regions of behavior are evident: in region A the rate of transport decreases from $X_{Os} = 1.0$ to ca. 0.50, then becomes relatively independent (region B) of X_{Os} when $X_{Os} = 0.50$–0.15, and (region C) decreases further at $X_{Os} < 0.15$. D_{ct} changes overall by ca. 10^2 times as the Os sites are isomorphically diluted from 1.2 to 0.10 M. This pattern of behavior has not been revealed in any of the prior redox site concentration studies[9b,9d] of D_{ct}.

We offer the following scheme in explanation of Figure 2:

$$Os^{2+} + [Ru^{2+},Os^{3+}] \rightarrow Ru^{2+} + [Os^{2+},Os^{3+}] \qquad (1)$$

$$[Os^{2+},Os^{3+}] \xrightarrow{\tau} [Os^{3+},Os^{2+}] \qquad (2)$$

$$Ru^{2+} + [Os^{3+},Os^{2+}] \rightarrow Os^{3+} + [Ru^{2+},Os^{2+}] \qquad (3)$$

The symbols represent different redox site locations in the polymer, and nearest neighbors are in brackets. The scheme assumes that electron hopping (reaction 2) occurs solely between nearest neighbor Os/Os site pairs, with time constant τ. Calculation of the rate of reaction 2 by a random walk model[6,11] in which the forward, reverse, and lateral electron-jump probabilities are defined as, respectively, $P(d_n,d_{n+1})$, $P(d_n,d_{n-1})$ (both equal to $X_{Os}^2/2$), and $P(d_n,d_n)$ $(=1 - X_{Os}^2)$ is in excellent agreement with experiment (dashed line, Figure 2). This shows that the X_{Os} dependence of D_{ct} in region A can be accounted for simply by the statistical population of Os/Os site pairs.

The simple statistical calculation fails for more dilute copolymers because it assumes that the redox polymer sites are completely stationary. We propose that in region B, polymer self-diffusive motions generate additional, reactive, Os/Os nearest neighbor pairs, as in reaction 1, and also by the elastic reverse diffusion reaction (3) act to aid translocation of electron-bearing Os^{2+} sites toward the electrode. These two factors conspire to make D_{ct} relatively insensitive to X_{Os} over region B.

The polymer motions must have considerable frequency since region B begins at a X_{OS} where the Os/Os nearest neighbor population is still high, approximately equal to that of Ru/Os neighbors. Interestingly, when X_{Os} is such that there are on the average *no* Os/Os nearest neighbor pairs (complex edge-to-edge distance exceeds ca. 11–12 Å), D_{ct} begins to decrease further, starting region C. Now, reaction 1 does not just supplement reaction 2 but is required for any electron transport at all. It is reasonable to assume that elastic polymer diffusive motions away from a site's equilibrium position occur considerably more slowly as they are required to occur with larger amplitude, and so D_{ct} in region C represents a concentration-dependent self-diffusion constant for Os redox sites in the polymer.

Activation barrier studies are consistent with the above assignments of regions A–C. The thermal barrier ΔE_a decreases in the order C > B > A (11.2, 6.4, and 3.6 kcal/mol, respectively) and remains approximately constant in region A. Furthermore, the differing barriers mean that Figure 2 can take on different shapes at different temperatures as the several kinetic factors change their relative importance. These effects will be described in the full paper.[6]

Finally, reactions 1 and 3 have cautioning implications for use of redox polymers as models to study distance-of-electron-transfer phenomena, since in them we regard the sites as not "stationary". The diffusive motions would blur attempts at exponential term correlation[14] of average site–site distances with the electron-transport rate. Also, when the redox sites are not affixed to the polymer as they are here but are counterions of ion exchange polymer films,[15] site mobility clearly plays a major and perhaps dominating role.

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(10) This method involves a potential step from 0.40 to 0.90 V, plotting anodic current for Os(2+ → 3+) reaction vs. $t^{-1/2}$ and taking D_{ct} from the linear short time slope by using the equation $i = nFAD_{ct}^{1/2}C_{Os}/(\Pi t)^{1/2}$. D_{ct} is reproducible to ca. 8% for a given electrode film and to ca. 15% for different films having the same X_{Os}. Potential steps to 0.98 V produce identical results, showing the Ru sites remain uninvolved in electron transport. Full details are reported elsewhere.[6]

(11) In the calculation, an electron originating at distance coordinate $d_n = 0$ is allowed to undergo a 250-step random walk a total of 20000 times, each time with notation of the final d_n coordinate of the particle, thus generating a curve for frequency of occurrence vs. displacement from origin. The variance σ^2 of this gaussian curve measured in terms of d is the rms displacement for an "average" electron,[12] thus $D_{ct} = \sigma^2/2(250)\tau$. These calculations done for a series of X_{Os} generated the result in Figure 2, dashed line, where $1/\tau = 1.3 \times 10^5$ s^{-1} is normalized for D_{ct} at $X_{Os} = 1$ and the jump distance[13] 14.2 Å. We are not aware of analogous random walk calculations having been done.

