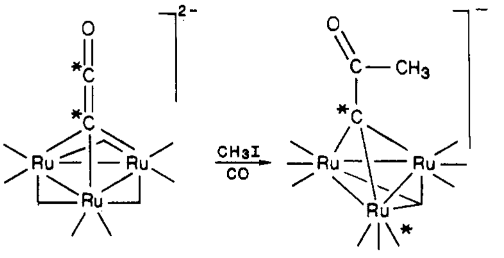
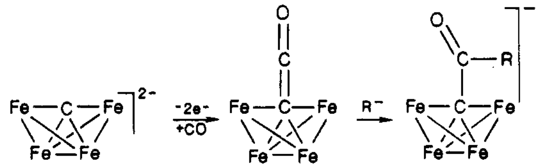
substantial driving force is expected for the postulated migration because carbon–carbon bonds are 30–40 kcal/mol stronger than M–CF_3 bonds and about 40–50 kcal/mol stronger than metal–carbon alkyl bonds.[22] Although alkyl migration to a carbide ligand has not been demonstrated previously in the literature, a recent labeling study in our laboratory supports an acyl to carbon ligand migration in reaction 6.[23] This result suggests prior reaction and CO insertion at a ruthenium center, followed by displacement of the labeled ketenylidene CO by a metal-bound acyl ligand.



(6)

An alternative mechanism involves a neutral ketenylidene species that is thought to be an intermediate in the reactions of $Fe_4(CO)_{13}C$ with nucleophiles.[24] This mechanism appears unlikely because of the observed carbon monoxide inhibition of the reaction and the lack of product 3 when 1 and RX are mixed together in an electrochemical cell under oxidizing conditions.



(7)

Conclusions. Our observations indicate that different reaction pathways are accessible for the reaction alkyl halides and carbocation alkylating reagents with 1. We suggest that direct attack on the carbon ligand gives the tetrahedral alkylidyne clusters in the case of strong carbocations. In reactions of 1 with alkyl halides, we suggest that the initial site of reactivity is a metal center.

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Silyltitanocene Complexes as Catalysts for the Hydrogenation, Isomerization, and Hydrosilation of Olefins

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The hydrogen evolution that normally accompanies the Cp_2TiMe_2-catalyzed dehydrogenative coupling of organosilanes is completely suppressed in the presence of olefins. Instead, the olefin undergoes hydrogenation. The rates of co-hydrogenation of several olefins (cyclohexene, 1- and 2-pentene, styrene, and norbornadiene) with a variety of silanes ($PhSiH_3$, $PhSiD_3$, $PhCH_2SiH_3$, $C_6H_{13}SiH_3$, c-$C_6H_{11}SiH_3$, and Ph_2SiH_2) parallel the rates of silane coupling in the absence of olefin but are considerably faster. Sterically hindered primary silanes and secondary silanes, which do not catalytically couple in the absence of olefin, dimerize in its presence. The rates of olefin co-hydrogenation are strongly dependent on olefin in the order cyclohexene < 2-pentene ≪ 1-pentene ≈ norbornene ≈ styrene. In the first two cases, a kinetic study reveals that the catalyst is largely in the form of previously described dimeric silyltitanium complexes. The rapidly hydrogenated olefins also give silylated products. In addition to the above reactions the complex $Cp_2Ti(\mu\text{-H})(\mu\text{-HSiHPh})TiCp_2$ also catalyzes the isomerization of 2-pentene and the hydrogenation of alkenes by H_2. A kinetic study of the isomerization reaction is also reported.

Introduction

Organotitanium compounds have played a key role in the developed of both synthetic organometallic and catalytic chemistry.[2] It was the discovery of their remarkable activity in the polymerization of 1-olefins that fueled much of the expansion of interest in transition-metal organometallic chemistry that began in the 1950s.[3] In spite of the practical importance of Ziegler–Natta catalysis and the vast amount of research that has been committed to understanding the mechanisms of the polymerization and related catalytic processes, we remain remarkably ignorant of the details of these reactions in comparison to our understanding of similar chemistry involving the later transition groups.[4] For example, very few of the known, iso-

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[1] On sabbatical leave from the Chemistry Department, Chungnam National University, Daejon, Korea.

[2] Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience; New York, 1980; Chapter 4. Bottrill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 3, Chapter 22. Boor, J. *Ziegler-Natta Catalysis and Polymerizations*; Academic: New York, 1979. Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1.

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[4] At least two plausible, distinct mechanisms have been proposed for the propagation step,[5,6] neither of which has been excluded for the most important case of 1-olefin polymerization.

[5] Cossee, P. *Tetrahedron Lett.* **1960**, *17*, 12. See also ref 2.

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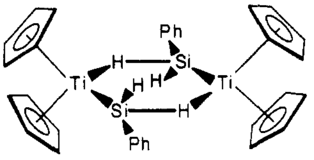
lated, and characterized organotitanium compounds catalyze the polymerization of 1-olefins with a rate comparable to that of the commercial Ziegler–Natta catalysts, and it is virtually impossible to predict new systems that will show such activity.

Other catalytic reactions effected by organotitanium species are the hydrogenation of olefins,[7,8] isomerization of olefins,[8] the cyclooligomerization of dienes,[9] and the ring-opening polymerization of strained cyclic olefins.[10] The last mentioned reaction has recently been analyzed mechanistically with the kind of detail one associates with the catalytic reactions of the later transition groups.[10] In the other cases, the nature of the catalytic species is usually unknown and the complexity and reactivity of the titanium compounds preclude detailed mechanistic study.

