

Hydrocarbon bridged metal complexes. XXXIV. Synthesis, structure and attempted decarbonylation of a *trans* 11,12-bis(dicarbonylcyclopentadienylironacyl) substituted dihydro 9,10-ethanoanthracene¹

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Abstract

The diiron bisacyl complex of 9,10-ethanoanthracene-*trans*-11,12-dicarboxylic acid was obtained from the corresponding acid dichloride and Na[Fe(CO)₂Cp]. Its crystal structure was determined. Photo- and thermolysis reactions were studied, giving not the expected bisacyl complexes but elimination of the metal dimer and formation of 9,10-ethanoanthracene. The reaction of phthaloyl chloride and [Fe(CO)₂Cp]⁻ yields [Fe(CO)₂Cp]₂ and *trans*-biphthalyl.

Keywords: Hydrocarbon bridged metal complexes; X-ray structure; Cyclopentadienyl; Carbonyl; Iron; Acyl; Dihydro-ethanoanthracene

1. Introduction

Bimetallic complexes **A**–**C** linked by unsubstituted C₂ bridges of bond orders from one to three are isolobal [2] to ethane, ethene and ethyne (Scheme 1). A complete series of these complexes is thus an interesting aim for preparative organometallic chemistry. So far, such a complete series has only been obtained for a heterobimetallic system [Ru, Zr] by Bullock and coworkers [3].

We reported the unsubstituted, homobimetallic complexes of type **A** [4] and **C** [5] [ML_n = Re(CO)₅]. The unsubstituted ethenediide bridged **B** is so far missing, though the stability of substituted bridges **B2** and **B3** has been proven [6,7]. Also, compound **B1** [8] has correct hybridization at the C₂ bridge, but dipolar resonances limit its olefin character (Scheme 1).

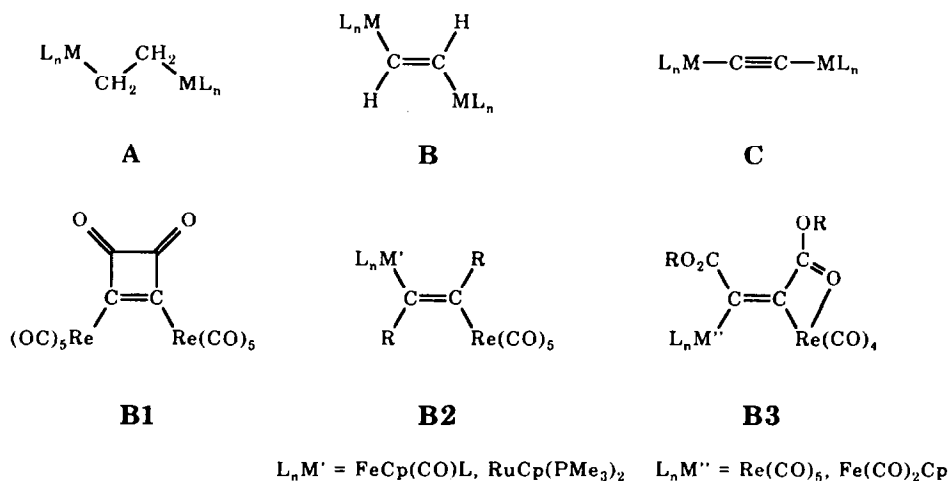
A promising route to **B** is the decarbonylation of acyl

complexes. This is exemplified by the reaction of difluorofumaroyl chloride with NaCo(CO)₄, giving directly the difluorethenediide bridged complex [9]. A bisacyl complex of fumaric acid [ML_n = Fe(CO)₂Cp] had been obtained by Gompper and Kottmair [10]. However, our attempts to obtain bisacyl complexes from fumaroyl chloride and pentacarbonylmetalates surprisingly produced 2,4-bis(pentacarbonylmanganese and -rhenium)-but-3-enolides [11]. Thus it seemed reasonable to attempt the synthesis of complexes of type **B** by a step-wise procedure (Scheme 2): standard Diels–Alder reactions require an electron-poor double bond, in our case the fumaroyl dichloride, and an electron-rich diene. Thus, the *trans*-substituted double bond of the fumaroyl chloride can be masked by the stereoselective [2 + 4]-cycloaddition. Our strategy was based upon converting the electron-poor “olefin” in the cycloadduct via formation of the bisacyl complex and its decarbonylation into a dimetallated electron-rich “olefin”. Now it should be possible to release this olefin by a thermally allowed cycloreversion. The concept of the reversible protection of a double bond by the Diels–Alder reaction has recently been used successfully for the synthesis of (*Z*)-ethenethiols [12].

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¹ For Part XXXIII, see Ref. [1]. Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

² X-ray structural analysis.



Scheme 1.

