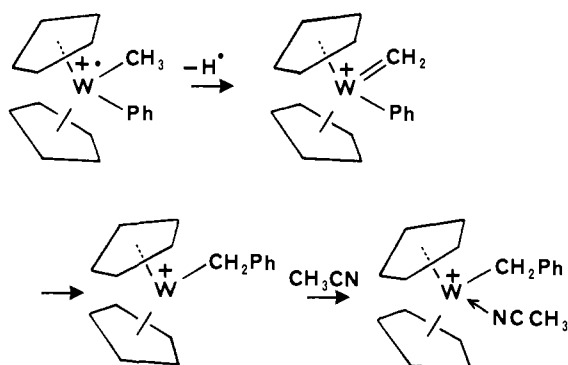Scheme I

rocene was removed by trituration with toluene and the brick-red powder obtained was dried under vacuum to give [W(η-C$_5$H$_5$)$_2$(CH$_3$)Ph]PF$_6$ (0.23 g, 0.40 mmol ≡ 86%). Analytical samples were obtained in 50% yield by rapidly concentrating a CH$_2$Cl$_2$ solution and collecting the resulting red needles by decantation, but the crude salt, identical by IR and ESR with recrystallized material, was typically used for subsequent experiments without further purification. ¹H NMR spectra showed the absence of diamagnetic tungstenocene derivatives, and the compound was characterized by analysis and by ESR.[9] This showed the presence of a single major paramagnetic species with an ⟨g⟩ value similar to that observed for other tungstenocene dialkyl cations[2,7] and somewhat higher than the values reported for tungstenocene dihalo cations.[10] Chemical characterization of the complex included reduction back to [W(η-C$_5$H$_5$)$_2$(CH$_3$)Ph] (ca. 60%) using saturated aqueous KOH/acetone.[11]

Hydrogen atom abstraction from [W(η-C$_5$H$_5$)$_2$(CH$_3$)Ph]PF$_6$ was accomplished by stirring the salt (0.12 g, 0.22 mmol) in CH$_3$CN (60 mL) with an excess (0.57 mmol) of the trityl radical dimer[6] at room temperature. After 2.5 h the intense red color of the cation was replaced by an orange color. The solvent was removed and the triphenylmethane formed (¹H NMR) washed off together with excess dimer (diethyl ether). The organometallic product was recrystallized from CH$_2$Cl$_2$ as brown-orange rods and plates by slow concentration of a saturated solution. Analysis and ¹H NMR showed that the product was the acetonitrile complex [W(η-C$_5$H$_5$)$_2$(CH$_2$Ph)(NCCH$_3$)]PF$_6$[12] (56%).

Formation of [W(η-C$_5$H$_5$)$_2$(CH$_2$Ph)(NCCH$_3$)]PF$_6$ (Scheme I) presumably follows generation of a methylidene–aryl cation which undergoes migratory insertion to give a 16-electron benzyl complex. Since this species lacks a β-hydrogen (unlike its ethyl or propyl analogues[1,2]), it cannot form an alkene hydride complex (eq 1), but instead coordinates a solvent molecule to give the observed product. The acetonitrile complex can also be prepared from a preformed benzyl complex by heating a solution of [W-(η-C$_5$H$_5$)$_2$(C$_2$H$_4$)CH$_2$Ph]PF$_6$[13] in acetonitrile at 45 °C. Solvent displacement of ethylene is complete within 48 h, and the product can be isolated in 44% recrystallized yield.

It is possible that the polar solvent participates more directly in the insertion step than is indicated in Scheme I. Coordination of CH$_3$CN to the cationic tungsten center could be responsible, for example, for the difference between the reactivity observed

for [W(η-C$_5$H$_5$)$_2$(CH$_2$)Ph]$^+$ and that reported for [Nb(η-C$_5$H$_5$)$_2$CH{OZrH(η-C$_5$Me$_5$)$_2$}Ph];[5] although this complex contains an electrophilic carbene ligand, it does not undergo migratory insertion (for either kinetic or thermodynamic reasons) under the conditions examined.

