between energy and electron-transfer quenching is an active field of inquiry.[12] Our results are the first to show the driving force dependence of the electron-transfer component. Lee, Bakac, and Espenson have found that quenching of the doublet excited state of $Cr(bpy)_3^{3+}$ by ferrocene can be partitioned into electron and energy transfer components, but a correlation with Marcus theory was not established.[13]

With Fc quenching of $Ru(bpy)_3^{2+}$ the driving force for electron transfer of ~ 0.4 eV is insufficient to overcome the preference for energy transfer quenching, which is 0.4 eV downhill in all cases. Although electron transfer can occur at a longer distance than energy transfer the extra solvent and internal reorganization energy needed to accommodate the electron transfer strongly favors quenching by energy transfer at equal driving force. We find that in the systems studied an electron transfer driving force of ~ 1.5 eV is necessary to achieve equal quenching by electron and energy transfer.

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Zirconium-Catalyzed, Highly Regioselective Hydrosilation Reaction of Alkenes and X-ray Structures of Silyl(hydrido)zirconocene Derivatives[1]

Tamotsu Takahashi*

Coordination Chemistry Laboratory
Institute for Molecular Science
Myodaiji, Okazaki 444, Japan

Maki Hasegawa, Noriyuki Suzuki, and Masahiko Saburi

Department of Industrial Chemistry
The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Christophe J. Rousset,[†] Phillip E. Fanwick, and
Ei-ichi Negishi*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907
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Hydrosilation reactions catalyzed by late transition metals[2] have been extensively studied. In contrast, few examples have been reported for hydrosilation catalyzed by early transition metals.[3]

[†] D. Ross Fellow, Purdue University (1988-1990).
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**Table I.** Hydrosilation of Alkenes Catalyzed by Zirconocene and Related Complexes[a]

silane	alkene	catalyst	product	yield,[b] %
H_2SiPh_2	1-octene	Cp_2ZrEt_2	n-OctSiHPh$_2$	73 (65[c])
H_2SiPh_2	1-octene	$Cp_2Zr(n$-Bu$)_2$	n-OctSiHPh$_2$	75
H_2SiPh_2	1-octene	Cp_2ZrMe_2	n-OctSiHPh$_2$	10
H_2SiPh_2	1-octene	Cp_2TiEt_2	n-OctSiHPh$_2$	9
H_2SiPh_2	1-octene	Cp_2NbEt_2	n-OctSiHPh$_2$	tgrace
H_2SiPh_2	2-octene	Cp_2ZrEt_2	n-OctSiHPh$_2$	53
H_2SiPh_2	1-decene	Cp_2ZrEt_2	n-DecSiHPh$_2$	– (70[c])
H_2SiPh_2	styrene	Cp_2ZrEt_2	$Ph(CH_2)_2SiHPh_2$	78
H_2SiPh_2	β-methylstyrene	Cp_2ZrEt_2	$Ph(CH_2)_3SiHPh_2$	65
H_3SiPh	1-octene	Cp_2ZrEt_2	n-OctSiH$_2$Ph	41

[a] The reaction was run in THF at 50 °C; alkene/silane/catalyst = 1/1.2/0.1. [b] By GLC. [c] Isolated yield.

Scheme I
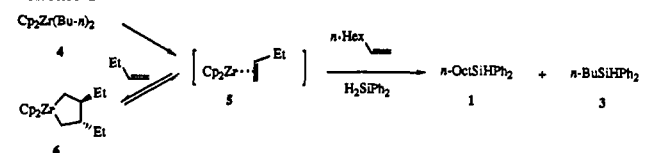
One possible competing reaction in the latter is polymerization of silanes catalyzed by early transition metals, which can take place even in the presence of alkenes.[4] We report herein a highly regioselective, zirconium-catalyzed hydrosilation reaction of 1-alkenes, which promises to be of considerable generality and synthetic utility.

