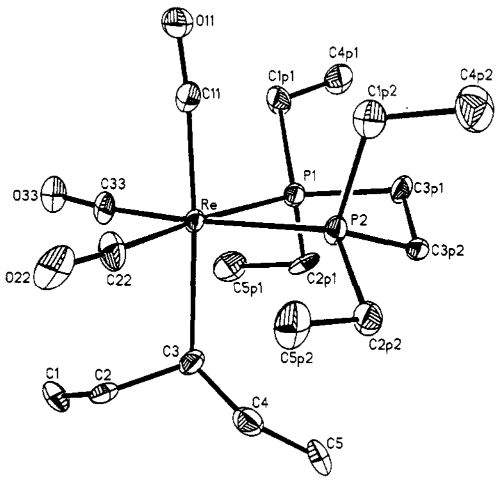
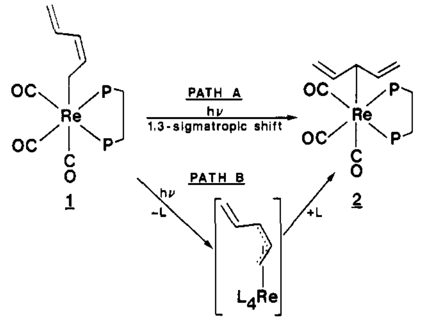


Figure 2. ORTEP drawing of (3-η^1-pentadienyl)Re(CO)$_3$(Et$_2$PCH$_2$CH$_2$PEt$_2$) (2). Bond distances and angles: Re–P1, 2.492 (4) Å; Re–P2, 2.449 (4) Å; Re–C11, 1.94 (2) Å; Re–C22, 1.91 (2) Å; Re–C33, 1.94 (1) Å; Re–C3, 2.35 (2) Å; C1–C2, 1.36 (3) Å; C2–C3, 1.46 (3) Å; C3–C4, 1.47 (2) Å; C4–C5, 1.32 (3) Å; P1–Re–P2, 80.4 (1)°; P1–Re–C11, 90.4 (5)°; P1–Re–C22, 176.2 (6)°; P1–Re–C33, 89.8 (5)°; P1–Re–C3, 88.6 (4)°; P2–Re–C11, 89.2 (5)°; P2–Re–C22, 97.6 (6)°; P2–Re–C33, 170.0 (6)°; P2–Re–C3, 96.8 (4)°; C11–Re–C22, 92.8 (8)°; C11–Re–C33, 89.3 (7)°; C11–Re–C3, 173.6 (6)°; C22–Re–C33, 92.4 (7)°; C22–Re–C3, 88.5 (8)°; C33–Re–C3, 84.4 (7)°; C1–C2–C3, 123 (2)°; Re–C3–C2, 108 (1)°; Re–C3–C4, 112 (1)°; C2–C3–C4, 109 (2)°; C3–C4–C5, 127 (2)°.

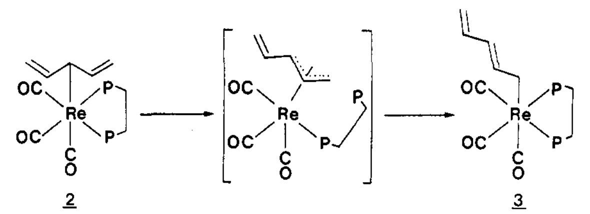
Scheme I



The mechanism of the photoconversion of 1 to 2 is still unclear. The two most likely possibilities are outlined in Scheme I. Pathway A involves a 1,3-sigmatropic shift with no ligand dissociation. Although photochemical 1,3-sigmatropic shifts involving transition metals have not been previously observed, thermal 1,5-sigmatropic shifts are quite common in organotransition-metal chemistry.[10] Hence, pathway A seems reasonable under the reaction conditions. However, ligand dissociation/association processes involving η^3-pentadienyl intermediates (pathway B) cannot be ruled out. Experiments designed to distinguish between these mechanistic possibilities (e.g., photolysis in the presence of labeled CO or phosphine) have proved inconclusive.

