Synthesis of a new iron tricarbonyl (η^4) -α-pyrone complex by reaction of iron vinyldiketone complexes with methyllithium under a CO atmosphere

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Abstract

The reaction between a new (η^4)-trans-1,2-α,β-unsaturated diketone-Fe(CO)$_3$ complex derived from trans-1,2-dibenzoylethylene or the corresponding (η^2)-Fe(CO)$_4$ complex with MeLi under a CO atmosphere leads to the formation of an (η^4)-α-pyrone-Fe(CO)$_3$ complex 3 via the respective (η^4)-ketene-Fe (O) complex. The structure of the complex was determined by mass spectrometry, IR, ^{1}H and ^{13}C NMR spectroscopies and was confirmed by X-ray diffraction studies. © 1997 Elsevier Science S.A.

1. Introduction

We are currently interested in preparing vinylketene-Fe (O) complexes which are readily available as stable yet reactive starting materials, due mainly to the investigations of Richards and Thomas [1], Hill et al. [2], Saberi and Thomas [3], Benyunes and Gibson [4], Morris et al. [5,6], Saberi et al. [7,8] and Alcock et al. [9,10] related to the reactions of alkyllithium with iron tricarbonyl complexes of vinylketones under a carbon monoxide atmosphere.

In our previous work concerning the preparation of novel (η^2), (η^2,η^2) and (η^4)-Fe (O) complexes derived from dibenzylideneacetone [11,12], the Thomas' method has been succesfully applied to the subsequent transformation to vinylketene-Fe (O) complexes.

The purpose of this investigation was to prepare a ketene complex from the (η^2)-trans-1,2-dibenzoylethylene-Fe (O) complex 1, which was reported by Andri-

anov et al. [13]. While preparing complex 1, a new complex was also isolated, namely the (η^4)-trans-1,2-dibenzoylethylene-Fe (O) complex 2. Therefore our interest in these compounds was to bring to light the influence of the supplementary α-positioned C=O group on the course of the reaction.

Here we report the results obtained in the study of the reactivity of the (η^2) and the new (η^4)-trans-1,2-dibenzoylethylene-Fe (O) complexes 1 and 2 toward MeLi under a CO atmosphere (Scheme 1).

2. Results and discussion

2.1. Synthesis of the η^2-trans-1,2-dibenzoylethylene-Fe(CO)$_4$ complex 1 and η^4-trans-1,2-dibenzoylethylene-Fe(CO)$_3$ complex 2

Trans-1,2-dibenzoylethylene reacts with an excess of Fe$_2$(CO)$_9$ in anhydrous THF at room temperature yielding 1 and 2 after 6 h. Silica gel chromatography of the reaction mixture affords complexes 1 and 2 with yields

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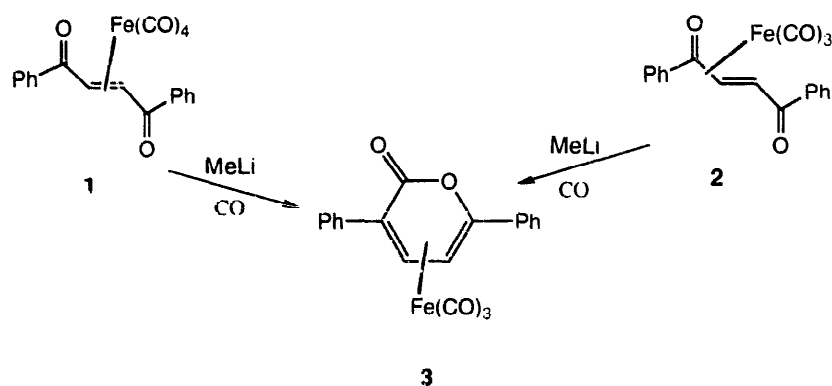
Scheme 1.

of 70% and 17% respectively. The structures of these complexes were assigned spectroscopically and, in the case of **2**, the structure was confirmed by X-ray diffraction studies.

Complex **1**, a yellow solid, exhibited absorption bands in its IR spectrum at 2100, 2023 and 1990 cm^{-1} and a band at ν(CO) 1630 cm^{-1} for an α,β-unsaturated CO group. The ^{1}H NMR spectrum (200 MHz, CDCl$_3$) showed the signals at δ 8.2–7.5 ppm for aromatic protons (10H) and a singlet (2H) at δ 5.1 ppm corresponding to vinylic protons. The ^{13}C NMR (50 MHz, CDCl$_3$) spectrum exhibited signals at δ 204 ppm attributed to M–CO groups, at δ 197 ppm the peak for a nonmetallic CO group, at δ 137–126 ppm for the aromatic carbons, and at δ 48 ppm for vinylic carbons. The mass spectrum displayed the molecular ion at m/z 404, which matches the expected molecular weight for **1**, and the peaks for successive loss of four CO groups.

