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POLYMERISATION OF PENTADIENYL COMPOUNDS IN THE PRESENCE OF TRANSITION-METAL COMPOUNDS: THE POLYMORPHIC COMPOUND DECA-1,3,7,9-TETRAENEDIIRON HEXACARBONYL

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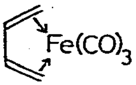
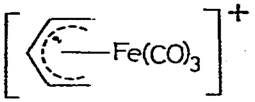
Summary

The reaction between $Fe(CO)_5$ and penta-1,4-dien-3-ol gives two forms of di(pentadienyliron tricarbonyl).

The pentadienyl compounds are interesting potential ligands because they offer scope for the formation of a diverse range of products. Firstly, conjugated dienes such as C_5H_7X may form conventional complexes, I, similar to butadieneiron tricarbonyl, by acting as four-electron donors [1]. Secondly, the pentadienyl group itself contains five π-electrons, so that 5-electron analogues of the π-allyl complexes are also possible: this possibility has been realised in the *cisoid* structure of the π-pentadienyltricarbonyliron cation, II [2,3]. Alternatively, only three electrons might be donated to the metal to form a conventional π-allyl linkage [4—6], and leave an uncomplexed double bond in the ligand, III.



(I)



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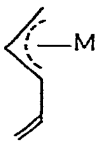

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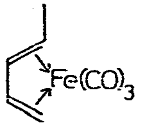
Trans- and *cis*-structural isomers of penta-1,3-dieneiron tricarbonyl exist, IV and V, and it is interesting that only the *cis*-isomer undergoes hydride abstraction reactions to form a π-pentadienyl complex cation, II, although some workers suggest that a *trans-* pentadienyl complex could also be stable. [7] Fourthly, the five-carbon chain is sufficiently long and flexible to coordinate to two separate metal atoms. This possibility has also been realised in the compound VI, bis(pentadienyl)dinickel, which is considered to involve a trimethylaluminium-like bridging system [8].



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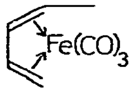

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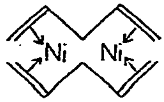
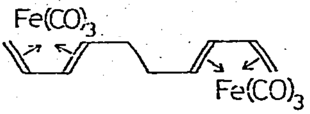


(VI)

In addition to these variations, the pentadienyl system offers considerable scope for chemical reaction of the ligand. For example, there is the possibility of an essentially metal-catalysed rearrangement reaction to a 2-methylbutadiene derivative. More interesting is the possibility of polymerisation reactions and, in this context, it is noteworthy that pentadienyl Grignard reagents are readily converted to a variety of C_{10} compounds [9]. Such a decapolyene is sufficiently large to either wrap itself around a single metal or to bond to two separate metal atoms. There are many precedents for such a transition-metal catalysed polymerisation. For example, butadiene undergoes a trimerisation reaction with $RuCl_3$ and forms the complex dichloro(dodeca-2,6,10-triene-1,12-diyl)-ruthenium(IV) [10], which is thought to be related to intermediates in some catalytic polymerisation reactions [4], while allene itself reacts with $Fe_2(CO)_9$ to give, inter alia, a 2,2′-bis(allene) complex of the $Fe_2(CO)_9$ grouping [11].

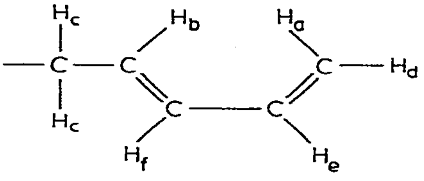
We have investigated the reactions of a number of derivatives of piperylene, C_5H_8, with transition-metal compounds. The ligands used were: piperylene itself (penta-1,3-diene), penta-1,4-diene-3-ol $(CH_2{=}CH)_2CH(OH)$, which was prepared by the reaction of acrolein with vinylmagnesium bromide [12], 1-chloropenta-2,4-diene $(CH_2{=}CHCH{=}CHCH_2Cl)$, which was obtained by treatment of $(CH_2{=}CH)_2CH(OH)$ with hydrochloric acid at 0° C [12], and the relatively unstable *trans*-penta-2,4-dien-1-ol $(CH_2{=}CHCH{=}CHCH_2OH)$, which was prepared by hydrolysis of the corresponding chloride. Using these ligands we isolated products in which a transition-metal system was bonded to a polymerised pentadienyl group and these received further study because of the intrinsic interest of possible models for intermediates in catalytic polymerisation reactions.

