Journal of Organometallic Chemistry, 260 (1984) 105–113
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF COORDINATED CYCLIC POLYOLEFINS * ADDITION OF CARBONYLCARBENES TO TRICARBONYL(CYCLOHEPTATRIENE)IRON AND THE X-RAY STRUCTURE OF TRICARBONYL[(η-5,6,7,8)-2,3-DIPHENYL-4*H*-CYCLOHEPTA[*b*]FURAN]IRON

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(Received August 12th, 1983)

Summary

The copper catalysed reaction of ethyl diazoacetate with tricarbonyl(cycloheptatriene)iron gave the expected 8-ethoxycarbonyl-homotropylidene complex. However, the analogous reaction with azibenzil afforded the unusual oxidized adduct, tricarbonyl[(η-5–8)-2,3-diphenyl-4*H*-cyclohepta[*b*]furan]iron, whose structure was confirmed by a single crystal X-ray diffraction study. In both reactions hexacarbonyl(bicycloheptatrienyl)diiron was obtained.

Introduction

Until recently there were only two reports on the direct cyclopropanation of tricarbonyl(polyene)iron complexes with carbenes. Reger and Gabrielli [2] were the first to describe the successful addition of methylene, generated from the Simmons–Smith reagent, to tricarbonyl(cycloheptatriene)iron (I) [3]. Recently, Taylor reported the addition of dichlorocarbene to I and to a series of cyclic and acyclic polyene complexes using chloroform and potassium t-butoxide [4]. The reluctance of these complexes to react with carbenes was attributed to steric and electronic effects [4]. However, it may also be ascribed to the high affinity of carbenes for the metal center of the complex [5], which competes with reactions at the organic ligand site. Other cyclopropanation reactions of coordinated polyolefins e.g., the thermal decomposition of Δ′-pyrazolines to homotropone complexes [6] and the addition of

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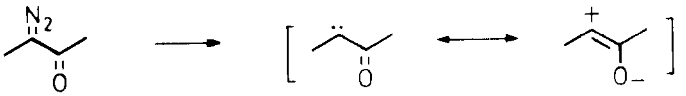
* See ref. 1 for previous paper in this series.

0022-328X/84/$03.00

sulphur ylids to electrophilic hexatriene complexes [7], have also been described recently [8].

To our knowledge there have been no reports on the addition of the highly electrophilic carbonylcarbenes [9] to polyene complexes. Our continued interest in cycloaddition reactions of coordinated cyclic polyolefins [10] led us to examine the



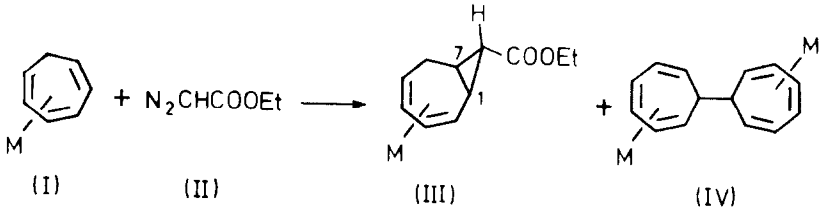
(1)

reaction of I with carbonylcarbenes prepared from the corresponding diazo compounds (eq. 1) and we now describe the results of a study of the copper catalysed addition of ethyl diazoacetate (II) [9,11] and azibenzil (V) to the cycloheptatriene complex I.

Results and discussion

The reactions were relatively straightforward when carried out in excess of cycloheptatriene complex I, which served as the solvent, in the presence of catalytic amounts of the soluble Cu^{II} chelate of salicylaldehyde-aniline Schiff's base [12]. No reaction was observed at room temperature but at ca. 50°C an exothermic reaction commenced with evolution of N_2.