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Generation of Superoxide in a Cobalt(II) Tetraphenylporphyrin–Thiolate–Oxygen System

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Superoxide, O_2^-, has been shown to be generated in several biochemical and chemical reactions[1,2] such as the xanthine oxidase system,[3] hydrogen peroxide–periodate system,[3] pulse radiolysis of oxygenated aqueous solution,[4] electrochemical reduction of oxygen in an organic solvent,[5] and potassium superoxide in Me_2SO.[6,7] In these studies, EPR spectroscopy has proved useful for unambiguous identification of superoxide. The first clear evidence for the presence of the superoxide was obtained by the rapid freezing technique of Bray.[3] The asymmetric free radical, O_2^-, gives an EPR signal with a $g_\perp$ at about 2.00 and a $g_\parallel$ component of low amplitude at about 2.08.

Since oxygen acitvation in heme proteins such as cytochrome *P*-450 monooxygenases and some oxidases involving electron transfer from iron plays a central role in the catalytic activities of these enzymes,[8] it is essential to construct model systems involving a one-electron reductant for oxygen using metal ion such as iron and cobalt ions. In fact, studies have been made on a number of superoxide complexes of transition metals, especially cobalt, prepared by reacting a lower valence transition-metal complex with O_2.[9-12] However, little is known about the gen-

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(7) Abbreviations: Me_2SO, dimethyl sulfoxide; EPR, electron spin resonance; TPP, *meso*-tetraphenylporphyrinato; Me_4NOH, tetramethylammonium hydroxide; TGE, thioglycolic acid ethyl ester; P-450$_{cam}$, cytochrome *P*-450 from *Pseudomonas Putida.*

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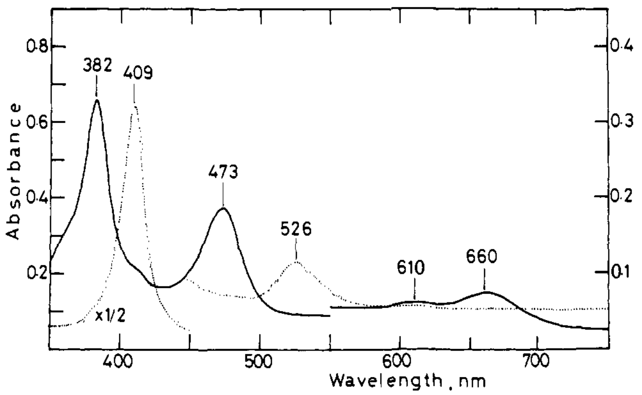


Figure 1. Electronic spectrum of dithiolate–Co(III)TPP complex at room temperature. A mixture (---) consisting of Co(II)TPP (0.25 mM dissolved in CH_2Cl_2, 0.05 mL) and TGE (0.05 M in acetone, 0.2 mL) in acetone solvent (2.75 mL) was added to Me_4NOH (1 M in methanol, 1 μL) (—) under air at room temperature (20 °C). Thus the solvent composition is CH_2Cl_2–acetone–methanol = 1.67:98.30:0.03.

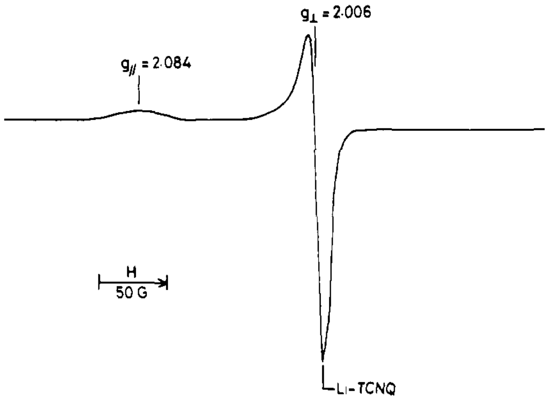


Figure 2. EPR spectrum of superoxide at 77 K. Superoxide was produced under air and at room temperature (20 °C) by mixing Co(II)TPP (1 mM in CH_2Cl_2, 0.5 mL), TGE (0.5 M in acetone, 0.02 mL), Me_4NOH (1 M in methanol, 0.01 mL), and acetone (0.47 mL). Thus the solvent composition is CH_2Cl_2–acetone–methanol = 50:49:1.

