Inorganica Chimica Acta, 41 (1980) 171–178
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Reactivity of Cycloheptatrienyl Tricarbonyl Ferrate(−1): Synthesis and Stereochemistry of Ditropylium Metal Carbonyl Complexes

M. AIROLDI, G. DEGANELLO*, G. DIA, P. SACCONE

Istituto di Chimica Generale ed Inorganica, Facoltà di Scienze dell'Università, Via Archirafi, 26-28, 90123 Palermo, Italy

and J. TAKATS

Department of Chemistry, University of Alberta, Edmonton, Alta., T6G 2E1, Canada

Received January 2, 1980

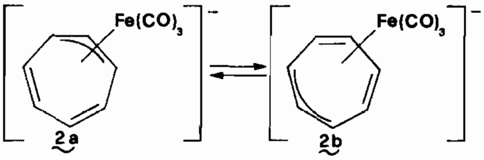
Exo-*deprotonation of* [*Fe*(*CO*)$_3$(*η*^{4}-*C*$_7$*H*$_8$)] (*1*) (*C*$_7$*H*$_8$ = *cyclohepta-1,3,5-triene*) *gives the anionic compound* [*Fe*(*CO*)$_3$(*η*^{3}-*C*$_7$*H*$_7$)]$^-$ (*2*). *The reactivity of* 2 *towards several electrophiles has been studied. Mixed ditropylium complexes of the type* [*FeM*(*CO*)$_6$(*C*$_{14}$*H*$_{14}$)] (*3*) *are obtained on treating* 2 *with* [*M*(*CO*)$_3$(*η*^{7}-*C*$_7$*H*$_7$)]$^+$ (*M* = *Cr, Mo, W*). *A minor product of these reactions is a ditropylium hexacarbonyldiiron derivative which becomes the major product in the reaction of* 2 *with several alkyl and allyl halides. The* exo-*stereochemistry of the ditropylium complexes is discussed on the basis of spectroscopic data and reactivity.*

Introduction

Coordination of metals to cyclic polyolefins is known to modify the electronic distribution of the ring carbon atoms thus allowing substitution of hydrogens by various reagents [1]. Complexes of different metals, coordinated in the same fashion to the same polyolefin, can show different reactivity. For instance [PdCl$_2$(2,3,6,7-η^4-C$_9$H$_{10}$)] **(C$_9$H$_{10}$ = bicyclo [6.1.0] nona-2,4,6-triene) is reactive towards nucleophiles [2] while [Fe(CO)$_3$(2,3,6,7-η^4-C$_9$H$_{10}$)] [3, 4] reacts with electrophiles [5]. Coordination of metals in different fashion to the same polyolefin also offers interesting examples of differing reactivity. Reaction of [(CPh$_3$)BF$_4$] with [M(CO)$_3$(η^6-C$_7$H$_8$)] (C$_7$H$_8$ = cyclohepta-1,3,5-triene, M = Cr, Mo, W) affords the corresponding tropylium complexes [M(CO)$_3$(η^7-C$_7$H$_7$)]$^+$ [7, 8] by abstraction of hydride from the methylenic carbon atom of the ring. The same reaction carried out on [Fe(CO)$_3$(η^4-C$_7$H$_8$)] (*1*) produces the ring addition product [Fe(CO)$_3$(η^4-C$_7$H$_8$CPh$_3$)]$^+$ [9, 10].

Although formation of an intractable product has been mentioned in a previous report [10] when *1* was treated with phenyl lithium, [Fe(CO)$_3$(C$_7$H$_7$)]$^-$ (*2*) has been detected and spectroscopically characterized upon reaction of *1* with butyl lithium in THF, at −78 °C [11]. Subsequently, deprotonation of *1* was achieved at room temperature using a variety of reagents such as t-Bu OK [12], [Si(CH$_3$)$_2$N] Na [13], and metal hydrides [14].

The possibility of two structures for *2* has been proposed on the basis of its preliminary reactivity towards some electrophiles [12] (Scheme 1).



Scheme 1

However, theoretical calculations based on energy profiles of the anion *2* as a function of the coordination number have shown that form *2a* is energetically more stable by 3.4 Kcal/mol [15]. An X-ray structural determination of *2* as tetraphenylarsonium salt confirms that *2a* is the actual structure of this anionic complex [16], *in* the solid state.

Complex *2* is an actractive starting material and substituted cycloheptatriene tricarbonyl iron complexes have been prepared from it [12, 17], as well as η^3-cycloheptatrienyl tricarbonyl iron derivatives [18] and Fe–M bonded bridging cycloheptatrienyl complexes [19].

In this paper we describe the synthesis from *2* of ditropylium complexes, their spectroscopic characterization and reactivity.*

---

*Author to whom correspondence should be addressed.

**Similar behaviour is manifested by [PdCl$_2$(η^4-C$_{10}$H$_{12}$)] (C$_{10}$H$_{12}$ = bicyclo [6.2.0] deca-2,4,6-triene), but comparison with [Fe(CO)$_3$(η^4-C$_{10}$H$_{12}$)] is not feasible, owing to rearrangement of the polyolefin to tricyclo [4.4.0.0^{2,5}] deca-7,9-diene in the latter complex [6].

*Part of this work has been communicated previously [12].

Experimental

IR spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer 457 spectrometer or in the 2200–1650 region with a Perkin-Elmer 580 spectrometer, using 1 mm NaCl cells. Calibrations are obtained with a polystyrene film. ^1H NMR spectra were obtained with a 60 MHz Varian NV-14 and a 400 MHz Bruker WH-400 spectrometer, in $CDCl_3$ as the solvent with TMS as the internal standard, at 30 °C. Mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6D operating at 70 eV, using the direct inlet technique for the introduction of the samples.

