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Synthesis and Crystal Structure of a Dinuclear Iron Tetracarbonyl Complex Containing a Ligand, η^5,η^5-$C_5Me_4CH_2CH_2CH_2C_5Me_4$

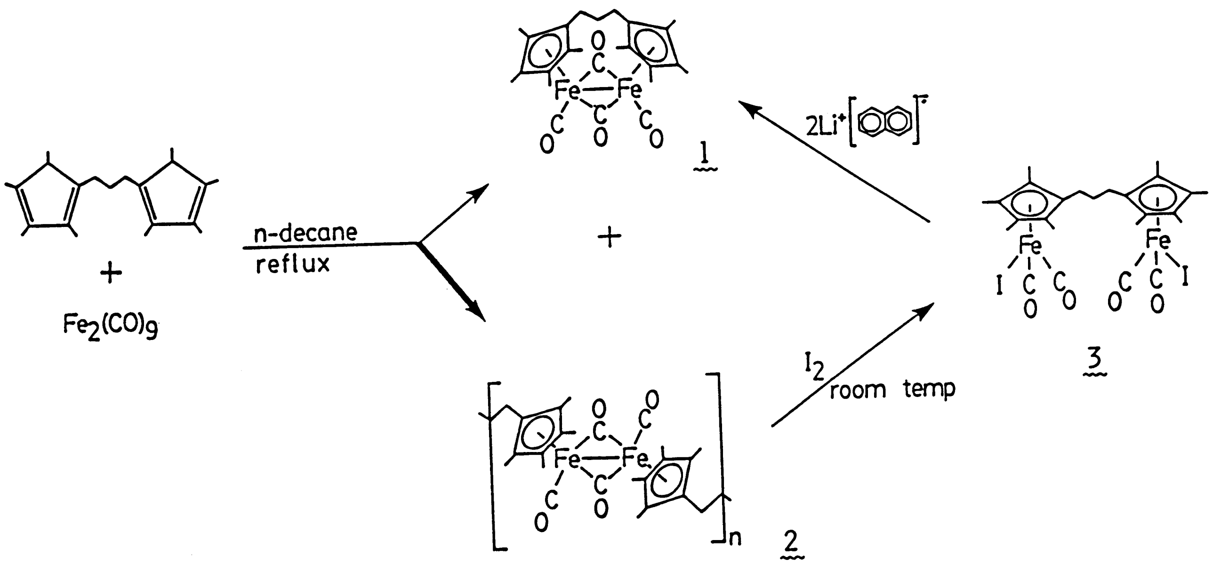
Hiromi TOBITA, Hiroki HABAZAKI, Mamoru SHIMOI, and Hiroshi OGINO*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

A dinuclear iron carbonyl complex with trimethylene-bridged permethylcyclopentadienyl rings as a ligand, $[Cp_2^{(3)}Fe_2(CO)_4]$ (**1**) and its oligomeric derivative $[Cp_2^{(3)}Fe_2(CO)_4]_n$ (**2**) were synthesized, where $Cp_2^{(3)}$ represents the ligand, η^5,η^5-$C_5Me_4CH_2CH_2CH_2C_5Me_4$. The oligomeric mixture **2** was easily converted to monomer **1** , and crystal structure of **1** was determined.

A diiron complex $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ and its derivatives are highly useful as precursors of a variety of organoiron complexes. That is why modifications of cyclopentadienyl rings, particularly permethylation$^{1)}$ and linking$^{2-5)}$ of the cyclopentadienyl rings, have been extensively studied. However, to our knowledge, there is no report on the synthesis of this type of iron complex with linked permethylcyclopentadienyl rings as a ligand. We report here the synthesis and crystal structure of a dinuclear iron carbonyl complex, $[Cp_2^{(3)}Fe_2(CO)_4]$ (**1**) ($Cp_2^{(3)}=\eta^5,\eta^5$-$C_5Me_4CH_2CH_2CH_2C_5Me_4$), the formation of an oligomeric mixture, $[Cp_2^{(3)}Fe_2(CO)_4]_n$ (**2**), and the easy conversion of **2** to **1**.

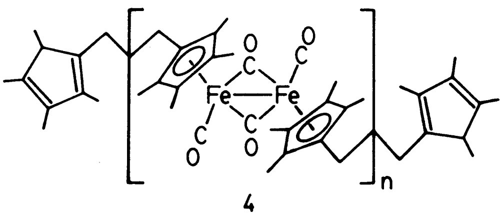
A precursor of the bridging ligand, $HMe_4C_5CH_2CH_2CH_2C_5Me_4H$ ($H_2Cp_2^{(3)}$), was synthesized by an application of the method for the synthesis of pentamethylcyclopentadiene developed by Threlkel and Bercaw:$^{6)}$ Dimethyl glutarate was treated with four equivalents of 2-lithio-2-butene followed by hydrolysis. The dehydration and cyclization of the resulting intermediate, 1,1,5,5-tetrakis(1-methylprop-1-enyl)pentane-1,5-diol, were brought about by *p*-toluenesulfonic acid. The reaction product $H_2Cp_2^{(3)}$ was purified to ca. 70% purity by its conversion to dilithium salt followed by hydrolysis.$^{7)}$

