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PREPARATION AND RESOLUTION OF (η^4-1,3-DIENECARBOXYLIC ACID)Fe(CO)$_3$ COMPLEXES

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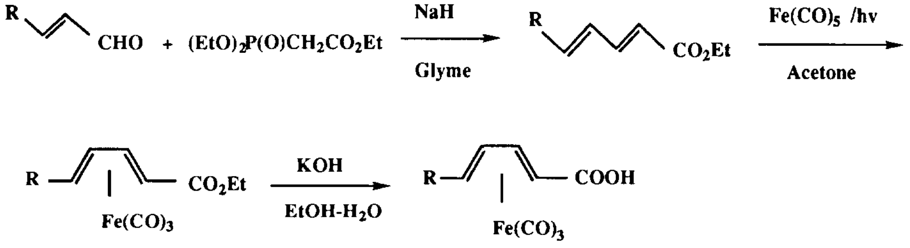
Abstract: (η^4-1,3-dienecarboxylic acid)Fe(CO)$_3$ complexes **1** were prepared, starting from a Horner-Emmons reaction of α,β-unsaturated aldehydes, followed by complexation with Fe(CO)$_5$ and hydrolysis of the ester groups. Reaction of **1** with (*S*)-2-octanol gave a mixture of diastereomeric esters which can be easily separated by column chromatography. Enantiomerically pure (η^4-1,3-dienecarboxylic acid)Fe(CO)$_3$ complexes were obtained by hydrolysis of the esters thus separated without racemization and decomposition of the complexes.

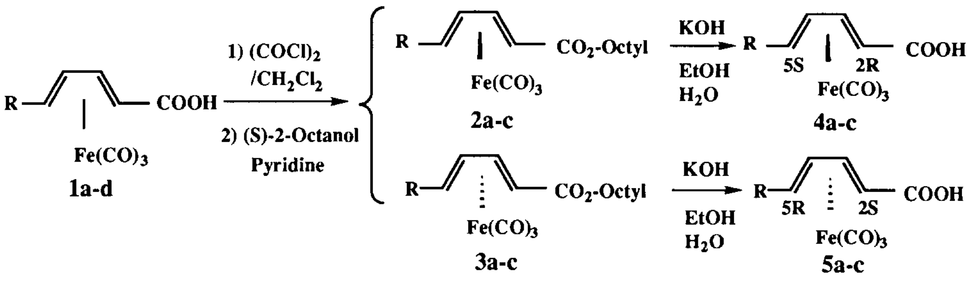
Planar chiral (η^4-diene) Fe(CO)$_3$ complexes have attracted great interest as a powerful source for asymmetric organic synthesis.[1] They can serve as chiral auxiliary and also protected functional group to introduce the 1,3-diene fragment into organic molecules. For this purpose (η^4-2,4-pentadienal)Fe(CO)$_3$ and its derivatives have been widely used.[2] However, utilization of (η^4-1,3-dienecarboxylic acid)Fe(CO)$_3$ complexes **1** has been little developed[3] and only one resolution method of **1** has been hitherto exploited.[4] We report here a preparation of (η^4-1,3-dienecarboxylic acid)Fe(CO)$_3$ complexes **1** and a facile resolution of **1** via esterification with (*S*)-2-octanol.



1b-d

b: R=Ph, **c: R=CH$_3$CH$_2$CH$_2$,** **d: R=2-Furyl**

Scheme 1



a: R=CH_3, b: R=Ph, c: R=$CH_3CH_2CH_2$, d: R=2-Furyl

Scheme 2

Racemic complexes **1** were prepared starting from the Horner-Emmons reaction of the corresponding phosphite and aldehydes as shown in Scheme 1. All the acid complexes **1a-d** are slightly soluble in most organic solvents.