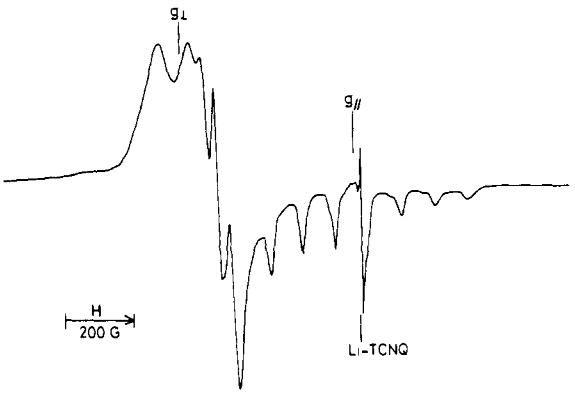
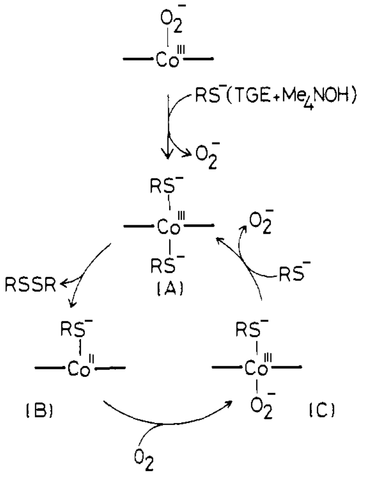


Figure 3. EPR spectrum of Co(II)TPP–TGE–Me_4NOH system at 77 K under reduced pressure. Concentrations of each component are the same as for Figure 2. The components were prepared separately then mixed under reduced pressure at room temperature and frozen.

Chart I. Possible Reaction Mechanism for Superoxide Generation by Chemical Model



eration of superoxide from these complexes. Before us, the first demonstration of superoxide generation with metalloporphyrin was reported by Billecke et al. by using osmium(II) porphyrins.[13]

During investigations on models of cytochrome P-450,[14,15] we found that superoxide could be generated readily under air by the reaction of Co(II)TPP and TGE in the thiolate form in an organic solvent at room temperature. Superoxide was detected by the usual method of EPR spectroscopy but not by the rapid freezing procedure. This paper reports a simple method for preparation of superoxide in a Co(II)TPP–TGE(thiolate form)–O_2 system and detection of superoxide.

Aerobic addition of Me_4NOH to a mixture of Co(II)TPP and TGE in acetone at room temperature (20 °C) resulted in formation of two new split Soret bands at 382 and 473 nm with broad bands at 610 and 660 nm (Figure 1). The half-life of this new pale green complex was about 13 min under these conditions. A very similar spectrum was already reported for the dithiolate ferric complex[15,16] and the dithiolate adduct complex of cobalt-substituted cytochrome P-450_{cam} in the oxidized form,[17] in which the spectrum has been classified as a d-type hyperporphyrin spectrum.[18] The EPR spectrum of the pale green complex had no observable signal due to Co(II) ion, but its g values ($g_\perp = 2.006$ and $g_\parallel = 2.084$ at 77 K) provided evidence for the formation of free superoxide species, as shown in Figure 2. The observed anisotropic g factors were akin to those observed in frozen solution.[3,5] On standing, the complex gradually changed from green to red-brown, and no EPR signal ascribed to the superoxide was detected. When oxygen was then bubbled through, the solution changed from red-brown to green again with reappearance of the EPR signal due to superoxide. This reaction cycle under air continued until all the added TGE had been fully oxidized. Therefore, the estimation of superoxide[13] in this system is essentially important in order to evaluate the efficiency of the superoxide generation. Work is continuing in this effort, and the results will be reported. Under reduced pressure without oxygen, the complex involving Co(II)TPP, TGE, and Me_4NOH turned red-brown and gave the characteristic EPR signal of Co(II) ion[9] (Figure 3). When air was bubbled through the solution, it became green and developed the EPR signal of superoxide. Complexes of Co(II)TPP–TGE–O_2, Co(II)TPP–Me_4NOH–O_2, and Co(II)TPP–O_2 in the same solvent formed not a free superoxide but a superoxide complex of cobalt porphyrin as reported previously.[9-11] From EPR studies on these model systems in several solvents, we deduced that the reaction mechanism for generating superoxide in the Co(II)TPP–TGE(thiolate form)–O_2 system is as shown in Chart I. A is a new hyperporphyrin complex having a dithiolate–Co(III)TPP coordination mode, deduced by spectrophotometry, as well as ligand-exchange reactions with various types

