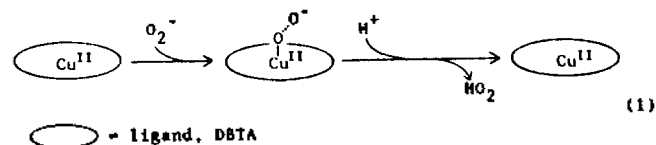


interaction of Cu(II)DBTA with superoxide results in an ERP-silent five-coordinate complex.

Cyclic voltammogram of Cu(II)DBTA plus superoxide (>1.0 equiv) in CH₃CN under the anaerobic condition showed a new irreversible wave centered at -0.47 V, using 0.1 M TBABF₄ as supporting electrolyte and a glossy carbon electrode. The new wave centered at -0.47 V is attributed to reduction of coordinated superoxide to peroxide followed by irreversible oxidation.

Addition of ca. 1 equiv of superoxide to solution of Cu(II)DBTA in CH₃CN under the anaerobic condition caused a little blue shift and an increase in intensity at the short-wavelength absorption band. Similar visible spectra were obtained from interaction of Cu(II)DBTA with (CH₃)₄NOH or C₆H₅-CH₂ONa in CH₃CN. The similarity of the visible spectra of the products formed by interaction with O₂⁻, OH⁻, and C₆H₅CH₂O⁻ implies that they are all structurally similar five-coordinate Cu(II) complexes.

On the basis of the EPR spectra, visible spectra, and cyclic voltammetric studies, the interaction of Cu(II)DBTA with superoxide in CH₃CN under the anaerobic condition leads to the formation of copper(II)-superoxide complex, which can be easily decomposed to HO₂ and the copper(II) complex by a proton source (eq. 1).



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Formation and Characterization of the 19-Electron Rhenium Radical

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Paramagnetic 17- or 19-electron complexes play a vital role in the organometallic chemistry because many reactions have been found in which these complexes are involved as intermediates.¹ For example, several substitution reactions have been found to proceed more rapidly when a small anodic or cathodic current was passed through the solution.² The isolation and characterization of paramagnetic complexes are relatively rare due to the instability of transient species. Recently, Brown and coworkers³ described the formation of persistent metal-centered substituted transition metal carbonyl radical, M(CO)₃L₂ (M = Mn, Re; L = P-c-Hx₃), whose stability is ascribable to the large cone angle of the phosphine ligand. The 19-electron complex, Co(CO)₃L₂ [L₂ = 2,3-bis(diphenylphosphino) maleic anhydride], was first synthesized from Co₂(CO)₈ and L₂ by Fenske⁴,

who showed that the unpaired electron is delocalized over the Co atom and the π* system of the L₂ ligand. Further evidence for the formation of 19-electron adducts has been obtained by photochemical reaction of a metal-metal bonded complex with ligands possessing a low-energy π* orbital such as quinones⁵, α-diimines⁶, and substituted pyridines⁷. The ease of the formation of transient Re(CO)₅ radical from the dimer Re₂(CO)₁₀ by photochemical method⁸ prompted us to study the 19-electron species, Re(CO)₄L₂ with ESR spectroscopy.

The ESR spectrum of a THF solution of Re₂(CO)₁₀ (10 mM) and L₂ [2,3-bis(diphenylphosphino) maleic anhydride] (10 mM) in the dark at room temperature is shown in Figure 1. The radical, which is stable four hours in the dark, exhibits the 1:2:1 triplets arising from two equivalent ³¹P nuclei. The

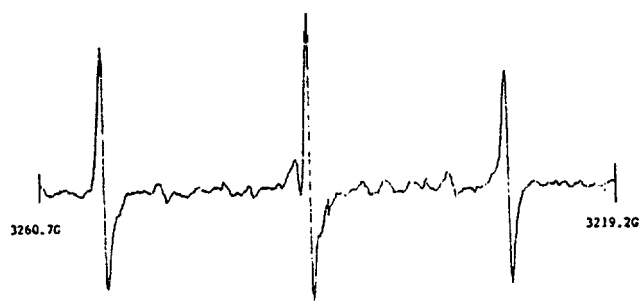


Figure 1. The ESR spectrum of the THF solution containing $\text{Re}_2(\text{CO})_{10}$ and 2,3-bis(diphenylphosphino) maleic anhydride in the dark at room temperature. The triplet is due to a negatively charge diphosphine ligand arising from two equivalent ^{31}P nuclei.

