.89; H, 13.74; Si, 6.84. ^1H NMR ($CDCl_3$) δ 1.31 (large m), 0.86 (m), 0.38 (m), −0.1 (s); ^{13}C NMR δ 33.9, 32.02, 29.75, 29.35, 23.96, 22.72, 14.07, 13.88, −5.18 (SiMe); ^{29}Si NMR δ +2.83; GCMS identical with the $Me(decyl)Si(octyl)_2$ in the Air Force sample (above).

Relative Rate of Pt and Rh with Bulky R_3SiH. The trioctylsilane + $(vinyl)SiMe_3$ stock solution consisted of $(octyl)_3SiH$ (5 mL, 11.1 mmol) and $(vinyl)SiMe_3$ (1.62 mL, 11.1 mmol). Reaction initiated with addition of 0.26 μmol of either the Pt or

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[21] Lewis, L. N., manuscript in preparation.

[22] There is a characteristic multiplet present in these compounds due to the abx_2 spin system, which we fondly call a Colborn multiplet (CM): Colborn, R. E. *J. Chem. Educ.*, in press.

[23] Lamoreaux, H. F. U.S. Patent 3,197,432, 1965.

Rh colloid solution. Analysis of the reaction product by GCMS showed the expected single product, (octyl)$_3$SiCH$_2$CH$_2$SiMe$_3$, *m/e* 468 (25%, M$^+$), 367 (85%, M$^+$ – CH$_2$CH$_2$SiMe$_3$), 355 (25%, M$^+$ – octyl), 255 (80%), 243 (100%).

Relative Activity of Et$_3$SiH and Et$_2$SiH$_2$. For the triethylsilane reaction the stock solution contained (vinyl)SiMe$_3$ (4 mL, 27.5 mmol), Et$_3$SiH (0.44 mL, 2.77 mmol), and decane (0.4 mL, 2 mmol). For the diethylsilane reaction the stock solution contained (vinyl)SiMe$_3$ (4 mL, 27.5 mmol), Et$_2$SiH$_2$ (0.35 mL, 2.7 mmol), and decane (0.4 mL). The reactions were initiated by addition of the Pt Karstedt catalyst (7 μL of a 5% Pt solution, 1.8 μmol of Pt). The Rh-catalyzed reactions were carried out in exactly the same way except Rh colloid solution was used (58 μL of a 0.3% Rh colloid solution, 1.7 μmol). For the Rh-catalyzed reaction, the diaddition product was obtained in >98% conversion. GCMS analysis showed the expected product, Et$_2$Si[CH$_2$CH$_2$SiMe$_3$]$_2$, *m/e* 288 (25%, M$^+$), 187 (80%, M$^+$ – CH$_3$CH$_2$SiMe$_3$), 171 (80%), 158 (70%), 157 (80%), 87 (100%), 73 (100%). The authentic monoaddition product, Et$_2$Si(H)(CH$_2$CH$_2$SiMe$_3$), was prepared to confirm its retention time and response factor on the GC. In an addition funnel was placed (vinyl)SiMe$_3$ (5.63 mL, 38.8 mmol) and Rh colloid catalyst (35 μL of a 0.3% Rh solution, 0.5 μmol of Rh). In a three-neck flask was placed Et$_2$SiH$_2$ (5 mL, 38.8 mmol). The diethylsilane was heated to reflux, and then the (vinyl)SiMe$_3$/Rh mixture was slowly added. Analysis by GC showed complete conversion to the single monoaddition product Et$_2$Si(H)(CH$_2$CH$_2$SiMe$_3$). GCMS analysis showed *m/e* 187 (35%, M$^+$ – 1), 159 (20%, M$^+$ – Et (100%)). The product of Et$_3$SiH and (vinyl)SiMe$_3$ was consistent with Et$_3$SiCH$_2$CH$_2$SiMe$_3$:

$$(\underset{a}{CH_3}\underset{b}{CH_2})_3Si\underset{c}{CH_2}\underset{d}{CH_2}Si(\underset{e}{CH_3})_3$$

^{1}H NMR (CDCl$_3$) δ 0.95 (t, 9 Hz, a), 0.55 (m, b), 0.42 (m, c + d), 0.02 (s, e); ^{13}C NMR (CDCl$_3$) δ 9.08 (c), 7.88 (b), 3.34 (a + d), –1.91 (e); HRMS 216.1729 (M$^+$, calcd for C$_{11}$H$_{28}$^{28}Si$_2$ 216.1729).

