

Chemical synthesis with metal atoms: preparation and reactivity of (η^6 -cyclohepta-1,3,5-triene)(η^4 -cycloocta-1,5-diene) iron(0) [☆]

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Abstract

The complex (η^6 -cyclohepta-1,3,5-triene)(η^4 -cycloocta-1,5-diene)iron(0), **1**, stable at low temperature (-30°C), has been prepared by co-condensation of iron atoms with cycloocta-1,5-diene at -196°C followed by condensation of cyclohepta-1,3,5-triene. Complex **1** furnishes, reacting with carbon monoxide and trimethylphosphite, the compounds monocarbonyl(1-4- η -cyclohepta-1,3,5-triene)(η^4 -cycloocta-1,5-diene)iron(0), **2**, and (1-4- η -cyclohepta-1,3,5-triene)tristrimethylphosphiteiron(0), **3**, respectively. The X-ray crystal structure of **2** [orthorhombic space group, *Pbca*; unit cell dimensions: $a = 12.491(4)$ Å, $b = 13.170(4)$ Å, $c = 16.119(5)$ Å; final *R* value, 0.0485 on 1142 data] reveals that the C7 ring is butadiene-like bonded to the metal.

Keywords: Iron; Metal vapour synthesis; Cycloocta-1,5-diene; Cyclohepta-1,3,5-diene; Carbon monoxide; Phosphine

1. Introduction

Iron vapours are powerful reagents in organometallic chemistry, providing useful routes to a wide range of interesting compounds [1]. $\text{Fe}(\eta^4\text{-COD})_2$ (COD = cycloocta-1,5-diene) [2], $\text{Fe}(\eta^5\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$ [3], $\text{Fe}(\eta^4\text{-diene})\text{L}_3$ [4], $\text{Fe}(\eta^6\text{-arene})\text{L}_2$ [5] and $\text{Fe}(\eta^6\text{-arene})(\eta^4\text{-diene})$ [5] (L = phosphorous ligands) are examples of iron vapour-derived complexes, which are difficult, if not impossible, to obtain by traditional methods [6]. We report here the preparation of the new compound $\text{Fe}(\eta^6\text{-CHT})(\eta^4\text{-COD})$, **1**, (CHT = cyclohepta-1,3,5-triene), by co-condensation of iron atoms with COD and CHT. This complex and, more generally, bis(cycloolefin)metal complexes containing different cycloolefins bound to the metal are of special interest in preparative chemistry and in catalysis, because of the expected diverse bond strength and reactivity of the two ligands, as observed for similar Ru(0) complexes [7]. The reactions of **1** with CO and $\text{P}(\text{OMe})_3$, which afford the complexes $\text{Fe}(1\text{-}4\text{-}\eta\text{-CHT})(\eta^4\text{-}$

COD)(CO), **2** and $\text{Fe}(1\text{-}4\text{-}\eta\text{-CHT})[\text{P}(\text{OMe})_3]_3$, **3**, respectively, are also described.

2. Results and discussion

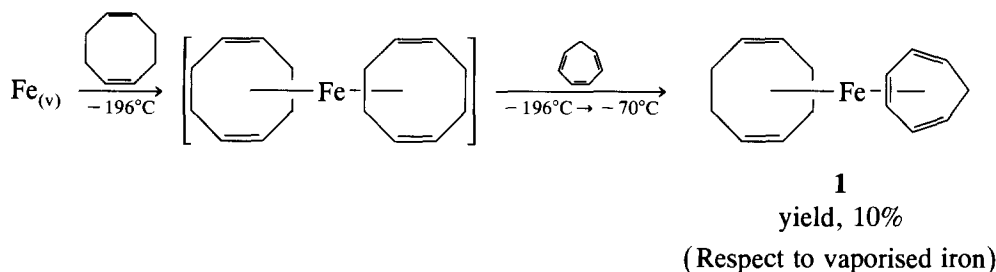
2.1. Synthesis and characterization of (η^6 -cyclohepta-1,3,5-triene)(η^4 -cycloocta-1,5-diene)iron(0), **1**

The complex $\text{Fe}(\eta^6\text{-CHT})(\eta^4\text{-COD})$, **1**, was prepared as reported in Scheme 1, by co-condensation of iron atoms with COD over a liquid nitrogen-cooled surface followed by condensation of CHT over the solid matrix at the same temperature. On warming at -70°C , a red solution was obtained from which, after removal under vacuum of excess ligands and chromatography (Al_2O_3) at -40°C , complex **1** was recovered as a red-brown solid, stable at low temperature (-30°C), soluble in aliphatic and aromatic hydrocarbons and THF.

It is worth noting that the synthesis of **1** by simultaneous co-condensation of iron atoms with COD and CHT did not result because of the contemporary formation of the complex (η^5 -cycloheptadienyl)(η^5 -cycloheptatrienyl)-iron [3]. In addition, an attempt to prepare **1** by ligand-exchange reaction between preformed $\text{Fe}(\eta^4\text{-COD})_2$ [2] and CHT at -30°C was unsuccessful.

[☆] Dedicated to Professor Henri Brunner on the occasion of his 60th birthday.

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Scheme 1.