Melting points were determined in a Büchi melting point apparatus, and are uncorrected.

Elemental analyses were performed by Dörnis and Kolbe, Mülheim (West Germany).

Reagents and Preparations

Iron pentacarbonyl was filtered before use. Cycloheptatriene was freshly distilled. Potassium terbutylate was dried under vacuum several hr before use. Solvents (THF, benzene, petroleum (boiling range 40–70 °C)) were refluxed on sodium-potassium-benzophenone, and distilled before use. Florisil (60–100 mesh) was used as received, alumina of activity III was prepared from a Merck reagent (70–230 Mesh). Other reagents were used as received. $[Fe(CO)_3(\eta^4\text{-}C_7H_8)]$ [20], $[M(CO)_3(\eta^6\text{-}C_7H_8)]$ (M = Cr, Mo, W) [21], $[M(CO)_3(\eta^7\text{-}C_7H_7)]^+$ [21], were prepared according to published methods. $[Fe(CO)_3(\eta^4\text{-}C_7H_7OCH_3]$ was obtained from $C_7H_7OCH_3$ and $[Fe(CO)_3(BDA)]$. The pure complex was protonated with anhydrous HBF_4–diethyl ether complex and the yellow precipitate of $[Fe(CO)_3(\eta^5\text{-}C_7H_7)]^+$ was filtered, washed with ether, dried and used immediately. $[Fe(CO)_3(BDA)]$ was prepared with a slight modification of the literature method [22] by irradiating for 8 hr a 150 ml benzene solution containing $Fe(CO)_5$ (10 ml) and BDA (4 g) with a mercury lamp (450 W). The yield, after chromatography on an alumina or silica column, and crystallization was 4.6 g (m.p. 87–88 °C).

All preparations and subsequent manipulations in solution were carried out under nitrogen atmosphere.

Potassium Cycloheptatrienyl Tricarbonyl Ferrate-(−1), $[K\{Fe(CO)_3(\eta^3\text{-}C_7H_7)\}]$ (2)

Addition of solid t-BuOK to a stirred THF solution of $[Fe(CO)_3(\eta^4\text{-}C_7H_8)]$ (*1*) or dropwise addition of a THF solution of *1* to a magnetically stirred THF slurry of t-BuOK gave comparable results. The two reagents are used in 1 to 1 ratio. Usually 5 mmol scale preparations with 25 ml of THF were used. The resulting dark red solution is stirred till the absorption bands due to *1* (2050 s, 1975 s, br in THF) are completely replaced by those (1945 s, 1870 s, br) of *2*. This requires about 4 hr. The reaction mixture is used for the successive reactions assuming 95% yield of *2*, or evacuated in high vacuum overnight to give *2* as a dark-red pyrophoric powder. Elemental analyses were not carried out owing to the very high air sensitivity of the product.

Mixed Bis-cycloheptatrienyl Hexacarbonyl Dimetals, $[FeCr(CO)_6(C_{14}H_{14})]$ (3a)

To a magnetically stirred THF (10 ml) slurry of $[Cr(CO)_3(\eta^7\text{-}C_7H_7)]BF_4$ [21] was added dropwise a THF solution of *2* obtained from a 5 mmol preparation. An orange-red precipitate is obtained after 1 hr while the solution turns orange. The reaction mixture is evaporated to dryness and extracted several times with a CH_2Cl_2/ether 1:1 mixture until the extracts are almost colorless. The extracts are concentrated to about 10 ml to give some orange red crystalline material which is filtered off and washed with ether. The ether washing is added to the filtrate, concentrated and chromatographed on an alumina column. Elution with petroleum gives traces of *1* and a tiny amount of $[Fe(CO)_3(\eta^4\text{-}C_7H_7)]_2$ (see later). The red orange band which remains on the top of the column is eluted with ether. Evaporation of the solvent gives orange-red solid which is combined with the previous crop and crystallized from ether/petroleum. Analytical and spectroscopic data except ^1H NMR are listed in Table I. $[FeMo(CO)_6(C_{14}H_{14})]$ (*3b*) and $[FeW(CO)_6(C_{14}H_{14})]$ (*3c*) were prepared by analogous route and work up, starting from *2* and the corresponding tropylium derivative (Table I).

Bis-cycloheptatrienyl Hexacarbonyl Diiron

Procedure A: Reaction of 2 *with $CH_2{=}CH_2{-}CH_2Cl$ or $CH_3{-}CH{=}CH{-}CH_2Br$*

As mentioned in the discussion $[Fe(CO)_3(C_7H_7)]_2$ is a by-product in almost all the reactions involving the anion *2*. It becomes a major product of the reaction when *2* (obtained from 5 mmol preparation) is reacted with $CH_2{=}CH{-}CH_2Cl$ or $CH_3{-}CH{=}CH{-}CH_2Br$ in excess. The reaction mixture upon addition of the allyl halide turns rapidly yellow. After 2 hr it is evaporated to dryness and extracted with petroleum. The pale yellow extract is concentrated to few ml and chromatographed on Florisil column using petroleum as eluent. After a small amount of $[Fe(CO)_3(\eta^4\text{-}C_7H_8)]$ (*1*) a yellow band is developed which is collected and evaporated to give a waxy pale yellow solid. Crystallization from petroleum at −30 °C gives the product as pale-yellow needles. Y = 60% (see Table I for other analytical and spectroscopic data).

Procedure B: Reaction of 2 *with $[Fe(CO)_3(\eta^5\text{-}C_7H_7)]^+$*

Addition of a THF solution of *2* (obtained from 1 mmol preparation) to a stirred THF solution of $[Fe(CO)_3(\eta^5\text{-}C_7H_7)]BF_4$ (0.44 g) results in a yellow

TABLE I. Analytical and Spectroscopic Data of Ditropylium Complexes.

