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Studies on the Reaction between Bis((trimethylsilyl)cyclopentadienyl)niobium Trihydride and Styrene

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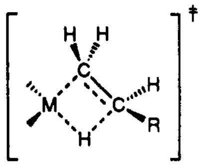
Bis((trimethylsilyl)cyclopentadienyl)niobium hydride styrene, $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(\eta^2\text{-}PhCH{=}CH_2)$ (3), has been prepared both from the reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$ (1) with styrene and from that of $Nb(\eta^5\text{-}C_5H_4SiMe_3)Cl_2$ (2) with $PhCH_2CH_2MgBr$. The first method gives rise to two isomeric products (endo, where the olefinic substituent is central, and exo, with the olefinic substituent lateral in the equatorial plane), while the latter leads exclusively to the endo isomer. The mechanism of the formation of 3 is discussed in terms of a model which implies a consecutive reaction with a reversible step and a first-order rate dependence with respect to 1. Finally, the kinetics of the olefin–hydride insertion have been studied by ^{1}H NMR spectroscopy using coalescence techniques.

Introduction

Bis(cyclopentadienyl)–hydride–olefin complexes of group 5 metals are among the more interesting hydride–olefin complexes. After the preparation of the first such complex $Nb(\eta^5\text{-}C_5H_5)_2(H)(\eta^2\text{-}C_2H_4)$, by Tebbe and Parshall[1] from the reaction of $Nb(\eta^5\text{-}C_5H_5)_2H_3$ and C_2H_4 under elevated pressure, several hydride–olefin complexes of Nb and Ta were synthesized by employing two alternative processes, namely the reaction of $M(\eta^5\text{-}C_5R_5)_2Cl_2$ and $M(\eta^5\text{-}C_5R_5)_2H_3$ (M = Nb, Ta) with various alkylmagnesium halides and olefins, respectively.[2] The first reaction proceeds via a stereospecific β-H elimination from the monoalkyl complexes $(M(\eta^5\text{-}C_5R_5)_2R$ and the second one by thermal elimination of H_2 followed by olefinic coordination to the $M(\eta^5\text{-}C_5R_5)_2H$ species.

Olefin–hydride–metal systems are of special interest in several catalytic processes; in particular, the insertion of olefins into metal–hydride bonds and its microscopic reverse, β-elimination, are very common steps in industrial catalytic reactions such as olefinic isomerization, hydrogenation, and hydroformylation.[3] In spite of this importance, to date few mechanistic studies of these processes have been described,[4] in part probably because the olefin insertion/elimination step is often reversible and fast with regard to other steps and therefore direct measurement of its kinetics is not easy. In two elegant and extensive papers Bercaw and co-workers described[2d,e] NMR studies of the dynamic processes in the olefin–hydride complexes $M(\eta^5\text{-}C_5R_5)_2(H)(\eta^2\text{-}RCH{=}CH_2)$ (R = H, Me; M = Nb, Ta). The rates of insertion of olefins were determined by magnetization transfer and coalescence techniques (^{1}H NMR). A model based on a typical planar, delocalized, four-centered cyclic transition state[5] in which the migrating hydrogen is attached to both the metal center and to one of the olefinic carbons was proposed:



Changes in both the electronic and steric factors in the olefin and/or ligand environment were extensively evaluated. In Bercaw's mechanism the olefin inserts into the metal–hydride bond, forming a 16-electron σ-alkyl species in which the metal center has a "pyramidal" structure. Rotation of the alkyl group around the C_α–C_β bond followed by β-elimination gives the olefin–hydride complex. Green and co-workers have also studied[2f] the fluxional processes with other species, $M(\eta^5\text{-}C_5H_5)_2(H)(\eta^2\text{-}RCH{=}CH_2)$ (M = Nb, Ta), using magnetization and spin-saturation transfer along with two-dimensional exchange NMR techniques, and they have proposed an alternative mechanism for the insertion/elimination step proceeding via in place rotation in 18-electron agostic alkyl intermediates.

