formed from the precatalyst Ir(OEP)H by electrochemical oxidation at the beginning of the cathodic scan.[17] As the potential becomes more negative than E_f, the catalytic activity is diminished upon formation of Ir(OEP)H, which reacts with $\mathrm{O_2}$ relatively slowly to form $\mathrm{Ir(OEP)O_2H}$, which is not an intermediate in the fast four-electron catalytic cycle. Rapid oxidative dimerization of Ir(OEP)H to a very effective catalyst, $[\mathrm{Ir(OEP)}]_2$, is therefore the key to the remarkable activity of this system.[19] This work is currently being expanded to include diiridium cofacial porphyrins. Further studies to elucidate the mechanistic details are also in progress.

Acknowledgment. We thank C. R. Leidner for the synthesis of $[\mathrm{Ir(OEP)}]_2$ and assistance in data analysis and M. G. Finn, F. C. Anson, R. W. Murray, N. S. Lewis, and G. T. Yee for helpful discussions. We acknowledge the Bio-Organic, Biomedical Mass Spectrometry Resource, supported by the NIH Division of Research Resources Grant RR01614, and the National Science Foundation (Grant FSVCHE83-18512) for support.

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(17) The following cyclic voltammetric data is consistent with the reversible electrochemical interconversion of Ir(OEP)H and $[\mathrm{Ir(OEP)}]_2$.[20] (a) Both Ir(OEP)H and $[\mathrm{Ir(OEP)}]_2$ on graphite exhibit the same redox wave under $\mathrm{N_2}$. (b) One electron per Ir(OEP)H is passed in the redox process;[9] however, the full width at half-maximum peak height (fwhm) is considerably narrower (~57 mV) that would be expected for a simple one-electron transfer, suggesting the presence of some other phenomenon, including a dimerization reaction. For the case of electron transfer followed by a dimerization reaction, the expected fwhm is a complicated function of the rate of dimerization and scan rate.[21] When the dimerization rate is much faster than the scan rate, the fwhm is calculated to be 47 mV for a one-electron process, close to the observed value.

(18) Wan, G. X.; Shigehara, K.; Tsuchida, E.; Anson, F. C. *J. Electroanal. Chem.* **1984**, *179*, 239.

(19) We believe that the inability of adsorbed Ir(TTP)H to show a surface redox wave and to catalyze the reduction of oxygen results from an inhibition of the rapid oxidative dimerization reaction, either by a different surface morphology or an intrinsic steric barrier to dimerization.

(20) It should be noted that the interconversion of Ir(OEP)H and $[\mathrm{Ir(OEP)}]_2$ has not been demonstrated in solution. Cyclic voltammetry of Ir(OEP)H (0.2 M $\mathrm{Bu_4NPF_6}$ in $\mathrm{CH_2Cl_2}$ at a Pt electrode with Ag wire pseudoreference, $\mathrm{FeCp_2}^{0/+}$ = 0.33 V) showed the following features: (1) irreversible reduction at ~−1.8 V; (2) one irreversible oxidation at 1.4 V and one reversible wave at 1.7 V; (3) a chemically and electrochemically irreversible oxidation at ~0.6 V. Features 1 and 2 are presumably ligand-centered processes. The nature of the oxidation at 0.6 V is not yet established.

(21) Laviron, E. *Electrochim. Acta* **1971**, *16*, 409.