At room temperature, (3-η^1-pentadienyl)Re(CO)$_3$(depe) (2) isomerizes quite rapidly to the *trans*-η^1-pentadienyl isomer 3 *even in the absence of light.*[11] Hence, this second step in the overall conversion of 1 to 3 is thermal. Furthermore, it can be shut down by adding an excess of depe or PMe$_3$ to 2, strongly suggesting that the rearrangement of 2 to 3 involves phosphine loss, specifically the dissociation of one arm of the depe ligand (Scheme II).

Scheme II



In summary, we conclude that the conversion of the *cis*-η^1-pentadienyl ligand in 1 to its *trans*-η^1 isomer proceeds in two well-defined steps. The first step is photochemical and results in the formation of a 3-η^1-pentadienyl intermediate. The second step is thermal and proceeds via ligand dissociation/association. Further studies of these novel η^1-pentadienyl–rhenium complexes are in progress.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8520680) is gratefully acknowledged. Washington University's High Resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, torsional angles, and significant least-squares planes including subtended dihedral angles for 1 and 2 (18 pages); listings of observed and calculated structure factor amplitudes for 1 and 2 (35 pages). Ordering information is given on any current masthead page.

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(11) **Synthesis of (*trans*-η^1-Pentadienyl)Re(CO)$_3$(Et$_2$PCH$_2$CH$_2$PEt$_2$) (3) from 2.** (3-η^1-Pentadienyl)Re(CO)$_3$(Et$_2$PCH$_2$CH$_2$PEt$_2$) (2) (0.20 g, 3.7×10^{-4} mol) was dissolved in 30 mL of benzene and stirred at room temperature for 2 days. The solvent was then removed under vacuum. The residue was treated with diethyl ether, and the resulting extract was filtered through Celite. Cooling of the filtrate to −30 °C produced 0.14 g (70%) of 3. NMR spectra of 3 obtained by this method were identical with those of 3 obtained from 1 (see ref 6).

Photochemistry of Cyclopentadienyliron(II) Alkylborate Salts: Rapid Intra-Ion-Pair Electron Transfer Gives Alkyl Free Radicals

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Summary: Irradiation of tetrahydrofuran solutions of appropriate alkylborate [RB(Ph)$_3$]$^-$ salts of cyclopentadienyliron (II) arene cations [CpFeArH]$^+$ initiates an intra-ion-pair electron-transfer reaction to form a neutral 19-electron iron(I) species and a neutral boranyl radical [RBPh$_3$]$^\bullet$. Cleavage of the alkyl carbon–boron bond in the boranyl radical occurs more rapidly than does energy-wasting back electron transfer to regenerate the starting salt. The alkyl radical formed is detected by laser flash photolysis and by its characteristic chemical reactions in solution.

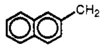
The electronically excited-state lifetimes of organometallic compounds in solution are typically very short. This fact often restricts reactions of these species to unimolecular ligand dissociations: Except at very high concentration of reagent, bimolecular reactions often cannot compete with the nonreactive, usually radiationless decay. A typical case is that of the cationic $[CpFeArH]^+X^-$ complexes. The photochemistry of these compounds has been explored from both synthetic and mechanistic viewpoints. Their irradiation in a ligand-containing solution leads to release of the arene and formation of a new, triply ligated iron(II) complex, $[CpFeL_3]^+$.[1] The mechanism of this reaction is complex. Studies by Mann and co-workers,[2] Catheline and Astruc,[3] and our investigation[4] have shown that the reactive state of these complexes is a short-lived triplet ($\tau < 1.5$ ns). The labilized arene ligand of the triplet state is thought to slip from η^6 to η^4, thereby opening a coordination site on the iron for attack by ligand or by the counterion X^-.