We have previously described[6] the anomalous spectroscopic properties of various niobium trihydride derivatives and observed that those bearing electron-withdrawing

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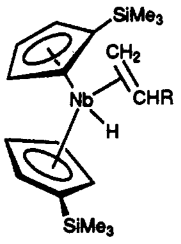
substituents, $SiMe_3$, display the largest H–H coupling constants, in agreement with the importance of a nearly dihydrogen state. Furthermore, ab initio calculations show that niobium trihydrides possess a thermally accessible hydride–dihydrogen state.[7,8] With these precedents we decided to examine the behavior of a niobocene trihydride, $Nb(\eta^5\text{-}C_5H_4Me_3)_2H_3$, toward styrene and determine the mechanism of hydride–olefin complex formation. NMR studies of the dynamic process for the olefin insertion/elimination step using coalescence techniques have also been carried out and constitute a complementary contribution to the above-mentioned works. We describe in this paper the synthesis and spectroscopic properties of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(\eta^2\text{-}PhCH{=}CH_2)$ and the results of the kinetic studies for the formation of the hydride–olefin complex and for the olefin insertion/elimination.

Results and Discussion

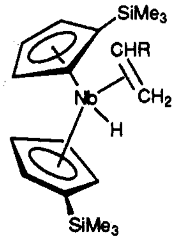
Synthesis and Characterization of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(\eta^2\text{-}PhCH{=}CH_2)$ (3). $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$ (1) reacts with 2 equiv or more of styrene at room temperature in toluene over a period of 48 h to give, after appropriate workup, yellowish microcrystals of the hydride–olefin complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(\eta^2\text{-}PhCH{=}CH_2)$ (3), in accordance with eq 1.

$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3 + 2PhCH{=}CH_2 \rightarrow Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(\eta^2\text{-}PhCH{=}CH_2) + PhEt \quad (1)$$

Alternatively, 3 can be formed when solutions of 1 in toluene are warmed to 65 °C for 3 h. Ethylbenzene is also obtained in the reaction mixture due to the hydrogenation of excess styrene. 3 was isolated as a mixture of endo and exo isomers in almost equal proportions. However, it has been pointed out that the endo isomer is sterically favored over the exo isomer. Bercaw and co-workers[2d] obtained the endo isomer with the sterically bulkier C_5Me_5 ring, while a mixture of endo and exo isomers was isolated with the C_5H_5 ring:



endo



exo

Therefore, it is not surprising that we isolated a mixture of both isomers employing the $C_5H_4SiMe_3$ ring. However, we have selectively prepared the endo isomer only (vide infra) of 3 by reacting $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ (2) with 2 equiv of $PhCH_2CH_2MgBr$ in diethyl ether, in accordance with eq 2.

$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2 + 2PhCH_2CH_2MgBr \rightarrow Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(\eta^2\text{-}PhCH{=}CH_2) \quad (2)$$

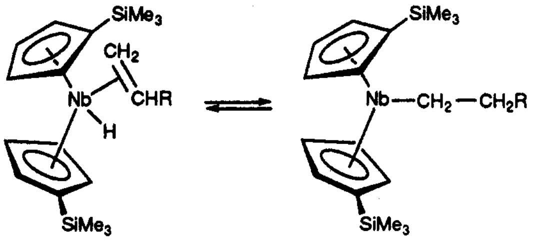
This synthetic method, which was initially described several years ago by Teuben,[2a,c] has subsequently been employed by Bercaw[2d,e] and Green[2f] in their studies. The last step of the reaction probably proceeds via stereospecific β-elimination from the monoalkyl species $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CH_2CH_2Ph)$, which has not been detected. The thermal treatment of the endo isomer with an excess of styrene for several days gives a mixture of endo and exo isomers.

Attempts to prepare other hydride–olefin complexes by reaction of 1 with olefins, namely 2,3-dimethyl-2-butene, 2-methyl-2-pentene, and cyclohexene, were not successful, because complex mixtures of products were obtained which were not characterized.

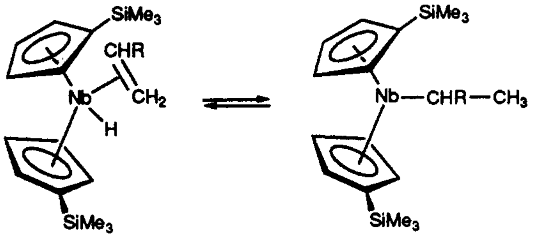
The IR spectrum of 3 shows a weak broad band at 1730 cm^{-1} assigned to ν(Nb—H). The ^1H NMR spectrum of 3, via reaction of 1 with styrene, shows the resonances of both endo and exo isomers. The spectrum of the major product corresponds to the endo isomer, which is alternatively obtained via reaction 2; both isomers show similar but slightly shifted resonances (see Experimental Section). The ^1H NMR spectrum in $(CD_3)_2CO$ shows the hydride resonances at δ −2.67 and −3.21 for the endo and exo isomers, respectively. Due to the lateral coordination of styrene the two (trimethylsilyl)cyclopentadienyl rings are inequivalent, and in the spectrum two resonances appear for the $SiMe_3$ groups of each isomer along with eight resonances for the protons of cyclopentadienyl rings. The olefinic protons exhibit a typical ABX spin system similar to that previously reported for $Nb(\eta^5\text{-}C_5R_5)_2(H)(\eta^2\text{-}PhCH{=}CH_2)$ (R = H, Me).[2d,e]

