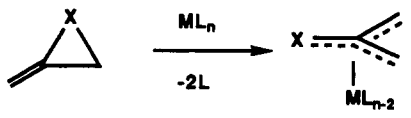
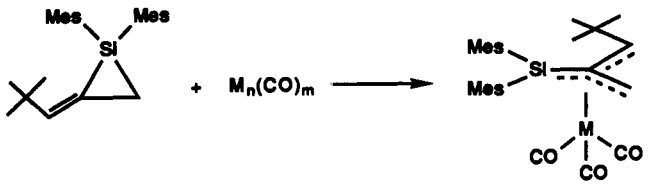
Scheme I



11 1

X=S, SiR_2

Scheme II



2 3a; $Fe_2(CO)_9$ 3b; $Ru_3(CO)_{12}$ 1a; M=Fe 1b; M=Ru

Conclusive evidence was obtained from an X-ray analysis. Recrystallization of the iron analogue (**1a**) from hexane at 0 °C yielded well-formed prisms. The molecule crystallized in space group $Pna2_1$; an ORTEP drawing is shown in Figure 1 together with selected bond lengths and angles.[9] The silatrimethylenemethane ligand is bound in an η^4 fashion and staggered relative to the three carbonyl ligands. The bond distances C(1)-Si, C(1)-C(2), and C(1)-C(3) are 1.840 (8), 1.42 (1), and 1.46 (1) Å, which falls midway between C-Si or C-C single and double bonds.[8] Especially the C(1)-Si distance is somewhat longer than the values found in other silene complexes:[1i-h] $Cp^*RuHPCy_3(\eta^2\text{-}CH_2{=}SiMe_2)$, 1.78-1.79 Å; $Cp^*IrPMe_3(\eta^2\text{-}CH_2{=}SiPh_2)$, 1.810 Å; $Cp_2W(\eta^2\text{-}CH_2{=}SiMe_2)$, 1.800 Å. The cross-conjugative interaction with the C-C double bond may be responsible for the slightly longer values of the C(1)-Si bond. The methylene and methine protons in **1a** were located and refined, allowing discussion of the nonplanarity of the ligand. The sum of the angles around silicon and the three carbons C(1), C(2), and C(3) are 346.6°, 343.9°, 350°, and 341°, between the 360° and 329.1° values expected for sp^2 and sp^3 hybridization. The central carbon C(1) lies above the plane of the other three atoms, while planes containing C(11)-Si-C(12), C(31)-C(2)-H(2), and H(31)-C(3)-H(32) are bent away from the $Fe(CO)_3$ fragment. Thus, the η^4-silatrimethylenemethane ligand adopts an umbrella shape, as it is in the structurally characterized trimethylenemethane[6b] and its hetero analogue.[2a,h] The low yield realized for **1b** is in part due to the competitive formation of an alkylidenesilirane-containing triruthenium complex, which structure will be reported elsewhere.

The successful construction of title complexes **1a** and **1b** suggests the ring opening of hetero-analogous methylenecyclopropane and η^4-complexation by transition metals to be more general than expected.

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Supplementary Material Available: Detailed information on the X-ray crystal analysis of **1a** and 2D NMR spectra of **1a** and **1b** (21 pages); listing of observed and calculated structure factors for **1a** (5 pages). Ordering information is given on any current masthead page.

(9) Crystal data for **1a**: $C_{28}H_{34}O_3SiFe$, M = 502.51, orthorhombic with a = 10.254 (2) Å, b = 14.402 (2) Å, c = 18.151 (3) Å, V = 2680.5 Å^3, space group $Pna2_1$, Z = 4, μ(Mo Kα) = 6.3 cm^{-1}, ρ_{calcd} = 1.25 g/cm^3. The 1710 independent reflections [$2\theta \le 50°$; $|F_o^2| > 3\sigma|F_o^2|$] were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an ω-2θ scan. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically and hydrogen atoms refined with fixed thermal parameters to R = 0.044 and R_w = 0.048.

Regioselectivities and Stereoselectivities of Singlet Oxygen Generated by Cyclodextrin Sandwiched Porphyrin Sensitization. Lipoxygenase-like Activity

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Singlet oxygen has been attracting significant attention from physical and organic chemists due to its unique properties, and various types of reactions involving this highly reactive molecular oxygen have been investigated.[1] Although some of these reactions are very useful even for synthetic purposes, the reactions are usually nonregio- and/or nonstereoselective because of the high reactivity of singlet oxygen. For example, oxidation of linoleic acid by singlet oxygen results in nonselective oxidation of the $\Delta^{9,10}$ and $\Delta^{12,13}$ double bonds to give 9-, 10-, 12-, and 13-hydroperoxy derivatives as ene reaction products.[2] This observation is quite in contrast with that for biological oxidation catalyzed by enzymes such as dioxygenase which gives hydroperoxy products in regio- and stereospecific fashion; for example, soybean lipoxygenase exclusively produces L-13-hydroperoxy-9,11-*cis,trans*-octadecadienoate from linoleic acid.[3]

We report here the first example of regio- and stereospecific oxidation of linoleic acid by singlet oxygen which is generated by cyclodextrin sandwiched porphyrin sensitization. Although both specificities are still not perfect, the present results suggest the interesting possibility of reaction control of singlet oxygen.