Complex **1** was characterized by MS spectrometry and NMR spectroscopy. The MS spectrum exhibits peaks at m/z 256 and m/z 148, assigned to the ions M^+ and $M^+ - \text{COD}$, respectively. The ^1H NMR spectrum (Fig. 1) shows two sets of absorption between 1.8 ppm and 3.0 ppm and between 4.8 ppm and 5.2 ppm that have been assigned by bidimensional analysis DQF-COSY (double-quantum-filtered correlated spectroscopy). The carbon absorptions (Fig. 2) have been attributed by bidimensional analysis HETCOR (heteronuclear correlation). The corresponding proton and carbon spectral parameters of **1** are summarized in Table 1.

2.2. Reaction of $(\eta^6\text{-cyclohepta-1,3,5-triene})(\eta^4\text{-cycloocta-1,5-diene})\text{iron}(0)$, **1**, with CO and $P(\text{OMe})_3$

2.2.1. Carbon monoxide

Complex **1** in pentane reacts with CO (1 atm) (Scheme 2) to form the new compound monocarbonyl-

$(1\text{-}4\text{-}\eta\text{-cyclohepta-1,3,5-triene})(\eta^4\text{-cycloocta-1,5-diene})\text{iron}(0)$, **2**, as a yellow solid, soluble in hydrocarbons, THF, diethyl ether and acetone, and stable under inert atmosphere at room temperature both in the solid state and in solution.

Interestingly, complex **2** is also obtained by reaction under CO pressure (10 atm). No polycarbonyl derivative (i.e. $\text{Fe}(\eta^4\text{-COD})(\text{CO})_3$ [8] or $\text{Fe}(\eta^4\text{-CHT})(\text{CO})_3$ [9]) is formed, pointing out the stability of the monocarbonyl complex **2**.

The MS spectrum of **2** shows peaks at m/z 284, m/z 256 and m/z 164 assigned to the ions M^+ , $M^+ - \text{CO}$ and $M^+ - (\text{CO} + \text{CHT})$, respectively. The IR spectrum exhibits a very strong band at 1965 cm^{-1} attributed to $\nu(\text{CO})$ [10].

The X-ray molecular structure of **2** is shown in Fig. 3 and a list of the more relevant bond distances and angles are given in Table 2. X-ray analysis shows that the cycloocta-1,5-diene and cyclohepta-1,3,5-triene are

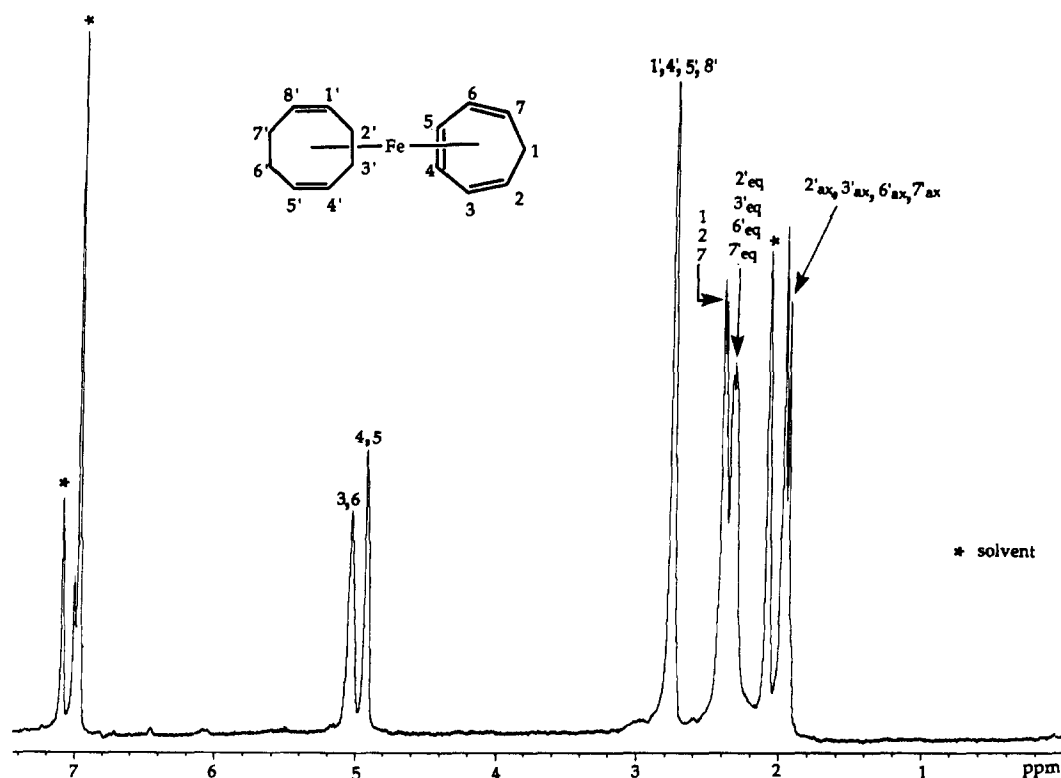


Fig. 1. ^1H NMR (300 MHz, toluene- d_8 , 25°C) spectrum of $\text{Fe}(\eta^6\text{-CHT})(\eta^4\text{-COD})$, **1**.



