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OLIGOMERIZATION CATALYSTS

VII. THE ROLE OF DIOLEFIN MONOCARBONYL IRON(0) COMPLEXES IN BUTADIENE OLIGOMERIZATION AND POLYMERIZATION*

A. CARBONARO and F. CAMBISI
Montecatini Edison S.p.A., Centro Ricerche Milano, Via G. Colombo, 81–Milan (Italy)

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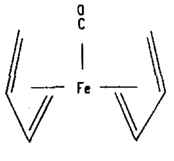
SUMMARY

As an extension of research on dibutadienecarbonyliron (I) and butadienecyclooctatetraenecarbonyliron(IV), the synthesis and some properties of the homologous diisoprenecarbonyliron(II), di-1,3-pentadienecarbonyliron(III), isoprenecyclooctatetraenecarbonyliron (V) and 1,3-pentadienecyclooctatetraenecarbonyliron (IV) complexes are described. All these compounds smoothly oligomerize butadiene. In the presence of protic acids, (I), (II) and (III) readily induce butadiene polymerization, whereas (IV), (V) and (VI) are transformed into stable allylic derivatives.

Possible mechanisms for conjugated diolefins oligomerization and polymerization are discussed.

FOREWORD

In 1970, 40 years after the discovery of butadienetricarbonyliron, dibutadienemonocarbonyliron (I) was prepared by three independent research groups. The X-ray structure of (I) was first described by Davis, Cupper and Simpson[1] who, however, did not give details of its preparation. Almost simultaneously, one of the present authors reported the synthesis of (I) via carbonylation of an ethereal solution of $FeCl_3$, butadiene and isopropylmagnesium chloride[2]. The preparation of (I) by UV irradiation of a mixture of $(CO)_5Fe$ and butadiene was later reported by Körner von Gustorf *et al.*[3]. Butadienecyclooctatetraenecarbonyliron (IV), was also reported by Carbonaro and Greco[2,4]. In this paper we describe the preparation and some properties of the two series of compounds having structures analogous to those of (I) and (IV), *viz.*:



(I)

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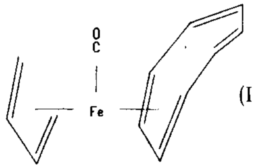
* For Part VI, see ref. 4.


(IV)

(Isoprene)$_2$FeCO (II), (1,3-pentadiene)$_2$FeCO (III), (isoprene)(cyclooctatetraene)FeCO (V), and (1,3-pentadiene)(cyclooctatetraene)FeCO (VI). (II)[3,4] and (III)[4] have previously been briefly described in the literature.

EXPERIMENTAL

Preparation of iron complexes

The new iron complexes were prepared by the method used for (I) and (IV)[4]. The molar ratio between magnesium and iron compounds ranged from 3 to 5, the CO pressure from 1 to 10 atm (yields increase slightly with the pressure) and the reaction times from 2–8 h at 0°.

The mixed complexes (IV)–(VI) were prepared starting either from (COT)$_2$Fe, as described for (IV)[4], or preferably from FeCl$_3$ and i-C$_3$H$_7$MgCl in the presence of COT and the appropriate diolefin, as for (I).

Ferric chloride (1 g) was dissolved in a glass flask in diethyl ether (50 ml) freshly distilled from LiAlH$_4$. COT (4 ml, 0.35 moles) and diolefin (0.18 moles) were added. The stirred solution was cooled to $-30°$, and a 3.1 *M* ethereal solution of i-C$_3$H$_7$MgCl (7.2 ml) was slowly added. The red solution was maintained at 0° for about 1 h, or at room temperature for about 10 min. The subsequent carbonylation was carried out in a stainless steel autoclave for 8 h at 0° under ca. 10 atm of CO pressure. The solution was evaporated under vacuum and the residue sublimed (0.01 mmHg, 50–70°). The pure compounds were obtained by recrystallization from cooled ($-78°$) n-hexane solutions. Yields were in the 20–30% range based on the ferric chloride taken.

