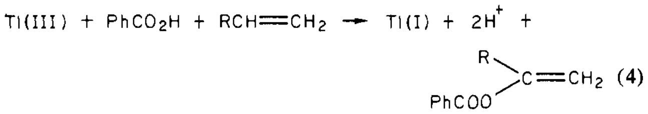

$$\mathrm{Tl(III) + PhCO_2H + RCH{=}CH_2 \rightarrow Tl(I) + 2H^+ + R(PhCOO)C{=}CH_2} \qquad (4)$$

action mixture. Therefore, good yields of epoxides are formed only if excess thallium(III) relative to **2** is employed.

Our future work will be directed toward cocatalysts that avoid this side reaction and allow conversion of this stoichiometric epoxidation into a catalytic system.

Acknowledgment. We thank J. Smith, H. Njuguna, and E. McCarthy for GC-MS and MS analysis.

Registry No. 1-Octene, 111-66-0; propylene, 115-07-1; cobalt, 7440-48-4; thallium, 7440-28-0.

Epoxidation of Cyclic Alkenes by Bis(acetonitrile)chloronitropalladium(II): On the Role of Heterometallacyclopentanes and β-Hydrogen Elimination in the Catalytic Oxidation of Alkenes

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Selective (nonradical) alkene oxidation, epoxidation in particular, is a commercially important but technologically difficult procedure. Transition-metal dioxygen[1,2] and alkyl peroxide[3,4] complexes have been widely investigated in this regard, the latter being key intermediates in the Halcon propylene epoxidation process.[4b,d,5] Unsolved problems include the production of stoichiometric coproducts[6] and the lack of definitive mechanistic information due in large measure to the absence of detectable reaction intermediates. Catalysts based on the nitro–nitrosyl redox couple[7–9] offer a potential solution to the coproduct problem since symmetrical oxygen cleavage preceeds interaction with the substrate (eq 1 and 2). We report here the first example of the

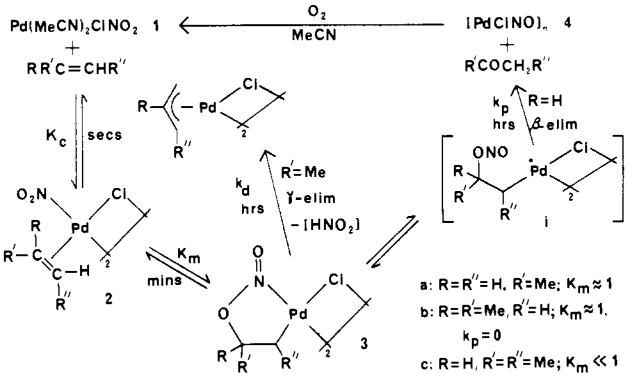
$$\mathrm{M(NO) + {}^1/_2O_2 \rightarrow M(NO_2)} \qquad (1)$$

$$\mathrm{M(NO_2) + L \rightarrow M(NO) + LO} \qquad (2)$$

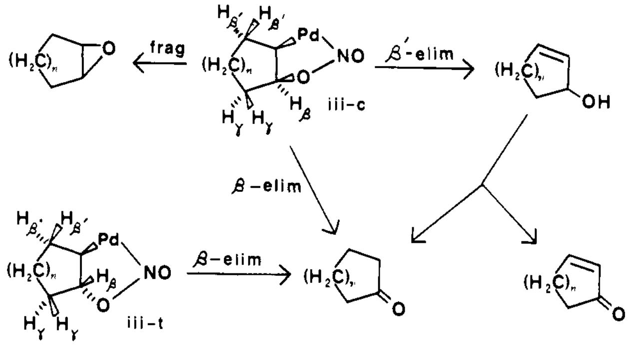
application of this type of catalyst to alkene epoxidation,[10] together with the isolation and characterization of an intermediate heterometallacyclopentane of type Ia. Related metallacyclic in-

termediates Ib and Ic have been widely proposed without substantiation in the oxidation of unactivated alkenes by dioxygen[1a,b,2a,c,d] and alkyl peroxide[3a,b,4c] complexes, respectively.