Reaction of enantiomerically pure (*S*)-2-octanol with (η^4-2,4-hexadienoyl chloride) $Fe(CO)_3$, generated in situ by treatment of **1a** with oxalyl chloride in dichloromethane, gave diastereomeric mixtures of esters **2a** and **3a** (1 : 1) in quantitative yields. The diastereomers thus obtained were separated by column chromatography on silica gel using hexane and dichloromethane (1:1) as eluents. Similar treatment of **1b, c** with (*S*)-2-octanol also afforded the corresponding diastereomeric ester complexes **2b, c** and **3b, c** which were separated in the same manner. No ester complexes were obtained from **1d**. The properties of the diastereomers are listed in Table 1. The structures of the complexes were confirmed by spectroscopy.[5] Use of (-)-menthol, (+)-neomenthol and 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose in place of (*S*)-2-octanol gave a mixture of corresponding diastereomeric ester complexes of **1a** in good yield. However, separation of these diastereomeric complexes was not effected by column chromatography.

Hydrolyses of the ester complexes thus separated were carried out in ethanol-water (3:1) in the presence of KOH (0.5 M) under reflux to give carboxylic acid complexes **4** and **5** in good yields. The properties of the chiral acid complexes were summarized in Table 2. The specific rotation of the complexes **4a** and **5a** thus obtained are in fair agreement with those of reported.[3] Consequently racemization of the complexes did not occur under these conditions. Under more drastic conditions (2 M KOH) or acidic conditions (4M HCl), racemization and decomposition of the complexes proceeded considerably.

The absolute configuration of the ester complexes was not examined by X-ray analysis because all of the complexes are oily compounds. It is known that the structure of dextrorotatory isomer **5a** is the (*2S, 5R*) configuration (Table 2).[3b, 4, 6] The structures of the ester complexes **2a** and **3a** were determined on the basis of the configuration of the acid complexes derived from the ester complexes. Molecular models of the ester complexes **2** and **3** indicate that **3** is more polar than **2**. This is in

Table 1. Properties of Ester Complexes

Complex	Yield[a]/%	Rf value[b]
2a	41	0.42
3a	40	0.37
2b	39	0.40
3b	44	0.36
2c	42	0.46
3c	38	0.41

a) Isolated yield.
b) Silica gel, hexane : dichloromethane (1 : 1).

Table 2. Properties of Acid Complexes

Complex	Yield[a]/%	$[\alpha]_D^{20}$ [b]
4a	67	-205 (lit[3] -204)
5a	75	+210 (lit[3] +213)
4b	76	+142
5b	82	-139
4c	65	-222
5c	74	+206

a) Isolated yield.
b) Measured in acetone (C : 0.05-0.1).

accord with the Rf values of the ester complexes. The configuration of the other ester complexes was predicted by their Rf values.

To get an insight into the configuration of the (η^4-1,3-diene)Fe(CO)$_3$ fragment, CD spectra of these complexes were measured. As an example, those of **4c** and **5c** are illustrated in Fig. 1. Grée and the coworkers[6] reported that the configuration of (η^4-1,3-diene)Fe(CO)$_3$ fragment is correlated with their CD spectrum and also the specific rotation in the case of (η^4-1,3-diene)Fe(CO)$_3$ complexes bearing carbonyl and alkyl groups at 1,4-positions. Thus, the complexes having (*2S,5R*) configuration exhibit a negative band at long wavelength (around 400 nm) and positive rotation values. This empirical rule can be applied to **4a-c** and **5a-c**, that is, all the complexes **4a-c** showed a positive band and **5a-c** showed a negative band at 400 nm. However, the relation between Rf values and specific rotations is in opposite sense in the case of **4b** and **5b**. This disagreement is probably due to a different chromophole of phenyl group.

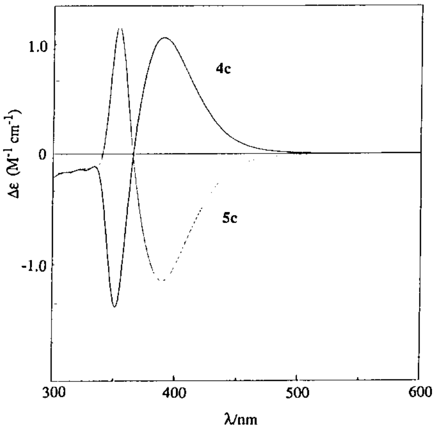


Fig. 1. CD spectra of **4c** and **5c**.