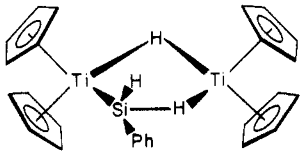
The dehydrogenative coupling of organosilanes was recently added to the list of reactions effectively catalyzed by organotitanium compounds.[11] Our studies of that reaction led to the discovery of some unusual silyltitanium(III) complexes which could be isolated as stable crystalline compounds and whose structures suggested that they might exhibit activity for other reactions.[12] In this paper we describe some investigations of the titanocene derivative catalyzed hydrogenation, isomerization, and silylation of olefins in the presence of organosilanes.

Results and Discussion

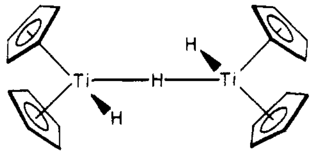
Silane Polymerization/Olefin Co-hydrogenation. The dehydrogenative coupling of primary organosilanes catalyzed by dimethyltitanocene has recently been shown to involve the three complexes **1**, **2**, and **3**.[12] The spontaneous transformation of **1** to **2** to **3** occurs with concomitant formation of polysilane. The transformations of **3** to **2** and **2** to **1** are effected by reaction with silane and result in the liberation of H_2. Cycling through these reactions leads to the catalytic process depicted in (1).



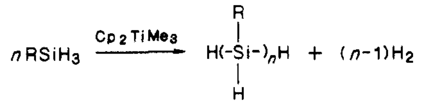
1



2



3



$$n\,\mathrm{RSiH_3} \xrightarrow{\mathrm{Cp_2TiMe_2}} \mathrm{H(-\overset{\displaystyle R}{\underset{\displaystyle H}{Si}}-)_{\mathit{n}}H} + (n-1)\mathrm{H_2} \qquad (1)$$

However, the rates of these reactions are too slow to account for the rate of the catalytic reaction. When reaction 1 is carried out in the presence of an olefin, the evolution of H_2 is suppressed and hydrogenation of the olefin takes place. In the cases of cyclohexene, styrene, and norbornene the hydrogenation occurs without the complication of accompanying olefin isomerization, but for linear alkenes isomerization occurs very rapidly and complicates the interpretation of hydrogenation results.

Table I. Kinetic Data for Co-hydrogenation of Cyclohexene with Phenylsilane[a]

10^2-$[Cp_2TiMe_2]$, M	$[PhSiH_3]$, M	$[C_6H_{12}]$, M	10^5R_i, $M\cdot s^{-1}$	$10^4k'$, s^{-1}
1.9	0.46	1.15	9.2	9.8
2.1	0.46	1.15	9.3	9.5
3.7	0.46	1.15	10.4	8.0
6.2	0.46	1.15	19.2	11.3
8.3	0.46	1.15	20.3	10.4
1.9	0.23	1.15	4.7	7.2
1.9	0.69	1.15	9.8	8.7
1.9	0.92	1.15	10.1	7.8
1.9	1.15	1.15	13.2	9.1
2.1	0.46	2.42	10.6	9.8
2.1	0.46	3.63	9.3	9.8

[a] All experiments in C_7D_8 at 30 °C.

Table II. Dependence of Initial Cyclohexene Co-hydrogenation Rate on Structure of Silane[a]

silane	10^5R_i, $M\cdot s^{-1}$	silane	10^5R_i, $M\cdot s^{-1}$
$PhSiH_3$	13.2	(benzyl)SiH_3	1.0
$PhSiD_3$	3.6	(cyclohexyl)SiH_3	0.5
(*p*-tolyl)SiH_3	9.8	$PhMeSiH_2$	4.6
(*n*-hexyl)SiH_3	1.0	$PhSiH_3$[b]	3.0

[a] $[Cp_2TiMe_2] = 1.9 \times 10^{-2}$ M; [silane] = 1.2 M; $[C_6H_{10}] = 1.1$ M. All experiments at 30 °C in C_7D_8. [b] Rate of polymerization in absence of olefin.

Compound **2** is an excellent catalyst for the direct hydrogenation of olefins with H_2. Although rate constants for direct hydrogenation have not been measured, the reaction rates for direct hydrogenation are much greater than silane effected cohydrogenation.

Co-hydrogenation of Cyclohexene. A kinetic study of the hydrogenation of cyclohexene in the presence of phenylsilane and catalytic amounts of dimethyltitanocene was undertaken. The results of this study are summarized in Table I. From these results, the rate law for the reaction was deduced to be of the form

$$\text{rate} = k'_1[\text{catalyst}]^{1/2}[\text{silane}]^{1/2}[\text{olefin}]^0 \qquad (2)$$

Such a rate law suggests a mechanism in which the active species in the rate-controlling step is in equilibrium with a dimeric precursor. A reasonable candidate for this equilibrium is shown in (3). If it is assumed that equi-

$$\underset{\textbf{2}}{\mathrm{Cp_2Ti(H)(SiH_2Ph)TiCp_2}} + \mathrm{PhSiH_3} \overset{K_1}{\rightleftharpoons} \underset{\textbf{4}}{\mathrm{2Cp_2Ti(H)(SiH_2Ph)}} \qquad (3)$$

$$\mathrm{Cp_2Ti(H)(SiH_2Ph)} \xrightarrow{k_1} \text{products} \qquad (4)$$

librium 3 is rapidly established and mostly in the direction of reactants, the concentration of the supposed Ti(IV) hydrido silyl complex **4** is given by

$$[\mathbf{4}] = K_1^{1/2}[\mathbf{2}]^{1/2}[\mathrm{PhSiH_3}]^{1/2} \qquad (5)$$

The rate-controlling, unimolecular decomposition of **4** to

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[6] Ivin, R. J.; Rooney, J. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1978**, *604*. Turner, H. W.; Schrock, J. D.; Fellman, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942.