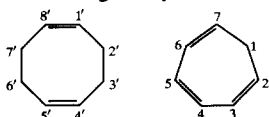
Fig. 2. ^{13}C NMR (75 MHz, toluene- d_8 , -30°C) spectrum of $\text{Fe}(\eta^6\text{-CHT})(\eta^4\text{-COD})$, **1**.

Table 1
Analytical and spectroscopic data for compounds 1–3

Compound	Analysis ^a (%)		NMR data ^{b,c}			
	C	H	$^1\text{H-NMR}$ ^d		$^{13}\text{C-NMR}$ ^e	
			Olefin	Methylene	Olefin	Methylene
$\text{Fe}(\text{CHT})(\text{COD})$ 1			2.37 (2H, 2, 7) 2.80 (4H, 1', 4', 5', 8') 4.92 (2H, 4, 5) 5.04 (2H, 3, 6)	1.95 (4H; ax: 2', 3', 6', 7') 2.25 (4H; eq: 2', 3', 6', 7') 2.36 (2H, 1)	38.3 (2, 7) 71.5 (1', 4', 5', 8') 93.4 (4, 5) 104.6 (3, 6)	26.1 (1) 33.4 (2', 3', 6', 7')
$\text{Fe}(\text{CHT})(\text{COD})(\text{CO})$ 2	67.53 (67.65)	7.30 (7.07)	0.71 (1H, 4) 0.88 (1H, 7) 2.18 (1H, 5') 2.21 (1H, 8') 2.73 (1H, 4') 3.19 (1H, 1') 4.96 (2H, 2) 5.33 (1H, 6) 5.55 (1H, 3) 5.64 (1H, 5)	1.52 (3H; ax: 1, 6', 7') 1.62 (1H, 2' _{ax}) 1.63 (1H, 3' _{ax}) 2.53 (1H, 3' _{eq}) 2.54 (2H; eq: 6', 7') 2.55 (1H, 1 _{eq})	50.3 (4) 54.7 (7) 77.6 (1') 78.3 (4') 82.9 (5') 83.6 (8') 92.9 (6) 100.0 (5) 121.9 (2) 131.2 (3)	29.6 (7' or 6') 30.3 (2') 31.1 (6' or 7') 31.7 (1, 3')
$\text{Fe}(\text{CHT})[\text{P}(\text{OMe})_3]_3$ ^f 3	36.04 (36.93)	6.95 (6.73)	2.78 (1H, 4) 2.89 (1H, 7) 4.90 (1H, 6) 5.18 (1H, 5) 5.26 (1H, 2) 6.16 (1H, 3)	2.23 (1H, 1 _{ax}) 2.58 (1H, 1 _{eq})	45.2 (4) 49.0 (7) 83.1 (6) 89.7 (5) 122.9 (2) 132.2 (3)	31.9 (1)

^a Calculated values are given in parentheses.

^b Labelling for cycloocta-1,5-diene and cyclohepta-1,3,5-triene:



^c The signals were assigned by analysis of DQF-COSY and HETCOR bidimensional maps.

^d Spectra were measured at 300 MHz, in C_6D_6 ; δ scale; ax, axial proton; eq, equatorial proton.

^e Spectra were measured at 75 MHz, in toluene- d_8 at -30°C for compound **1** and in C_6D_6 at 25°C for compounds **2** and **3**, δ scale.

^f Analysis: P%: 18.10 (17.88). NMR data for $\text{P}(\text{OCH}_3)_3$: ^1H : 3.40–3.65 ppm (27 H); ^{13}C : 51.5 ppm; ^{31}P : 183 ppm.

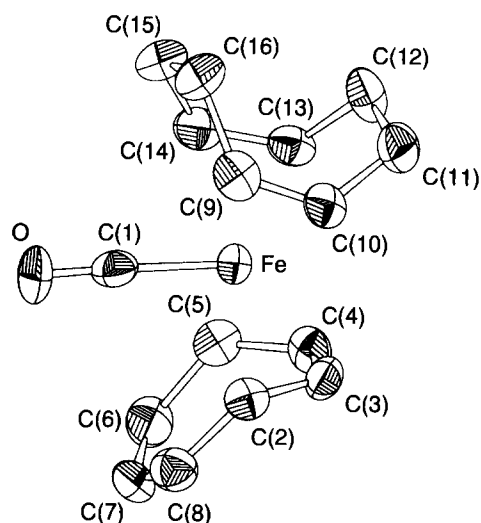
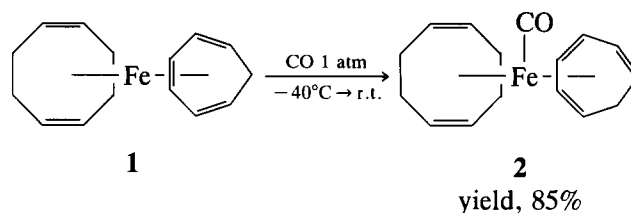


Fig. 3. ORTEP view of the molecular structure of Fe(1-4- η -COD)(η^4 -COD)(CO), **2**, with the atomic numbering scheme. Thermal ellipsoids are represented at 50% probability.

both η^4 bonded on opposite sides to the iron atom. The planes of the donor atoms, C(9), C(10), C(13), C(14)¹ for COD and C(2), C(3), C(4), C(5) for CHT, respectively, are not exactly parallel but make an acute dihedral angle of 18.4(4)°. This “open book” disposition of the two planes allows the coordination of the carbon monoxide C(1)–O to the iron atom on the side where the planes are more open. Similar Fe–C distances and a similar divergence of the coordination planes of the ligands have also been observed in the complexes monocarbonyl(η^4 -buta-1,3-diene)(η^4 -cycloocta-1,5-diene)-iron [11] and monocarbonyl bis(η^4 -cyclohexa-1,3-diene)iron [12].