Sigmatropic [1,3]-Hydrogen Migration in a 1-Silapropene

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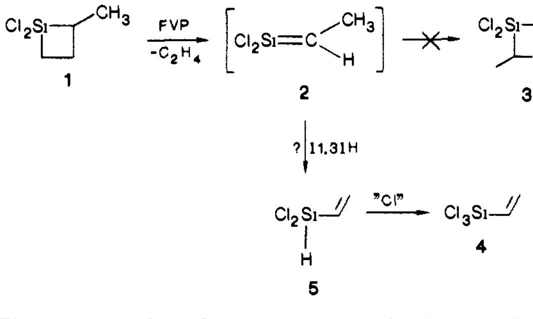
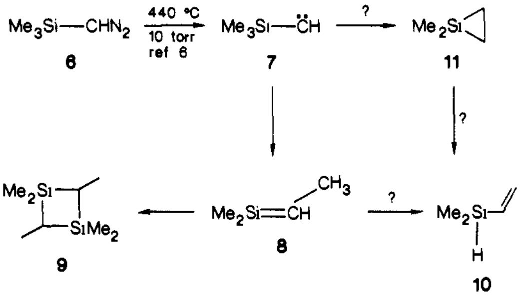
Suprafacial sigmatropic [1,3] shifts are symmetry-forbidden unless there is accompanying inversion of the migrating group, while the symmetry-allowed antarafacial [1,3] shift is rendered extremely awkward at best by geometric constraints.[1] Thus, although there are rare examples of the [1,3]-sigamtropic shifts of carbon,[2] to our knowledge the [1,3]-sigmatropic migration of hydrogen has not been observed. MINDO/CI calculations by Dewar[3] predict an activation energy of 49.2 kcal/mol for the 1,3-allylic hydrogen shift in propene.

In view of the above, it was with considerable surprise that we observed in the flash vacuum pyrolysis (FVP) of 1,1-dichloro-2-methyl-1-silacyclobutane (**1**) none of the expected dimer **3** of silene **2** and a 46% yield of vinyltrichlorosilane (**4**).[4] As silacyclobutane pyrolysis is a standard route to the silicon–carbon double bond,[5] it was difficult to ignore the possibility that **4** arose from a rearrangement of the anticipated 1,1-dichloro-1-silapropene (**2**). If, indeed, silene **2** rearranged via a [1,3]-hydrogen shift, the product would be dichlorovinylsilane **5** and not the trichloro species **5**. However, the facile H/Cl redistribution on silicons makes it possible that we might not actually observe **5** from this reaction mixture.[6]



The question of [1,3]-hydrogen migration in 2-methylsilenes has arisen before. In 1975 Shechter[7] reported that trimethylsilyldiazomethane (**6**) thermally produced carbene **7** which isomerized to 1,1,2-trimethylsilene (**8**) as evidenced by the formation of its head-to-tail dimer **9** in ca. 40% yield. Of considerable interest was the concomitant formation of dimethylvinylsilane (**10**) albeit in quite low yield (3–4%). It was recognized that the vinylsilane could either arise from rearrangement of **8** or from isomerization of 1,1-dimethylsilacyclopropane (**11**), derived directly from carbene **7**. Indeed, this latter process had literature precedent in the proposal of Skell[8] that reaction of $\mathrm{Me_3SiCHCl_3}$ with Na–K vapor at 260 °C produced **10** via silirane **11**.



The obvious experiment for distinction between **8** and **11** as progenitors of **10** is deuterium labeling of the carbenic carbon of **7**. This experiment was conducted by Shechter but, unfortunately, insufficient **10-D** was produced for the crucial determination of the position(s) of deuterium substitution. The only clue was the formation of 2,5-dideuterio-3,3,4,4-tetramethyl-3,4-disilahex-1-ene (**12**) which was reasonably assumed to arise from insertion of **8-D** into the Si–H bond of **10-2D** and thus to deductively establish the position of the deuterium in **10-D**. Unfortunately, that interpretation now suffers from the absence of precedent for such an insertion reaction,[9] our inability to produce the formation of **12** under our conditions of FVP (vide infra), and an alternative mechanistic possibility for the formation of **12** (Scheme I). We note that **12** could have been produced by head-to-head dimer-

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(1) Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1971.

(2) Baldwin, J. E. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II.

(3) Bingham, R. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9107.

(4) At 810 °C there is 99% conversion of **1**. The yield of **4** assumes that two molecules of **1** are required to produce one of **4**.

(5) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(6) Cherneyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A.; Sokolov, V. V. *Zh. Obsh. Khim.* **1978**, *48*, 830. These authors report that the addition of $\mathrm{:SiCl_2}$ to ethylene affords both **5** (7%) and **4** (18%), thus weakening our suggestion. We will more completely discuss this point and present alternative mechanistic pathways in a complete report on the thermochemistry of chlorosilacyclobutanes.

