Reaction between Mono-olefins and Ferrocenylcarbene Complexes of Chromium; Formation of 3-Amino- and 5-Amino-pent-1-enes

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The reactions of 1,1-diphenylethylene and dimethyl fumarate with the carbene complexes, $[(CO)_5CrC(X)Fc]$ (X = OMe or NC_4H_8, Fc = ferrocenyl) at 136° in a nitrogen atmosphere are described. Although the methoxy-compound reacts with dimethyl fumarate to give a 1-ferrocenyl-1-methoxycyclopropane derivative in 50% yield, the pyrrolidinyl compound reacts with dimethyl fumarate to give dimethyl 5-[ferrocenyl(pyrrolidin-1-yl)methyl]-3,4-bis-methoxycarbonylhex-2-enedioate (32%) and with 1,1-diphenylethylene to give 3-ferrocenyl-1,1,5,5-tetraphenyl-3-pyrrolidin-1-ylpent-1-ene (7%). The course of these reactions is discussed briefly and it is suggested that they are not consistent with the participation of a free carbene species, Fc(X)C:. The intervention of zwitterionic intermediates in the reactions of aminocyclopropanes is considered.

Cycloaddition of a carbene, $R^1R^2C:$, to an olefin is an important method for the synthesis of cyclopropanes. This reaction has been employed in several experiments designed to determine the spin multiplicity of the carbene involved.[1]

Recent studies of ferrocenylcarbenes generated from tosylhydrazone precursors have indicated that the carbenes possess a triplet multiplicity which was thought to be determined by the iron atom.[2]

We have described the preparation and characterisation of a number of carbene complexes of chromium, tungsten, and manganese in which the carbene ligand contains a ferrocenyl (Fc) group adjacent to the co-ordinatively unsaturated carbene carbon atom. The close analogy between the carbene ligand in these complexes and a ferrocenylcarbonium ion has been demonstrated.[3]

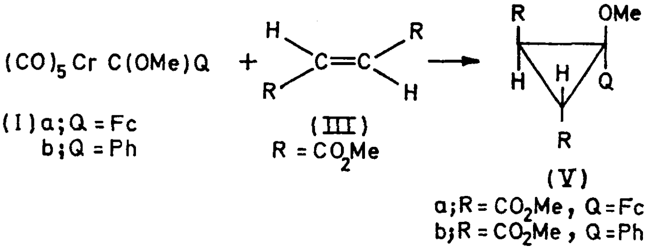
We report now a comparative study of the reactions of two ferrocenyl carbene complexes $[(CO)_5CrC(Fc)OMe]$ (Ia) and $[(CO)_5CrC(Fc)NC_4H_8]$ (II) with each of the olefins dimethyl fumarate (III) and 1,1-diphenylethylene (IV). This has been carried out in order to establish whether or not the inclusion of a heteroatom substituent or a change in the olefinic substrate will influence the reactions of the complex and to examine whether or not free carbenes may be involved in such reactions.

RESULTS AND DISCUSSION

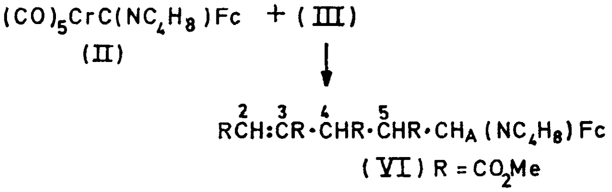
Reactions of the Alkoxy-complex (Ia).—Compound (Ia), m.p. 134—135°, was heated with a large excess of the diester (III), an electrophilic olefin, at 136° under nitrogen to give the cyclopropane (Va) in moderate yield (50%) after 0·75 h.† This result is consistent with the finding that the cyclopropane (Vb) is formed in comparable yield when compound (Ib) is heated with (III) at 110° for 2·5 h.[4]

Compound (Ia) was heated at the same temperature (136°) with a large excess of the nucleophilic, triplet-trapping olefin (IV) for 3 h, *i.e.* four times the period required for complete reaction with (III). The majority of the complex (Ia) (66%) was then recovered unchanged. Apart from decomposition products, no other material [such as a 1 : 1 adduct of (Ia) with (IV)] was obtained.

Reactions of the Pyrrolidinyl Complex (II).—Compound (II), m.p. 132—133°, was completely consumed when heated in a large excess of the diester (III) for 1·5 h at 136°. The product was shown (see later) to be the pentene derivative (VI). Compound (VI) was also produced from compounds (II) and (III) in refluxing pyridine.



