796. *Ferrocene Derivatives. Part XIV.* Polyarylcyclopentadienyliron Compounds*

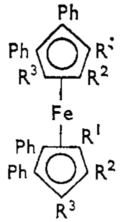
By S. McVey and P. L. Pauson

Reactions of polyarylcyclopentadienes with iron carbonyl or their anions with ferrous chloride have given a range of highly substituted ferrocenes and cyclopentadienyliron carbonyls. Bromopenta-(or tetra-)phenylcyclopentadiene reacts with pentacarbonyliron to give dicarbonylbromopenta-(or tetra-)phenylcyclopentadienyliron.

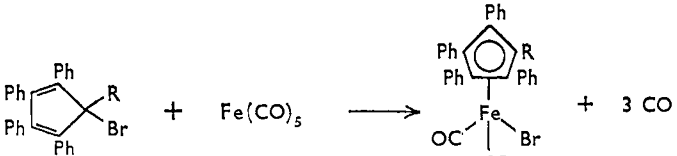
Polyarylferrocenes have previously been prepared from the lithium salts of polyarylcyclopentadienes and ferric chloride [1] and in one case from the cyclopentadiene and iron carbonyl.[2] The former method failed with cyclopentadienes having more than two adjacent phenyl groups.[1] However Weinmayr [3] was able to obtain octaphenylferrocene (I; $R^1 = H$, $R^2 = R^3 = Ph$) from the sodium salt of tetraphenylcyclopentadiene and ferrous chloride. This suggested that the earlier difficulty may have arisen, at least in part, at the stage involving reduction of the ferric to ferrous derivatives.

We have now investigated the behaviour of various polysubstituted cyclopentadienides with ferrous chloride, and have at the same time extended the metal carbonyl route.[2]

1,3-Diphenylcyclopentadiene, which had previously been shown to be convertible into 1,3,1′,3′-tetraphenylferrocene, both by the original ferric chloride method[1] and with iron carbonyl,[2] gave a 40% yield of the same ferrocene derivative under Weinmayr's conditions [3] for octaphenylferrocene. This was increased to 68% when the sodium salt of the diene was prepared with dimsylsodium [4] in tetrahydrofuran in place of sodium amide. This



(I)



(II) (III)

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* Part XIII, P. L. Pauson and W. E. Watt, *J.*, 1963, 2990.

[1] P. L. Pauson, *J. Amer. Chem. Soc.*, 1954, **76**, 2187.

[2] B. F. Hallam and P. L. Pauson, *J.*, 1956, 3030.

[3] V. Weinmayr, *J. Amer. Chem. Soc.*, 1955, **77**, 3012.

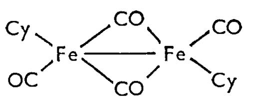
[4] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 866.

modified method gave octaphenylferrocene in 20% yield, whereas we were unable to reproduce its preparation under the original conditions. In our hands the best yield of this substance (32%) was obtained on heating tetraphenylcyclopentadiene with pentacarbonyliron. 1,2,3,1′,2′,3′-Hexaphenylferrocene (I; $R^1 = R^2 = H$, $R^3 = Ph$) was also prepared by both these methods, but in this case the dimsylsodium technique proved preferable.

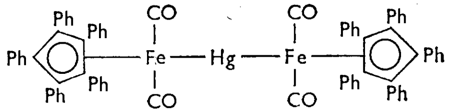
Neither the above, nor a variety of other conditions, proved applicable to pentaphenylcyclopentadiene and all our attempts to obtain decaphenylferrocene have remained unsuccessful. Despite the recent description [5] of bis(pentaphenylcyclopentadienyl)molybdenum it is difficult to find an explanation other than steric hindrance for this failure. That the bond from iron to a pentaphenylcyclopentadienyl group is not intrinsically unstable is shown by the ease of preparing the compounds with only one such group. The first of these, bromodicarbonylpentaphenylcyclopentadienyliron (III; R = Ph), was readily formed from bromopentaphenylcyclopentadiene (II; R = Ph) and pentacarbonyliron in boiling benzene. Although this reaction may be compared with the behaviour of simple allylic halides,[6] the bromotetraphenylcyclopentadiene (II; R = H) reacted only under vigorous conditions giving the corresponding iron derivative (III; R = H) in poor yield.

