901. *Ferrocene Derivatives. Part IX.* Some Disubstituted Derivatives.*

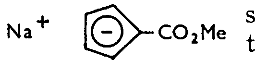
By J. M. OSGERBY and P. L. PAUSON.

Novel preparations of dimethyl ferrocene-1,1′-dicarboxylate, 1,1′-bis-(dimethylaminomethyl)ferrocene, ferrocene-1,1′-dicarboxyaldehyde, and 1,1′-dicyanoferrocene are described. Some reactions of ferrocene-mono- and -di-carboxyaldehyde are reported.

THE synthesis of substituted ferrocenes directly from the corresponding cyclopentadiene derivatives rather than by substitution of the parent compound is hampered by the inaccessibility of most such derivatives. It has therefore been limited to a few alkyl and aryl derivatives.[1]

The work described in this and the following papers was based on the consideration that substituted cyclopentadienide ions were frequently more accessible than the corresponding free cyclopentadienes and should be capable of reacting directly with ferrous chloride or other transition-metal salts. This principle has already been utilized by Benson and Lindsey [2] in their elegant synthesis of dihydroxyferrocenes.

Thiele [3] described the condensation of cyclopentadiene with diethyl oxalate, ethyl nitrite, and ethyl nitrate in presence of an excess of alkali, obtaining the sodium salts of ethoxalyl-, nitroso-, and nitro-cyclopentadiene respectively. In each case the free cyclopentadiene is unobtainable, since its liberation with acid is followed by rapid dimerisation. The salts contain the resonance-stabilised cyclopentadienide ion and are stable as monomers. Unfortunately we have not so far been able to convert any of these salts into the corresponding ferrocenes. However, when cyclopentadienylsodium was treated with methyl chloroformate in presence of excess of sodium so as to produce the sodium salt (I) of methyl cyclopentadienecarboxylate, and then with ferrous chloride, dimethyl ferrocene-1,1′-dicarboxylate was produced in 30% yield. Though illustrating the validity of the method in principle, this offers no advantage over the preparation of ferrocenedicarboxylic acid by the method of Nesmeyanov *et al.*[4] While our work was in progress Peters [5] used the same method to prepare the salt (I) and his isolation of a dicarboxylic ester provides an explanation of the low yields observed. No tri- or tetra-carboxylate of ferrocene was found in our work, whence it seems that, in common with Thiele's salts, Peters's dimethyl sodiocyclopentadienedicarboxylate is too inert towards ferrous chloride. There has also appeared a patent [6] in which the same approach is used to prepare diacetylferrocene from cyclopentadienylsodium and acetyl chloride: no detail or yield is given here: we obtained only a 2% yield of diacetylferrocene under the same conditions as used for the diester.



(I)

---

* Part VIII, preceding paper.

[1] Pauson, *J. Amer. Chem. Soc.*, 1954, **76**, 2187; Reynolds and Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 3; Riemschneider and Nehring, *Monatsh.*, 1959, **90**, 568.

[2] Benson and Lindsay, *J. Amer. Chem. Soc.*, 1957, **79**, 5471.

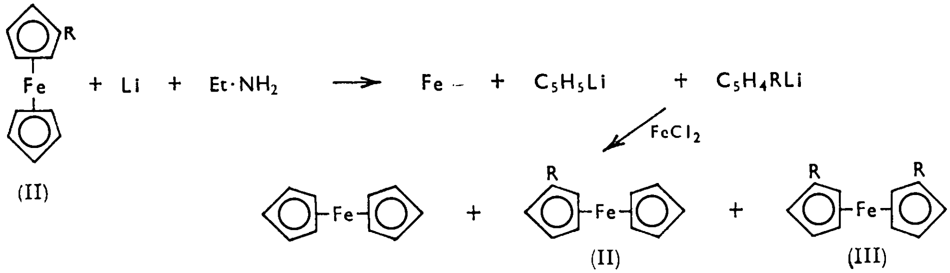
[3] Thiele, *Ber.*, 1900, **23**, 666; 1901, **24**, 68.

