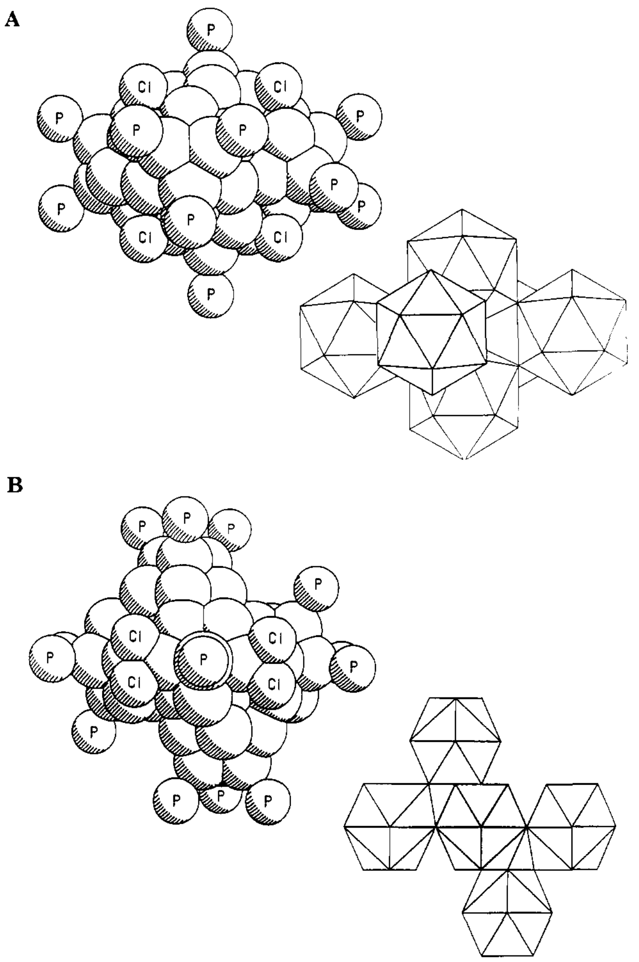

Figure 2. Space-filling representation of the proposed structure for $Au_{67}(PPh_3)_{14}Cl_8$ viewed (A) plan and (B) elevation. The phosphine positions are labeled P (with phenyl rings omitted for clarity), all unlabeled atoms are Au. The icosahedral framework is indicated in the accompanying line drawings.

and I_4.[10] Similar, but less symmetric, clusters can also be proposed. In particular an I_6, M_{67} cluster sharing eleven vertices can be postulated (Figure 2). This can be visualized as two tetrahedral I_4 units sharing two icosahedra in a centrosymmetric manner.

In known supraclusters, $[Au_{12}Ag_{13}(PPh_3)_{12}Cl_6]^{m+}$ (**2**)[9] (I_2, linear), $\{Au_{18}Ag_{19}[P(Tol)_3]_{12}Br_9\}^{2+}$ (**3**)[8] (I_3, trigonal + one capping Ag), and $Au_{22}Ag_{24}(PPh_3)_{12}Cl_{10}$[10] ($I_4$, tetrahedral), the phosphine ligands are bound only to those metal atoms which are *not* involved in binding to the other icosahedra. If this is a general condition, then 14 phosphines would be attached to I_6 (Figure 2). With triphenylphosphine as the ligand the metallic core is well encapsulated allowing for conventional cone angles.[11] The number of anions is more problematic. Electron-counting rules[12] predict 12 or 13 Cl^- ions, but elemental analysis[2] indicates eight. As physical data must be preferred to theory eight anions are included in our model (Figure 2).

The zones in the mass spectra observed for "Au_{55}" are therefore due to the fragmentation of I_6, $Au_{67}(PPh_3)_{14}Cl_8$ (at ca. 16 600 *m/z*); I_4, $Au_{46}(PPh_3)_{12}Cl_6$ (at ca. 12 800 *m/z*); and I_2, $Au_{25}(PPh_3)_{12}Cl_6$ (at ca. 8590 *m/z*).[13] The two samples contain differing amounts of these three supraclusters. (A) can be reprecipitated by dissolving in CH_2Cl_2 and adding pentane, giving (C) (Figure 1). The ratio of I_4:I_6 increases markedly, suggesting that an equilibrium exists in solution between these various supraclusters[14] and that the mole ratios in the solid sample depend on the rate of precipitation.