The olefinic protons of the endo isomer show three sets of doublets of doublets, the C*H*R resonance appearing at δ 3.25 and those of the CH_2, groups at δ 1.34 and 0.92. However, the olefinic protons of the exo isomer exhibit a pseudotriplet for C*H*R at δ 2.58 and two broad resonances at δ 1.57 and 1.15 for the CH_2 protons (see Experimental Section).

When the temperature is raised, an exchange of the hydride ligand with the hydrogen atoms of the olefin takes place (vide infra). A transformation of the doublet of doublets of δ 3.25 (H_X) to a triplet was observed as the result of the hydride insertion in the CHPh group to give a CH_2Ph group in the complex obtained from reaction 2. This observation supports our assignment for this species as the endo isomer. In the same way, in the spectrum of the mixture of products from reaction 1, in addition to this transformation the pseudotriplet at δ 2.58 is transformed to a quartet by the hydride insertion in the CH_2 group to give a CH_3 group in the exo isomer.



endo



exo

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Table 1. Relationship between Initial Concentrations of Reactants and Kinetic Constant Values

expt	$[Nb]_0$ (M)	$[PhCH{=}CH_2]_0$ (M)	10^5k_{app} (s^{-1})	$t_{1/2}$ (min)
I	0.13	0.19	2.75 (±0.01)	420
II	0.13	0.27	4.09 (±0.04)	282
III	0.13	0.46	8.23 (±0.04)	140
IV	0.13	0.69	9.08 (±0.06)	127
V	0.13	1.15	10.77 (±0.09)	107
VI	0.13	2.30	11.06 (±0.02)	104
VII	0.13	3.45	10.76 (±0.09)	107
VIII	0.26	2.60	10.50 (±0.09)	110

We have tried to confirm the assignment to the ^{1}H NMR resonances by difference NOE experiments which would allow the correlation of the cyclopentadienyl ligands with the neighboring olefin and hydride ligands, but unfortunately no detectable NOE on the different signals was observed. ^{13}C NMR spectra for the endo and exo isomers of **3** each show 2 resonances for the $SiMe_3$ group as well as 10 resonances for the carbon atoms of both nonequivalent cyclopentadienyl rings. In addition the olefinic signals appear at characteristic values for sp^3 carbon atoms, which suggests an appreciable metallacyclopropane character (see Experimental Section). DEPT experiments were carried out to assign the different resonances.

It was discovered that **1** polymerized styrene when an excess of this compound was present at 65 °C for 3 days, giving rise to an atactic polystyrene (a-PS) with an average molecular weight ($\bar{M}_w$) of 16 000, a melting point of 155 °C, and a value for the polydispersity ($\bar{M}_w/\bar{M}_n$, M_n = number-average molecular weight) of 1.62, which was close to the theoretical value of a homogeneous Ziegler–Natta catalyst system, indicating that the catalytic system under discussion is homogeneous.[9] The structure of the polymer was determined by ^{1}H and ^{13}C NMR spectroscopy. The polymer, in fact, shows resonances characteristic of an a-PS.[10] A typical mechanism of polymerization can be proposed, the first step being the elimination of H_2 to give Nb(η^5-$C_5H_4SiMe_3$)$_2$H, followed by coordination of styrene. The chain growth would take place through consecutive insertions of styrene into the niobium–carbon bond. The simultaneous formation of endo and exo hydride–olefin isomers could explain the loss of stereospecificity in the polymer formation. Obviously the result is not very interesting in the field of stereospecific polymerization of styrene, but it constitutes a new example of the few described group 5 metal catalysts for styrene polymerization, for instance Nb(OC_2H_5)$_5$.[11] We are currently focusing our efforts on preparing modified niobocene trihydrides in order to produce a syndiospecific polymerization of styrene.