For the new complex **2**, obtained as an orange solid, the IR spectrum showed three absorption bands ν(CO) at 2070, 2010 and 1998 cm^{-1} and at 1642 cm^{-1} for a nonmetallic CO group. The ^{1}H NMR spectrum (200

MHz, CDCl$_3$) revealed at δ 8.2–7.4 ppm the signals for aromatic protons (10H), at δ 6.9 ppm a doublet (1H, $J = 7.7$ Hz) and at δ 3.5 ppm another doublet (1H, $J = 7.7$ Hz) corresponding to the vinylic protons. The ^{13}C NMR (50 MHz, CDCl$_3$) spectrum displayed signals at δ 209.1–202.5 ppm for the carbons of M–CO groups, at δ 196 ppm for nonmetallic CO groups, at δ 145–127 ppm for aromatic carbons, and at δ 74 and 52 ppm for vinylic carbons. The mass spectrum showed a molecular ion with m/z of 376, and the peaks for successive loss of three CO groups.

The structure of complex **2** was finally determined by X-ray diffraction. Its ORTEP projection appears in Fig. 1, some selected bond distances (Å) and bond angles (degrees) are listed in Table 1.

The asymmetric unit consists of two crystallographic independent molecules. The fragments C(1)–C(2)–C(3)–C(4) and C(21)–C(22)–C(23)–C(24) are fairly planar (0.04 Å) in both molecules. The bond distance between C(1)–C(2) [1.485(11) Å] is larger than C(3)–C(4) [1.427(11) Å], indicating the coordination to iron. The phenyl groups [C(5)–C(10) and C(11)–C(16)] form
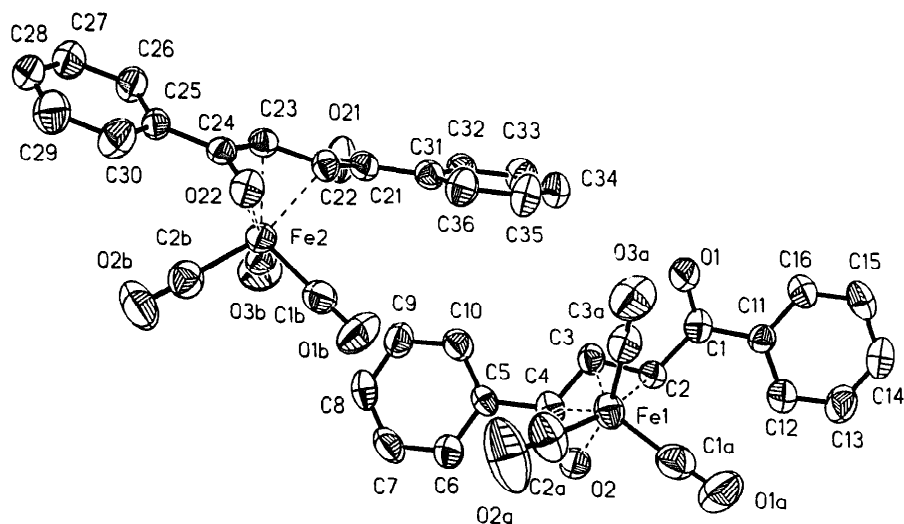
Fig. 1. The molecular structure and atom numbering scheme for **2**.

an angle of 11.8° and 14.5° respectively, with the former and phenyl groups [C(25)–C(30) and C(31)–C(36)] making an angle of 11.7° and 14.3° with the second moiety. This compound can be described by a