The reaction with ethyldiazoacetate (II) (eq. 2) afforded two irontricarbonyl coordinated products which were separated by column chromatography. The major product was assigned structure III based on the analytical and spectral data. The IR



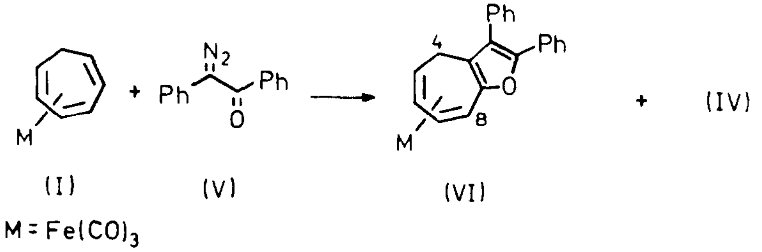
(2)

M = Fe(CO)$_3$

spectrum shows characteristic strong bands of the ligand carbonyls at 2040 and 1965 cm^{-1} and a carbonyl absorption band of a cyclopropane ester at 1710 cm^{-1}. The ^{1}H NMR spectrum of III is diagnostic of an anti condensed cycloheptadiene system [4,10b], since it displays a low field signal, centered at δ 5.06 ppm, of the two inner protons of the diene complex (H(3) and H(4)). The high field region consists of the two terminal proton signals at δ 3.09 (H(5)) and 3.49 (H(2)), the ring methylene protons at δ 2.30, and the three cyclopropane protons at δ 1.2, 1.54 and 1.92 ppm. The ethoxy protons resonate as a triplet, δ 1.23, and a quartet, δ 4.20 (J 7 Hz), as expected. There remains the stereochemical assignment of the carbethoxy group at C(8). Unfortunately we could not directly determine the stereochemistry from our spectral data since only one isomer was isolated, but on the basis of previous reports which established the *exo* configuration for the cyclopropanation product of uncoordinated cycloheptatriene with ethyl diazoacetate [13], it appears reasonable to assign the *exo* configuration to the carbethoxy group of complex III.

The minor product, m.p. 120–122°C, shows a molecular ion at m/e 462 and fragment ions which correspond to the presence of two $Fe(CO)_3$ units. The IR spectrum shows only ligand carbonyl absorptions bands at 2040 and 1970br cm^{-1} and the ^1H NMR spectrum resembles that of cycloheptatriene complex I. This is consistent with the structure IV, and this was confirmed by comparison with the spectral data recently reported [14,3].

The copper catalysed decomposition of a solution of azibenzil (V) and complex I (eq. 3) commenced at 45°C as indicated by evolution of N_2. Two products were



(3)

isolated by chromatography. The minor product was again the dimer IV. However, the major product, obtained in rather low yield, was not the expected ketone IX, since there was no ketone carbonyl absorption in the IR spectrum. Instead, in addition to the ligand CO bands at 2045 and 1975 cm^{-1}, there was a band at 1595 cm^{-1} characteristic of a furan C=C stretching [15]. This together with the elemental analysis and mass spectrum suggested structure VI as the product. The structure of VI was further confirmed from the ^1H and ^{13}C magnetic resonance data. The ^1H NMR spectrum showed the presence of only six nonaromatic protons at δ 2.59 (2H methylene), 3.54 (H(5)), 3.75 (H(8)), 5.40 (H(6) and H(7)) ppm. The ^{13}C NMR showed five non-aromatic carbon resonances at δ 29.39 (C(4)), 55.39. 65.89 (C(5) and C(8)), 91.64, 92.50 (C(6) and C(7)) ppm.

In order to establish the structure of VI unequivocally, a single crystal X-ray analysis was carried out.

Crystal structure analysis of VI

X-ray diffraction data were recorded on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator, employing Mo-K_α radiation (λ 0.71069 Å). The unit-cell dimensions were determined from 2θ measurements of 25 carefully centered reflections and refined by the method of least-squares. Intensity data were collected in the ω-2θ mode with a scan width of $0.9 + 0.3 \tan\theta$ out to $2\theta = 54°$. The scan rate varied according to the detected intensity between 1.2 and 4° min^{-1}. The data were corrected for background counts, variable measuring time and the Lorentz-polarization factor, but not for absorption or secondary extinction.