Equimolar amounts of $H_2Cp_2^{(3)}$ and $Fe_2(CO)_9$ were refluxed for four hours in *n*-decane. Two reddish brown products, $[Cp_2^{(3)}Fe_2(CO)_4]$ (**1**) and $[Cp_2^{(3)}Fe_2(CO)_4]_n$ (**2**), were isolated in 0.3 and 53% yields, respectively, by fractional crystallization (Scheme 1). It was shown by gel permeation chromatography (polystyrene gel; solvent $CHCl_3$) that **2** is a mixture of some oligomers with different *n*'s. This fact was further supported by its ^1H NMR spectrum which showed some broad signals in the range of δ 0.7 to 2.5 ppm, and by its mass spectrum. In contrast with these spectra, the IR spectrum of **2** is quite simple and shows only two sharp CO-stretching bands at 1920 (terminal CO) and 1755 (bridging CO) cm^{-1}. Therefore, it is considered that **2** is a mixture of cyclic oligomers and/or acyclic oligomers **4** which have non-coordinated C_5Me_4H rings at



Scheme 1.

their both ends. On the other hand, **1** displays distinct NMR signals [^{1}H NMR(C_6D_6) δ 1.37 (6H, m, CH_2), 1.72 (12H, s, CH_3), 1.81 (12H, s, CH_3); ^{13}C NMR($CDCl_3$) δ 9.4, 9.8 (CH_3), 21.5, 26.2 (CH_2), 93.7, 100.9 (C_5Me_4), 211.9 (CO), 280.7 (μ-CO)] and M^+ of its mass spectrum at *m/e* 506 (27%) as might be expected from its monomeric structure. The *cis*-configuration of **1** and the *trans*-configuration of **2** are obvious from the similarity of the IR patterns of CO-stretching bands between **1** ($\nu_{max.}$ 1960, 1915, 1750 cm^{-1}) and *cis*-[(η^5-$C_5H_5)_2Fe_2(CO)_4$],[8] and between **2** ($\nu_{max.}$ 1920, 1755 cm^{-1}) and *trans*-[(η^5-$C_5H_5)_2Fe_2(CO)_4$].[8] One of the interesting facts revealed by synthesizing **1** is on the difference of electronic spectra between *cis*- and *trans*-isomers of [(η^5-$C_5R_5)_2Fe_2(CO)_4$]. The absorption maxima of the *cis*-complex **1** [$\lambda_{max.}$ (ε) 503 sh (600), 358 (9400) nm] appear in shorter wavelength region than those of the *trans*-complex **2** [$\lambda_{max.}$ (ε) 535 (1300), 364 (8900) nm] and of [(η^5-$C_5Me_5)_2Fe_2(CO)_4$] ($\lambda_{max.}$ 534, 363 nm), which is fixed to *trans*-configuration.[9] This trend is in accord with the expectation from puckered $Fe_2(CO)_4$ core for *cis*-isomer and planar one for *trans*-isomer.[10]



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It has been reported that a dinuclear iron carbonyl complex containing two C_5H_4 rings connected by $SiMe_2$[2] or $Me_2SiCH_2CH_2SiMe_2$[5] was prepared in high yield from the reaction of $Fe(CO)_5$ and the corresponding precursor of the bridging ligand, respectively. In these papers, there is no description on the formation of oligomers. Therefore, **2** is the first example of the oligomeric mixture of this type. One of the reasons why oligomeric mixture **2** with *trans*-configuration was the major product is thought to be the absence of sterically demanding substituents on the trimethylene chain. It has been known that the introduction of the suitably positioned sterically demanding substituents, heteroatoms, double and triple bonds to the methylenic chain of a bridging ligand makes chelation favorable.[11,12]

It was found that **2** can be easily converted to **1** by the following procedure (see Scheme 2). Reaction of **2** with I_2 in CH_2Cl_2 causes the breakup of the $Fe_2(\mu\text{-}CO)_2$ framework[13] to give diiodo complex **3**[14] in 49% yield. Treatment of **3** with lithium naphthalenide in tetrahydrofuran at -78 °C afforded **1** in 75% yield.