Scheme I



Scheme II



We have shown that bis(acetonitrile)chloronitropalladium(II) (**1**) reacts with linear alkenes to give ketones via spectroscopically detectable alkene (**2**) and heterometallacyclopentane (**3**) complexes (Scheme I).[7] While complex **2** has precedent in the well-known dichloro analogue $[\mathrm{Pd(alkene)Cl_2}]_2$,[11] metallacycle **3** represents a new structural type.[12] Our attempts to isolate and fully characterize such a complex have been hampered by facile equilibria and decomposition reactions (Scheme I). Ketone formation may proceed via i, a ring-opened isomer of **3** (Scheme I),[13] where coordinative unsaturation[14] and of 0° Pd–C–C–H dihedral angle[14b] favorable to elimination are more readily accessible than in metallacycle **3** itself. This additional reaction path, which is not available to carbametallacyclopentanes, may account for the scarcity of heterometallacyclopentanes compared to their ubiquitous carbocyclic analogues.[14b,15]

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[1] (a) Mimoun, H.; Serée de Roch, I.; Sajus, L. *Tetrahedron* **1970**, *26*, 37–50. (b) Igersheim, F.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 161–166, 711–713. (c) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295–296. (d) Sheldon, R. A.; Van Doorn, J. A. *J. Organomet. Chem.* **1975**, *94*, 115–129.

[2] Dioxygen complexes are implicated in a number of other systems: (a) Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 883–888. (b) Holland, D.; Milner, D. J. *Ibid.* **1975**, 2440–2443. (c) Tang, R.; Mares, F.; Neary, N.; Smith, D. E. *J. Chem. Soc. Chem. Commun.* **1979**, 274–275. (d) Mimoun, H.; Perez Machirant, M. M.; Serée de Roche, I. *J. Am. Chem. Soc.* **1978**, *100*, 5437–5444. (e) Nyberg, E. D.; Drago, R. S. *Ibid.* **1981**, *103*, 4966–4968.

[3] (a) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047–1054. (b) Bregeault, J.-M.; Mimoun, H. *Nouv. J. Chim.* **1981**, *5*, 287–289. (c) Strukul, G.; Ros, R.; Michelin, R. A. *Inorg. Chem.* **1982**, *21*, 495–500.

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[5] Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; pp 115–117.

[6] Epoxidations based directly or indirectly on molecular oxygen, the reagent of choice, invariably lead to the loss of one oxygen atom per O_2 molecule to coproduct formation, e.g., alcohols or carbon dioxide and water.

[7] Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 2894–2896.

[8] Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 6616–6618.

[9] Ugo, R.; Bhaduri, S.; Johnson, B. F. G.; Khair, A.; Pickard, A. *J. Chem. Soc., Chem. Commun.* **1976**, 694–695.

[10] Just prior to submission of this work, we learned of the demonstration of metal nitro catalyzed epoxidation of terminal alkenes: Diamond, S. E.; Mares, F.; Szalkiewicz, A.; Muccigrosso, D. A.; Solar, J. P. *J. Am. Chem. Soc.*, preceeding paper in this issue.

[11] Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882–884.

[12] Two reports have described nonmetallacyclic alkyl nitrite complexes: (a) Read, C. A.; Roper, W. F. *J. Chem. Soc., Dalton Trans.* **1972**, 1243–1246. (b) Walsh, J. L.; Bullock, R. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 865–869.

[13] The Pd–N bond in metallacycle **3** must be relatively weak since alkyl nitrites do not displace the labile acetonitrile ligands in bis(acetonitrile)dichloropalladium(II) (M.A.A., unpublished observation).

[14] (a) Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789–2794. (b) McDermott, J. X.; White, J. F.; Whitesides, G. M. *Ibid.* **1976**, *98*, 6521–6528.

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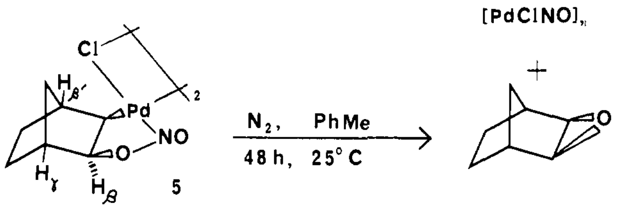
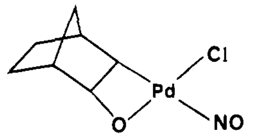
Table I. Reactions of $Pd(CH_3CN)_2ClNO_2$ with Cycloalkenes[a]

				product yields, %				
ring size	alkene/Pd	T, °C	time, h	epoxide	ketone	enol[b]	enone[c]	other(s)
C_5[d]	1:1	20	6	4	3	27	1	25
C_6	1:1	60	2	0	3	34	5	18
C_7	1:1	20	20	21	4	2	32	8
C_7	1:1	60	2	34	2	9	17	6
C_7	10:1	60	1	32	10	20	40	25
C_7[e]	10:1	60	4	69	41	80	106	40
C_7[e,f]	10:1	60	5	88	53	60	85	45
C_7[g]	1:1	20	24	0	14	12	24	7
c-C_8	1:1	60	3	12	6	7	0	10
t-C_8	1:1	20	24	4, 1[h]	45	0	0	10