The bromodicarbonylpentaphenylcyclopentadienyliron (III; R = Ph) was subjected to a number of reactions which it was hoped might ultimately lead to decaphenylferrocene. Unlike the unsubstituted bromodicarbonylcyclopentadienyliron its pyrolysis afforded none of the corresponding ferrocene, but only a low yield of an unidentified product, along with pentaphenylcylopentadiene.

It was hoped that other derivatives, especially the dimeric carbonyl (IV; Cy = C_5Ph_5), might undergo such pyrolysis more smoothly. The bromide (III; R = Ph) was therefore subjected to two reduction procedures. Sodium amalgam afforded two products. One of these was identified as the mercury derivative (V). The other was too insoluble and unstable to permit full purification, analysis, or molecular-weight determination. Its infrared spectrum showed " terminal " and " bridging " carbonyl frequencies compatible with the expected structure (IV; Cy = C_5Ph_5), but its green colour and insolubility suggest a more complex (*e.g.*, tetrameric) structure. Both these products on pyrolysis afforded only pentaphenylcyclopentadiene. Reduction of the bromide (III; R = Ph) with sodium borohydride afforded dicarbonyl(pentaphenylcylopentadienyl)hydridoiron (VI; X = H). The same product has been obtained by Hübel [5b] along with tricarbonylpentaphenylcyclopentadieneiron (footnote in ref. 5*a*). To confirm the hydride formulation we have subjected this compound to Nyholm and Vrieze's reaction [7] with mercuric halides and obtained the halogenomercuri-derivatives (VI; X = HgCl or HgI). The high stability of this hydride (VI; X = H) relative to unsubstituted dicarbonylcylopentadienylhydridoiron is noteworthy.



(IV)



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The bromide (III; R = Ph) reacted smoothly with benzene in the presence of aluminium chloride to give the expected cation (VII) isolated as the water-insoluble but acetone-soluble bromide, as the iodide and as the reineckate.

Pentaphenyl- and tetraphenyl-cyclopentadienylsodium and 1,2,3-triphenylcyclopentadienyl-lithium each caused only reduction of the bromo-compound (III; R = Ph)

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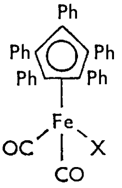
[5] (*a*) W. Hübel and R. Merenyi, *J. Organometallic Chem.*, 1964, **2**, 213; (*b*) W. Hübel, personal communication.

[6] H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, 1962, **45**, 1927.

[7] R. S. Nyholm and K. Vrieze, *Proc. Chem. Soc.*, 1963, 138.

to the same green solid obtained with sodium amalgam. Surprisingly 1,3-diphenylcyclopentadienylsodium reacted with this bromide with displacement of pentaphenylcyclopentadiene giving 1,3,1′,3′-tetraphenylferrocene. Only the unsubstituted cyclopentadienylsodium reacted in the expected fashion to yield the σ-cyclopentadienyl derivative



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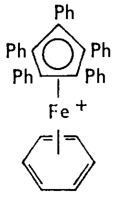

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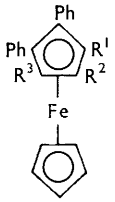

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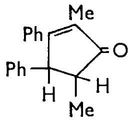

(IX)

(VI; X = C_5H_5). This was considerably more stable than the unsubstituted parent compound [2] but lost carbon monoxide on heating to give 1,2,3,4,5-pentaphenylferrocene (VIII; $R^1 = R^2 = R^3 =$ Ph). Reduction was again the only effect of treating unsubstituted bromodicarbonylcyclopentadienyliron with either sodiopenta- or lithiotetraphenylcyclopentadiene, the bromide being converted into the tetracarbonyl (IV; Cy = C_5H_5) and the cyclopentadienes recovered.