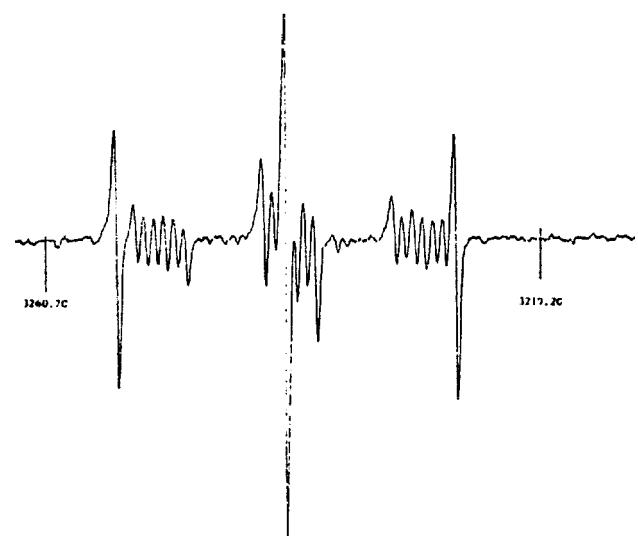


Figure 2. The ESR spectrum after the irradiation of the solution for 2 min.

coupling constant of the reduced ligand ($a_p = 8.92\text{G}$) indicates that the unpaired electron density is polarized toward the phosphorus atoms. The large value of a_p is in good contrast with that of the reduced form in L_2 ($a_p = 3.10\text{G}$)⁹, which indicates that the unpaired electron is polarized toward the oxygen atoms. The g value ($g = 2.0036$) is close to the free electron value ($g_e = 2.0023$) and the g factors reported by Stufkens and coworker¹⁰ for $\text{Re}(\text{CO})_3\text{L}_2$ ($\text{L} = \text{-i-Pr-DAB}$, $t\text{-Bu-DAB}$, $p\text{-tol-DAB}$) radical complexes.

The progress of irradiation without cutoff filter results in a homolytic splitting of the metal-metal bond and in the formation of radical species, $\text{Re}(\text{CO})_4\text{L}_2$. The ESR spectra of $\text{Re}(\text{CO})_4\text{L}_2$ in THF at room temperature are shown in Figure 2 and 3 for the irradiation of the solution for 2 and 15 min., respectively. The formation of radical complex is complete within 20 min. The radical, which is stable for 24 hours, exhibits three groups of sextets arising from one $^{185,187}\text{Re}$ nucleus ($I = 5/2$) and two equivalent ^{31}P ($I = 1/2$) nuclei. The large phosphorus coupling constant ($a_p = 14.17$) and small rhenium coupling constant ($a_{\text{Re}} = 0.835$) indicate that the unpaired electron has a greater interaction with the phosphorus atoms in the complexes due to the delocalization of the electron onto the $\text{Re}(\text{CO})_4$ portion of the molecule. Best-fit simulated ESR spectrum (see Figure 4) was obtained for the

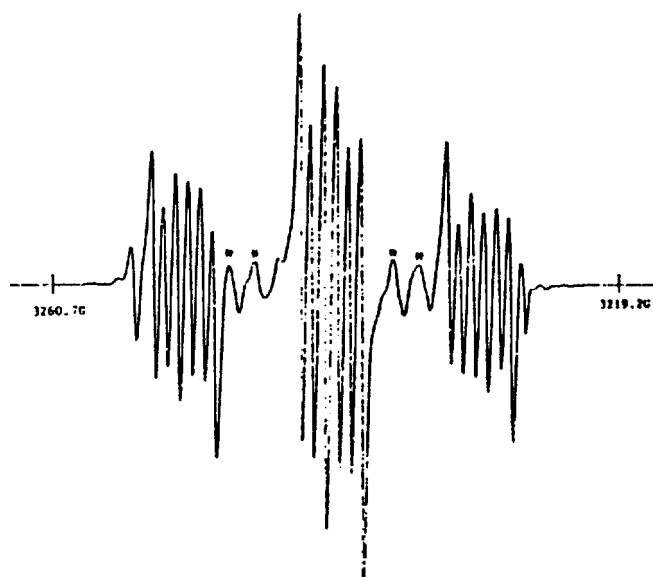


Figure 3. The ESR spectrum after the irradiation of the solution for 15 min. The asterisks are due to the impurity.

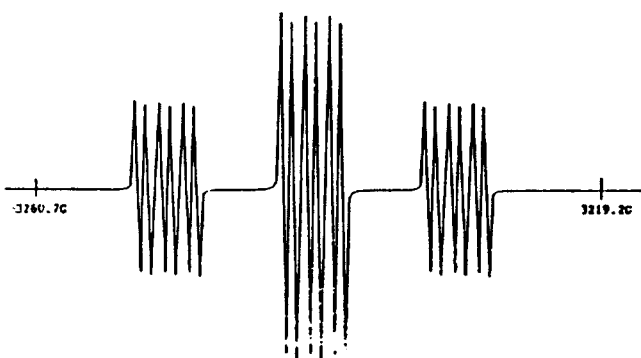


Figure 4. Best-fit simulated ESR spectrum of Fig. 3.