[4] Nesmeyanov, Perevalova, and Beinoravichute, *Doklady Akad. Nauk S.S.S.R.*, 1957, **112**, 439.

[5] Peters, *J.*, 1959, 1757.

[6] Lynch and Brantley, B.P. 785,760.

Another source of substituted cyclopentadiene salts is the substituted ferrocenes. Trifan and Nicholas[7] showed that ferrocene is rather smoothly degraded by lithium and ethylamine. The isolation of free cyclopentadiene on hydrolysis of the reaction mixture indicates that the cleavage leads initially to cyclopentadienyl-lithium. If the same reaction is applied to a monosubstituted ferrocene (II) a mixture of cyclopentadienyl-lithium and a substituted cyclopentadienyl-lithium results. Addition of ferrous chloride should convert this into a mixture of starting material, disubstituted ferrocene, and ferrocene. If the first step is complete and if the second takes the statistical course, then 50% of starting material (II) would be recovered and 25% of the disubstituted product (III) should result. We studied dimethylaminomethylferrocene (II; $R = CH_2 \cdot NMe_2$) since it may be made quantitatively by direct aminomethylation[8] of ferrocene, whereas the corresponding disubstitution product (III) cannot be obtained at all in this way. It was found that a rather large excess of lithium was required to effect even 80% completion of the first stage [as ascertained by decomposition of the reaction mixture with water and isolation of unchanged (II)], but addition of ferrous chloride then afforded the three products in very nearly the statistical ratio. The optimum yield of the diamine (III; $R = CH_2 \cdot NMe_2$) was ~15% (based on total iron present). It was also found that free dimethylaminomethylcyclopentadiene could not be isolated from the initial reaction mixture, which emphasised the value of direct treatment with ferrous chloride. Cyanoferrocene and methylthioferrocene failed to yield products other than ferrocene itself in a similar reaction: in both cases it appears reasonable to assume that the substituted cyclopentadienyl-lithium does not survive under the vigorous reducing conditions. The diamine (III; $R = CH_2 \cdot NMe_2$) was characterised as its picrate and dimethiodide, and the structure of the latter was demonstrated by the close similarity of its infrared spectrum to that of ferrocenylmethyltrimethylammonium iodide (II; $R = CH_2 \cdot NMe_3^+I^-$), as well as by hydrolysis to the known diol (III; $R = CH_2 \cdot OH$). Other reactions of the bis-quaternary salt are under investigation. The diol (III; $R = CH_2 \cdot OH$) is better obtained by the Russian method.[4] Using manganese dioxide,[9] we oxidised it to the dialdehyde (III; R = CHO), a stable red solid, in 33% yield. The intermediate hydroxyaldehyde was obtained as a by-product.



The dialdehyde was characterised as dioxime which was dehydrated in excellent yield to the dinitrile (III; R = CN). Nesmeyanov and Reutov[10] recently obtained the same dinitrile from ferrocenedicarboxylic acid through the diamide. The infrared spectra of these disubstituted ferrocenes (III; $R = CH_2 \cdot NMe_3I$, CHO, CN) are listed in Table 1 with those of their monosubstituted analogues for comparison.

An attempt has been made to produce derivatives in which the two rings are bridged by condensing the dialdehyde with acetone and with *o*-phenylenediamine.

The product obtained from *o*-phenylenediamine proved difficult to purify completely

[7] Trifan and Nicholas, *J. Amer. Chem. Soc.*, 1957, **79**, 2746.

[8] Osgerby and Pauson, *J.*, 1958, 656.

[9] Hauser, Lindsay, Lednicer, and Cain, *J. Org. Chem.*, 1957, **22**, 717.

[10] Nesmeyanov and Reutov, *Doklady Akad. Nauk S.S.S.R.*, 1958, **120**, 1267.

and its low solubility and poor stability in solution prevented us from determining its molecular weight. Its analysis is in approximate agreement with the bridged structure (IV).

