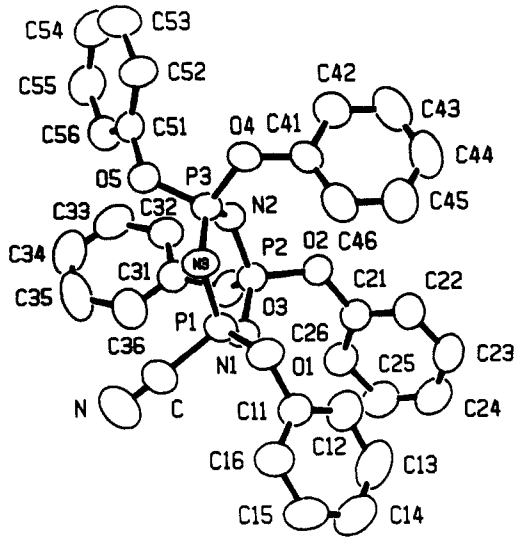

Figure 1. ORTEP representation of the structure of monocyanopentaphenoxycyclotriphosphazene (**1**).

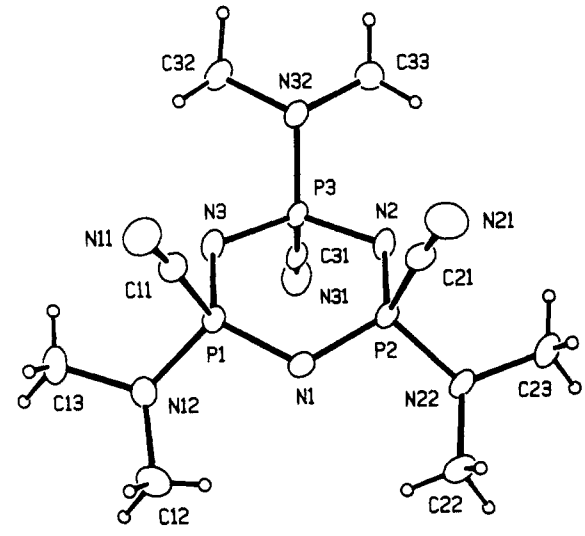

Figure 2. ORTEP representation of the structure of non-*gem*-*trans*-tris(dimethylamino)tricyanocyclotriphosphazene (**2**).

Table I. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

		Compound **1**	
P(1)-N(1)	1.564 (2)	N(1)-P(1)-N(3)	119.3 (1)
P(1)-N(3)	1.567 (2)	N(1)-P(2)-N(2)	117.4 (1)
P(2)-N(1)	1.585 (2)	N(2)-P(3)-N(3)	117.4 (1)
P(2)-N(2)	1.570 (2)	P(1)-N(1)-P(2)	120.9 (1)
P(3)-N(2)	1.574 (2)	P(2)-N(2)-P(3)	122.6 (1)
P(3)-N(3)	1.577 (2)	P(1)-N(3)-P(3)	121.4 (1)
P(1)-C	1.781 (3)	O(2)-P(2)-O(3)	99.6 (1)
C-N	1.134 (3)	O(4)-P(3)-O(5)	100.7 (1)
		O(1)-P(1)-C	101.6 (1)
		P(1)-C-N	177.1 (3)
		Compound **2**	
P(3)-C(31)	1.819 (2)	N(1)-P(1)-N(3)	118.58 (9)
P(2)-C(21)	1.812 (2)	N(1)-P(2)-N(2)	117.86 (8)
P(1)-C(11)	1.815 (2)	N(2)-P(3)-N(3)	119.71 (9)
C(11)-N(11)	1.145 (3)	P(1)-N(1)-P(2)	119.5 (1)
C(21)-N(21)	1.139 (3)	P(2)-N(2)-P(3)	119.6 (1)
C(31)-N(31)	1.145 (3)	P(1)-N(3)-P(3)	119.4 (1)
P(3)-N(32)	1.625 (2)	P(1)-C(11)-N(11)	176.0 (2)
P(2)-N(22)	1.628 (2)	P(2)-C(21)-N(21)	176.3 (2)
P(1)-N(12)	1.623 (2)	P(3)-C(31)-N(31)	176.7 (2)
ring P-N(av)	1.587		

31.30; H, 5.22; N, 36.52. Found: C, 31.34; H, 5.25; N, 36.70. Low-resolution mass spectral analysis showed the expected molecular ion at *m/e* 345. The infrared spectrum contained a cyano stretching peak at 2180 cm^{-1}. The ^{31}P NMR spectrum consisted of a singlet at −7.8 ppm. Crystals suitable for X-ray analysis were grown by slow evaporation of a solution of **2** in hexane. The structure of **2** is illustrated in Figure 2, and important structural parameters are given in Table I.[9]

Both compounds, **1** and **2**, are stable in contact with the atmosphere and are unaffected when heated to moderate temperatures.

