$(O_2CCF_3)(O_2\text{-}t\text{-}Bu)]_4$.[3a] We find that this alkyl peroxide complex reacts (slowly) with cycloheptene to give, in contrast to nitro complex **1**, only products attributable to β- and/or β'-hydrogen elimination (e.g., enone (33%), enol (11%), and ketone (1%)).[28] These results are consistent with a higher metallacycle to open-chain isomer ratio for nitrogen-bonded Ia vs. oxygen-bonded Ib as would be expected from the greater ligating strength of nitrogen vs. oxygen donors to Pd(II). They also suggest that epoxidation and β-hydrogen elimination are nearly competitive and that catalyst modification should allow for the epoxiation of terminal alkenes. Thus, it is tempting to speculate that the universal formation of epoxides in the case of high-valent, oxophilic d^0 transition-metal catalysts results from the stability of proposed oxygen-bonded metallacyclic intermediates Ib and Ic toward β-hydrogen elimination.[29] The intermediacy of metallacycles in these d^0 systems is highly controversial, however, since alternative nonmetallacyclic mechanisms[1c,4a,b,d,5] are at least as consistent with the extensive but inconclusive available data.

Acknowledgment. We are grateful to Dr. F. Mares for agreeing to joint publication of our related investigations and to Dr. K. Loening of Chemical Abstracts for assistance with nomenclature. This research was carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

Registry No. 1, 77933-52-9; **5**, 82135-64-6; $[Pd(O_2CCF_3)(O_2\text{-}t\text{-}Bu)]_4$, 73644-24-3; norbornene, 498-66-8; *exo*-epoxynorbornene, 3146-39-2; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; 2-cyclohepten-1-ol, 4096-38-2; *cis*-cyclooctene, 931-87-3; *trans*-cyclooctene, 931-89-5.

Supplementary Material Available: Experimental details for syntheses and reactions (3 pages). Ordering information is given on any current masthead page.

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(28) Norbornene does give *exo*-epoxynorbornene (50%), but no intermediates were detectable.

(29) Stability toward β-hydrogen elimination in these systems would result from both π electron donation by the oxygen ligands[30] and from the inhibition by the strong metal-oxygen bonds of ring opening.

(30) Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440-1447.

Pulsed-Laser Photocatalytic Isomerization and Hydrogenation of Olefins

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A central prerequisite for organometallic catalysis is coordinative unsaturation at the active site. In most homogeneous systems this requirement is satisfied thermally by pyrolysis of the catalyst precursor in the presence of substrate.[1] Photodissociation is also an effective initiation technique in many cases, as evidenced by the growing number of known photocatalytic systems.[2] This communication introduces a new initiation method of great promise for the study of organometallic catalysis. We have used sustained near-ultraviolet pulsed irradiation to produce catalytically active organo-transition metal fragments on a nanosecond time scale under mild liquid-phase conditions. These catalysts show high thermal activity under the ambient conditions of the medium and revert between laser pulses to catalytically inert precursors.

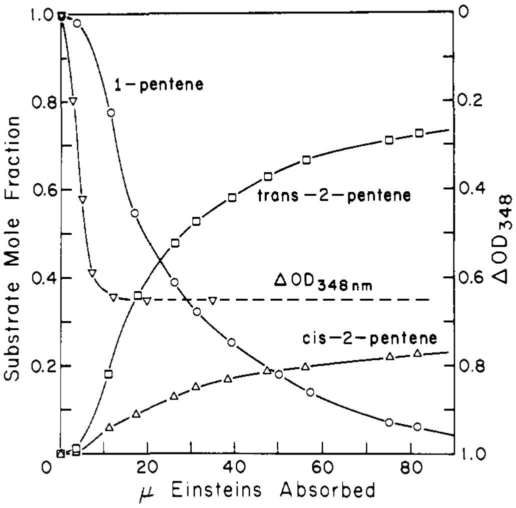

Figure 1. Time dependence of photocatalytic isomerization and change in optical density at 348 nm plotted as a function of μeinsteins absorbed under conditions of 2×10^{-3} M $Fe(CO)_5$ in pure 1-pentene, 300 K, 4.0-Hz laser-pulse repetition rate.

The initial subjects of our investigation have been the iron carbonyl catalyzed isomerization and hydrogenation of olefins, systems long noted for their high photocatalytic activity. Previous photolytic[3,4] and thermal[5] studies have implicated $Fe(CO)_3$ as the recurring catalytic unit. This communication reports intrinsic turnover and parametric reversion rates for laser-initiated catalytic isomerization and presents data in support of a proposed complete mechanistic cycle.