The conformation of COD in **2** is saddle-like, as generally observed in this kind of complex; i.e., it can be met in the aforementioned monocarbonyl(η^4 -buta-1,3-diene)(η^4 -cycloocta-1,5-diene)iron and in the compound tricarbonyl(η^4 -cycloocta-1,5-diene)iron [13]. Several cases of substituted cyclohepta-1,3,5-trienes, η^4 bonded to iron, have been reported: tricarbonyl(1-4- η -7-R-cyclohepta-1,3,5-triene)iron (R = cycloheptatrienyl [14], phenyl [15] and styryl [16]) can be considered examples close to **2**. In these compounds the conformation of the substituted seven-membered ring is the same as that observed for CHT in **2** and the carbon–carbon distances in the ring are similar.

The molecule of **2** in the crystal has no element of symmetry. Nevertheless the mean plane defined by the atoms Fe, C(1), C(7) and the mid points of C(3)–C(4), C(11)–C(12) and C(15)–C(16) bonds are approximately



Scheme 2.

Table 2

Structural parameters in the complex **2** (distances in Å, angles in degrees, e.s.d.'s are given in parentheses)

Fe–C(1)	1.761(8)	C(4)–C(5)	1.428(10)
Fe–C(4)	2.053(7)	C(5)–C(6)	1.484(10)
Fe–C(3)	2.066(6)	C(6)–C(7)	1.437(11)
Fe–C(5)	2.084(7)	C(7)–C(8)	1.361(11)
Fe–C(2)	2.110(6)	C(9)–C(10)	1.374(10)
Fe–C(10)	2.146(7)	C(9)–C(16)	1.514(11)
Fe–C(14)	2.155(7)	C(10)–C(11)	1.489(10)
Fe–C(9)	2.158(7)	C(11)–C(12)	1.521(10)
Fe–C(13)	2.167(7)	C(12)–C(13)	1.497(10)
C(1)–O	1.154(8)	C(13)–C(14)	1.388(10)
C(2)–C(3)	1.433(10)	C(14)–C(15)	1.510(11)
C(2)–C(8)	1.482(10)	C(15)–C(16)	1.494(12)
C(3)–C(4)	1.390(10)		
C(1)–Fe–C(4)	127.2(3)	C(14)–Fe–C(13)	37.5(3)
C(1)–Fe–C(3)	125.9(3)	C(9)–Fe–C(13)	89.0(3)
C(4)–Fe–C(3)	39.5(3)	O–C(1)–Fe	177.8(7)
C(1)–Fe–C(5)	90.3(3)	C(3)–C(2)–C(8)	124.2(6)
C(4)–Fe–C(5)	40.4(3)	C(3)–C(2)–Fe	68.3(4)
C(3)–Fe–C(5)	71.8(3)	C(8)–C(2)–Fe	116.5(5)
C(1)–Fe–C(2)	88.7(3)	C(4)–C(3)–C(2)	119.6(6)
C(4)–Fe–C(2)	71.8(3)	C(4)–C(3)–Fe	69.8(4)
C(3)–Fe–C(2)	40.1(3)	C(2)–C(3)–Fe	71.6(4)
C(5)–Fe–C(2)	83.8(3)	C(3)–C(4)–C(5)	119.4(6)
C(1)–Fe–C(10)	120.3(3)	C(3)–C(4)–Fe	70.8(4)
C(4)–Fe–C(10)	108.5(3)	C(5)–C(4)–Fe	71.0(4)
C(3)–Fe–C(10)	83.5(3)	C(4)–C(5)–C(6)	125.1(7)
C(5)–Fe–C(10)	148.6(3)	C(4)–C(5)–Fe	68.6(4)
C(2)–Fe–C(10)	89.7(3)	C(6)–C(5)–Fe	119.7(5)
C(1)–Fe–C(14)	82.2(3)	C(7)–C(6)–C(5)	121.7(6)
C(4)–Fe–C(14)	113.1(3)	C(8)–C(7)–C(6)	124.6(7)
C(3)–Fe–C(14)	147.8(3)	C(7)–C(8)–C(2)	126.1(7)
C(5)–Fe–C(14)	95.2(3)	C(10)–C(9)–C(16)	124.6(7)
C(2)–Fe–C(14)	170.9(3)	C(10)–C(9)–Fe	70.9(4)
C(10)–Fe–C(14)	95.7(3)	C(16)–C(9)–Fe	112.1(5)
C(1)–Fe–C(9)	84.4(3)	C(9)–C(10)–C(11)	126.2(7)
C(4)–Fe–C(9)	145.6(3)	C(9)–C(10)–Fe	71.8(4)
C(3)–Fe–C(9)	113.9(3)	C(11)–C(10)–Fe	110.6(5)
C(5)–Fe–C(9)	173.9(3)	C(10)–C(11)–C(12)	113.9(6)
C(2)–Fe–C(9)	99.2(3)	C(13)–C(12)–C(11)	112.3(6)
C(10)–Fe–C(9)	37.2(3)	C(14)–C(13)–C(12)	123.3(7)
C(14)–Fe–C(9)	81.0(3)	C(14)–C(13)–Fe	70.8(5)
C(1)–Fe–C(13)	119.5(3)	C(12)–C(13)–Fe	113.6(5)
C(4)–Fe–C(13)	86.0(3)	C(13)–C(14)–C(15)	124.4(7)
C(3)–Fe–C(13)	111.6(3)	C(13)–C(14)–Fe	71.7(4)
C(5)–Fe–C(13)	90.8(3)	C(15)–C(14)–Fe	111.2(6)
C(2)–Fe–C(13)	151.4(3)	C(16)–C(15)–C(14)	113.4(7)
C(10)–Fe–C(13)	80.3(3)	C(15)–C(16)–C(9)	115.6(7)