The cluster produced by Schmid[2] (A) is therefore formulated to be $Au_{67}(PPh_3)_{14}Cl_8$ with smaller clusters as impurities. This formulation fits the analytical data and observed molecular weight better than $Au_{55}(PPh_3)_{12}Cl_6$. The slight, but necessary modification of Teo's supracluster model[8] allows us to predict the existence of many more supraclusters of low rotational symmetry. ^{252}Cf-PDMS can provide essential information about these large clusters in spite of considerable fragmentation.

Acknowledgment. We thank Professor Gunther Schmid for providing us with a sample of the gold cluster and for helpful comments on the manuscript. We also thank Professor Boon Teo for his sample of the $Au_{12}Ag_{13}$ cluster and Professor Ron Macfarlane for discussions. This work was supported by the National Science Foundation, Grants CHE-8708625 and CHE-8604609, and the Robert A. Welch Foundation.

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(9) Teo, B. K.; Keating, K. *J. Am. Chem. Soc.* **1984**, *106*, 2224.

(10) Teo, B. K.; Shi, X.; Zhang, H. *Chem. Eng. News.* **1989**, *67(2)*, p 6.

(11) Tollman, C. A. *Chem. Rev.* **1977**, *77*, 313. In $Au_{67}(PPh_3)_{14}Cl_8$ the distance between the centers of the bases of the triphenylphosphine "cones" is 6.0 Å cf. sterically required 6.3 Å.

(12) Teo, B. K.; Zhang, H. *Inorg. Chem.* **1988**, *27*, 414.

(13) Additional peaks may be caused by the presence of supraclusters "capped" by individual Au atoms and associated anions as seen in the M_{37} and M_{38} clusters reported previously (ref 8). The number of anions attached to the smaller supraclusters is uncertain.

(14) Reprecipitation of sample (B) gave a sample with an identical spectrum to that of (B); this indicates that the solution equilibrium is close to that in the solid sample (B). Very slow reprecipitation, by vapor diffusion of pentane at low temperatures, gave a gold mirror.

Zirconium-Mediated Ring Construction from Dienes: Remarkable Effect of Ligands on Stereochemistry[†]

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Received March 6, 1989

Recently there has been growing interest in transition-metal-mediated cyclization of enynes and diynes as a tool for organic synthesis.[2] It is therefore surprising that the synthetic potential of the corresponding intramolecular cyclometalation of nonconjugated dienes has remained unexplored.[3] We have recently discovered conditions that allow such cyclometalations to be carried out efficiently. Our preliminary studies suggest that these transformations will prove quite useful in organic synthesis.

Our approach allows the selective cyclization of 1,6-dienes to either cis- or trans-1,2-disubstituted cyclopentanes. Treatment of 1,6-heptadiene with zirconocene dichloride (1 equiv) and butyllithium (2 equiv)[4] followed by bromination at −78 °C as shown in eq 1a afforded *trans*-1,2-bis(bromomethyl)cyclopentane in 88% isolated yield (crude product 97% trans by GLC).[5] In contrast

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[†] Dedicated to Dr. George W. Parshall on the occasion of his 60th birthday, Sept 19, 1989.

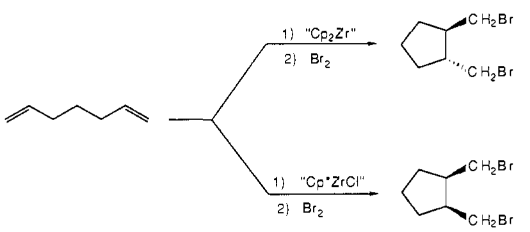
[‡] Contribution No. 5062.

