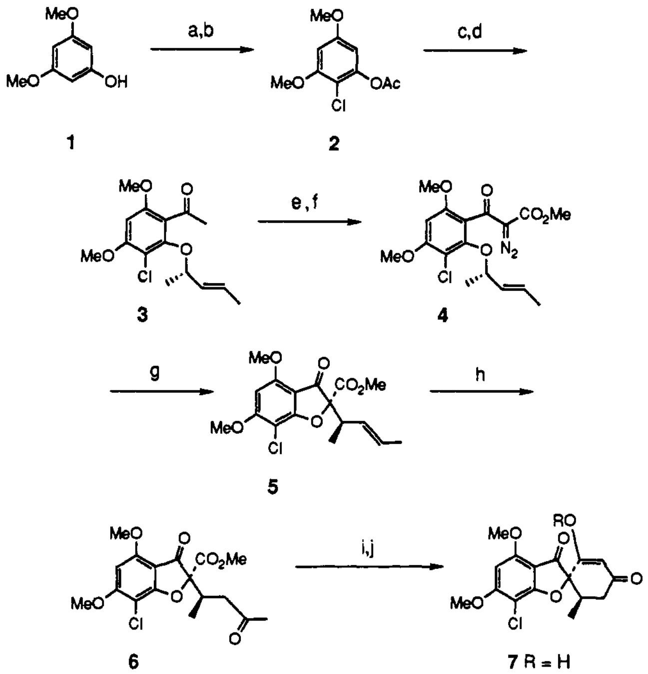
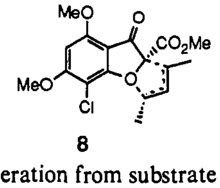
**Scheme I**[a]



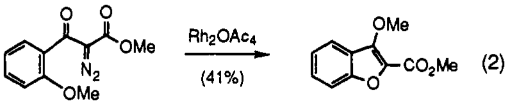
[a] (a) $SO_2Cl_2$, 68% (ref 7); (b) $Ac_2O$, pyridine, 93%; (c) $AlCl_3$, chlorobenzene, reflux, 30 min, 94%; (d) (*R*)-pent-3-en-2-ol, diisopropylazodicarboxylate, tributylphosphine, 73%; (e) 2 equiv of LHMDS, $NCCO_2Me$, THF, -78 °C, 78%; (f) $MsN_3$, $Et_3N$, 95%; (g) $Rh_2(piv)_4$, benzene, 1 h, reflux, 62%; (h) (1) $O_3$, $CH_2Cl_2/MeOH$, DMS; (2) $Ph_3P{=}C(CH_3)CO_2$-*t*-Bu, THF, room temperature, 70%; (3) TFA, 100%; (4) diphenyl phosphorazidate, $Et_3N$; reflux, toluene, then $HCl/H_2O$, reflux, 2 h, 80%; (i) NaOMe, MeOH, room temperature, 49%; (j) $CH_2N_2$, THF, room temperature, 95% (3:2 mix).

ee (prepared by resolution).[9] Asymmetry is thereby introduced and used in the elaboration of the spirocyclic stereocenter. The *S* ether **3** ($[\alpha]_D$ +22.8°) is methoxycarbonylated using Mander's reagent,[10] and the resulting β-keto ester is subjected to diazo transfer[11] to provide the key diazo ketone intermediate ($[\alpha]_D$ −6.9°). Decomposition of **4** is conducted with 5 mol % of rhodium pivalate catalyst in refluxing benzene for 1 h, providing the sigmatropic rearrangement product **5** ($[\alpha]_D$ −59.9°) in 62% yield after purification. No other stereoisomers or regioisomers can be detected in the crude reaction mixture. The stereochemistry of this process can be understood in terms of a transition-state model **8** that resembles an oxabicyclo[3.3.0]octane ring system with the key, stereochemistry-defining methyl group located on the convex face. The synthesis is completed by conversion of **5** to methyl ketone **6** ($[\alpha]_D$ +120.6°), which in racemic form has earlier served as an intermediate in griseofulvin synthesis.[5d] Its Dieckmann cyclization is conducted under superior conditions to provide griseofulvic acid (**7**) and thence griseofulvin. The material obtained (5% from **1**) is identical by NMR, IR, TLC (4:1 ethyl acetate/hexane), and optical rotation to the natural product.