Compound	Color	M.p. °C	Yield %	Analysis Found	Analysis Calcd	Mass Spectrum (highest peak)	IR ν(CO)
$[FeCr(CO)_6(C_{14}H_{14})]$ *3a*	orange-red	146–149	75	C = 52.6 H = 3.02 Fe = 11.9	52.4 3.08 12.2	458 (P)	2058 s 1978 s, br 1920 s 1893 s
$[FeMo(CO)_6(C_{14}H_{14})]$ *3b*	red	126–130	77	C = 47.69 H = 2.75 Fe = 11.21	47.8 2.8 11.16	502 (P)	2056 s 1988 vs, br 1922 s 1898 s
$[FeW(CO)_6(C_{14}H_{14})]$ *3c*	red-wine	124–126	62	C = 41.1 H = 2.2 Fe = 9.3	40.7 2.4 9.5	590 (P)	2055 s 1985 vs, br 1918 ms 1890 s
$[Fe_2(CO)_6(C_{14}H_{14})]$ *5*	pale-yellow	120–124	variable (see text)	C = 52.12 H = 3.01 Fe = 24.15	51.95 3.03 24.44	204 (P–CO)	2059 s 1990 s 1979 s

solution which is evaporated after 2 hr. The residue is extracted with petroleum and worked up as in procedure A. Yield 50%.

Procedure C: Reaction of $[Fe(CO)_3(\eta^4\text{-}C_{14}H_{14})]$ *with* $[Fe(CO)_3(BDA)]$

$[Fe(CO)_3(\eta^4\text{-}C_{14}H_{14})]$ (0.6 g) is dissolved in benzene and $[Fe(CO)_3(BDA)]$ (0.5 g) is added. The reaction mixture is magnetically stirred at 65 °C for 48 hr. After evaporation of the solvent the residue is extracted with petroleum and chromatographed on an alumina column, activity III, using petroleum as eluent. A yellow band is collected, while orange-red $[Fe(CO)_3(BDA)]$ and orange yellow (BDA) are left behind. The yellow solution after usual work up gives 0.3 g of $[Fe(CO)_3(\eta^4\text{-}C_7H_7)]_2$.

Bis-cycloheptatrienyl Tricarbonyl Iron, $Fe(CO)_3(\eta^4\text{-}C_{14}H_{14})$

Procedure A: Demetalation of 3b *with* $(NH_2CH_2CH_2)_3N$

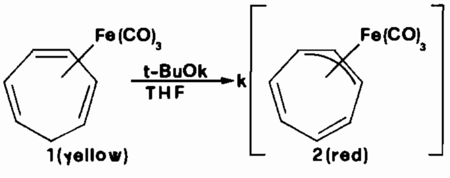
Complex *3b* (0.5 g) is dissolved in CH_2Cl_2 (10 ml) and treated with 1.5 molar excess of $(NH_2CH_2CH_2)_3N$. The reaction mixture is magnetically stirred for 24 hr, at room temperature. The filtered orange-yellow solution is evaporated to dryness and extracted with petroleum. Chromatography of the extract on an alumina column, activity III, by elution with petroleum gives an orange-yellow band that is evaporated to give 0.11 g of a waxy orange-yellow compound identified as $[Fe(CO)_3(\eta^4\text{-}C_{14}H_{14})]$, by ^1H NMR spectroscopy.

Procedure B: Reaction of 2 *with* $[C_7H_7(BF_4)]$

Addition of a THF solution of *2* (obtained from a 8 mmol preparation to $[C_7H_7(BF_4)]$ (1.42 g) in 10 ml of THF) results in the formation of an orange yellow mixture. After stirring for 4 hr, at room temperature, the solution is evaporated to dryness and the residue extracted with petroleum. Three distinct yellow bands are obtained by elution of the mixture with petroleum on an alumina column of activity III: the first and the second bands contain small amount of *1* and $[Fe(CO)_3(\eta^4\text{-}C_7H_7)]_2$, respectively while the third band gives, after usual work up, 0.61 g of $[Fe(CO)_3(\eta^4\text{-}C_{14}H_{14})]$, identified by ^1H NMR spectroscopy (Y = 25%).

Results and Discussion

Reaction of $[Fe(CO)_3(\eta^4\text{-}C_7H_8)]$ (*1*) with potassium terbutylate, in THF at room temperature, under rigorously anhydrous and oxygen-free conditions, results in rapid formation of a dark-red solution [12] (Scheme 2). The ^1H [11] and ^{13}C NMR [14, 18] spectra of *2* show a single line down to –80 °C, suggesting the occurrence of a rapid interconversion among equienergetic or isomeric forms of *2*. The simplest explanation of this behaviour involves a series of 1,2 shifts of the tricarbonyliron unit around the cycle (Scheme 3).



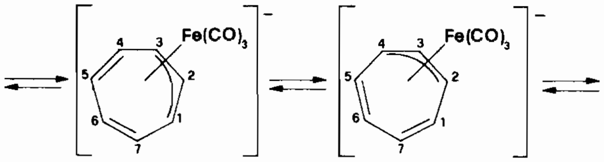
Scheme 2

The participation of the η^4-coordinated form *2b*, as intermediate in this mechanism, has been proposed

TABLE II. ^{1}H NMR Data for Ditropylium Metal Carbonyl Complexes[a].