(1) Du Pont Visiting Research Scientist 1988-89. Permanent address: Department of Chemistry, University of Delaware, Newark, DE 19716.

(2) For a review, see: Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047-1058.

(3) The literature contains several reports of cyclization of 1,7-octadiene by early transition metals to give isomeric mixtures of metallaindanes: McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529-6536. Grubbs, R. H.; Miyashita, A. *J. Chem. Soc., Chem. Commun.* **1977**, 864-865. McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558-4570. Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244-246.

(4) This superb "zirconocene equivalent" was developed and first applied to organic synthesis by Negishi and co-workers: Negishi, E.-i.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829-2832.

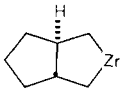


(1a)

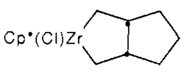
(1b)

(eq 1b), treatment of the same diene with Cp*ZrCl$_3$[6] (1 equiv) and 0.5% sodium amalgam (2 equiv) at −20 °C followed by bromination cleanly produced the isomeric cis dibromide (78% isolated yield; crude product 99% cis by GLC):[7]

In each case the reaction is presumed[8] to proceed through the corresponding zirconacyclopentane, i.e., **1** or **2**, respectively. Thus our results indicate that *the stereochemical course of metallacycle formation can be essentially reversed by changing the ancillary ligands.*[9]



1



2

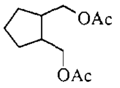
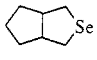
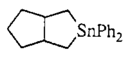
Treatment of metallacycles **1** and **2** with electrophiles other than bromine provides a stereoselective route to a variety of functionalized cyclopentanes (Table I).[10] Oxidation to the corresponding diols is carried out by bubbling dioxygen through the cyclized product (15 min, room temperature) prior to hydrolytic workup.[11] The straightforward synthesis of both cis- and trans-fused heterobicycles is illustrated in Table I by reactions with diphenyltin dichloride and with selenium monochloride, Se$_2$Cl$_2$. Many other heterocycles should be accessible by this approach since we have shown[12] that "metallacycle transfer" from zirconium to main-group halides is a general and facile reaction.

The Cp$_2$ZrCl$_2$-mediated cyclization of *substituted* 1,6-heptadienes likewise consistently affords trans-disubstituted cyclopentanes (Table II).[10] Moreover, the reaction is not limited to simple terminal olefins; disubstituted double bonds participate as exemplified by entries 2 and 3. *However, the trans stereochemistry of Cp$_2$ZrCl$_2$-mediated cyclization of 1,6-heptadienes cannot be generalized to other types of diene substrates.* The cyclization of 1,7-octadiene (entries 5 and 6) gives predominantly the cis-disubstituted product (entry 5, crude dibromide 81% cis by GLC). Heteroatom-containing dienes such as diallyldimethylsilane and diallylaniline can be utilized (entries 7 and 8) although again for the latter cyclization the isolated (principal) product proved to be cis fused (crude product 67% cis by GLC).

In contrast, the Cp*ZrCl$_3$-mediated cyclization gives cis-fused products in all cases studied to date. For example, treatment of the cyclic ketal substrate from entry 4 of Table II with the Cp*ZrCl$_3$-based reagent followed by bromination gave a 74% yield of the corresponding *cis*-bis(bromomethyl)cyclopentane as the only isolated product. Cp*ZrCl$_3$-mediated cyclization/thiolation of *N,N*-diallylaniline afforded the same cis-fused thiazabicyclooctane as shown in Table II (entry 8) but in somewhat higher (58%) yield.