TABLE I

ANALYSES

Compd.	*Formula*	*Found (%)*			*Calcd. (%)*		
		C	*H*	*Fe*	*C*	*H*	*Fe*
(II)	$C_{11}H_{16}FeO$	59.86	7.31	25.32	60.02	7.27	25.42
(III)		59.90	7.36	25.50			
(V)	$C_{14}H_{16}FeO$	65.60	6.29	22.02	65.63	6.24	21.84
(VI)		65.39	6.41	21.94			

Properties of the new complexes

Spectroscopic characterizations were performed on a Perkin–Elmer 125 IR spectrophotometer (KBr optics), a Jeol JNM 4H 100 MHz NMR spectrometer (C$_6$D$_6$ solution, room temperature, C$_6$H$_6$ reference), and a Hitachi RMU 6 E (70 eV) mass spectrometer.

(I)–(VI) are thermally stable below their melting points, and are very soluble in hydrocarbons. Solutions in chlorinated solvents decompose at room temperature.

(II) (orange needles, m.p. 115°) shows a mass spectrum parent peak at *m/e* 220 and principal fragments at *m/e* 192, 56, 125, 190, 67, 89, 96. ^{1}H NMR signals are at δ 4.0 (1 H), 1.75 (3 H), 1.4 (2 H), and −0.2 (2 H) ppm to TMS. Medium to strong bands in the IR spectrum (2500–650 cm^{-1} range) are at 1965 vs, 1470, 1425, 1378, 1198, 1027, 925, and 817 cm^{-1}. The UV spectrum shows maxima at 211 (log ε 4.277) and 230 (log ε 4.124) nm.

(III) is a low-melting red-orange solid (m.p. about 25°). It can be prepared either from a mixture of *trans*- and *cis*-1,3-pentadiene or from the pure isomers, but the *cis*-isomer gives the highest yields. The mass spectrum parent peak is at *m/e* 220, and fragments at *m/e* 124, 56, 82, 192, 96. The NMR spectrum shows four complex bands centered at δ 4.4 (2 H), 0.8 (4 H), 0.2 (1 H) and −0.4 (1 H) ppm. The IR spectrum contains absorptions at 1960 vs, 1482, 1446, 1375, 1223, 1193, 1055, 1027, 990, 948, 922–897, 660, 580 vs, 540 vs, 510, 460, and 417 cm^{-1}. The UV maxima are at 232 (log ε 4.715) and 206 (log ε 4.857) nm.

(V) (brown needles, m.p. 96°) shows a mass spectrum parent peak at *m/e* 256, and fragments at *m/e* 78, 104, 39, 68, 56, 134, 51, 53, 160, 103. The NMR spectrum shows a singlet at δ 4.4 ppm (8 H) and multiplets centered at δ 4.1 (1 H), 1.5 (5 H), and −0.25 (2 H) ppm. Bands in the IR spectrum are at 1963 vs, 1575, 1424–1417, 1477, 1453, 1380, 1204, 1031, 862, 818, 777, 709 vs, and 693 vs cm^{-1}. The UV spectrum shows maxima at 207 (log ε 4.373), 258 (log ε 4.116), and 292 (log ε 4.078) nm.

(VI) (brown crystals, m.p. 104°) has the mass spectrum parent peak at *m/e* 256, and fragments at *m/e* 56, 134, 78, 68, 104, 160, 39. The NMR spectrum shows a singlet at δ 4.5 ppm (8 H), and multiplets at δ 4.2 (2 H), 1.6 (1 H), 1.1 (3 H), 0.5 (1 H), and −0.15 (1 H) ppm. IR bands are at 1963 vs, 1570, 1475, 1453–1431, 1414, 1372, 1235, 1198, 1028, 957, 898, 882, 860, 775, 709 vs, 693 vs, and 653 cm^{-1}. The UV maxima are at 292 (log ε 3.754), 265 (log ε 3.767), and 209 (log ε 4.045) nm.

Decomposition of the complexes in CCl_4

(I) or (II) (10–20 mg) was dissolved in CCl_4 (1 ml) containing 1% wt of n-nonane as internal standard. After 12 h at room temperature, quantitative GLC analysis of the solution (C.Erba, Fractovap C, methylsilicone SE 30, 2 m, 150°, He) gave 1,5-cyclooctadiene from (I) (90–95% of the calculated based on butadiene) and 1,5-dimethyl-1,5-cyclooctadiene* from (II) (60–90% of the calcd.).