Crystal data. $C_{24}H_{16}FeO_4$, $M_r = 424.2$, monoclinic, a 9.653(3), b 18.243(4), c 11.293(2) Å, β 102.54(2)°, V 1941.3 Å^3, $Z = 4$, d_c 1.451 g cm^{-3}, $F(000) = 872$, space group $P2_1/c$.

The structure was solved by a combination of direct methods (MULTAN 80) and Fourier techniques. Refinement was carried out by full-matrix least-squares calculation, including the atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms. All hydrogens were located directly from electron density difference maps, and were assigned isotropic temperature factors. No attempt was made however to refine their atomic parameters. The final discrepancy index at the end of the refinement was $R = 0.039$ for 2398 observations above threshold of 3σ of the intensity. The final difference-Fourier map was essentially featureless, showing no indications of incorrectly placed or missing atoms. The refined atomic parameters

TABLE 1

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS OF COMPOUND VI [a]

Atom	x	y	z	U_{eq}/U (Å^2)
Fe(1)	0.2469(1)	0.0950(0)	0.3749(0)	0.0458
C(2)	0.0819(5)	0.1038(2)	0.4176(4)	0.0662
O(3)	−0.0281(4)	0.1081(2)	4413(3)	0.1063
C(4)	0.3414(4)	0.1438(2)	0.5060(4)	0.0594
O(5)	0.4017(4)	0.1762(2)	0.5876(3)	0.0853
C(6)	0.2897(4)	0.0023(2)	0.4199(3)	0.0547
O(7)	0.3168(3)	−0.0570(2)	0.4448(3)	0.0863
C(8)	0.4385(4)	0.0403(2)	0.2191(3)	0.0465
C(9)	0.4256(4)	0.1050(2)	0.2891(3)	0.0510
C(10)	0.3211(4)	0.1613(2)	0.2547(3)	0.0556
C(11)	0.1794(4)	0.1435(2)	0.2078(3)	0.0542
C(12)	0.1346(4)	0.0687(2)	0.1944(3)	0.0477
C(13)	0.1870(4)	0.0108(2)	0.1183(3)	0.0485
C(14)	0.3431(3)	−0.0029(2)	0.1458(3)	0.0427
C(15)	0.4186(3)	−0.0655(2)	0.1157(3)	0.0419
C(16)	0.5580(3)	−0.0551(2)	0.1701(3)	0.0424
O(17)	0.5715(2)	0.0097(1)	0.2356(2)	0.0463
C(18)	0.3514(3)	−0.1307(2)	0.0488(3)	0.0383
C(19)	0.2809(4)	−0.1259(2)	−0.0718(3)	0.0540
C(20)	0.2176(4)	−0.1874(2)	−0.1313(3)	0.0701
C(21)	0.2203(5)	−0.2530(2)	−0.0722(4)	0.0685
C(22)	0.2868(4)	−0.2582(2)	0.0479(4)	0.0616
C(23)	0.3525(4)	−0.1977(2)	0.1084(3)	0.0491
C(24)	0.6908(3)	−0.0929(2)	0.1689(3)	0.0406
C(25)	0.8151(4)	−0.0733(2)	0.2519(3)	0.0535
C(26)	0.9420(4)	−0.1073(2)	0.2493(3)	0.0629
C(27)	0.9478(4)	−0.1619(2)	0.1659(4)	0.0610
C(28)	0.8255(4)	−0.1819(2)	0.0835(3)	0.0523
C(29)	0.6977(4)	−0.1477(2)	0.0846(3)	0.0469
H(9)	0.527	0.127	0.333	0.050
H(10)	0.354	0.217	0.268	0.050
H(11)	0.093	0.181	0.198	0.050
H(12)	0.027	0.055	0.179	0.050
H(13A)	0.149	0.021	0.025	0.050
H(13B)	0.149	−0.040	0.141	0.050
H(19)	0.272	−0.065	−0.104	0.050
H(20)	0.167	−0.183	−0.214	0.050
H(21)	0.172	−0.299	−0.120	0.050
H(22)	0.291	−0.311	0.086	0.050
H(23)	0.409	−0.196	0.202	0.050
H(25)	0.813	−0.024	0.301	0.050
H(26)	1.032	−0.089	0.314	0.050
H(27)	1.047	−0.191	0.177	0.050
H(28)	0.833	−0.225	0.023	0.050
H(29)	0.612	−0.172	0.023	0.050

[a] For non-hydrogen atoms U_{eq} represents the equivalent value of the anisotropic Debey-Waller factor.

are listed in Table 1. Bond lengths and bond angles are given in Table 2. Figure 1 shows an ORTEP drawing of VI. Tables of observed and calculated structure factors may be obtained from the authors.

