

In summary, the results presented here demonstrate the remarkable catalytic effect that one-electron oxidation can have on the rearrangement of vinylcyclopropanes to cyclopentenones.

**Acknowledgment.** Research support was provided by the National Science Foundation (CHE86-10404) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

### Electron-Transfer Reactions in Cyanine Borate Ion Pairs: Photopolymerization Initiators Sensitive to Visible Light

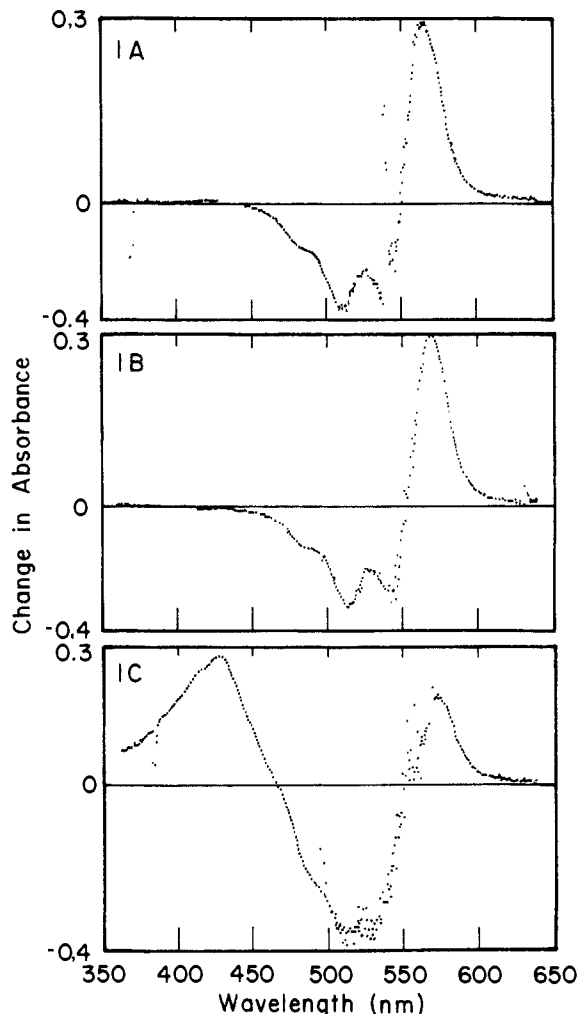
Subhankar Chatterjee,<sup>1</sup> Peter Gottschalk,<sup>2</sup> Paul D. Davis,<sup>2</sup> and Gary B. Schuster\*<sup>1</sup>

Department of Chemistry, Roger Adams Laboratory  
University of Illinois, Urbana, Illinois 61801  
Mead Imaging Incorporated, 3385 Newmark Drive  
Miamisburg, Ohio 45342  
Received December 21, 1987

Photoinitiation of polymerization is a process of immense practical, economic, and theoretical importance. In typical examples the polymerization of an acrylate or styrene-derived monomer is initiated by irradiation of a sensitizer with ultraviolet light. The excited state of the sensitizer may dissociate directly to form active free radicals as in the case of the benzoin ethers,<sup>3</sup> or it may first undergo a bimolecular electron-transfer reaction whose products initiate polymerization as is the case in the benzophenone-dimethylaniline system.<sup>4</sup> Efforts to extend the range of useful photoinitiators of free-radical polymerization to the visible region of the spectrum have heretofore met with only modest success.<sup>5</sup> These special initiators typically are sensitive only to blue light or suffer from thermal instability and have low quantum efficiencies. We report herein the discovery that triphenylalkylborate salts of cyanine dyes (Chart I) are photoinitiators of free-radical polymerization whose sensitivity throughout the entire visible spectral region is the result of a novel intra-ion-pair electron-transfer reaction.