Simple bonding considerations (eq 3) suggest that a useful analogy can be drawn between migratory insertions in cationic alkylidene–alkyl complexes and 1,2-alkyl shifts within carbonium ions.[14] When such Wagner–Meerwein rearrangements involve

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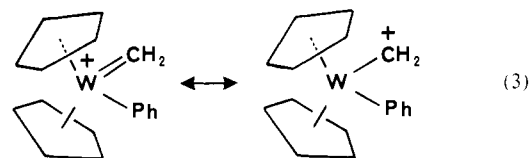
aryl migration it is usually assumed that their facility reflects the ability of the aromatic p-orbital on the migrating carbon to interact simultaneously with the carbon atoms at both termini of the migration, and it is to be expected that this bridging ability would also facilitate aryl migration in cationic alkylidene–aryl complexes of transition metals. This pathway does, however, require that the aryl group be oriented with the ring perpendicular to the plane containing the M=CH$_2$ bond and the migrating carbon, and this arrangement could result in unfavorable steric interactions with other ligands. In the tungstenocene system such contacts do not apparently prevent the migration, although the steric interactions observed between the ring hydrogens and the ethylidene ligand in [Ta(η-C$_5$H$_5$)$_2$(CHCH$_3$)CH$_3$][15] would suggest that similar interactions with the perpendicular phenyl in [W(η-C$_5$H$_5$)$_2$-(CH$_2$)Ph]$^+$ are probably marked.

(14) Kirmse, W. *Top. Curr. Chem.* **1979**, *80*, 125.
(15) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.

Spectroscopy and Photochemistry of Binuclear Iridium(I) Complexes

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Extensive spectroscopic studies on Rh$_2$b$_4^{2+}$ (b is 1,3-diisocyanopropane) and Pt$_2$(P$_2$O$_5$)$_4$H$_8^{4-}$ indicate that the ¹A$_{1g}$ (D_{4h}) ground state is weakly metal–metal bonding, and the lowest electronic excited states are a triplet (³A$_{2u}$) and a singlet (¹A$_{2u}$) derived from the (dσ)^2(dσ*)^1(pσ)^1 electronic configuration.[2] Interestingly, the luminescent ³A$_{2u}$ excited state, which is strongly metal–metal bonding,[2c,3] undergoes reversible electron-transfer

(9) ESR (CH$_2$Cl$_2$, 25 °C,, 9.439 GHz): ⟨g⟩ = 2.049. IR (KBr): 3133 s, 3068 w, 3052 mw, 2970 w br, 2902 w, 1571 m, 1560 w, 1438 s br, 1420 ms, 1385 m, 1337 w, 1316 w, 1304 w, 1245 w, 1211 w, 1128 w, 1070 mw, 1025 m sh, 1019 ms, 1000 m, 969 mw, br, 850 vs br, 741 s, 703 ms, 552 s, 490 w, 365 mw br. Anal. Calcd for C$_{17}$H$_{18}$F$_6$PW: C, 37.04; H, 3.30. Found (Galbraith Laboratories, TN): C, 37.07; H, 3.34.
(10) Lindsell, W. E. *J. Chem. Soc., Dalton Trans.* **1975**, 2548.
(11) The tungstenocene dialkyl radical cations which we have prepared previously[2,7] are characteristically reduced to the parent W(IV) complexes under these conditions.
(12) ¹H NMR (acetone-d_6, 80 MHz): δ 7.20–7.00 (c, 5 H, C$_6$H$_5$), 5.43 (s, 10 H, 2C$_5$H$_5$), 2.81 (s, 3 H, CH$_3$CN), 2.65 (s, satellites J_{183w} = 8.1 Hz, 2 H, CH$_2$). Anal. Calcd for C$_{19}$H$_{20}$F$_6$NPW: C, 38.60; H, 3.42. Found (Schwarzkopf Laboratories, NY): C, 38.33; H, 3.52.
(13) Benfield, F. W. S.; Cooper, N. J.; Green, M. L. H. *J. Organomet. Chem.* **1974**, *76*, 49.

