predicts that a plot of $RT \ln (k'_q)$ vs. $E^\circ(A^+/A)$ should be linear for quenchers with values of $E^\circ(A^+/A)$ less than or approximately equal to $E^\circ(Ir_2^+/^3Ir_2^*)$ and approach a diffusion-limited value for $E^\circ(A^+/A)$ greater than or approximately equal to the value of $E^\circ(Ir_2^+/^3Ir_2^*)$.[11] The data accord fully with these predictions (Figure 2); the slope of 0.48 in the linear region of this curve (quenchers **7–13**) is in excellent agreement with the theoretical value of 0.5. Since electron transfer between $^3Ir_2^*$ and these pyridinium quenchers is reversible, net photochemistry is not observed. However, with acceptors whose initial electron-transfer products are unstable, we have found that **1** undergoes multielectron photochemical processes.[12] Thus the C_{2v} d^8–d^8 complexes may prove to be versatile photoreagents for the reductive activation of many inert substrates.

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Registry No. 1, 89710-83-8; $[Ir(\mu\text{-}3\text{-}CH_3\text{-}5\text{-}CF_3(pz))(COD)]_2$, 89726-03-4; $[Ir(\mu\text{-}3,4,5\text{-}(CH_3)_3(pz))(COD)]_2$, 89726-04-5; 4-cyano-*N*-methylpyridinium, 13441-45-7; 4-carbomethoxy-*N*-methylpyridinium, 38117-49-6; 4-amido-*N*-ethylpyridinium, 71258-88-3; 3-amido-*N*-benzylpyridinium, 16183-83-8; 3-amido-*N*-methylpyridinium, 3106-60-3; *N*-ethylpyridinium, 15302-96-2; 2-methoxy-*N*-methylpyridinium, 15121-44-5; 4-methyl-*N*-methylpyridinium, 18241-35-5; 4-*tert*-butyl-*N*-ethylpyridinium, 46061-24-9; 2,6-dimethyl-*N*-methylpyridinium, 33718-19-3; 2,3,6-trimethyl-*N*-methylpyridinium, 55508-48-0; 2,4,6-trimethyl-*N*-methylpyridinium 2,6-dimethyl-4-methoxy-*N*-methylpyridinium, 89746-09-8.

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[11] For a more complete description of the dependence of k'_q on $E^\circ(A^+/A)$, see ref 10a.

[12] Caspar, J. V.; Gray, H. B. *J. Am. Chem. Soc.*, following paper in this issue.

Photoinduced Oxidative Addition Chemistry of Bis(1,5-cyclooctadiene)bis(μ-pyrazolyl)diiridium(I)

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In the previous paper[2] it was demonstrated that the long-lived $^3B_2(d\sigma^*p\sigma)$ metal-localized excited state of the complex $[Ir(\mu\text{-}pz)(COD)]_2$ (**1**) (pz is pyrazolyl, COD is 1,5-cyclooctadiene) is subject to rapid electron-transfer quenching by a wide variety of organic electron acceptors. The facility with which the photogenerated $^3B_2$ excited state of **1** reduced these organic substrates coupled with the presence of adjacent vacant coordination sites at the two iridium centers suggested to us that the proper choice of substrate might lead to unique photochemical reactivity. The extensive thermal chemistry of **1** and related compounds[3] provided a further basis for this suggestion. Thus we have investigated the thermal and photochemical reactions of **1** with a number of chlorinated and brominated hydrocarbon substrates, and we report here the results for 1,2-dichloroethane (DCE) and methylene chloride.

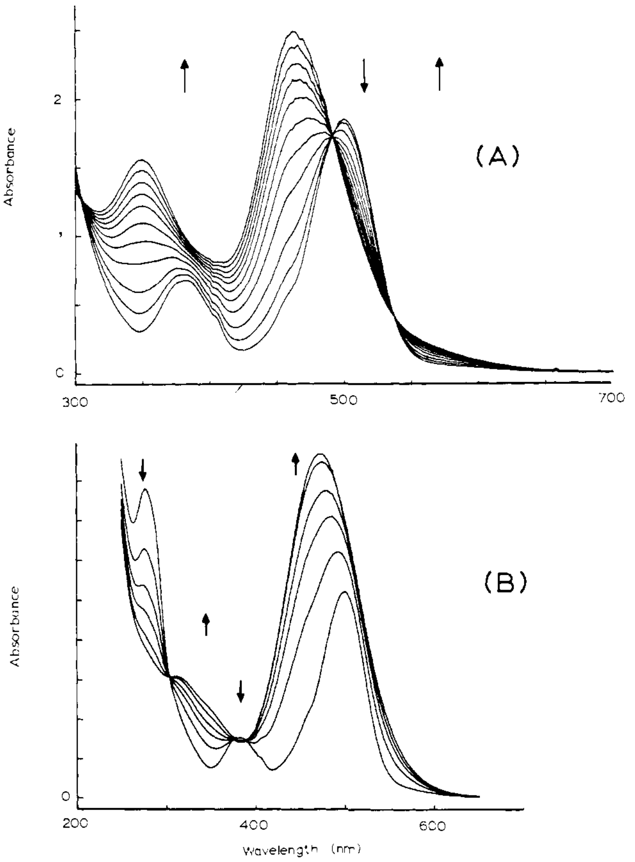
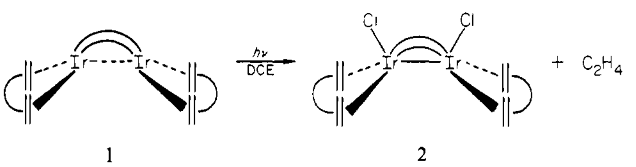