**8**

Oxonium ylide generation from substrate **4** raises an important issue of reaction selectivity because there are two *o*-alkoxy groups. Ylide formation might occur at either, with the product ratio being determined by their relative rates of formation and available reaction pathways. To discern the possible fate of an *O*-methyl ylide, we prepared a diazo ketone from *o*-anisic acid. The product of its rhodium-catalyzed decomposition, isolated in 41% yield, is a benzofuran derived from 1,4-migration (eq 2). In the case of the griseofulvin synthesis, no products derived from the *O*-methyl ylide could be found. This result suggests that a Curtin–Hammett situation obtains. The symmetry-allowed [2,3]-sigmatropic rearrangement pathway having the lowest activation barrier is exclusively observed. Any *O*-methyl ylide formed from **4** must reverse.



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**Supplementary Material Available:** Experimental procedures and spectral data for **1–7** (4 pages). Ordering information is given on any current masthead page.

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# Competitive Energy and Electron-Transfer Quenching of Excited Ruthenium Polypyridyls by Ferrocene Derivatives

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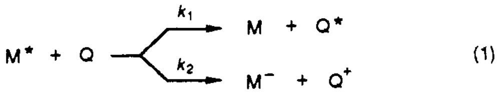
We report results showing that quenching of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and $Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine) by ferrocene and several methyl derivatives occurs competitively by both energy and electron transfer, eq 1. The relative fraction of electron transfer to total quenching can be tuned by varying the driving force for electron transfer as anticipated by Marcus theory.[1] The series of quenchers used is ferrocene (Fc), 1,1′-dimethylferrocene ($Me_2Fc$), 1,2,3,4,5-pentamethylferrocene ($Me_5Fc$), 1,1′,2,2′,3,3′,4,4′-octamethylferrocene ($Me_8Fc$), and decamethylferrocene ($Me_{10}Fc$). This series is useful in our study because the $E_{1/2}$ values vary from 0.38 to −0.11 V vs SCE in $CH_3CN$/0.1 M $[n\text{-}Bu_4N]PF_6$, whereas the lowest triplet excited states of ferrocenes are ligand field states of nearly the same energy, 1.8 eV.[2] The oxidizing power of excited $Ru(bpy)_3^{2+}$ and $Ru(bpz)_3^{2+}$ is 0.80 V vs SCE and 1.36 V vs SCE, respectively,[3] whereas the lowest excited-state energies, 2.15 eV, are essentially the same.[4] Therefore variation of either ferrocene quencher or



$$M^* + Q \begin{cases} \xrightarrow{k_1} M + Q^* \\ \xrightarrow{k_2} M^- + Q^+ \end{cases} \qquad (1)$$

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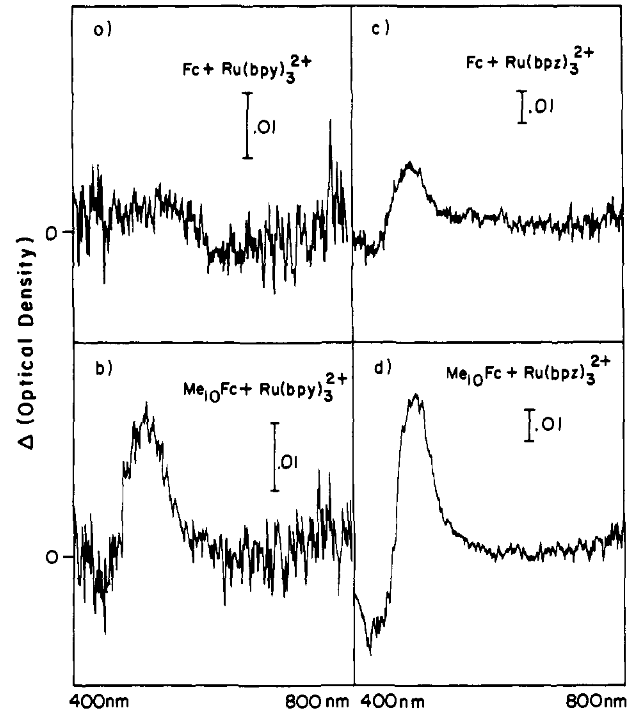