¹ Note that the crystallographic numbering system for **2** differs from that used in discussing the NMR spectra (Table 1).

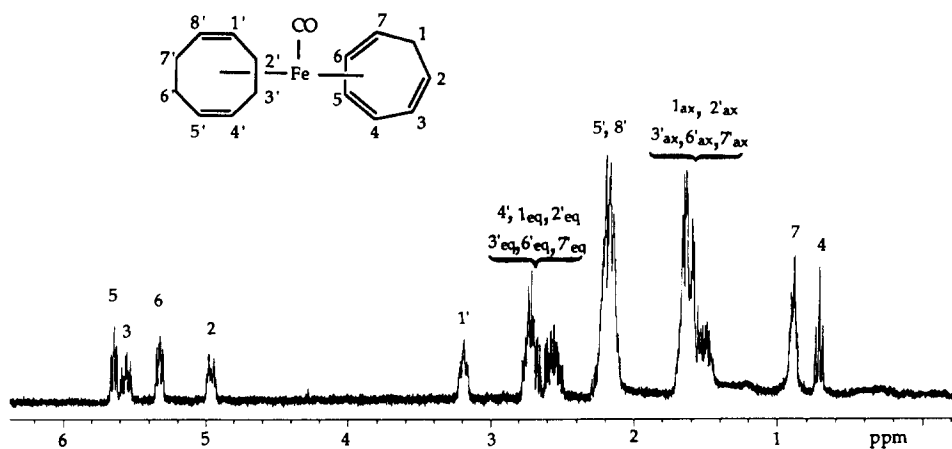


Fig. 4. ^1H NMR (300 MHz, benzene- d_6 , 25°C) spectrum of $\text{Fe}(1\text{-}4\text{-}\eta\text{-CHT})(\eta^4\text{-COD})(\text{CO})$, **2**.

a mirror plane, so, although in the solid state the molecule is asymmetric, it can reasonably be considered to have a C_s symmetry in solution.

The ^1H and ^{13}C NMR spectra of **2** are shown in Figs. 4 and 5, respectively. A complete attribution of the proton and carbon resonances has been performed by DQF-COSY and HETCOR analyses; the corresponding data are reported in Table 1. The presence of carbon monoxide in **2** introduces a loss of symmetry, relatively to complex **1**, which is well reflected in both the proton and carbon spectra (Fig. 4 compared to Fig. 1, for proton, and Fig. 5 compared to Fig. 2, for carbon): indeed, in the case of **2** all the proton and carbon nuclei of the two ligands CHT and COD are inequivalent and show distinct absorptions. Concerning the diene moiety of CHT bound to the iron, it is noteworthy that, in the

^1H NMR spectrum (Fig. 4), two very high-field shifted resonances are found, at 0.71 ppm and 0.88 ppm, corresponding to the protons H_4 and H_7 , respectively. Similar signals have been also observed in other 1-4- η -diene-iron complexes [9,17] and, according to literature data [18], can be reasonably related to a large σ contribution in the Fe–C bond. Also the ^{13}C NMR spectrum and the X-ray molecular structure of **2** reflect this situation. The first (Fig. 5 and Table 1) exhibits two high field shifted absorptions at 50.3 ppm and 54.7 ppm due to the carbon atoms C_4 and C_7 carrying the protons H_4 and H_7 . The second shows (Table 2) that the C(3)–C(4) bond (equivalent to $\text{C}_5\text{--C}_6$ in Table 1) is the shortest (1.39 Å) among the carbon–carbon bonds of the 1-4- η -diene moiety, indicating that this bond is of olefinic character.