$$RCH{=}CH_2 + H_2SiPh_2 \xrightarrow{\text{cat. } Cp_2ZrR'_2} RCH_2CH_2SiHPh_2 \quad (1)$$
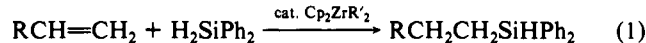
R = n-Hex, n-Oct, Ph, etc.; R' = Et or n-Bu

Typically, to a mixture of Cp_2ZrCl_2 (0.1 mmol) and THF (5 mL) was added EtMgBr (0.3 mmol) at -78 °C. After the mixture was stirred for 1 h, 1-octene (1.0 mmol) and H_2SiPh_2 (1.1 mmol) were added, and the mixture was stirred at 25 °C for 1 h. Complete consumption of H_2SiPh_2 was observed, and the desired hydrosilation product, n-OctSiHPh$_2$ (1), was obtained in 73% yield with >99% regioselectivity along with EtSiHPh$_2$ (2) obtained in 10% yield based on H_2SiPh_2. No dimer of H_2SiPh_2 was detected. The use of just 2 equiv of EtMgBr, i.e., 0.2 mmol, led to only a $\sim 10\%$ yield of 1. The experimental results are summarized in Table I, and the following are noteworthy. First, no reaction is observed with 1-octene and H_2SiPh_2 in the absence of the zirconocene-based catalyst. The use of $Cp_2Zr(n$-Bu$)_2$ in place of Cp_2ZrEt_2 led to a 75% yield of 1 and a 10% yield of n-BuSiHPh$_2$ (3). On the other hand, the use of Cp_2ZrMe_2 led only to a 10% yield of 1. Reagents generated in situ by the reaction of Cp_2TiCl_2 and Cp_2NbCl_2 with 2-3 equiv of EtMgBr gave insignificant amounts (<10%) of the desired hydrosilation products. Secondly, not only simple 1-alkenes, such as 1-octene and 1-decene, but also styrene and internal alkenes, such as 2-octene and β-methylstyrene, are convertible to the corresponding terminally silated products. Thirdly, the regioselectivity in all cases investigated to date is >99%. This high regioselectivity is particularly noteworthy in view of the moderate regioselectivity observed with the previously known catalysts.[2d-f,3c] In the case of internal alkenes, their pos-

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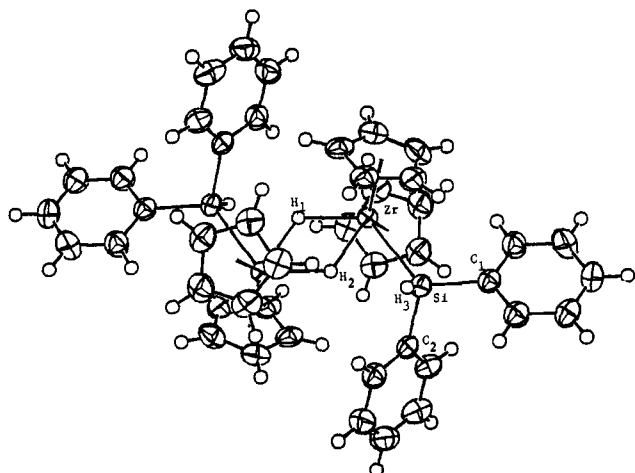
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Figure 1. Selected bond distances (Å) and angles (deg) are as follows: Zr–Si = 2.7590 (8), Zr–H$_1$ = 2.01 (2), Zr–H$_2$ = 1.96 (3), Si–H$_3$ = 1.43 (3), Si–C$_1$ = 1.902 (3), H$_1$–Zr–H$_2$ = 60 (1), Zr–H–Zr = 120 (1), Si–Zr–H$_2$ = 63.5 (7), Si–Zr–Cp = 102.25 (8), Cp–Zr–Cp = 122.67 (1), H$_1$–Zr–Cp = 102.2 (7).
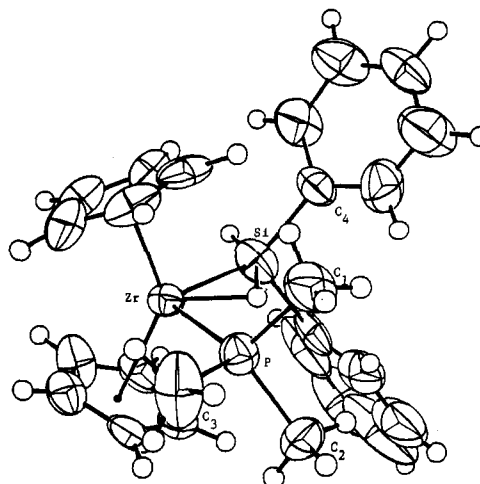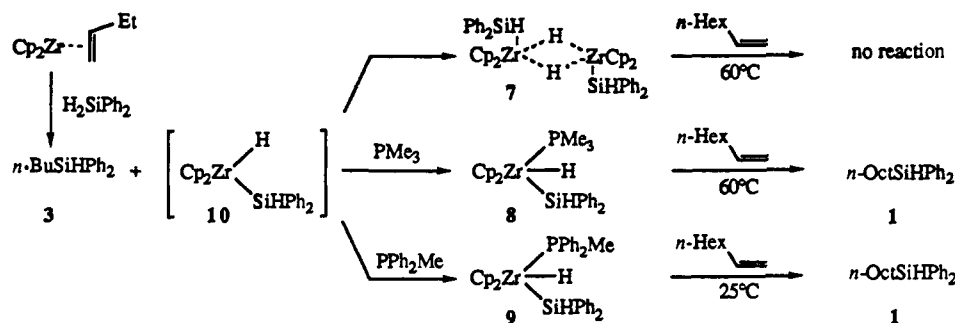