Kinetic Studies of the Reaction of 1 with Styrene. The reaction between **1** and styrene (at 35 °C) was monitored in C_6D_6 by ^{H} NMR by systematically changing the concentration of styrene (see Table 1). A stacked plot of the hydride proton region of the NMR spectrum taken at various time intervals during the course of the reaction (experiment V; see Table 1) along with peak intensity changes of the signals for the hydride ligands of **1** are shown in Figures 1 and 2, respectively. A possible mechanism is shown in Scheme 1, which corresponds to a consecutive reaction with a reversible step.[12] In the scheme, $K'_2 = K_2[PhCH{=}CH_2]_0$, for a high initial concentration of styrene.

This mechanism is widely encountered, and it explains important reactions such as enzymatic catalysis, acid–base, heterogeneous, unimolecular reactions in the gaseous phase, etc. It can be assumed that B reaches a steady state, $K'_2 \gg K_1$, and in this state we have an apparent pseudo-first-order rate constant which should be $K_{app} = (K_1K'_2)/(K_{-1} + K'_2)$. As K_{-1} becomes negligible in comparison to K'_2, this K_{app} value for the disappearance of A becomes K_1. A plot of ln(intensity of signals) versus time results in a straight-line segment whose slope gives the value of K_{app} (Figure 3). Different values for K_{app} for several experiments are shown in Table 1.

At high concentrations of styrene a negligible dependence on the rate constant was observed such that the formation of Nb(η^5-$C_5H_4SiMe_3$)H must be the rate-limiting step and a first-order dependence of the reaction rate with respect to the concentration of **1** may be considered. Values of K_{app} at several temperature values (Table 2) for a 0.69 M concentration of styrene (experiment IV, Table 1) were calculated. The K_{app} values satisfactorily fit the Arrhenius plot (Figure 4); $K_{app} = A \exp(-E_a/RT)$. A value of 20.6 kcal mol^{-1} has been found for E_a.

Kinetic Studies of the Insertion of Styrene into the Niobium–Hydride Bond in 3. Variable-temperature NMR studies on the mixture of endo and exo isomers of **3** indicate the presence of a dynamic process corresponding to a reversible insertion and β-elimination process. The hydride of the exo isomer, which shows a value of 20 °C for the coalescence temperature, reaches the fast exchange at a lower temperature than the endo isomer. The assignation of the exchange is based on the transformations observed for the signals from the CHPh and CH_2 olefinic groups which have been mentioned previously (vide supra).

In fact, when the temperature is raised, an insertion to form the alkyl tautomer followed by rapid rotation about the Nb–C bond and a subsequent fast β-elimination occurs, in accordance with Bercaw's proposal.[2d,e] The alkyl ligand probably occupies the central site.[2f]

This behavior may affect site exchange for the two (trimethylsilyl)cyclopentadienyl rings, and the two ^{1}H NMR resonances from the $SiMe_3$ groups of both nonequivalent cyclopentadienyl rings coalesce (see Table 3).

A line-shape analysis was carried out for the $SiMe_3$ groups.[13] In the case of slow exchange at −50 °C $\delta\nu$ (differences between the signals) has values of 46 and 5 Hz for the endo and exo isomers, respectively. Several values for the line widths and rate constants (K) obtained using the appropriate equations are shown in Table 3. It is possible to obtain the free energy of activation ΔG^* from the coalescence point by using the corresponding equation.[13a] The temperature-dependent variable activation energy E_a for the K values is calculated by the Arrhenius equation (Table 4).

Obviously the plot of ln K vs $1/T$ would give the activation parameters ΔH^* and ΔS^*, but the values obtained in this manner are often inaccurate,[13a] and they have not been evaluated.

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[9] Keii, T.; Doi, Y. *Shiyokubai, Jpn.* **1979**, *21*(1), 32.