(1) (a) California Institute of Technology, Pasadena, CA 91125. (b) University of Victoria, Victoria, British Columbia, Canada.
(2) (a) Rice, S. F.; Milder, S. J.; Gray, H. B.; Goldbeck, R. A.; Kliger, D. S. *Coord. Chem. Rev.* **1982**, *43*, 349 and references therein. (b) Che, C-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796. (c) Rice, S. F.; Gray, H. B. *Ibid.* **1983**, *105*, 4571.
(3) (a) Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 1593. (b) Dallinger, R. F.; Miskowski, V. M.; Gray, H. B.; Woodruff, W. H. *Ibid.* **1981**, *103*, 1595. (c) Che, C-M.; Butler, L. G.; Gray, H. B.; Crooks, R. M.; Woodruff, W. H. *Ibid.* **1983**, *105*, 5492.
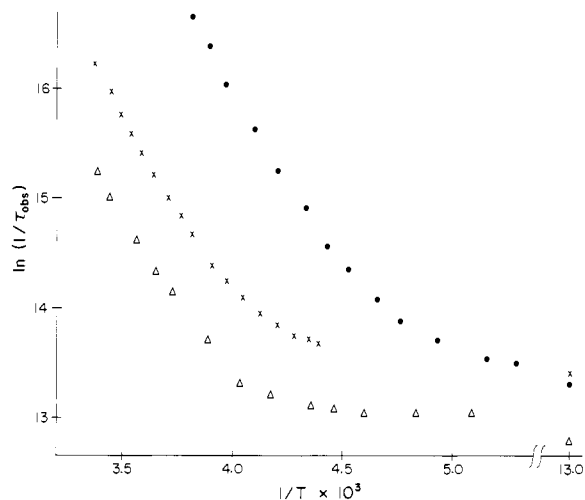
Figure 1. Arrhenius plots of the $^3B_2(d\sigma^*p\sigma)$ excited-state lifetimes: ●, $[Ir(\mu\text{-}3\text{-}CH_3\text{-}5\text{-}CF_3(pz))(COD)]_2$; ×, $[Ir(\mu\text{-}3,4,5\text{-}(CH_3)_3(pz))(COD)]_2$; △, $[Ir(\mu\text{-}pz)(COD)]_2$.

reactions with a variety of acceptors and donors.[2b,4] As evidenced by our results reported here, the description of the metal–metal interactions in these D_{4h} species may be extended to d^8–d^8 complexes of C_{2v} symmetry. In contrast to the "face-to-face" systems, the metals in these lower symmetry complexes are more accessible to potential substrates, enhancing the possibility of multielectron excited-state reactivity.

Our studies have focused on pyrazolyl-bridged iridium complexes of the form $[Ir(\mu\text{-}pz)(COD)]_2$ (pz is pyrazolyl, COD is 1,5-cyclooctadiene) (**1**). In the parent complex, **1**, the iridium–
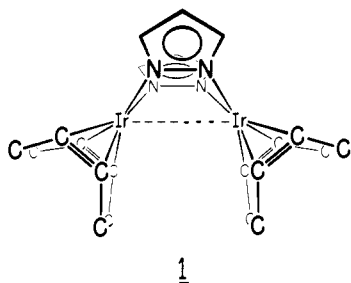
1

iridium separation is 3.216 (1) Å,[5] consistent with weak metal–metal bonding in the ground state. The absorption spectrum of **1** in acetonitrile is similar to that of the "face-to-face" systems, and by analogy, the bands centered at 498 ($\epsilon_{max} = 9100$ M^{-1} cm^{-1}) and 585 nm ($\epsilon_{max} = 260$ M^{-1} cm^{-1}) are assigned as the singlet and triplet components, respectively, of the $d\sigma^* \rightarrow p\sigma$ transition. Luminescence is observed from both these states ($^1B_2$ and $^3B_2$), and the excited-state lifetimes are 250 ns for the phosphorescence ($\lambda_{max} = 687$ nm, $\phi_p = 7.8 \times 10^{-3}$) and less than 100 ps for the fluorescence ($\lambda_{max} = 564$ nm, $\phi_f = 1 \times 10^{-4}$) in acetonitrile at ambient temperature.[6]