Since [2 + 4]-cycloadditions and -reversions occur stereospecifically [13], the geometry of fumaric acid should be preserved and the cycloreversion should give the *trans*-dimetallated olefin. While this isomer may undergo β -hydride elimination as observed by Bullock and coworkers [3], two metal fragments *cis* to each other would be more disfavoured due to sterical interactions.

2. Results and discussion

Retro-Diels–Alder reactions proceed under milder conditions if the resulting diene is stabilized by aromatization [14]. We thus chose anthracene as the diene component. By heating fumaroyl dichloride and anthracene for 24 h in toluene we obtained the *trans*-dicarboxylic acid dichloride **1**, which could be crystallized in 36% yield from hexane. This synthesis had already been mentioned in a footnote [15]; a one-step procedure is preferred to the previously described syntheses. **1** had also been obtained from the reaction of ethanoanthracene dicarboxylic acid with SOCl_2 /pyridine [16] or SOCl_2 [17].

The reaction of **1** with $\text{NaFe(CO)}_2\text{Cp}$ at -78°C gives, in almost quantitative yield, the diiron bisacyl compound **2**. In contrast, we did not succeed in synthesizing the corresponding dirhenium bisacyl; here the anion decomposed, probably giving a cluster compound [$\nu_{\text{C=O}}$ 1900 cm^{-1}].

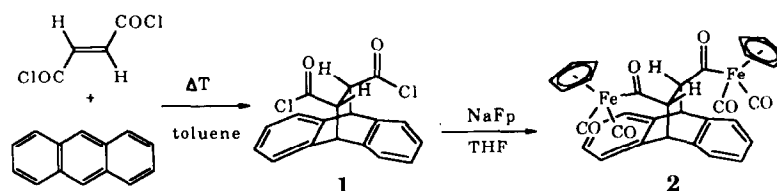
In the Diels–Alder reaction the *trans*-geometry of the fumaroyl chloride is maintained stereospecifically [13]. **1** is obtained as the racemic mixture (R,R) and (S,S) enantiomers. Under achiral conditions, neither can be distinguished spectroscopically; the presence of two chiral carbon atoms complicates the NMR spectra. The spectral data of **1** are in accordance with those reported for the (+)-(S,S)-enantiomer [17]. At low resolution the aromatic protons of **1** and **2** seem to give an ABCD-spin system. However, at high resolution the higher order of the spin system results in more lines, so the signals are characterized as “multiplets”. The bridgehead protons (9,10-H) and those on the ethano bridge (11,12-H) have an almost rectangular orientation. As a consequence, predicted by the Karplus graph, only very small coupling constants are observed. This results in only one, slightly broadened line for each group. Gaussian multiplication results in pseudo triplets, with $|J_{\text{AE}} + J'_{\text{AE}}| = 0.9 \text{ Hz}$ as the virtual coupling constant of this AA'EE' spin system.

The ^{13}C -NMR spectrum of **2** shows, as expected, six signals for the carbon atoms of the aromatic rings. For the $\text{Fe(CO)}_2\text{Cp}$ fragment one observes, due to the chirality of the bridge carbons, two diastereotopic carbonyl ligands. The IR spectrum of **2** is in accordance with its structure, clearly showing the presence of two terminal and one acyl carbonyl groups.

Yellow plates of **2** suitable for X-ray diffraction were obtained by cooling an acetone solution to -28°C . Details of the data collection and refinement parameters



Scheme 2.



Scheme 3.

are given in the Experimental Section. Table 1 contains selected bond distances and angles. Final atomic parameters are listed in Table 2. The unit cell of **2** contains two pairs of independent molecules (centrosymmetric space group); both are the same diastereomeric pair (Fig. 1 shows the *S,S*-enantiomer of both molecules). The main difference between the molecules consists in the relative orientation of the (cyclopentadienyl)dicarbonyliron fragments. In molecule **2** both fragments are located on different sides of the backbone, resulting in an approximate C_2 -axis through the centre of the dihydroanthracene. In molecule **1** the fragment around Fe(1) is rotated about 90° around the Fe(1)–C(117) bond.

A representation of the unit cell of **2** (Fig. 2) shows one cyclopentadienyl group always located in the hydrophobic pocket of the dihydroanthracene skeleton of another molecule. Interestingly, derivatives of ethanoanthracene–11,12-dicarboxylic acid had been recognized as hosts for clathrate formation [16], but there the host–guest interaction was based on hydrogen bonds to polar substituents on the ethano bridge.