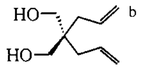
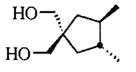
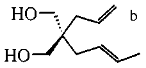
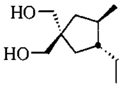
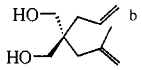
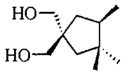
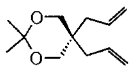
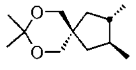
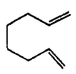
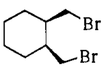
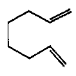
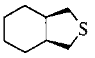
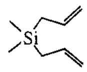
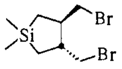
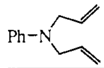
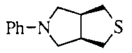
When an allylic substituent is present in the substrate, preliminary experiments suggest that the Cp$_2$Zr-mediated cyclization can proceed with high levels of 1,2-induction. For example, the

Table I. Synthesis of 1,2-Disubstituted Cyclopentanes from 1,6-Heptadiene

Electrophile	Reagent[a]	Product	Stereochemistry	Yield (%)[b]
O$_2$[c]	A	 OAc OAc	trans	80
O$_2$[c]	B		cis	55
Se$_2$Cl$_2$[d]	A	 Se	trans	51
Se$_2$Cl$_2$[d]	B		cis	53
Ph$_2$SnCl$_2$[d]	A	 SnPh$_2$	trans	67
Ph$_2$SnCl$_2$[d]	B		cis	60

[a] A = Cp$_2$ZrCl$_2$/2*n*-BuLi; B = Cp*ZrCl$_3$/2Na(Hg). [b] Isolated yield after chromatography. [c] 1 atm of O$_2$, 15 min; crude diol acetylated with 1:1 pyridine/acetic anhydride prior to chromatography. [d] Solution of cyclometalated diene treated with 1.0 equiv of electrophile (25 °C, 16 h).

Table II. Cyclization of Representative Dienes with Cp$_2$ZrCl$_2$

	Diene	Electrophile	Product	Yield[a]
1	 HO HO b	H$^+$	 HO HO	75%[c]
2	 HO HO b	H$^+$	 HO HO	75%[d]
3	 HO HO b	H$^+$	 HO HO	73%
4	 O O	H$^+$	 O O	66%[e]
5		Br$_2$	 Br Br	63%[f]
6		S$_2$Cl$_2$	 S	74%[f]
7	 Si	Br$_2$	 Si Br Br	59%[f]
8	 Ph−N	S$_2$Cl$_2$	 Ph−N S	46%[f]

[a] Yields given are for pure chromatographed material.[10] [b] An additional 2 equiv of *n*-BuLi was added at the beginning of the cyclization. [c] Trans/cis ratio = 10:1. [d] Trans/cis ratio = 3.7:1. [e] Trans/cis ratio = 10:1. [f] The diastereomeric products separated on chromatography. Yield reported is for the major diastereomer.

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(5) To a solution of 1,6-heptadiene (385 mg, 4.0 mmol) and zirconocene dichloride (1.17 g, 4.0 mmol) in THF (50 mL) at −78 °C was added via syringe 1.6 M butyllithium in hexane (5.0 mL, 8.0 mmol). After 10 min the mixture was allowed to warm to room temperature and stirring was continued for 2 h. The mixture was cooled to −78 °C and a solution of bromine (1.50 g, 9.4 mmol) in carbon tetrachloride (10 mL) was added. The reaction was quenched (room temperature) with 10% H$_2$SO$_4$ (50 mL), extracted into ether (3 × 50 mL), washed with aqueous sodium bicarbonate and water, and dried (MgSO$_4$). Removal of solvent followed by flash chromatography (hexane) afforded *trans*-1,2-bis(bromomethyl)cyclopentane as a colorless liquid (0.90 g, 88%). Anal. (C$_7$H$_{12}$Br$_2$) C, H, Br. ^{13}C NMR (CDCl$_3$): δ 23.93, 32.05, 38.05, 45.84.

(6) Cp* = pentamethylcyclopentadienyl ligand. Blenkers, J.; de Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383–393. Commercially available CpZrCl$_3$ gave cis/trans = 95:5.