The π-pentadienyliron tricarbonyl cation may be obtained by reacting the diene complex formed in the reaction between iron pentacarbonyl and *trans*-penta-2,4-dien-1-ol [2] with a strong acid. The hydroxyl group appears to be an important feature of this reaction system, and we therefore investigated the reaction between penta-1,4-dien-3-ol and iron pentacarbonyl. 16 g of $Fe(CO)_5$ and 2 g of penta-1,4-dien-3-ol were dissolved in 20 ml of 130/140 petroleum spirit and refluxed under nitrogen for 36 h. After heating, the excess solvent and unchanged $Fe(CO)_5$ were removed by vacuum distillation leaving a blackish residue. The latter was dissolved in 40/50 petroleum spirit and filtered under reduced pressure to remove the majority of the pyrophoric iron present. Crystallisation gave 1 g of pale yellow crystals which were later identified as a mixture of two varieties of di(pentadienyliron tricarbonyl) (VII).



(VII)

A mixture of two diasteroisomers resulted from the reaction, one a *meso* form, the other a racemate. This was originally diagnosed from the variation in the always sharp melting point following recrystallisation from various solvents and/or chromatographic separation and, secondly, the associated marked variation in the relative intensity of two carbonyl bands at 1977 and 1987 cm^{-1} (Table 1) in the infrared spectra of the solutions. There was some indication of separate plate-like and needle-like crystals on microscope examination and although crystal-sorting was possible, this did not prove to be a reliable method of separating the two forms. Indeed, we were unable to effect a complete separation. All of the mixed products obtained gave analysis in good agreement with the formula $[C_5H_7Fe(CO)_3]_x$. The dimeric nature (i.e. $x = 2$) in benzene solution was established by osmometric determination of the molecular weight as 420 g mol^{-1} ($C_{10}H_{14}(Fe(CO)_3)_2$ = 414 g mol^{-1}). The NMR and mass-spectral of the two forms appear practically identical as does the IR data except for the ν(CO) intensity variation (Table 1). The parent ion was observed at $m/e = 414$; many strong peaks at lower mass numbers correspond to loss of successive carbonyl groups. The principal features of the NMR spectrum in $CDCl_3$ at room temperature are a broad multiplet at τ 4.81 ppm (integration 2), two further broad multiplets at τ 8.30 (3) and τ 9.02 ppm (1) and a doublet of doublets at τ 9.73 ppm (1). These are tentatively assigned to the proton sets $H_e + H_f$, $2H_c + H_d$, H_b and H_a respectively (see VIII). The fluxional properties of the compound were not investigated. In an attempt to obtain some direct evidence on the nature of the ligand in this species, the products of flash pyrolysis at 610° C were investigated by the GLC/MS technique. The products divided into three



(VIII)

TABLE 1

IR SPECTRA OF $C_{10}H_{14}Fe_2(CO)_6$, n-HEXANE AS SOLVENT

M.p. of crystals (°C)	ν(CO) (cm^{-1})		
130	2056s	1987s	1977ms
86	2056s	1987s	1977s

main classes: aromatic hydrocarbons like benzene, toluene, xylenes and naphthalene were formed in significant quantities, but aliphatic C_{10} polyenes were the dominant products. Thus, 1,2,3 and 1 products of formulae $C_{10}H_{12}$, $C_{10}H_{14}$, $C_{10}H_{16}$ and $C_{10}H_{18}$ respectively were identified with the decatetraenes predominant. Iron-containing products included ferrocene, a decatriene complex and a compound of formula $C_8H_{10}Fe(CO)_2$, perhaps a π-xyleneiron dicarbonyl.

Mahler et al. reported that, when *syn*-1-methylpentadienyliron tricarbonyl salts are reacted with zinc dust or alcoholic alkali, a mixture of two diastereoisomers of 5,6-dimethyldeca-1,3,7,9-tetraenediiron hexacarbonyl is formed, one a racemate and the other a *meso*-compound [3]. Apart from the methyl substituents, these compounds are evidently very similar to those that we prepared. This was confirmed by an X-ray investigation of single crystals of the two forms of deca-1,3,7,9-tetraenediiron hexacarbonyl carried out in these laboratories. [13]. The two structures are shown in Fig. 1. The *meso*-compound has strict C_i symmetry whereas the other has approximately C_2 symmetry, the centrosymmetric unit cell containing a pair of enantiomeric molecules.