The X-ray structural information for both **1** and **2** is consistent with a cyano rather than an isocyano arrangement,[10] and this is confirmed by the infrared spectra.[11] The triple bonds of the cyano groups in **2** are slightly longer than that in **1**, but no evidence could be found for multiple bonding between the cyano groups and the phosphazene ring. The carbon–phosphorus bond lengths are similar to those reported elsewhere for cyano groups attached to phosphorus through single bonds.[12]

Acknowledgment. We thank the U.S. Army Research Office for the support of this work.

(9) X-ray analysis of **2**: space group $P\bar{1}$; unit cell, a = 6.715 (3) Å, b = 8.538 (5) Å, c = 14.910 (6) Å, α = 92.10 (4)°, β = 105.41 (4)°, γ = 95.75 (4)°; 2861 unique reflections measured on an Enraf-Nonius CAD4 diffractometer at 140 K; solved by direct and Fourier methods; full-matrix least-square calculations; hydrogen atoms from difference map and refined isotropically; final R = 0.044 and R_w = 0.061 for 2460 observed reflections $I > 3\sigma(I)$.

(10) Refinement of the three cyano groups in **2** as isocyano units caused the structure to converge with R = 0.058 and R_w = 0.089, significantly higher values than found for the cyano-type arrangement.[9]

(11) For example, see: Seyferth, D.; Kahleen, N. *J. Am. Chem. Soc.* **1960**, *82*, 1080.

(12) Emerson, K.; Britton, D. *Acta Crystallogr.* **1964**, *17*, 1134.

Stereocontrol in Intramolecular Hydrosilation of Allyl and Homoallyl Alcohols: A New Approach to the Stereoselective Synthesis of 1,3-Diol Skeletons[1]

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We report herein a new methodology for the regio- and stereocontrolled synthesis of 1,3-diols from certain allyl and homoallyl alcohols via intramolecular hydrosilation followed by oxidative cleavage of the carbon–silicon bond.

Much attention has recently been paid to the regio- and stereoselective olefin functionalization through olefin cyclization induced by external[2] or internal[3] electrophiles. Intramolecular hydrometalation, however, has scarcely been studied so far from the viewpoint of regio- and stereocontrol in acyclic systems,[4] despite the potential utilities.

We have now developed an intramolecular hydrosilation as a new promising methodology for such purposes. The intramolecular

(1) Silafunctional Compounds in Organic Synthesis. 31. (a) Part 30: Tamao, K.; Tanaka, T.; Nakajima, T.; Sumiya, R.; Arai, H.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 3377. (b) A review on this subject: Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; pp 231–242.

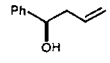
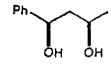
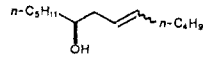
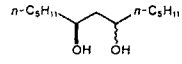
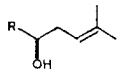
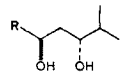
(2) Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 411–454.

(3) E.g., the Sharpless oxidation: (a) Sharpless, K. B.; Woodard, S. S.; Finn, M. G. *Pure Appl. Chem.* **1983**, *55*, 1823. (b) Mihelich, E. D.; Daniels, K.; Eickhoff, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 7690.

(4) Sequential hydroboration of dienes by boron dihydrides has been reported: Still, W. C.; Darst, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 7385.