Both the emission quantum yield and the lifetime of the $^3B_2(d\sigma^*p\sigma)$ excited state of **1** increase dramatically at 77 K ($\tau(295$ K$) = 250$ ns, $\tau(77$ K$) = 2.68$ μs), implying that the temperature dependence of the lifetime is primarily due to variations in the rate constant for nonradiative decay, k_{nr}. The temperature dependence of the triplet lifetime (Figure 1) can be fit to a two-term expression of the form $(1/\tau_{obsd}) = k_0 + k_1 e^{-E_a/kT}$, where $(1/\tau_{obsd})$
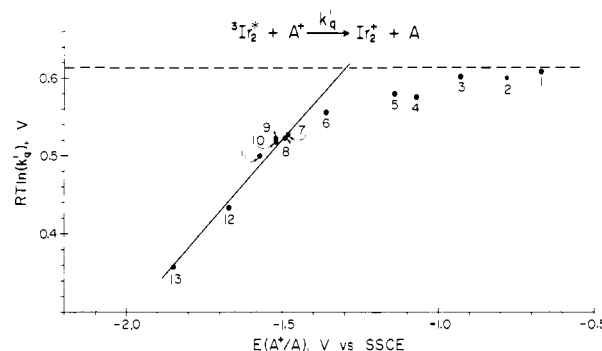
**Figure 2.** Plot of $RT \ln (k'_q)$ vs. $E(A^+/A)$ for the electron-transfer quenching of the $^3B_2(d\sigma^*p\sigma)$ excited state of $[Ir(\mu\text{-}pz)(COD)]_2$ in CH$_3$CN at 22 ± 2 °C: $[[Ir(\mu\text{-}pz)(COD)]_2] = 10^{-4}$ M, $\mu = 0.1$ M $[(n\text{-}C_4H_9)_4NPF_6]$. The quenchers are PF$_6^-$ salts. The rate constants (k'_q) are corrected for diffusion effects. For quenchers 1–3, $E(A^+/A) = E_{1/2}(A^+/A)$. For quenchers 4–13, the reductions are irreversible; therefore, the values of $E(A^+/A)$ are the cathodic peak potentials, E_p- (A^+/A), measured at a constant scan rate (200 mV s^{-1}). Both $E_{1/2}$- (A^+/A) and $E_p(A^+/A)$ were measured by cyclic voltammetry (CH$_3$CN, $\mu = 0.1$ M $[(n\text{-}C_4H_9)_4NPF_6]$, 22 ± 2 °C). 4-Cyano-N-methylpyridinium (**1**), 4-carbomethoxy-N-methylpyridinium (**2**), 4-amido-N-ethyl-pyridinium (**3**), 3-amido-N-benzylpyridinium (**4**), 3-amido-N-methyl-pyridinium (**5**), N-ethylpyridinium (**6**), 2-methoxy-N-methylpyridinium (**7**), 4-methyl-N-methylpyridinium (**8**), 4-tert-butyl-N-ethylpyridinium (**9**), 2,6-dimethyl-N-methylpyridinium (**10**), 2,3,6-trimethyl-N-methyl-pyridinium (**11**), 2,4,6-trimethyl-N-methylpyridinium (**12**), 2,6-di-methyl-4-methoxy-N-methylpyridinium (**13**).

approximates k_{nr} because ϕ_p is <0.1 at high temperature. For the $^3B_2(d\sigma^*p\sigma)$ excited state of $[Ir(\mu\text{-}pz)(COD)]_2$, the activation energy, E_a, is 2600 cm^{-1}, which is similar to the values of E_a for the substituted pyrazolyl complexes, $[Ir(\mu\text{-}3\text{-}CH_3\text{-}5\text{-}CF_3(pz))\text{-}(COD)]_2$ and $[Ir(\mu\text{-}3,4,5\text{-}(CH_3)_3(pz))(COD)]_2$ (2300 and 2500 cm^{-1}, respectively). We have noted similar behavior in the temperature dependence of k_{nr} for several D_{4h} d^8–d^8 systems,[2a] and we are currently investigating the nature of this thermal deactivation.

From spectroscopic and electrochemical measurements,[7] the $^3B_2(d\sigma^*p\sigma)$ excited state of $[Ir(\mu\text{-}pz)(COD)]_2$ is predicted to be a powerful reductant, as illustrated in the modified Latimer diagram below (Ir$_2$ is $[Ir(\mu\text{-}pz)(COD)]_2$).
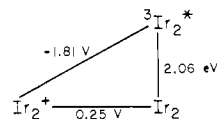
Electron-transfer quenching of this excited state by methyl viologen (MV^{2+}, $E_{1/2}$(MV^{2+}/MV$^+$) = -0.45 V vs. SSCE[8]) is rapid, proceeding at a diffusion-limited rate of 1.6×10^{10} M^{-1} s^{-1}. Flash spectroscopic studies of the thermal back-electron-transfer reaction ($k_b = 1.2 \times 10^9$ M^{-1} s^{-1}) (eq 1) reveal the presence of the transient

$$Ir_2^+ + MV^+ \xrightarrow{k_b} Ir_2 + MV^{2+} \tag{1}$$
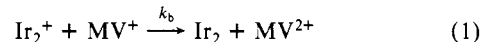
radical cation, MV$^+$,[9] which confirms that quenching of the triplet excited state proceeds via electron transfer.

We have confirmed that **1** is a powerful photoreductant in acetonitrile solution from a detailed investigation of the kinetics of electron-transfer quenching of the $^3B_2(d\sigma^*p\sigma)$ state by a series of alkylated pyridinium acceptors with widely varying reduction potentials. The classical theory of outer-sphere electron transfer[10]

(4) (a) Milder, S. J.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 6761. (b) Fukuzumi, S.; Hironaka, K.; Nishizawa, N.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2220.