Unsymmetrical ferrocenes of the type (VIII) have previously been obtained [2] both by the above procedure and by heating tetracarbonylbiscyclopentadienyldi-iron (IV; Cy = C_5H_5) with a substituted cyclopentadiene. We have extended the latter procedure to three additional examples, (VIII; $R^1 = R^3 =$ H, $R^2 =$ Ph), (VIII; $R^1 =$ H, $R^2 = R^3 =$ Ph), and (VIII; $R^1 = R^2 = R^3 =$ Me). In each case it was found however that reaction at 180° led to partial displacement of the unsubstituted cyclopentadiene ring and the expected products (VIII) were therefore accompanied by the corresponding symmetrical ferrocenes (I). With 1,2,3-triphenylcyclopentadiene this (I; $R^1 = R^2 =$ H, $R^3 =$ Ph) was the exclusive product, while pentaphenylcyclopentadiene gave only a trace of the pentaphenylferrocene (VIII; $R^1 = R^2 = R^3 =$ Ph), but the symmetrical ferrocene again failed to form.

The above preparation of 1,2,3,4-tetraphenylferrocene (VIII; $R^1 =$ H, $R^2 = R^3 =$ Ph) confirms this structure for Nakamura and Hagihara's product [8] obtained from dicarbonylcyclopentadienylmethyliron, $C_5H_5Fe(CO)_2CH_3$, and tolane.

The hexamethyltetraphenylferrocene (I; $R^1 = R^2 = R^3 =$ Me) is only the second fully substituted ferrocene derivative; one other example,[9] decaethylferrocene, was described while this work was in progress. We recovered only the hydrocarbon from an attempt to obtain the same ferrocene (I; $R^1 = R^2 = R^3 =$ Me) by adding ferrous chloride to the lithium salt of 1,2,5-trimethyl-3,4-diphenylcyclopentadiene. Moreover, at 150°, this cyclopentadiene reacted with iron carbonyl giving exclusively the tetracarbonyl (IV; Cy = $C_5Me_3Ph_2$). Although this corresponds with the behaviour of cyclopentadiene itself and of its simple derivatives, it contrasts with that of tetraphenyl- (*vide infra*) and 1,3-diphenyl-cyclopentadiene [2] which give the corresponding ferrocenes without isolation of such intermediate carbonyls.[10] 1,4-Dimethyl-2,3-diphenylcyclopentadiene, in contrast to its higher homologue, readily afforded the corresponding ferrocene (I; $R^2 =$ H; $R^1 = R^3 =$ Me) when its lithium salt was allowed to react with ferrous chloride.

EXPERIMENTAL

All reactions involving organo-sodium or -lithium compounds were conducted in an atmosphere of nitrogen. M. p.s of all organometallic compounds were determined in sealed evacuated capillaries. Ligroin refers to the fraction of b. p. 60—80°. Ferrous chloride was prepared

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[8] A. Nakamura and N. Hagihara, *J. Chem. Soc. Japan*, 1963, **84**, 344.

[9] K. Schlögl and M. Peterlik, *Monatsh.*, 1962, **93**, 1328.

[10] The tetracarbonylbis(1,3-diphenylcyclopentadienyl)di-iron (IV; Cy = 1,3-$Ph_2C_5H_3$) has however recently been obtained by another route (R. Bruce and G. R. Knox, personal communication).

by the method of Kovacic and Brace.[11] Chromatography was carried out on alumina (Spence's Grade " H " which had been partially deactivated by exposure to air for 6 hr.). Molecular weights were determined cryoscopically in benzene. Infrared spectra were recorded as KCl discs.

1,3,1′,3′-*Tetraphenylferrocene*.—(*a*) *Sodamide method*.[3] Sodamide was prepared from sodium (0·5 g., 0·022 g.-atom) in liquid ammonia (50 ml.). To this was added 1,4-diphenylcyclopentadiene (2·18 g., 0·01 mole) followed, after 1 hr., by anhydrous ferrous chloride (3·0 g., 0·023 mole). After addition of xylene (25 ml.), the ammonia was allowed to distil off and the mixture was stirred at room temperature overnight. The precipitated solid was filtered off and washed with hot xylene. The combined xylene solutions were evaporated and the residue was crystallised from acetone to give orange-red prisms of 1,3,1′,3′-tetraphenylferrocene (0·9 g.; 40%), m.p. 220—222° (lit.,[1] m. p. 220—222°), identical with an authentic sample.