Bond distances and angles of **2** (Table 1) show no peculiarities. The ethano bridges [154.0(5)/154.1(5) pm] are comparable with the bond length of ethane [153.4 pm], though considerably shorter than the bond length found in a chelating 1,6-diphospha-1,5-hexadiene [155.4(13) pm] with the same backbone [15]. The bonds

connecting the ethano bridge to the backbone are elongated owing to strain in the molecule [from C(206)–C(216) 157.6(6) to C(213)–C(215) 159.0(5)pm]. Thus, this effect is even stronger than for the diacid and its clathrate, where distances of 156.5(5) to 157.9(4) pm had been found [16]. Angles at the carbon atoms of the ethano bridges containing both bridge atoms towards the backbone are close to the tetrahedral angle [108.3(3) to 108.9(3)°]. However, towards the acyl groups they are significantly widened [113.3(3) to 114.3(3)°], reflecting the strain between the two organometallic groups.

Compound **2** was submitted to a differential thermal analysis (DTA). At 189°C a sharp peak was observed, characteristic of an endothermic decomposition (68 kJ mol^{-1}). A second endothermic process (broad signal around 255°C) took place at higher temperature. A second sample was heated rapidly to 210°C and cooled. IR spectroscopy exhibited only bands assignable to $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ (Fp_2), showing clearly that **2** had collapsed completely. A further sample was thermolysed for 5 min at 200°C in a stoppered NMR tube and then dissolved in CDCl_3 . $^1\text{H-NMR}$ showed signals of acetylene (1.89 ppm), anthracene (8.43 s, 2H; 8.01 dd, 4H; 7.47 dd, 4H), Fp_2 (4.77 s) and one further compound. By its signal pattern this could be identified as 9,10-ethenoanthracene (dibenzobarrelene). The aromatic and bridge regions of the spectrum both form an AA'EE'

Table 1
Selected interatomic distances (pm) and angles ($^\circ$) with standard deviations for **2**

C(115)–C(116)	154.0(5)	C(215)–C(216)	154.1(5)
Fe(1)–C(117)	200.4(4)	Fe(3)–C(217)	200.3(4)
Fe(2)–C(118)	199.8(4)	Fe(4)–C(218)	199.7(4)
C(117)–O(101)	120.6(5)	C(217)–O(201)	120.0(5)
C(118)–O(102)	120.4(5)	C(218)–O(202)	120.1(5)
C(117)–C(115)	153.3(5)	C(217)–C(215)	154.0(6)
C(118)–C(116)	153.7(5)	C(218)–C(216)	154.8(5)
C(113)–C(115)	158.2(5)	C(213)–C(215)	159.0(5)
C(106)–C(116)	158.1(5)	C(206)–C(216)	157.6(6)
C(113)–C(115)–C(117)	109.8(3)	C(213)–C(215)–C(217)	109.4(3)
C(113)–C(115)–C(116)	108.9(3)	C(213)–C(215)–C(216)	108.3(3)
C(117)–C(115)–C(116)	114.0(3)	C(217)–C(215)–C(216)	113.3(3)
C(106)–C(116)–C(115)	108.8(3)	C(206)–C(216)–C(215)	108.4(3)
C(106)–C(116)–C(118)	110.4(3)	C(206)–C(216)–C(218)	110.0(3)
C(115)–C(116)–C(118)	114.3(3)	C(215)–C(216)–C(218)	113.9(3)