(7) Shechter, H.; Kreeger, R. L. *Tetrahedron Lett.* **1975**, 2061.

(8) Skell, P. S.; Goldstein, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 1442.

(9) Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1984**, *3*, 918.

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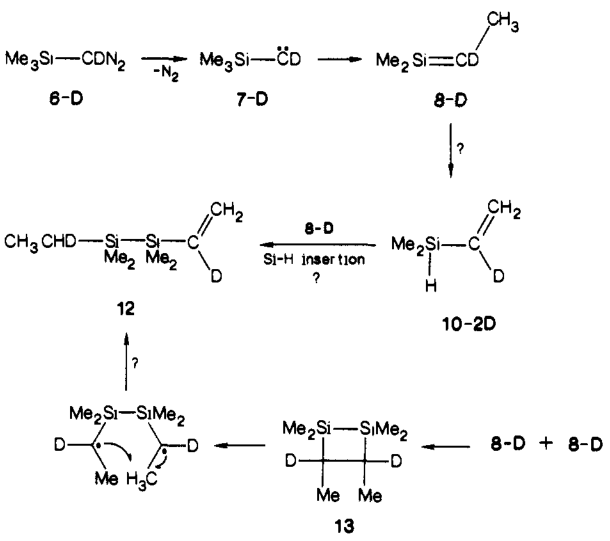
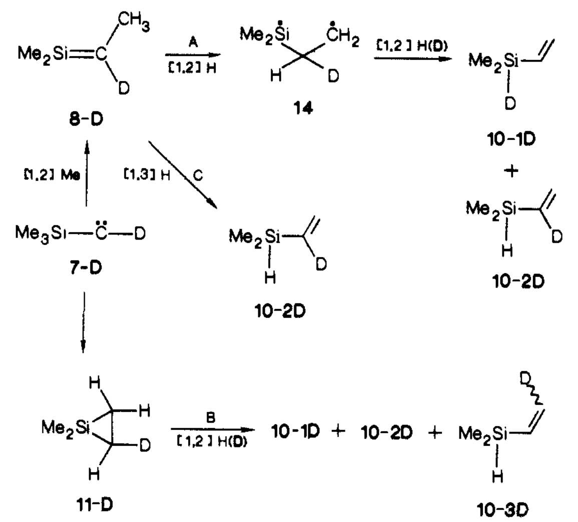
Scheme I

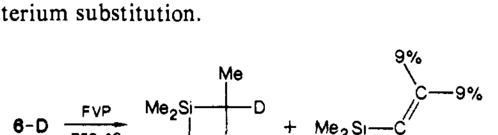


Scheme II



ization[10] of **8-D** to form **13**, C–C bond homolysis, and intramolecular hydrogen abstraction.

We have carried out a detailed study of the FVP (750 °C, ca. 0.01 torr) of **6-D**[11] and find from deuterium NMR that the deuterium in **10-D** is scrambled in a nonrandom fashion, while in **9-2D** it is located only on the ring carbons. Scrambling of the deuterium positions in **10-D** *after* formation is eliminated by the observation that FVP (750 °C) of $Me_2DSiCH=CH_2$ (**10-1D**) returns this compound with complete integrity of the position of deuterium substitution.



9-2D (40%) **10-D** (3%)
(only monodeuterated)

The labeling distribution of **10-D** is consistent with competing processes of silirane (**11-D**) and silene (**8-D**) isomerizations to the vinylsilane (Scheme II) and if k_H/k_D for both is unity would thus represent 64% [1,3]-sigmatropic hydrogen migration and 36% silacyclopropane rearrangement. However, there is yet another conceivable pathway to produce products **10-1D** and **10-2D**, namely, a [1,2]-hydrogen shift to afford 1,3-diradical **14** which proceeds to product by a 1,2-shift of either H or D (path A, Scheme II).