(III) was decomposed in CCl_4 containing 1% wt. of n-nonane and about 1% wt. of thiophene: 3,4-dimethyl-1,5-cyclooctadiene* was found by GLC (50–55% of the calcd.) as well as *trans*-1,3-pentadiene (about 40% of the calcd.).

(IV)–(VI) decompose similarly in CCl_4. The reaction products, containing 1/1 adducts COT/diolefin, were not characterized.

Reaction of the complexes with acids

A solution of (I) or (IV) (40–50 mg) in toluene (5 ml) was cooled to −78° and a 0.2 *M* hydrochoric acid solution in dry n-hexane was added slowly with stirring.

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* Shown to be identical with an authentic sample prepared as described in the literature[5].

After addition of an equimolar amount of acid, an insoluble compound separated in a few minutes; chemical analysis showed that the compounds formed were impure, but according to the mass spectrum, mainly $FeCl_2$ was produced from (I).

The composition of the compound (VII) obtained from (IV) is close to that for $(C_8H_9)(C_4H_6)Fe(CO)Cl$. The mass spectrum (70°) shows a parent peak at *m/e* 348 and fragments at *m/e* 320, 266, 216, 238, 134, 105, 91 and 78, corresponding to the formula $(C_8H_9)_2(C_4H_6)FeCO$. The IR spectrum contains absorptions at 2002 vs, 1498, 1460 vw, 1430, 1409, 1375, 1235, 1225, 1168, 1133, 1110, 1068, 1047, 1027, 1010, 945, 906, 889, 851, 833, 768 and 742 cm^{-1}.

Reaction of (I) with hydrochloric acid in the presence of butadiene

A solution of (I) (48 mg) was in toluene (4 ml) containing butadiene (3.9 g) was cooled to −78° and a 0.2 *M* HCl solution in n-hexane (1.25 ml) was added. After 2 h at 0°, a white insoluble organic compound (35 mg) was obtained, the IR spectrum of which indicated a predominant 1,2-polybutadiene structure.

Reaction of (I) with trichloroacetic acid in the presence of butadiene

(I) (13 mg) was dissolved in a mixture of toluene (6 ml) and butadiene (3.9 g). After cooling to −10°, a 0.07 *M* CCl_3COOH solution in n-hexane (1 ml) was added. The reaction mixture was maintained overnight at −10°. From the yellow solution 1 g of polymer was obtained by addition of excess methanol, and had a mol. wt. of 4700 (mechrolab); IR analysis indicated that it consisted of 80% of *cis*-1,4- and 20% of 1,2-butadiene units.

Preparation of tri-2-thienylaluminum

This compound was prepared as previously described[6].

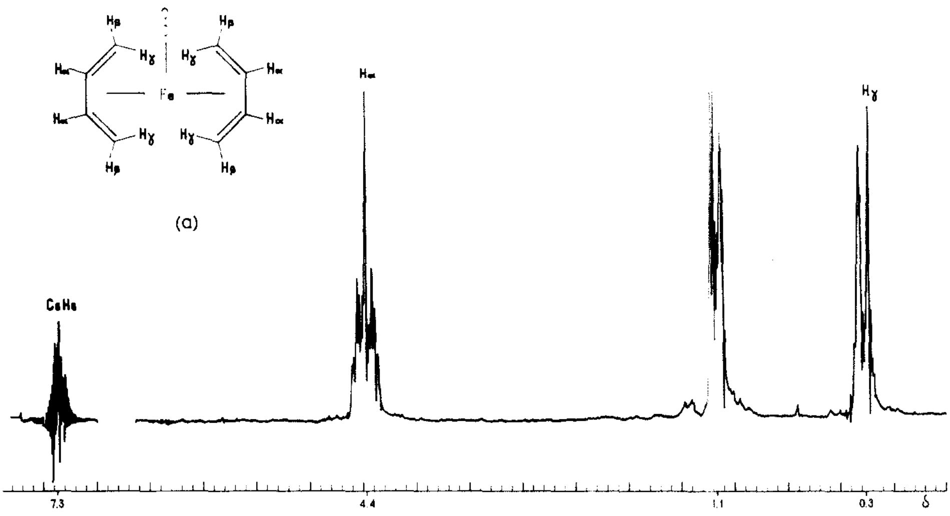
Di-2-thienylmercury (2 g)[7], and aluminum turnings (1 g) were allowed to react in boiling toluene (70 ml) for about 90 min. The filtered solution was concentrated to 5 ml and then diluted with n-heptane (10 ml). From the cooled (−35°) toluene/heptane solution, white crystals were obtained (0.92 g), m.p. 160–165° (dec.). (Found: C, 53.12; H, 3.62; Al, 9.71; S, 33.35. $AlC_{12}H_9S_3$ calcd.: C, 52.17; H, 3.26; Al, 9.79; S, 34.80%.) Bands in IR spectrum are at 1465, 1398–1378, 1205, 1177, 1080, 965, 905, 845, 752, 743, 710 vs and 673 cm^{-1}.