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2

Atom	x	y	z	U_{eq}
C(101)	-2025(4)	-586(3)	3633(3)	49(1)
C(102)	-2013(5)	-916(3)	4332(3)	59(1)
C(103)	-2742(5)	-694(4)	4796(3)	59(1)
C(104)	-3512(4)	-135(3)	4588(2)	44(1)
C(105)	-3533(4)	196(3)	3900(2)	37(1)
C(106)	-4270(4)	848(3)	3596(2)	35(1)
C(107)	-5074(4)	396(3)	2741(2)	36(1)
C(108)	-6408(4)	180(3)	2422(3)	44(1)
C(109)	-6995(5)	-273(3)	1616(3)	52(1)
C(110)	-6268(5)	-494(3)	1150(3)	53(1)
C(111)	-4927(4)	-277(3)	1467(2)	45(1)
C(112)	-4331(4)	163(3)	2265(2)	37(1)
C(113)	-2891(4)	439(3)	2705(2)	36(1)
C(114)	-2780(4)	-20(3)	3424(2)	39(1)
C(115)	-2426(3)	1549(3)	3020(2)	33(1)
C(117)	-923(4)	1940(3)	3335(2)	40(1)
O(101)	-376(3)	2224(3)	4039(2)	60(1)
Fe(1)	134(1)	1938(1)	2566(1)	38(1)
C(119)	482(4)	3171(3)	2742(3)	49(1)
O(103)	-2001(4)	1558(3)	1112(2)	74(1)
C(120)	-1173(5)	1710(3)	1698(3)	48(1)
O(104)	718(4)	3974(3)	2858(2)	76(1)
C(121)	2075(4)	2002(4)	2603(3)	56(1)
C(122)	1201(5)	1259(4)	1990(3)	54(1)
C(123)	411(4)	616(3)	2329(3)	50(1)
C(124)	822(4)	969(3)	3149(3)	52(1)
C(125)	1840(4)	1835(3)	3323(3)	53(1)
C(116)	-3123(4)	1773(3)	3637(2)	32(1)
C(118)	-3653(4)	2602(3)	3543(2)	37(1)
O(102)	-4260(3)	2650(2)	2897(2)	60(1)
Fe(2)	-3270(1)	3577(1)	4527(1)	43(1)
C(127)	-4766(6)	3762(4)	4200(4)	79(2)
O(105)	-4253(5)	2123(3)	5347(2)	115(2)
C(126)	-3869(6)	2694(4)	5010(3)	70(2)
O(106)	-5731(5)	3926(4)	4000(4)	133(2)
C(128)	-1244(5)	3875(4)	4976(4)	72(2)
C(129)	-1649(6)	4372(4)	5522(3)	84(2)
C(130)	-2196(5)	4996(4)	5152(4)	78(2)
C(131)	-2090(5)	4859(4)	4383(3)	69(2)
C(132)	-1493(5)	4189(4)	4285(3)	64(1)
C(201)	-461(4)	7451(3)	3749(3)	48(1)
C(202)	709(5)	8207(3)	3990(3)	56(1)
C(203)	1291(5)	8537(3)	3440(3)	58(1)
C(204)	725(4)	8123(3)	2627(3)	50(1)
C(205)	-444(4)	7374(3)	2386(2)	41(1)
C(206)	-1188(4)	6826(3)	1545(2)	42(1)
C(207)	-1453(4)	5778(3)	1531(3)	48(1)
C(208)	-1166(5)	5144(4)	1023(3)	63(1)
C(209)	-1541(6)	4188(4)	1081(4)	78(2)
C(210)	-2195(6)	3889(4)	1609(4)	73(2)
C(211)	-2493(5)	4519(3)	2107(3)	60(1)
C(212)	-2107(4)	5471(3)	2070(3)	47(1)
C(213)	-2330(4)	6261(3)	2575(2)	43(1)
C(214)	-1036(4)	7044(3)	2946(2)	40(1)
C(215)	-3186(4)	6737(3)	2014(2)	35(1)
C(217)	-4636(4)	6103(3)	1740(2)	41(1)
O(201)	-5061(3)	5533(3)	1119(2)	66(1)
Fe(3)	-5815(1)	6292(1)	2396(1)	46(1)
C(219)	-4696(6)	6458(4)	3327(3)	71(2)
O(203)	-4016(5)	6550(4)	3961(3)	120(2)
C(220)	-6389(7)	5080(4)	2289(4)	90(2)
O(204)	-6809(7)	4270(4)	2208(4)	176(3)

Table 2 (continued)

Atom	x	y	z	U_{eq}
C(221)	-7052(8)	7006(6)	2738(5)	90(2)
C(222)	-5932(9)	7659(5)	2690(4)	97(2)
C(223)	-5884(8)	7479(5)	1924(5)	95(2)
C(224)	-6960(8)	6698(7)	1478(4)	99(2)
C(225)	-7679(7)	6411(7)	2031(6)	116(3)
C(216)	-2608(4)	6910(3)	1319(2)	37(1)
C(218)	-2556(4)	7875(3)	1097(2)	40(1)
O(202)	-2290(3)	8561(2)	1614(2)	56(1)
Fe(4)	-2996(1)	7888(1)	-61(1)	43(1)
C(226)	-1789(6)	7427(5)	-221(3)	78(2)
O(205)	-1019(6)	7120(5)	-365(3)	138(2)
C(227)	-1960(5)	9066(4)	167(3)	63(1)
O(206)	-1283(5)	9838(3)	309(3)	104(2)
C(228)	-4690(6)	6709(4)	-523(4)	87(2)
C(229)	-4942(5)	7395(6)	-47(3)	90(2)
C(230)	-4762(6)	8181(5)	-376(3)	77(2)
C(231)	-4429(5)	7993(4)	-1061(3)	65(1)
C(232)	-4393(5)	7086(4)	-1158(3)	71(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

spin system, having the appearance of double doublets [18].

Ethanoanthracene has been obtained by the pressure reaction of acetylene and anthracene (40 to 60 h, 25 atm, 180–200°C) [19], dehalogenation of 11,12-dichloroethanoanthracene [20], or by oxidation of ethanoanthracene dicarboxylic acid with lead tetraacetate [21]. The relative amounts of anthracene and ethanoanthracene formed in this experiment were approximately 1:1. As we were not applying pressure, it seems plausible that ethanoanthracene was not formed from anthracene and acetylene, but rather may be an intermediate in their formation.