(7) To a solution of 1,6-heptadiene (385 mg, 4.0 mmol) and (pentamethylcyclopentadienyl)zirconium trichloride (1.33 g, 4.0 mmol) in THF (50 mL) at −30 °C was added dropwise 0.5% sodium amalgam (40 g, 8.7 mmol). The mixture was stirred 2 h at −20 °C and 2 h at 0 °C. Bromination and workup as in note 5 afforded *cis*-1,2-bis(bromomethyl)cyclopentane as a pale yellow liquid (0.80 g, 78%). Anal. (C$_7$H$_{12}$Br$_2$) C, H, Br. ^{13}C NMR (CDCl$_3$): δ 22.63, 30.30, 33.97, 44.92.

(8) We have confirmed structures **1** and **2** (chloride-bridged dimer) by X-ray crystallography. For the structure of a tantalum metallacyclopentane related to **2**, see: Churchill, M. R.; Youngs, W. Y. *Inorg. Chem.* **1980**, *19*, 3106–3112.

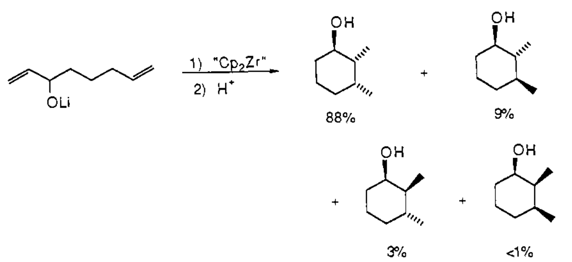
(9) We are currently investigating the origin of this effect and will report our results in a forthcoming full paper.

(10) Products in Tables I and II refer to material purified by flash chromatography and characterized by ^{1}H and ^{13}C NMR and combustion analysis (±0.40%).

(11) Compare: Blackburn, T. F.; Labinger, J. A.; Schwartz, J. *Tetrahedron Lett.* **1975**, 3041–3044.

(12) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310–2312. Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137–7141.

lithiated allylic alcohol in eq 2 was cyclized in 64% chemical yield;



(2)

the 1,2-trans 1,3-cis isomer constituted 88% of the product. We intend to further explore and develop this potentially useful observation.

In summary, the zirconium-mediated cyclization of nonconjugated dienes provides an efficient, versatile,[13] and stereoselective route to functionalized carbocycles and heterocycles.

Supplementary Material Available: Details of the synthesis, isolation, and characterization (^{1}H NMR, ^{13}C NMR, HRMS, elemental analysis) for all reported products (8 pages). Ordering information is given on any current masthead page.

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(13) Known limitations: Cyclization failed for 1,5-hexadiene and 1,8-nonadiene; diethyl diallylmalonate underwent competitive reduction of the carbonyl group; substrates containing the allyl ether functionality gave significantly diminished yields.

An ENDOR Study of Spin Distributions in Octaethylmetalloporphyrin π Cation Radicals

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Received March 7, 1989

π cation radicals of the metalloporphyrin family are biologically important species, found as primary products of the photochemical reaction in photosynthetic reaction centers and as oxidized intermediates in the enzymatic cycles of horseradish peroxidase and catalase.[1] Classic ESR studies by Fajer and co-workers have demonstrated that stable porphyrin π cation radicals of either the $^2A_{2u}$ or $^2A_{1u}$ ground state can be formed. $^2A_{2u}$ species such as Zn tetraphenylporphyrin radical are distinguishable by large, ESR resolvable nitrogen hyperfine couplings, whereas the ESR spectra of $^2A_{1u}$ complexes, such as Mg octaethylporphyrin radical (MgOEP$^+$), display either meso proton couplings of only moderate size or no resolved structure at all.[2] For systems without evident hyperfine structure attempts have been made to assign ground states based on optical spectra; the visible spectra of Co^{III}OEP$^{\bullet+}$2Br$^-$ and Co^{III}OEP$^{\bullet+}$2Cl$^-$ are thought to be characteristic of $^2A_{1u}$ radicals, whereas the distinctive spectra of Cu^{II}OEP$^{\bullet+}$2ClO$_4^-$ and Co^{III}OEP$^{\bullet+}$2ClO$_4^-$ were taken as signatures of the $^2A_{2u}$ state.[3] Although these assignments have formed the basis for much of the discussion in the porphyrin radical literature,[4] they have been brought into question by several independent EPR,[5] NMR,[6] and resonance Raman studies.[7] ESR hyperfine coupling is the physical parameter most unequivocally related to electron spin density in organic radicals; unfortunately, none of the ESR spectra of the principal species in question (Cu^{II}OEP$^{\bullet+}$2ClO$_4^-$, Co^{III}OEP$^{\bullet+}$2ClO$_4^-$, Co^{III}OEP$^{\bullet+}$2Br$^-$, Co^{III}OEP$^{\bullet+}$2Cl$^-$) display resolved hyperfine structure.[8] We report here measurements of