Figure 2. Selected bond distances (Å) and angles (deg) are as follows: Zr–P = 2.676 (5), Zr–Si = 2.707 (5), Si–C$_4$ = 1.90 (2), P–C$_1$ = 1.78 (2), Cp–Zr–Si = 101.2 (5), Cp–Zr–Cp = 127.2 (7), Cp–Zr–P = 102.5 (7), P–Zr–Si = 112.6 (2), C$_1$–P–C$_2$ = 102.1 (9). The two hydrogen hydrides were located, but their positions were not refined.

Scheme II

itional isomerization rather than silane isomerization appears to take place prior to hydrosilation, because cyclic alkenes, such as cyclohexene and cyclooctene, do not give any noticeable amounts of hydrosilation products. Fourthly, the reaction of 1-octene with H$_3$SiPh catalyzed by 10 mol % of Cp$_2$ZrEt$_2$ gave *n*-OctSiH$_2$Ph in 41% yield, although the corresponding reaction with HSiEt$_3$ did not proceed under the same conditions.

We have so far been mainly concerned with the scope and synthetic potential of the reaction. However, the following results shed some light on its mechanism. The reaction of Cp$_2$Zr(*n*-Bu)$_2$ (**4**) with 1 equiv of H$_2$SiPh$_2$ gave *n*-BuSiHPh$_2$ (**3**) in 53% yield. Since it has recently been shown[5] that **4** decomposes to give **5**, it is likely that **5** is an intermediate in the reaction. Even **6**[6] reacted with H$_2$SiPh$_2$ to give **3** in 67% yield, indicating that **6** may serve as a reservoir of **5** (Scheme I).

The reaction of **4** with 2 equiv of H$_2$SiPh$_2$ produced not only **3** in 70% yield but also a yellow crystalline compound in 85% yield, which has been fully identified as the double-hydrido-bridged

dimer of Cp$_2$Zr(H)SiHPh$_2$, i.e., **7** (Scheme II). Its X-ray ORTEP diagram is shown in Figure 1. Although X-ray diffraction analysis of a similar but unsymmetrically substituted dimer, i.e., Cp$_2$Zr-(SiHMePh)(μ-H)$_2$(PhMe$_2$Si)ZrCp$_2$, has very recently been disclosed,[7] its X-ray structure has not been fully resolved. Some other ZrCp$_2$ dimers with two hydrido bridges have also been suggested.[8] However, only a few have been characterized by X-ray analysis.[9] The formation of **7** clearly indicates that some Cp$_2$Zr[II] derivatives, e.g., **5**, undergo oxidative addition to H$_2$SiPh$_2$ to give **7**. To our surprise, **7** has proven to be inert to 1-octene, which rules out the intermediacy of **7** in the hydrosilation. The dimer **7** was also inert to acetone, PMe$_3$, or even 3 N HCl at 25 °C.