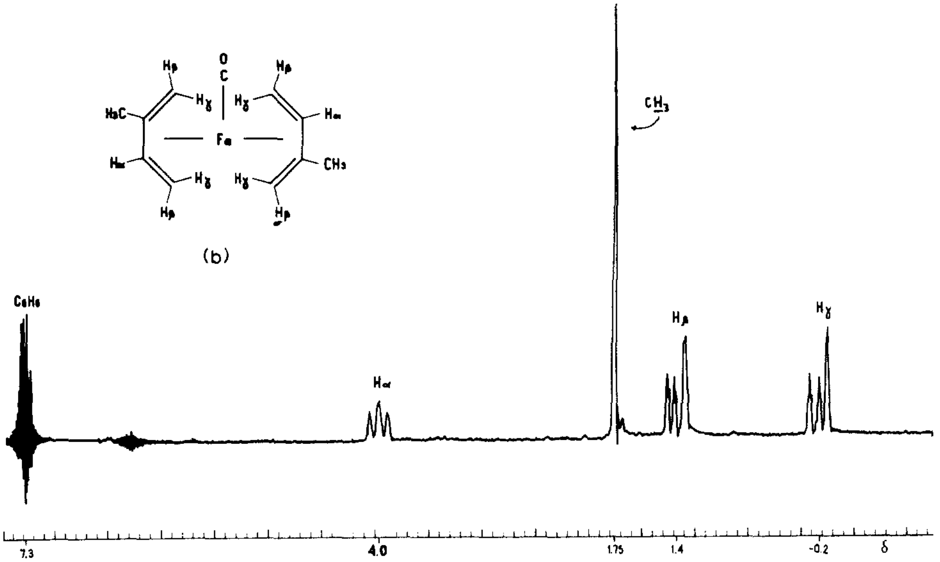
The compound is rapidly decomposed by water: with D_2O, 2-deuteriothiophene is formed (NMR). Hydrolysis with C_2H_5OH gave over 90% of the theoretical amount of thiophene. The cryoscopic molecular weight in benzene was 558 (calcd. for dimer 552).