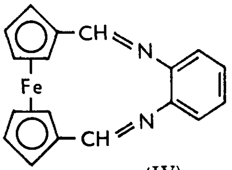
TABLE 1.

Infrared spectra of mono- and di-substituted ferrocenes (cm.$^{-1}$) (as KBr discs).

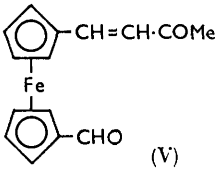
CHO		CN		$CH_2{\cdot}NMe_3{}^+I^-$	
Mono	Di	Mono	Di	Mono	Di
1671s *	1696s	2242s	2240s	1483s	1483s
1381s	1452s			1469s	1469s
		1442m	1438m	1445s	1455s
1414m	1408m			1407m	1397m
1388m	1384m	1388m	1389m	1380m	1377m
1371s	1365s	1373m	1375m		
1332m	1332m				
1247s	1240s	1233s	1227s		
1203m	1209m			1131m	1129m
1106s		1109s		1104s	
1033s	1037s	1052s	1048s	1044m	1040m
1026s	1023s	1032s	1030s	1037m	1021m
1004s		1006s		1005s	
		912s	908s	990s	987s
		859m	861m	974s	971s
826s	830s	825s	829s	914s	924s
745s	746s			880s	877s
				851m	853m

* Doublet.

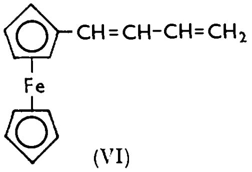
Acetone led to a product giving a positive iodoform test, whose analysis and dark colour suggested formulation as (V), but its infrared spectrum appears incompatible with such a structure. Its lowest-wavelength maximum in the carbonyl region occurs at 1652 cm.$^{-1}$, whereas 1-(3-oxobut-1-enyl)ferrocene (II; R = $CH{:}CH{\cdot}CO{\cdot}CH_3$) prepared for comparison from the monoaldehyde and acetone has a peak at 1674 cm.$^{-1}$.



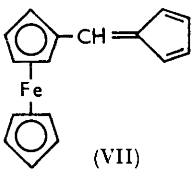
(IV)



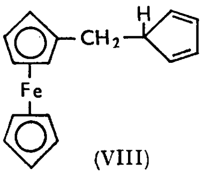
(V)



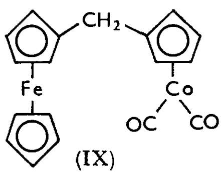
(VI)



(VII)



(VIII)



(IX)

We also performed some new reactions of the monoaldehyde (II; R = CHO). In addition to the methods previously recorded, this aldehyde has now been obtained, albeit in very low yield, by the McFadyen–Stevens[11] method from ferrocenecarboxylic acid (II; R = CO_2H). The aldehyde was reduced by the Clemmensen method to methylferrocene (II; R = Me), also obtained by Emde reduction of ferrocenylmethyltrimethylammonium iodide (II; R = $CH_2{\cdot}NMe_3{}^+I^-$). While the present work was in progress, the latter method was described independently by Nesmeyanov *et al.*[12] who also obtained methylferrocene by reducing methyl ferrocenecarboxylate (II; R = CO_2Me) with a large

---

[11] McFadyen and Stevens, *J.*, 1936, 584.

[12] Nesmeyanov, Perevalova, Shilovtseva, and Beinoravichute, *Doklady Akad. Nauk S.S.S.R.*, 1958, **121**, 117.

excess of lithium aluminium hydride. Ferrocenecarboxyaldehyde undergoes Wittig condensation with allyltriphenylphosphinylide, giving ferrocenylbutadiene (VI). The aldehyde condenses with cyclopentadiene, to afford α-ferrocenylfulvene (VII). These two products are of interest as precursors of ferrocene-containing polymers. The closely related ferrocenylmethylcyclopentadiene (VIII) has been obtained by reaction of ferrocenylmethyltrimethylammonium iodide (II; $R = CH_2{\cdot}NMe_3^+I^-$) with cyclopentadienylsodium and reacts readily with dicobalt octacarbonyl, the product being however rather unstable: although not obtained analytically pure, this undoubtedly has the expected structure (IX) and is a compound of novel type, containing two different transition metals in one molecule. Numerous examples of this type are being studied in our laboratories.