Pulsed-laser irradiation of $Fe(CO)_5$ in hydrocarbon solutions of linear pentenes or hexenes rapidly yields an equilibrated isomeric mixture, as illustrated for 1-pentene in Figure 1. Laser pulse lengths are 6-12 ns, depending on the choice of wavelength (N_2 337 nm and XeF 351 nm are used for most experiments). Pulse repetition rate and average laser power are variable.[6] All experiments are conducted under an N_2 or Ar atmosphere. Irradiated mixtures are analyzed by infrared and optical spectroscopy and by gas chromatography.

No unsaturated organic products are observed other than linear isomers of the initial olefin. When $Fe(CO)_5$-pentene mixtures are irradiated under an H_2 atmosphere, no aliphatic product other than pentane is seen. Under conditions of low $Fe(CO)_5$ concentration ($>10^{-2}$ M) we find no spectroscopic evidence for organometallic complexes other than $Fe(CO)_5$ and $Fe(CO)_4$(pentene) over the entire course of the isomerization run. However, visible absorption bands attributable to organo-transition metal clusters are observed in the case of prolonged irradiation of concentrated $Fe(CO)_5$ solutions. Significantly, holding substrate constant and $Fe(CO)_5$ concentration in the range 10^{-4}-10^{-2} M allows the rate of reaction to depend only on the number of photons absorbed, i.e., within this range, higher $Fe(CO)_5$ concentrations with compensatingly lower laser intensities give identical conversion rates. The proportional rate decreases at higher concentrations. Both of these observations are highly inconsistent with a recently proposed binuclear isomerization mechanism.[7]

The time dependence of the pulsed-laser photocatalytic isomerization reaction (Figure 1) is qualitatively identical with the results previously obtained with $Fe(CO)_5$ and other closely related catalyst precursors.[8] The reaction can be divided into two distinct parts: (1) an induction period, during which the rate of reaction

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(1) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

(2) Moggi, L.; Juris, A.; Sandrini, D.; Manfrin, M. F. *Rev. Chem. Intermed.* **1981**, *4*, 171-223.

(3) Wrighton, M. S.; Ginley, D. S.; Schroeder, M. A.; Morse, D. L. *Pure Appl. Chem.* **1975**, *41*, 671.

(4) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551.

(5) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248.

(6) In all quantitative work laser fluence is less than 5 mJ/cm^2, so that multiphoton events are negligible.

(7) Swartz, G. L.; Clark, R. J. *Inorg. Chem.* **1980**, *19*, 3191.

(8) See, for example, ref 3-5 and 8 and references therein.

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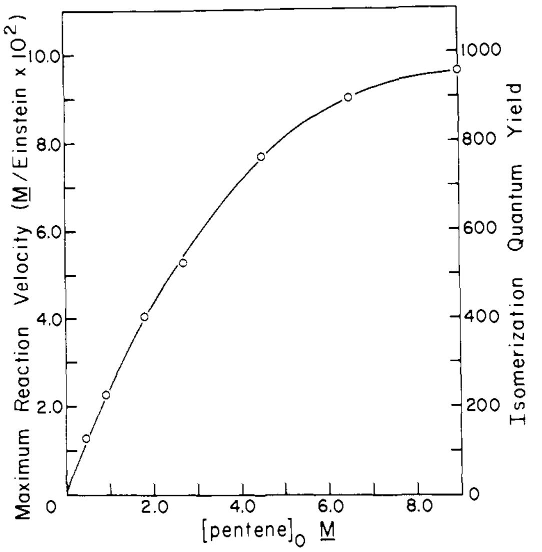
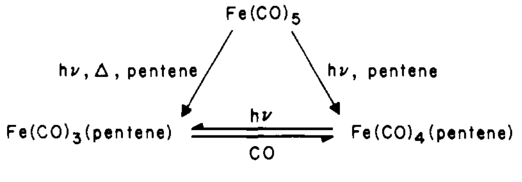


Figure 2. Reaction velocity vs. substrate concentration for photocatalytic isomerization 2×10^{-3} M $Fe(CO)_5$ in pentane/1-pentene solution, 300 K, 4.0-Hz laser-pulse repetition rate.