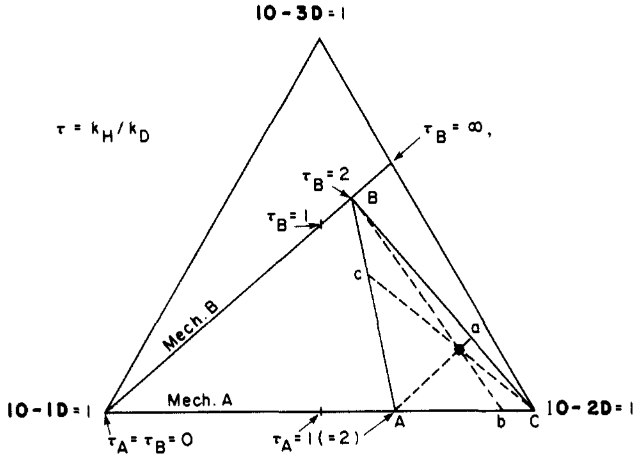


Figure 1. Tertiary component plot for products **10-1D**, **-2D**, and **-3D** from mechanisms A, B, and C with variable k_H/k_D (τ). The experimental point is 73% **10-2D**, 18% **10-3D**, and 9% **10-1D**. This example assumes $\tau_A = \tau_B = 2$.

Analysis of the problem of three mechanisms and three products is mathematically simple but tedious when repeated for a variety of assumed k_H/k_D (τ) values for mechanisms A and B. However, this situation is conveniently handled with a tertiary component plot (Figure 1) where each interior point in the equilateral triangle represents a product distribution of **10-1D**, **-2D**, and **-3D**. Mechanism A is on the base (the particular composition point being set by τ_A) since this route produces no **10-3D**, mechanism B is an internal line with components for each of the three products (except where $\tau_B = 0, \infty$), and mechanism C is only the lower right apex since it affords only product **10-2D**. One assumes values for τ_A and τ_B, connects the three mechanisms to form an inner triangle, segments the sides by dropping lines from each mechanism's composition point through the experimental point, and determines the fractions of reactant consumed by each of the three paths from the ratios of the line segments. Figure 1 shows this analysis where $\tau = 2$ for both "A" and "B". The operative fraction by mechanism A, f_A, is given by

$$f_A = C_bB_c/[A_cC_b + A_bB_c + C_bB_c]$$

and f_B and f_C are given by corresponding expressions.[13]

If k_H/k_D for both mechanisms A and B lies between 1 and 2, as seems likely from the results of Rabinovitch[14] on cyclopropane to propene isomerization, the formation of vinylsilane **10** is due both to a [1,3]-sigmatropic H-migration (64–53%)[16] and to isomerization of an intermediate silacyclopropane (36–31%).

These conclusions are dependent upon the validity of the assumption that vinylsilane **10** arises in a unimolecular fashion from

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(10) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.

(11) Compound **6-D** was prepared by the method of Mori[12] and enriched to 87% D_1 by sequential reaction with MeLi and D_2O.

(12) Mori, S.; Sakai, I.; Aoyama, T.; Shioiri, T. *Chem. Pharm. Bull.* **1982**, *30*, 3380.

(13) The concepts employed here in the tertiary component plot analysis are those which are described for phase diagrams in any standard physical chemistry text. To our knowledge, a kinetic application of these principles has not appeared before, and we plan to publish a more detailed description of this technique in the near future.

(14) Rabinovitch, B. S.; Gilderson, P. W.; Blades, A. T. *J. Am. Chem. Soc.* **1964**, *86*, 2994. In fact, in their studies of cyclopropane and cyclopropane-d_6, these authors found an inversion of k_H/k_D at ca. 10^{-2} torr with a limiting value of ca. 0.8. The limiting high-pressure value was determined by Blades[15] to be 1.96. Our data will not support that an inverse isotope effect as the experimental point can only accommodate τ values between 1.0 and 8.11; however, the pressure in our reaction zone is not accurately known and is quite likely on the edge of the inversion point.

(15) Blades, A. T. *Can. J. Chem.* **1961**, *39*, 1401.