**Figure 1.** Transient absorption spectra with 10-ns resolution taken 300 ns after excitation at 416 nm. Chromophore concentration is $2 \times 10^{-4}$ M, and ferrocene concentration is $2 \times 10^{-3}$ M in $CH_3CN$ with 0.1 M [$n$-$Bu_4N$]$PF_6$. Note the different absorbance scales for the four spectra. The absorption in (b) is due to Ru(bpy)$_3^+$ and in (c) and (d) is due to Ru(bpz)$_3^+$.

excited-state reagent changes the driving force for electron transfer but not for energy transfer.

All of the ferrocene derivatives quench the luminescence of the excited Ru(bpy)$_3^{2+}$ [5a] and Ru(bpz)$_3^{2+}$, and the quenching obeys the Stern–Volmer relationship.[5b] The quenching rate constants in $CH_3CN$ with 0.1 M [$n$-$Bu_4N$]$PF_6$ are 1.1 (±0.2) × $10^{10}$ $M^{-1}$ $s^{-1}$, the diffusion-controlled limit. The nature of the quenching process, energy or electron transfer is, of course, not revealed by the values of the quenching constants. Electron-transfer quenching can be measured by monitoring transient absorption at 510 nm ($\epsilon = 1.2 \times 10^4$ $M^{-1}$ $cm^{-1}$)[6] for Ru(bpy)$_3^+$ or 490 nm ($\epsilon = 1.2 \times 10^4$ $M^{-1}$ $cm^{-1}$)[4,7] for Ru(bpz)$_3^+$, following pulsed laser excitation of the chromophore in the presence of quencher, Figure 1. The magnitude of the transient absorption at the absorption maximum for the reduced Ru species 300 ns after a 10-ns, 416-nm excitation pulse can be related to the relative amounts of electron-transfer quenching, since only the reduced chromophore undergoes significant change in absorbance in the 450–550-nm region. Fc itself gives no detectable electron-transfer quenching of excited Ru(bpy)$_3^{2+}$, Figure 1a, whereas Me$_{10}$Fc clearly yields transient absorption due to Ru(bpy)$_3^+$, Figure 1b. Assuming that the electron-transfer products from quenching all have the same cage escape efficiency (vide infra), the Me$_{10}$Fc can be regarded as giving a greater degree of electron-transfer quenching owing to the greater driving force (~0.5 eV) compared to Fc. The amount of Ru(bpy)$_3^+$ following quenching by other methylated ferrocenes correlates with their $E_{1/2}$ values. Excited Ru(bpz)$_3^{2+}$ has ~0.5 eV greater oxidizing power than excited Ru(bpy)$_3^{2+}$. Ru(bpz)$_3^{2+}$ shows electron-transfer product accompanying quenching by Fc, Figure 1c. Quenching of excited Ru(bpz)$_3^{2+}$ by Me$_{10}$Fc shows the largest amount of transient absorption and has the largest driving force for electron transfer, Figure 1d.[8]