The cyclodextrin sandwiched porphyrin used here is an equimolar mixture of diagonal type isomers (**1a** and **1b**).[4] Tetrakis(*p*-sulfonatophenyl)porphyrin (**2**) is also used as a reference sensitizer having no substrate binding site (Figure 1).

The major products of present reactions are hydroperoxy dienes **4a-d**, and the trans,trans isomers corresponding to **4a** and **4d** are also detected as the minor rearranged products as reported previously.[2] The results are summarized in Table I together with experimental details.

The most remarkable result is obtained when nearly equimolar amounts of **1** and the substrate are employed (run 6), i.e., the hydroperoxidation takes place selectively at the $\Delta^{12,13}$ double bond to yield **4a** and **4b** in 82% specificity [(**4a** + **4b**)/total].[5] The product distribution, **4a**/**4b**/**4c**/**4d** (51/31/11/7), indicates that the attack of singlet oxygen in the present system is more facile at the position remote from the carboxyl end of **3**. The importance of the binding sites of the cyclodextrin in the present reaction is clearly shown by the observation that, as expected, sensitization by a simple water-soluble porphyrin, **2** (runs 1-3), results in nonselective hydroperoxidation at the $\Delta^{9,10}$ and $\Delta^{12,13}$ double bonds, though the product ratios **4a**/**4b** and **4c**/**4d** vary according to the reaction conditions.[2] It should be noted that a combination of **2** as a sensitizer and a large excess of β-cyclodextrin as a complexation host does not change the nonselective reaction course of singlet oxygen generated by sensitization with **2** (run 4). These observations strongly suggest that the existence of both **3** and

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(5) The product ratios including trans,trans isomers corresponding to **4a** and **4d**, **4a**/*trans,trans*-**4a**/**4b**/**4c**/**4d**/*trans,trans*-**4d**, are 49/3/30/10/7/1 for run 6 and 31/1/18/17/31/2 for run 5, respectively.

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Table I. Hydroperoxidation of Linoleic Acid by Singlet Oxygen Generated by Photosensitization[a]

run	sensitizer	concn, μM		product distribution		ee,[b] %		yield,[c] %
		[1] or [2]	[3]	$\Delta^{12,13}$(4a/4b)	$\Delta^{9,10}$(4c/4d)	4a	4b	
1	2	10	1780	49 (40/9)	51 (11/40)			3
2	2	98	89	50 (40/10)	50 (10/40)			12
3	2 (in MeOH)	10	1780	51 (30/21)	49 (20/29)			17
4	2 (+ β-CD)[d]	98	89	50 (31/19)	50 (19/31)	∠2[e]	∠2[e]	6
5	1	10	1780	51 (32/19)	49 (17/32)	∠2[e]	∠2[e]	28
6	1	98	89	82 (51/31)	18 (11/7)	20	12	14

[a] The aqueous reaction mixture (1 mL) containing linoleic acid (3) and a sensitizer (1 or 2) was sonicated for 15 min and, bubbling with O_2 (100 mL/min), irradiated with a 500-W Xe lamp through a 380 nm cutoff filter at 0 °C for 1 h. The products were reduced by triphenylphosphine, methylated by a slight excess of diazomethane, and analyzed by a silica gel HPLC column (Wakosil 5Sil, 0.46 × 75 cm, hexane/*i*-PrOH = 99/1). The products corresponding to **4a** and **4d** were detected at 234 nm and those corresponding to **4b** and **4c** at 202 nm. [b] Enantiomeric excess (see footnote 6). [c] Total yields based on used 3. [d] The solution was saturated with β-cyclodextrin (6×10^{-3} M). [e] The values of ee are below the experimental error limit of HPLC integration.