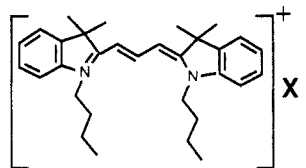
The absorption spectra of the di-*n*-butyltetramethylindocarbocyanines (**1a-c**) in ethyl acetate, di-*n*-butyl suberate (DBS), or *n*-butyl acrylate solution exhibit modest solvatochromic shifts with maxima at ca. 556 nm ( $\epsilon_{\max} = 1.8 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) that are essentially independent of the identity of the counter ion. In acetonitrile solution, this absorption maximum shifts to 545 nm ( $\epsilon_{\max} = 1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ). Solutions of cyanine borate (**1c**) in butyl acrylate are stable in the dark, but polymerization occurs rapidly when they are irradiated with visible light. In contrast, irradiation of butyl acrylate solutions of the cyanine bromide (**1a**) or the hexafluorophosphate (**1b**) does not initiate polymerization. Other cyanine dyes absorbing at various wavelengths throughout the visible spectral region behave similarly.

The mechanism for operation of these cyanine borate initiators was investigated by steady-state and time-resolved methods. Irradiation of cyanine borate **1d** in  $\text{N}_2$ -purged ethyl acetate solutions containing increasing amounts of tri-*n*-butylstannane gives propylbenzene in 45% yield with a quantum efficiency of ca. 0.14 at extrapolated infinite stannane concentration. This finding signals generation of the phenylpropyl radical in this case and, by implication, the *n*-butyl radical from cyanine borate **1c**. Etter



**Figure 1.** Transient absorption spectra recorded 1  $\mu\text{s}$  after irradiation of the cyanine dyes at 532 nm: (1A) irradiation of cyanine borate (**1c**) in acetonitrile solution; (1B) irradiation of cyanine hexafluorophosphate (**1b**) in ethyl acetate solution; (1C) irradiation of cyanine borate (**1c**) in ethyl acetate solution.

**Chart I**



- 1a:** X = Br  
**1b:** X = PF<sub>6</sub>  
**1c:** X = [n-C<sub>4</sub>H<sub>9</sub>B(Ph)<sub>3</sub>]  
**1d:** X = [Ph(CH<sub>2</sub>)<sub>3</sub>B(Ph)<sub>3</sub>]

and co-workers<sup>6</sup> likewise inferred radical formation from bleaching studies of cyanine borates in the absence of traps. A related process operates in the reaction of these borates with excited-state cyanoarenes.<sup>7</sup>

Cyanines **1** fluoresce with quantum yields and lifetimes that vary with the nature of the solvent but, surprisingly, are essentially independent of the identity of the anion, Table I. The emission in the ester solutions, solvents of relatively low dielectric constant, has maxima at ca. 583 nm and efficiencies and lifetimes that clearly depend on the solvent viscosity. In acetonitrile solution,

(6) Etter, M. C.; Holmes, B. N.; Kress, R. B.; Filipovich, G. *Isr. J. Chem.* **1985**, *25*, 264.

(7) Lan, J. Y.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 4261. Lan, J. Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 6710.

(1) University of Illinois.

(2) Mead Imaging.

(3) Pappas, S. P.; Chattopadhyay, A. *J. Am. Chem. Soc.* **1973**, *95*, 6484. Merlin, A.; Fouassier, J. P. *J. Chim. Phys.* **1981**, *78*, 267. Gaur, H. A.; Groenenboem, C. J.; Hagemen, H. J.; Hakvoort, G. T. M.; Oosterhoff, P.; Overeem, T.; Polman, R. J.; van der Werf, S. *Makromol. Chem.* **1984**, *185*, 1795.

(4) Block, H.; Ledwith, A.; Taylor, A. R. *J. Polym. Sci.* **1972**, *10*, 3137. Bevington, J. C. *Radical Polymerization*; Wiley: New York, 1966.

(5) Eaton, D. F. *Adv. Photochem.* **1985**, *13*, 427.