Scheme I



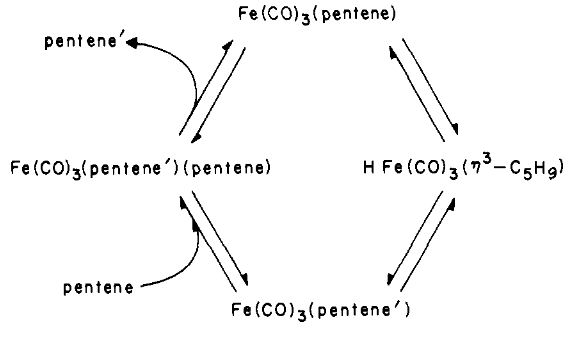
I

increases with time; (2) a steady-state period, in which the rate decreases monotonically as the system approaches equilibrium substrate concentrations. After reaching equilibrium, the addition of more 1-pentene followed by further irradiation rapidly equilibrates the added substrate, but now *without* an induction period. Similar behavior is seen in hydrogenation where for an 800-torr over-pressure of H_2 we observe typical raw quantum efficiencies of from 2 to 4.

We have recorded changes in the optical spectra of photocatalytic isomerization mixtures, with the following results: (1) an immediate and permanent spectral change takes place in the near ultraviolet region, resulting in a new absorption band centered at 348 nm; (2) on continued irradiation the intensity of this spectral feature grows with a time dependence that tracks the induction period. After the induction period, no further spectral changes are observed as the substrates are equilibrated. The time dependence of the change in optical density in this region is shown in Figure 1.

We associate this induction period with the complete conversion of $Fe(CO)_5$ to the stable catalyst precursor $Fe(CO)_4$(pentene).[9] There is considerable evidence that near ultraviolet irradiation of $Fe(CO)_5$ in solution[10] or in the gas phase[11,12] directly photogenerates $Fe(CO)_3$. Taking these processes into account we modify previously proposed photochemical initiation and termination steps for photocatalytic isomerization as in Scheme I. The unsaturated complex $Fe(CO)_3$(pentene) is identified as before as the phenomenological catalyst.[3] Its ready recombination with CO accounts for the unchanging optical spectrum throughout the post-induction period.

Scheme II



II

From this initiation mechanism it is clear that not every absorbed photon creates a catalytically active complex and that the reversion rate depends on CO pressure.[13] It is nonetheless instructive to measure quantum yields of the pentene isomerization under pulsed irradiation conditions. Figure 2 shows the dependence of the initial reaction velocity and quantum yield on substrate concentration. The catalyst is apparently not saturated by substrate even in neat 1-pentene, an indication of very high catalytic activity. At 70 °C, a temperature at which thermally initiated catalysis is negligible, we observe minimum quantum yields[14] exceeding 1000, i.e., a minimum average of 1000 complete catalytic cycles for each absorbed photon.[15] Turnover numbers for the system regularly exceed 10^4, indicating that the catalyst reverts to a catalyst precursor capable of reactivation.

By varying the repetition rate of the laser, we have been able to establish the conditions under which the laser pulses act independently of each other and thereby obtain a lower bound for the turnover rate of the isomerization catalyst. In neat 1-pentene the quantum efficiency of the system increases with decreasing repetition rate, indicating that laser pulses are irradiating catalytic intermediates. However, below 4 Hz the quantum efficiency is independent of this parameter. We thus estimate the lifetime of the catalyst, τ_{cat}, to be 0.2 s. Combining this number with observed quantum yield under the same conditions allows a straightforward calculation of the turnover rate:

$$\text{turnover rate} = \frac{\phi_{isom}}{\tau_{cat}} = \frac{800}{0.2\ \text{s}} = 4 \times 10^3\ \text{s}^{-1}$$

A previous lower bound estimate[16] yielded a value nearly 50 times smaller.

In the full report on this system we provide further evidence for the steady-state catalytic cycle shown below in Scheme II.[17] Though it features a substitutionally labile dialkene complex, as proposed by Schroeder and Wrighton,[3] it is important to note that this cycle differs in one respect from the generally accepted 1–3 hydrogen shift mechanism.[4,18] Taking into account the instability

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(9) These complexes are not thermally catalytic under mild conditions but have been shown to be active photocatalysis. See ref 3.

(10) Instead of direct photodissociative loss of two CO ligands, a possible route to $Fe(CO)_3$ in solution is photolysis to produce $Fe(CO)_4$ followed by thermolysis of the weak $Fe(CO)_3$–CO linkage, a path which, if present, must compete unfavorably with stabilization by reaction with pentene to form $Fe(CO)_4$(pentene); see ref 19.