0002-7863/86/1508-6090$01.50/0

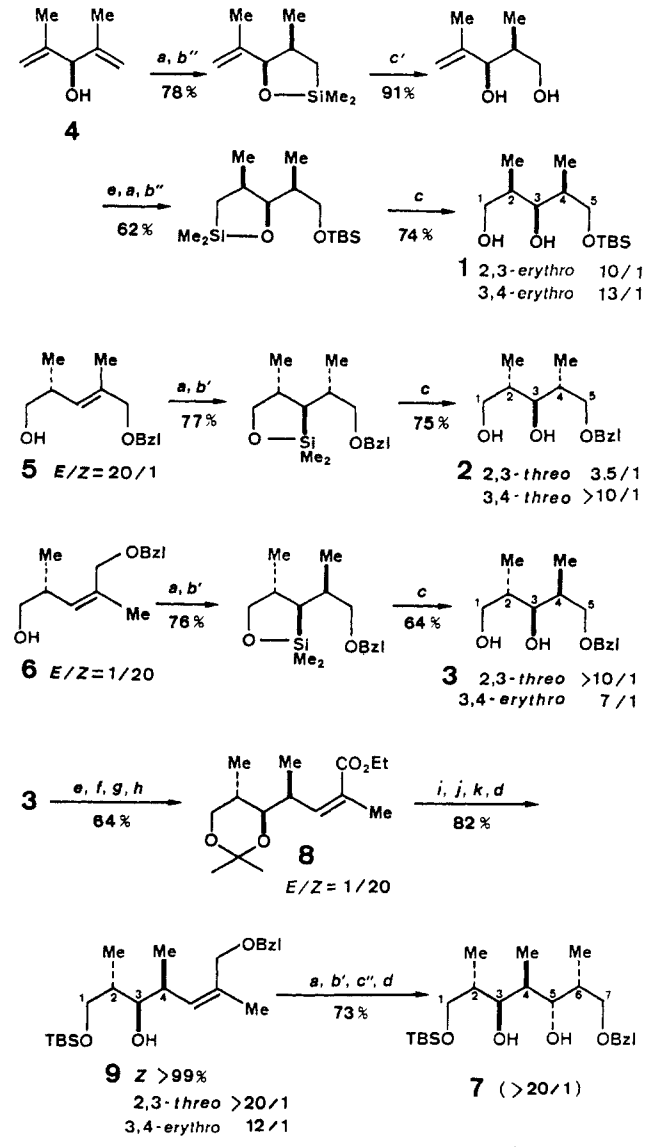
Table I. Stereoselectivity of 1,3-Diol Synthesis via Intramolecular Hydrosilation of Allyl and Homoallyl Alcohols Catalyzed by $H_2PtCl_6 \cdot 6H_2O$[a]

entry	alcohol[b]	major isomer of product 1,3-diol	selectivity[c]	yield,[d] %
1			>100 : 1	73[e]
2			>100 : 1	52
3			5.7 : 1	71[f]
4	 *E* or *Z*		~1 : 1	63-95
				
5	R = *n*-C_5H_{11}		5.3 : 1	72
6	R = *i*-Pr		3.5 : 1	33
7	R = Ph		3.3 : 1	53
8			1.6 : 1	40
9			6.1 : 1	67
				
10	R = *n*-Bu		2.4 : 1	73
11	R = *i*-Pr		24 : 1	66
12	R = *t*-Bu		>100 : 1	52
13	R = Ph		6.7 : 1	55

[a] Reaction conditions have not yet been optimized. Reactions were carried out usually on 3-mmol scales: (1) $(HMe_2Si)_2NH$ (0.6–2 equiv), (2) $H_2PtCl_6 \cdot 6H_2O$ (ca. 0.1 mol %)/room temperature–60 °C/10 min–24 h, (3) 30% H_2O_2 (2–6 equiv/Si–C bond)/$NaHCO_3$ (1 equiv)/MeOH/THF/60 °C/10–15 h. [b] Alcohols are all racemic. [c] Determined by GLC analysis of the corresponding acetonides, with the exception of entries 1 and 2 determined by 400-MHz NMR. [d] Isolated overall yields based on the starting alcohols. [e] Hydrosilation was catalyzed by $RhCl(PPh_3)_3$ (0.1 mol %) at 100 °C. [f] A mixture of 1,3- and 1,4-diols in the ratio of 88/12.

hydrosilation may be attained with a hydrosilyl group anchored to a neighboring hydroxy group in the presence of transition-metal catalysts such as platinum and rhodium.[5] The regio- and stereochemistry should be controlled during the addition of a transition-metal hydride to the coordinated olefin and the final oxidative cleavage of the resultant carbon–silicon bond should form the stereodefined diols, since the oxidative cleavage has been shown to proceed with retention of configuration at carbon.[6] Indeed, we have recently noted the dramatic acceleration and the high regioselectivity in the intramolecular hydrosilation of certain allyl and homoallyl alcohols.[1a] Most significantly, this method has made possible for the first time the direct hydrosilation of internal di- and trisubstituted olefins under mild conditions. This report describes the stereochemical aspects and applications of this new procedure.