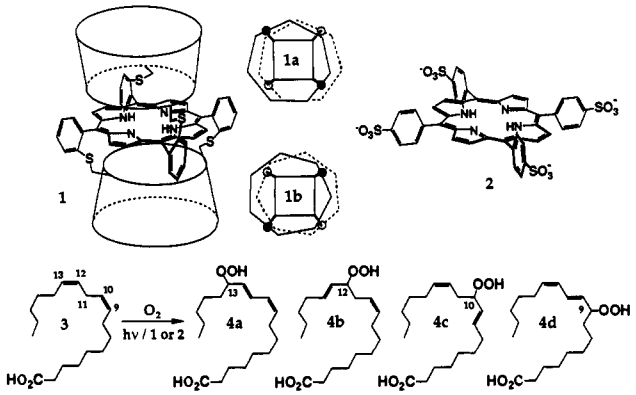

Figure 1. Porphyrin sensitizers and hydroperoxidation of linoleic acid by singlet oxygen.

singlet oxygen in the hydrophobic pocket of **1** during the reaction is essential for the present selective hydroperoxidation. This conclusion is further supported by the more interesting result that the main products obtained from the reaction using **1** (run 6) are significantly chiral, i.e., **4a** and **4b** have 20% (L-predominant) and 12% enantiomeric excess, respectively.[6] Since the reaction using **3** (45 μM) and an excess amount of **1** (196 μM) leads to the same chiral induction within the limit of error, the observed enantiomeric excess seems to reflect the chiral environment around the $\Delta^{12,13}$ double bond in the 1/1 complex of **3** and **1**. Thus, the hydrophobic cavity of **1** regulates not only the attacking position but also the attacking face of the alkene for singlet oxygen under the present conditions. To our knowledge, this is the first example of a chiral induction observed for the reaction of singlet oxygen.

In contrast with these observations, even when **1** is employed as a sensitizer, both regio- and stereospecificities are lost in the presence of a large excess of **3** (run 5) and the product distribution becomes practically the same as those of runs 3 and 4 where **2** is used as a sensitizer. This result may be due to the large contribution of the reaction of **3** with singlet oxygen outside of the cyclodextrin cavity of **1**. Since the lifetime of singlet oxygen in water is known to be ca. 2 μs, which corresponds to a ca. 100-nm diffusion distance,[7] such "outside" reaction is expected to be significant under the conditions of run 5. Finally, it should be noted that the "radical contribution" in the present photooxygenation which is evaluated from the product ratio of conjugated and nonconjugated diolefin products (**4a**/**4b** or **4c**/**4d**) seems to be more significantly suppressed in the system containing β-cyclodextrin or **1** than that in pure water (runs 1 and 2).[2d,8]

(6) The stereospecificity of **4a** was determined by comparison with standard samples are prepared enzymatically [soybean lipoxygenase (Sigma), **4a**/**4d** = 87/13, ee(L-**4a**) = 97%, cf. ref 3b] using a chiral HPLC column (Daicel Chiralcel OD, hexane/*i*-PrOH = 99/1), though the absolute configuration of **4b** obtained predominantly in this work was not known.

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Although it is evident that further investigation is necessary for the elucidation of the origin of the present regio- and stereospecificities, the system shown here provides a highly interesting example which suggests the relationships between molecular recognition and selectivity in the reaction of activated molecular oxygen.

Toward a Dinitrogen Electroreduction Catalyst: Characterization of a Bis-Ammine, a μ_2-Hydrazine, a μ_2-Diazene, and a Remarkably Stable μ_2-Dinitrogen Complex of a Ruthenium Cofacial Diporphyrin

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Since the discovery of μ_2-$N_2[Ru(NH_3)_5]_2[BF_4]_4$ in 1968,[3] bridging dinitrogen complexes have been pursued as model complexes in the context of both biological and chemical dinitrogen reduction.[4] Because of the successful application of bis-cobalt cofacial diporphyrins to the electrocatalytic reduction of dioxygen,[5] we are exploring analogous cofacial systems as possible dinitrogen reduction catalysts. If the two metals of a cofacial metallodiporphyrin can jointly bind and promote the protonation and reduction of dinitrogen, perhaps an electrode catalyst could be devised. Herein we report the synthesis and spectroscopic properties of (1) a remarkably stable, bridged dinitrogen complex of a cofacial metallodiporphyrin, μ_2-$N_2Ru_2(*L)_2DPB$ (Figure 1), and (2) the putative reduction intermediates of the dinitrogen complex: the μ_2-diazene, μ_2-hydrazine, and bis-ammine complexes (Figure 2).

Addition of 2 equiv of 1-*tert*-butyl-5-phenylimidazole, *L, to a benzene solution of the metal–metal-bonded bis-ruthenium cofacial diporphyrin, Ru_2DPB,[6] under a dinitrogen atmosphere

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(2) Abbreviations: OEP = octaethylporphyrinato dianion, DPB = biphenylenediporphyrinato tetraanion, TMP = *meso*-tetramesitylporphyrinato dianion, THF = tetrahydrofuran.

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