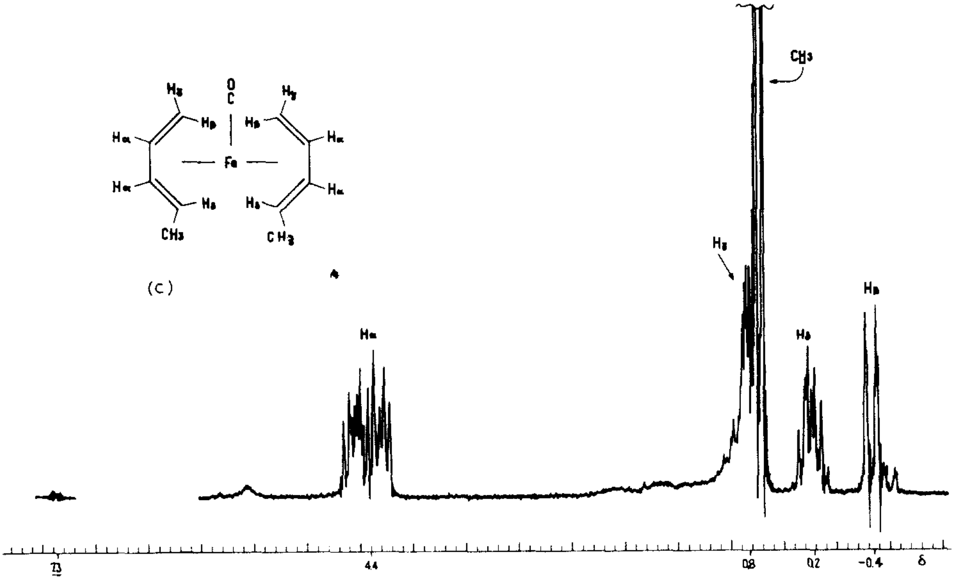
RESULTS AND DISCUSSION

Structures of the new complexes

A comparison is made in Fig. 1 (a and b) between the ^1H NMR spectrum of (II) and that previously described for (I)[4]: apart from the signal of methyl protons at δ 1.75 ppm, other peaks are analogously attributed to =CH− (δ 3.95), and to outside and inside $=CH_2$ hydrogens (δ 1.40 and −0.2, respectively) of isoprene molecules. The IR spectrum of (II) shows the intense absorption band for carbonyl groups (1965 cm^{-1}) and weaker bands attributable to complexed diolefin units (1425 and 1470