Scheme I



[a] $(HMe_2Si)_2NH$/room temperature–60 °C/1–9 h. [b] $H_2PtCl_6 \cdot 6H_2O$ (0.1 mol %)/20 °C/1 h. [b'] $H_2PtCl_6 \cdot 6H_2O$ (0.1 mol %)/60 °C/3 h. [c] 30% H_2O_2/KF/$KHCO_3$/MeOH/THF/room temperature/10 h. [c'] 30% H_2O_2/$NaHCO_3$/MeOH/THF/60 °C/12–48 h. [c''] 30% H_2O_2/15% KOH/MeOH/THF/50 °C/2.5 h. [d] *t*-$BuMe_2SiCl/Et_3N$/DMAP/CH_2Cl_2/room temperature/2 h. [e] $Me_2C(OMe)_2$/TsOH. [f] Li/liquid NH_3. [g] $(COCl)_2/Me_2SO/Et_3N$. [h] $(EtO)_2P(O)$-$CHMeCO_2Et$/NaH/THF/<–50 °C. [i] LAH/Et_2O/–30 °C. [j] $PhCH_2Br$/NaH/THF. [k] $AcOH/H_2O$/40 °C.

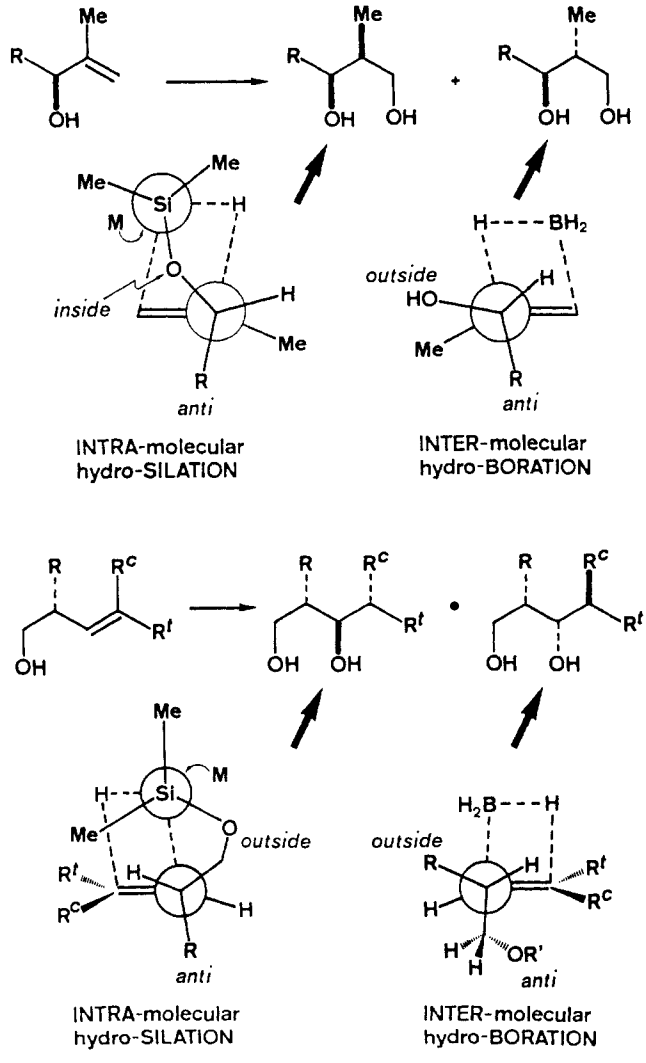
The preliminary results summarized in Table I show the following features.[7] (1) Cyclic homoallylic alcohols gave *cis*-1,3-diols solely (entries 1 and 2). (2) In acyclic homoallylic alcohols (entries 3–9), the 1,3-stereocontrol varied from erythro rich for a terminal olefin (entry 3) to threo rich for trisubstituted olefins (entries 5–7); little stereoselection was observed in *E*- and *Z*-disubstituted olefins (entry 4). (3) 1,2-Stereocontrol in the 1,3-diol synthesis from homoallyl alcohols favored the formation of threo isomers (entries 8 and 9), the *Z* isomer showing the much higher stereoselectivity than the *E* isomer. (4) Another type of 1,2-stereoselection was achieved in allylic alcohols (entries 10–13); erythro isomers were

(5) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Harrod, J. F.; Chalk, A. J. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 673–704.

(6) (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. (b) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37.