The data given in Tables 1 and 2 as shown in Fig. 1 are very similar to those found for the dimethyl analogue which was prepared by an independent route and whose structural features were discussed in great detail by El Borai et al. [16]. We note the square-pyramidal geometry around the pentacoordinate iron with two carbonyl groups (C(2)O(3) and C(6)O(7)) and the two diene double bonds defining the basal plane, and the remaining carbonyl (C(4)O(5)) forming the apex of the

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°) IN COMPOUND VI

Fe(1)–C(2)	1.769(5)	C(14)–C(15)	1.435(5)
Fe(1)–C(4)	1.797(4)	C(15)–C(16)	1.365(4)
Fe(1)–C(6)	1.788(4)	C(15)–C(18)	1.480(4)
Fe(1)–C(9)	2.161(4)	C(16)–O(17)	1.385(4)
Fe(1)–C(10)	2.059(4)	C(16)–C(24)	1.459(5)
Fe(1)–C(11)	2.057(3)	C(18)–C(19)	1.387(4)
Fe(1)–C(12)	2.145(3)	C(18)–C(23)	1.395(5)
C(2)–O(3)	1.153(6)	C(19)–C(20)	1.380(5)
C(4)–O(5)	1.142(5)	C(20)–C(21)	1.367(6)
C(6)–O(7)	1.135(5)	C(21)–C(22)	1.372(6)
C(8)–C(9)	1.441(5)	C(22)–C(23)	1.378(5)
C(8)–C(14)	1.350(4)	C(24)–C(25)	1.399(4)
C(8)–O(17)	1.375(4)	C(24)–C(29)	1.392(5)
C(9)–C(10)	1.432(5)	C(25)–C(26)	1.380(5)
C(10)–C(11)	1.394(6)	C(26)–C(27)	1.380(6)
C(11)–C(12)	1.429(5)	C(27)–C(28)	1.384(5)
C(12)–C(13)	1.517(5)	C(28)–C(29)	1.385(5)
C(13)–C(14)	1.492(5)		
C(4)–Fe(1)–C(2)	93.2(2)	C(14)–C(15)–C(16)	106.5(3)
C(6)–Fe(1)–C(2)	100.0(2)	C(14)–C(15)–C(18)	124.8(3)
C(6)–Fe(1)–C(4)	100.9(2)	C(18)–C(15)–C(16)	128.4(3)
C(10)–Fe(1)–C(2)	126.1(2)	C(15)–C(16)–O(17)	109.2(3)
C(10)–Fe(1)–C(4)	93.7(2)	C(15)–C(16)–C(24)	135.4(3)
C(10)–Fe(1)–C(6)	130.6(2)	C(24)–C(16)–O(17)	115.3(3)
C(11)–Fe(1)–C(2)	94.9(2)	C(16)–O(17)–C(8)	107.3(2)
C(11)–Fe(1)–C(4)	123.0(2)	C(15)–C(18)–C(19)	121.2(3)
C(11)–Fe(1)–C(6)	132.5(2)	C(15)–C(18)–C(23)	120.0(3)
Fe(1)–C(2)–O(3)	177.3(4)	C(23)–C(18)–C(19)	118.6(3)
Fe(1)–C(4)–O(5)	178.4(4)	C(18)–C(19)–C(20)	119.9(3)
Fe(1)–C(6)–O(7)	177.9(3)	C(19)–C(20)–C(21)	120.9(3)
C(14)–C(8)–C(9)	133.3(3)	C(20)–C(21)–C(22)	119.9(4)
O(17)–C(8)–C(9)	116.6(3)	C(21)–C(22)–C(23)	120.1(3)
O(17)–C(8)–C(14)	109.7(3)	C(22)–C(23)–C(18)	120.5(3)
C(8)–C(9)–C(10)	125.3(3)	C(16)–C(24)–C(25)	120.0(3)
C(9)–C(10)–C(11)	120.8(3)	C(16)–C(24)–C(29)	121.2(3)
C(10)–C(11)–C(12)	120.7(3)	C(29)–C(24)–C(25)	118.7(3)
C(11)–C(12)–C(13)	126.5(3)	C(24)–C(25)–C(26)	120.5(3)
C(12)–C(13)–C(14)	116.4(3)	C(25)–C(26)–C(27)	120.4(3)
C(8)–C(14)–C(15)	107.2(3)	C(26)–C(27)–C(28)	119.6(3)
C(13)–C(14)–C(8)	123.6(3)	C(27)–C(28)–C(29)	120.5(3)
C(13)–C(14)–C(15)	128.8(3)	C(28)–C(29)–C(24)	120.3(3)