The authors thank Arakawa Chemical Industries, LTD. for the gift of (*S*)-2-octanol.

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5) All new compounds were characterized by their spectral data. Selected data: **1b**: Yellow solids. mp; 215-217 °C. IR (KBr) 2064, 2002, 1978, 1669 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 1.74 (1H, d, J=8.0, Hz, CH=), 2.99 (1H, d, J=9.6, Hz, CH=), 5.91 (1H, dd, J=8.0, 4.8 Hz, CH=), 6.36 (1H, dd, J=9.6, 4.8 Hz, =CH), 7.10-7.55 (5H, m, arom), 10.87 (1H, br, COOH); **1c**: Yellow solids. mp; 153-155 °C. IR (KBr) 2063, 2000, 1978, 1674 cm^{-1}.^{1}H NMR (DMSO-d_6) δ 0.85 (3H, d, J=6.9 Hz, CH$_3$), 1.23 (1H, d, J=8.5, Hz, CH=), 1.35-1.78 (5H, m, CH=, CH$_2$), 5.50 (1H, dd, J=8.5, 5.1 Hz, CH=), 5.73 (1H, dd, J=8.5, 5.1 Hz, =CH); 10.54 (1H, br, COOH); **1d**: Yellow solids. mp; 192-194 °C. IR (KBr) 2060, 2003, 1982, 1669 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 1.56 (1H, d, J=8.6, Hz, CH=), 3.00 (1H, d, J=8.6, Hz, CH=), 5.88 (1H, dd, J=8.6, 5.2 Hz, CH=), 6.06 (1H, dd, J=8.6, 5.2 Hz, =CH), 6.37-6.38 (2H, m, CH=), 7.56 (1H, s, CH=), 10.33 (1H, br, COOH); **2a**: IR (Neat) 2058, 1986, 1709 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 0.87 (3H, d, J=6.5 Hz, CH$_3$), 1.00 (1H, d, J=8.0, Hz, CH=), 1.18 (3H, d, J=6.5 Hz, CH$_3$), 1.25-1.55 (11H, m, CH$_2$, =CH), 1.50 (3H, d, J=6.0 Hz, CH$_3$), 4.81-4.88 (1H, m, OCH), 5.19 (1H, dd, J=8.0, 4.8 Hz, CH=), 5.74 (1H, dd, J=8.0, 4.8 Hz, =CH).^{13}C NMR (CDCl$_3$) δ 14.04, 19.13, 19.70 (CH$_3$), 22.57, 25.40, 29.14, 31.75, 35.85 (CH$_2$), 46.75 (CH), 58.86, 71.15, 82.81, 88.11(C=), 171.86 (C=O), 212.5 (CO); **3a**: IR (Neat) 2058, 1988, 1709 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 0.87 (3H, d, J=6.5 Hz, CH$_3$), 1.00 (1H, d, J=8.0 Hz, CH=), 1.18 (3H, d, J=6.5 Hz, CH$_3$), 1.25-1.55 (11H, m, CH$_2$, =CH), 1.50 (3H, d, J=6.0 Hz, CH$_3$), 4.87-4.94 (1H, m, OCH), 5.20 (1H, dd, J=8.0, 4.8 Hz, CH=), 5.76 (1H, dd, J=8.0, 4.8 Hz, =CH). ^{13}C NMR (CDCl$_3$) δ 14.06, 19.13, 20.08 (CH$_3$), 22.57, 25.24, 29.10, 31.77, 36.07 (CH$_2$), 46.55 (CH), 58.88, 70.96, 82.83, 88.15 (C=), 171.86 (C=O), 212.8 (CO);

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