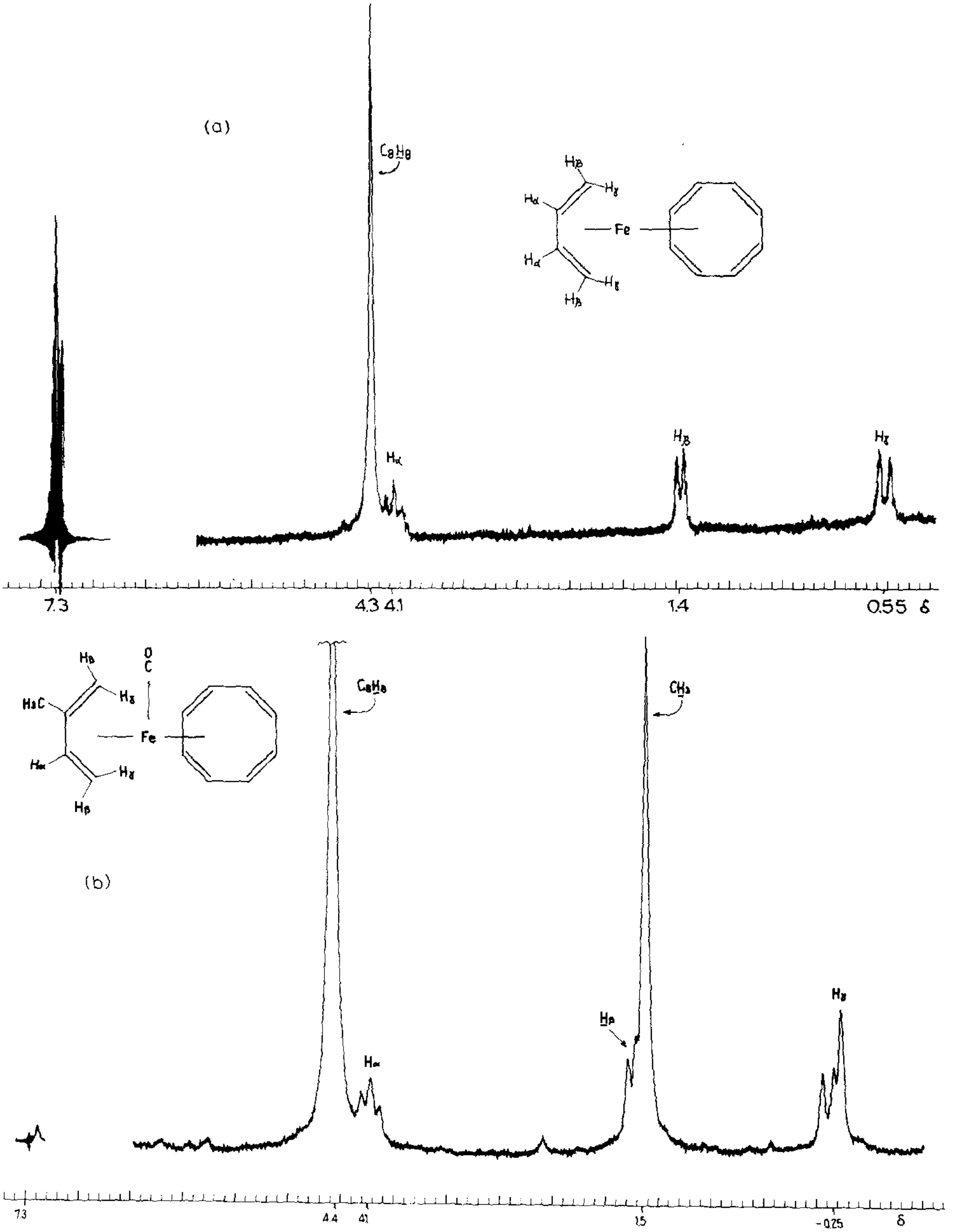

Hβ
Hγ
Hα
Fe
(a)
C6H6
Hα
Hγ
7.3
4.4
1.1
0.3
δ


O
C
Hβ
Hγ
H3C
Hα
Fe
CH3
(b)
C6H6
Hα
CH3
Hβ
Hγ
7.3
4.0
1.75
1.4
-0.2
δ


O
C
Hγ
Hβ
Hα
Fe
Hδ
CH3
(c)
Hγ
CH3
Hα
Hδ
Hβ
7.3
4.4
0.8
0.2
-0.4
δ

cm^{-1}). The formation of 1,5-dimethyl-1,5-cyclooctadiene from (II) in CCl_4 as the sole product of isoprene dimerization suggests structure (II).

The NMR spectrum of (III) is shown in Fig. 1c. It is far more complex than those of (I) or (II), especially as far as coupling is concerned. Clearly, the δ 0.85 ppm system consists of two bands: a sharp doublet at δ 0.75 ppm and a downfield multiplet ($\approx\delta$ 0.90 ppm). The following assignment appears reasonable: =CH– hydrogens at δ 4.4 ppm; outside hydrogen of the $=CH_2$ group at δ 0.85 ppm; methyl protons at



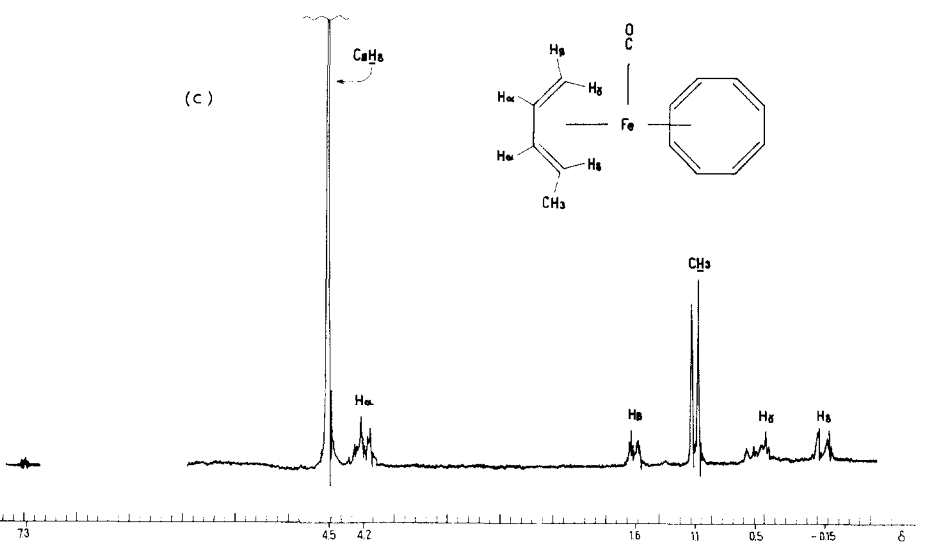
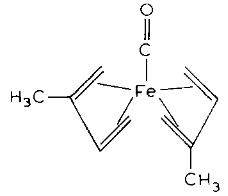


Fig. 2. ^1H NMR spectra (100 MHz, C_6D_6 solution, room temperature, C_6H_6 reference) of (IV), (a), (V), (b) and (VI), (c).