Astruc and co-workers discovered that one-electron reduction by chemical or electrochemical means of appropriately substituted $[CpFeArH]^+$ complexes leads to formation of stable "19-electron", neutral iron species $[CpFeArH]^\bullet$.[5,6] Single electron transfer reactions of organometallic complexes are known to be initiated by their irradiation with visible or UV light in the presence of an appropriate ligand[7] or reagent.[8] We recently reported that one-electron oxidation of alkyltriphenylborates $[RB(Ph)_3^-]$ gives a boranyl radical $[RB(Ph)_3^\bullet]$ which undergoes rapid bond scission to form triphenylborane and an alkyl radical $[R^\bullet]$.[9] Herein we describe the preparation of thermally stable (2-naphthylmethyl)triphenylborate $[NpCH_2B(Ph)_3]^-$ salts of $[CpFeArH]^+$ cations. Irradiation of these salts in tetrahydrofuran solution initiates a reaction that generates the 2-naphthylmethyl free radical (eq 1).

$$[CpFeC_6H_5X]^+[NpCH_2B(Ph)_3]^- \xrightarrow{h\nu} [CpFeC_6H_5X]^\bullet + Ph_3B + NpCH_2^\bullet \quad (1)$$

X = CN, CH$_3$ Only X = CN

NpCH$_2$ =



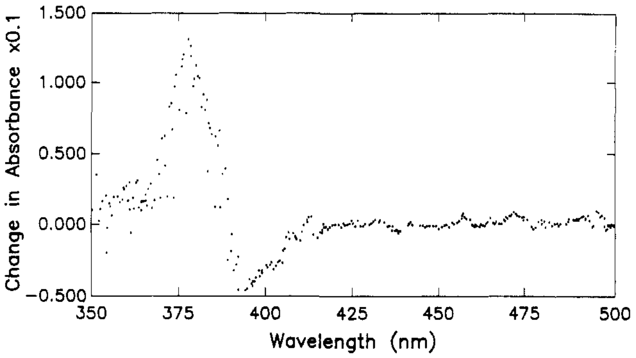
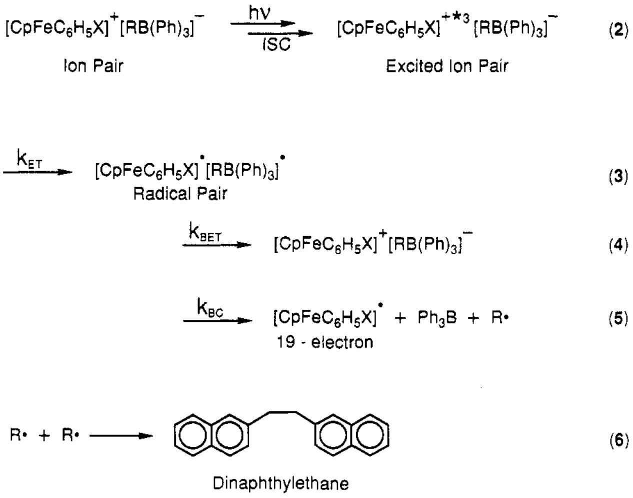


Figure 1. Absorption spectrum recorded 100 ns after excitation of a tetrahydrofuran solution of $[CpFeC_6H_5CN]^+[NpCH_2B(Ph)_3]^-$ at 343 nm with a 20-ns wide laser pulse.

Scheme I



The $[NpCH_2B(Ph)_3]^-$ salts of $[CpFeC_6H_5CN]^+$ and $[CpFeC_6H_5CH_3]^+$ were prepared from the previously reported[10] iron arene hexafluorophosphate(1−) salts by exchange with $K^+[NpCH_2B(Ph)_3]^-$. These new compounds are stable in the dark and were characterized by ^1H NMR spectroscopy and by elemental analysis.[11]

The photolyses of ca. 10^{-3} M tetrahydrofuran solutions of the iron arene borate salts with the Pyrex-filtered output of a medium-pressure Hg-vapor lamp for 2–3 h were monitored by gas chromatography. The products obtained are dependent on the nature of the arene ligand bound to the iron. When the C_6H_5CN complex is irradiated, 1,2-di(2-naphthyl)ethane is formed in ca. 40% yield. Formation of dinaphthylethane signals the intermediacy of the 2-naphthylmethyl free radical, a conclusion supported by time-resolved absorption spectroscopy (see below). In contrast, identical irradiation of the $C_6H_5CH_3$ complex does not give a detectable amount of the dinaphthylethane.