Table I. Fluorescence Efficiencies and Lifetimes

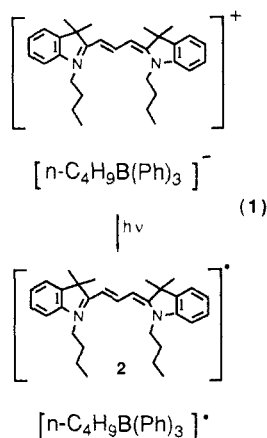
Cy <sup>+</sup> X <sup>-</sup>	solvent	$\Phi_f^a$	$\tau$ (ps)
[ <i>n</i> -C <sub>4</sub> H <sub>9</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	EtOAc <sup>b</sup>	0.13 ± 0.02	300 ± 35
PF <sub>6</sub> <sup>-</sup>	EtOAc	0.16 ± 0.03	303 ± 40
Br <sup>-</sup>	EtOAc	0.14 ± 0.03	360 ± 20
[ <i>n</i> -C <sub>4</sub> H <sub>9</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	DBS	0.53 ± 0.03	1040 ± 100
PF <sub>6</sub> <sup>-</sup>	DBS	0.55 ± 0.04	915 ± 100
Br <sup>-</sup>	DBS	0.55 ± 0.01	1070 ± 100
[ <i>n</i> -C <sub>4</sub> H <sub>9</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	DES	0.42 ± 0.014	690
Br <sup>-</sup>	DES	0.45 ± 0.012	670
[ <i>n</i> -C <sub>4</sub> H <sub>9</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	CH <sub>3</sub> CN	0.03 ± 0.01	120 ± 30
PF <sub>6</sub> <sup>-</sup>	CH <sub>3</sub> CN	0.03 ± 0.01	115 ± 30
Br <sup>-</sup>	CH <sub>3</sub> CN	0.04 ± 0.01	130 ± 40

<sup>a</sup> Determined by comparison with rhodamine B = 0.5 in C<sub>2</sub>H<sub>5</sub>OH.

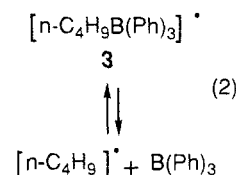
<sup>b</sup> EtOAc is ethyl acetate; DBS is dibutyl suberate; DES is diethyl succinate.

the emission maximum shifts to 577 nm, and its lifetime decreases to 125 ± 25 ps.

Irradiation of cyanines **1a**, **1b**, or **1c** in acetonitrile solution (ca. 5 × 10<sup>-5</sup> M) with the frequency-doubled output of a Nd-YAG laser (532 nm, 20 ns, 60 mJ) results in partial bleaching of the dye absorption and an immediate increase in absorption at 580 nm due to formation of a *cis*-cyanine isomer;<sup>8</sup> no additional new features are observed under these conditions, Figure 1A. Similarly, flash photolysis of the cyanine bromide or hexafluorophosphate in ethyl acetate solution reveals only the new absorption for the photoisomer, Figure 1B. In striking contrast, laser irradiation of cyanine borate **1c** in ethyl acetate solution gives the *cis* isomer and a second intermediate with an apparent absorption maximum at ca. 430 nm, Figure 1C. The second intermediate is formed within the laser pulse and then decays slowly over a period of several hundred microseconds. The species absorbing at 430 nm is not the triplet state of the cyanine. In general, the singlet states of nonrigid cyanines intersystem cross with immeasurably low efficiency and absorb at longer wavelengths than the dye itself.<sup>9</sup> The species absorbing at 430 nm is identified as the reduced, neutral cyanine radical **2** (eq 1) on the basis of its independent generation by electrochemical reduction of **1a** and by reaction of excited singlet **1a** with tetramethylphenylenediamine. Also, the absorption spectrum of **2** is similar to that of other closely related cyanine radicals.<sup>10</sup>



Single electron transfer from the alkyltriphenylborates, but not bromide or hexafluorophosphate, to the excited cyanine is expected to occur with a rapid rate from calculations based on the Weller equation.<sup>11</sup> This reaction will generate the cyanine radical **2** and an alkylphenylboranyl radical **3**. Previous electrochemical<sup>12</sup> and photochemical<sup>6,7</sup> investigations have revealed that boranyl radicals such as **3** fragment to form an alkyl radical and triphenylborane, eq 2. This alkyl radical can be captured by the stannane, or, when in the presence of a suitable monomer, initiate polymerization.