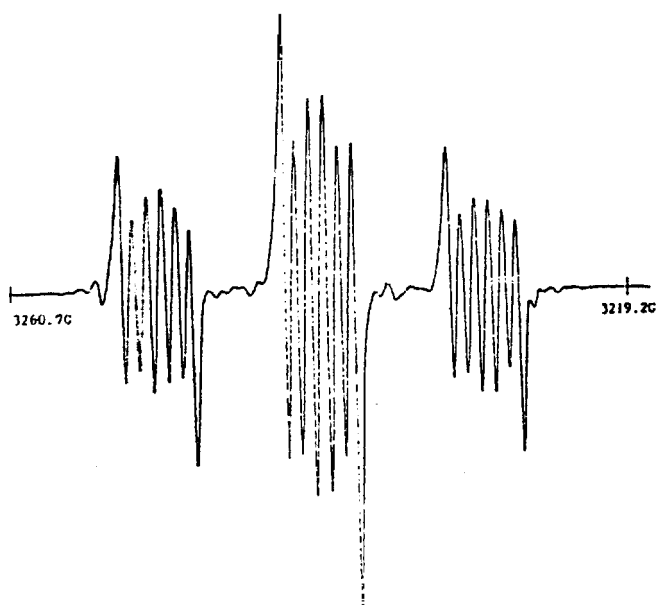


Figure 5. The ESR spectrum of a mixture of $\text{Re}(\text{CO})_4\text{L}_2$ ($\text{L}_2 = 2,3\text{-bis(diphenylphosphino) maleic anhydride}$) and $\text{P}(\text{OMe})_3$ at room temperature.

$\text{Re}(\text{CO})_4\text{L}_2$ radical by direct comparison of the experimental spectrum with line shapes calculated for a wide variety of hyperfine parameters. The g value ($g = 2.0033$) of radical complex is still close to the free electron value. This means that the unpaired electron resides at the ligand, and the radical is considered as the 18 electron anion complex in which rhenium is surrounded by four carbonyl groups and a negatively charge diphosphine ligand. The next question still remains as to whether the radical is 17- or 19-electron complex. The IR spectrum of the radical complex in THF shows four absorption bands at 2078, 2009, 1900, and 1975 cm^{-1} in the carbonyl region, as expected from C_{2v} symmetry group ($2\text{A}_1 + \text{B}_1 + \text{B}_2$). The peaks are very similar to those of the known $\text{Mn}(\text{CO})_4\text{L}_2$ complex.⁴

Since it is known that the 19-electron complex is substitutionally labile, we attempted to react $\text{Re}(\text{CO})_4\text{L}_2$ with phosphite ligand in THF. Unexpectedly, the product was turned out to be a diamagnetic compound rather than one substituted phosphite product. The ESR spectrum, immediately taken from the addition of $\text{Re}(\text{CO})_4\text{L}_2$ and $\text{P}(\text{OMe})_3$ at room temperature is shown in Figure 5. The ESR spectrum taken after leaving the mixture for one hour, is completely silent, indicating that the product is diamagnetic due presumably to the formation of dimer. This is in striking contrast with the substitution reactions of the $\text{Co}(\text{CO})_3\text{L}_2$ with phosphines.⁹

From these results, we could draw three salient aspects:

- a) 19-electron complex of a stable $\text{Re}(\text{CO})_4\text{L}_2$ can be obtained *via* a homolytic splitting of the metal-metal bond, although it is difficult to obtain the radical complex under a mild condition.
- b) The unpaired electron essentially resides on the ligand.

c) The radical complex is substitutionally unstable, decomposing to the formation of dimer.

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Reactions of α, β -Dinitroolefins with *p*-Toluenethiol

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α, β -Dinitroolefins as a group of compounds have not been extensively investigated though they have been known for more than 30 years. They are generally synthesized by three synthetic routes: 1) dimerization of germinal halo-nitroalkanes by base,¹ 2) addition of nitrogen tetroxide on acetylene², and 3) addition of one mole halogen on disodium salt of vicinal dinitroalkanes³. Nitration of acetylene by nitrogen tetroxide produces predominantly *E* dinitroolefins with *Z* isomers as minor components². Dimerization of germinal haloalkanes, on the other hand, was known to produce only *Z* products¹. However, in this work some *E* isomers were found in the reaction mixture from the previously discarded low boiling fractions⁴. We also found that *E* isomer could be obtained by isomerization of *Z* isomer in the presence of hydrobromic acid or bromine in ethanol⁵.

One of the two nitro groups is easily replaced by nucleophiles such as azide⁶, ammonia⁷, aniline⁷ and mercaptans⁶ giving furoxans, α -amino-, α -phenylamino-, and α -mercap-

to- β -nitroolefins. The mechanism of nucleophilic vinylic substitution reactions has drawn some interest for sometimes. One of the major tools to investigate this reaction has been the comparison of configuration of starting olefins and products⁸. Convergence of stereochemistry, meaning the same ratio of *E/Z* products or in the extreme case a single product starting from either *E* or *Z* olefin, strongly supports multi-step mechanism.

We have examined a few cases of converged nucleophilic vinylic substitution of α, β -dinitroolefins. *E*- and *Z*- α, β -dinitroolefins separately or combined reacted with ammonia and primary amines as nucleophiles to yield single products. A few α -amino- β -nitroolefins were synthesized from either *E*- and *Z*- α, β -dinitroolefins and their *Z* configuration were deduced through spectral interpretation⁹. This configuration is the only one known for this type of compound. On the other hand, either *E*-(3) or *Z*-3,4-dinitro-3-hexene(4) was reacted with *p*-toluenethiol to produced the mixture of *E*-(7)