(II)

δ 0.75 ppm; the clearly non-equivalent inside hydrogens should lie upfield (δ 0.25 and 0.35 ppm). The IR spectrum suggests the presence of carbonyl groups and of complexed diolefin (bands at 1960, 1482 and 1446). Like (I) and (II), (III) decomposes in CCl_4 at room temperature, but dimers as well as trimers and higher oligomerization products of 1,3-pentadiene are found. By operating in the presence of thiophene, formation of higher products is avoided and only the dimer, 3,4-dimethyl-1,5-cyclooctadiene is formed. The monomeric pentadiene evolved is the pure *trans* isomer independent of the isomer used for the complex preparation. On the basis of this evidence, we suggest structure (III).

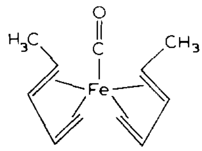
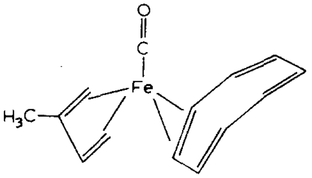
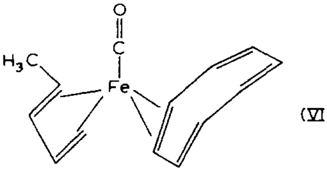

(III)

Figure 2 (a and b) presents a comparison between the NMR spectrum of (V) and that of the analogous butadiene derivative (IV), which was previously described[4]. Apart from the peak of the COT protons at δ 4.4 ppm, assignments similar to those for (II) can be made for (V). The IR spectrum reveals CO groups (band at 1963 cm^{-1}) and is consistent with the presence of COT (1424–1417 cm^{-1}) and isoprene (1477 and 1453 cm^{-1}). The cyclooctatetraene ligand is fluxional in solution at room temperature, as observed for (IV). The structure of (V) may be represented as shown:



(V)

The NMR spectrum of (VI) (Fig. 2c) shows analogies with that of (III) and (IV): assignments are indicated in the Figure. Taking account also of the IR and UV data, we suggest structure (VI).



(VI)

Reactions of the complexes

The diolefin monocarbonyliron complexes, (I)–(VI), are surprisingly stable. They smoothly decompose above their melting points, but are fairly stable in alcoholic solutions, and towards air and water.

The olefinic ligands can with difficulty be replaced by Lewis bases: *e.g.*, (I) does not react with triphenylphosphine, bis(diphenylphosphino)ethane, or 2,2′-bipyridine even at 100°, but does react with 2-butyne or cyclooctatetraene, to yield new complexes which are being investigated*.

Compounds (I)–(VI) react with protic acids in anhydrous hydrocarbons. The reaction is fast, even at low temperature. Inorganic (HCl) as well as organic acids (CCl_3COOH) can be used. A stoichiometric amount of acid (1–1.1 moles/Fe) is sufficient to produce colourless solutions with the COT-containing compounds (IV), (V) and (VI), whereas a large excess (3–5 moles) is necessary to do this for (I), (II) and (III). The products formed are always insoluble suggesting that they are ionic in character. Starting from (IV), (V) and (VI), new organometallic compounds are isolable, in which π-cycloenyl–Fe bonds are present: the compound (VIII) obtained from (IV) and HCl probably has the formula $[(C_8H_9)(C_4H_6)FeCO]^+Cl^-$.

Further evidence for the presence of the protonated COT nucleus in the products obtained by treatment of the mixed complex with acids comes from the NMR spectrum of (IV) in CF_3COOH. The solutions are moderately stable at room temperature, and show several peaks of the $C_8H_9^+$ ion instead of the COT singlet observed for (IV) in hydrocarbons. Multiplets are centered at δ 8.15 (1 H), 5.65 (2 H), 5.20 (2 H), 4.45 (2 H), 2.45 (2 H), 1.95 (2 H), 1.05 (1 H), and 0.45 (3 H) ppm. In addition to the butadiene peaks at δ 4.45, 1.95 and (in part) 0.45 ppm (slightly shifted with respect to the starting compound in C_6D_6), the spectrum shows significant analogies with that of $[C_8H_9Fe(CO)_3]^+$ for which a bicyclic C_8H_9 structure was proposed[8]. On treat-

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* The complex obtained from (I) and 2-butyne crystallizes as red-brown needles. It contains CO and hexamethylbenzene. From (I) and cyclooctatetraene brown compounds of variable composition are formed.

ment of the acid solution with water, butadiene is evolved, but no butenes: only the cyclic ligand of (IV) is protonated, and no π-crotyl–Fe bonds are formed.