To further probe the possible intermediacy of silyl(hydrido)-zirconocene derivatives, Cp$_2$Zr(*n*-Bu)$_2$ was mixed with H$_2$SiPh$_2$ (2 equiv) and PMe$_3$ (1.3 equiv) at –78 °C, and the mixture was warmed to 25 °C to produce **3** in 80% GLC yield. The ^{1}H NMR spectrum of this reaction mixture indicated the formation in 90% yield of a Cp$_2$Zr derivative, which exhibited a Cp signal of δ 5.32 (d, *J* = 3 Hz) and has been isolated as a pale yellow powder and identified as a 5:1 mixture of **8**[10] and an isomeric byproduct. A purer sample of **8** was obtained by recrystallization (THF), and

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an ORTEP diagram of its molecular structure is shown in Figure 2. In contrast with **7**, treatment of **8** with 3 N HCl readily gave H_2SiPh_2. Although the reaction of **8** with 1-octene was very sluggish at 25 °C, it proceeded smoothly at 60 °C to give *n*-OctSiHPh₂ in 80% yield in 6 h. Similarly, the reaction of **4** with H_2SiPh_2 (2 equiv) in the presence of PPh_2Me (1.3 equiv) gave **3** in quantitative yield and a $ZrCp_2$ species (70%), tentatively identified as $Cp_2ZrH(SiHPh_2)(PMePh_2)$ (**9**) on the basis of a ^1H NMR Cp signal at δ 5.27 (d, $J = 3$ Hz). This complex reacted with 1-octene even at 25 °C to give a 75% yield of *n*-OctSiHPh₂ (**1**). The corresponding reactions of **9** with 2-octene also gave **1** in 90% yield. However, attempts to isolate and purify **9** were unsuccessful. These results suggest that, under the catalytic conditions, the monomer of **7**, i.e., $Cp_2ZrH(SiHPh_2)$ (**10**), probably is generated in situ and reacts with alkenes to give hydrosilated products before dimerization to produce **7**. Such a hydrosilation may involve either hydrozirconation[11] or silylzirconation[12] followed by reductive elimination to form a C–Si or C–H[8] bond. All but reductive elimination to form a C–Si bond are precedented. However, elucidation of these mechanistic details requires further investigation.

Supplementary Material Available: Experimental details for the syntheses of **1**, **7**, and **8**, ^1H and ^{13}C NMR, IR, and mass spectral data for **7**, **8**, and various diphenylsilanes, and ORTEP representations of **7** and **8** (5 pages). Ordering information is given on any current masthead page.

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Spectrophotometric Detection of a Modified Flavin Mononucleotide (FMN) Intermediate Formed during the Catalytic Cycle of Chorismate Synthase

Manoj N. Ramjee,† John R. Coggins,‡ Timothy R. Hawkes,§ David J. Lowe,† and Roger N. F. Thorneley*,†

AFRC Institute of Plant Science Research
Nitrogen Fixation Laboratory, University of Sussex
Brighton, Sussex, BN1 9RQ U.K.
Department of Biochemistry, University of Glasgow
Glasgow, G12 8QQ U.K.
ICI Agrochemicals, Jealotts Hill Research Station
Bracknell, Berks, RG12 6EY U.K