Scheme 1



Scheme 2

A mixture of products was obtained when the complex (II) was heated with a large excess of (IV) at 136° for 3·5 h [10% of (II) was recovered]. The principal product was the pentene derivative (VII), and chromatography of the reaction mixture also produced 3,3-diphenylpropionylferrocene and ferrocenecarbaldehyde. We believe that these latter compounds are produced from the decomposition of a metal carbonyl complex containing the 3-aminopentene (VII), as a ligand, which is probably of the type $[(VII)Cr(CO)_5]$. This complex could be recognised by the i.r. spectrum of a solution in hexane, which differs from that of the starting material (II). However, all attempts to isolate and purify the

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† The stereochemistry of the alkene (III) is retained in the cyclopropane product (Va) as established by the n.m.r. spectrum (J_{AB} 7·5 Hz).

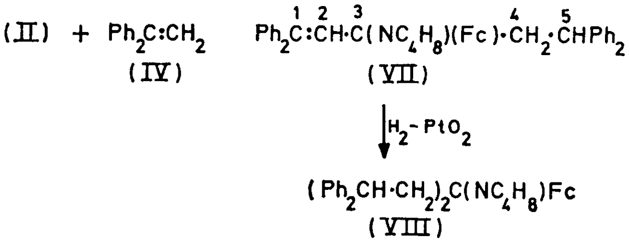
[1] T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes, and Arynes,' Nelson, London, 1969.

[2] A. Sonoda and I. Moritani, *Bull. Chem. Soc. Japan*, 1970, **43**, 3522; *J. Organometallic Chem.*, 1971, **26**, 133.

[3] J. A. Connor and J. P. Lloyd, *J.C.S. Dalton*, 1972, 1470.

[4] K. H. Dötz and E. O. Fischer, *Chem. Ber.*, 1972, **105**, 1356.

complex by chromatography resulted in its decomposition, as shown by the appearance of a brown band. This decomposition was greatly accelerated by light. Elution of the brown band with benzene gave 3,3-diphenylpropionylferrocene, ferrocenecarbaldehyde, and hexacarbonylchromium.



Scheme 3

When ferrocenecarbaldehyde was heated with the olefin (IV) at 136° for 3·5 h, the materials were recovered unchanged, showing that 3,3-diphenylpropionylferrocene is not formed by this route. Furthermore, when compound (II) was heated in the absence of (IV) under identical conditions, no trace of ferrocenecarbaldehyde was found. These results taken together show that neither 3,3-diphenylpropionylferrocene nor ferrocenecarbaldehyde is a primary product of the reaction between (II) and (IV), and indicate that these compounds may arise from the complex of the 3-aminopentene (VII) already mentioned either by photolytic or by hydrolytic decomposition on the deactivated chromatographic material. Care was taken to ensure the rigorous deoxygenation of the materials used both in the reaction and in its subsequent elaboration, so that it is most unlikely that the volume of oxygen required to produce the amounts of 3,3-diphenylpropionylferrocene and ferrocenecarbaldehyde isolated could have been present. We believe that the carbonyl group in 3,3-diphenylpropionylferrocene is derived from the carbene carbon atom in (II) rather than the CO ligands in the compound.

Characterisation of the Substituted Pentenes (VI) *and* (VII).—Quantitative analysis and mass spectrometry showed that (VI) and (VII) have the formulae $C_{27}H_{33}FeNO_8$ and $C_{43}H_{41}FeN$, respectively, each case corresponding to two molecules of olefin and one carbene ligand ($C_{15}H_{17}FeN$) unit.

The n.m.r. spectrum of compound (VI) (see Experimental section) contains two broad multiplets produced by the pyrrolidine ring protons at chemical shift values similar to those found in *N*-alkylpyrrolidines. For three single proton signals comprising two doublets and a double doublet the coupling constants lie in the range 5—9 Hz, consistent with $^3J_{HH}$. Of the two methoxycarbonyl signals at δ 3·59 and 3·65 p.p.m. the former is tentatively assigned to the olefinic substituents. The mass spectrum of (VI) shows a strong molecular ion peak which was shown to be $C_{27}H_{33}FeNO_8$ by mass measurement. Similar measurements on the ions at *m*/*e* 412 and 286 showed that they had the compositions $C_{21}H_{26}FeNO_4$ and $C_{12}H_{14}O_8$, respectively. The former could arise by rupture of the C(3)–C(4) bond, while the latter could arise by rupture at C-5 and loss of hydrogen, possibly giving a tetrasubstituted butadiene ion together with $FcCH_2NC_4H_8$ (*m*/*e* 269). Evidence for this is provided by the observation of a metastable transition at *m*/*e* 147·4 [$555^+ \longrightarrow 286^+ + 269$].

