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HPLC OPTICAL RESOLUTION OF TRICARBONYL(2,3-DIHYDROTROPONE)IRON AND ITS ABSOLUTE CONFIGURATION

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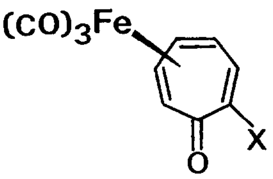
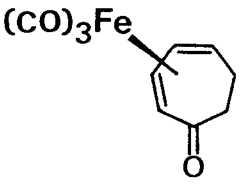
Dedicated to Professor George Büchi on the occasion of his 65th birthday

Summary: Optical resolution of (±)-tricarbonyl(2,3-dihydrotropone)-iron was carried out, and the absolute configuration was determined by X-ray diffraction and CD spectroscopic studies.

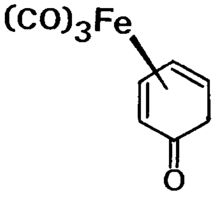
Determination of the absolute configuration of optically active (η^4-polyene)$Fe(CO)_3$ complexes, and their chemical application in asymmetric organic syntheses are an importnat and challenging subject in contemporary organometallic chemistry. The absolute configuration of $Fe(CO)_3$ complex of 5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanone was recently determined by single crystal X-ray diffraction analysis and CD spectroscopic measurements.$^{1)}$ We have already reported optical resolution by HPLC and CD spectra of (tropone)$Fe(CO)_3$ (1a) and (2-acyloxytropone)$Fe(CO)_3$ (1b), and kinetic data of 1,3-haptotropic metal shift.$^{2)}$ Very recently, a successful diastereomeric separation of (tropone)$Fe(CO)_2L$ [L = (+)-(neomenthyl)PPh_2] is reported.$^{3)}$ However, the absolute configuration of these complexes remains unresolved.$^{4)}$



(+)-1



(+)-2



(+)-3

a : X = H, b : X = $OCOCH_3$

Herein we report optical resolution and the absolute configuration by X-ray analysis of (2,3-dihydrotropone)$Fe(CO)_3$ [(cyclohepta-2,4-dienone)$Fe(CO)_3$]

(**2**) which is not amenable to resolution using presently available methods. Furthermore, the CD spectrum of the resolved complex **2** in conjunction with its chemical conversion from **1a** establishes the absolute configuration of **1a**. Optical resolution and CD spectrum of (cyclohexa-2,4-dienone)Fe(CO)$_3$ (**3**) are also described, though the absolute configuration of (-)-**3** was defined to be 2*S* in a process of the stereospecific derivation of naturally occuring cryptone from partially active (+)-(1-methoxy-1,3-cyclohexadiene)Fe(CO)$_3$.[5]

A racemic complex (±)-**2** was derived from (±)-**1a** by catalytic hydrogenation according to the literature.[6] Optical resolution of (±)-**2** (mp 105-106°C) was carried out on a column packed with DAICEL CHIRALPAK OC, using hexane/2-propanol (9 : 1) as eluent, to give optically pure (+)-**2** (mp 93-94°C) with $[\alpha]_D^{20}$ +490° (*c* 0.263, $CHCl_3$) and (-)-**2** (mp 93-94°C) with $[\alpha]_D^{20}$ -486° (*c* 0.262, $CHCl_3$). A racemic complex (±)-**3** (mp 103-106°C, decomp.) was resolved on a column packed with DAICEL CHIRALPAK OB to give (+)-**3** (mp 127.5-128.5°C, decomp.) with $[\alpha]_D^{20}$ +535° (*c* 0.131, $CHCl_3$) and (-)-**3** (mp 127.5-128.5°C, decomp.) with $[\alpha]_D^{20}$ -526° (*c* 0.112, $CHCl_3$).

Absorption and CD spectra of (+)-**2** are represented in Fig. 1 together with those of (+)-**3**. Optical active complex (+)-**2** exhibits almost the same profile as that of (+)-**3**, indicating the same chirality inherent in the complexes. The longest wavelength CD band of (+)-**2** and (+)-**3** at *ca*. 380 nm which corresponds to that observed at around 450-500 nm newly and commonly in (tropone)Fe(CO)$_3$[2,7] is stronger in intensity than that of (tropone)Fe(CO)$_3$ complexes, and subjected to the blue-shift on changing solvent from non-polar to polar. Considering the blue-shift in conjunction with the low intensity of absorption, the longest wavelength CD band is considered to be the intramolecular CT transition. The CD extrema at *ca*. 300 nm observed both in (+)-**2** and (+)-**3** are considered to arise from the n → π* transition within the dienone chromophore.