(*b*) *Dimsylsodium method*. Dimsylsodium [4] was prepared from dimethyl sulphoxide (6 ml.) and sodium hydride (0·52 g., 50% dispersion, 0·01 mole). To this was added a solution of 1,4-diphenylcyclopentadiene (1·6 g., 7·3 mmole) in tetrahydrofuran (50 ml.) and the mixture was stirred for 1 hr. Ferrous chloride (0·63 g., 5 mmole), was then added and stirring continued overnight. Evaporation of the filtered solution gave the above ferrocene (1·2 g.; 68%).

1,2,3,4,1′,2′,3′,4′-*Octaphenylferrocene* (I; $R^1 = H$, $R^2 = R^3 = Ph$).—(*a*) *Dimsylsodium method*. To dimsylsodium [from NaH (1·04 g., 50% dispersion, 0·02 mole) and Me_2SO (8 ml.)] was added 1,2,3,4-tetraphenylcyclopentadiene (5·2 g., 0·014 mole) in tetrahydrofuran (100 ml.). The mixture was stirred for 2 hr. at 40°. Ferrous chloride (1·25 g., 0·01 mole) was then added and stirring continued overnight. The filtered solution was evaporated and the residue was redissolved in benzene and chromatographed to give octaphenylferrocene (1·0 g.; 20%) as deep red prisms, m. p. 322° (lit.,[3] m. p. 322°), identical with an authentic sample.[3]

(*b*) *Carbonyl method*. Pentacarbonyliron (1·5 ml., 0·01 mole) and 1,2,3,4-tetraphenylcyclopentadiene (3·7 g., 0·01 mole) were heated for 4 hr. at 180° under an atmosphere of carbon dioxide in an autoclave. The residue was extracted with hot benzene. The extract was concentrated and chromatographed to give octaphenylferrocene (1·2 g., 32%), m. p. 322° (from chlorobenzene).

1,2,3,1′,2′,3′-*Hexaphenylferrocene* (I; $R^1 = R^2 = H$, $R^3 = Ph$).—(*a*) *Carbonyl method*. Substitution of 1,2,3-triphenylcyclopentadiene [1] (3 g., 0·01 mole) for the tetraphenyl derivative in the preceding experiment afforded 1,2,3,1′,2′,3′-*hexaphenylferrocene* (0·75 g., 21%), m. p. 266—268°, identical with the product described in (*b*).

(*b*) *Dimsylsodium method*. This was carried out as described above for 1,3,1′,3′-tetraphenylferrocene except for the use of 1,2,3-triphenylcyclopentadiene (2·06 g., 7 mmole). The resulting hexaphenylferrocene (1 g., 45%) crystallised from chlorobenzene as red prisms, m. p. 266—268° (Found: C, 86·1; H, 5·5. $C_{46}H_{34}Fe$ requires C, 86·0; H, 5·3%).

1,4,1′,4′-*Tetramethyl*-2,3,2′,3′-′*tetraphenylferrocene* (I; $R^2 = H$, $R^1 = R^3 = Me$).—To phenyl-lithium [prepared from PhBr (0·8 g., 5 mmole) and Li (0·07 g., 0·01 g.-atom) in ether] was added 1,4-dimethyl-2,3-diphenylcyclopentadiene [12] (1·23 g., 5 mmole) and the mixture was refluxed for 2 hr. with stirring. After addition of ferrous chloride (0·32 g., 2·5 mmole) stirring was continued at room temperature overnight. Ice–water was then added and the organic layer was separated, dried, and evaporated. The residual 1,4,1′,4′-*tetramethyl*-2,3,2′,3′-*tetraphenylferrocene* (0·63 g., 46%) crystallised from acetone as orange-red prisms, m. p. 232—233° (Found: C, 83·2; H, 6·8. $C_{38}H_{34}Fe$ requires C, 83·3; H, 6·2%).

Tetracarbonylbis-(1,2,3-*trimethyl*-4,5-*diphenylcyclopentadienyl*)*di-iron* (IV; Cy = $C_5Me_3Ph_2$).—Pentacarbonyliron (0·75 ml., 5 mmole) and 1,2,5-trimethyl-3,4-diphenylcyclopentadiene [12] (1·3 g., 5 mmole) were heated for 4 hr. at 150° under an atmosphere of carbon dioxide in an autoclave. Extraction of the product with benzene and concentration of this solution gave almost black crystals of *tetracarbonylbis*-(1,2,3-*trimethyl*-3,4-*diphenylcyclopentadienyl*)*di-iron* (0·9 g.; 48·5%), m. p. 330° (decomp.), $\nu_{max.}$ 1953, 1773 cm.$^{-1}$ (terminal and bridging CO, respectively) (Found: C, 70·8; H, 5·4. $C_{44}H_{38}Fe_2O_4$ requires C, 71·2; H, 5·1%).