The electron-transfer reaction from the borate to the excited cyanine has several unique and special characteristics. The cyanine borates must exist entirely as ion pairs tightly bound by Coulombic attraction in the nonpolar ester solvents.<sup>13</sup> This preordained arrangement ensures encounter between the borate and the excited cyanine despite the very short lifetime of the latter. In support of this postulate we note that no cyanine radical is detected from irradiation of **1c** in acetonitrile solution since in this solvent the ion pairs may dissociate. This sort of inverted solvent polarity dependence, similarly attributed to ion pairing, has been reported in the electron-transfer reactions of excited pyridinium iodides<sup>14</sup> and some diazonium salts.<sup>15</sup>

The fluorescing state of the cyanine is not the state that is reduced by the borate. Cyanine dyes have been studied extensively<sup>9</sup> because of their utility as laser mode-lockers and as sensitizers in silver halide photography. Direct excitation of the essentially planar *trans* dye forms its fluorescing singlet state.<sup>16</sup> The predominant decay mode of this singlet in relatively nonviscous solvents is nonradiative relaxation by rotation to a "twisted" excited state. Internal conversion of the twisted state reforms the original *trans*-cyanine or gives a *cis* photoisomer.<sup>8,9</sup> If electron transfer in the cyanine borate reduced the fluorescing singlet state, then both its emission efficiency and lifetime must be less than they are for the inactive cyanine bromide or hexafluorophosphate. The data, Table I, are inconsistent with this hypothesis and imply instead that the active intermediate is one derived from the fluorescing state, the twisted singlet, for example.

The time dependence for formation of cyanine radical **4** was probed with ca. 15-ns resolution for irradiation of cyanine borate **1c** in several solvents. In ethyl acetate solution, the cyanine radical is formed immediately and irreversibly on this time scale. It may be significant that electron transfer in the ion pair neutralizes the charges on the cyanine and borate to leave a repulsive force suddenly without balance by Coulombic attraction. Immediate recoil of the radical pair may accelerate their separation and inhibit energy-wasting back electron transfer. Classical mechanical models support this view.<sup>17</sup>

(11) Rehm, D.; Weller, A. *Ber. Bunsenges Phys. Chem.* **1969**, *73*, 834. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.  $E_{ox}(n\text{-BuPh}_3\text{B}^-) = 0.92$  V (irreversible) versus SCE;  $E_{red}(\text{Cy}^+) = -0.86$  (reversible) versus SCE;  $\Delta E_{00}^* = 2.21$  eV.  $\Delta G_{ET} = -0.43$  eV in CH<sub>3</sub>CN.  $E_{ox}(\text{Br}^-) = 1.5$  V (irreversible) versus SCE;<sup>15b</sup>  $\Delta G_{ET} = 0.11$  eV in CH<sub>3</sub>CN.

(12) Bancroft, E. E.; Blount, H. N.; Janzen, E. G. *J. Am. Chem. Soc.* **1979**, *101*, 3692.

(13) Güsten, H.; Schulte-Frohlinde, D. *Chem. Ber.* **1971**, *104*, 102. Reichardt, C.; Dimroth, K. *Fortschr. Chem. Forsch.* **1968/69**, *11*, 1.

(14) Kosower, E. M.; Lindqvist, L. *Tetrahedron Lett.* **1965**, 4481. Görner, H.; Gruen, H. *J. Photochem.* **1985**, *28*, 329. Görner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1985**, *89*, 4105. Görner, H. *J. Phys. Chem.* **1985**, *89*, 4112. Görner, H. *J. Phys. Chem.* **1986**, *91*, 1887.