(7) For a general procedure and some special precautions, see ref 1a. All the starting materials and the final products showed the consistent spectral and/or analytical data.

Scheme II



formed preferentially, the selectivity increasing with an increase of bulkiness of the allylic substituent.

The synthetic utility of the intramolecular hydrosilation is demonstrated herein by the simple, highly stereoselective synthesis of racemic forms of three isomeric triols having three consecutive chiral centers **1**–**3** (Scheme I),[7,8] which are often found in many natural products such as polyoxy ionophores, macrolides, and ansamycins.[9] While for the synthesis of **1** the erythro stereoselection has been used in a reiterative manner, for **2** and **3** the threo-selective hydrosilation has been applied to the stereodefined trisubstituted olefin moieties; the 3,4-relative stereochemical outcomes depend on the olefin geometries. In this connection, the latter two results with **5** and **6** have provided the first clear-cut experimental evidence for the stereospecific cis process of the platinum-catalyzed hydrosilation of acyclic olefins.[10] Similarly, as shown in Scheme I, **3** was converted further into a tetraol having five consecutive chiral centers, **7**, a segment of narasin, salinomycin, elaiophilin, etc.;[9,11] carefully purified (*Z*)-**8** afforded isomerically almost pure **7** after isolation by preparative TLC.

The extents of stereoselection in these examples are comparable to or mugh higher than those attained by intermolecular hydroboration in the related systems.[9b,12] Far more important is that the preferred configurations are opposite each other. These differences are schematically visualized by Scheme II, where the most favorable transition structures for our systems[13] are deduced on the basis of the inspection of the molecular models and Houk's staggered models which have been proposed for the intermolecular hydroboration.[14] Thus, in the hydroboration the preferred positions of the allylic and homoallylic oxygen groups are *outside* and *anti*, respectively;[14] in the intramolecular hydrosilation these oxygen groups should be inevitably oriented *inside* and *outside*, respectively, with the larger R group being kept out of the most crowded *inside* region in both cases.

Refinement, further applications, and mechanistic studies are now in progress in our laboratories.

Acknowledgment. We thank Professor Emeritus M. Kumada for encouragement, Haruo Fujita for measurements of 400-MHz NMR spectra, and Shin-etsu Chemical Industrial Co., Ltd., for a gift of organosilicon compounds.

Registry No. 1, 103668-53-7; **2**, 79027-32-0; **3**, 103729-90-4; **4**, 38614-40-3; (*E*)-**5**, 74130-36-2; (*Z*)-**5**, 74130-40-8; **7**, 103668-57-1; (*E*)-**8**, 103668-55-9; (*Z*)-**8**, 103729-91-5; **9**, 103668-56-0; (±)-PhCH(OH)$CH_2CH{=}CH_2$, 80735-94-0; (±)-PhCH(OH)$CH_2CH(OH)CH_3$ (major isomer), 103729-81-3; (±)-PhCH(OH)$CH_2CH(OH)CH_3$ (minor isomer), 103729-86-8; (±)-Ph-CH(OH)$(CH_2)_3OH$, 103668-47-9; (±)-(*E*)-$CH_3(CH_2)_4CH(OH)CH_2CH{=}CH(CH_2)_3CH_3$, 103668-34-4; (±)-(*Z*)-$CH_3(CH_2)_4H(OH)CH_2CH{=}CH(CH_2)_3CH_3$, 103668-40-2; (±)-$CH_3(CH_2)_4CH(OH)CH_2CH(OH)(CH_2)_4CH_3$ (isomer 1), 103729-82-4; (±)-$CH_3(CH_2)_4CH(OH)CH_2CH(OH)(CH_2)_4CH_3$ (isomer 2), 103729-85-7; (±)-$CH_3(CH_2)_4CH(OH)CH_2CH{=}C(CH_3)_2$, 103668-35-5; (±)-$CH_3(CH_2)_4CH(OH)CH_2CH(OH)CH(CH_3)_2$ (major isomer), 103668-42-4; (±)-$CH_3(CH_2)_4CH(OH)CH_2CH(OH)CH(CH_3)_2$ (minor isomer), 103668-48-0; (±)-*i*-PrCH(OH)$CH_2CH{=}C(CH_3)_2$, 103668-36-6; (±)-*i*-PrCH(OH)$CH_2CH(OH)CH(CH_3)_2$ (major isomer), 103668-43-5; (±)-*i*-PrCH(OH)$CH_2CH(OH)CH(CH_3)_2$ (minor isomer), 65534-62-5; (±)-PhCH(OH)$CH_2CH{=}C(CH_3)_2$, 103668-37-7; (±)-PhCH(OH)-$CH_CH(OH)CH(CH_3)_2$ (major isomer), 103668-44-6; (±)-PhCH(OH)-$CH_2CH(OH)CH(CH_3)_2$ (minor isomer), 103668-49-1; (±)-(*E*)-$HOCH_2CH(CH_3)CH{=}CHCH_3$, 103729-79-9; (±)-$HOCH_2CH(CH_3)$-$CH(OH)CH_2CH_3$ (major isomer), 103729-83-5; (±)-$HOCH_2CH$-$(CH_3)CH(OH)CH_2CH_2$ (minor isomer), 103729-87-9; (±)-(*Z*)-$HOCH_2CH(CH_3)CH{=}CHCH_3$, 80375-06-0; (±)-BuCH(OH)C-$(CH_3){=}CH_2$, 79605-66-6; (±)-BuCH(OH)$CH(CH_3)CH_2OH$ (major isomer), 103668-45-7; (±)-BuCH(OH)$CH(CH_3)CH_2OH$ (minor isomer), 103668-50-4; (±)-*i*-PrCH(OH)$C(CH_3){=}CH_2$, 103668-38-8; (±)-*i*-PrCH(OH)$CH(CH_3)CH_2OH$ (major isomer), 103729-84-6; (±)-*i*-PrCH(OH)$CH(CH_3)CH_2OH$ (minor isomer), 103729-88-0; (±)-*t*-BuCH(OH)$C(CH_3){=}CH_2$, 103668-39-9; (±)-*t*-BuCH(OH)CH-$(CH_3)CH_2OH$ (major isomer), 103668-46-8; (±)-PhCH(OH)C-$(CCh_3){=}CH_2$, 103729-80-2; (±)-PhCH(OH)$CH(CH_3)CH_2OH$ (major isomer), 51451-31-1; (±)-PhCH(OH)$CH(CH_3)CH_2OH$ (minor isomer), 51451-32-2; (±)-$H_2C{=}C(CH_3)CH(OH)CH(CH_3)CH_2OH$ (stereo iso-