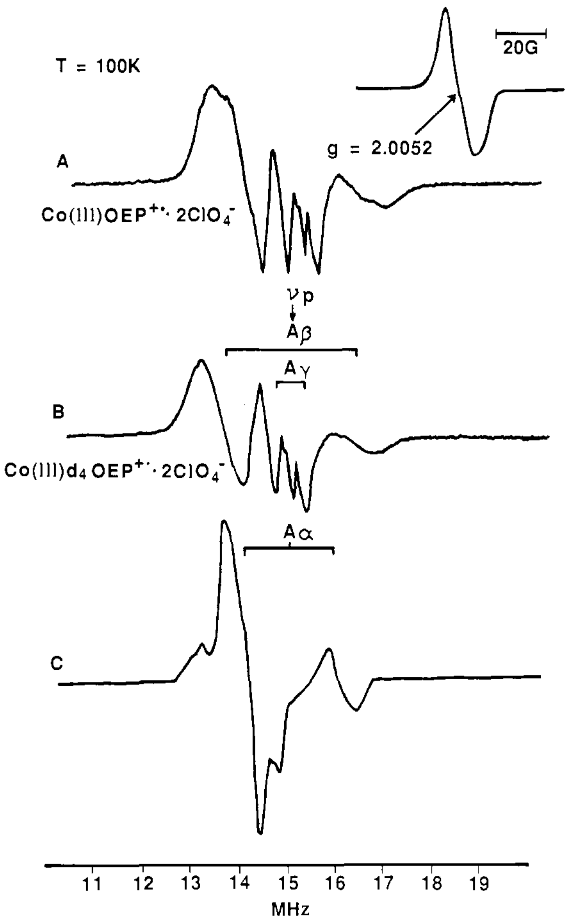

Figure 1. ESR and proton ENDOR spectra of Co^{III}OEP$^{\bullet+}$2ClO$_4^-$ glassed in 1:1 CH$_2$Cl$_2$/toluene at 100 K. Insert: ESR spectrum, 0.65 mW microwave power, 0.5 G$_{pp}$ 12.5 KHz field modulation, 200 s sweep time, 200 ms time constant. A: ENDOR spectrum of 1 mM Co^{III}OEP$^{\bullet+}$-2ClO$_4^-$. B: ENDOR spectrum of 1 mM Co$^{III}d_4$OEP$^{\bullet+}$2ClO$_4^-$. ENDOR spectra were taken at 16 mW micowave power, 150 W rf power, 25 KHz rf modulation, 2000 s sweep time, 2 s time constant, with the magnetic field set at 3458.0 G (9.7027 GHz). C: Difference of spectra A and B showing meso proton ENDOR features (note that the ordinate scale has been expanded).

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† Present address: Department of Chemistry, University of California-Santa Barbara, Santa Barbara, CA 93106.

(1) (a) Dolphin, D.; Felton, R. H. *Acc. Chem. Res.* **1974**, *7*, 26–32. (b) Frew, J. E.; Jones, P. In *Advances in Inorganic and Bioinorganic Mechanism*; Academic Press; New York, 1984; Vol. 3, pp 175–215.

(2) (a) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 4, pp 197–256. (b) Fajer, J.; Borg, D. C.; Forman, A.; Felton, R. H.; Vegh, L.; Dolphin, D. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 349–364.

(3) Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J.; Felton, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 614–618.

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0002-7863/89/1511-6437$01.50/0