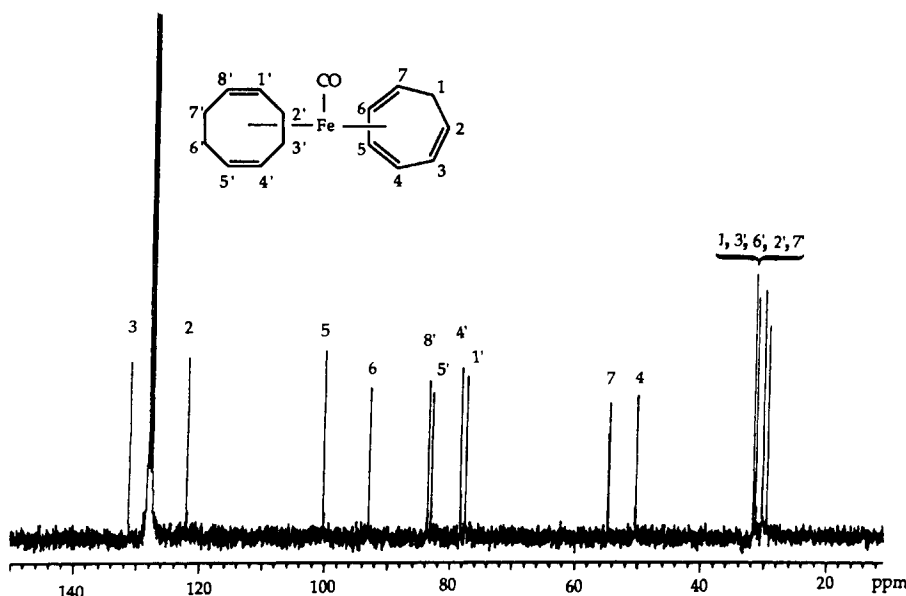


Fig. 5. ^{13}C NMR (75 MHz, benzene- d_6 , 25°C) spectrum of $\text{Fe}(1\text{-}4\text{-}\eta\text{-CHT})(\eta^4\text{-COD})(\text{CO})$, **2**.

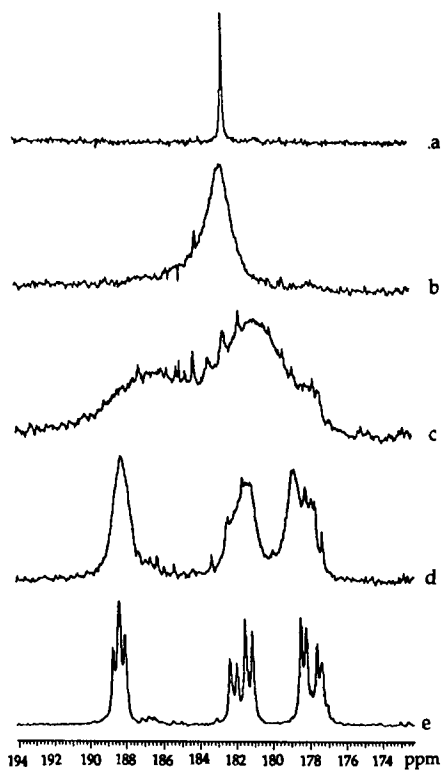


Fig. 6. ^{31}P NMR (121 MHz, toluene- d_8) spectrum of $\text{Fe}(\eta^4\text{-CHT})[\text{P}(\text{OMe})_3]_3$, **3**: a: 25°C; b: -20°C; c: -40°C; d: -60°C; e: -80°C.

2.2.2. Trimethyl phosphite

The reaction of **1** with $\text{P}(\text{OMe})_3$ (molar ratio 1:5) at 0°C in pentane furnishes yellow-orange crystals of the complex **3**, characterized as (1-4- η -cyclohepta-1,3,5-triene)tristrimethylphosphiteiron [4] (Scheme 3).

The MS spectrum of **3** shows the peak with the highest mass at m/z 396, corresponding to the ion $\{\text{Fe}(\text{CHT})[\text{P}(\text{OMe})_3]_2\}^+$.

The presence in **3** of three phosphorous atoms per iron atom was unambiguously established by ^{31}P NMR analysis (Fig. 6). At room temperature a single phosphorus signal is observed (Fig. 6a), which broadens progressively on lowering the temperature and decoalesces into three distinct resonances at -60°C (Fig. 6c). These are completely resolved at -80°C (Fig. 6d), showing the typical coupling pattern of the ABC spin system, where two phosphorous nuclei couple each other and couple with the third nucleus which couples only with the other two, thus originating two double

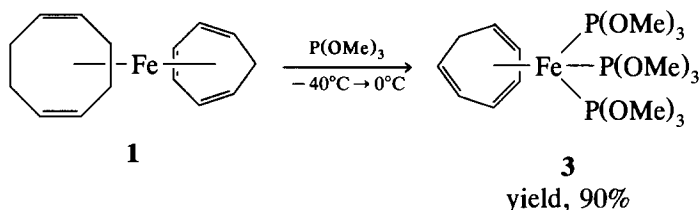
doublets and a triplet respectively. Therefore, the presence of three unequivalent phosphite ligands is revealed at low temperatures becoming fast exchanging on the NMR time scale at higher temperatures (greater than -20°C).

The fluxional behaviour of **3** was previously reported by Ittel et al. [4], who prepared **3** by simultaneously co-condensing iron atoms with CHT and $\text{P}(\text{OMe})_3$. Our results are identical to those found by Ittel et al. although a better resolution in the spectrum of **3** at -80°C was observed by us. The ^1H and ^{13}C NMR data of **3**, not previously described, are reported in Table 1.