Table 1
Selected bond lengths (Å) and bond angles (°) for compound 2

Fe(1)–C(1A)	1.809(9)	Fe(2)–C(1B)	1.822(8)
Fe(1)–C(2A)	1.798(11)	Fe(2)–C(2B)	1.812(10)
Fe(1)–C(3A)	1.772(8)	Fe(2)–C(3B)	1.778(7)
Fe(1)–O(2)	2.015(5)	Fe(2)–O(22)	2.012(4)
Fe(1)–C(2)	2.097(7)	Fe(2)–C(22)	2.089(7)
Fe(1)–C(3)	2.045(6)	Fe(2)–C(23)	2.040(6)
Fe(1)–C(4)	2.111(6)	Fe(2)–C(24)	2.119(6)
O(1A)–C(1A)	1.137(11)	O(1B)–C(1B)	1.144(10)
O(2A)–C(2A)	1.145(14)	O(2B)–C(2B)	1.142(13)
O(3A)–C(3A)	1.146(9)	O(3B)–C(3B)	1.145(9)
O(1)–C(1)	1.228(9)	O(21)–C(21)	1.233(8)
O(2)–C(4)	1.293(8)	O(22)–C(24)	1.313(7)
C(1)–C(2)	1.485(11)	C(21)–C(22)	1.463(10)
C(1)–C(11)	1.493(11)	C(21)–C(31)	1.480(12)
C(2)–C(3)	1.416(11)	C(22)–C(23)	1.415(10)
C(3)–C(4)	1.427(11)	C(23)–C(24)	1.422(10)
C(4)–C(5)	1.479(11)	C(24)–C(25)	1.473(11)
C(1A)–Fe(1)–C(2A)	101.9(4)	C(1B)–Fe(2)–C(2B)	103.6(4)
C(1A)–Fe(1)–C(3A)	97.5(3)	C(1B)–Fe(2)–C(3B)	97.3(3)
C(2A)–Fe(1)–C(3A)	89.0(4)	C(2B)–Fe(2)–C(3B)	88.5(4)
C(1A)–Fe(1)–O(2)	100.6(3)	C(1B)–Fe(2)–O(22)	98.8(3)
C(2A)–Fe(1)–O(2)	91.8(3)	C(2B)–Fe(2)–O(22)	92.2(3)
C(3A)–Fe(1)–O(2)	161.2(3)	C(3B)–Fe(2)–O(22)	163.2(2)
C(1A)–Fe(1)–C(2)	94.1(3)	C(1B)–Fe(2)–C(22)	94.5(3)
C(2A)–Fe(1)–C(2)	162.6(3)	C(2B)–Fe(2)–C(22)	160.8(3)
C(3A)–Fe(1)–C(2)	95.7(3)	C(3B)–Fe(2)–C(22)	95.4(3)
O(2)–Fe(1)–C(2)	78.4(2)	O(22)–Fe(2)–C(22)	78.7(2)
C(1A)–Fe(1)–C(3)	133.4(4)	C(1B)–Fe(2)–C(23)	133.5(3)
C(2A)–Fe(1)–C(3)	123.0(4)	C(2B)–Fe(2)–C(23)	120.9(3)
C(3A)–Fe(1)–C(3)	95.2(3)	C(3B)–Fe(2)–C(23)	96.6(3)
O(2)–Fe(1)–C(3)	68.7(2)	O(22)–Fe(2)–C(23)	68.7(2)
C(2)–Fe(1)–C(3)	40.0(3)	C(22)–Fe(2)–C(23)	40.1(3)
C(1A)–Fe(1)–C(4)	135.2(3)	C(1B)–Fe(2)–C(24)	134.2(3)
C(2A)–Fe(1)–C(4)	93.6(4)	C(2B)–Fe(2)–C(24)	92.2(3)
C(3A)–Fe(1)–C(4)	124.8(3)	C(3B)–Fe(2)–C(24)	126.2(3)
O(2)–Fe(1)–C(4)	36.4(2)	O(22)–Fe(2)–C(24)	36.9(2)
C(2)–Fe(1)–C(4)	69.9(3)	C(22)–Fe(2)–C(24)	70.3(3)
C(3)–Fe(1)–C(4)	40.1(3)	C(23)–Fe(2)–C(24)	39.9(3)
Fe(1)–C(1A)–O(1A)	176.0(9)	Fe(2)–C(1B)–O(1B)	177.4(8)
Fe(1)–C(2A)–O(2A)	179.5(7)	Fe(2)–C(2B)–O(2B)	177.9(6)
Fe(1)–C(3A)–O(3A)	177.6(8)	Fe(2)–C(3B)–O(3B)	177.9(7)
Fe(1)–O(2)–C(4)	75.8(3)	Fe(2)–O(22)–C(24)	75.9(3)
O(1)–C(1)–C(2)	120.3(7)	O(21)–C(21)–C(22)	119.9(7)
O(1)–C(1)–C(11)	119.5(7)	O(21)–C(21)–C(31)	118.8(7)
C(2)–C(1)–C(11)	120.2(6)	C(22)–C(21)–C(31)	121.2(6)
Fe(1)–C(2)–C(1)	119.8(4)	Fe(2)–C(22)–C(21)	120.1(5)
Fe(1)–C(2)–C(3)	68.1(4)	Fe(2)–C(22)–C(23)	68.1(4)
C(1)–C(2)–C(3)	119.6(6)	C(21)–C(22)–C(23)	120.5(5)
Fe(1)–C(3)–C(2)	72.0(3)	Fe(2)–C(23)–C(22)	71.8(4)
Fe(1)–C(3)–C(4)	72.4(4)	Fe(2)–C(23)–C(24)	73.0(4)
C(2)–C(3)–C(4)	116.0(6)	C(22)–C(23)–C(24)	117.4(5)
Fe(1)–C(4)–O(2)	67.7(3)	Fe(2)–C(24)–O(22)	67.1(3)
Fe(1)–C(4)–C(3)	67.4(4)	Fe(2)–C(24)–C(23)	67.0(3)
O(2)–C(4)–C(3)	114.8(7)	O(22)–C(24)–C(23)	113.4(6)
Fe(1)–C(4)–C(5)	132.7(5)	Fe(2)–C(24)–C(25)	133.9(5)
O(2)–C(4)–C(5)	121.7(6)	O(22)–C(24)–C(25)	120.4(6)
C(3)–C(4)–C(5)	123.4(6)	C(23)–C(24)–C(25)	126.2(5)