The photolysis of **2** in THF (15 min, room temperature, high pressure Hg immersion lamp) proceeds more selectively than the thermolysis. After quick removal of the THF the $^1\text{H-NMR}$ spectrum shows only the signals of Fp_2 and ethanoanthracene. No further cleavage to anthracene and acetylene occurs, since the [4 + 2]-cycloreversion is thermally allowed, but photochemically forbidden. It had been observed [22] that by UV-irradiation in THF, ethanoanthracene can rearrange to dibenzosemibullvalene and *sym*-dibenzocyclooctatetraene. Under our conditions these products were not detected.

From our experiments it is not possible to determine via which processes ethanoanthracene is formed. It is well known that the dissociation of a terminal carbonyl ligand is the rate limiting step in the decarbonylation of acyl complexes [23]. Recent studies of the UV-photolysis of $\text{H}_3\text{CC(O)Fe(CO)}_2\text{Cp}$ using time-resolved FT-IR spectroscopy report clean decarbonylation or substitution [24]. The formation of $[\text{Fe(CO)}_2\text{Cp}]_2$ was not observed. According to these studies a two-fold decarbonylation of **2** to an ethanediide bridged complex is

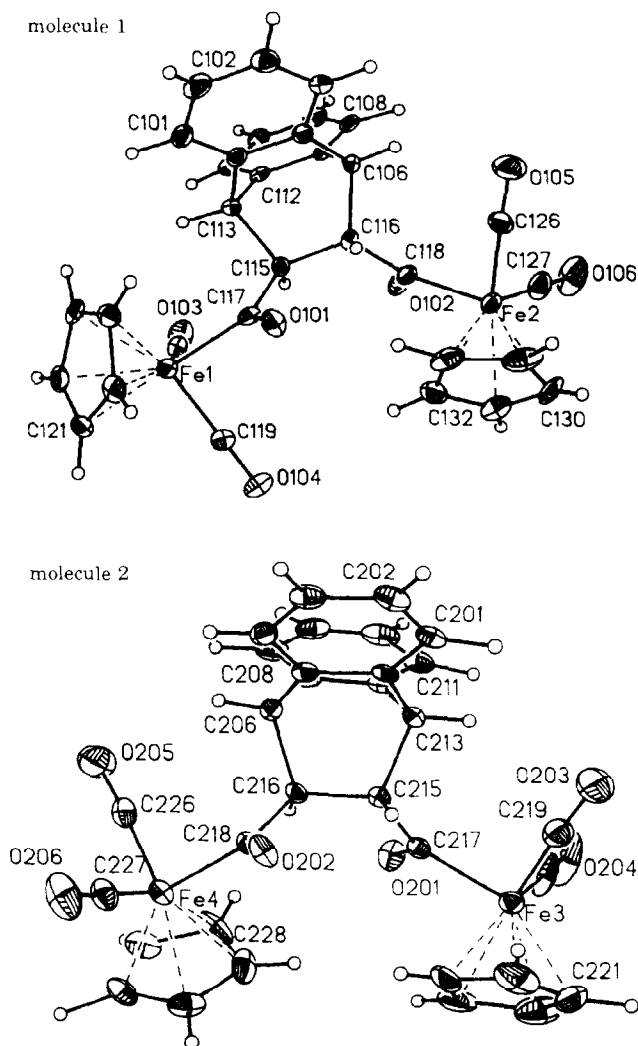


Fig. 1. Crystal structure of **2**. The thermal ellipsoids of non-hydrogen atoms represent 20% probability.