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[8] Pez, G. P.; Kwan, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 8079.

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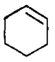
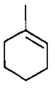
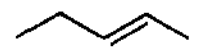
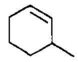
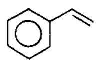
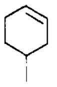
[10] Gillom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

[11] Aitken, C.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11.

[12] Aitken, C.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

Table III. Initial Rates of Co-hydrogenation of Different Olefins

olefin	R_i, M·s^{-1}	olefin	R_i, M·s^{-1}
	13.2×10^{-5}		>0.01
	no reaction		24.0×10^{-5}
			$>2.1 \times 10^{-3}$
	8.6×10^{-5}		>0.01
	10.8×10^{-5}		

a species which rapidly hydrogenates olefin thus yields eq 2 with

$$k'_1 = k_1K_1^{1/2} \qquad (6)$$

The rate of co-hydrogenation of cyclohexene was found to depend strongly on the nature of the silane used. The initial rates of reaction for a number of different silanes, under the same experimental conditions are shown in Table II. A value for the initial rate of phenylsilane polymerization in the absence of added olefin is included for comparison. The considerable polymerization rate increase accompanying co-hydrogenation may reflect the fact that hydrogen accumulation and evolution from solution is a rate-determining factor in the case of the straight polymerization reaction.

The only obvious factor with which the observed reactivities of the different primary silanes correlate is their steric bulk, to which the reaction shows a remarkable sensitivity. This correlation does not seem to hold for methylphenylsilane, which reacts an order of magnitude faster than cyclohexylsilane, but it is likely, as discussed further below, that these silanes react by a different mechanism from the more reactive, less hindered ones. Neither of these silanes undergoes straight polymerization at a measurable rate in the absence of olefin, and the coupling in the presence of olefin leads to disilane in both cases. The other primary silanes all produce oligomers of the same chain length in the presence and absence of olefin.

It can also be seen from Table II that there is a considerable isotope effect operating in $PhSiD_3$ relative to $PhSiH_3$. An isotope effect would be expected to operate at the level of equilibrium 3, but NMR examination of reaction mixtures also shows that compound 1 is about twice as abundant in the deuteriosilane reaction as in the undeuteriated reaction. This shows that much of the isotope effect is due to slowing down of the decomposition of 1 to 2 and an increase in the total amount of titanium tied up in the form of 1. A similar accumulation of the analogue of 1 is observed for cyclohexylsilane, suggesting that the decomposition of 1 may be rate determining. However, since the spontaneous rate of decomposition of 1 is known to be much too slow to account for the rates of catalytic reactions described herein, its effect on the rate is likely to be diversion of active species out of the catalytic cycle rather than a direct participation in that cycle.

Mass analysis of the cyclohexane produced from the reaction of cyclohexene with $PhSiD_3$ revealed the following percent abundances of deuteriocyclohexanes: d_0, 7; d_1, 27; d_2, 45; d_3, 18; d_4, 4.

The reactivities of a number of different olefins toward co-hydrogenation with phenylsilane are listed in Table III. Apart from 1-methylcyclohexene, which is completely unreactive, the methylcyclohexenes exhibit very similar activity to cyclohexene and follow the same rate law. The reactions of the other olefins will be dealt with individually below.

Table IV. Kinetic Data for the Catalytic Isomerization of 1-Pentene[a]

10^3[catalyst], M	[1-pentene], M	10^2R_i, M·s^{-1}	$10^4k'_2$, M^{-2}·s^{-1}
3.6	2.6	0.46	8.3
3.6	1.2	0.22	8.7
1.8	1.2	0.07	7.8
1.2	1.2	0.04	8.2

[a] Conditions as in Table I.

Hydrogenation and Hydrosilation of 2-Pentene. 2-Pentene underwent catalytic co-hydrogenation in the presence of $PhSiH_3$ according to the same rate law as cyclohexene and gave a rate constant, $k = 0.0023$ s^{-1}, roughly twice that of cyclohexene. This difference in rate constant is probably due to the fact that (3) is not a true equilibrium but rather a pseudoequilibrium in a complex cycle of steps in a steady state. Thus, in a many-step cycle which involves the decomposition of 4 and the eventual regeneration of 2 from the decomposition products, a variation in structure of the olefin can alter the rate of a step in the cycle and thereby the steady-state concentrations of 2 and 4, without introducing an olefin dependence in the rate law. This remains true as long as the criteria outlined in the derivation of eq 5 hold.

Analysis of the final product of the pentene/$PhSiH_3$ reaction showed the pentene to have been converted to pentane (97%) and pentylphenylsilanes (3%).

Hydrogenation, Hydrosilation, and Isomerization of 1-Pentene. Under conditions that lead to the complete co-hydrogenation of cyclohexene or 2-pentene in a few hours, 1-pentene undergoes about 24% hydrogenation, 18% hydrosilation, and 58% isomerization to 2-pentene in a few minutes. Although experimental difficulties precluded full kinetic analysis of the hydrogenation reaction in this case, the observed conversion permitted the assignment of a lower limit rate for the hydrogenation, $R > 2.1 \times 10^{-3}$ M·s^{-1}, roughly an order of magnitude greater than that measured for 2-pentene.