Table 2
Selected bond lengths(Å) and bond angles(°) for compound 3

|			
Fe(1)–C(1A)	1.801(7)	Fe(2)–C(1B)	1.793(7)
Fe(1)–C(2A)	1.777(7)	Fe(2)–C(2B)	1.790(7)
Fe(1)–C(3A)	1.808(8)	Fe(2)–C(3B)	1.823(8)
Fe(1)–C(1)	2.122(7)	Fe(2)–C(21)	2.115(7)
Fe(1)–C(2)	2.078(6)	Fe(2)–C(22)	2.059(7)
Fe(1)–C(3)	2.067(6)	Fe(2)–C(23)	2.057(7)
Fe(1)–C(4)	2.126(6)	Fe(2)–C(24)	2.133(6)
O(1A)–C(1A)	1.140(9)	O(1B)–C(1B)	1.142(8)
C(2A)–O(2A)	1.144(9)	O(2B)–C(2B)	1.136(9)
C(3A)–O(3A)	1.146(11)	O(3B)–C(3B)	1.131(10)
O(1)–C(1)	1.414(8)	O(21)–C(21)	1.440(7)
O(1)–C(5)	1.371(9)	O(21)–C(25)	1.377(6)
O(2)–C(5)	1.215(9)	O(22)–C(25)	1.206(8)
C(1)–C(2)	1.427(10)	C(21)–C(22)	1.433(9)
C(1)–C(12)	1.490(10)	C(21)–C(32)	1.478(8)
C(2)–C(3)	1.395(11)	C(22)–C(23)	1.378(7)
C(3)–C(4)	1.446(9)	C(23)–C(24)	1.449(8)
C(4)–C(5)	1.468(11)	C(24)–C(25)	1.459(9)
C(4)–C(6)	1.502(10)	C(24)–C(26)	1.482(7)
C(1A)–Fe(1)–C(2A)	96.1(3)	C(1B)–Fe(2)–C(2B)	96.2(3)
C(1A)–Fe(1)–C(3A)	91.5(3)	C(1B)–Fe(2)–C(3B)	91.3(3)
C(2A)–Fe(1)–C(3A)	101.4(3)	C(2B)–Fe(2)–C(3B)	101.5(3)
C(1A)–Fe(1)–C(1)	98.4(3)	C(1B)–Fe(2)–C(21)	96.8(3)
C(2A)–Fe(1)–C(1)	88.4(3)	C(2B)–Fe(2)–C(21)	92.1(3)
C(3A)–Fe(1)–C(1)	165.3(3)	C(3B)–Fe(2)–C(21)	163.3(3)
C(1A)–Fe(1)–C(2)	98.0(3)	C(1B)–Fe(2)–C(22)	97.0(3)
C(2A)–Fe(1)–C(2)	127.6(3)	C(2B)–Fe(2)–C(22)	131.6(3)
C(3A)–Fe(1)–C(2)	128.2(3)	C(3B)–Fe(2)–C(22)	124.4(3)
C(1)–Fe(1)–C(2)	39.7(3)	C(21)–Fe(2)–C(22)	40.1(2)
C(1A)–Fe(1)–C(3)	126.3(3)	C(1B)–Fe(2)–C(23)	125.4(3)
C(2A)–Fe(1)–C(3)	133.5(3)	C(2B)–Fe(2)–C(23)	135.3(3)
C(3A)–Fe(1)–C(3)	96.3(3)	C(3B)–Fe(2)–C(23)	93.8(3)
C(1)–Fe(1)–C(3)	69.1(3)	C(21)–Fe(2)–C(23)	69.6(2)
C(2)–Fe(1)–C(3)	39.3(3)	C(22)–Fe(2)–C(23)	39.1(2)
C(1A)–Fe(1)–C(4)	166.5(3)	C(1B)–Fe(2)–C(24)	165.6(3)