Reactions of Substituted Cyclopentadienes with Tetracarbonylbiscyclopentadienyldi-iron.—The tetracarbonyl (0·9 g., 2·5 mmole) was heated with the substituted cyclopentadiene (2·5 mmole) for 3 hr. at 180° under an atmosphere of carbon dioxide in a small autoclave (40 ml.).

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[11] P. Kovacic and N. O. Brace, *J. Amer. Chem. Soc.*, 1954, **76**, 5491.

[12] P. Bladon, S. McVey, and P. L. Pauson, in preparation.

In each case the product was then extracted with benzene, the extract filtered through a short column of alumina, and evaporated. The mixtures of ferrocenes so obtained were separated by fractional crystallisation from acetone with the following results (all known products being identified by comparison with authentic samples): (i) 1,2,4-Triphenylcyclopentadiene (0·73 g.) yielded 1,2,4-*triphenylferrocene* (VIII; $R^1 = R^3 = H$, $R^2 = Ph$) (0·41 g.; 37%) as orange prisms, m. p. 167—169° (Found: C, 81·3; H, 5·9. $C_{28}H_{22}Fe$ requires C, 81·2; H, 5·3%), and 1,2,4,1′,2′,4′-hexaphenylferrocene (I; $R^1 = R^3 = H$, $R^2 = Ph$) [1] (0·06 g.; 7%): (ii) 1,2,3-Triphenylcyclopentadiene (0·73 g.) yielded only 1,2,3,1′,2′,3′-hexaphenylferrocene (I; $R^1 = R^2 = H$, $R^3 = Ph$) (see above) (0·99 g.; 10%): (iii) 1,2,3,4-Tetraphenylcyclopentadiene (0·9 g.) yielded 1,2,3,4-*tetraphenylferrocene* (VIII; $R^1 = H$, $R^2 = R^3 = Ph$) (0·53 g.; 43%) as orange red prisms, m. p. 226° (lit.,[8] m. p. 226°) (Found: C, 82·7; H, 5·8. $C_{34}H_{36}Fe$ requires C, 82·9; H, 5·4%), and 1,2,3,4,1′,2′,3′,4′-octaphenylferrocene (I; $R^1 = H$, $R^2 = R^3 = Ph$) [3] (0·14 g.; 15%): (iv) 1,2,3,4,5-Pentaphenylcyclopentadiene (1·1 g.) yielded only 1,2,3,4,5-pentaphenylferrocene (VIII; $R^1 = R^2 = R^3 = Ph$) (trace) as orange-yellow needles, m. p. 356—358° (see below): (v) 1,2,5-Trimethyl-3,4-diphenylcyclopentadiene (0·4 g., 1·6 mmole) and tetracarbonylbiscyclopentadienyldi-iron (0·6 g., 1·6 mmole) yielded 1,2,3-*trimethyl*-4,5-*diphenylferrocene* (VIII; $R^1 = R^2 = R^3 = Me$) (0·23 g., 40%) as golden yellow needles, m. p. 204—206° (Found: C, 79·2; H, 7·0. $C_{25}H_{24}Fe$ requires C, 78·9; H, 6·3%), and 1,2,3,1′,2′,3′-*hexamethyl*-4,5,4′,5′-*tetraphenylferrocene* (I; $R^1 = R^2 = R^3 = Me$) (40 mg., 9%) as red prisms, m. p. 192—193° (Found: C, 83·6; H, 7·5. $C_{40}H_{38}Fe$ requires C, 83·6; H, 6·6%).