The catalytic behaviour of the complexes

As previously reported[9], carbon monoxide-free iron(0) complexes, such as dicyclooctatetraeneiron(0), are very active in catalyzing the formation of dimers and trimers. The above monocarbonyl complexes also promote such oligomerizations, without any polymerization, although their activity is markedly lower. The type of oligomer and their quantitative composition differ from those obtained with the CO-free complexes, and they consist essentially of vinylcyclohexane and 1,5-cyclooctadiene, along with minor amounts of n-dodecatetraene*. 2-Butyne and norbornadiene are oligomerized at 70–90° to hexamethylbenzene and polycyclic dimers, respectively.

The lowering of the catalytic activity is probably to be attributed to the stabilizing action of carbon monoxide. In spite of this stabilization, no intermediates containing stable σ-alkenyl– or π-allyl–iron bonds could be isolated. This is in agreement with our previous assumption, that such bonds are not responsible for diolefin oligomerization catalysis[9,10]. On the contrary we believe, in agreement with other authors[11,12] that π-allyl bonds may promote the diolefin polymerization. To confirm this, we have studied the reaction between the above monocarbonyliron complexes and protic acids in the presence of excess butadiene. As examples, the results obtained with (I) and (IV) are summarized in Scheme 1.

SCHEME 1

$$(C_4H_6)_2FeCO + \text{butadiene} \rightarrow \text{oligomers} \tag{1}$$

$$+HCl \rightarrow FeCl_2 \tag{2}$$

$$+HCl + \text{butadiene} \rightarrow \text{polybutadiene (1,2)} \tag{3}$$

$$+CCl_3COOH + \text{butadiene} \rightarrow \text{polybutadiene } (\textit{cis}\ 1,4) \tag{4}$$

$$(C_4H_6)(C_8H_8)FeCO + \text{butadiene} \rightarrow \text{oligomers} \tag{5}$$

$$+HCl \rightarrow \text{compound (VII)} \tag{6}$$

$$+HCl + \text{butadiene} \rightarrow \text{compound (VII)} \tag{7}$$

Very different results are obtained depending on whether the cyclooctatetraene ligand is present or not. The COT-free complexes, which under the action of acids do not form stable organometallic compounds, induce butadiene polymerization. The COT-containing complexes, which under comparable conditions form stable allyl–iron bonds, are catalytically inactive.

The above differences may be a matter of the degree of stability of the allyl–iron bonds: in the cases (1) and (5), no allyl–iron bonds seem to be formed; in case (2) the proposed allyl–iron bonds would be very unstable, and lead to decompositions of the complex; in the cases (3) and (4), such a bond may be sufficiently stable to induce

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* These results differ from those reported by Körner von Gustorf *et al.*[3], who found cyclododecatriene as the greatly dominant product.

polymerization, but not to allow isolation; finally, in the cases (6) and (7) the allyl–iron bonds are too stable to give rise to catalytic activity in butadiene polymerization, and the complexes may be isolated.

Observations made with two- and three-component systems are in agreement with the above scheme: *e.g.*, the tris(acetylacetonato)iron/triethylaluminum/-triphenylphosphine system catalyzes selective butadiene polymerization, whereas the analogous two-component phosphine-free system promotes di-and trimerization[13]. That an insertion mechanism is involved in such a polymerization is indicated by the observation that the polybutadiene produced with a $FeCl_3$/tri-2-thienylaluminum catalyst, contains 2-thienyl groups. To conclude, the behaviour of the iron catalysts, giving both polymers and oligomers of butadiene, may be associated with two different kinds of initiator: (*i*) π-olefinic complexes which induce oligomerization*, and (*ii*), C–Fe containing compounds of suitable stability which promote polymerization via a characteristic insertion mechanism. The different structures of the polymers obtained in various amounts on treatment with the different acids are probably due to the counterion effect (polarity effect) already observed for some anionic polymerizations of butadiene[12].

ACKNOWLEDGEMENT

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* Fe^0 complexes appear to be true catalysts and not stable intermediates: we recover most (>50%) of the $(C_4H_6)_2FeCO$ used in butadiene oligomerization.