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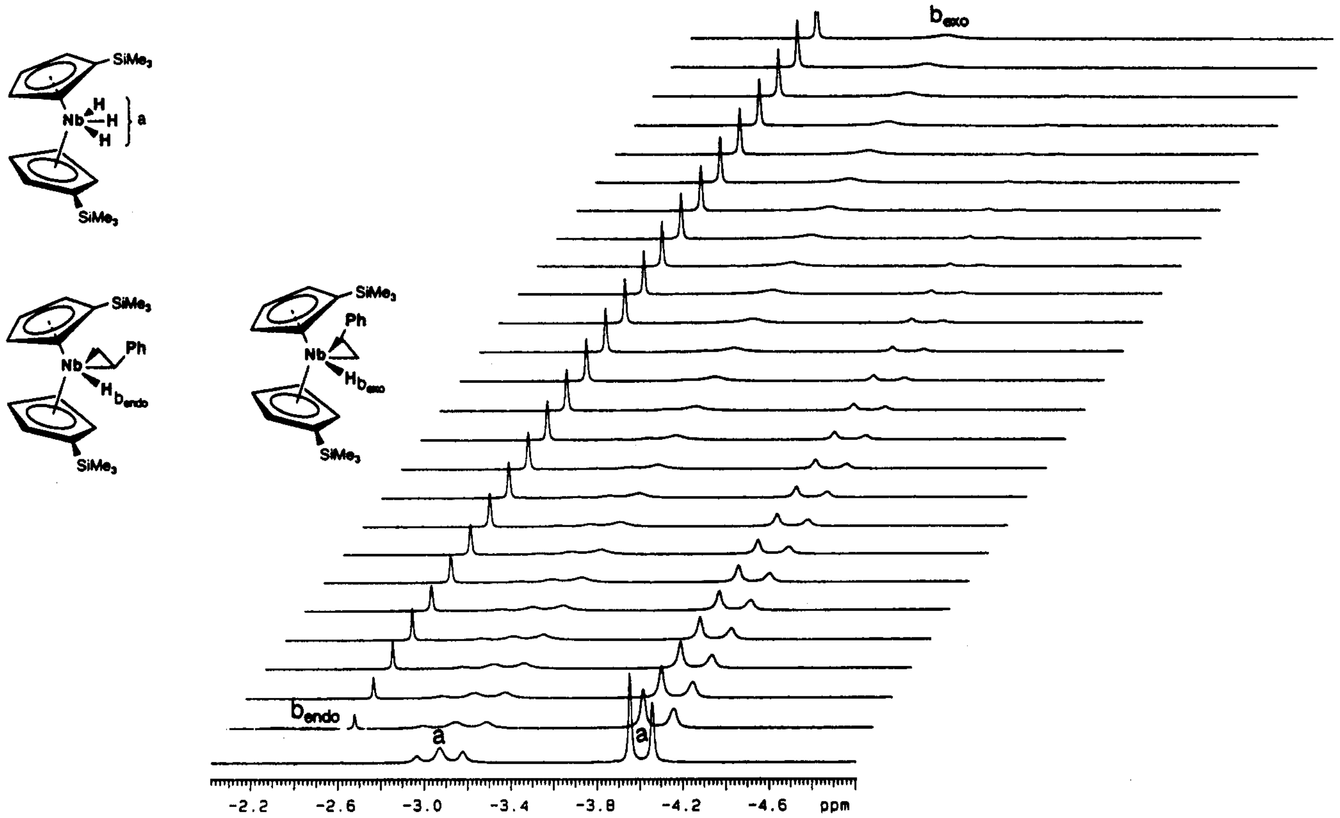


Figure 1. Hydride region of the NMR spectrum shown at various times during the course of reaction 1.

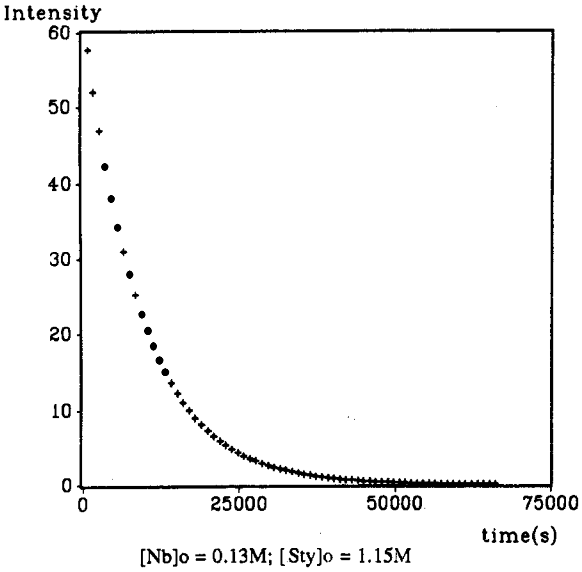
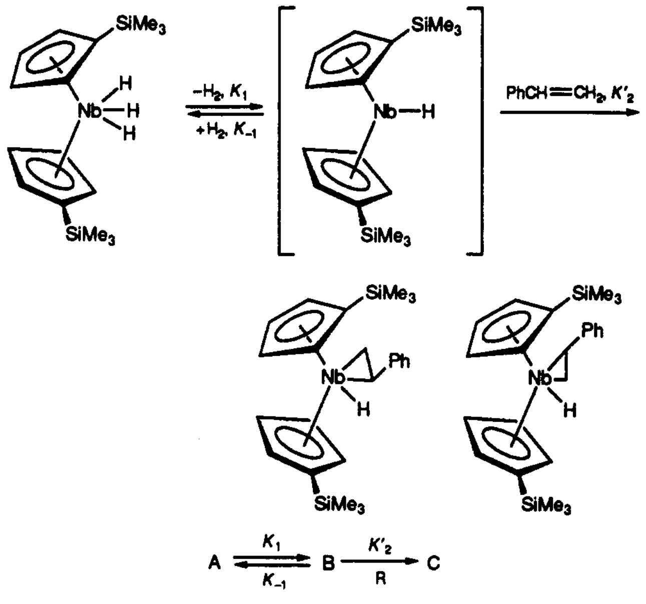