Allylpalladium chloride is formally a 34-electron system. We therefore at-

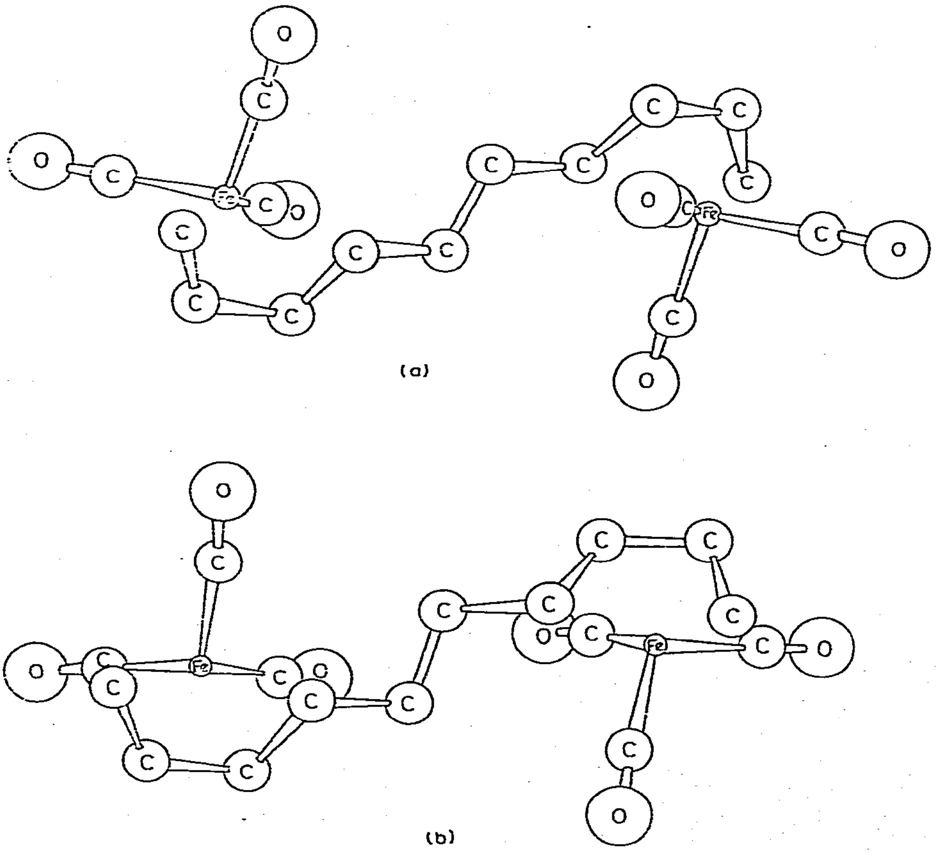


Fig. 1. Structure of deca-1,3,7,9-tetraenediiron hexacarbonyl, (a) *meso* , (b) racemic.

tempted to prepare the 36-electron pentadienyl analogue of this compound by the reaction of 1-chloropenta-2,4-diene with Na_2PdCl_4 in the presence of CO using methanol as solvent [14]. A yellow solid is immediately precipitated in high yield, but this material is of very low solubility and little thermal stability. It was slightly soluble in aromatic hydrocarbons and chlorinated solvents, but it separated from these as an intractible yellow oil. Similar oils and gums were obtained by the reactions of piperylene or 1-chloropenta-2,4-diene with Na_2PdCl_4 in the absence of CO. When these materials were reacted with thallous acetylacetonate (or acetylacetone in the presence of $BaCO_3$), a good yield of bis(acetylacetonato)palladium was obtained.

Ethylenediamine also appeared to strip off the ligand and red colourations were obtained from the gums on treatment with $(Ph_2PCH_2)_2$ in CH_2Cl_2 but no new products could be isolated from these reactions. Despite repeated efforts involving a variety of techniques the insolubility and lack of volatility of the products prevented their purification and absolute characterisation. A GLC/MS investigation of the volatile products of flash pyrolysis was carried out for each species. In all cases the dominant products were aliphatic dienes together with smaller amounts of aromatic hydrocarbons, but there were no volatile palladium-containing products.

Acknowledgement

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