EXPERIMENTAL

Ligroin refers to the solvent of b. p. 60—80° unless otherwise specified. Alumina refers to Spence's grade " H " which had been exposed to air for 6 hr.

Dimethyl Ferrocene-1,1′-*dicarboxylate*.—Cyclopentadiene (6·6 g., 0·1 mole) in tetrahydrofuran (20 ml.) was added dropwise with stirring to powdered sodium (4·6 g.; 0·2 g.-atom) under the same solvent (50 ml.) in an atmosphere of nitrogen and the mixture was stirred for 1½ hr. A solution of methyl chloroformate (9·45 g., 0·1 mole) in tetrahydrofuran (20 ml.) was added dropwise, producing an immediate red colour. After a further 5 hours' stirring all the sodium had dissolved and anhydrous ferrous chloride (prepared from 20 g. of ferric chloride [13]) was added as a slurry in tetrahydrofuran, and the mixture stirred overnight. After removal of the solvent, the residue was extracted with benzene, and this extract concentrated and chromatographed on neutralised alumina. The main red material was eluted with benzene, recovered, and crystallised from ligroin, giving dimethyl ferrocene-1,1′-dicarboxylate (4·3 g., 28·5%), m. p. and mixed m. p. 107—109°.

1,1′-*Diacetylferrocene*.—The above procedure was repeated, but with acetyl chloride (7·85 g., 0·1 mole) in place of methyl chloroformate. 1,1′-Diacetylferrocene (0·55 g., 2%), identical in m. p. and mixed m. p. with an authentic sample, was isolated.

1,1′-*Bis*(*dimethylaminomethyl*)*ferrocene* (III; $R = CH_2{\cdot}NMe_2$).—A solution of dimethylaminomethylferrocene (II; $R = CH_2{\cdot}NMe_2$) (5·44 g., 0·02 mole) in anhydrous ethylamine (100 ml.) was poured on lithium metal (3·0 g., 0·43 g.-atom) as rapidly as the vigorous reaction permitted (in ~2 min.). The mixture was stirred for 20 min. and then poured on ferrous chloride [from ferric chloride (6 g., 0·04 mole)] tetrahydrofuran being used to rinse the original reaction vessel and added to the mixture which was then stirred at room temperature overnight. After removal of the solvents the residue was chromatographed in benzene on alumina. Three bands developed; benzene eluted ferrocene (0·59 g., 14·5%). This was followed by dimethylaminomethylferrocene (II; $R = CH_2{\cdot}NMe_2$) (1·94 g., 36%; eluted with ether); and 1,1′-bis(dimethylaminomethyl)ferrocene (III; $R = CH_2{\cdot}NMe_2$) (1·0 g., 15%) was eluted with acetone. The last was characterised as its picrate, m. p. 150° (decomp.), and *dimethiodide*, m. p. 260° (decomp.) (Found: C, 36·5, 37·6; H, 5·3, 5·4; N, 5·0. $C_{18}H_{30}FeI_2N_2$ requires C, 37·0; H, 5·2; N, 4·8%).

A similar experiment without ferrous chloride yielded 1·02 g. (18·2%) of the unchanged amine (II; $R = CH_2{\cdot}NMe_2$); thus the initial decomposition was over 80% complete under these conditions.

The dimethiodide, on hydrolysis with 5N-sodium hydroxide at 180° for 3 hr. in a sealed tube, gave a low yield of the diol (III; $R = CH_2{\cdot}OH$), m. p. and mixed m. p.[14] 107—108° (correct infrared spectrum).