pyramid [17]. The ring fold conformation of the cycloheptatriene is typical to cyclic systems containing the dieneiron tricarbonyl moiety [17,18]. The C(16)–C(24) bond is significantly shorter (1.459 Å) than its counterpart C(15)–C(18) bond (1.480 Å). Obviously, the phenyl at C(16) and the furan ring lying approximately in the same plane, are more strongly conjugated than the furan and the twisted phenyl at C(15).

Formation of homotropylidene complex (III) in the reaction of I with diazoacetate II parallels the formation of uncomplexed 8-carbethoxy-tropylidene from cycloheptatriene and II [13]. Thus the uncoordinated double bond of I enters cyclopropanation reactions with the carbethoxycarbenoid, as with other electrophilic carbenes [2,4], like a regular olefinic π-bond. With azibenzil (V) however, the reaction takes another course. The free double bond reacts as a dipolarophile in a formal 1,3-dipolar addition [19] with benzoylphenylcarbene (VII) to give an intermediate (VIII) which is subsequently oxidized to the cyclohepta[*b*]furane complex (VI).

In principle, two mechanistic pathways for the formation of VI are conceivable; (a) a concerted 1,3-dipolar cycloaddition to VIII followed by spontaneous dehydrogenation (eq. 4), and (b) initial cyclopropanation to give ketone IX which under the reaction conditions rearranges, via the zwitterion X, to VIII (eq. 5).

While there is ample precedent for the formation of furan derivatives in metal catalyzed additions of carbonylcarbenes to unsaturated systems, there are relatively