(11) Nathanson, G.; Gitlin, B.; Rosan, A. M.; Yardley, J. T. *J. Chem. Phys.* **1981**, *74*, 361, 370.

(12) Whetten, R. L.; Fu, K. J.; Grant, E. R., to be submitted for publication.

(13) Removal of CO from dead volume above the solution greatly enhances rate but leads eventually to loss of catalytic activity. It should be noted that experiments are not reproducible unless the dead volume is fixed. We calculate the accumulated CO pressure as approximately 200 torr above an irradiated 5×10^{-3} M $Fe(CO)_5$ solution in a cell for which the gas to liquid ratio is 0.5. This observation explains various reports of irreproducible dark catalytic activity following periods of irradiation. See ref 3 and 8.

(14) Quantum yield is defined here as in ref 3 by taking the number of substrate molecules transformed divided by the number of photons absorbed.

(15) Continuous photochemical initiation, ref 6, produces a maximum initial quantum yield of approximately 400. At lower repetition rates we observe much higher quantum yields under otherwise similar conditions. Thus a substantial efficiency advantage exists for the use of pulsed over continuous irradiation to initiate photocatalysis.

(16) Mitchener, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 975.

(17) Whetten, R. L.; Fu, K. J.; Grant, E. R., to be submitted for publication.

of $Fe(CO)_4$ with respect to CO loss,[19] we propose that instead of iron tetracarbonyl the cycle is carried by di- and monoolefin-substituted iron tricarbonyl complexes.[20] Termination is by recombination of $Fe(CO)_3$(pentene) with CO.

From all experiments performed thus far, it appears the pulsed-laser initiation method yields time-averaged results identical with conventional thermal and continuous photochemical systems. The time resolution of this method (limited only by the length of the laser pulse), however, will permit transient spectroscopic studies of previously unobservable intermediates and dynamics of organometallic catalytic systems. In work currently in progress we are attempting to spectroscopically and dynamically characterize the $Fe(CO)_5$-based systems by direct, time-resolved observation of intermediates in both liquid and entirely gas-phase photocatalytic systems.

Acknowledgment. We gratefully acknowledge Koppers Company Inc. for generous support of this research.

Registry No. $Fe(CO)_5$, 13463-40-6; 1-pentene, 109-67-1; *trans*-2-pentene, 646-04-8; *cis*-2-pentene, 627-20-3.

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(18) Masters, C. "Homogeneous Transition-Metal Catalysis"; Chapman and Hall: London, 1981.

(19) Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569.

(20) This mechanism is supported by the comparison to the behavior of group 6 systems where diolefin complexes are stable and where isomerization appears to require the absorption of more than one photon per conversion. For relevant experiments see: Wrighton, M. S.; Hammond, G. H.; Gray, H. B. *J. Organomet. Chem.* **1974**, *70*, 283. Tumas, W.; Gitlin, B.; Rosan, A. M.; Yardley, J. T. *J. Am. Chem. Soc.* **1982**, *104*, 55. The problem is analyzed theoretically in Elian and Hoffmann (Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

Circular Dichroism of 1,1′-Spirobi[benzindans]: Demonstration of Nongenerality of the C_2 Rule

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Previously, Hug and Wagnière presented the rule of C_2 symmetry (C_2 rule) whereby they pointed out that if the chirality of a chromophore in a C_2 molecule is right handed, transitions of *A* symmetry will lead to negative Cotton effects and transitions of *B* symmetry to positive ones. They gave evidences in support of this rule for many different types of C_2 molecules.[2,3]

However, the C_2 rule cannot be considered a general one in view of the fact that the *chirality of chromophore*[4] is independent of the *helicity of transition*.[5] This situation is shown schematically by use of an exciton model (Figure 1). For both cases a and b, the chirality of the chromophore is left handed and the coupling mode of local transition moments ($\vec{\mu}_1$ and $\vec{\mu}_2$) is of *A* symmetry. The rotational strength R^A is evaluated as follows:[6]

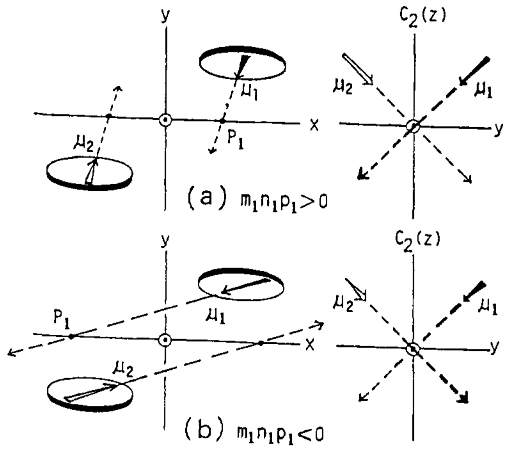

Figure 1. *A* symmetry coupling of local transitions in a left-handed chirality of a chromophore. The chromophore is located in the +*z* region and viewed along the $C_2(z)$ axis (left) and *x* axis (right).