[a] $Pd(CH_3CN)_2ClNO_2$ (29 mM) in 1,2-dichloroethane under nitrogen, GC yields. [b] 2-Cycloalken-1-ol. [c] 2-Cycloalken-1-one. [d] Dichloromethane solution. [e] Under air. [f] One equivalent of BHT added. [g] 2-Cyclohepten-1-ol used in place of cycloheptene. [h] *trans*-Epoxide.

By employing the strained bicyclic alkene norbornene as substrate, it has been possible to circumvent these reactivity problems. Reaction of nitro complex **1** with 1 equiv of norbornene in acetone leads to the nearly instantaneous and quantitative formation of metallacycle **5** ($K_m >> 1$), which can be isolated as a bright yellow solid.[16,17] Decomposition of this metallatricycle under nitrogen in toluene solution gives *exo*-epoxynorbornene (>90% GC yield, >99% selectivity) at an initial rate of only 3%/h at 25 °C (vs. 2-decanone at ~30%/h for **1** + 1-decene). Part of this stability and change in product selectivity is attributed to the allylic bridgeheads, which preclude (Bredt's rule[21]) both exometallacyclic β'-hydrogen elimination and allyl complex formation[3a,7] (γ-hydrogen elimination). Furthermore, intrametallacyclic β-hydrogen elimination, even in the ring-opened isomer of **5**, is restricted by both the rotational rigidity of the bicyclic norbornane skeleton (which prevents attainment of a 0° Pd–C–C–H dihedral angle) and by the attendant reintroduction of ring strain. Epoxide formation from **5** may involve a concerted fragmentation[3a] or a ring contraction[15a,c] to ii followed by reductive elimination.[22] The air epoxidation of norbornene by nitro complex **1** is catalytic with about seven turnovers obtained in ethylacetate at 60 °C.





ii

The formation of epoxides is not restricted to the specialized case of norbornene. Simple monocyclic alkenes also react with nitro complex **1** to give the corresponding epoxide, together with a number of other products (Table I).[16] Metallacyclic intermediates are not detectable in these reactions ($K_m << 1$), even for the highly strained *trans*-cyclooctene.[23] The saturated cyclic ketones probably result from intrametallacyclic β-hydrogen elimination (Scheme II), while the other nonepoxide products (as well as a fraction of the saturated ketones) are most likely decomposition products of an initially formed allyl alcohol produced by exometallacyclic β'-hydrogen elimination.[24] For *trans*-cyclooctene, the large ring and trans-metallacyclic ring juncture iii-t should make attainment of an intrametallacyclic (β) 0° Pd–C–C–H angle more facile than in the cis-isomer iii-c, consistent with the significantly enhanced yields of cyclooctanone from the trans alkene. Conversely, with cyclopentene and cyclohexene the small cis-substituted ring inhibits intrametallacyclic β elimination, thus exometallacyclic β' elimination is observed. For cycloheptene neither β nor β' elimination appears to be as favorable, and epoxidation becomes a competing pathway. It is significant that monocyclic alkenes give even low yields of epoxides since in all cases there is more than adequate conformational flexibility to achieve an exometallacyclic (β') 0° Pd–C–C–H dihedral angle.[25]

Our final observations concern the general role that heterometallacyclopentanes might have in transition-metal-mediated alkene oxidations. Despite widespread suggestions of their involvement,[1a,b,d,2a,c,d,3a,b,4c] the only well-characterized examples of type I metallacycles prior to the present work are those derived from the reaction of ML_2O_2 (M = Pd, Pt; L = PR_3) with highly functionalized, electron-deficient alkenes.[1d,26,27] Mimoun, for example, has proposed metallacycle Ib as an intermediate in the conversion of terminal alkenes to ketones by [Pd-

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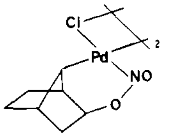
(15) (a) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610–5618. (b) McAlister, D. R.; Irwin, D. K.; Bercaw, J. E. *Ibid.* **1978**, *100*, 5966–5968. (c) Grubbs, R. H.; Miyashita, A. *Ibid.* **1978**, *100*, 7418–7420.