Figure 1. Spectral changes observed on visible irradiation ($\lambda > 400$ nm) of $[Ir(\mu\text{-}pz)(COD)]_2$ in rigorously degassed 1,2-dichloroethane (A) and methylene chloride (B) at 25 °C (scan intervals, ~15 s).

In the absence of light, solutions of **1** in methylene chloride or DCE are stable for a period of at least several days as monitored by absorption spectroscopy. Figure 1 shows the spectral changes that were observed upon visible irradiation of **1** in DCE and methylene chloride (1000-W high-pressure Hg/Xe lamp filtered to give $\lambda > 400$ nm). Both reactions exhibit clean isosbestic points initially, although the reaction with methylene chloride becomes more complicated as it proceeds, due to the onset of a secondary photoreaction. For this reason our mechanistic studies have focused primarily on the DCE reaction.

Isolation of the product of the photoreaction with DCE gave a brown crystalline material whose properties are consistent with the structure $[Ir(Cl)(\mu\text{-}pz)(COD)]_2$ (**2**).[4] The same optical absorption spectrum was generated upon thermal oxidation of **1** with Cl_2, which also is expected to produce **2**.[3] Toepler pumping of the photochemical reaction mixture gave 1.0 ± 0.02 equiv of ethylene (determined by mass spectrometry). Thus the photoreaction between **1** and DCE is that shown in eq 1, wherein one



1 2

(1)

photon of visible light has been used to effect the two-electron reduction of DCE with the concomitant formation of a binuclear iridium(II) species.[5]

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[1] E. I. du Pont DeNemours and Co., Inc., Central Research and Development Department, Experimental Station, Wilmington, DE 19898.

[2] Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.*, preceding paper in this issue.

[3] (a) Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R.; Atwood, J. L.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 920. (b) Coleman, A. W.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J.; Atwood, J. L. *Ibid.* **1982**, *104*, 922.

[4] The product was isolated by photolyzing to completion a 50-mg sample of **1** in 10 mL of DCE followed by cooling to −10 °C, which gave **2** as dark brown crystals in quantitative yield: NMR (CD_2Cl_2) (90 MHz) δ 7.65 (d, 4 H), 6.10 (t, 2 H), 5.15 (m, 4 H), 4.35 (m, 4 H), 3.02 (m, 4 H), 2.55 (m, 12 H). Anal. Calcd for $[Ir(\mu\text{-}pz)(COD)Cl]_2 \cdot 0.75DCE$: C, 32.08; H, 3.77; N, 6.39. Found: C, 32.02; H, 3.78; N, 6.29. The presence of 0.75 free DCE molecules of crystallization was confirmed by NMR.

[5] The observed reaction quantum yield was independent of incident light intensity indicating that only one photon is required.

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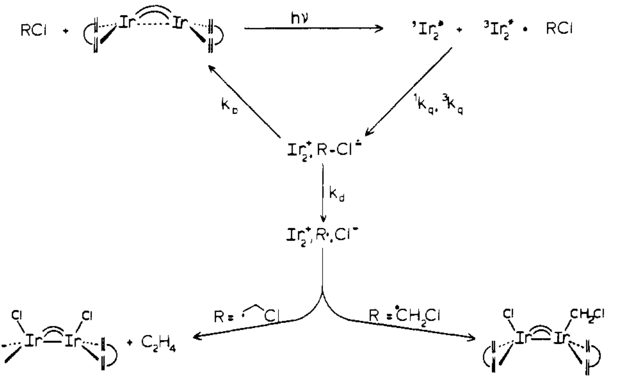
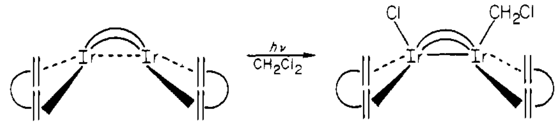


Figure 2. Proposed mechanism for the photochemical reaction of $[Ir(\mu\text{-pz})(COD)]_2$ with RCl.