Complex	Chemical Shift (τ)[b]									
	H_5	H_6	$H_{2,3}$	$H_{1,4}$	H_7	$H_{10,11}$	$H_{9,12}$	H_8	H_{13}	H_{14}
$[FeCr(CO)_6(C_{14}H_{14})]$ *3a*	4.22	5.3[c]	4.71	7.04	9.12	4.06	5.12	6.23	6.43	7.48
$[FeMo(CO)_6(C_{14}H_{14})]$ *3b*	4.16	5.1[c]	4.66	6.95	8.64	3.98	5.00	5.97	6.18	7.26
$[FeW(CO)_6(C_{14}H_{14})]$ *3c*	4.20	5.2[c]	4.73	7.03	8.63	4.05	5.18	6.06	6.27	7.23
$[Fe(CO)_3(C_7H_7)]_2$ *6*	3.90–5.25[d]		6.70–7.25[d]							
$[Fe(CO)_3(C_{14}H_{14})]$ *7*	4.08	4.8[c]	4.62	6.95	8.18[e]	3.37	3.78	4.7[c]	4.7[c]	7.0[c,e]

[a]Solvent $CDCl_3$, TMS as internal reference. [b]Numerical values refer to the center of the complex signal, following the numbers shown in Fig. 1. [c]Approximate chemical shift, signal overlapped by other multiplets. [d]See Fig. 3 for more precise assignments. [e]C.S. values of H_7 and H_{14} given here may be reversed (see Discussion).



Scheme 3

[15]. However, it does not appear necessary for understanding the phenomenon.

Although *2a* can be isolated, as a pyrophoric powder, by prolonged evaporation of the condensable products (THF, t-BuOH) under high vacuum, we have not found it inconvenient to use the THF solution directly for further reactions*. When the red THF solution of *2a* is treated with the tropylium complexes $[M(CO)_3(\eta^7\text{-}C_7H_7)]^+$, (M = Cr, Mo, W), red crystals have been obtained in 60–75% yield which analyze as $[FeM(CO)_6(C_{14}H_{14})]$ (*3a, b, c*) as shown in Table I. Since the $Fe(CO)_3$ and the $M(CO)_3$ groups show very small changes in their carbonyl frequencies in the IR spectrum compared to those of $[Fe(CO)_3(\eta^4\text{-}C_7H_8)$ and $[M(CO)_3(\eta^6\text{-}C_7H_8)]$ (M = Cr, Mo, W), the formation of a metal–metal bond can be ruled out safely**. The carbon–carbon bond position can be deduced from the ^{1}H NMR spectra of the complexes. Since the spectra of *3a, 3b,* and *3c* are very similar (Table II) we will discuss only the ^{1}H NMR spectrum of *3c* (Fig. 1 and Table III). This spectrum is indeed reducible to the sum of that of *1* [10] and of $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ [24], at least in the olefinic region, the only difference being the position of H_7 and H_{14} signals, as expected. This similarity implies that the two cycloheptatrienyl units are linked through their 7-carbon atoms. The uncertainty to be solved in the interpretation of the spectrum of Fig. 1 is the stereochemistry in both the cycloheptatrienyl tricarbonyl metal units. The possible combinations are shown in Fig. 2.

TABLE III. 400 MHz ^{1}H NMR Spectrum of $[FeW(CO)_6(C_{14}H_{14})]$ (*3c*), in $CDCl_3$.

Chemical Shifts	τ	Coupling Constants (Hz)	
$H_{10,11}$	4.01	H_5–H_7	1.5
H_5	4.19	H_5–H_6	10.6
$H_{2,3}$	4.71	H_5–H_4	7.8
H_6	5.04[a]	H_7–$H_{1,6}$	4.6
$H_{9(12)}$	5.04[a]	H_7–H_{14}	8.5
$H_{12(9)}$	5.17	H_{14}–$H_{8,13}$	8.5
H_8	6.02		
H_{13}	6.26		
H_1	6.97		
H_4	7.04		
H_{14}	7.22		
H_7	8.66		

[a]Approximate chemical shifts since H_6 and $H_{9(12)}$ are overlapping.

A detailed study of ^{1}H NMR spectra of compounds of the type $[Cr(CO)_3(\eta^6\text{-}C_7H_7R'')]$ (R″ = alkyl) [25] showed that the position (*endo* or *exo*) of the R″ unit with respect to the coordinated $Cr(CO)_3$ group is clearly determined by the chemical shift of H_7 and by its coupling constant with $H_1(H_6)$. When R″ is in the *endo* position the H_7 signal appears at $\tau = 9.1$ while τ_{H_7} is shifted 1–1.5 ppm downfield if

---

*The yields of the products in this case are about 3–4% lower.

**The formation of a σ-intermediate, $[(\eta^3\text{-}C_7H_7)Fe(CO)_3(\eta^1\text{-}C_7H_7)M(CO)_3]$, cannot be excluded *a priori*. The first stable σ-cycloheptatrienyl derivative of a transition metal, *i.e.* $[Re(CO)_5(\eta^1\text{-}C_7H_7)]$, has been synthesized recently [23].

