

마크로싸이클 리간드에 의해 안정화된 유기금속 화합물의
합성 및 특성 연구. I. 완전히 공액된 마크로싸이클
리간드의 철 착화합물의 산화환원*

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**Synthesis and Characterization of Organometallic Compounds
Stabilized by Macrocyclic Ligands. I. Oxidation-Reduction
of Iron Complexes of a Fully Conjugated Macrocyclic Ligand***

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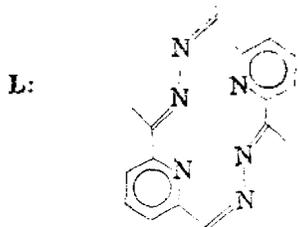
The organometallic compounds, especially alkyl or hydride transition metal complexes, are attractive as catalysts because of their ability to transfer alkyl or hydride groups to the substrates.^{1,2} However, simple hydride or alkyl complexes of transition metals are unstable because of the accumulation of electron density on the metals, and most of the known alkyl or hydride complexes contain electron accepting ligands such as carbon monoxide or phosphine. Although vitamin B₁₂ coenzyme has been known for quite a long time as a porphyrin derivative containing a cobalt-alkyl σ bond,^{3,4} there has been little research on the analogous synthetic ligand complexes, especially the iron macrocyclic complexes.⁵⁻⁸

In an attempt to prepare the organometallic compounds containing macrocyclic ligands, we have searched for the suitable macrocyclic ligands

that lower the electron density of the metal ion, and, consequently, stabilize the metal-alkyl or metal-hydride σ bonds. The earlier studies on the stretching frequencies of carbon monoxide in the iron (II) carbon monoxide complexes containing various macrocyclic ligands revealed that the Fe-CO bond is weakened as the degree of the double bond conjugation in the macrocyclic ligand increases.⁹ This implicates that the electron density of the iron atom is reduced as the degree of conjugation in the macrocyclic ligand increases.

In order to obtain further information on the electronic effects exerted by the extensively conjugated macrocyclic ligands and on the stabilization of the alkyl derivatives of the iron complexes by such ligands, we have investigated the electrochemical behavior of the iron complexes of [2, 5, 11, 14-tetramethyl-3, 4, 12, 13, 15, 17-decaene-N³, N¹², N¹⁹, N²⁰] (L).¹⁰

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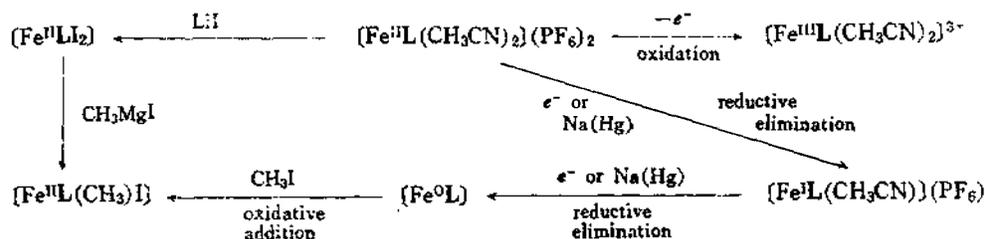
The electrochemical reactions of the iron complexes of **L** were carried out in acetonitrile with tetraethylammonium hexafluorophosphate added as the electrolyte. Cyclic voltammetry of $[\text{Fe}^{\text{II}}\text{L}(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ exhibited one well defined reversible oxidation wave at +1.05 volts and two well defined reversible reduction waves at -0.49 volts and -1.40 volts against the Ag/AgCl reference electrode. These correspond to one-electron oxidation, one-electron reduction, and two-electron reduction, respectively.

The oxidation potential and the reduction potentials measured in the present study are higher than those observed with other iron(II) complexes of macrocyclic ligands with less degree of conjugation.¹²⁻¹⁴ This indicates that the fully conjugated macrocyclic ligand **L** is more efficient in attracting the electron density from the iron atom and more favoring the low oxidation states of the iron atom than other macrocyclic complexes.

Reduction of the iron complexes of **L** with sodium amalgam was also carried out. Treat-

ment of an acetonitrile solution of $[\text{Fe}^{\text{II}}\text{L}(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ with sodium amalgam under rigorous exclusion of air and moisture-free conditions led to red precipitates (I). Further reduction of an acetonitrile suspension of I with sodium amalgam resulted in a green solution(II). The red and the green colored reduction products were extremely sensitive to air and decomposed to brownish materials upon slight exposure to air. The IR spectrum of I showed a broad PF_6^- band around 840cm^{-1} indicating the presence of the counter-anion. From the data available at present, I appears to be a $\text{Fe}^{\text{I}}(\text{d}^7)$ species with the formula of $[\text{Fe}^{\text{I}}\text{L}(\text{CH}_3\text{CN})](\text{PF}_6)$ and II appears to be a $\text{Fe}^0(\text{d}^8)$ species with the formula of Fe^0L .

Attempts to prepare an organometallic complexes of **L** were made. Treatment of II with methyl iodide under inert atmosphere gave purple crystals. The IR spectrum of the purple crystals revealed the absence of the counter-anion, PF_6^- . Apparently the same crystals, probably $[\text{Fe}^{\text{II}}\text{L}(\text{CH}_3)\text{I}]$, were obtained by reacting methylmagnesium iodide with $[\text{Fe}^{\text{II}}\text{L}(\text{CH}_3\text{CN})_2](\text{PF}_6)$ and lithium iodide. The reactions described in this letter are summarized in Scheme 1. The detailed characterization of the extremely air- and light-sensitive organometallic compound will appear elsewhere.



Scheme 1.

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10. The complex $[\text{FeL}(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ was synthesized from $[\text{FeL}(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ ¹¹ by exchanging the perchlorate anion with ammonium hexafluorophosphate.
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14. The potentials reported in ref. 13 and 14 were measured against a Ag/Ag^+ (0.1M) reference electrode. The absolute values of the oxidation potentials and the reduction potentials measured against this reference electrode are smaller by 0.30 volts than the corresponding values measured against the Ag/AgCl reference electrode.