C(2A)–Fe(1)–C(4)	96.1(3)	C(2B)–Fe(2)–C(24)	96.7(3)
C(3A)–Fe(1)–C(4)	91.9(3)	C(3B)–Fe(2)–C(24)	92.5(3)
C(1)–Fe(1)–C(4)	76.0(3)	C(21)–Fe(2)–C(24)	76.3(2)
C(2)–Fe(1)–C(4)	69.8(2)	C(22)–Fe(2)–C(24)	69.5(2)
C(3)–Fe(1)–C(4)	40.3(2)	C(23)–Fe(2)–C(24)	40.4(2)
Fe(1)–C(1A)–O(1A)	175.6(6)	Fe(2)–C(1B)–O(1B)	178.7(7)
Fe(1)–C(2A)–O(2A)	175.0(7)	Fe(2)–C(2B)–O(2B)	177.0(8)
Fe(1)–C(3A)–O(3A)	175.3(7)	Fe(2)–C(3B)–O(3B)	178.1(6)
C(1)–O(1)–C(5)	115.3(5)	C(21)–O(21)–C(25)	113.9(5)
Fe(1)–C(1)–O(1)	107.1(4)	Fe(2)–C(21)–O(21)	108.2(3)
Fe(1)–C(1)–C(2)	68.5(4)	Fe(2)–C(21)–C(22)	67.8(4)
O(1)–C(1)–C(2)	116.9(5)	O(21)–C(21)–C(22)	115.6(5)
Fe(1)–C(1)–C(12)	121.8(4)	Fe(2)–C(21)–C(32)	122.7(5)
O(1)–C(1)–C(12)	111.5(6)	O(21)–C(21)–C(32)	110.6(5)
C(2)–C(1)–C(12)	123.8(6)	C(22)–C(21)–C(32)	125.1(5)
Fe(1)–C(2)–C(1)	71.8(3)	Fe(2)–C(22)–C(21)	72.0(4)
Fe(1)–C(2)–C(3)	69.9(3)	Fe(2)–C(22)–C(23)	70.4(4)
C(1)–C(2)–C(3)	114.6(6)	C(21)–C(22)–C(23)	115.7(5)
Fe(1)–C(3)–C(2)	70.8(3)	Fe(2)–C(23)–C(22)	70.5(4)
Fe(1)–C(3)–C(4)	72.1(3)	Fe(2)–C(23)–C(24)	72.6(4)
C(2)–C(3)–C(4)	115.7(7)	C(22)–C(23)–C(24)	115.5(5)
Fe(1)–C(4)–C(3)	67.7(3)	Fe(2)–C(24)–C(23)	67.0(3)
Fe(1)–C(4)–C(5)	103.0(4)	Fe(2)–C(24)–C(25)	104.5(4)
C(3)–C(4)–C(5)	116.6(6)	C(23)–C(24)–C(25)	115.2(5)
Fe(1)–C(4)–C(6)	119.1(4)	Fe(2)–C(24)–C(26)	120.1(5)
C(3)–C(4)–C(6)	120.1(7)	C(23)–C(24)–C(26)	121.2(5)
C(5)–C(4)–C(6)	118.3(6)	C(25)–C(24)–C(26)	117.5(5)
O(1)–C(5)–O(2)	118.5(7)	O(21)–C(25)–O(22)	114.4(6)
O(1)–C(5)–C(4)	115.6(6)	O(21)–C(25)–C(24)	116.9(5)
O(2)–C(5)–C(4)	125.9(7)	O(22)–C(25)–3C(24)	128.7(5)
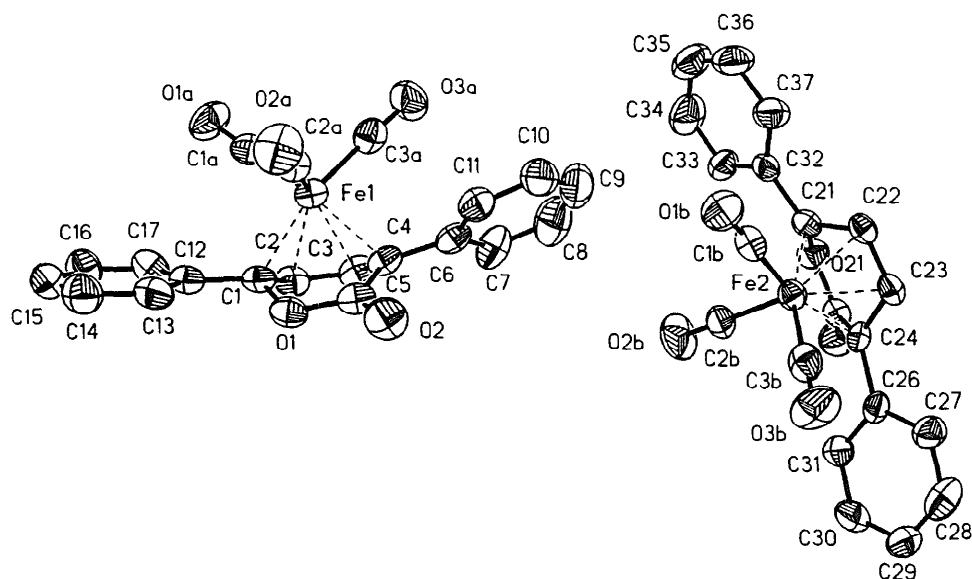
Fig. 2. The molecular structure and atom numbering scheme for 3. The plots were made at 40% probability.