(15) (a) Macrae, P.; Wright, T. R. *J. Chem. Soc., Chem. Commun.* **1971**, 898. (b) Becker, H. G. O.; Israel, G.; Oertel, U.; Vetter, H.-U. *J. Prakt. Chem.* **1985**, *327*, 399.

(16) Allmann, R.; Anis, H.-J.; Benn, R.; Grahn, W.; Olenjek, S.; Waszkowska, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 876.

(17) A similar concept has been suggested when electron transfer forms two similarly charged ions: Holten, D.; Windsor, M. W.; Parson, W. W.; Gouterman, M. *Photochem. Photobiol.* **1978**, *28*, 951.

(8) Åkesson, E.; Sundström, V.; Gillbro, T. *Chem. Phys. Lett.* **1985**, *121*, 513. Åkesson, E.; Sundström, V.; Gillbro, T. *Chem. Phys.* **1986**, *106*, 269. Dietz, F.; Rentsch, S. K. *Chem. Phys.* **1985**, *96*, 145.

(9) Chibisov, A. K. *J. Photochem.* **1976/77**, *6*, 199. Pierce, R. A.; Berg, R. A. *J. Chem. Phys.* **1969**, *51*, 1267. Dempster, D. N.; Morrow, T.; Rankin, R.; Thompson, G. F. *J. Chem. Soc. Faraday Trans. 2* **1972**, 1479. Arthurs, E. G.; Bradley, D. J.; Roddie, A. G. *Chem. Phys. Lett.* **1973**, *22*, 230. Knudtson, J. T.; Eyring, E. M. *J. Phys. Chem.* **1974**, *78*, 2355. Madge, D.; Windsor, M. *Chem. Phys. Lett.* **1974**, *27*, 31. Rullière, C. *Chem. Phys. Lett.* **1976**, *43*, 303. Kuzmin, V. A.; Darmanyan, A. P. *Chem. Phys. Lett.* **1978**, *54*, 159. Jaraudias, J. *J. Photochem.* **1980**, *13*, 35. Velsko, S. P.; Fleming, G. R. *Chem. Phys.* **1982**, *65*, 59. Blimes, G. M.; Tocho, J. O.; Braslavsky, S. E. *Chem. Phys. Lett.* **1987**, *134*, 335.

(10) Siegel, J.; Friedrich, M.; Kuehn, V.; Von Grossman, J.; Fassler, D. *J. Inf. Rec. Mater.* **1986**, *14*, 215.

In sum, the cyanine borates are unique compounds whose irradiation leads to intra-ion-pair electron transfer from a nonvertical excited state and to subsequent formation of reactive free radicals.

**Acknowledgment.** We thank Professor Faulkner and Michael Walsh of the U of I Chemistry Department for their help with the spectroelectrochemistry measurements. The emission lifetimes were determined at the Laboratory of Fluorescence Biodynamics of the University of Illinois with the assistance of Cathy Royer; John Wilkey helped with the NMR spectra. The work at the University of Illinois was supported in part by a grant from Mead Imaging and in part by a grant from the National Science Foundation.

**Registry No. 1a**, 113352-39-9; **1b**, 113352-41-3; **1c**, 113352-42-4; **1d**, 113378-60-2; poly(butylacrylate), 9003-49-0.

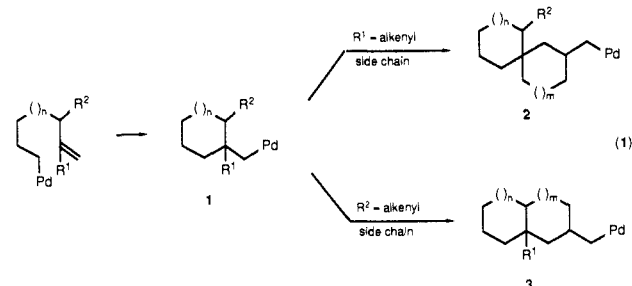
## Palladium-Catalyzed Polyene Cyclizations of Dienyl Aryl Iodides