A low intensity optical absorption band of the iron arene complexes near 650 nm has been assigned to the ground-state singlet to excited triplet transition.[2] Direct irradiation into this band will bypass the excited singlet and generate the triplet state of the complex directly. Photolysis of the iron arene borate salts with red light (RG-610 cutoff filter) gives the dinaphthylethane in the case of the C_6H_5CN derivative, but not for the $C_6H_5CH_3$ complex. This finding indicates that in suitable cases, the triplet

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(11) (a) $[CpFeC_6H_5CH_3]^+[NpCH_2B(Ph)_3]^-$ ^1H NMR δ 7.30 (br s, 8 H), 6.5–7.0 (m, 19 H), 5.41 (s, 5 H, Cp), 2.65 (q, 2 H, CH_2B), 2.51 (s, 3 H). Anal. Calcd for $C_{41}H_{37}BFe$: C, 82.55; H, 6.21. Found: C, 82.05; H, 6.19. (b) $[CpFeC_6H_5CN]^+[NpCH_2B(Ph)_3]^-$: mp 148–150 °C; ^1H NMR δ 7.5–7.6 (m, 1 H), 7.27–7.4 (br s, 7 H), 7.06–7.25 (m, 3 H), 6.72–7.05 (m, 13 H), 6.4–6.6 (br m, 3 H) 5.31 (s, 5 H, Cp), 2.76 (q, 2 H, CH_2B). Anal. Calcd for $C_{41}H_{34}NBFe$: C, 81.08; H, 5.64; N, 2.31. Found: C, 81.02; H, 5.66; N, 2.30.

state of the iron arene complex is capable of reacting with its borate counterion.

Laser flash photolysis of the iron arene borate salts confirms formation of the 2-naphthylmethyl radical for the C_6H_5CN complex. Irradiation of a tetrahydrofuran solution of $[CpFeC_6H_5CN]^+[NpCH_2B(Ph)_3]^-$ with a 20-ns light pulse at 343 nm produces a sharp transient absorption at ca. 385 nm characteristic of the 2-naphthylmethyl radical[12] (Figure 1). The absorption of the radical rises instantaneously on the time scale of this experiment and then decays following a complex kinetic law with a lifetime of 5–10 μs. In a control experiment we found that irradiation of $Me_4N^+[NpCH_2B(Ph)_3]^-$ does not give a detectable (<5% that from the complex iron salt) absorption for the naphthylmethyl radical. Significantly, laser flash photolysis of $[CpFeC_6H_5CH_3]^+[NpCH_2B(Ph)_3]^-$ in tetrahydrofuran solution also does not give evidence for the formation of the naphthylmethyl radical. Similarly, irradiation of $[CpFeC_6H_5CN]^+[NpCH_2B(Ph)_3]^-$ in acetone solution, where in contrast to the ion pairs in tetrahydrofuran, the salt should exist primarily as freely solvated ions, gives no evidence for the formation of the naphthylmethyl radical.

Astruc and co-workers report that the 19-electron species formed from the reduction of $[CpFeArH]^+$ have weak (ϵ_{max} = ca. 100 M^{-1} cm^{-1}) absorption bands at ca. 700 nm.[13] We searched unsuccessfully for the absorption of this species in the laser flash photolysis of the C_6H_5CN complex. The low extinction coefficient of this intermediate makes it difficult to detect under these conditions; its formation in a concentration equal to that of the observed naphthylmethyl radical would produce a maximum change in absorbance of only ca. 0.002 at 700 nm.

The photochemistry of the iron arene alkylborate salts can be understood within the mechanism outlined in Scheme I. Excitation of the ion pair leads to the triplet of the iron-arene complex either directly, from red light irradiation, or via the singlet excited state by means of rapid intersystem crossing (ISC) (eq 2). Electron transfer (eq 3) can occur despite the short lifetime of the triplet state because ion-pairing insures the appropriate positioning of the donor (borate) next to the acceptor (iron arene) at the moment of excitation.