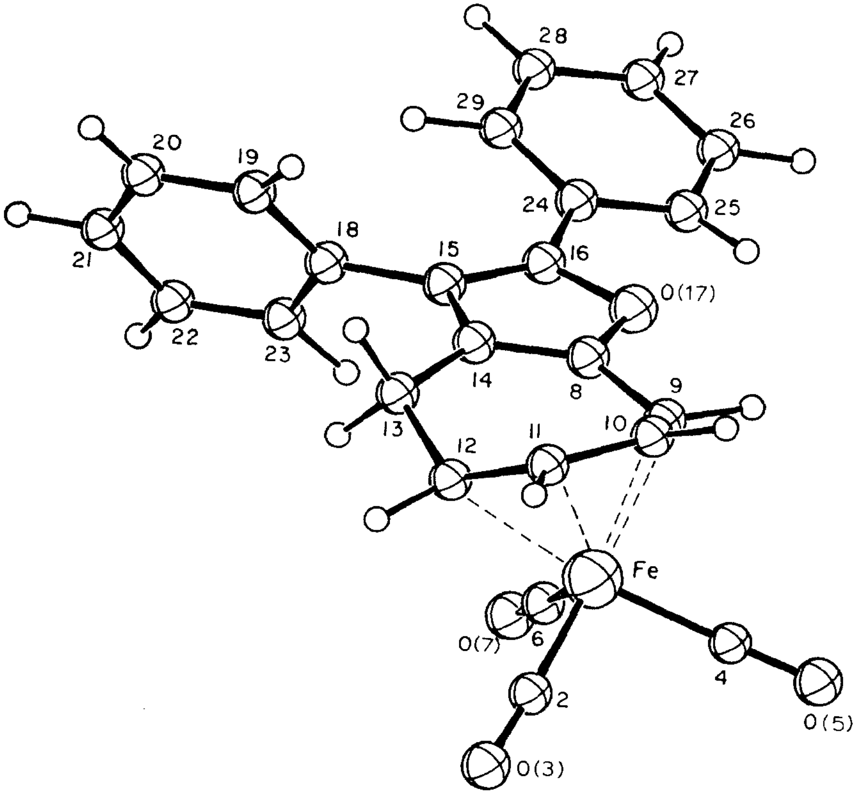
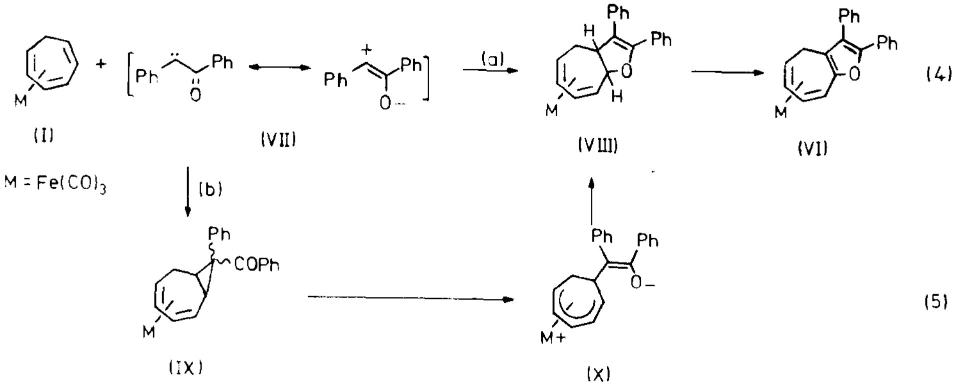


Fig. 1. The molecular structure of cyclohepta[*b*]furan (VI).



few confirmed examples of 1,3-dipolar additions which do not involve isomerization of an initially formed cyclopropane intermediate [9]. Benzoylphenylcarbene (VII) was previously mainly trapped by 1,3-dipolar additions [20]. Scott and Cotton [20a] have demonstrated that the interception of benzoylphenylcarbene (VII) with *trans*-stilbene in the presence of $ZnBr_2$ proceeds via a direct 1,3-dipolar addition, which presumably does not involve the intermediacy of the corresponding cyclopropane. The ability of the free bond in tricarbonyl(tropone)iron and some acyclic complexes to undergo 1,3-dipolar additions with diazoalkanes [6,7] and diphenylnitrilimine [21] further supports the concerted mechanism (a) (eq. 4). However, the bipolar mechanism (b) (eq. 5) cannot be disregarded since activated cyclopropanes are known to be readily cleaved under these conditions [9]. Furthermore, ready cleavage of related complexes with strained cyclobutanone ring [1] has also been observed. Hence, although the concerted route seems probable, this is by no means firmly established. The question of the detailed mechanism thus remains open.

A final comment on the oxidation steps involved in the formation of dimer IV and furan VI is in order. Johnson et al. were first to report the formation of IV during attempts to add methylene to I under Simmons-Smith conditions [3]. Also, Alper and Amaratunga noted the insertion of dibromocarbene into saturated carbon–hydrogen bonds of dieneiron tricarbonyl complexes [22]. Since insertion reactions often involve the formation of radicals by hydrogen abstraction [9], it is reasonable to suggest that IV is obtained by dimerization of tricarbonyl(tropylium)iron radical.