Figure 2. Normalized reactant ^1H NMR intensities plotted vs time (experiment V, Table 1).

Scheme 1



This is the first time that the use of coalescence methods has allowed the determination of the insertion rate constants for both endo and exo isomers. In some cases[2a] a lower thermal stability of the complexes hindered the application of these methods. The exo isomer 3 was found to have a much lower barrier to insertion (2.2 kcal mol^{-1} less) than the corresponding endo isomer, but the latter exhibits a faster rate constant value at the coalescence point. Although a complete study has not been performed, these results suggest that there is a kinetic control (higher E_a value) for the endo isomer whose coalescence point is reached at a higher temperature than for the exo isomer, where a thermodynamic control (lesser value of $\Delta G^{\ddagger}$) may be considered. Finally, we must point out that η^5-C_5H_4-SiMe$_3$ niobocene derivatives insert more readily than do the η^5-C_5H_5 and η^5-C_5Me_5 analogues (see Table 4).

Experimental Section

General Procedure. All handling was conducted under an inert atmosphere of dry nitrogen using standard Schlenk-tube techniques. Solvents were distilled from appropriate drying agents and degassed before use. Distilled styrene (Aldrich, 99%) and $PhCH_2CH_2Br$ (Jansen, 99%) were used without further purification. The complexes Nb(η^5-$C_5H_4SiMe_3)_2H_3$ and Nb(η^5-$C_5H_4SiMe_3)Cl_2$ were prepared as described in the literature.[6,14]

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(14) Hitchcock, P. B.; Lappert, M. F.; Milne, C. R. C. *J. Chem. Soc., Dalton Trans* 1981, 180.

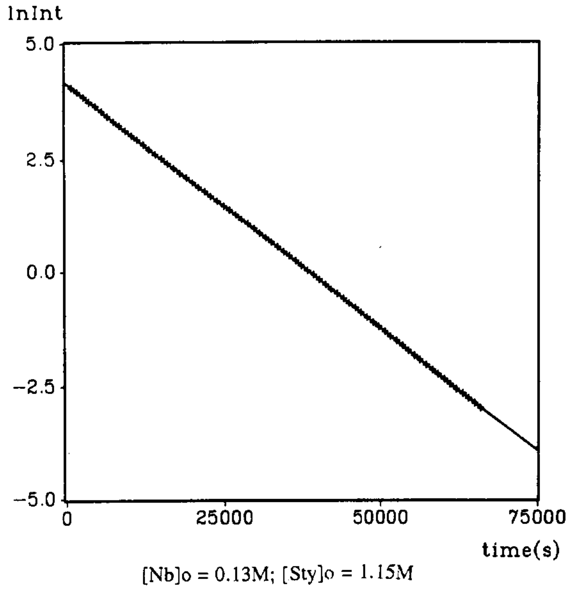


Figure 3. Pseudo-first-order rate plot for reaction 1 (experiment V, Table 1).

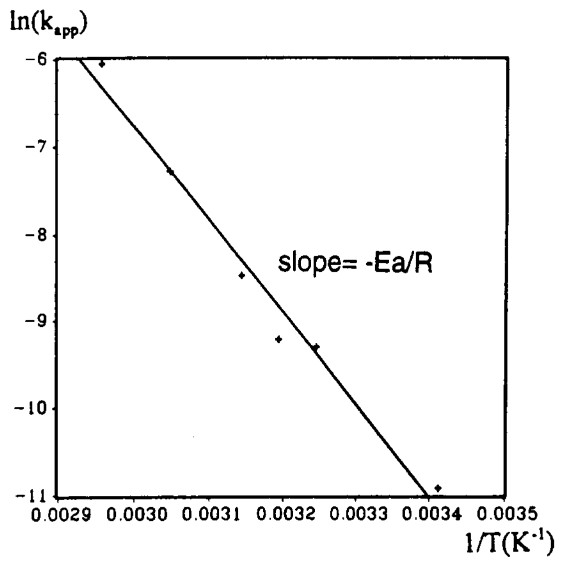


Figure 4. Arrhenius plot for reaction 1.