Bromodicarbonyl(tetraphenylcyclopentadienyl)iron (III; R = H).—Pentacarbonyliron (0·5 ml., 3·3 mmole) and 5-bromo-1,2,3,4-tetraphenylcyclopentadiene [13] (1·0 g., 2·2 mmole) were refluxed in chlorobenzene (20 ml.) for 2 hr. The filtered solution was evaporated under reduced pressure and the residue was dissolved in benzene and chromatographed. A small purple band was eluted giving *bromodicarbonyl(tetraphenylcyclopentadienyl)iron* which crystallised from methylene chloride–ligroin as dark red prisms, m. p. 175—177° (decomp.), $\nu_{max.}$ 2041 and 2000 cm.$^{-1}$ (CO) (Found: C, 67·7; H, 4·3. $C_{31}H_{21}BrFeO_2$ requires C, 66·3; H, 3·8%).

Bromodicarbonyl(pentaphenylcyclopentadienyl)iron (III; R = Ph).—Pentacarbonyliron (2·0 ml., 13 mmole) and 5-bromopentaphenylcyclopentadiene (6·5 g., 12 mmole) were refluxed in benzene (150 ml.) for 2 hr. The mixture was filtered and concentrated *in vacuo* to small bulk. The product which crystallised was collected and recrystallised from methylene chloride–ligroin giving *bromodicarbonyl(pentaphenylcyclopentadienyl)iron* (5·0 g.; 65%) as dark red needles, which decompose above 230° without melting; $\nu_{max.}$ 2040 and 2000 cm.$^{-1}$ (CO) (Found: C, 69·9; H, 4·2; Fe, 8·8. $C_{37}H_{25}BrFeO_2$ requires C, 69·7; H, 3·9; Fe, 8·8%).

Pyrolysis of Bromodicarbonyl(pentaphenylcyclopentadienyl)iron (III; R = Ph).—This bromo-compound (0·5 g.) was heated at 200° *in vacuo* (0·1 mm.) for 2 hr. Extraction of the residue with benzene, evaporation to small bulk, and addition of ligroin gave a red solid (0·05 g.). Recrystallisation from chlorobenzene gave deep red needles, m. p. 264—266° (Found: C, 52·6, 53·1; H, 3·7, 3·0%). Chromatography of this substance (35 mg.) led to a green and a blue band. The former, eluted by benzene as a green fluorescent solution, gave on evaporation only a trace (3 mg.) of a yellow solid. The latter was eluted by benzene–ether (2 : 1) and gave a blue solid (12·5 mg.), m. p. 110—130°. It was reprecipitated from its ligroin solution on cooling to −70°, but decomposed on keeping and could not be purified completely.

Reaction of Bromodicarbonyl(pentaphenylcyclopentadienyl)iron (III; R = Ph) *with Sodium Amalgam*.—The bromo-compound (1 g., 1·5 mmole) was dissolved in tetrahydrofuran (40 ml.) and stirred with 1% sodium amalgam (1·52 g., 0·0015 g.-atom Na) for 2 hr. A green powder (0·5 g.), m. p. above 360° (decomp.), was filtered off; this was insoluble in common organic solvents; it showed two strong infrared maxima of comparable intensity at ν 1965 (terminal) and 1786 cm.$^{-1}$ (bridging carbonyl). Its pyrolysis (200°/1 mm/2 hr.) afforded 1,2,3,4,5-pentaphenylcyclopentadiene. The filtrate was evaporated and the residue chromatographed in benzene to give *bis(dicarbonylpentaphenylcyclopentadienyliron)mercury* (0·3 g.; 30%) crystallising from methylene chloride as orange prisms, m. p. 262—264°, $\nu_{max.}$ 1970, 1931 cm.$^{-1}$ (CO) (Found: C, 67·0; H, 3·9; Fe, 7·7. $C_{74}H_{50}Fe_2HgO_4$ requires C, 67·6; H, 3·8; Fe, 8·5%). Its pyrolysis (200°/1 mm.) afforded only 1,2,3,4,5-pentaphenylcyclopentadiene.