When the catalyst concentration was reduced from 0.02 to 0.0037 M, the time to completion was increased from a few minutes to about 70 h. The percent composition of the final reaction mixture, based on 1-pentene, was as follows: pentane, 36; *cis*-2-pentene, 26; *trans*-2-pentene, 20; 1-pentene, 0.5; pentylated silanes, 18.

Compound 2 catalyzes the isomerization of 1-pentene in the absence of silane. Some relevant kinetic data are shown in Table IV. With use of the data in Table IV, the rate law for the isomerization reaction was found to be

$$\text{rate} = k'_2[2]^{3/2}[\text{1-pentene}]^{1/2} \qquad (7)$$

Such a rate law can be accommodated by a mechanism involving initial splitting of 2 by olefin in a fast pseudoequilibrium, followed by a rate-determining step involving a second molecule of 2. A schematic representation of such a mechanism is the following

$$2 + \text{ol} \overset{K_2}{\rightleftharpoons} \text{“Ti(ol)”} + \text{“Ti”} \qquad (8)$$

$$2 + \text{“Ti(ol)”} \xrightarrow{k_2} \text{products} \qquad (9)$$

$$\text{ol} = \text{1-pentene}$$

Earlier studies of the reaction of 2 with CO favor the choice of a heterolytic cleavage for reaction[12] with “Ti(ol)” being a bis(cyclopentadienyl)titanium(II) olefin complex[13] and

Table V. GC/MS Analyses of Products from Reactions of 1-Pentene with $PhSiH_3$

compd	retentn time[a] s	yield,[b] %		fragment, m/e (% base)
1-$C_5H_{11}SiH_2Ph$[c]	504		2	M – 8 H; 170 (2); M – C_2H_2, 152 (2); M – C_3H_6, 136 (4); M – Ph, 101 (98); M – C_6H_6, 100 (100); M – $PhSiH_3$, 70 (4)
1-$C_5H_{11}(SiHPh)_2H$[c]	996		16	M – C_5H_{11}, 213 (1); M – $PhSiH_2$, 177 (12); $PhSiH_2$, 107 (83); M – $C_5H_{12}Si$, 100 (100): M – $Ph_2Si_2H_3$, 72 (34); SiH, 29 (30)
2-$C_5H_{11}(SiHPh)_2H$[d]	972		3	M – H, 283 (1); M – C_2H_5, 255 (2); M – C_3H_7, 241 (3); M – C_4H_9, 227 (5); M – C_6H_8, 205 (5); M – $PhSiH_4$, 175 (30); $PhSiC_3H_7$, 148 (13); $PhSiCH_4$, 121 (27); $C_5H_{13}Si$, 100 (53); $PhSiH_2$, 107 (100), PhSi, 105 (73)
1-$C_5H_{11}nSiHPh)_2H$[d]	996[e]		6	as above
$(C_5H_{11})_2(SiHPh)_2$[d]	1002[e]		9	M – H, 353 (2); M – C_5H_{11}, 283 (10); M – $C_5H_{12}Si$, 254 (11); M – C_8H_{18}, 240 (13); M – $PhSiC_5H_{14}$, 175 (100); $C_5H_{12}Si$, 100 (73)
$H(SiHPh)_2H$	1044	6.0	trace	M – H; 213 (1); Ph_2SiH_2, 184 (4); PhSiH, 106 (100)
$H(SiHPh)_4H$	1146	1.0	2.0	M – 5 H, 421 (1); M – C_6H_9, 345 (2); M – $PhSiH_4$, 317 (1); $Ph_3Si_2H_2$, 289 (9); Ph_3Si, 259 (3); $Ph_2Si_3H_2$, 240 (11); $Ph_2Si_2H_2$, 212 (34); Ph_2Si, 182 (38); PhSi, 105 (100); SiH, 29 (29)
$H(SiHPh)_5H$	1896	trace	trace	M – C_6H_{11}, 450 (1); M – $PhSi_2H_4$ and $Ph_4Si_3H_3$, 395 (2); M – $Ph_2Si_2H_3$ and $Ph_3Si_3H_4$, 319 (18); Ph_3Si, 259 (14); $Ph_3Si_3H_2$, 240 (8); Ph_2Si_2H, 211 (13); Ph_2Si, 182 (10); PhSi2H, 134 (13); PhSi, 105 (100)

[a] Sample size 1.6 μL; inlet, 170 °C; column (initial), 30 °C, column (final), 150 °C; heating rate, 10 deg/min. [b] Based on initial [1-pentene]. [c] $[Cp_2TiMe_2]$ = 0.021 M; [silane] = 1.2 M; [1-pentene] = 1.2 M. [d] $[Cp_2TiMe_2]$ = 0.004 M; [silane] = 1.0 M; [1-pentene] = 1.0 M. [e] These fractions were not completely separated.