distorted trigonal bipyramidal if we consider C(2)–C(3) and C(4)–O(2) bonds as being one site of coordination, so that the metal atom is five coordinated. This is consistent with a η^4-coordination of the O(2)–C(4)–C(3)–C(2) fragment of the dibenzoylethylene ligand to a Fe(CO)$_3$. The bond distance for C(1)–O(1) is 1.228 Å whereas that for C(4)–O(2) is 1.293 Å, confirming the coordination of the latter CO group.

It must be pointed out that when complex 1 is refluxed in THF during 1 h, the complex 2 is obtained with a yield of 17% along with 52% of an organic compound, isolated as white crystals, which was characterized as 1,2-dibenzoylethane according to its physical constants and spectroscopic data.

2.2. Reaction of complexes 1 and / or 2 with MeLi / CO: formation of the (η^4)-3,6-diphenyl-α-pyrone–Fe(CO)$_3$ complex 3

Treatment of complex 1 or 2 with methyllithium under a carbon monoxide atmosphere led to a new complex 3. The complex 3, isolated as a dark-red solid

in 20% yield, proved to be the (η^4)-3,6-diphenyl-α-py-rone–Fe(CO)$_3$ complex, based on its spectroscopic data. In addition the structure was confirmed by an X-ray diffraction study. The IR spectrum displayed absorption bands ν(CO) at 2055, 2000 and 1985 and at 1732 for a (CO) lactonic group. The ^{1}H NMR spectrum (200 MHz, CDCl$_3$) showed, besides those signals for two phenyl groups at δ 7.6–7.2 (10H), signals at δ 6.9 and 6.2 ppm (2H, $J = 6.0$ Hz) as two doublets arising from the protons of the coordinated dienic system. The ^{13}C NMR (50 MHz, CDCl$_3$) spectrum revealed a signal arising from a CO group at δ 169.1 ppm. In addition the aromatic carbons can be observed at δ 136.3–123.1 ppm as well as four signals at δ 101.9, 86.7, 71.7 and 67.1 ppm which correspond to the dienic system.

The structure of this complex was finally confirmed by an X-ray diffraction study. Fig. 2 represents an ORTEP projection of the complex. Selected bond distances (Å) and angles (degrees) are listed in Table 2. As in complex (1), the asymmetric unit consists of two crystallographic independent molecules.

The six-membered ring of the α-β, γ-δ-unsaturated
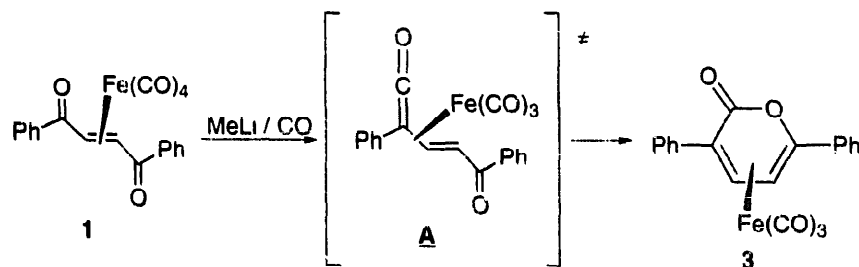
Scheme 2.

lactone can be considered as in a quasi-boat conformation. The coordination fragment C(1)–C(2)–C(3)–C(4) is fairly planar and makes an angle of 39.5(5)° with the moiety O(1)–C(1)–C(5)–C(4) in one molecule while the angle in the other molecule [C(21)–C(22)–C(23)–C(24) with C(21)–O(21)–C(25)–C(24)] is 41.2(1)°. This compound can be described as a distorted trigonal bipyramidal which is consistent with an η^4-coordination of the C(1)–C(2)–C(3)–C(4) moiety ligand to a Fe(CO)$_3$ fragment. By the same token C(1)–C(2) [1.427(10) Å], C(3)–C(4) [1.446(9) Å] and C(21)–C(22) [1.433(9) Å], C(23)–C(24) [1.449(8) Å] bonds are larger than a normal C=C double bond (1.33 Å) owing to the coordination with the Fe(CO)$_3$ fragment.