Matthew M. Abelman<sup>1</sup> and Larry E. Overman\*

Department of Chemistry, University of California  
Irvine, Irvine, California 92717

Received December 11, 1987

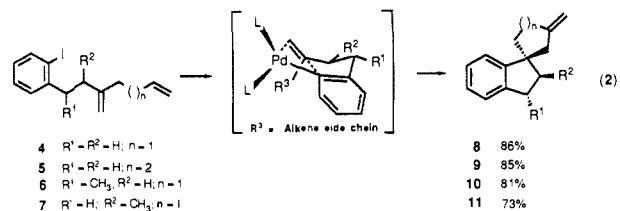
Metal-catalyzed additions of carbon fragments to alkenes have found wide application in organic synthesis.<sup>2</sup> The utility of this chemistry would be greatly expanded if the newly created carbon-metal bond could be routinely transformed to a new carbon-carbon bond. In this communication, we report that ( $\sigma$ -alkyl)palladium intermediates **1**, produced by intramolecular Heck cyclization,<sup>3,4</sup> can be efficiently captured by neighboring double bonds to give bis-cyclization products of either spiro **2** or fused **3** geometry (see eq 1).<sup>5,6</sup> Since the regiochemistry for the reaction



of organopalladium intermediates with alkenes can be opposite to that of related radical or carbonium ion intermediates,<sup>7</sup> pal-

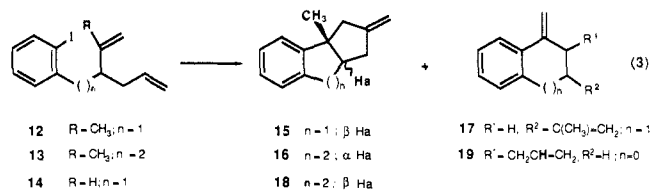
ladium-catalyzed polyene cyclizations hold exciting potential for organic synthesis.

By using Heck reaction conditions we recently described,<sup>4c</sup> dienyl aryl iodide **4**<sup>8</sup> was cyclized in acetonitrile at room temperature in the presence of 1 mol% of Pd(OAc)<sub>2</sub>, 4 mol% of Ph<sub>3</sub>P, and 1 equiv of Ag<sub>2</sub>CO<sub>3</sub> to afford tricyclic alkene **8**<sup>9</sup> in 86% yield (see eq 2). The initially formed bicyclic ( $\sigma$ -alkyl)palladium



intermediate can be trapped also by insertion into a 4-pentenyl side chain as demonstrated by cyclization of **5** under identical conditions at 70 °C to afford **9**<sup>9</sup> in 85% yield. Useful levels of relative asymmetric induction at the newly formed quaternary center were observed in cyclizations of diene substrates containing a stereogenic center in the chain connecting the aromatic ring with the exocyclic double bond. Thus, cyclization<sup>10</sup> of **6** proceeded in 81% yield with 13:1 diastereoselectivity to provide **10**<sup>9</sup> as the major stereoisomer, while **7** was cyclized<sup>10</sup> (73% yield, 6.5:1 diastereoselectivity) to afford **11**<sup>9</sup> as the predominant product. Suprafacial insertion<sup>3,11</sup> of an initially formed (aryl)palladium intermediate via a conformation which places the substituents in favored pseudoequatorial positions (see eq 2) provides a rationale for the observed diastereoselectivities.<sup>12</sup> It merits note that the facility of these transformations and the lack of isomerization of the exocyclic double bond of tricyclic alkene products **8-11** provide a dramatic illustration of the advantages<sup>4c,13</sup> of employing a Ag(I) additive in alkenyl palladations.

Bis-cyclizations in the fused mode were examined with substrates **12-14** (see eq 3). Cyclization<sup>10</sup> of **12** yielded, as the major



products, tetralin **17**<sup>9</sup> and tricycle **15**<sup>9</sup> in a 1.5:1 ratio, respectively.<sup>14</sup>

(7) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Academic: London, 1986; Chapter 4. Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, Chapter 5.