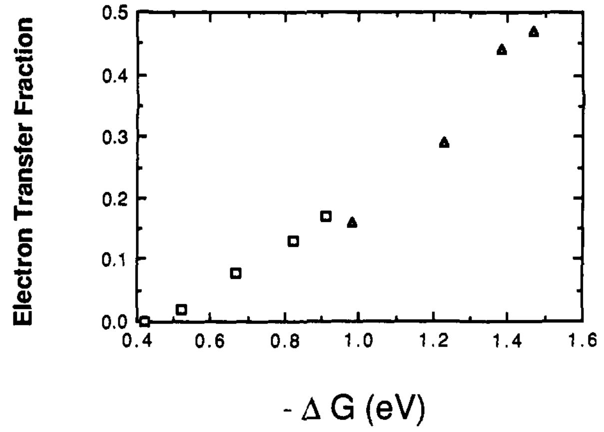

**Figure 2.** Fraction of total quenching by electron transfer versus driving force for electron transfer for the quenching of excited-state Ru(bpy)$_3^{2+}$ (□) and Ru(bpz)$_3^{2+}$ (△) by ferrocene derivatives. The data points for each excited-state reagent correspond to quenching studies with Fc, Me$_2$Fc, Me$_5$Fc, Me$_8$Fc, or Me$_{10}$Fc to give variations in $\Delta G$ for electron-transfer quenching.

The actual fraction of electron-transfer quenching by the ferrocene quenchers can be established by comparing the transient absorption at 510 or 490 nm to that obtained using *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, TMPD, as a quencher, eq 2. The $E_{1/2}$ for TMPD$^{+/0}$ is close to that for the ferrocenes, but TMPD

$$M^* + TMPD \rightarrow M^- + TMPD^+ \qquad (2)$$

has no low-lying excited states so the quenching is only by electron transfer.[9,10] The ion pair solvent cage escape efficiency of Fc$^+$ or TMPD$^+$ and Ru(bpy)$_3^+$ or Ru(bpz)$_3^+$ is assumed to be the same. Other studies involving Ru(II) polypyridyls in organic solvents find cage escape for neutral donors consistently near unity,[10a,b] while in mixed aqueous/organic solvents the cage escape is dependent on the driving force for ion pair recombination.[10b,c,4,6c] We have determined that the cage escape efficiency of TMPD$^+$ and Ru(bpy)$_3^+$ or Ru(bpz)$_3^+$ is the same, even though the driving force for back electron transfer is ~0.5 V larger with Ru(bpy)$_3^+$. This shows that despite the increase in back electron transfer rate expected for the increased driving force, the cage escape rate is sufficiently high that the escape efficiency is unaffected. Assuming the ferrocenium cage escape efficiencies are similarly insensitive to driving force, the fraction of electron-transfer quenching can be determined by comparing transient absorption values for the TMPD and ferrocene quenching after pulsed laser excitation of Ru(bpy)$_3^{2+}$ and Ru(bpz)$_3^{2+}$, Figures 1 and 2.

In the literature, quenching of Ru(bpy)$_3^{2+}$ by either electron transfer[9] or energy transfer[11] is well-established, and competition

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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]

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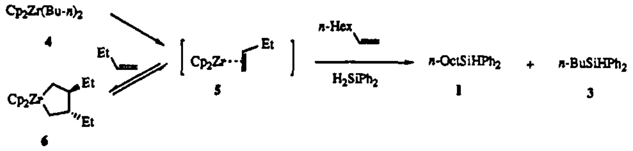
Hydrosilation reactions catalyzed by late transition metals[2] have been extensively studied. In contrast, few examples have been reported for hydrosilation catalyzed by early transition metals.[3]

**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 | $Cp_2Zr(n\text{-}Bu)_2$ | *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*-$OctSiH_2Ph$ | 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.

$$RCH{=}CH_2 + H_2SiPh_2 \xrightarrow{\text{cat. }Cp_2ZrR'_2} RCH_2CH_2SiHPh_2 \qquad (1)$$

$$R = n\text{-Hex},\ n\text{-Oct},\ Ph,\ etc.;\ R' = Et \text{ or } n\text{-Bu}$$

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 ~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 $Cp_2Zr(n\text{-}Bu)_2$ 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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† D. Ross Fellow, Purdue University (1988–1990).

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