compressing the valence angle ($C_2C_3C_4$) lowers the antibonding orbital of the allyl unit thus favoring more suitable orbital interaction.

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Electronic and Stereoelectronic Effects on the Intervalence Transfer Transition in Biferrocene Cations

Sir:

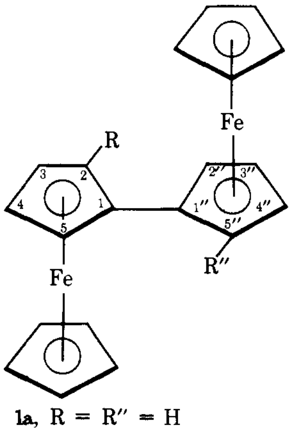
The mixed valence monocation of biferrocene (**1a**) has been thoroughly characterized by a variety of physical measurements.[1] A low energy transition, observed in the near-infrared, has been assigned to an intervalence transfer transition:

$$[\mathrm{Fe(II)—Fe(III)}] \xrightarrow{h\nu} [\mathrm{Fe(III)—Fe(II)}]^*$$

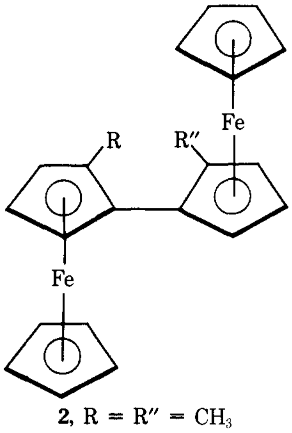
A simple model for intervalence transfer transitions has been proposed by Hush[2] and expounded by Day.[3] A corollary states that the energy of the Franck-Condon transition for a one-electron transfer in a symmetrical compound is determined by the amount of reorganizational energy involved. For an electron transfer in an unsymmetrical compound, the band is expected to be blue shifted because of a difference in energy between the initial and final states at the equilibrium configurations.

The intensity of the transition, however, depends on the amount of interaction (i.e., delocalization) between donor and acceptor sites.[4] Mayoh and Day[5] have recently shown that, in the absence of direct metal-metal overlap, the metal centers in mixed-valence compounds interact via ligand π and π^* orbitals.

In order to investigate the usefulness of this simple model in interpreting results in the biferrocene series, we examined the mixed-valence cations of three disubstituted biferrocenes (**1b**, **1c**, and **2**).[6,7]



1a, R = R″ = H
b, R = R″ = CH_3
c, R = CH_3; R″ = CH_2OH



2, R = R″ = CH_3

It has been shown that the presence of substituents adjacent to the fusion between the ferrocenyl groups affects the overall conformation of the molecule.[7,8] The 2,5″-disubstituted compounds (**1b** and **1c**) may adopt a trans conformation,[9] whereas the 2,2″ derivative (**2**), because of steric hindrance, probably adopts a skewed conformation. As a result, a reduced π interaction in the "fulvalene" ligand is expected. It was shown that this effect satisfactorily explains the blue shift and reduced intensity in the $\pi \rightarrow \pi^*$ transition of the neutral 2,2″-disubstituted compounds.[7] The nonplanarity of the fused cyclopentadienyl rings should, in turn, reduce the extent of interaction between the mixed-valence metal centers in the cation but have little or no effect on the reorganizational energy.

Table I. Half-Wave Potentials for Substituted Biferrocenes[a,b]

Compd	$E_{1/2}(1)$	$E_{1/2}(2)$	$\Delta E_{1/2}$[c]
1a	0.285	0.600	0.315
1b	0.310	0.605	0.295
2	0.370	0.630	0.260
1c	0.350	0.675	0.325

[a] Volts vs. SCE at 100 mV/sec (platinum disk electrode). [b] Acetonitrile containing Et_4NClO_4 (0.1 *M*). [c] $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$.