Table VI. GC/MS Analyses of Products from Reactions of Norbornene with $PhSiH_3$

compd	retentn time, s	yields,[b] %		fragment, m/e (% base)
		c	d	
$NBSiH_2Ph$[e]	510	3.0	trace[f]	M – 5 H, 197 (7); M – SiH_8, 166 (3); M – C_5H_7, 135 (2); M – C_6H_8, 122 (100); $PhSiH_2$, 107 (46)
$NB(SiHPh)_2H$	1104[g]	16.0	49.0	M – C_2H_7, 277 (19); M – Ph, 231 (18); M – $PhSiH_2$, 201 (100); M – $PhSi_2H_2$, 171 (52); M – Ph_2SiH_3, 123 (21); NB, 95 (29)
$NE(SiH_2Ph)_2$[h]	1104[g]			M – C_2H_7, 277 (2); M – Ph, 231 (29); M – C_4H_{12}, 248 (3); M – PhSiH, 202 (5); M – $PhSi_2H_3$, 172 (46); M – Ph_2SiH_2, 124 (98); $PhSiH_2$, 107 (100); NB, 95 (53)
$NE[(SiHPh)_2H]_2$	1344	trace	trace	M – Ph, 443 (7); M – 2Ph, 366 (6); Ph_3Si_2H, 288 (2); M – Ph_3Si and Ph_3SiH_2, 261 (100); M – Ph_4SiH_4, 180 (43); PhSi, 105 (40)
$NB(SiHPh)_4H$	1788	trace	3.0	M – NBH_3, 422 (1), M – $PhSi_2H_4$, 383 (34); M – $Ph_2Si_2H_3$, 307 (49); M – $Ph_2Si_3H_5$, 277 (100); M – $Ph_3Si_2H_7$, 226 (16); M – $Ph_3Si_3H_7$, 198 (16); M – $Ph_3Si_4H_6$, 171 (20); PhSi, 105 (78)

[a] Sample, 1.6 μL; inlet, 270 °C; column (initial), 30 °C; column (final), 250 °C; heating rate, 10 deg/min. [b] Based on initial [norbornene]. [c] $[Cp_2TiMe_2]$ = 0.019 M; [silane] = 1.1 M; [norbornene] = 1.2 M. [d] $[Cp_2TiMe_2]$ = 0.004 M; [silane] = 0.89 M; [norbornene] = 0.93 M. [e] NB = C_7H_{11}. [f] Detectable but below 1%. [g] These peaks were not resolved by the column. The presence of two compounds was clearly evident from scanning the initial and final parts of the peak. [h] NE = C_7H_{10}.

"Ti" being **4**. In order for reactions 8 and 9 to give the rate law 7, the pseudoequilibrium 8 must lie mostly to the left and there must be a compensating process that keeps the concentrations of "Ti(ol)" and "Ti" roughly equal. It is not necessary for (9) to immediately follow (8), and it is possible that "Ti(ol)" undergoes fast reactions to a downstream intermediate which eventually reacts with a second molecule of **2**.

Co-hydrogenation/Hydrosilation of Styrene and Norbornene. The co-hydrogenations of styrene and norbornene are so fast that it is extremely difficult to do reproducible kinetic measurements because of the sensitivity of the catalyst to oxygen and other impurities at the low levels required to slow down the reactions. The activity of these two olefins is more than a hundredfold faster than those of 2-pentene and cyclohexene, and there is clear visual evidence that the titanium is in a different form than in the reactions of cyclohexene and 2-pentene. At catalyst levels of ca. 0.02 M, the reacting solution is orange-brown in the case of styrene, while that of norbornene is green. On complete depletion of the styrene, the styrene reaction mixture turns bluish green. Reaction media during co-hydrogenation of 2-pentene and cyclohexene are the typical royal blue color of compound **1**, whose presence is detected by NMR.[12]

The rate selectivity described above is much greater than is normally observed in homogeneous hydrogenation of these olefins. Although 1-olefins are generally more reactive than internal olefins, the disparity in rates for the present system is greater than usual and the disparity between cyclohexene and norbornene is particularly exaggerated.[14]

NMR analysis showed that the co-hydrogenation of norbornene with $PhSiD_3$ leads exclusively to the cis-exo dideuterio product.[15] No hydrogen/deuterium exchange between $PhSiD_3$ and the vinyl protons of the norbornene was observed by mass spectrometry.

Co-hydrogenation of norbornene by $PhSiH_3$ at low concentrations (~0.004 M) of Cp_2TiMe_2 gave results significantly different from those obtained at higher (~0.02 M) catalyst concentrations. As has been previously described, the reaction of Cp_2TiMe_2 with silanes is subject to an induction period.[12] Under conditions where the induction period is short, the catalytic chemistry is due to the intermediacy of compounds **1**–**3** and whatever species may arise from their reactions with substrates. At very low catalyst concentrations the induction period for the formation of **1**–**3** can be of the order of days. A 0.004 M solution of Cp_2TiMe_2 in phenylsilane/norbornene/toluene is very pale yellow and remains so for about 24 h before turning gray/green over a period of about an hour. During the induction period the norbornene is transformed completely into an approximately 1:1 mixture of norbornane and norbornyl-terminated oligosilanes of the

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(13) Such complexes have been proposed as intermediates in other reactions. See, e.g.: McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

(14) Hussey, A. S.; Takeuchi, Y. *J. Org. Chem.* **1970**, *35*, 643.

(15) Brown, H. C.; Murray, K. J. *J. Org. Chem.* **1961**, *26*, 631.

general formulae $C_7H_{11}(SiHPh)_nSiH_2Ph$ and $C_7H_{10}[(SiHPh)_nSiH_2Ph]_2$ (see Table VI). After the lower boiling species (solvent, reactants, and norbornane) are stripped off, the major volatile components of the oily residue are, by GC/MS, the $n = 1$ products. Higher oligomers, $n = 2$–4, both norbornyl- and hydrogen-terminated, are also detected in rapidly declining abundances.

Behavior similar to that described above for norbornene was also observed for 1-pentene and styrene, but a detailed product analysis was not carried out in the case of styrene.