(8) Prepared from 2-(chloromethyl)-1-iodobenzene, allyl bromide, and ethyl acetoacetate by using conventional alkylation and Wittig chemistry. Other cyclization substrates<sup>9</sup> were prepared in related fashions.

(9) New compounds showed IR, 500 MHz <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectra in accord with their assigned structures. Molecular composition was determined by high resolution MS or elemental analysis, while isomer ratios were determined by capillary GC analysis. Stereochemistry was typically assigned on the basis of NOE studies.

(10) Cyclizations were conducted with 1 mol% of Pd(OAc)<sub>2</sub>, 4 mol% of Ph<sub>3</sub>P, and 1 equiv of Ag<sub>2</sub>CO<sub>3</sub> in CH<sub>3</sub>CN (~0.1 M) at room temperature for 2-8 h, unless noted otherwise.

(11) For a recent theoretical study of the insertion of the Pd-H bond and leading references, see: Fujimoto, H.; Yamasaki, T. *J. Am. Chem. Soc.* **1986**, *108*, 578.

(12) The R<sub>2</sub> side chain may occupy one of the ligand sites on Pd. Coordination of the second double bond during the first insertion step does not appear possible for the bis-cyclizations reported in eq 4. These and other mechanistic and stereochemical issues will be discussed in more detail in a subsequent full account of this work.

(13) (a) For example, the cyclization of **4** was complete at room temperature within 3 h in the presence of 1 equiv of Ag<sub>2</sub>CO<sub>3</sub>. An identical cyclization conducted with Et<sub>3</sub>N in place of Ag<sub>2</sub>CO<sub>3</sub> required 24 h for completion and provided **8** together with 10% of two endocyclic alkene isomers. (b) The effect of Ag(I) additives on the rate of Heck arylations was originally described by Hallberg and co-workers, see, e.g.: Andersson, C.-M.; Karabelas, K.; Hallberg, A.; Anderson, C. *J. Org. Chem.* **1985**, *50*, 3891.

(1) NIH NRSA Postdoctoral Fellow (GM-11332), 1986-1987. American Cancer Society Postdoctoral Fellow (PF-3066), 1987-1988.

(2) See, e.g.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: 1987, Chapters 6 and 17.

(3) (a) Davison, S. F.; Maitlis, P. M. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. L., de Jonge, C. R. H. I., Ed.; Plenum Press: New York, 1986; pp 482-488. (b) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985. (c) Trost, B. M. In *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 8, pp 867-874. (d) Heck, R. F. *Org. React. (NY)* **1982**, *27*, 345.

(4) Recent publications, not reviewed in ref 3, include the following: (a) Negishi, E.-I.; Tour, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 8289. (b) Kasahara, A.; Izumi, T.; Murakami, S.; Yanai, H.; Takatori, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 927. (c) Mori, M.; Kanda, N.; Ban, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1375. (d) Grigg, R.; Sridharan, V.; Stevenson, P.; Worakan, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1697. (e) Abelman, M. M.; Oh, T.; Overman, L. E. *J. Org. Chem.* **1987**, *52*, 4130. (f) Larock, R. C.; Babu, S. *Tetrahedron Lett.* **1987**, *28*, 5291.

(5) There are, to the best of our knowledge, no reported examples<sup>3,4</sup> of Heck-type polyene cyclizations. There are a few important reports<sup>6</sup> of the intramolecular trapping by alkenes of ( $\sigma$ -alkyl)palladium intermediates generated in other fashions.

(6) (a) Trost, B. M.; Burgess, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1084. (b) Hegedus, L. S.; Allen, G. F.; Olsen, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 3583. (c) Danishefsky, S.; Taniyama, E. *Tetrahedron Lett.* **1983**, *24*, 15. (d) Fugami, K.; Oshima, K.; Utimoto, K. *Ibid.* **1987**, *28*, 809.