(8) The starting materials **5** and **6** were prepared by Kishi's method[9b] from $THPOCH_2CHMeCHO$ which was prepared from the THP ether of methallyl alcohol by ordinary hydrosilation/oxidation[6] followed by the Swern oxidation.

(9) Synthesis of these segments. (a) Epoxidation/cuprates: Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873. (b) Epoxidation/cuprates and hydroboration: Johnson, M. R.; Nakata, T.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4343. (c) Hydroboration: Oikawa, Y.; Nishi, T.; Itaya, H.; Yonemitsu, O. *Tetrahedron Lett.* **1983**, *24*, 1987. (d) Reduction of carbonyl groups: Nakata, T.; Fukui, M.; Ohtsuka, H.; Oishi, T. *Tetrahedron* **1984**, *40*, 2225. (e) Aldol reaction: Masamune, S.; Choy, W.; Peterson, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. (f) Diels–Alder reaction: Danishefsky, S.; Harvey, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 6647. For natural products which contain these chiral units, see references cited therein and the following reviews: (g) Westley, J. W. *Adv. Appl. Microbiol.* **1977**, *22*, 177. (h) Paterson, I.; Mansuri, M. M. *Tetrahedron* **1985**, *41*, 3569.

(10) The cis process of the hydrosilation of olefins has been shown only with a rigid cyclic system, 1-methylcyclohexene: Selin, T. G.; West, R. *J. Am. Chem. Soc.* **1962**, *84*, 1863.

(11) Seebach, D.; Chow, H. F.; Jackson, R. F. W.; Lawson, K.; Sutter, M. A.; Thaisrivongs, S.; Zimmermann, J. *J. Am. Chem. Soc.* **1985**, *107*, 5292.

(12) (a) Schmid, G.; Fukuyama, T.; Akasaka, K.; Kishi, Y. *J. Am. Chem. Soc.* **1979**, *101*, 259. (b) Still, W. C.; Barrish, J. C. *Ibid.* **1983**, *105*, 2487. (c) Heathcock, C. H.; Jarvi, E. T.; Rosen, T. *Tetrahedron Lett.* **1984**, *25*, 243.