A Mechanistic Proposal. While the chemistry described above is very complex, certain self-consistent patterns emerge. The interconnection of **1**, **2**, and **3** by reaction loops has already been outlined, as has the tendency of **2** to dissociate into titanocene(II) and hydridosilytitanocene(IV) fragments.[12] The rate laws for the co-hydrogenation of cyclohexene and 2-pentene point to a mechanism in which the cleavage of the binuclear complex **2** by silane is a key step and that the product(s) of that cleavage is (are) involved in the rate-determining step. The cleavage of **1** as the key step is less likely since **2** catalyzes both direct hydrogenation and isomerization without the need for the additional silane that would be necessary to generate **1**. It is more difficult to exclude the possibility that **3** may be the key binuclear species since we known very little of its chemistry.[12] It is most likely that the hydrogenations and isomerizations described in the present work involve the same intermediates as the reactions described by Pez and Kwan.[9]

Following the conventional format for coordination-catalyzed reactions of olefins, compound **4** itself, or a hydridic decomposition product, could insert olefin into the Ti–H bond. The resulting alkyl species then leads to the formation of the various observed products. Rapid reversible insertion/β-hydride elimination leads to olefin isomerization, as observed for 1-pentene, or H/D exchange, as observed for the cyclohexene/$PhSiD_3$ reaction. The hydrogenation products may arise from direct transfer of H from an Si–H or Ti–H moiety. A rapid hydrogenolysis involving free H_2 produced in the silane oligomerization loop is also a possibility since it has been shown that the direct hydrogenation of olefin by H_2 is faster than co-hydrogenation.

The strong dependence of the overall rate on the nature of the silane points to the fact that the rate of reaction 4 is strongly silane-dependent. Although there is no direct evidence for the existence of the species **4**, a zirconium analogue, which is dimerized through two hydrogen bridges, has been prepared by reaction of $PhSiH_3$ with dimethylzirconocene.[16] We believe that the key step in the dehydrogenative coupling of primary silanes is the loss of hydrogen from **4** with the formation of a metal silylene species. It is in this process that the steric properties of the silyl substituents appear to play an important role, perhaps through a strong conformational requirement for a transition state involving departure of the H from silicon across the empty Ti LUMO to form a hydrogen molecule with the Ti–H.

The unusual colors of the co-hydrogenation reaction mixtures and the very high reaction rates observed for 1-pentene, styrene, and norbornene suggest a major shift in the locus of the rate-determining step(s) and major changes in the steady-state concentrations of the catalytic intermediates. In these cases a larger proportion of the titanium is probably in the form of olefin complex or, more likely, alkyl complex. The color of the styrene reaction medium indicates that virtually none of the titanium is in the form of the dinuclear species **1**–**3**.

Scheme I

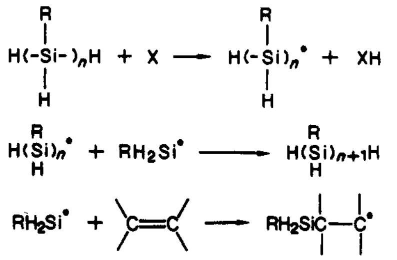
$$Cp_2TiMe_2 + RSiH_3 \rightarrow Cp_2TiMe(SiH_2R) + CH_4 \quad (10)$$

$$Cp_2TiMe(SiH_2R) \rightarrow Cp_2TiMe + RH_3Si^\bullet \quad (11)$$

$$2Cp_2TiMe + RSiH_3 \rightarrow Cp_2Ti(H)Me + Cp_2TiMe(SiH_2R) \quad (12)$$

$$2Cp_2Ti(H)Me \rightarrow 2Cp_2TiMe + H_2 \quad (13)$$

$$2RH_2Si^\bullet \rightarrow RH_2SiSiH_2R \quad (14)$$



$$H(-\underset{H}{\overset{R}{Si}}-)_nH + X \rightarrow H(-\underset{H}{\overset{R}{Si}})_n^\bullet + XH \quad (15)$$

$$H(\underset{H}{\overset{R}{Si}})_n^\bullet + RH_2Si^\bullet \rightarrow H(\underset{H}{\overset{R}{Si}})_{n+1}H \quad (16)$$

$$RH_2Si^\bullet + \rangle C{=}C\langle \rightarrow RH_2Si\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^\bullet \quad (17)$$

X = any radical species

The qualitative difference in behavior of the phenylsilane/norbornene, -styrene, and -1-hexene systems at high and at low catalyst concentrations is remarkable. The difference is related to whether or not the induction period for the formation of compounds **1**–**3** is completed before a significant proportion of the olefin has undergone reaction. At very low catalyst concentration, reaction of the olefin can be essentially complete before the induction period is over. Under such conditions the norbornene/phenylsilane reaction yields significant amounts of oligophenylsilanes, of norbornyl-terminated di- and oligosilanes, and of bis(silyl)norbornylenes. Under conditions where most of the olefin reacts after the formation of compounds **1**–**3**, the formation of norbornyl-terminated polysilanes is not observed. It is clear that the catalytic species involved during and after the induction period are quite different. Although we are far from a complete understanding of what occurs during the induction period, the following facts are known: (1) reaction of dimethyltitanocene with reactive silanes under an atmosphere of CO leads to slow formation of titanocene dicarbonyl and the formation of **1**–**3** is suppressed;[12] (2) reaction of dimethyltitanocene with triphenylgermane gives methyltriphenylgermyltitanocene and methane;[17] (3) diphenylgermane undergoes highly selective coupling to tetraphenyldigermane under induction period conditions but gives higher oligo(diphenylgermylenes) under post-induction period conditions.[17]

From the above it seems very likely that the key species in the catalytic reactions occurring during the induction period is a silylmethyltitanocene. If this is the case, the persistence of a methyl ligand in the coordination sphere of the titanium blocks the formation of **4** and the critical step (4), which is the key to post-induction period silane polymerization. A possible candidate for the induction period catalysis is a free radical chain of the type shown in Scheme I.