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of ligands, as will be reported elsewhere. B is a thiolate–Co(II)TPP complex, although the possibility of a dithiolate–Co(II)TPP coordination is not thoroughly ruled out yet. C was not detected by usual EPR spectroscopy, suggesting that this complex is very unstable and has a short half-life.

Since superoxide is very reactive,[1,2] it is interesting that it can be detected during formation of a simple complex. The value of $g_{\parallel}$ in the EPR spectrum of superoxide is known to depend on the nature of the solvent or environment of the superoxide.[5] Recently Bray et al. reported that $g_{\parallel}$ value of superoxide shifts markedly toward $g_{\perp}$ in the presence of cations such as Ca(II), Ba(II), and Na(I), indicating solvent-shared ion-pair formation.[19] Judging from the $g_{\parallel}$ value in the spectrum of superoxide observed in our system, there may be little interaction between superoxide and cobalt ion or solvent.

This work provides the direct evidence for the generation of superoxide in a chemical model, a cobalt–porphyrin complex. We believe that this system provides not only a simple method for generation of superoxide but also an insight into the mechanism for oxygen activation depending on heme proteins in many biological processes.

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Registry No. A, 82555-90-6; B, 82555-91-7; C, 82571-32-2; Co^{II}TPP, 14172-90-8; TGE, 623-51-8; Me$_4$NOH, 75-59-2; O_2^-, 11062-77-4; O_2, 7782-44-7; cytochrome P450, 9035-51-2; oxidase, 9035-73-8; monooxygenase, 9038-14-6.

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Optically Active Allylsilanes. 1. Preparation by Palladium-Catalyzed Asymmetric Grignard Cross-Coupling and Anti Stereochemistry in Electrophilic Substitution Reactions

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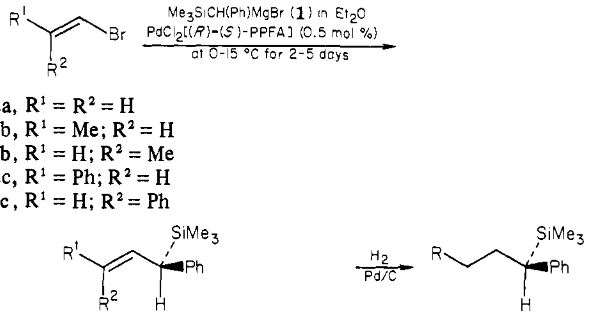
We have succeeded, for the first time, in a simple and efficient synthesis of optically active allylsilanes with high optical purity, by the aid of the catalytic asymmetric Grignard cross-coupling.[1] The allylsilanes contain an asymmetric carbon atom directly bonded to the silicon atom and could hardly be obtained by other methods. We report here the first general procedure for preparation of the optically active allylsilanes and the first unambiguous stereochemistry (anti attack) of S_E' reaction[2] of the allylsilanes with various electrophiles.

Dichloro[(*R*)-*N*,*N*-dimethyl-1-{(*S*)-2-(diphenylphosphino)-ferrocenyl}ethylamine]palladium(II) (PdCl$_2$[(*R*)-(*S*)-PPFA])[1,3] was found to be an effective catalyst for the cross-coupling of α-(trimethylsilyl)benzylmagnesium bromide[4] (**1**) with vinyl bromide (**2a**), (*E*)- and (*Z*)-1-bromopropene (**2b**), and (*E*)- and (*Z*)-β-bromostyrene (**2c**) to give, in good yields, the corresponding allylsilanes (**3**)[5] in an optically active form without *E–Z* isomerization of the olefinic double bond. The results summarized in Scheme I[6] show that the allylsilanes with high optical purity were obtained in the reaction of **2a**, (*E*)-**2b**, and (*E*)-**2c** and that the *R* isomer was formed preferentially in every case. The se-