Dicarbonyl(pentaphenylcyclopentadienyl)hydridoiron (VI; X = H).—To bromodicarbonyl-(pentaphenylcyclopentadienyl)iron (1·0 g., 1·5 mmole) in tetrahydrofuran (30 ml.), excess of

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[13] H. Kainer, *Annalen*, 1952, **578**, 232.

sodium borohydride dissolved in water (3 ml.) was added. The mixture was stirred for 3 hr. The aqueous layer was withdrawn and the tetrahydrofuran solution was acidified with glacial acetic acid. When this solution was cooled in ice, a crystalline product separated. Recrystallisation from acidified (HOAc) tetrahydrofuran yielded *dicarbonyl(pentaphenylcyclopentadienyl)-hydridoiron* as yellow prisms, m. p. 277—279° (decomp.). Its infrared spectrum showed maxima in the metal–carbonyl stretching region at ν 2000 and 1942 cm.$^{-1}$ and was indistinguishable from a spectrum kindly supplied by Dr. W. Hübel.[5] Because of the instability of this compound accurate analyses could not be obtained (Found: C, 75·8; H, 5·0. $C_{37}H_{26}FeO_2$ requires C, 79·0; H, 4·7%) but the structure assigned is confirmed by the following reactions with mercuric halides: To acidified tetrahydrofuran solutions of the hydride, saturated solutions of the appropriate mercuric halide in ethanol were added and the resulting mixtures were shaken for 10 min. The precipitated products were recrystallised from aqueous tetrahydrofuran yielding *dicarbonyl(pentaphenylcyclopentadienyl)chloromercuri-iron* (VI; X = HgCl) as yellow-orange needles, decomp. above 150°, $\nu_{max.}$ 2000 and 1970 cm.$^{-1}$ (CO) (Found: C, 57·0; H, 3·8; Fe, 7·0. $C_{37}H_{25}ClFeHgO_2$ requires C, 56·0; H, 3·2; Fe, 7·1%) and the corresponding *iodomercuri-derivative* (VI; X = HgI) as orange needles, m. p. 245° (decomp.), $\nu_{max.}$ 2010 and 1960 cm.$^{-1}$ (CO) (Found: C, 52·5; H, 3·6; Fe, 6·5. $C_{37}H_{25}FeHgIO_2$ requires C, 50·2; H, 2·8; Fe, 6·3%).

Benzene(pentaphenylcyclopentadienyl)iron Salts (VII).—Benzene (30 ml.), bromodicarbonyl-(pentaphenylcyclopentadienyl)iron (III; R = Ph) (1 g., 1·5 mmole), and aluminium chloride (0·20 g., 1·5 mmole) were refluxed for 1 hr. The mixture was poured into water, precipitating *benzene(pentaphenylcyclopentadienyl)iron bromide* (0·75 g., 75%) which crystallised from acetone as orange prisms, m. p. 256—258° (decomp.) (Found: C, 75·3; H, 5·3; Fe, 8·5. $C_{41}H_{31}BrFe$ requires C, 74·5; H, 4·7; Fe, 8·2%). Treatment of aqueous acetone solutions of this salt with ammonium reineckate and with potassium iodide in the same solvent mixture precipitated, respectively, the corresponding *reineckate* as bright red needles, m. p. 219—221° (decomp.), and *iodide*, as orange needles, crystallising from acetone, m. p. 253—254° (decomp.) (Found: C, 69·2; H, 4·9; Fe, 8·1. $C_{41}H_{31}FeI$ requires C, 69·7; H, 4·4; Fe, 7·9%).

Reactions of Bromodicarbonyl(pentaphenylcyclopentadienyl)iron (III; R = Ph) *with Substituted Cyclopentadienides*.—The bromo-compound (III; R = Ph) (3·19 g., 5 mmole) was treated with approximately equimolar proportions of each of the following reagents under the conditions specified: (*a*) 1,2,3-Triphenylcyclopentadienyl-lithium (prepared from the hydrocarbon and phenyl-lithium) with stirring in ether for 1 hr. (*b*) Tetraphenylcyclopentadienylsodium (prepared from the hydrocarbon and dimsylsodium) with stirring in tetrahydrofuran for 2 hr. (*c*) Pentaphenylcyclopentadienylsodium (prepared from the hydrocarbon with dimsylsodium) with stirring in tetrahydrofuran for 2 hr. In each case the same green solid (0·4, 1·2, and 1·4 g., respectively), identical with that obtained by sodium amalgam reduction of the bromide (III; R = Ph), was precipitated. Chromatography of the soluble products afforded 1,2,3,4,5-pentaphenylcyclopentadiene in each case, accompanied in (*a*) and (*b*) by 1,2,3,-tri- and by 1,2,3,4-tetra-phenylcyclopentadiene, respectively. An analogous reaction was carried out between the bromo-compound (III; R = Ph) (1·28 g., 2 mmole) in tetrahydrofuran (30 ml.) and 1,3-diphenylcyclopentadienylsodium [prepared by stirring dimsylsodium (from 0·11 g., 2 mmole, 50% NaH dispersion and 2 ml. Me_2SO) with 1,4-diphenylcyclopentadiene (0·44 g., 2 mmole) in tetrahydrofuran (20 ml.) for 1 hr.]. The mixture was stirred for 1 hr., then refluxed for 4 hr., filtered, and the filtrate evaporated. Extraction with hot acetone gave, on cooling, 1,2,3,4,5-pentaphenylcyclopentadiene (0·65 g.; 73%) and a solution from which 1,3,1′,3′-tetraphenylferrocene (0·1 g.; 20%), m. p. and mixed m. p. with an authentic specimen [1] 221—223°, was obtained after evaporation and chromatography (in benzene).