In this type of mechanism, the silane oligomerization resembles a condensation reaction, and in the initial stages the amounts of the various oligomers fall off steeply with increasing degree of polymerization. Such is the behavior observed with the norbornene/phenylsilane system, in sharp contrast to the post-induction period polymerization reaction where only polymer of the ultimate molecular weight is observed from the beginning of the reaction. At the same time, one is forced to the conclusion that one or more of the methyltitanium species in reaction 12 is ca-

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(16) Harrod, J. F.; Aitken, C.; Samuel, E. *Can. J. Chem.* **1986**, *64*, 1677.

(17) Harrod, J. F.; Malek, A., unpublished results.

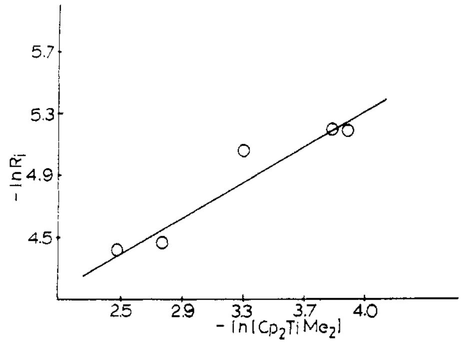

Figure 1. ln/ln plot of initial rate vs. catalyst concentration for the co-hydrogenation of cyclohexene by phenylsilane (least-squares slope = 0.54; correlation coefficient (R) = 0.96).

pable of effecting hydrogenation of the olefinic substrate. In the cases of hindered primary silanes and of secondary silanes, the rapid oligomerization process is suppressed and even the post-induction period chemistry probably proceeds by a mechanism more like that characteristic of the induction period for the more active silanes.

Experimental Section

All manipulations were carried out under argon by using standard inert-atmosphere techniques. Toluene was freshly distilled from Na/benzophenone. Fisher Scientific Co. anhydrous ether was used directly from the freshly opened can. Benzene-d_6 and toluene-d_8 were purchase from Merck, Sharpe and Dohme. All solvents, silanes, and olefins were purged by repeated evacuation and saturation with argon before use. Liquid olefins were prepurified by distillation and passage through an activated alumina column immediately prior to use. Norbornene, obtained from Aldrich Chemical Co., was sublimed under vacuum. All hydrosilanes were prepared from the chlorosilanes by a standard literature procedure.[18] Chlorosilanes were purchased from Petrarch Chemical Co. and used as received.

Compound 2 was prepared according to the previously described procedure.[12]

Kinetic measurements were carried out by using a Varian T-60 NMR spectrometer. NMR measurements for purposes of compound identification were carried out on Varian XL-300 and XL-200 FT-NMR spectrometers. The GC analyses reported in Tables V and VI were performed on a Shimadzu GC-8A chromatograph using a 30 × 0.25 mm column packed with a lu film of 95% dimethyl- and 5% diphenylpolysiloxane. GC/MS analyses were carried out on a Finnegan 700 ion trap detector, with a Varian 3500 capillary gas chromatograph.

Kinetic Measurements. A typical procedure for a co-hydrogenation experiment is the following. Stock solutions of Cp_2TiMe_2 (0.13 M), $PhSiH_3$ (1.6 M), and olefin (8.0 M) were prepared in toluene-d_8. NMR tubes were filled with appropriate aliquots of the stock solutions and made up to 0.7-mL total volume with deuteriotoluene. Following the completion of the induction period, signaled by the sudden appearance of an intense blue color, the tube was immediately placed in the NMR probe and the disappearance of reactants and appearance of products was monitored by periodic integration of the appropriate signals. Absolute concentrations were determined by calibration with standards. Limitations on the integration procedure were estimated to give a lower limit on the concentration precision of ±5%. Reactions were usually followed to about 80% completion. A few test co-hydrogenation reactions were run by using pre-prepared 2 as catalyst instead of the more convenient Cp_2TiMe_2. The rate law and rate constant were the same as those obtained by using Cp_2TiMe_2.

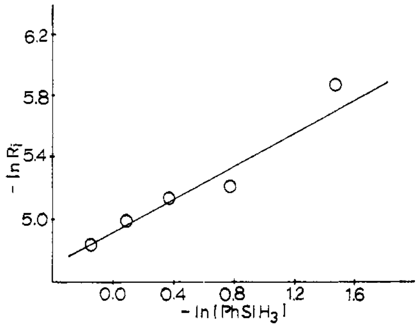

Figure 2. ln/ln plot of initial rate vs. phenylsilane concentration for the cohydrogenation of cyclohexene by phenylsilane (slope = 0.58; R = 0.95).

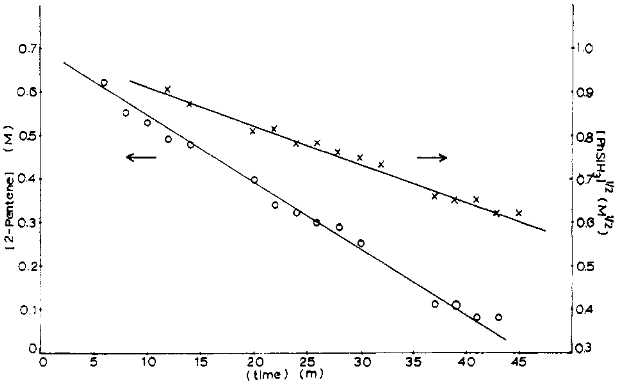

Figure 3. Zero-order (2-pentene) and half-order (phenylsilane) plots for the cohydrogenation of 2-pentene ($[Cp_2TiMe_2]$ = 0.019 M; $[PhSiH_3]_i$ = 1.15 M; $[2\text{-pentene}]_i$ = 0.77 M).