Table II. Spectral Data for Biferrocene Cations

	Monocations[a] λ_{max}, nm (ϵ)[c]		Dications[b] λ_{max}, nm (ϵ)[c]
Compd	Near-infrared	Visible	Visible
1a	1800 (750)	545 (2160)[d]	480 (920), 660 (1000)
1b	1800 (560)	560 (1850)[d]	485 (860), 670 (1100)
2	1800 (340)	560 (1030)[d]	480 (480), 660 (910)
1c	1680[e] (520)	545 (2000)[d]	485 (900), 665 (1100)

[a] Acetonitrile containing Et_4NClO_4 (0.1 *M*). [b] Methylene chloride containing $n\text{-}Bu_4NBF_4$ (0.1 *M*). [c] Reproducible within 5%. [d] Shoulder at longer wavelength. [e] Because of solvent absorption, values in 1660–1740 nm region are interpolated.

To obtain absorption spectra of the mono- and dications of compounds **1b**, **1c**, and **2**, 10^{-3} *M* solutions were generated electrochemically. Oxidation by precisely 1 F/mole yields the monocations, while exhaustive coulometric oxidation results in consumption of precisely 2F/mole and formation of the dications. The stability and identity of the cations were demonstrated by cyclic voltammetry and polarography.[10] Half-wave potentials for these compounds as measured by cyclic voltammetry are given in Table I. Each compound undergoes two reversible one-electron oxidations. A difference in peak potentials of 60 mV between the oxidation and reduction waves was used as the criterion for reversibility. Spectral data in the visible and near-infrared regions are given in Table II.

The spectral results obtained for the monocations in the near-infrared region do indeed reflect the predictions of the simple model. Within experimental limits, the maximum for the two dimethylbiferrocene cations is the same, whereas the intensity of the band is significantly reduced in the skewed 2,2″-dimethyl derivative.[11] In the case of the cation of the unsymmetrically substituted hydroxymethyl compound (**1c**), the intervalence transfer band is blue shifted some 120 nm (0.05 eV) as expected.

These results demonstrate the usefulness of the simple model in interpreting the results in the biferrocene series.[12] Mixed-valence biferrocenes fulfill the prerequisite of the Hush model[2,3] in that there is weak interaction between the donor and acceptor sites. Consequently, transitions due to the ferrocene and ferrocenium portions are expected to be seen. Table II lists the absorption maxima and intensities of the visible bands of the biferrocene mono- and dications. The 617-nm band observed for the ferrocenium ion has been assigned to a symmetry-allowed ligand to metal transition based on the effect of substituents.[13] A ferrocenyl group is electron donating[14] and as such should induce a red shift. The visible bands of the biferrocene monocations, however, are broad and unsymmetrical with maxima around 560 nm and shoulders at lower energy (~650 nm). We previously suggested that a second band in the visible region results from an excited state intervalence transfer.[1] In view of our present observation of two distinct bands in the visible spectra of all the biferrocene dications (see Table II), it seems more reasonable to propose that these bands result from separate ligand to metal transitions from the cyclopentadienyl ligands (at lower energy) and the fulvalene ligand. In the monocations, the bands coalesce. This would explain the lower intensity of the 560-nm transition in the 2,2″-dimethyl monocation and the 480-nm transition in the dication. Further experiments to evaluate these assignments are in progress.

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References and Notes

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(4) According to Hush,[2] the intensity of an intervalence band is dependent on several factors:

$$\epsilon_{\max} \simeq \bar{\nu} r^2 \alpha^2 / 4.5 \times 10^{-4} \Delta_{1/2}$$

where $\epsilon_{\max}$ is the molar absorptivity, r is the donor–acceptor distance, α is the interaction parameter, $\Delta_{1/2}$ is the band half-width, and $\bar{\nu}$ is the frequency.
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(11) Estimates of the band width are the same for both dimethyl compounds. (The full band is not observed because of the onset of solvent absorptions.)
(12) A study of 1,1′-polyferrocene cations is reported elsewhere: G. M. Brown, T. J. Meyer, D. O. Cowan, C. LeVanda, F. Kaufman, P. V. Roling, and M. D. Rausch, *Inorg. Chem.*, to be published.
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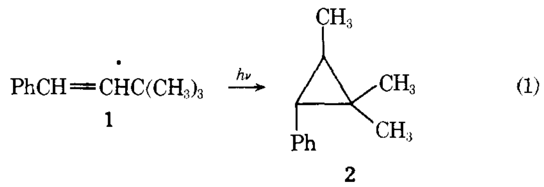
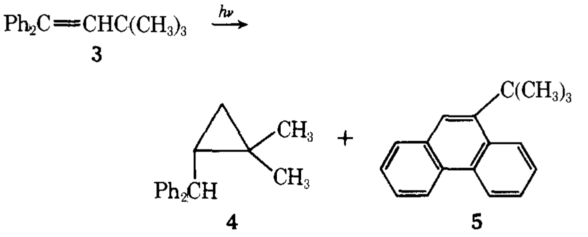
Photochemistry of β-*tert*-Butyl-1,1-diphenylethylene. Evidence for an Unusual Olefin to Carbene Transformation