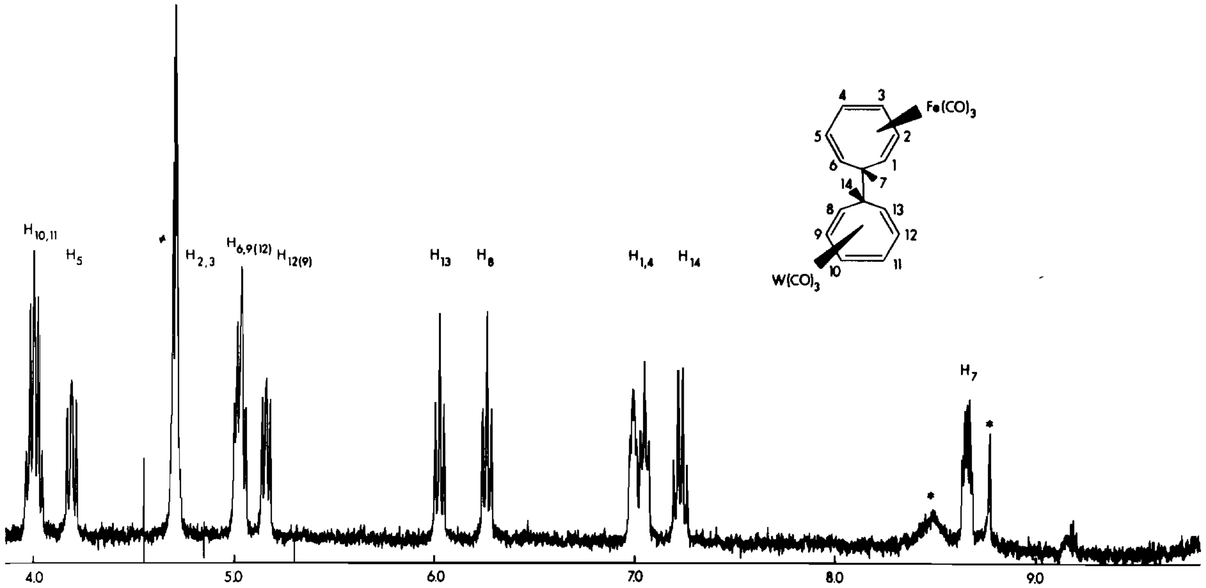
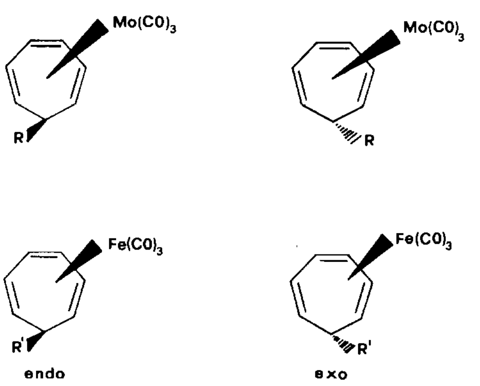


Fig. 1. The 400 MHz ^1H NMR spectrum of $[FeW(CO)_6(C_{14}H_{14})]$ (*3c*) in $CDCl_3$.



$R = -C_7H_7Fe(CO)_3$
$R' = -C_7H_7Mo(CO)_3$

Fig. 2. The possible stereochemistry for the $[M(CO)_3(\eta^6\text{-}C_7H_7R)]$ and $[Fe(CO)_3(\eta^4\text{-}C_7H_7R')]$ in complexes of type *3*.

R″ is in the *exo*-position, due to the absence of the shielding effect of the cycloheptatriene moiety in the latter case. Moreover the empirical Karphus curve [26] anticipates coupling constants of 4 Hz and 8 Hz, respectively. In our case the chemical shift of the signals attributable to protons in the 7-position are respectively at τ = 7.22 and 8.66. Selective decoupling experiments conclusively established that the signal at τ = 7.22 belongs to H_{14}. The position and the shape of the signal (quartet with $J_{H_{8,13}-H_{14}}$ = 8.5 Hz) are very close to that of $[Cr(CO)_3(\eta^6\text{-}C_7H_7R'')]$ complexes with *exo* stereochemistry. Accordingly we attribute the stereochemistry *exo* (Fig. 2) to the $[M(CO)_3(\eta^6\text{-}C_7H_7R)]$ portion of complexes *3a, b, c*.

More variable values for chemical shifts and coupling constants ($J_{H_{1,6}-H_7}$) are found in complexes of the type $[Fe(CO)_3(\eta^4\text{-}C_7H_7R')]$. In the case of $[Fe(CO)_3(\eta^4\text{-}C_7H_7GeMe_3)]$ (*4*) the substituent occupies the 7-*exo* position as shown by a X-ray diffraction analysis [27]. However, application of the empirical Karplus curve [26] to the coupling constants ($JH_{1,6}$–H_7) of *4* would predict a value larger than 6.5 Hz for the *exo*-isomer and lower than 3.0 Hz for the *endo*-isomer. Although this empirical correlation has been used successfully for the correct prediction of $J_{H_{1,6}-H_7}$ for the $[Cr(CO)_3(\eta^6\text{-}C_7H_7R)]$ complexes, it appears not to be decisive in the assignment of the stereochemistry of $[Fe(CO)_3(\eta^4\text{-}C_7H_7R')]$. In *4* $J_{H_{1,6}-H_7}$ is 5.0 Hz, a value which does not indicate a clear choice [28]. The X-ray analysis of *4*, as mentioned, however establishes an *exo*-stereochemistry [27]. The chemical shift of H_7 in *4* has a value of τ = 8.19 [28], somewhat lower than the value found in our mixed ditropylium complexes *3* (Table II, H_7). The nature of the substituent also appears to have a great influence on the chemical shift of H_7. For instance in $[Fe(CO)_3(\eta^4\text{-}C_7H_7GePh_3)]$ τ_{H_7} = 7.06 (in $[Fe(CO)_3(\eta^4\text{-}C_7H_7Ph)]$ for which an *exo*-stereochemistry also has been established by X-ray analysis [29], τ_{H_7} is not available).

On the basis of the above information and considering that similar preparative routes have been used for the synthesis of *3* and *4*, we are confident in assigning the *exo*-stereochemistry to the $[Fe(CO)_3$-

---

It is obvious that the arguments used by Pauson and coworkers [25] for the chromium complex are extensible to the corresponding molybdenum and tungsten complexes. Moreover, the spectra of *3a, 3b,* and *3c* are very similar (Table II).