Ferrocene-1,1′-*dicarboxyaldehyde* (III; R = CHO).—" Active " manganese dioxide (100 g.) was added to a solution of 1,1′-di(hydroxymethyl)ferrocene [4] (10 g.) in chloroform (200 ml.). The mixture became warm and was left in the dark for 12 hr. After filtration, the red solution was evaporated and the dry residue chromatographed in benzene on alumina. Benzene eluted *ferrocene*-1,1′-*dicarboxyaldehyde* (3·4 g., 34%) which formed bright red needles, m. p. 183—184°, from cyclohexane (Found: C, 59·4; H, 4·3. $C_{12}H_{10}FeO_2$ requires C, 59·5; H, 4·2%). A second band, eluted with ether, afforded 1′-*hydroxymethylferrocene*-1-*carboxyaldehyde* which

---

[13] Kovacic and Brace, *J. Amer. Chem. Soc.*, 1954, **76**, 5491.

[14] Rinehart, Frerichs, Kittle, Westman, Gustafson, Pruett, and McMahon, *J. Amer. Chem. Soc.*, 1960, **82**, 4111.

crystallised from cyclohexane as orange plates (1 g., 10%), m. p. 39—40° (Found: C, 59·4; H, 5·1. $C_{12}H_{12}FeO_2$ requires C, 59·05; H, 5·0%). The *semicarbazone* of the latter formed orange crystals (from acetone), m. p. 166—167° (Found: C, 52·3; H, 5·4; N, 13·7. $C_{13}H_{15}FeN_3O_2$ requires C, 51·9; H, 5·0; N, 14·0%).

Ferrocene-1,1'-*dialdoxime*.—A solution of hydroxylamine hydrochloride (0·17 g.) in water (1 ml.) was added to a solution of ferrocene-1,1'-dicarboxyaldehyde in (0·08 g.) in ethanol (5 ml.). Sodium hydroxide (0·3 g.) was then added. The solution was refluxed for 1 hr., cooled, poured into water, and neutralised by solid carbon dioxide. The *dioxime* (0·06 g., 67%) was filtered off and recrystallised from benzene; it had m. p. 135° (Found: C, 52·3; H, 4·5; N, 10·1. $C_{12}H_{12}FeN_2O_2$ requires C, 53·0; H, 4·5; N, 10·3%).

1,1'-*Dicyanoferrocene*.—A solution of ferrocene-1,1'-dialdoxime (0·815 g., 1 mol.) and dicyclohexylcarbodi-imide (1·27 g., 2 mol.) in dry benzene (20 ml.) was refluxed for 15 hr. After cooling and removal of dicyclohexylurea (1·18 g., 90%), the solution was concentrated under reduced pressure. The remaining dinitrile was purified by chromatography on alumina in benzene and, crystallised from the same solvent, had m. p. 166—167° (lit.,[10] m. p. 166—167·5°) (0·70 g., 98%).

Condensation of the Dialdehyde with o-*Phenylenediamine*.—Ferrocene-1,1'-dicarboxyaldehyde (0·39 g.) and *o*-phenylenediamine (0·19 g.) were refluxed in ethanol for 2 hr. The solvent was removed *in vacuo*, the brown residue was dissolved in chloroform and chromatographed on alumina, and the only coloured band eluted with the same solvent. The orange-brown *compound* (IV?) (0·38 g.) obtained on evaporation did not crystallise but was purified by precipitation from chloroform with benzene as an orange powder, m. p. 210° (Found: C, 69·6; H, 4·95; N, 8·15. $C_{18}H_{14}FeN_2$ requires C, 68·8; H, 4·5; N, 8·9%).

Condensation of the Dialdehyde with Acetone.—Ferrocene-1,1'-dicarboxyaldehyde (0·49 g., 1 mol.), acetone (0·12 g., 1 mol.), and an excess of potassium hydroxide were refluxed in ethanol (20 ml.) for 1·5 hr. The precipitated purple solid (0·36 g.) was filtered off from the cooled mixture, washed with ethanol, and chromatographed in chloroform on alumina. Only one band was formed which, on elution, gave a deep purple crystalline *substance*, which did not melt below 300° and could not be recrystallised (Found: C, 64·1; H, 4·9; Fe, 19·7. $C_{15}H_{14}FeO_2$ requires C, 63·9; H, 5·0; Fe, 19·8%). The compound gave a positive iodoform test and showed strong maxima in the infrared at 1652, 1619, and 1587 $cm.^{-1}$.