(16) Wiberg[17,18] has reported that 2-(trimethylsilyl) silenes readily undergo 1,3-Si-to-Si migrations of methyl.

(17) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

(18) Wiberg, N.; Wagner, G.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

carbene **7**. Thus, it was necessary to explore the possibility that **10** arose from decomposition of the major product, silene dimer **9**. FVP of **9** at 750 °C produced only a trace of **10** (detectable only by GC MS), but at 850 °C the complex product mixture contained 9% of **10**. FVP of **9-2D** at 850 °C afforded **10-D** in which 66% was **10-2D**, 10% **10-3D**, 5% **10-1D**, and 18% deuterium incorporation into the methyl groups. Therefore, it appears that little, if any, of vinylsilane **10** originates from silene dimer decomposition, and the little that does almost certainly comes from reversion of dimer **9** to silene **8**, judging from the similarity of deuterium distribution.

Acknowledgment. The support of this work by the National Science Foundation is gratefully acknowledged. David K. Hoffman thanks the Department of Energy for support of his portion of this work.

Photoisomerization of the Ruthenium Cluster $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$, an Unprecedented Oxygen-to-Carbon Alkyl Migration

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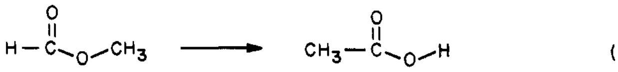
The formation of carbon-carbon bonds from simple C_1 precursors is a topic of major interest in both heterogeneous and homogeneous catalysis chemistry.[1] For example, a potentially important transformation is the isomerization of methyl formate (which can be formed by the base catalyzed methanolysis of carbon monoxide)[2] to acetic acid (eq 1). Although catalysts for this

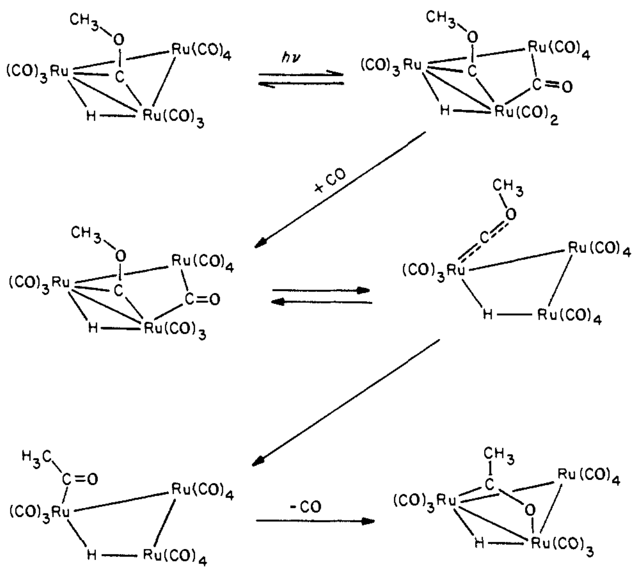


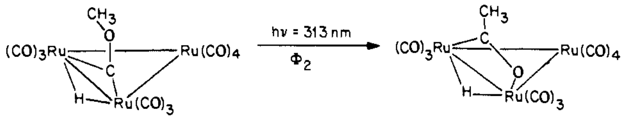
$$H-\overset{\overset{O}{\|}}{C}-O-CH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-H \qquad (1)$$

transformation have been reported,[3] the conditions are relatively extreme and mechanisms are unknown. To our knowledge, simple molecular models for methyl migration from oxygen to carbon are unprecedented. Here we describe such a molecular transformation, in this case, the result of photochemical excitation of the bridging methylidyne triruthenium cluster $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$.[4]