2.2.1. Formation of 3 from 1 and / or 2

A mechanism which would account for the formation of complex 3 is given in Scheme 2.

It is well known that treatment of η^2-complexes of α,β-unsaturated ketones with MeLi/CO leads to stable η^4-vinylketene complexes [12]. In this case, the ketene $\overline{A}$ intermediate could not be isolated and possibly via a simple six electron electrocyclic ring closure [14] afforded the η^4-α-pyrone–Fe(CO)$_3$ complex 3.

3. Conclusion

We report for the first time the formation of a new (η^4)-α-pyrone–Fe(CO)$_3$ complex 3 from a ring-closure reaction of a likewise new (η^4-trans-1,2-α,β-unsaturated diketone–Fe(CO)$_3$ complex or the corresponding (η^2)–Fe(CO)$_4$ complex with MeLi under a CO atmosphere. Ketene intermediates are suggested for these ring closures. Iron complexes similar to 3 have been already synthesized by other methods [15].

4. Experimental section

4.1. General methods

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 300S spectrometer and IR spectra were recorded on a Perkin-Elmer 283 B or 1420 spectrometer. The electronic impact (EI) ionization mass spectra were acquired on a JEOL JMS-AX505 HA mass spectrometer operated in the positive ion mode. The acquisition conditions were ion source temperature 230°C, ionization energy 70 eV, emission current 0.14 μA and ionization current 100 μA. Melting points were measured using a Mel-Temp II apparatus and are uncorrected. Column chromatography was performed with Merck silica gel (70–230 mesh) using ethyl acetate:hexane in different ratios as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under nitrogen at-

mosphere in carefully dried glassware. THF was distilled from sodium-benzophenone under an argon atmosphere.

4.1.1. Synthesis of the (η^2)-trans-1,2-dibenzoylethylene–Fe(CO)$_4$ complex 1 and (η^4)-trans-1,2-dibenzoylethylene–Fe(CO)$_3$ complex 2 of η^4,η^4-1

A solution of trans-1,2-dibenzoylethylene (3.78 g, 16 mmol) in anhydrous THF was treated with Fe$_2$(CO)$_9$ (8.74 g, 24 mmol) under reflux for 6 h. After reaction was completed, the solvent was evaporated under vacuum and the mixture reaction chromatographed on silica gel. Elution with hexane/ethyl acetate in a 98:2 ratio gave 1 (70%) and 2 (17%).

Complex 1: mp, 117°C; IR (KBr): ν(CO) 2070, 2015, 1995 cm^{-1}, ν(CO) 1630 cm^{-1}. ^{1}H NMR (200 MHz, CDCl3): δ 8.18–8.05 (m, 4H, Ar), 7.54–7.01 (m, 6H, Ar), 5.06 (s, 2H, vinylic Hs); ^{13}C NMR (50 MHz, CDCl$_3$): δ 204.5 (M–CO), 196.6 (CO), 137.1, 133.1, 129.1, 128.8, 128.6, 128.0, 127.1 (Ar), 48.6 (vinylic Cs); EI-MS, 404 (M$^+$), 376 (M$^+$–CO), 348 (M$^+$–2CO), 320 (M$^+$–3CO), 292 (M$^+$–4CO).

Complex 2: mp, 125°C; IR (KBr): ν(CO) 2100, 2030, 2000 cm^{-1}, ν(CO) 1642 cm^{-1}. ^{1}H NMR (200 MHz, CDCl3): δ 8.15 (d, 2H, J = 6.4 Hz, Ar), 8.03 (d, 2H, J = 6.4 Hz, Ar), 7.64–7.50 (m, 6H, Ar), 6.88 (d, 1H, J = 7.7 Hz, vinylic H), 3.48 (d, 1H, J = 7.7 Hz, vinylic H); ^{13}C NMR (50 MHz, CDCl3): δ 209.1, 205.4 (M–CO), 195.8 (CO), 144.5, 137.2, 133.2, 132.5, 129.1, 128.8, 127.5, 127.2 (Ar), 73.4, 51.8 (vinylic Cs). EI-MS, 376(M$^+$), 348 (M$^+$–CO), 320 (M$^+$–2CO), 292 (M$^+$–3CO).