Isolation of the product of the photoreaction of **1** with methylene chloride gave adduct **3** as identified by NMR.[6,7] Toepler pumping



(2)

1 3

showed the formation of no gaseous products. As in the case of DCE, net two-electron reduction of the substrate has occurred, leading in this case to the two-center oxidative addition product analogous to that observed in the thermal reaction of **1** with methyl iodide.[2]

The maximum quantum yield (0.047 ± 0.004) for the photoreaction with DCE was observed for 577-nm irradiation, corresponding to direct excitation of the $^1A_1 \rightarrow {}^3B_2$ electronic transition. However, both the $^1B_2$ and $^3B_2$ states appear to be reactive as shown by the fact that for hexane solutions of **1** with added methylene chloride or DCE both the $^1B_2$ emission intensity and the $^3B_2$ emission lifetime are quenched in accord with Stern–Volmer kinetics. The measured quenching rate constants (^3k_q) for the $^3B_2$ state by methylene chloride and DCE are 5.8×10^5 and 7.3×10^5 M^{-1} s^{-1}, respectively. The Stern-Volmer quenching constants for the $^1B_2$ state are 0.13 and 0.30 M^{-1}, which place lower limits of 1.3×10^9 and 3.0×10^9 M^{-1} s^{-1} on the singlet quenching rates (^1k_q), based on an upper limit of 100 ps for the singlet lifetime.[8]

Electrochemical reductions of halocarbons (RX) have been demonstrated to proceed via initial one-electron transfer to form the anion radical $RX^-\cdot$, which undergoes rapid unimolecular decomposition to form R· and X^- ($k_d = 3 \times 10^8$ s^{-1} for methyl chloride).[9] Because the reduction potentials for methylene chloride and DCE are −2.14 and ca. −2.1 V vs. SSCE,[10] respectively, outer-sphere reduction of either of these substrates by the $^3B_2$ excited state ($E° \sim -1.81$ V) is energetically feasible. The $^1B_2$ excited state also should be capable of reducing these materials, as it is predicted to be an even more powerful reductant ($E° \sim -2.1$ V vs. SSCE) than $^3B_2$. Using as a basis the results obtained for the rates of reversible electron-transfer quenching (k_q) of $^3B_2$ by simple organic electron acceptors,[2] we were able to obtain rough estimates for ^3k_q and ^1k_q for the halocarbon substrates. Neglecting effects due to changes in the reorganizational barrier to electron transfer, the experimentally determined dependence of ln (k_q) on quencher reduction potential predicts a value of $^3k_q = 1 \times 10^5$ M^{-1} s^{-1} for a halocarbon with a reduction potential of −2.1 V, in remarkably good agreement with the observed quenching rate constant. Analogous quenching data are not available for the singlet state; however, using an excited-state potential of −2.1 V and making the reasonable assumption that the overall shape of the quenching curve is the same as for the triplet state, we predict $^1k_q = 2 \times 10^6$ M^{-1} s^{-1}.

The results described above suggest that the mechanism of the observed photoreactions of **1** is that shown in Figure 2. The absence of radical recombination or disproportionation products indicates that the organic radical intermediates are effectively trapped within the solvent cage. Note that in the mechanistic scheme we have assumed that the only singlet and triplet reactivity difference is in the rate of the initial quenching step. However, the possibility of rate differences in reactions of the singlet- and triplet-generated radical pairs cannot be ruled out.

Acknowledgment. We thank Janet Marshall and Stephen Stobart for helpful discussions. This research was supported by National Science Foundation Grant CHE81-20419.

Registry No. 1, 89710-83-8; **2**, 89710-84-9; **3**, 89710-85-0; DCE, 107-06-2; methylene chloride, 75-09-2.

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(6) Photolysis of 300 mg of **1** in 25 mL of methylene chloride for 1 h followed by the addition of 50 mL hexane and cooling to −10 °C for 48 h gave **3** as a red-brown powder in low yield (ca. 10%): NMR (CD_2Cl_2) (90 MHz) δ 7.70 (d, 2 H), 7.45 (d, 2 H), 6.14 (t, 2 H), 4.90 (s, 2 H). The COD protons appear as complicated multiplets in the range 2.0–4.7 (24 H). Irradiation of **1** in CD_2Cl_2 gave an identical NMR with the exception of the absence of the signal at δ 4.90. Calcd for $[Ir(\mu\text{-pz})(COD)]_2\cdot CH_2Cl_2$: C, 33.69; H, 3.93; N, 6.86. Found: C, 33.61; H, 3.97; N, 6.91.

(7) The iodo analogue of **3** has been structurally characterized (Stobart, S. R., private communication).

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Total Synthesis of *d,l*-Fulvine and *d,l*-Crispatine

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Considering their interesting and diverse biological activity,[1] 11-membered pyrrolizidine dilactones such as fulvine (**1**), crispatine (**2**), or monocrotaline (**3**) have attracted little synthetic attention. These compounds are challenging targets for total synthesis due to their potential for stereochemical equilibration, β-elimination, and intramolecular carbonyl interaction. A successful synthesis of the less substituted dicrotaline (**4**) by Robins et al. using a variant of Corey lactonization and related work by Meinwald et al. on crobarbatine acetate[3] suggested to us that a general solution to these problems might be at hand. We were therefore somewhat surprised to find that none of the published techniques involving carboxyl activation were successful when applied to the more complex but structurally similar substrates **5a–c**, Potential preursors of crispatine (**2**).[4] Recognizable byproducts could be isolated from the 2-pyridyl thioester **5b**, which decomposed to protected crispatic anhydride **7**, and from the mixed phosphoric anhydride **5c**, which suffered a more peculiar but mechanistically related intramolecular cyclization.[5] We have

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