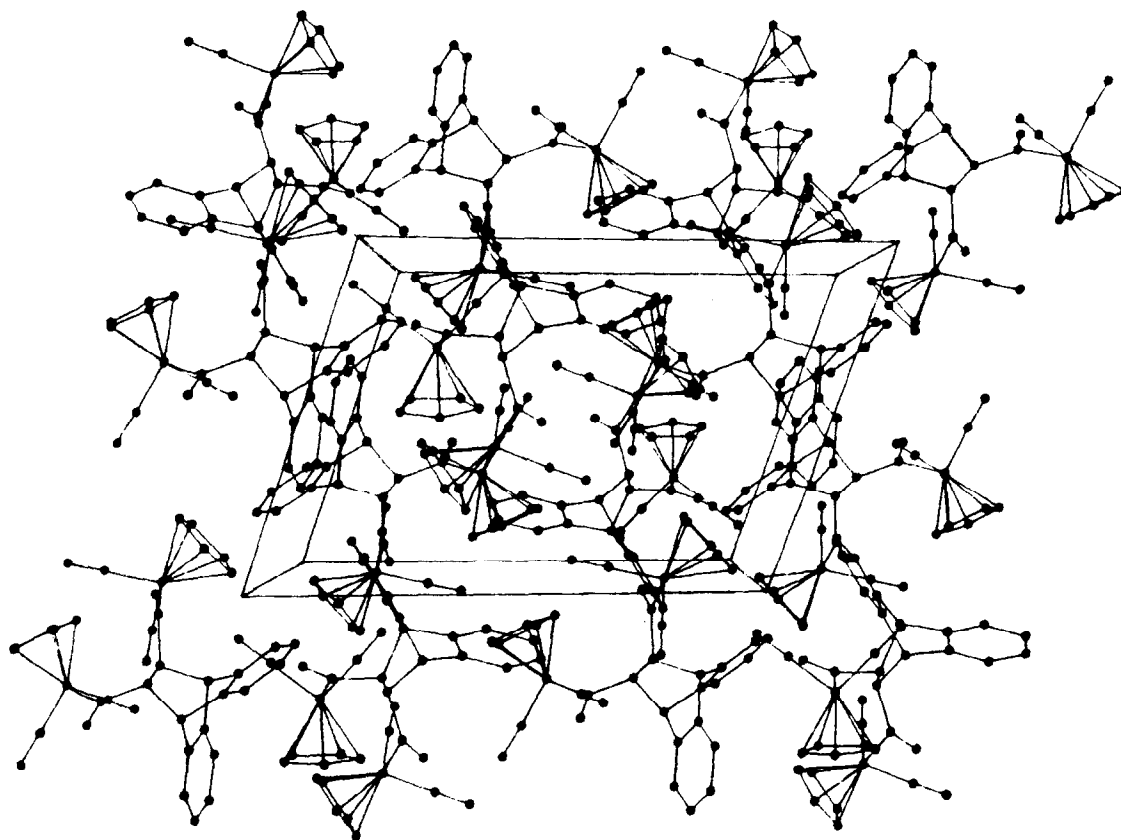


Fig. 2. Projection of the unit cell of **2** along the *c*-axis.

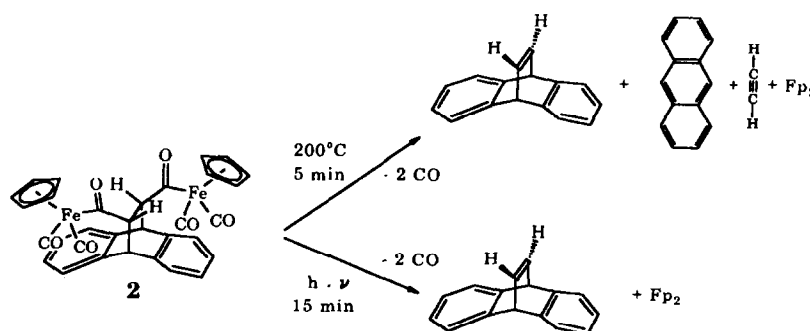
probable. Our results are in accordance with the assumption that this intermediate is sensitive to light and heat, and an immediate elimination of $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ takes place.

Especially for the photolytic pathway, a participation of radicals must be considered. Lappert and coworkers [25] studied the UV-photolysis of pentacarbonylmanganese acyl and alkyl complexes at -30°C . Alkyl and pentacarbonylmanganese radicals resulting from homolytic cleavage of the Mn–C bond were successfully trapped. Thus, the formation of ethenoanthracene may well proceed via radicals in a solvent cage.

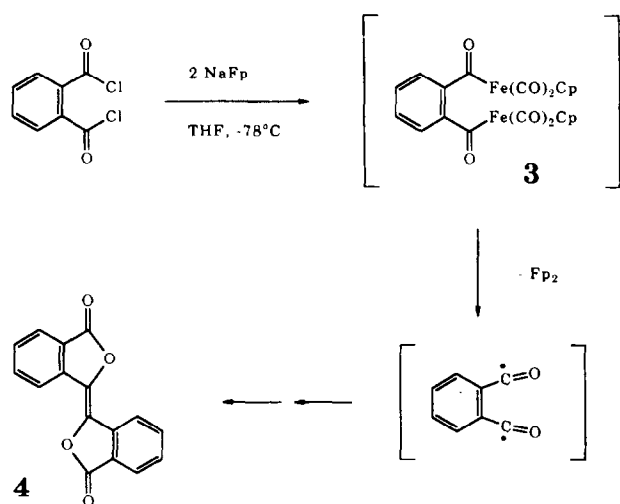
While the photolytic cleavage ends at the olefin, in

the case of the thermolysis the retro-Diels–Alder reaction follows. The enthalpy of decomposition observed in the differential thermal analysis must be interpreted as the sum of both steps.