Sir:

The study of the photochemical migration reactions of β-substituted styrenes and 1,1-diarylethylenes has proved to be a fascinating and fruitful area for research.[1] In such systems, the most commonly observed photochemical process is a 1,2 migration of a γ substituent to form a cyclopropane (e.g., **1** → **2**),[1a,d] though other migration processes have been noted.[2] We report here the new and unusual reaction course taken by photoexcited β-*tert*-butyl-1,1-diphenylethylene (**3**). Our observations are consistent with the occurrence of a novel olefin to carbene transformation.

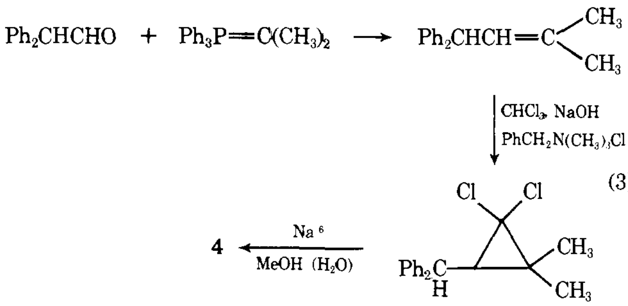


(1)



(2)

Irradiation[3] of **3** in cyclohexane solution produced, inefficiently, a major and a minor photoproduct in 36 and 6% yields, respectively, at 53% conversion of **1** (eq 2).[4] The NMR spectrum of the major product, isolated via tedious silica gel chromatography, strongly suggested that this material was the benzhydryldimethylcyclopropane **4**. That this structural assignment was indeed correct was unambiguously demonstrated by comparison of the NMR spectrum and gas chromatographic retention times of the **4** isolated from the photolysis of **3** with those of **4** independently synthesized as shown in eq 3.



(3)

The minor photoproduct was identified as 9-*tert*-butylphenanthrene (**5**) by comparison of its NMR spectrum and GC retention times with those of an authentic sample.[7] Benzophenone-sensitized irradiation of **3** gave no **4** or **5** (or **7**).

To probe the molecular details of the rearrangement of **3**, **3-*d*** containing deuterium (>95% *d*) at the vinyl position was prepared using standard procedures and irradiated. Inspection of the NMR spectrum of the resulting **4-*d*** proved very revealing. The signals for the methyl groups (δ 1.10 and 0.99) and the cyclopropane methylene protons (multiplets centered at δ 0.51 and 0.32) in **4-*d*** were clearly present and identical with those in the nondeuterated **4**. However, the prominent doublet for the benzhydryl proton at δ 3.39 in **4** had completely disappeared. The deuterium at C-2 in starting olefin **3** has therefore become attached to the benzhydryl carbon in product **4**. An insufficient amount of **5-*d*** was produced for accurate NMR analysis in this experiment.

Though one may conceive of other pathways leading from **3** to **4** and **5**,[8] we feel the most likely scheme is that shown in eq 4. The reactive excited singlet state of **3** undergoes a 1,2 shift of its vinyl hydrogen to form carbene **6**. The latter in turn is trapped by insertion into one of the γ C–H bonds of the neighboring methyl groups to form **4**, a reaction typical of β-methylcarbenes.[9a] In addition, the expected phenyl migration occurs[9b] to form α-*tert*-butylstilbene **7** (not isolated) which undergoes the expected photochemical cyclization to phenanthrene **5**.[10] Reversion of **6** to starting material via β C–H insertion most likely also occurs, but this would go undetected. Our isolation of the products