1-(3-*Oxobut*-1-*enyl*)*ferrocene*.—Ferrocenecarboxyaldehyde (0·1 g.) and potassium hydroxide (0·1 g.), dissolved in water (1 ml.) and acetone (5 ml.), were refluxed for 1 hr. More water was added, the product extracted with benzene, and the dried extract concentrated to small bulk and then chromatographed on alumina. Unchanged aldehyde was eluted first, followed by the *ketone* which crystallised from ligroin in bright red plates, m. p. 85° (Found: C, 66·5; H, 5·6. $C_{14}H_{14}FeO$ requires C, 66·2; H, 5·6%). It gave a positive iodoform reaction and yielded a semicarbazone, m. p. 176°, $\nu_{max.}$ 1674, 1647, and 1622 $cm.^{-1}$.

Ferrocenecarboxyhydrazide (with G. D. BROADHEAD).—Methyl ferrocenecarboxylate (6 g., 1 mol.) and hydrazine hydrate (15 ml., 12 mol.) were refluxed in methanol (30 ml.) for 8 hr. Water was then added, the solution concentrated, and the *ferrocenecarboxyhydrazide* (4 g., 60%) which separated as orange-yellow plates recrystallised from methanol; it had m. p. 159—160° (Found: C, 54·4; H, 5·4. $C_{11}H_{12}FeN_2O_2$ requires C, 54·1; H, 5·4%).

N'-*Benzenesulphonylferrocenecarboxyhydrazide*.—Benzenesulphonyl chloride (0·22 g.) was added to the above hydrazide (0·30 g.) in pyridine (15 ml.). After 1 hr. at room temperature the mixture was poured on ice and hydrochloric acid, and the orange precipitate filtered off, washed with dilute hydrochloric acid and water, and dried. Crystallisation from chloroform afforded the *benzenesulphonyl derivative* (0·4 g., 85%), m. p. 203°, decomp. 222° [Found: C, 52·8; H, 4·3; N, 7·3; S, 8·5. $C_{17}H_{16}FeN_2O_3S$ requires: C, 53·1; H, 4·2; N, 7·3; S, 8·4%).

Ferrocenecarboxyaldehyde.—*N'*-Benzenesulphonylferrocenecarboxyhydrazide (0·164 g.) was heated in ethylene glycol (4 ml.) to 160°. An excess of sodium carbonate (0·12 g.) was then added in one portion, causing a brisk effervescence. The bath-temperature was maintained at 160° for 35 min. The mixture was then cooled, diluted with water, and extracted with ether, and the ether extract was washed with water, dried, and evaporated. The very small orange residue crystallised from light petroleum (b. p. 40—60°) and was identified as ferrocenecarboxyaldehyde by its m. p. and mixed m. p.

Methylferrocene.—Ferrocenecarboxyaldehyde (1 g.) in glacial acetic acid (20 ml.) was added to amalgamated zinc needles (7 g.) and concentrated hydrochloric acid (20 ml.) under nitrogen.

The mixture was heated on a steam bath for 15 min., cooled, and poured into water; the mixture was filtered and the solid material washed with benzene. The two layers in the filtrate were separated, the aqueous layer was extracted three times with benzene, and the combined benzene solutions were washed with water, aqueous sodium hydrogen carbonate, and water and dried (Na_2SO_4). Removal of benzene under reduced pressure left a yellow oil (0·8 g.), slightly volatile with benzene. Distillation of this oil at 86°/0·4 mm. afforded methylferrocene (0·6 g., 66%) which, crystallised from ligroin, had m. p. 36° undepressed by a sample obtained by reduction of ferrocenylmethyltrimethylammonium iodide with sodium and ethanol or sodium amalgam[11] (Found: C, 66·2; H, 6·1%; *M*, 204. Calc. for $C_{11}H_{12}Fe$: C, 66·0; H, 6·05%; *M*, 200).