Dicarbonyl-σ-cyclopentadienyl-π-pentaphenylcyclopentadienyliron (VI; X = C_5H_5).—Cyclopentadienylsodium [prepared by stirring cyclopentadiene (0·13 g., 2 mmole) with a 20% sodium dispersion (0·23 g., 0·002 g.-atom) in tetrahydrofuran for 1 hr.] and bromodicarbonyl(pentaphenylcyclopentadienyl)iron (III; R = Ph) (1·28 g., 2 mmole) were stirred in tetrahydrofuran (50 ml.) for 2 hr. The orange precipitate was filtered off and recrystallised from methylene chloride. *Dicarbonyl-σ-cyclopentadienyl-π-pentaphenylcyclopentadienyliron* (0·8 g.) formed orange-red prisms, m. p. 343—345° (decomp.), $\nu_{max.}$ 2010 and 1961 cm.$^{-1}$ (CO). A further 0·2 g. were obtained from the filtrate (total 1·0 g., 78%) (Found: C, 79·6; H, 5·0; Fe, 9·0%; *M*, 622. $C_{42}H_{30}FeO_2$ requires C, 81·0; H, 5·8; Fe, 9·0%; *M*, 623).

1,2,3,4,5-*Pentaphenylferrocene*. (VIII; R′ = R^2 = R^3 = Ph).—The above dicarbonyl (VI; X = C_5H_5) (0·2 g.) was heated to 200° *in vacuo* (0·5 mm.) for 1·5 hr. Extraction of the residue with benzene, evaporation, and recrystallisation from chlorobenzene gave 1,2,3,4,5-*pentaphenylferrocene* (0·175 g., 95%) as orange needles, m. p. 356—358° (Found: C, 84·6; H, 5·9%; *M*, 518. $C_{40}H_{30}Fe$ requires C, 84·8; H, 5·3%; *M*, 566).

Reaction of Bromodicarbonylcyclopentadienyliron with Tetra- and Penta-phenylcyclopentadienides.—This bromo-compound (1·04 g., 4 mmole or 1·28 g., 5 mmole) was stirred in tetrahydrofuran (40 or 20 ml.) overnight or for 2 hr., respectively, with with following substituted cyclopentadienides: (*a*) Tetraphenylcyclopentadienyl-lithium [prepared in benzene (20 ml.) from 1,2,3,4-tetraphenylcyclopentadiene (1·7 g., 4 mmole) and phenyl-lithium (from 0·056 g., 0·008 g.-atom: Li; 0·628 g., 4 mmole PhBr and 5 ml. ether)]: (*b*) Pentaphenylcyclopentadienylsodium [prepared in tetrahydrofruran (40 ml.) from dimsylsodium (5 mmole) and 1,2,3,4,5-pentaphenylcyclopentadiene (2·23 g., 5 mmole)]. Chromatography of the products in benzene yielded in each case only tetracarbonylbis(cyclopentadienyliron) (IV; Cy = C_5H_5) (0·46 g., 68% and 0·85 g., 72% respectively) and recovered tetra- (1·62 g., 95%) or penta-phenylcyclopentadiene (2·1 g., 94%).

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