Finally, it is important to note that the reaction between **1** and $\text{P}(\text{OMe})_3$ carried out at 0°C, using a molar ratio 1:1, gives complex **3** as the only product with unreacted **1**, indicating that the reaction pathway is not dependent on the ratio of the reagents (see Scheme 3) and that $\text{P}(\text{OMe})_3$, unlike CO, is able to remove COD from the species $\{\text{Fe}(\text{CHT})(\text{COD})[\text{P}(\text{OMe})_3]\}$, probably the first product of the reaction.

4. Experimental details

All reactions were carried out under a dry oxygen-free argon atmosphere, using conventional Schlenck-tube techniques. Solvents were dried by conventional methods and stored on sodium, under argon atmosphere. Cyclohepta-1,3,5-triene and cycloocta-1,5-diene were commercial samples and were dried by distillation on sodium, under argon atmosphere and stored on sodium. Trimethylphosphite, commercially available, was degassed and stored under argon atmosphere. The co-condensation of iron and cycloocta-1,5-diene was carried out in a static reactor, previously described [19]. All NMR spectra (^1H , ^{13}C , ^{31}P , DQF-COSY and HETCOR) were recorded using a Varian VXR-300 spectrometer operating at 300 MHz for ^1H , 75 MHz for ^{13}C and 121 MHz for ^{31}P . The temperature was controlled to $\pm 0.1^\circ\text{C}$. The double-quantum-filtered (DQF-COSY) experiments were performed in the phase-sensitive mode with a spectral width of 2500 Hz; 512 increments of 8 scans and 2K data points were acquired. The relaxation delay was 10s. The data were zero-filled to $2\text{K} \times 1\text{K}$ and a Gaussian function was applied for processing in t_2 . The ^1H - ^{13}C heterocorrelate experiments (HETCOR) were performed using a proton spectral width of 4000 Hz and a carbon spectral width of 16500 Hz, with 2K data



Scheme 3.

points and 512 increments of 32 scans. Mass spectra (EI) were carried out on a VG 7070 E spectrometer. IR Spectra were recorded at room temperature in nujol on IR-FT Perkin-Elmer 1710 spectrometer. Melting points were measured on a polarizer Reichert Thermovar microscope. Microanalyses were performed by the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, Italy.

4.1. Preparation of $(\eta^6\text{-cyclohepta-1,3,5-triene})(\eta^4\text{-cycloocta-1,5-diene})\text{iron}(0)$, **1**

In a typical experiment Fe vapour (4–5 g) (obtained by a resistively heated crucible) was co-condensed simultaneously with cycloocta-1,5-diene (20 ml) on a heptane matrix at liquid nitrogen temperature over a period of 1 h. Cyclohepta-1,3,5-triene (10 ml) in heptane (20 ml) was then distilled into the reactor at the same temperature. The mixture was allowed to warm to -70°C and siphoned out. Heptane and excess ligands were removed under vacuum (10^{-5} mmHg, 0°C) and the residue was taken up in pentane at -70°C . The red-brown solution was chromatographed on an alumina column (20 cm, neutral grade, activity II–III) at -40°C . Pentane eluted a red fraction that gave at -78°C red-brown crystals of **1** (1.47 g; yield 10% with respect to vaporised iron). **1** is thermodynamically unstable, decomposing to metal and ligands, and must be stored at -30°C , under an argon-atmosphere. MS-IE m/z (% rel. int.): 256, M^+ (35); 164, $M^+ - \text{CHT}$ (100); 148, $M^+ - \text{COD}$ (70).

4.2. Reaction of **1** with CO: preparation of monocarbonyl(1-4- η -cyclohepta-1,3,5-triene)(η^4 -cycloocta-1,5-diene)iron, **2**

4.2.1. Under atmospheric pressure

Complex **1** (0.2 g, 0.78 mmol) was dissolved in pentane (25 ml) at -40°C . The argon was removed under vacuum from the Schlenck-tube and carbon monoxide (1 atm) was introduced. The red solution was allowed to warm to room temperature under magnetic stirring for 8 h, turning to yellow-orange. The volume of solution was reduced to 5 ml and, at -78°C , yellow-orange crystals of **2** (0.188 g, 0.66 mmol) were obtained (m.p. = $67\text{--}69^\circ\text{C}$). IR (nujol): 1965 cm^{-1} , $\nu(\text{C-O})$. MS m/z (% rel. int.): 284, M^+ (5); 256, $M^+ - \text{CO}$ (60); 164, $M^+ - \text{CO} - \text{CHT}$ (60); 148, $M^+ - \text{COD} - \text{CHT}$ (100).

4.2.2. Under 10 atm

A glass vial, containing **1** (100 mg, 0.39 mmol) and pentane (25 ml) cooled at -40°C was introduced into a 125 ml stainless-steel rocking autoclave under nitrogen. The gas was removed under vacuum and the autoclave was charged with carbon monoxide (10 atm). The auto-

clave was stirred at room temperature for 8 h. It was discharged and the solid material present in the reaction mixture was filtered off under nitrogen atmosphere. The yellow solution obtained was cooled to -30°C to give yellow-orange crystals (0.077 g; yield, 70%) of **2**.