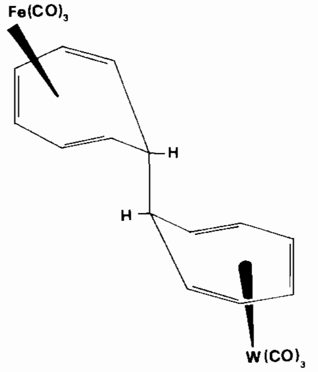


Fig. 3. The *exo*-stereochemistry of *3*, deduced from a model.

(η^4-C_7H_7R')] units in *3* (Fig. 2) and therefore the overall stereochemistry of *3* is that shown in Fig. 3*. Having established the *exo*-stereochemistry for complexes *3* it would be of interest to elucidate the mechanism of their formation. As mentioned in the introduction the anion *2* exists in the form *2a* [15, 16]. This structure could imply a localization of the negative charge mostly on iron which could be the preferable site of attack for the entering electrophile in our reactions (see footnote at page 9). However molecular orbital calculations indicate a lower negative charge on the cycloheptatrienyl ring for the η^4-bonded structure *2b* as compared to the η^3-bonded structure *2a* [15]. This finding is dictated by the localization of the 2a″ orbital on the coordinated diene system. Although this result may not be discriminating for the site of attack of the entering electrophile, since compounds of the type [Fe(CO)$_3$-MPh$_3$(η^3-C_7H_7)] have been isolated in the reaction of *2* with Cl MPh$_3$ (M = Sn, Pb) [28], it does suggest the possibility of a direct attack on the ring. Formation of *3* should then require a reorganization of the electron density on the ring. The alternative explanation [12] of a direct attack of the electrophile on the ring in the form *2b* appears therefore, in the light of the above calculations, less probable or at least not necessary.

Minor products in the reaction of *2* with [M(CO)$_3$-(η^7-C_7H_7)]$^+$ are [Fe(CO)$_3$(η^4-C_7H_8)] (*1*) and [Fe(CO)$_3$(η^4-C_7H_7)]$_2$ [12] (*5*). While the formation of *1*** can be attributed to the presence of trace amounts of water, the most likely explanation for the formation of *5* is an electron transfer between reagents followed by coupling. The yield of *5* is greatly increased if the reaction of *2* is carried out with weak electrophiles such as CH$_3$I or especially allyl halides. The mass spectrum (highest peak at 204 m/e) suggest a dimeric nature for the complex, although the parent peak (232 m/e) is not detected. A symmetric configuration for *5* is evident (three sharp carbonyl bands in the IR spectrum (Table I). The ^{1}H NMR spectrum (Fig. 4) clearly shows that the linkage is again between the C$_7$ atoms of the two rings, with the same stereochemistry for both [Fe(CO)$_3$(η^4-C_7H_7R')] units.

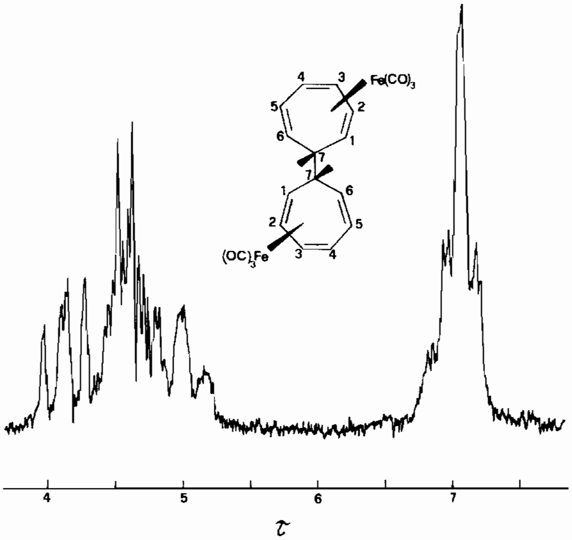


Fig. 4. The 60 MHz ^{1}H NMR spectrum of [Fe(CO)$_3$(η^4-C_7H_7)]$_2$ (*5*), in CDCl$_3$.

The stereochemistry at the C–C junction remains somewhat debatable. As we pointed out before, the ^{1}H NMR criteria, so successful in predicting the stereochemistry of [M(CO)$_3$(η^6-C_7H_7R)] complexes appear not to be applicable in a reliable fashion to [Fe(CO)$_3$(η^4-C_7H_7R')] compounds. Indeed, although the overlapping of the signals due to H$_{1,4}$ and H$_7$ precludes a detailed analysis, the apparently small coupling constants, $J \leqslant 2.5$ Hz, would suggest an *endo* stereochemistry. On the other hand, the position of the signals attributed to H$_7$, much lower than in the mixed ditropylium complexes, 3, is diametrically opposed to this and would suggest *exo* stereochemistry in this compound as well.

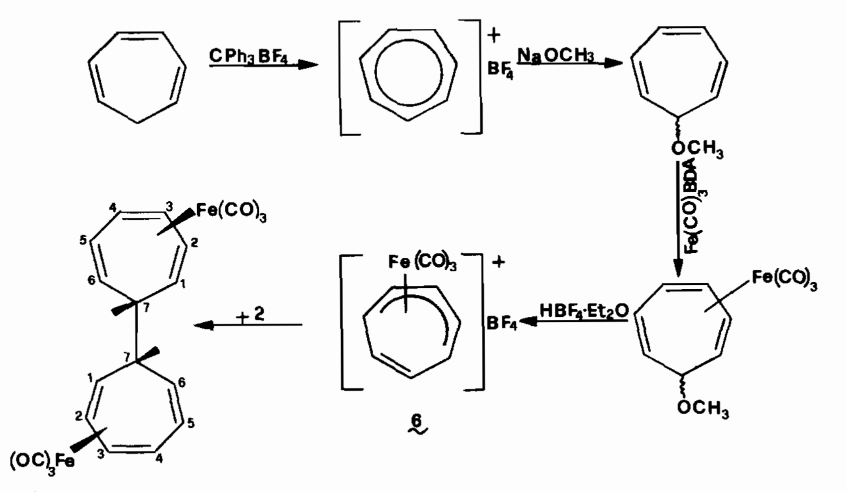
More convincing evidence against the *endo*-stereochemistry in *5* is given by some reactions we carried out with the aim of elucidating the structure of *5*. Reaction of *2* with [Fe(CO)$_3$(η^5-C_7H_7)]$^+$ (*6*) [30] obtained in good yield via the route outlined in Scheme 4, gives only *5*.