The rate constant for electron transfer, k_{ET}, will depend on the free energy change for this reaction (ΔG_{ET}). This value may be calculated by means of eq 7. The oxidation potential ($E_{ox.}$) of the naphthylmethyl borate was estimated by cyclic voltammetry in acetonitrile solution to be ca. 0.3 V vs SCE from the peak of its irreversible wave. The reduction potential ($E_{red.}$) of the iron complex in acetonitrile solution is −1.10 when C_6H_5CN is the arene ligand and −1.46 V for the $C_6H_5CH_3$ complex.[14] These values can be crudely adjusted for the change of solvent from acetonitrile to tetrahydrofuran by application of the Born equation:[15] $(E_{ox.} - E_{red.})_{THF}$ = 1.86 and 1.50 V for the toluene and benzonitrile complexes in tetrahydrofuran, respectively. The triplet energies (E^{*3}) of the $[CpFeArH]^+$ complexes were calculated from their singlet–triplet absorption spectra to be 2.0 V. And the Coulombic work necessary to combine the charges (E_{work}) was estimated[15] to be 0.33 V for a center-of-charge separation in the ion pair of 6 Å in a medium with the dielectric constant of bulk tetrahydrofuran. Substitution of these values into eq 7

$$\Delta G_{ET} = E_{ox} - E_{red} - E^{*3} + E_{work} \qquad (7)$$

shows that electron transfer from the borate to the C_6H_5CN complex is exothermic (ΔG_{ET} = −0.16 V). On the other hand, this calculation predicts that the electron transfer will be endothermic (+0.19 V) for reaction of the $C_6H_5CH_3$ complex. The precise values for ΔG_{ET} revealed by these calculations must be regarded with skepticism since the oxidation of the borate is irreversible. Nevertheless, the trend is reliable and is consistent with rapid electron transfer only for the C_6H_5CN complex. This finding accounts for the observed difference in photochemistry between the C_6H_5CN and $C_6H_5CH_3$ iron complexes.

Electron transfer from the borate to the excited iron complex generates a neutral radical pair. In many such reactions back electron transfer to regenerate ground-state starting materials (eq 4) overwhelms other reaction paths. In the present case, cleavage of the carbon–boron bond in the boranyl radical (eq 5) must be sufficiently rapid to give a measurable yield of the alkyl radical, whose dimerization (eq 6) completes the reaction sequence and gives the observed product.

In summary, photolysis of iron arene cation–alkyl borate salts initiates an intra-ion-pair electron-transfer reaction when the free energy change for such a reaction is favorable. The electrically neutral radical pair produced goes on to give unique products.

Acknowledgment. We thank M. Kropp and A. Strezo of this Department for the preparation of the naphthylmethylborate and for measuring its oxidation potential and Professor T. L. Brown for his advice concerning this manuscript. This work was supported by grants from Mead Imaging and from the National Science Foundation for which we are grateful.

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Electron-Transfer Activation of Coordinated Thiophene: Preparation and Desulfurization of $(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$

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Summary: Cyclic voltammetry studies show that $[(C_5Me_5)Rh(C_4Me_4S)]^{2+}$ undergoes two reversible one-electron reductions at low potentials. The reduced product was synthesized by cobaltocene reduction and was characterized as $[(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)]$. ^1H and ^{13}C NMR spectroscopic results are consistent with a symmetrical, reduced thiophene ligand. An X-ray crystallographic study confirms that the reduced complex contains a nonplanar η^4-thiophene ligand with an uncoordinated sulfur atom. The reduced complex reacts with $Fe_3(CO)_{12}$ to give $(C_5Me_5)RhC_4Me_4Fe(CO)_3$ which is analogous to a major product in the $Fe_3(CO)_{12}$ desulfurization of thiophenes. Electron-transfer activation is proposed to be relevant to the desulfurization of thiophenes by metal surfaces.