Photolysis (λ_{irr} 313 nm)[5] of a 10^{-4} M solution of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ (I) in CO-saturated cyclohexane led to significant changes in the electronic spectrum. The absorption band characteristic of the starting cluster λ_{max} 384 nm (ϵ = 6900 M^{-1} cm^{-1}) diminished in intensity and underwent a shift to slightly lower wavelengths, accompanied by rising absorbance at longer wavelengths. Isosbestic points observed at 436 and 358 nm, for >40% reaction, clearly indicated that the initial cluster had undergone a clean transformation to a single product (or to several products in constant proportion), which is significantly less sensitive to secondary photolysis at 313 nm. Although the product infrared spectrum proved virtually identical with that of I, significant changes in the proton NMR spectra (300 MHz) were evident. The starting complex I, in CO-saturated benzene-d_6 solution, displayed singlets for the methylidyne CH_3– group at 3.64 ppm and for the hydride proton at −14.90 ppm in the expected 3:1 ratio. After several hours of photolysis (313 nm) these had significantly diminished and a new methyl resonance at 2.07 ppm and a new hydride resonance at −13.98 ppm in a 3:1 ratio had appeared. All three spectral properties (electronic, IR, and ^1H NMR) are fully consistent with identification of the product as the $\mu\text{-}\eta^2$-acyl cluster $HRu_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C(O)CH_3)$ (II),[6] the result of overall oxygen-to-carbon migration of the methyl group (eq 2).

Scheme I

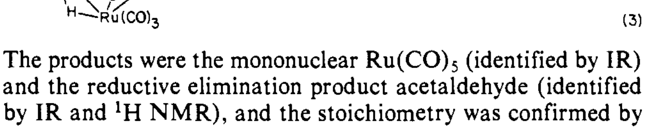




(2)

Quantum yields for eq 2 (Φ_2), determined by using standard techniques,[5] were found to be notably dependent both on the CO concentration and on the irradiation wavelength λ_{irr}. Although the resulting optical changes were the same for different λ_{irr}, the quantum yields in CO-saturated cyclohexane varied from $<10^{-5}$ mol/einstein at λ_{irr} = 405 nm to 4.9×10^{-2} at 313 nm. Furthermore, Φ_2 was found to be strongly dependent on P_{CO} and to vary linearly from 1.2×10^{-4} at $P_{CO} = 0$ (P_{N_2} = 1.0 atm) to 4.9×10^{-2} mol/einstein at P_{CO} = 1.0 atm for 313-nm photolysis in cyclohexane.

Long-term photolysis (313 nm) of II in CO-saturated cyclohexane eventually did lead to fragmentation of the cluster (eq 3).



(3)

The products were the mononuclear $Ru(CO)_5$ (identified by IR) and the reductive elimination product acetaldehyde (identified by IR and ^1H NMR), and the stoichiometry was confirmed by IR spectral techniques. This photoreaction was studied quantitatively by using authentic samples of $HRu_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C(O)CH_3)$ (10^{-4} M), and the quantum yield at 313-nm irradiation was found to be 1.1×10^{-3} mol/einstein.

The mechanism of the unprecedented transformation shown in eq 2 is unclear from the present data. Of particular note is the promotion of this photoreaction by CO, although additional CO is not required by the stoichiometry of eq 2. In earlier studies of the photolytic fragmentation of the triangular cluster $Ru_3(CO)_{12}$,[7] a key step in the proposed mechanism[7c-f] was the heterolytic

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(1) *Catalysis in C_1 Chemistry*; Keim, W., Ed.; Reidel: Dordrect, Holland, 1983.

(2) Aguilo, A.; Horlenko, T. *Hydrocarbon Process.* **1980**, *59*, 120.

(3) Pruett, R. L.; Kacmarcik, R. T. *Organometallics* **1982**, *1*, 1693-1699.

(4) Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* **1983**, *2*, 219.

(5) Cyclohexane and benzene-d_6 were freshly distilled from $LiAlH_4$, freeze degassed, and then saturated with the appropriate gas. Photolyses were performed at λ_{irr} 313, 334, 365, and 405 nm by using apparatus and procedures described previously (Hintze, R. E.; Ford, P. C. *J. Am. Chem. Soc.* **1975**, *97*, 2664-2671). Light intensities were measured by ferrioxalate or Actinochrome IR actinometry.

(6) Boag, N. M.; Kampe, C. E.; Lin, Y. C.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704-1708.

0002-7863/86/1508-7851$01.50/0