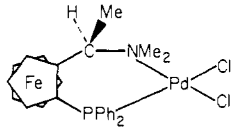
Scheme I



2a, R^1 = R^2 = H
(*E*)-2b, R^1 = Me; R^2 = H
(*Z*)-2b, R^1 = H; R^2 = Me
(*E*)-2c, R^1 = Ph; R^2 = H
(*Z*)-2c, R^1 = H; R^2 = Ph

	yield, %	$[\alpha]^{20}_D$, deg^a	ee, %
(*R*)-3a:	42	−61.8	95
(*R*)-(*E*)-3b:	77	−36.3	85
(*R*)-(*Z*)-3b:	38	−21.3	24
(*R*)-(*E*)-3c:	93	−43.9	95
(*R*)-(*Z*)-3c:	95	−44.3	13

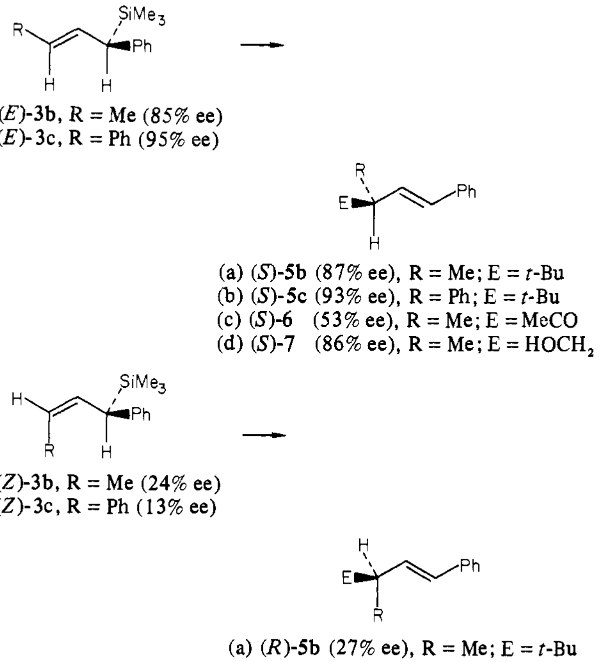
4a, R = H
4b, R = Me
4c, R = Ph



PdCl$_2$[(*R*)-(*S*)-PPFA]

^{a} Benzene.

Scheme II^a



(*R*)-(*E*)-3b, R = Me (85% ee)
(*R*)-(*E*)-3c, R = Ph (95% ee)

(a) (*S*)-5b (87% ee), R = Me; E = *t*-Bu
(b) (*S*)-5c (93% ee), R = Ph; E = *t*-Bu
(c) (*S*)-6 (53% ee), R = Me; E = MeCO
(d) (*S*)-7 (86% ee), R = Me; E = HOCH$_2$

(*R*)-(*Z*)-3b, R = Me (24% ee)
(*R*)-(*Z*)-3c, R = Ph (13% ee)

(a) (*R*)-5b (27% ee), R = Me; E = *t*-Bu
(b) (*R*)-5c (15% ee), R = Ph; E = *t*-Bu
(c) (*R*)-6 (19% ee), R = Me; E = MeCO

^{a} (a) 3b, *t*-BuCl/TiCl$_4$, CH$_2$Cl$_2$, −78 °C, 1 min; (b) 3c, *t*-BuCl/TiCl$_4$, CH$_2$Cl$_2$, 0 °C, 1 h; (c) 3b, MeCOCl/AlCl$_3$, CH$_2$Cl$_2$, −78 °C, 5 min; (d) 3b, HCHO or trioxane/TiCl$_4$, CH$_2$Cl$_2$, −78 °C, 5 min.

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[5] The reaction was carried out in a similar procedure to that described in ref 1. The physical data of the allylsilanes 3 are available as supplementary material.

[6] The configuration *R* and enantiomeric purity of the allylsilanes **3** were determined by comparing the optical rotation data of alkyltrimethylsilanes **4** obtained by hydrogenation of **3** with those of **4** obtained by palladium-catalyzed asymmetric hydrosilylation of styrene derivatives.[3] The maximum rotations of the alkylsilanes (*S*)-**4a**, -**4b**, and -**4c** are $[\alpha]_D^{20}$ +1.42, −9.55, and +2.36° (*c* 3–6, benzene), respectively. The asymmetric hydrosilylation will be fully described elsewhere.

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