The molecular structure of **1**, determined by an *X*-ray crystallographic analysis,[15] is shown in Fig. 1; the molecule has the expected *cis*-configuration. The Fe-Fe distance is 2.549(2) Å, a normal value for the complexes of this type. Geometry of the $Fe_2(CO)_4$ core is similar to that of *cis*-$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$.[8] Two permethylcyclopentadienyl rings are restricted to an eclipsed form with the trimethylene bridge, which presents a sharp contrast to the staggered cyclopentadienyl rings of *cis*-$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$.[8] The conformation of the trimethylene bridge is also eclipsed and the bite angles of this carbon chain [118.8(10), 114.2(10), and 116.8(11)°] are larger than the normal value, 109.5°. Methyl carbons [C(16), C(19), C(21), and C(24)] and bridging methylene carbon [C(15) and C(20)] are slightly bent away from the $Fe_2(CO)_4$ core out of cyclopentadienyl planes (0.12 - 0.23 Å) owing to the steric repulsion between these methyl or methylene groups and bridging carbonyl groups. Other methyl carbons are also bent out of the ring planes, but the deviation is smaller (0.01 - 0.07 Å). The dihedral angle between the two cyclopentadienyl ring planes is 73.2°, which is the smallest among the complexes of this type prepared so far: *cis*-$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$(92.8°),[8] $[(\eta^5,\eta^5\text{-}C_5H_4SiMe_2C_5H_4)Fe_2(CO)_4]$ (97.2°),[3] and $[(\eta^5,\eta^5\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4)Fe_2(CO)_4]$ (88.8°).[4] It seems to be due to the large steric interaction between trimethylene bridge, $Fe_2(CO)_4$ core, and methyl groups on cyclopentadienyl rings, so that the trimethylene bridge is fixed into the specific conformation. The compelling length of trimethylene chain may also contribute to this.

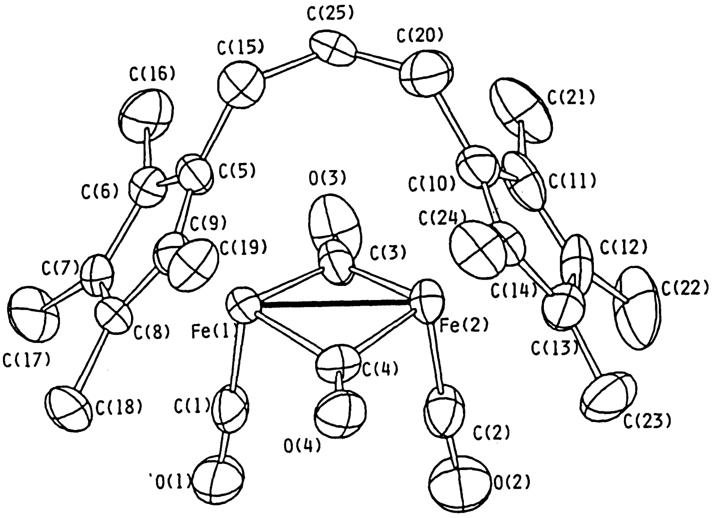

Fig. 1. Molecular structure of $[Cp_2^{(3)}Fe_2(CO)_4]$ (**1**) with the atom-labelling scheme.

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14) Spectral data for **3**: IR(KBr) $\nu_{\mathrm{max.}}$(CO) 2005, 1965 $\mathrm{cm^{-1}}$; ^{1}H NMR (90 MHz; $\mathrm{C_6D_6}$) δ 0.99 (2H, m, $\mathrm{CH_2}$), 1.49 (12H, s, $\mathrm{CH_3}$), 1.61 (12H, s, $\mathrm{CH_3}$), 1.96 (4H, m, $\mathrm{CH_2}$); ^{13}C NMR (22.5 MHz; $\mathrm{C_6D_6}$) δ 10.1, 10.4 ($\mathrm{CH_3}$), 25.7, 31.2 ($\mathrm{CH_2}$), 96.0, 98.2 ($C_5\mathrm{Me_4}$), 216.1 (CO).

15) Crystal data for **1**: $\mathrm{C_{25}H_{30}Fe_2O_4}$, M = 506.3, tetragonal, space group $P\bar{4}2_1c$ (No. 114), a = 23.026(5), c = 8.606(2) Å, U = 4562.9(17) Å^3, Z = 8, d_x = 1.48 g $\mathrm{cm^{-3}}$, μ(MoKα) = 13.3 $\mathrm{cm^{-1}}$. The structure analysis is based on 2179 independent reflections [$|Fo| > 3\sigma\,(Fo)$, $h \geq k$, $3° < 2\theta < 60°$] and R = 0.058 (Rw = 0.061). R = 0.063 when the inverse chirality was applied. Important bond lengths (Å) and angles (deg): Fe(1)-Fe(2) 2.549(2), Fe(1)-C(1) 1.730(11), Fe(2)-C(2) 1.740(12), Fe(1)-C(3) 1.918(10), Fe(1)-C(4) 1.912(9), Fe(2)-C(3) 1.916(10), Fe(2)-C(4) 1.905(9), average Fe(1)-C(5-9) 2.13(2), average Fe(2)-C(10-14) 2.15(2); Fe(2)-Fe(1)-C(1) 97.2(4), Fe(1)-Fe(2)-C(2) 97.0(4), Fe(1)-C(3)-Fe(2) 83.4(4), Fe(1)-C(4)-Fe(2) 83.8(4), C(5)-C(15)-C(25) 118.8(10), C(15)-C(25)-C(20) 114.2(10), C(10)-C(20)-C(25) 116.8(11).

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