We note that the reaction conditions for the reaction of *6* with *2* are very similar to those used for the synthesis of the *exo*-complexes *3*. The possibility that *5* in this reaction is again originated by oxidative coupling appears less probable.

---

*Effects of solvents on the chemical shift of *3* and *4* are considerable for the protons attached to the olefinic carbons, but negligeable for H$_7$ or H$_{14}$.

**The amount of *1* is variable, albeit low.



Scheme 4

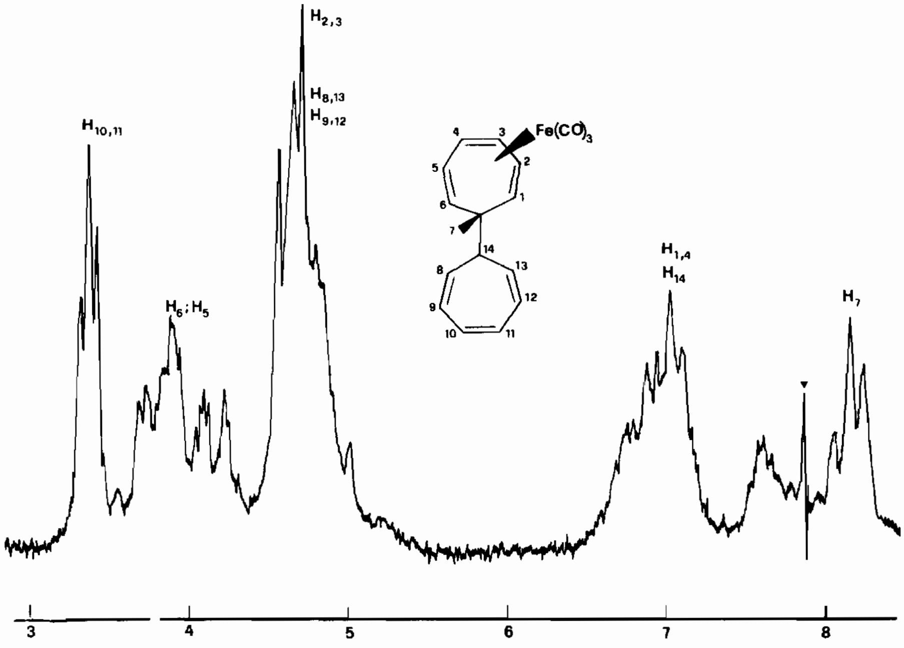


Fig. 5. The 60 MHz ^1H NMR spectrum of $[Fe(CO)_3(\eta^4\text{-}C_{14}H_{14})]$ (*7*), in $CDCl_3$.

Moreover, by treating complex *3b* with excess $[(H_2N\text{–}CH_2\text{–}CH_2)_3N]$, a known powerful chelating ligand for $Mo(CO)_3$ groups [31], selective demetalation of $Mo(CO)_3$ is achieved. The resulting complex $[Fe(CO)_3(\eta^4\text{-}C_{14}H_{14})]$ (*7*) has a ^1H NMR spectrum (Fig. 5) consistent with the chemical shifts reported for *7* obtained by a different synthetic approach [32]. Complex *7* can be synthesized in good yield by reaction of *2* with $[C_7H_7BF_4]$ in THF and is, surprisingly, a minor product of the reaction of *2* with $CH_2{=}CH_2\text{–}CH_2Cl$ (see experimental part).

Assignment of H_{14} to quartet centered at $\tau = 8.18$ ($J = 6.0$ Hz) is not certain and the signal of H_7 is part of a multiplet centered at $\tau = 6.85$. Although, as correctly noted [32] the assignments of τ_{H_7} and $\tau_{H_{14}}$ can be reversed, we believe that the stereochemistry of the $[Fe(CO)_3(\eta^4\text{-}C_7H_7R')]$ unit remains *exo* after demetalation. Again we note, whatever the correct assignment of the H_7 and H_{14} chemical shift, the difficulty in providing the correct stereochemistry on the basis of chemical shifts and coupling constants in $[Fe(CO)_3(\eta^4\text{-}C_7H_7R)]$ derivatives.

Reaction of *7* with $[Fe(CO)_3(BDA)]$ gives again *5*, albeit in low yield.

Finally, attempts to react *5* with t-BuOK to obtain the dianion corresponding to *2* failed suggesting again that *exo* stereochemistry is more appropriate for *5*. It is well established that *exo*-deprotonation occurs in

$Fe(CO)_3(\eta^4\text{-}C_7H_8)$] although a recent exception has been reported in the case of [$Fe(CO)_3(\eta^4\text{-}C_7H_7\text{-}GePh_3)$] which is *endo*-deprotonated by t-BuOK to give [$Fe(CO)_3(\eta^3\text{-}C_7H_6\text{-}GePh_3)$] [28].

In conclusion, although a definitive answer on the stereochemistry of the ditropylium complexes described here must await X-ray structural analysis*, we anticipiate an *exo*-stereochemistry for both *3* and *5*.