4.3. Reaction of **1** with $\text{P}(\text{OMe})_3$: preparation of (1-4- η -cyclohepta-1,3,5-triene)tristrimethylphosphiteiron, **3**

Complex **1** (0.2 g, 0.8 mmol) and $\text{P}(\text{OMe})_3$ (0.46 ml, 4 mmol) were dissolved in pentane (25 ml) at -40°C . The red solution was allowed to warm to 0°C under magnetic stirring for 8 h. The resulting yellow-orange solution was evaporated to dryness under vacuum pressure, removing $\text{P}(\text{OMe})_3$ in excess at 10^{-5} mmHg. The residue was dissolved in pentane (5 ml) giving, at -78°C , yellow-orange crystals of **3** (0.286 g, 0.55 mmol) (m.p. = $70\text{--}71^\circ\text{C}$). MS m/z (% rel. int.): 396, $M^+ - \text{P}(\text{OMe})_3$ (25); 304 $M^+ - \text{P}(\text{OMe})_3 - \text{CHT}$ (55); 124, $\text{P}(\text{OMe})_3$ (100).

4.4. Crystal structure analysis of monocarbonyl(1-4- η -cyclohepta-1,3,5-triene)(η^4 -cycloocta-1,5-diene)iron, **2**

Crystals of **2**, obtained by cooling a saturated pentane solution at -30°C , were sealed within Lindemann capillaries under nitrogen atmosphere and their diffraction patterns, obtained on a Weissenberg camera, were recorded. The radiation used at this first stage of the

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

Empirical formula	$\text{C}_{16}\text{H}_{20}\text{FeO}$
Formula weight	284.17
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Orthorhombic
Space group	$Pbca$ (n.61)
Unit cell dimensions	$a = 12.491(4)$ Å $b = 13.170(4)$ Å $c = 16.119(5)$ Å
Volume	$2651.7(14)$ Å ³
Z	8
Density (calculated)	1.424 Mg m^{-3}
Absorption coefficient	1.122 mm^{-1}
$F(000)$	1200
Crystal size	$0.41 \times 0.30 \times 0.17\text{ mm}$
Theta range for data collection	2.53 to 22.50 deg.
Index ranges	$0 \leq h \leq 13$, $0 \leq k \leq 14$, $\bar{1}7 \leq l \leq 0$
Independent reflections	1142
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1142/0/167
Goodness-of-fit on F^2	1.297
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0485$, $wR_2 = 0.1016$
Largest diff. peak and hole	0.308 and -0.409 eÅ^{-3}

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (0.0229P)^2 + 8.08P]$ where $P = [\text{MAX}(F_o^2, 0) + 2F_c^2] / 3$.

Table 4

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

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Fe	1363(1)	1703(1)	1835(1)	30(1)
C(1)	857(6)	461(6)	1735(4)	43(2)
O	517(5)	-352(4)	1696(4)	77(2)
C(2)	521(5)	1836(5)	2965(4)	35(2)
C(3)	1377(6)	2558(5)	2910(4)	40(2)
C(4)	2405(6)	2227(6)	2722(4)	42(2)
C(5)	2595(6)	1170(5)	2590(5)	41(2)
C(6)	2376(7)	356(5)	3204(5)	52(2)
C(7)	1374(8)	298(6)	3640(5)	56(2)
C(8)	531(6)	936(6)	3515(5)	46(2)
C(9)	93(6)	2100(6)	988(5)	43(2)
C(10)	482(6)	2970(5)	1349(5)	38(2)
C(11)	1220(7)	3717(5)	958(5)	51(2)
C(12)	2185(6)	3239(5)	536(5)	51(2)
C(13)	2512(7)	2263(6)	938(4)	43(2)
C(14)	2141(7)	1319(6)	684(5)	47(2)
C(15)	1334(8)	1158(7)	-1(5)	61(2)
C(16)	334(7)	1768(7)	108(5)	59(3)

crystallographic study was Cu K α , $\lambda = 1.54178 \text{ \AA}$. The diffraction symmetry and systematic absences indicated the space group *Pbca*.

The crystal showing the sharpest spots on the film was chosen for the following intensity data collection, performed on a four-circle automatic Ital-Structures diffractometer, following the experimental conditions summarized in Table 3. The absence of specimen decay was verified by the periodic rescan of the reflections 0 2 0 and 4 0 6. After correction of data for Lorentz and polarization effects the structure was solved by the automatic Patterson method, contained in the SHELX 86 [20] program. The data were not corrected for absorption, owing to the medium-low coefficient value and the relatively small dimensions of the crystal.

The hydrogen atoms were introduced in calculated positions and the refinement has been performed by full-matrix least-squares calculations, contained in the SHELX 93 [21] program, until a final value of 0.048 for reliability factor *R*. Table 3 summarizes some refinement details. The scattering factors were taken from the literature [22] and the ORTEP [23] program was used for drawing the molecule projections. The final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 4; a list of observed and calculated structure factors has been sent to the editor as supplementary material; full lists of anisotropic thermal parameters and coordinates of hydrogen atoms have been deposited with the Cambridge Crystallographic Data Centre and can be obtained by full citation of the present paper.

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