Relative Activity of (hexyl)$_3$SiH and (hexyl)SiH$_3$. For the reaction of eq 7, (vinyl)SiMe$_3$ (4 mL, 27.5 mmol), decane (0.4 mL, 2.06 mmol), and (hexyl)$_3$SiH (0.98 mL, 2.75 mmol) were combined. The reaction was initiated by addition of Pt colloid solution (35 μL of a 1.03; Pt solution, 1.8 μmol of Pt) or Rh colloid solution (116 μL of 0.3% Rh solution, 1.8 μmol of Rh). For the reaction of eq 8, (vinyl)SiMe$_3$ (4 mL, 27.5 mmol), decane (0.4 mL), and (hexyl)SiH$_3$ (0.44 mL, 2.72 mmol) were combined. The reaction was initiated with Pt or Rh as described for eq 7.

Acknowledgment. We thank Dave Williams, Silicone Products, for his technical assistance. NMR spectra were recorded by Dr. Elizabeth Williams and Paul Donahue. Hans Grade and Ralph May performed the GCMS analysis. Elemental analyses were performed by Winnie Balz and Nancy Marotta.

Mechanistic Studies of Processes Involving C–C Bond Cleavage in Gas-Phase Organometallic Reactions Using Product Kinetic Energy Release Distributions: Co$^+$ Reacting with Cyclopentane

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Received June 8, 1989

A reverse-geometry mass spectrometer is used to obtain product ion kinetic energy release distributions to probe the energetics and mechanisms of several gas-phase organometallic reactions. In particular, we examine the mechanism for C$_2$H$_4$ and C$_3$H$_6$ elimination from Co(cyclopentane)$^+$. The kinetic energy release distribution associated with these processes can be modeled by using phase space calculations assuming, for the C$_3$H$_6$ elimination process, propene rather than cyclopropane is being eliminated as the product neutral, and for the C$_2$H$_4$ elimination process, Co(propene)$^+$ rather than (cobaltacyclobutane)$^+$ is being formed as the product ion. In addition, we obtain a heat of formation for the cobalt ethylene ion of 255 kcal/mol at 0 K, corresponding to a bond dissociation energy of 42 kcal/mol at 0 K, by fitting the theoretical results to the experimental distribution. The proposed mechanism for cobalt ions reacting with cyclopentane involves a ring-opening process that eventually leads to a Co(1-pentene) ion complex, which then decomposes. The internal energy content of this Co(1-pentene)$^+$ complex is too low to allow elimination of C$_3$H$_6$ as cyclopropane, in contrast to the same complex formed directly from Co$^+$ and 1-pentene, where both cyclopropane and propene are eliminated.

Introduction

A variety of techniques are now available to probe mechanisms of gas-phase organometallic reactions.[1-16] Kinetic energy release distributions associated with the decomposition of nascent organometallic complexes generally provide additional insight into both the energetics and mechanisms of these reactions. For example, decarbonylation of cyclobutanone by either Fe$^+$ or Co$^+$ was shown to proceed via a metallacyclobutane intermediate,

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† Contribution No. 7957.

[1] For a recent review see: Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; Vol. 34, p 628, and references therein.

[2] See, for example: (a) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1985**, *89*, 5626. (b) Sunderlin, L.; Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 78. (c) Georgiadis, R.; Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 4251. (d) Schultz, R. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 411.

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