We are now investigating the influence of these bulky groups on the fluxional behaviour of [$Fe(CO)_3(\eta^4\text{-}C_7H_7R)$] complexes. According to recent reports which have established the occurrence of a fluxional process in [$Fe(CO)_3(\eta^4\text{-}C_7H_8)$] [34, 35]** and to the great influence of R on the activation energy of the process [36], we expect that *3* and *5* will be fluxional and amenable to conventional variable temperature NMR spectral studies.

Acknowledgements

We thank NATO (Grant N. 1209 to G. D. and J. T.), Italian CNR and Ministero della Pubblica Istruzione for financial support. We thank Drs. F. Vasile and S. Terranova for experimental assistance in the earlier stage of this work, and Drs. H. Reuvers and T. Nakashima for obtaining the 400 MHz spectrum of 3c.

---

*Crystals of *3a* and *5* are going to be studied by X-ray analysis by Professor V. W. Day of the University of Nebraska.

**Owing to the high activation energy of the process involved and to decomposition of *1* at ~100 °C, the fluxional behaviour of *1* has been established only by the use of the Forsen–Hoffmann saturation method both in the ^{13}C [34] and ^1H NMR [35] spectra of *1*.

References

1 G. Deganello, 'Transition Metal Complexes of Cyclic Polyolefins' Academic Press, London (1979).

2 P. L. Sandrini, R. A. Michelin, G. Deganello and U. Belluco, *Inorg. Chim. Acta, 17,* 65 (1976).

3 E. J. Reardon, Jr. and M. Brookhart, *J. Am. Chem. Soc., 95,* 4311 (1973).

4 G. Deganello, H. Maltz and J. Kozarich, *J. Organometal. Chem., 60,* 323 (1973); M. Airoldi, G. Deganello and J. Kozarich, *Inorg. Chim. Acta, 20,* L-5 (1976).

5 A. Salzer and W. von Philipsborn, *J. Organomet. Chem., 161,* 39 (1978).

6 F. A. Cotton and G. Deganello, *J. Organometal. Chem., 38,* 147 (1972); *J. Am. Chem. Soc., 95,* 396 (1973).

7 J. D. Munro and P. L. Pauson, *Proc. Chem. Soc.,* 267 (1959).

8 H. J. Dauben, Jr. and L. R. Honnen, *J. Am. Chem. Soc., 80,* 5570 (1958).

9 H. J. Dauben, Jr. and D. J. Bertelli, *J. Am. Chem. Soc., 83,* 497 (1961).

10 R. Burton, L. Pratt and G. Wilkinson, *J. Chem. Soc.,* 594 (1961).

11 H. Maltz and B. A. Kelly, *Chem. Comm., 1390* (1971).

12 G. Deganello, T. Boschi and L. Toniolo, *J. Organomet. Chem., 97,* C-46 (1975).

13 M. Moll, H. Behrens, R. Kellner, H. Knöckel and P. Wurstl, *Z. Naturforsch., 31b,* 1021 (1976).

14 J. Takats and J. G. Reuvers, *II Joint Meeting of the Chemical Institute of Canada.* The American Chemical Society, Montreal, May 29–June 2, 1977. Comm. C-90.

15 P. Hoffmann, *Z. Naturforsch., 33b,* 251 (1978).

16 E. Sepp, A. Pürzer, G. Thiele and H. Behrens, *Z. Naturforsch., 33b,* 261 (1978).

17 M. Moll, H. Behrens, R. Kellner, H. Knöckel, M. Moll and E. Sepp, *Z. Naturforsch., 31b,* 1019 (1976).

18 L. K. K. Li Shing Man and J. Takats, *J. Organomet. Chem., 117,* C-104 (1976).

19 M. J. Bennett, J. L. Pratt, K. A. Simpson, L. K. K. Li Shing Man and J. Takats, *J. Am. Chem. Soc., 98,* 4810 (1976).

20 L. Kruczinski and J. Takats, *Inorg. Chem., 15,* 3140 (1976).

21 R. B. King, 'Organometallic Syntheses', Vol. 1, p. 141, J. J. Eisch and R. B. King Eds., Academic Press (London) 1965.

22 M. Brookhart, G. W. Koszalka, G. O. Nelson, G. Sholes and R. A. Watson, *J. Am. Chem. Soc., 98,* 8155 (1976).

23 D. M. Heinekey and W. A. G. Graham, *J. Am. Chem. Soc., 101,* 6115 (1979).

24 R. B. King and A. Frozaglia, *Inorg. Chem., 5,* 1837 (1966).

25 P. L. Pauson, G. H. Smith and J. H. Valentine, *J. Chem. Soc. (C),* 1057 (1967) and 1061 (1967).

26 M. Karplus, *J. Chem. Phys., 30,* 11 (1959).

27 V. W. Day, personal communication (Sept. 1978).

28 J. G. A. Reuvers and J. Takats, *J. Organomet. Chem., 175,* C13 (1979).

29 J. A. D. Jefferys and C. Metters, *J. Chem. Soc., Dalton,* 729 (1977).

30 J. E. Mahler, D. A. K. Jones and R. Pettit, *J. Am. Chem. Soc., 86,* 3589 (1964).

31 W. Grimne, *Ber., 100,* 113 (1968).

32 P. McArdle, *J. Chem. Soc. Chem. Comm.,* 482 (1973).

33 M. Brookhart, K. J. Karel and L. E. Nance, *J. Organomet. Chem., 140,* 203 (1977).

34 B. E. Mann, *J. Organomet. Chem., 141,* C-33 (1977).

35 K. J. Karel and M. Brookhart, *J. Am. Chem. Soc., 100,* 1619 (1978).

36 C. S. Day, V. W. Day, G. Deganello, L. K. K. Li Shing Man, J. G. A. Reuvers and J. Takats, submitted to *J. Am. Chem. Soc..*