We would like to point out that by the conversion of **1** to **2** and its photolysis to ethenoanthracene, we have transformed a *trans*-dicarboxylic acid into an olefin. The reaction conditions are very mild. Reactions conventionally used for this transformation have been reviewed [26]. Most use strong oxidizing conditions, incompatible with many functional groups, such as lead tetraacetate, PbO_2 , CuO , $\text{K}_3\text{Fe}(\text{CN})_6$, anodic oxidation or the thermolysis of the *t*-butyl peresters [27]. Lead



Scheme 4.



Scheme 5.

tetraacetate had been used for the synthesis of ethenoanthracene from the isomeric ethanoanthracene dicarboxylic acids [21]. Even the milder elimination of CO and CO₂ from cyclic anhydrides by organometallic reagents such as Fe₂(CO)₉ or Ni(CO)₂(PPh₃)₂ still requires 80–200°C [28]. As shown here, the conversion of a 1,2-dicarboxylic acid to the bis(acyl) complex and its photolysis may thus be an interesting alternative using very mild conditions for olefin creation.

Hunter and Szigety [29] observed that the reaction of phthaloyl chloride with two equivalents of Na[Fe(CO)₂Cp] results in near quantitative formation of [Fp]₂. They did not report on the organic product that should arise from phthaloyl chloride. By repeating this experiment we found the yellow fluorescent compound to be (E)-[1,1']-biisobenzofuranylidene-3,3'-dione (*trans*-bi-phthalyl) (**4**). This is formed in about 50% yield and has previously been obtained by various routes [30]. The probable method of formation is shown in Scheme 5.

The organometallic compound **3** could not be isolated. The elimination of [Fe(CO)₂Cp]₂ occurs at much milder conditions than from **2**. Compound **4** was identified by its IR, ¹H- and ¹³C-NMR data [30].

3. Experimental

Reactions were performed under dried (molecular sieve 4 Å) argon using Schlenk techniques and dried solvents (THF, toluene: Na/Ph₂CO, CH₂Cl₂: CaH₂). Solid/liquid mixtures were separated using a centrifuge (Macrofuge 6-4, Heraeus-Christ) and PE-inserts for Schlenk tubes. The signals of the deuterated solvent were used as internal reference for ¹H- and ¹³C-NMR spectroscopy (resp. residual solvent protons). Differential thermal analysis in a nitrogen stream was performed in collaboration with the Institut für Pharmazeutische

Technologie, Universität München using a Mettler TC11 with TA4000-processor. C, H analyses were performed with a Heraeus VT.

3.1. 9,10-Ethanoanthracene-*trans*-11,12-dicarboxylic acid dichloride (**1**)

13 g (72.9 mmol) of anthracene were dissolved in 100 ml of toluene. 11 ml (15.57 g, 101.8 mmol) of fumaroyl chloride were added and the mixture was heated under reflux for 24 h. Toluene was evaporated from the dark red solution. The resulting oil was extracted with 250 ml of boiling hexane, which was then filtered hot through Celite, predried in vacuo at 200°C. Upon cooling a colourless powder precipitated, which was washed with hexane and dried in vacuo. 8.7 g (26.3 mmol) 36% yield. Anal. Found: C, 65.73; H, 4.22. C₁₈H₁₂Cl₂O₂ (*M* = 331.2) Calc.: C, 65.28; H, 3.65%. IR (cm⁻¹, hexane): 1749 ν_(C=O). ¹H-NMR (δ, 90MHz, CCl₄/TMS): 3.73s, br (2H, 11,12-H), 4.89s, br (2H, 9,10-H), 7.09–7.41m (8H, C_{ar}).

3.2. 9,10-Ethanoanthracene-*trans*-11,12-bis-[C(O)-Fe(C₅H₅)(CO)] (**2**)

750 mg (2.12 mmol) of [Fe(CO)₂Cp]₂ in 20 ml of THF were reduced with 1.5 ml of 0.7% sodium amalgam. The solution of the anion was separated and carefully cooled to -78°C. 702 mg (2.12 mmol) of the bis(acid chloride) **1** were rapidly weighed in air and added as a solid. The reaction mixture was stirred for 1 h at -78°C and for 30 min at room temperature. Removal of the THF in vacuo yielded an orange-red oil which was extracted three times, each with 10 ml of CH₂Cl₂. The combined extracts were evaporated. The resulting sticky solid was converted to a powder by freezing three times in liquid nitrogen with 15 ml each of hexane, bringing to room temperature and discarding the supernatant. The powder was extracted with 30 ml of hexane/CH₂Cl₂ 1:1, the extract was evaporated and again washed with 10 ml of hexane.