(5) (a) Coleman, A. W.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 922. (b) Beveridge, K. A.; Bushnell, G. W.; Stobart, S. R.; Atwood, J. L.; Zaworotko, M. J. *Organometallics* **1982**, *2*, 1447.

(6) The emission quantum yields are relative to that of Ru(bpy)$_3$(PF$_6$)$_2$ (ϕ_r = 0.062: Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583). Uncertainties are ±10%.

(7) From cyclic voltammetric measurements, $E_{1/2}$(Ir$_2^+$/Ir$_2$) = 0.25 V vs. SSCE (CH$_3$CN, μ = 0.1 M $[(n\text{-}C_4H_9)_4NBF_4]$, 22 °C).

(8) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710.

(9) For MV$^+$, ϵ(605 nm) = 1.07 × 10^4 M^{-1} cm^{-1} (Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524).

(10) (a) Scandola, F.; Balzani, V.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2519 and references therein. (b) Bock, C. R.; Connor, J. A.; Guitierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagel, J. K. *Ibid.* **1979**, *101*, 4815.

predicts that a plot of $RT \ln (k'_q)$ vs. $E°(A^+/A)$ should be linear for quenchers with values of $E°(A^+/A)$ less than or approximately equal to $E°(Ir_2^+/{}^3Ir_2^*)$ and approach a diffusion-limited value for $E°(A^+/A)$ greater than or approximately equal to the value of $E°(Ir_2^+/{}^3Ir_2^*)$.[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.

Acknowledgment. We thank Jonathan Caspar and Terry Smith for assistance with certain experiments and for helpful discussions. This research was supported by National Science Foundation Grant CHE81-20419.

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

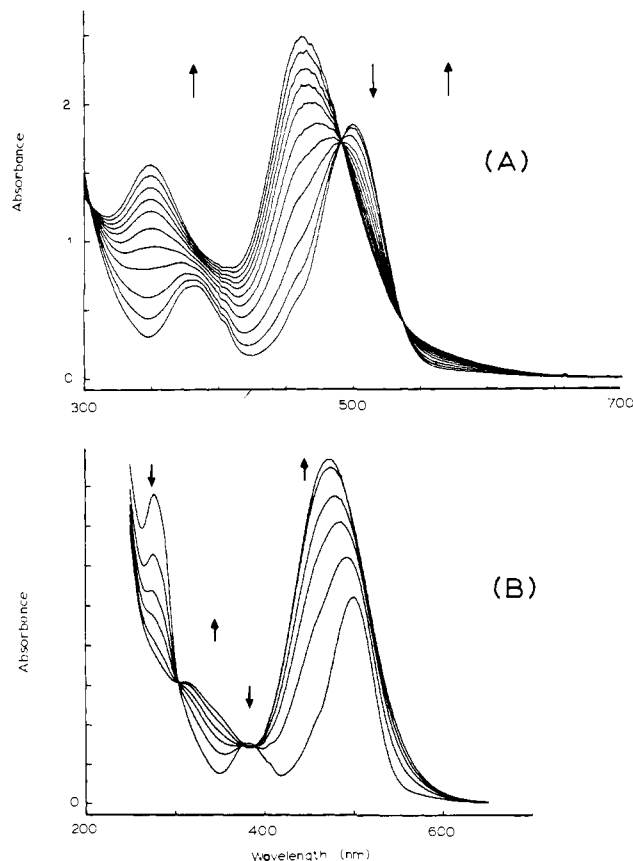(12) Caspar, J. V.; Gray, H. B. *J. Am. Chem. Soc.*, following paper in this issue.

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(μ-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.

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

(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.

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

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)(μ-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

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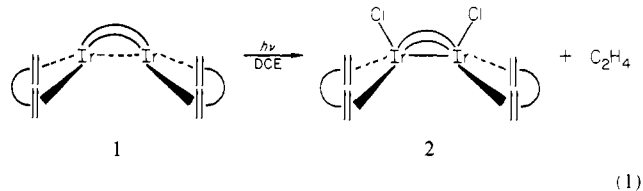
photon of visible light has been used to effect the two-electron reduction of DCE with the concomitant formation of a binuclear iridium(II) species.[5]

(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$_2$Cl$_2$) (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(μ-pz)(COD)Cl]$_2$·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.