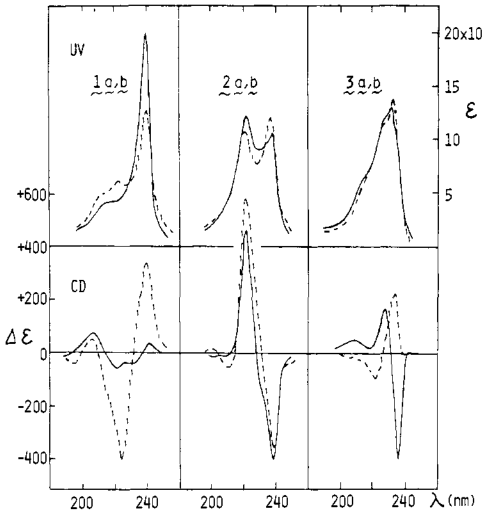

Figure 2. UV and CD spectra of 3,3′-di-*tert*-butyl-1,1′-spirobi[benzindans] **1**–**3**, in isooctane [(1*S*,3*R*,3′*R*)-**a** (—) and (1*S*,3*S*,3′*S*)-**b** (- - -)].

$$R^A = 2\pi\sigma\mu^2 m_1 n_1 p_1$$

where σ is the excitation wave number of the local chromophore, $\mu = |\vec{\mu}_1| = |\vec{\mu}_2|$, ($l_1$, m_1, n_1) denotes the direction cosines of the point dipole $\vec{\mu}_1$, and (p_1, 0, 0) are the coordinates of P_1, the point of intersection of $\vec{\mu}_1$ (or its extrapolation) and the *x* axis. Thus the rotational strength R^A assumes positive or negative value according to the sign of $m_1n_1p_1$, which corresponds with the helicity of transition (right handed for a and left handed for b). Evidently the C_2 rule takes only case a into consideration.[8] Therefore, it is not valid in principle to deduce the sign of the Cotton effect solely from the chirality of the chromophore and the symmetry of transition.

Moveover, even if the C_2 rule is accepted, its application to the prediction of absolute configurations will require an identification of the symmetry of transition for individual CD bands. For this purpose an apparent regularity that a transition of *B* symmetry is found at lower energy, followed by a transition of *A* symmetry, for many C_2 chromophores has often been employed.[3,9] However,

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(1) Present address: Suntory Institute for Biomedical Research, Wakayamadai, Shimamoto-cho, Mishima-gun, Osaka, 618 Japan.

(2) Wagnière, G.; Hug, W. *Tetrahedron Lett.* **1970**, 4765-8.

(3) Hug, W.; Wagnière, G. *Tetrahedron* **1972**, *28*, 1241-8.

(4) Hug and Wagnière[3] defined the chirality of a chromophore as follows: "A chromophore is visualized in the energetically most easily accessible planar conformation of effective C_{2v} symmetry. The C_2 axis lies in this plane and it divides the plane into a right part and a left part. The molecule (chromophore) is then twisted into its assumed real conformation. If the right-hand part of the molecule (chromophore) is twisted counterclockwise, the left part clockwise, then the chirality is right-handed." This is an expression of the handedness of the mutual arrangement between the local chromophores (molecular subunits) in the whole chromophore (molecule). We followed this definition throughout our arguments.

(5) Helicity of the transition refers to the helical relationship between local transition moments (transition moments in the local chromophores) which constitute the transitions (*A* and *B* symmetry) in the whole chromophore (molecule).

(6) This equation is derived from the general formula[7]

$$R = (\pi\sigma/2)(\vec{\mu}_1\cdot\vec{R}_{12}\vec{\mu}_2)$$

(7) Schellman, J. A. *Acc. Chem. Res.* **1968**, *1*, 144-51.

(8) Wagnière and Hug[2] indicated the mathematical underpinning of the C_2 rule by using a model that is virtually identical with Figure 1a.

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