(16) Experimental details of most syntheses and reactions reported here are available as supplemental material.

(17) Di-μ-chlorobis[3-(nitrosooxy)bicyclo[2.2.1]hept-2-yl-*C,N*]dipalladium: IR (KBr disk, significant peaks only, intensity, shift on ^{18}O labeling, tentative assignment[18]) 2973, 2944, 2871, 1610 (vs, −38, $\nu_{N=O}$), 1450, 1313 (s), 1138, 1083 (s), 1016 (s, −5), 985 (s, −8, ν_{C-O}), 939, 888 (s, −4), 871 (s, −2), 846 (s, −5), 774 (s, −3), 761 (s, −14, ν_{N-O}), 644 (w, −5), 597 (w, +12), 503 (w, −14, δ_{ONO}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.37 (1 H, q, J = 6, ~1.5 Hz), 4.29 (1 H, q, J = 6, 2.5 Hz), 2.57 (1 H, s), 2.44 (1 H, br s), 1.8–1.2 (6 H, m); ^{13}C NMR ($CDCl_3$) 94.9 (d), 69.5 (d), 44.0 (d), 42.0 (d), 34.7 (t), 26.7 (t), 23.2 (t); anal. ($C_{14}H_{20}Cl_2N_2O_4Pd_2$) C,H,Cl,N; MW (osmometry: calcd 564; obsd 550). An isomeric formulation a derived from a palladium-induced[19] norbornyl carbonium ion rearrangement can be ruled out on the basis of ^1H NMR coupling constants (e.g., second-order AB quartet at δ 4.3).[20] A single-crystal X-ray diffraction study of the dicyclopentadiene analogue of **5** is in progress.



a

(18) Cf.: Klaboe, P.; Jones, D.; Lippincott, E. R. *Spectrochim. Acta, Part A* **1967**, *23A*, 2957–2971.

(19) Sen, A.; Lai, T.-W.; *Inorg. Chem.* **1981**, *20*, 4036–4038.

(20) Cf.: Marshall, J. L.; Walter, S. R. *J. Am. Chem. Soc.* **1974**, *96*, 6358–6362.

(21) March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1968; p 122.

(22) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120–3128.

(23) It was initially presumed that the quantitative formation of metallacycle **5** ($K_m >> 1$) from the internal alkene norbornene was a result of ring strain relief. The lack of a detectable intermediate for the highly strained *trans*-cyclooctene and the presence of a metallacycle for the relatively unstrained bicyclo[2.2.2]oct-2-ene indicate that the stability of the alkene complex (or lack thereof) is also a factor.

(24) Cf. entry in Table I for 2-cyclohepten-1-ol and ref 2b.

(25) Cf. the stability of both α-methyl metallacycles[14b] and metallabicycles[15a] toward β-hydrogen elimination.

(26) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832–5839.

(27) A d^{10} mercury(II) metallacycle of type Ic has been characterized crystallographically: Halfpenny, J.; Small, R. W. H. *J. Chem. Soc., Chem. Commun.* **1979**, 879–880.

$(O_2CCF_3)(O_2\text{-}t\text{-Bu})]_4$.[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.

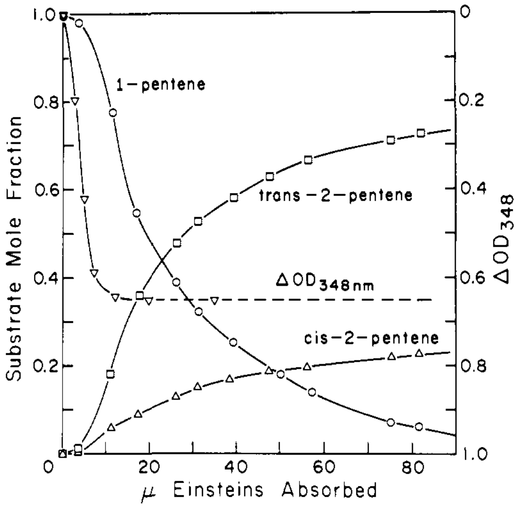

Figure 1. Time dependence of photocatalytic isomerization and change in optical density at 348 nm plotted as a function of μeinsteins absorbed under conditions of 2×10^{-3} M $Fe(CO)_5$ in pure 1-pentene, 300 K, 4.0–Hz laser-pulse repetition rate.

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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[†] National Science Foundation Graduate Fellow.

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(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/cm², 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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