Table 2. Relationship between Rate Constant Values and Temperature

temp (K)	k_{app} (s^{-1})	temp (K)	k_{app} (s^{-1})
293	$(1.80 \pm 0.02) \times 10^{-5}$	318	$(20.92 \pm 0.02) \times 10^{-5}$
308	$(9.09 \pm 0.06) \times 10^{-5}$	328	$(6.87 \pm 0.07) \times 10^{-4}$
313	$(9.93 \pm 0.06) \times 10^{-5}$	338	$(2.35 \pm 0.09) \times 10^{-3}$

Table 3. Olefin Insertion Rates for 3 Obtained by the Coalescence Method

temp (K)	endo		exo	
	$w_{1/2}$ (Hz)	k	$w_{1/2}$ (Hz)	k
223	1.8	$k \ll \delta\nu$	2.0	$k \ll \delta\nu$
288	2.0	0.6	2.4	1.3
293	2.9	2.9	coalescence	11.1 (coalescence)
303	3.0	3.5	3.4	19.6
323	3.7	5.9	3.0	24.5
343	6.2	13.8	1.4	$k \gg \delta\nu$
363	14.4	39.6		
373	coalescence	102.2 (coalescence)		

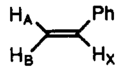
Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer. Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer. NMR spectra were recorded on a Varian Unity 300 spectrometer.

Table 4. Activation Parameters for the Hydride–Olefin Insertion Reaction of Hydride–Styrene Niobocene Complexes (in kcal mol^{-1})

isomer[e]	k	E_a	ΔG
endo (Cp′)	102.2[a]	11.4	18.6[a]
exo (Cp′)	11.1[a]	9.2	15.7[a]
endo (Cp*)[d]	29.5[a]	16.7	18.6[a]
endo (Cp)[d]	5.6[b]		20.1[b]
exo (Cp)[d]	2.2[c]		17.0[c]

[a] Calculated by coalescence techniques. [b] Calculated by magnetization transfer at 89 °C. [c] Calculated by magnetization transfer at 25 °C. [d] Data taken from ref 2d,e. [e] Abbreviations: Cp = C_5H_5; Cp′ = $C_5H_4SiMe_3$; Cp* = C_5Me_5.

Preparation of Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(η^2-PhCH=CH_2) (3) (Mixture of Endo and Exo Isomers). Compound 1 (0.300 g, 0.81 mmol) was dissolved in 20 mL of toluene. A 0.19-mL portion (1.62 mmol) of distilled styrene was added by syringe to the solution at room temperature. The mixture was warmed to 65 °C and stirred for 3 h. Alternatively the reaction can be carried out at room temperature over 48 h. The resulting solution was filtered and evaporated to dryness. The green-brown oily residue was extracted with 20 mL of hexane. After concentration and cooling, 0.34 g (90%) of complex 3 was obtained as a very air-sensitive yellowish microcrystalline solid.