1-(*Buta*-1,3-*dienyl*)*ferrocene* (VI).—As in Wittig and Haag's procedure,[15] allyltriphenylphosphonylide was obtained by addition of an excess of ethereal butyl-lithium to a suspension of allyltriphenylphosphonium bromide (2 g., 1 mol.) in ether (40 ml.). After this mixture has been stirred for 30 min., an ether solution of ferrocenecarboxyaldehyde (1·05 g., 1 mol.) was added and stirring continued overnight. Water was then added, the red ether layer separated, and the aqueous layer extracted with chloroform until colourless. The combined organic extracts were evaporated to dryness and a benzene solution of the residue was chromatographed on alumina. Unchanged aldehyde (0·5 g., 50%) was preceded on the column by 1-(*buta*-1,3-*dienyl*)*ferrocene* which distilled in a high vacuum and crystallised from ligroin (b. p. 40—60°) as red crystals (0·075 g., 12%), m. p. 80° (Found: C, 70·2; H, 6·0. $C_{14}H_{14}Fe$ requires C, 70·6; H, 5·9%).

α-*Ferrocenylfulvene* (VII).—Cyclopentadiene (1·0 g., 2 mol.) and ferrocenecarboxyaldehyde (1·6 g., 1 mol.), in ethanol (50 ml.), were added to a solution from sodium (2 g.) in ethanol (20 ml.). The mixture was heated on a steam bath for 30 min., then poured into water and extracted with ether. The ether extract was dried (Na_2SO_4) and evaporated, leaving a red oil which was chromatographed in benzene on alumina. Elution of the single coloured band with the same solvent afforded α-ferrocenylfulvene (1·9 g., 98%) as a deep red oil which polymerised on attempted distillation.

Ferrocenylmethylcyclopentadiene (VIII).—Ferrocenylmethyltrimethylammonium iodide (4·7 g., 1 mol.) was added to a solution of cyclopentadienylsodium prepared in tetrahydrofuran (50 ml.) from cyclopentadiene (4 g., 5 mol.) and an excess of powdered sodium. The mixture was stirred and refluxed under nitrogen for 15 hr. The solvent was removed *in vacuo*, and the residue treated with water and extracted with ether. The dried extract was evaporated and *ferrocenylmethylcyclopentadiene* (2·1 g., 65%) distilled at 104°/0·15 mm. as a mobile dark-red oil (Found: C, 72·6; H, 6·2. $C_{16}H_{16}Fe$ requires C, 72·8; H, 6·1%). The compound polymerised on storage, but the monomer was regenerated by distillation.

Dicarbonyl(*ferrocenylmethylcyclopentadienyl*)*cobalt* (IX).—A solution of the cyclopentadiene derivative (VIII) (0·9 g., 3·4 mol.) and dicobalt octacarbonyl (1·7 g., 5 mol.) in butyl ether (40 ml.) was refluxed for 1 hr. under nitrogen. The solvent was evaporated under a reduced pressure of nitrogen, and the residue extracted with benzene and chromatographed on alumina. A single red band was rapidly eluted with benzene. Removal of solvent left the product (IX) as a red oil (0·3 g., 13%) which decomposed gradually, was shown to contain cobalt, and had strong infrared maxima in the carbonyl–metal stretching region (2018 and 1962 cm.$^{-1}$).

The authors are indebted to the Minnesota Mining and Manufacturing Company for financial support and to E. I. du Pont de Nemours and Co. for gifts of ferrocene.

THE UNIVERSITY, SHEFFIELD, 10. [*Received, April* 10*th*, 1961.]

---

[15] Wittig and Haag, *Chem. Ber.*, 1955, **88**, 1654.