4.1.2. Formation of the (η^4)-3,6-diphenyl-α-pyrone–Fe(CO)$_3$ complex 3

A solution of complex 1 or 2 (1 g, 2.7 mmol) was treated with methyllithium under a carbon monoxide atmosphere at -78°C during 1 h, and then allowed to warm at room temperature with stirring for 18 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel giving 3 in 20% yield.

Complex 3: mp, 155°C; IR (KBr): ν(CO) 2055, 2000, 1985 cm^{-1}, ν(lactonic CO) 1732 cm^{-1}. ^{1}H NMR (200 MHz, CDCl3): 7.6–7.5 (m, 10H, Ar), 6.9 (d, 1H, J = 6 Hz, vinylic H), 6.2 (d, 1H, J = 6 Hz, vinylic H); ^{13}C NMR (50 MHz, CDCl3): δ 169.1 (CO), 136.3, 135.6, 128.9, 128.6, 128.4, 128.0, 123.1 (Ar), 71.7, 67.1 (vinylic Cs).

4.1.3. X-ray data collection, structure solution and refinements for 2 and 3

The single crystals of complex 2 were grown by slow evaporation from a hexane:dichloromethane solution to 0°C as orange regular crystals. For 3, crystals were grown by slow evaporation from a hexane:dichloromethane solution to 0°C as dark-red prismatic crystals.

Table 3
Crystal data and refinement details for compounds 2 and 3

	Compound 2	Compound 3
Formula	$C_{10}H_{12}O_5Fe$	$C_{20}H_{12}O_5Fe$
M_w	752.3	388.1
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	7.461(1)	6.614(1)
b (Å)	15.120(2)	13.547(2)
c (Å)	16.261(3)	20.343(2)
α (°)	109.91(1)	108.81(1)
β (°)	90.74(1)	91.523(1)
γ (°)	94.48(2)	100.856(1)
V (Å^3)	1717.9(5)	1686.9(5)
Z	4	4
D_c (g/cm^3)	1.454	1.528
μ (cm^{-1})	9.03	9.2
F (000)	768	792
Diffractometer	Siemens P4	Siemens p4
Radiation	Mo Kα	Mo Kα
Scan type	ω-2θ	ω-2θ
Scan range (Å)	$1.5 \le \theta \le 25$	$1.5 \le \theta \le 25$
Data collected	6369	6387
Data used (criterion)	3057 ($F \ge 4.0\sigma(F)$)	3359 ($F \ge 4.0\sigma(F)$)
$R(R_w)$ (%)	6.31 (6.50)	5.42 (5.06)
l.s. parameters	452	236
GOF	1.22	1.17

A crystal summary is given in Table 3. The crystal dimensions were 0.38 × 0.38 × 0.20 mm for 2 and 0.40 × 0.30 × 0.14 mm for 3. Both compounds were collected at room temperature and all data were corrected for usual Lorentz and polarizations effects [16]. Absorption corrections were applied using semi-empirical method based on psi-scan collection, the max./min. transmissions factors were 0.7345/0.8745 and 0.78267/0.9254 for 2 and 3 respectively. The structures were solved by direct methods [17] to the first atoms and the expansion structures were by Fourier map difference and refined by block-matrix least-squares [17]. All non-hydrogens atoms were refined anisotropically. The hydrogen atoms were located on the Fourier map difference and refined fixed isotropic thermal factor $U = 0.06$ Å. The minimized functions were $\sum w(F_o - F_c)^2$, with $w = [\sigma^2(F_o) + 0.0010(F_o)^2]$ and $w = [\sigma^2(F_o) + 0.0002(F_o)^2]$ for 2 and 3 respectively. Scattering factors were taken from International Tables for X-ray Crystallography (1974, Vol. IV).

4.2. Supplementary materials available

Tables giving all bond lengths (Tables S4, 4a), all bond angles (Tables S5, 5a), fractional coordinates (Ta-

bles S6, S6a), anisotropic thermal parameters (Tables S7, S7a), hydrogen atoms parameters (Tables S8) and structure factors for 2. Tables giving all bond lengths (Tables S9, 9a), all bond angles (Tables S10, 10a) fractional coordinates (Tables S11, S11a), anisotropic thermal parameters (Tables S12, S12a), hydrogen atoms parameters (Tables S13) and structure factors for 3.

Acknowledgements

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