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Chorismate synthase (EC 4.6.1.4), the seventh enzyme in the shikimate pathway,[1] catalyzes the conversion of 5-enolpyruvyl-shikimate 3-phosphate (EPSP) to chorismate in a reaction that involves the trans 1,4-elimination of the C-6-*pro-R* proton and the C-3 phosphate ion²⁻⁴ (Scheme I). Although this reaction does not involve an overall oxidation or reduction, a reduced flavin cofactor (i.e., $FMNH_2$) is required for activity.⁵⁻⁷ The enzyme
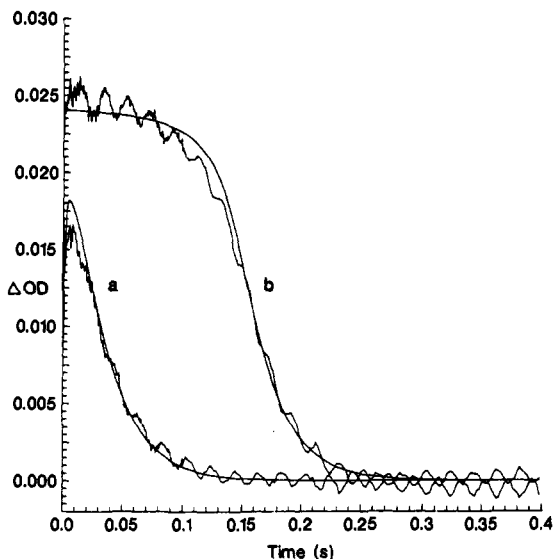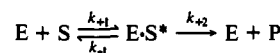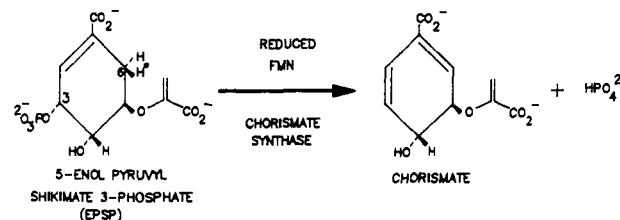
* Author to whom correspondence should be addressed.
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‡ University of Glasgow.
§ ICI Agrochemicals.

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Figure 1. Transient absorbance change at 400 nm for (a) a single-turnover experiment at 25 °C, pH 7.0 [chorismate synthase, 17 μM (sp act. 13 μmol of chorismate produced min⁻¹ mg⁻¹);[19,20] EPSP, 20 μM; $FMNH_2$, 40 μM; $Na_2S_2O_4$, 1 mM] and (b) a multiple-turnover experiment (concentrations as for Figure 1a except EPSP increased to 100 μM). The lines through the data were simulated using The values of

Scheme I. The C6-H* Proton and the C3-Phosphate Are Eliminated

5-ENOL PYRUVYL
SHIKIMATE 3-PHOSPHATE
(EPSP)

CHORISMATE

$$E + S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} E{\cdot}S^* \xrightarrow{k_{+2}} E + P$$

The values of the rate constants were constrained so that k_{+1} was 5 × 10⁷ M⁻¹ s⁻¹ (it must be >10⁷ M⁻¹ s⁻¹ as judged from the rise time observed in the traces) and so that k_{-1} = 70 s⁻¹ gave a K_s for EPSP of 2.2 μM (the same as the K_m determined for the *N. crassa* enzyme[10]). The best fit value of k_{+2} = 38 s⁻¹ is relatively insensitive to the precise values of k_{+1} and k_{-1} in these ranges. The absorbance change was assumed to be proportional to the concentration of the intermediate E·S*. We do not wish to imply that this intermediate is the only transient form of the enzyme nor that k_{+2} is necessarily associated with product release.

from *Escherichia coli* is therefore routinely assayed in the presence of 10 μM FMN and 1 mM sodium dithionite ($Na_2S_2O_4$).[8] The availability of purified enzyme either from *Neurospora crassa* or overproducing strains of *E. coli* has previously restricted mechanistic studies to steady-state kinetic determinations of K_m for EPSP (2.7 μM[9] and 2.2 μM[10]) and K_i for iso-EPSP (8.7 μM),[9] the detection of an isotope effect with (6R)-[6-²H]EPSP,[10] and one pre-steady-state rapid-quench experiment which failed to detect either a lag or a burst phase for P_i release.[11] The role of

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