(13) The proposed models for the intramolecular hydrosilation are based on the well-accepted mechanism of platinum-catalyzed intermolecular hydrosilation of olefins,[5] which involves addition of a transition-metal silyl hydride species to a coordinated olefin. The Si–M–H angle has been assumed to be 90°, in view of the cis process of the oxidative addition of the silicon–hydrogen bond to low-valent transition-metal complexes: Eaborn, C.; Tune, D. J.; Walton, D. R. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2255. Johnson, E. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531 and references cited therein. A four-centered mechanism for the addition of transition-metal hydride to olefin has also been well accepted: James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, Chapter 51, p 285. Although the ligands on the transition metal should play an important role for the stereoselection, they cannot be specified and are ignored at the present time.

(14) Houk, K. N.; Rondan, N. G.; Wu, Y.-D.; Metz, J. T.; Paddon-Row, M. N. *Tetrahedron* **1984**, *40*, 2257.

mer), 102745-52-8; (±)-3-cyclohexen-1-ol, 72137-22-5; (±)-(*cis*)-1,3-cyclohexanediol, 103668-41-3; (±)-2-cyclohexene-1-methanol, 103668-33-3; (±)-(*cis*)-2-(hydroxymethyl)-1-cyclohexanol, 96553-66-1; (±)-(*cis*)-5-isopropenyl-2,2,4-trimethyl-1-oxa-2-silacyclopentane, 103668-51-5; (±)-2,4,4-trimethyl-5-(2-*tert*-butyldimethylsilyloxy-1-methylethyl)-1-oxa-2-silacyclopentane (stereoisomer), 103668-52-6; (±)-2,2,4-trimethyl-3-(2-benzyloxy-1-methylethyl)-1-oxa-2-silacyclopentane (isomer 1), 103668-54-8; (±)-2,2,4-trimethyl-3-(2-benzyloxy-1-methylethyl)-1-oxa-2-silacyclopentane (isomer 2), 103729-89-1.

Supplementary Material Available: Preparative methods for the starting materials, stereochemical assignments of 1,3-diols listed in Table I, and 400-MHz ^{1}H NMR spectra of acetonides of **1**–**3** and **7** (6 pages). Ordering information is given on any current masthead page.

Membrane-Bound Cytochrome P-450 Mimic. Polymerized Vesicles as Microreactors

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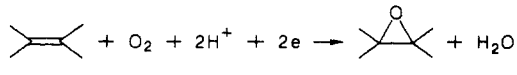
The Cytochrome P-450 dependent monooxygenases are membrane-bound enzymes that catalyze a great variety of reactions, among which is the epoxidation of alkenes by molecular oxygen.[1]



The active center of the enzymes contains an iron(III) protoporphyrin IX and axial thiolate ligand. After being reduced to iron(II) this center binds and cleaves molecular oxygen, whereupon water and a high-valent iron–oxo complex are formed. The latter species transfers its oxygen to a substrate molecule.[1,2] The electrons required in the process are provided by NADPH via a coupled electron transferring enzyme system.[1] We describe here a synthetic model system of cytochrome P-450 which incorporates all the features of the natural enzyme system, i.e., (i) a membraneously bound metalloporphyrin (complex **1**), (ii) an axial ligand (*N*-methylimidazole), (iii) an electron donor (colloidal Pt–H_2),[2a] (iv) an electron carrier (methylene blue), and (v) a membrane system (polymerized vesicles of **2**) which holds components within its bilayer or within its inner aqueous compartment (Figure 1).

[Tetrakis[4-(hexadecyloxy)phenyl]porphyrinato]manganese(III) acetate (**1**) was synthesized from the corresponding tetrakis(hydroxyphenyl) derivative and *n*-hexadecyl bromide by reaction with base in 3:1 v/v DMF–toluene. Compound **1** (2.7×10^{-5} M) and the isocyano surfactant **2**[3] (5×10^{-3} M) were cosonicated for 30 min in water at 25.0 °C. Subsequent polymerization[3] with nickel capronate (8.5×10^{-5} M) for 24 h yielded polymerized vesicles which had **1** incorporated into their bilayers. This was checked by dialysis and chromatographic procedures in combination with UV–vis. In a similar way, using an aqueous solution of K_2PtCl_4 (10^{-3} M), polymerized vesicles were prepared which, after passing over an anion-exchange resin (Dowex 1-X2, Cl^- form), contained **1** in their bilayers and Pt(II) (overall concentration 3.5×10^{-4} M) in their inner aqueous compartments. The Pt(II) ions within the vesicles were reduced to colloidal Pt by bubbling molecular hydrogen through the dispersions. Dynamic light-scattering experiments and electron micrographs revealed that the polymerized aggregates with Pt as well as those without had the same diameters, namely, 1000–3000 Å.