IR (Nujol; cm^{-1}): 1730, 1592, 1245, 1448. ^1H NMR ($(CD_3)_2CO$; δ): endo isomer, −2.67 (s, 1H, Nb–H), 0.25 (s, 9H, $SiMe_3$), 0.41 (s, 9H, $SiMe_3$), 0.92 (dd, J_{BA} = 6 Hz, J_{BX} = 15 Hz, 1H, H_B), 1.34 (dd, J_{AB} = 6 Hz, J_{AX} = 18 Hz, 1H, H_A), 3.25 (dd, J_{XA} = 18 Hz, J_{XB} = 15 Hz, 1H, H_X), 4.03 (s, 1H), 4.09 (s, 2H), 4.39 (s, 1H), 4.64 (s, 1H), 5.29 (s, 1H), 5.50 (s, 1H), 5.69 (s, 1H) (η^5-C_5H_4, exact assignment not possible), 6.70–7.20 (m, 5H, Ph); exo isomer, −3.21 (s, 1H, Nb–H), 0.29 (s, 9H, $SiMe_3$), 0.32 (s, 9H, $SiMe_3$), 1.15 (br, 1H, H_B, −30 °C), 1.57 (br, 1H, H_A, −30 °C), 2.58 (pst, J_{XB} = 9 Hz, ^1H, H_X, −30 °C), 3.48 (s, 1H), 3.82 (s, 1H), 4.35 (s, 1H), 4.45 (s, 1H), 5.32 (s, 1H), 5.50 (s, 1H), 5.75 (s, 1H), 5.90 (s, 1H) (η^5-C_5H_4, exact assignment not possible), 6.80–7.43 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$; δ): endo isomer, 0.59, 0.64 ($SiMe_3$), 14.5 (CH_2), 34.7 (CH), 94.7, 95.2, 96.9, 97.8, 99.8, 101.2, 103.3, 104.0, 104.6 ($C_5H_4SiMe_3$), 121.7, 126.7, 127.9, 152.0 (Ph); exo isomer, 0.50, 0.56 ($SiMe_3$), 10.8 (CH_2), 27.2 (CH), 91.1, 91.8, 95.1, 96.2, 96.3, 100.4, 100.6, 103.8, 105.6, 106.1 ($C_5H_4SiMe_3$), 122.1, 128.1, 129.1, 153.5 (Ph). Anal. Calcd for $C_{24}H_{35}Si_2Nb$: C, 61.05; H, 7.41. Found: C, 61.12; H, 7.43.

Preparation of *endo*-Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(η^2-PhCH=CH_2). To a suspension of 2 (1 g, 2.3 mmol) at 1 g, 2.3 mmol) at −20 °C in 50 mL of diethyl ether was added 2.5 mL of $PhCH_2CH_2MgBr$ (1.82 M). The mixture was stirred at 25 °C for 12 h. The resulting yellow suspension was filtered off and the filtrate evaporated to dryness. The residue was extracted with diethyl ether (3 × 20 mL). Complex 3 was obtained as a microcrystalline solid (0.38 g, 35%) after concentration and cooling of the solution.

Kinetics of the Reaction of 1 with Styrene. Determination of First-Order Rate Constants. A measured amount of 1 (40 mg) was dissolved in toluene-d_8 in a 5-mm NMR tube, and distilled styrene was added by syringe; the final volume was 0.8 mL, and the concentrations of styrene were systematically varied (see Table 1). The tube was vigorously shaken for about 5 s and then placed into the spectrometer. Each spectrum recorded at 35 °C was the result of coadding 16 transients which required nearly 1 min to acquire. Spectra were automatically recorded every 10 min using the software for kinetic analysis from Varian. Spectra were not transformed into the frequency domain until all measurements were completed. Variations of intensity of the more intense peak from the pseudodoublet for the hydride ligands in 1 were measured. A computer analysis method for intensities gives a straight-line segment in a plot of ln(intensity) against time. The error is given by the standard deviation in the regression analysis. Similar experiments were carried out for determined concentrations of styrene (at several temperature values; see Table 2).

Measurement of Styrene Insertion Rates Using Coalescence Techniques. The coalescence of two trimethylsilyl ($SiMe_3$) resonances from cyclopentadienyl rings in the endo and exo isomers forms of 3 was observed by ^1H NMR at 100 and 20 °C, respectively. A typical sample was prepared by dissolving 3 (0.5 g, 1.06 mmol) in toluene-d_8 (0.8 mL) in a 5-mm NMR tube. Spectra were automatically recorded at several temperatures in the range −50 to +100 °C. Line widths at half-height ($w_{1/2}$) for $SiMe_3$ resonances for each isomer were measured at various temperature values. Peak separation in the slow exchange limit ($\delta\nu$) was measured at −50 °C. The Gutowsky equation, $K = \pi\delta\nu(2^{1/2})$,[13a] was used to determine the rate constant at coalescence. $\Delta G^{\ddagger}$ can be calculated from the equation[13a]

$$\Delta G^{\ddagger}/RT_{\mathrm{c}} = \ln(2^{1/2}R/\pi Nh) + \ln(T_{\mathrm{c}}/\delta\nu) = 22.96 + \ln(T_{\mathrm{c}}/\delta_{\nu})$$

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Supplementary Material Available: Text giving additional details on the kinetic studies and figures giving variable-temperature ^1H NMR spectra for 3 and kinetic graphs for the reaction of 1 with styrene (36 pages). Ordering information is given on any current masthead page.

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