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First optically active organometallic free radical in the cymantrene series

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Abstract

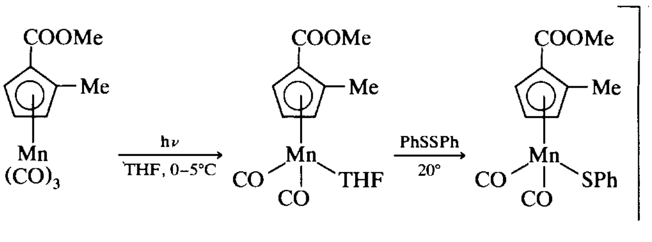
Replacement of one CO ligand in the enantiomeric 2-methylcymantrenecarboxylic acid ester for a radical ligand PhS results in the preparation of stable and optically active odd-electron complex $CH_3C_5H_3COOCH_3Mn(CO)_2SPh]^{\cdot}$ fully characterized by electron spin resonance, mass spectroscopy, UV–visible spectroscopy, IR spectroscopy and circular dichroism spectroscopy. This is the first example of an optically active organometallic free radical.

Keywords: Manganese; Chirality; Cyclopentadienyl; Radical; Sulfur

1. Introduction

The chemistry of 17-electron metal complexes with free radical ligands is a relatively new area of organometallic chemistry [1]. Previously Huttner and coworkers [2,3] had elaborated a procedure for preparing free-radical complexes of the type $Cp(CO)_2Mn(SR)]^{\cdot}$ (R = alkyl or aryl) (**1**) via the reaction of a well-known intermediate $Cp(CO)_2Mn(THF)$ (THF ≡ tetrahydrofuran) with either thiols RSH followed by oxidation in air or with disulphides RSSR. In the last case the S–S bond is broken. More recently we have shown that **1** are formed when $Cp(CO)_2Mn(THF)$ is reacted with trialkylthiophosphites $P(SR)_3$ when the rupture of the P–S bond occurs [4,5].

Now we wish to report the synthesis and circular dichroism (CD) study of the optically active analogue of **1** [6]. On the UV irradiation in THF at 5°C under an inert atmosphere, either of the enantiomers of planar chiral methyl 2-methylcymantrenyl carboxylate (**2a** and **2b**) affords the corresponding intermediates **3a** and **3b**; these react with PhSSPh at room temperature (without UV irradiation) to give optically active free radical complexes (+)- or (−)-**4** (**4a** and **4b**) which have been isolated using column chromatography on SiO_2 at room temperature (cf. [2,3]) after the solvent had been removed:



2a,b **3** **4a,b**

Enantiomers **4a** and **4b** have been obtained as non-crystallizable dark-blue oils very soluble in both polar and non-polar solvents. They are stable on keeping under argon at 0°C but very susceptible to oxidation and decompose rapidly in the presence of O_2 traces especially in solution.

The electron spin resonance (ESR) spectrum of **4a** and **4b** in toluene exhibit a broad sextet with $g = 2.032$ and $a(\mathrm{Mn}) = 51.6$ G, which is close to the g values for the thiyl radicals $RS^{\cdot}$. Hyperfine structure cannot be observed. The magnitude of $a(\mathrm{Mn})$ suggests strong delocalization of the spin density onto the metal atom. In the IR spectrum in hexane two absorption bands at 1950 (broad) and 2010 cm^{-1} due to CO ligands are observable, the intensity of the former being higher by

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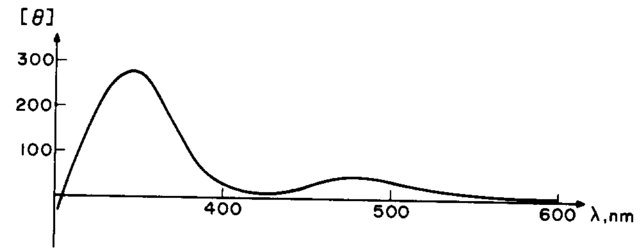

Fig. 1. CD spectrum of (+)-**4a** in hexane solution.

a factor of 2. The essential part of this spectrum is identical with that of unsubstituted radical $Cp(CO)_2MnSPh]^{\cdot}$ [3], in addition, ν(C=O) for the ester group appears at 1760 cm^{-1}.

In the mass spectra of **4a** and **4b** molecular ions have been observed. Precise measurement of m/e gave a value of 356.9997 which fit the calculated value of 356.9992 well. The most intense peak with $m/e = 301$ corresponds to the $M - 2CO$ fragment. This type of fragmentation is characteristic of many substituted cymantrenes.

Conversion of the even-electron precursors **2a** and **2b** into odd-electron species **4a** and **4b** results in sharp changes in UV–visible spectra. Compounds **2a** and **2b**, like many of cymantrene derivatives, are yellow colored owing to the absorption in the region 335–350 nm [7,8] whereas **4a** and **4b** are dark blue because of two bands of low intensity at about 520 nm (sh) and 613 nm (intensity ratio, 0.6:1). In the UV region (300–400 nm) the radicals **4a** and **4b** have a strong slope absorption without any characteristic bands with the exception of a shoulder at 396 nm. The UV–visible spectrum of **4a** and **4b** coincides with that of the parent radical $Cp(CO)_2MnSPh]^{\cdot}$ described in [3].

In the CD spectrum of (+)-**4a** (Fig. 1) there are two positive Cotton effects at 347 nm ($[\theta] = 290$) and at 480–500 nm ($[\theta] \approx 45$). The former is of the same position and intensity as in the CD spectrum of the precursor **2a** [7,8] and the latter is due to one of two "free-radical" bands in the UV–visible spectrum of **2a**. It is still observable in spite of low intensity; however, no Cotton effect has been recorded at longer wavelengths, which may be connected with the absorption band at 613 nm, probably because of its low intensity.

To our knowledge, this is the first example of optical activity in organometallic free radicals [9]. We are not confident that reliable evidence for any optically active organic free radicals is available.

2. Experimental part

All work has been carried out under an argon atmosphere with the solvents saturated with argon. IR, ESR, mass, UV–visible and CD spectra were obtained using UR-20, RE 1306, Finnigan MAT-212, Specord UV–visible, JASCO-500A and Dichrograph-III instruments respectively.

2.1. Preparation of 4a and 4b

The corresponding enantiomer of methyl 1,2-methylcymantrenylcarboxylate (2) [7,8] (1 mmol) in 15–20 ml of freshly distilled absolute THF was irradiated by UV light (mercury lamp PRK-2) in a quartz vessel with a cooling jacket (1.5 h at 0–5°C). To the dark-red solution formed which contains intermediate **3** (yield, about 70%) 0.5 mmol of PhSSPh in 5 ml of THF was added and the mixture was stirred without UV irradiation at room temperature for 14–16 h. During this period the colour changed gradually to dark blue, characteristic of free radicals **4**. After removal of THF in vacuo the dark-blue solid was chromatographed on the SiO_2 column (100/160 mesh). Unreacted complex **2** and disulphide were eluted with hexane or petroleum ether. For elution of **4a** and **4b** hexane–CH_2Cl_2 mixture, hexane–THF mixture (50:1) or pure THF were used. Final purification has been achieved by the reprecipitation from THF into hexane at −80°C.

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