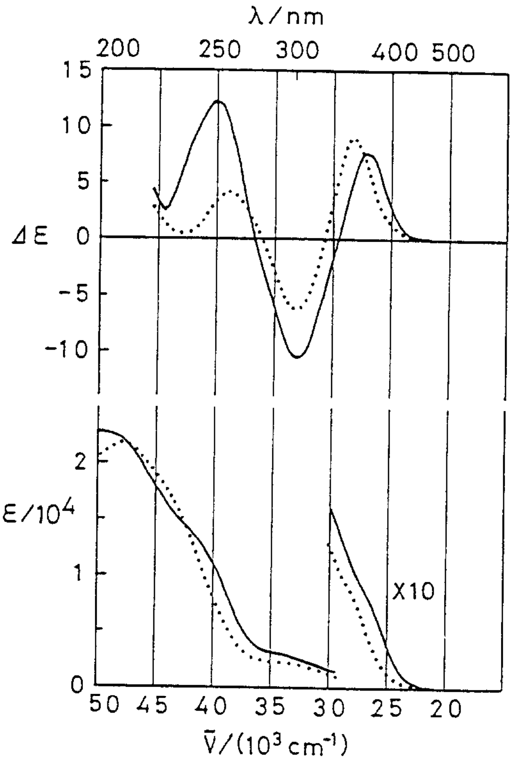


Fig. 1 Absorption (bottom) and CD (top) spectra of (+)-**2** (———) and (+)-**3** (·····) in *i*-octane at room temperature

The molecular and crystal structure of (+)-**2** were determined by single crystal X-ray analysis. In Fig. 2 molecular structure of (+)-**2** is reproduced.[8] The determined absolute configuration of optically active complex (+)-**2** coincides

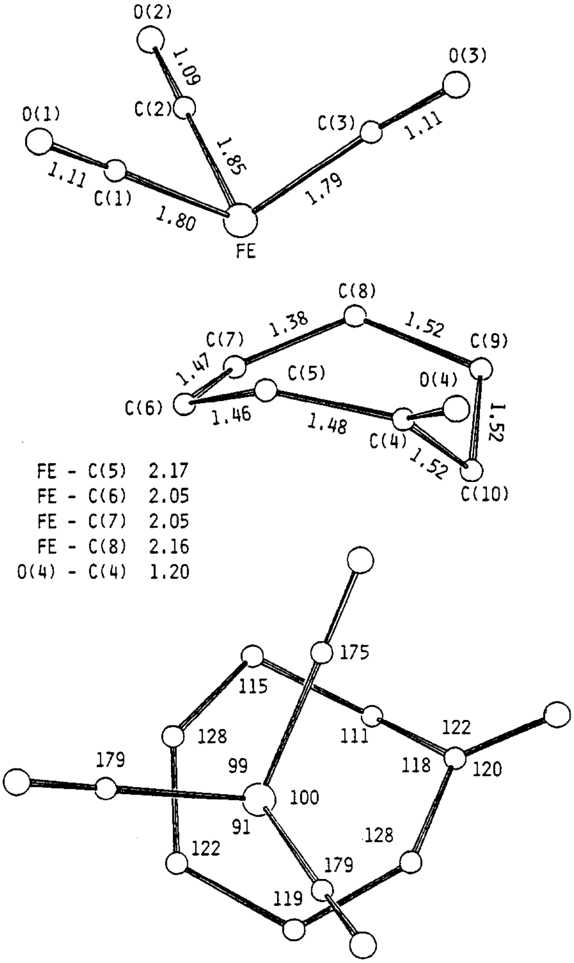


Fig. 2 Molecular structure of (+)-**2** with bond lengths in Å and angles in deg. The distances between the iron atom and the carbon atoms of 2,3-dihydrotropone are inserted in the figure.

with that drawn on the preceding diagram, with the iron tricarbonyl group upside on the left hand side of the 2,3-dihydrotropone ligand.

According to the Birch convention for nomenclature, the configuration of (+)-**2** is established to be 2*R*, while that of (+)-**3** turns to be also 2*R* in accordance with his definition.[5)]

Catalytic hydrogenation of optically pure complexes (+)-**1a** and (-)-**1a** afforded (+)-**2** and (-)-**2**, respectively, though in poor optical yield.[9)] This indicates the absolute configuration of (+)-**1a** and (-)-**1a** are 2*R* and 2*S*, respectively. This is also supported by stereospecific derivation of **1a** to (2,3-homotropone)Fe$(CO)_3$, which will be published in near future.

References and Notes

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8) Crystal data for (+)-**2** : $C_{10}H_8O_4Fe$, M = 248.0, orthorhombic, *a* = 13.305(2) Å, *b* = 10.612(1) Å, *c* = 7.628(1) Å, space group $P2_12_12_1$, z = 4, ρ_{calc} = 1.61 g/cm^3. The crystal size was *ca.* 0.15 x 0.15 x 0.25 mm. Two sets of independent reflections, *hkl* and $h\bar{k}l$, with $2\theta < 128°$ were measured at 25°C on a Rigaku automated four-circle diffractometer (AFC-5) usin Cu-K_α (λ = 1.548 Å) radiations, $\theta - 2\theta$ scan mode, a scan speed of 4° min^{-1} in 2θ. A total of 1620 reflections were measured and corrected for Lorentz and polarization effects, absorption correction being made.$^{10)}$ The structure was solved by the heavy atom method and refined by the block-diagonal least-square method. Including all calculated hydrogen atoms with isotropic temperature factors and the anomalous dispersion of the iron and oxygen atoms,$^{11)}$ the refinements terminated to give an R factor of 0.072 vs. 0.115 (R_w 0.092 vs. 0.135) for each enantiomorph. The difference was remarkably large and the absolute configuration of (+)-**2** was determined as shown in Fig. 2.

9) Rapid racemization of optically active **1**a takes place via 1,3-haptotropic rearrangement during the catalytic hydrogenation.

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