The spontaneous dehydrogenation of dihydrofurans is not commonly observed in carbene reactions [23]. However, in the presence of metal complexes, a mechanism involving intermolecular hydrogen transfer via metal hydride intermediate [24] is plausible. The formation of tricarbonyl(cycloheptadiene)iron from cycloheptatriene and iron pentacarbonyl [25] supports this premise, even though we could not isolate the diene complex in the present study.

Experimental

General. ^1H and ^{13}C NMR spectra were recorded on Varian Model EM-360A and Varian CFT-20 spectrometers, with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer Model 257 spectrometer. Mass spectra were determined with a GC/MS Finnigan Model 4000 spectrometer. Column chromatographic separations were performed under a slight positive nitrogen using Merck Kieselgel 60. Elemental analyses were determined in the analytical laboratories of the Hebrew University, Jerusalem. All reactions were conducted under nitrogen.

Tricarbonyl[(η-2,3,4,5)-8-ethoxycarbonyl-bicyclo[5.1.0]octa-2,4-diene]iron (III)

A solution of ethyldiazoacetate (II) (3.0 g, 26.3 mmol) in tricarbonyl(cycloheptatriene)iron (I) [26] (2.5 g) was added dropwise with vigorous stirring during 15 min, to I (7 g) containing the appropriate copper catalyst [12] (10 mg), at 75°C. When the evolution of N_2 had ceased the mixture was heated for an additional 15 min then diluted with hexane. The solution was filtered then chromatographed with hexane as eluent. The first fraction contained unreacted I followed by the hexacarbonyl(bicycloheptatrienyl)di-iron (IV) (70 mg) [14]. The ester (III) was eluted with toluene and kugelrohr distilled at 175°C (0.1 mmHg), to give an orange oil (3.4 g, 40% yield) which solidified at near room temperature (mp. 35°C); m/e 318 (M), 290, 262, 234, 278; IR (neat) 2040, 1965br (ligand CO), 1710 (ester CO) cm^{-1}; Anal. Found: C, 52.86; H, 4.44; $C_{14}H_{14}FeO_5$ calcd.: C, 53.16; H, 4.40%. ^1H NMR ($CDCl_3$) δ 1.23 (3H, t, J 7 Hz + 1H obscured), 1.54 (1H, m), 1.92 (1H, dd, J 6 and 4 Hz), 2.30 (2H, bt, J 4 Hz), 3.09 (1H, m), 3.49 (1H, dd, J 8 and 6 Hz), 4.20 (2H, 9, J 7 Hz), 5.06 (2H, m) ppm.

Tricarbonyl[(η-5,6,7,8)-2,3-diphenyl-4H-cyclohepta[b]furan]iron (VI)

Azibenzil (V) [27] (3.0 g, 13.5 mmol) dissolved in cycloheptatriene complex I (11.0 g) was added dropwise with stirring during 40 min to I (9.0 g) containing the copper catalyst (10 mg) at 65°C. Heating was continued for 20 min and the mixture was then chromatographed with hexane as solvent and eluent. Excess I and the di-iron complex IV (52 mg) were first eluted followed by the orange-red crystals of VI (0.51 g, 9%), mp. 177–178°C (CH_2Cl_2/hexane); m/e CI (CH_4)425 ($M+1$), 397, 369, 341, 285; IR ($CHCl_3$) 2045, 1975br (ligand CO), 1595 (furan C=C) cm^{-1}. Anal. Found: C, 67.86; H, 3.97. $C_{24}H_{16}FeO_4$ calcd.: C, 67.95 H, 3.80%. ^1H NMR ($CDCl_3$) δ 2.59 (2H, bd, J 4 Hz), 3.54 (1H, m), 3.75 (1H, m), 5.40 (2H, m), 7.22 (10H, m) ppm. ^{13}C NMR ($CDCl_3$) δ 29.39 (C(4)), 55.39, 65.89 (C(5) and C(8)), 91.64, 92.50 (C(6) and C(7)), 128.76, 130.41, 131.19, 132.60, 133.33 (aromatic) 215.47 (CO) ppm.

Acknowledgment

Financial assistance from the André Narboni and Leon Recanati Scholarship Funds (to S.A.) is gratefully acknowledged.

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