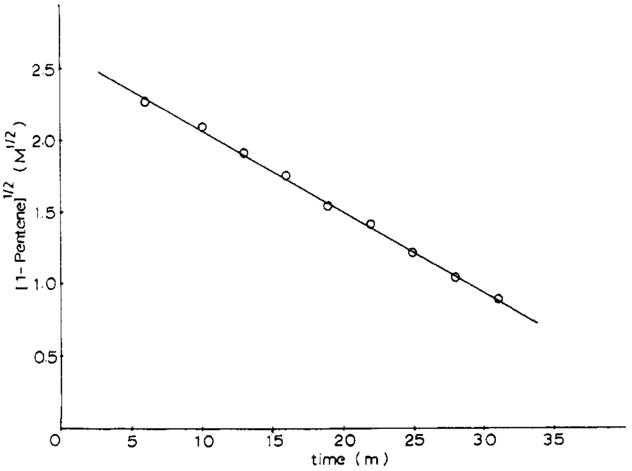

Figure 4. Half-order plot for the isomerization of 1-pentene by 2 ([2] = 0.0036 M; $[1\text{-pentene}]_i$ = 6.8 M).

Initial rates of reactions were determined by application of a nonlinear, least-squares curve fitting program to the experimental data. Reaction orders in the various reactants were determined by both log (initial rate) vs. log (concentration) plots and by linearization of concentration function vs. time plots over at least 3 half-lives. Some exemplary plots are shown in Figures 1–4.

Similar procedures were used to follow the isomerization of 2-pentene under the influence of 2 and the reaction of norbornene with phenylsilane in the induction period regime. In these cases the samples were inserted into the probe immediately since no induction period was involved. Product analyses of the complex mixtures of products arising from reactions of 1-pentene and norbornene with phenylsilane were identified by GC/MS. The identification of components, their abundances based on GC peak areas, and MS data are listed in Tables V and VI. A full description and interpretation of the mass spectra of oligophenylsilane will be published elsewhere.

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batical leave to carry out this work. We thank Dr. J. Finkenbine for the measurement of the mass spectra.

Registry No. 2, 102493-41-4; $PhSiD_3$, 18164-03-9; (p-tol)SiH_3, 931-70-4; $PhSiH_3$, 694-53-1; (n-hexyl)SiH_3, 1072-14-6; (benzyl)SiH_3, 766-06-3; (cyclohexyl)SiH_3, 18162-96-4; $PhMeSiH_2$, 766-08-5; Cp_2TiMe_2, 1271-66-5; D_2, 7782-39-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 3-methylcyclohexene, 591-48-0; 4-methylcyclohexene, 591-47-9; norbornene, 498-66-8; 2-pentene, 109-68-2; 1-pentene, 109-67-1; styrene, 100-42-5.

Theoretical and Experimental Studies of the Flash Pyrolysis of Trimethylsilyl Azide and Trimethylgermyl Azide: Generation and He I Photoelectron Spectra of Iminosilylene and Iminogermylene

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The generation and the detection of iminosilylene and its germanium analogue from trimethylsilyl (and germyl) azide by gas-phase flash pyrolysis (1100 K, 10^{-2} mbar) are described. The ab initio study of molecular rearrangements of the $(CH_3)_3SiN_3$ pyrolysis product after loss of N_2 predicts the possible formation of several compounds with the probability order $(CH_3)_2HSiN{=}CH_2 > Si{\equiv}NH + C_3H_8 > (CH_3)_2HSiCH{=}NH \gg Si{\equiv}NCH_3 + C_2H_6$. The comparison of the experimental and theoretical values of the first ionization potentials of the possible pyrolysis products indicates the formation of transient metallaisonitrile analogues $M{\equiv}NH$ (M = Si, Ge; iminosilylene and iminogermylene) and, in the case of the silyl derivative, of the imine $(CH_3)_2HSiN{=}CH_2$.

Introduction

The chemistry of unsaturated organometallic compounds with multiple bonds between a group 14 atom (except carbon) and a heteroatom has assumed increasing importance during the last several years, as shown by the large number of reviews[2-10] dealing with both theoretical and experimental aspects. The existence of these entities was proposed primarily on the basis of products obtained by chemical trapping. Relatively little work, however, has dealt with their isolation, since most are unstable and highly reactive. There exist only a limited number of spectroscopic data on this family, mostly generated in studies using argon matrix infrared spectroscopy for $R_2Si{=}O$[11-13] and $Si{\equiv}NH$,[14] mass spectroscopy for $R_2Si{=}S$,[15] and UV photoelectron spectroscopy for silane- and germanethiones,[16,17] germanone,[17,18] (phenylimino)silylene (phenylsilaisonitrile)[19] and various diatomic molecules such as SiO, GeO, GeS, GeSe, SnS, SnTe, and PbTe.[20-23] Most of these compounds were obtained by gas-phase flash pyrolysis from appropriate precursors. When the heteroatom was nitrogen, azides were found to be the most suitable precursors and thus the most often used[2,19,24,25] since they lose a nitrogen molecule relatively easy.

By analogy with results obtained by photolysis (in solution) and chemical trapping,[24,26-30] our initial aim was

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