Yellow powder, 1.06 g (1.72 mmol) 81% yield, decomp. [Fe(CO)₂Cp]₂ at 189°C (differential thermal analysis) Anal. Found: C, 62.61; H, 3.80. C₃₂H₂₂Fe₂O₆ (*M* = 614.2) Calc.: C, 62.58; H, 3.61%. IR (cm⁻¹, KBr): 2012vs, 1950vs, 1648s, 1484vw, 1468w, 1459w, 1434vw, 1417vw. ¹H-NMR (δ, 270 MHz, acetone-*d*₆) = 2.04: 3.65 (2H, ψt, *J*/0.9 Hz, 11,12-H), 4.95 (2H, ψt, *J*/0.9 Hz, 9,10-H), 5.00 (10H, s, Cp), 7.35–7.38 (2H, m), 7.20–7.24 (2H, m) (1,5-H/4,6-H), 7.01–7.12 (4H, m, 2,3,6,7-H). ¹³C-NMR (δ, 67.9 MHz, acetone-*d*₆): 252.8 (acyl), 216.1, 216.2 (Fe(CO)₂), 141.4, 145.1 (quart. C_{ar}), 126.3, 126.7 (β-C), 123.4, 125.6 (α-C), 87.9 (Cp, ¹*J* = 180.7 Hz), 75.0 (C-9,10, ¹*J* = 142.3 Hz), 46.5 (C-11,12, ¹*J* = 140.1 Hz).

Table 3
Crystal data and structure refinement for **2**

Empirical formula	C ₃₂ H ₂₂ Fe ₂ O ₆
Formula weight	614.22
Temperature (K)	293(2)
Diffractometer	Siemens R3
Radiation	Graphite monochromated
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	11.105(2)
<i>b</i>	15.091(4)
<i>c</i>	17.738(5)
α (°)	97.67(2)
β	104.04(2)
γ	106.40(2)
Volume	2700.6(12) Å ³
Z	4
Density (calculated)	1.511 Mg m ⁻³
Absorption coefficient	1.119 mm ⁻¹
<i>F</i> (000)	1256
Crystal size	0.90 × 0.70 × 0.20 mm ³
θ range for data collection	2.01 to 22.55°
Index ranges	−11 ≤ <i>h</i> ≤ 11, −16 ≤ <i>k</i> ≤ 16, −17 ≤ <i>l</i> ≤ 19
Reflections collected	12117
Independent reflections	7067 [<i>R</i> _{int} = 0.0407]
Absorption correction	ψ-scan
Max. and min. transmission	0.666 and 0.481
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	7066/0/722
Goodness-of-fit on <i>F</i> ²	1.049
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0473, <i>wR</i> ₂ = 0.1189
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0612, <i>wR</i> ₂ = 0.1294
Largest difference peak and hole	0.604 and −0.536 e Å ⁻³

Crystals suitable for X-ray structural analysis were obtained by slow cooling of a saturated solution of **2** in acetone to −28°C. After several weeks large crystals (yellow plates) were obtained.

3.3. X-ray crystal structure of **2**

Crystal data and relevant structure refinement parameters are given in Table 3. The structure was solved using the program XS from the program package SHELXTL-PLUS (Release 4.11/V, Siemens XRD, Madison, 1989) using direct methods. Early refinement was performed using the program XLS from the same package (on a MICROVAX II/VMS computer); the final refinement was done on a COMPAQ Prolinea MT 4/66 personal computer with the program SHELXL-PC (G.M. Sheldrick, 1993). This program uses refinement on *F*², while the former was based on *F*. The *R* value *wR*₂ refers to the *F*² refinement, while the (lower) *R*₁ value refers to the conventional refinement on *F*. The hydrogen atoms were positioned geometrically and refined using a riding model with an isotropic temperature

factor calculated from the equivalent isotropic temperature factor of the corresponding carbon atom using multiplication by 1.2 or 1.3, depending on the hybridization of C.

3.4. Reaction of Na[Fe(CO)₂Cp] with phthaloyl chloride

[Fe(CO)₂Cp]₂ (1 g, 2.82 mmol) in 10 ml of THF was reduced by vigorous stirring with 2 ml of 1% sodium amalgam for 2.5 h at room temperature. After cooling to −78°C the solution of Na[Fe(CO)₂Cp] was transferred via a cannula to 0.36 ml (2.5 mmol) of phthaloyl chloride in 3 ml of THF. The mixture was stirred for 30 min at −78°C, warmed up to room temperature and stirred for another 2 h. After removal of THF in vacuo, [Fe(CO)₂Cp]₂ was extracted with diethylether. The residue was put on a silica gel column. Elution with pentane and then dichloromethane gave a solution of **4** in CH₂Cl₂, which was evaporated in vacuo.

Yield of **4**: 160 mg, 0.6 mmol (48%). MS [*m/z*]: 264 (M).

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