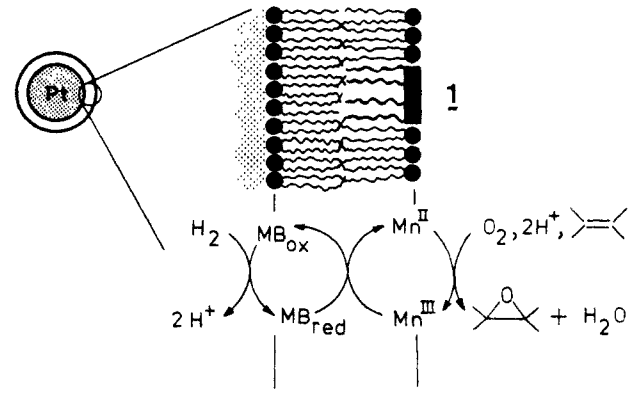


Figure 1. Polymerized vesicle as microreactor. MB_{ox} and MB_{red} stand for the oxidized and reduced forms of methylene blue, respectively.

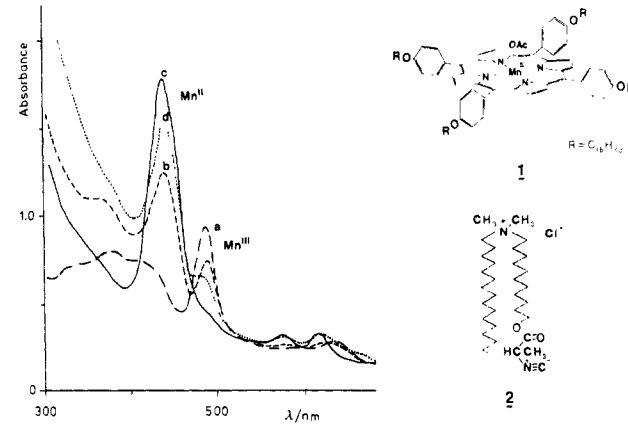


Figure 2. UV–vis spectra of manganese(III) porphyrin **1** in polymerized vesicles of **2**: (a) vesicles with or without Pt and without methylene blue after treatment with H_2; (b) same as (a) after treatment with sodium dithionite; (c) same as (b) after treatment with triton X-100; (d) vesicles with Pt and methylene blue after treatment with H_2 for 3 min.

The following experiment suggests that manganese porphyrin **1** is distributed equally between the inner and outer surfaces of the vesicles. To the polymerized vesicle dispersions (1.5 mL) containing **1**, sodium dithionite (1.5 mL, 2×10^{-3} M) was added externally. As shown by UV–vis, Mn^{III} partially reduces to Mn^{II} (50 ± 5%, Figure 2). Adding triton X-100, which causes the vesicles to leak, results in complete reduction of the manganese centers.

In order to establish the conditions under which alkenes are epoxidized by the aforementioned systems, a number of experiments had to be carried out. First, we investigated the reduction of Mn^{III} in the bilayers by molecular hydrogen. This reagent was bubbled through polymerized vesicle dispersions containing **1** and Pt in the concentrations mentioned above. Methylene blue was added in a concentration of 6.2×10^{-6} M. Blank experiments were done with vesicles without Pt and vesicles to which no methylene blue had been added. Figure 2 shows that Mn^{III} reduces to Mn^{II} when both Pt and methylene blue are present. However, when either of these components are omitted, no reduction takes place. In addition these experiments indicate that the manganese centers and Pt are located at different sites, i.e., in the vesicle bilayer and inner aqueous compartment, respectively.[4]

In a second series of experiments we tested the suitability of molecular oxygen as oxidant. Polymerized vesicles were prepared containing **1**, Pt, methylene blue, and in addition *N*-methyl-

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(2) For model studies on cytochrome P-450, see: (a) Tabushi, I.; Morimitsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 6871–6872. (b) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786–5791. (c) Razenberg, J. A. S. J.; Van der Made, A. W.; Smeets, J. W. H.; Nolte, R. J. M. *J. Mol. Catal.* **1985**, *31*, 271–287 and references cited.
(3) Roks, M. F. M.; Visser, H. G. J.; Zwikker, J. W.; Verkley, A. J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1983**, *105*, 4507–4510.

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