The n.m.r. spectrum of compound (VII) (see Experimental section) shows phenyl and ferrocenyl proton signals in the ratio 20 : 9. A two-proton doublet ($^3J_{HH}$ 8 Hz) at δ 3·58 p.p.m. (C-4 protons) and a single proton triplet ($^3J_{HH}$ 7·5 Hz) at δ 4·48 (5-H) are both at similar positions in the spectra of other $Ph_2CH{\cdot}CH_2X$ compounds (see Experimental section for X = CO_2H, COCl, or COFc). The mass spectrum contains a molecular ion shown to be $C_{43}H_{41}FeN$ by mass measurement: the base peak at *m*/*e* 446 was shown to be $C_{29}H_{28}FeN$ by a similar measurement. Two intense metastable transitions at *m*/*e* 317·2 and 227·9 correspond to the processes [$627^+ \longrightarrow 446^+ + 181$] and [$627^+ \longrightarrow 378^+ + 249$], respectively. The former involves simple rupture of the C(3)–C(4) bond; the latter is consistent with rupture of both the C(2)–C(3) bond and the C(3)–NC_4H_8 bond, with migration of the pyrrolidinyl group to C-2. The spectrum does not contain a peak of significant intensity (>0·5%) at *m*/*e* 358 which might correspond to the ion $[Ph_2C{\cdot}CH{:}CH{\cdot}CPh_2]^+$, whereas the mass spectrum of (V) contains an ion at *m*/*e* 286 (18%), shown to be consistent with $[RCH{\cdot}CR{:}CR{\cdot}CHR]^+$ (see before).

Mild hydrogenation of compound (VII) in methanol solution with Adams catalyst resulted in the fairly rapid uptake of 1 mol. equiv. of hydrogen and the deposition of yellow crystals of compound (VIII). Quantitative analysis and a mass measurement of the molecular ion established the molecular formula $C_{43}H_{43}FeN$. Two intense metastable transitions at 319 and at 227·2 correspond to the processes [$629^+ \longrightarrow 448^+ + 181$] and [$629^+ \longrightarrow 378^+ + 251$], respectively, both of which have their counterparts in the mass spectrum of (VII). A mass measurement of the ion *m*/*e* 448 indicated that it was $C_{29}H_{30}FeN$. The n.m.r. spectrum of (VIII) was very similar to that of (VII), with the important difference that the olefinic proton resonance observed for the latter is not present in the spectrum of the former. The two equivalent sets of methylene protons appear as a doublet ($^3J_{HH}$ 7·8 Hz) and the two methine protons as a triplet ($^3J_{HH}$ 7·0 Hz).

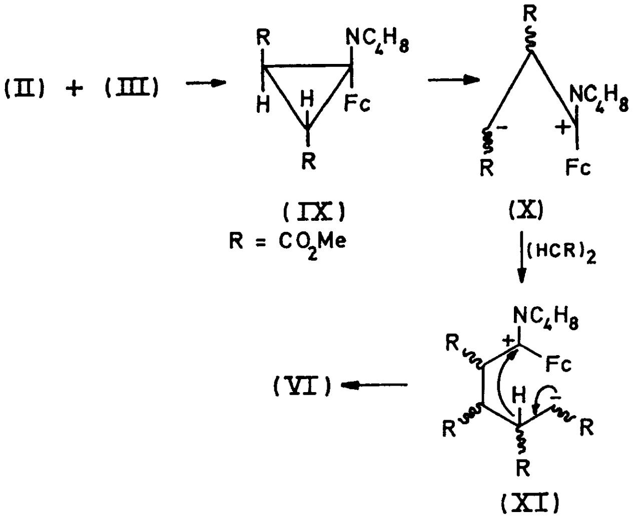
Cyclic structures considered for (VI) and for (VII) were eliminated by the evidence of the combined spectroscopic results and by the hydrogenation experiment [(VII) ⟶ (VIII)]. Other structures required the disruption and rearrangement of the carbene ligand, which seems unlikely in view of the ease with which (Va) is formed from (I), and yet others could not have acted as precursors of ferrocenecarbaldehyde and 3,3-diphenylpropionylferrocene in the manner already outlined.

CONCLUSIONS

The reactions reported appear to show an unexpected difference in reactivity between alkoxy- and aminocarbene complexes. Adducts of the type represented by (VI) and (VII) have not been isolated before from the reactions of carbene sources with olefins, so that the factors controlling the formation of such compounds must be the subject of speculation.

The large difference in the rate of reaction between the complex (Ia) and the olefins (III) and (IV) is less marked in the reactions of compound (II) with the same olefins. This suggests that, for compound (Ia) at least, the reactions are bimolecular, involving attack of the olefin on the carbene complex rather than a unimolecular decomposition of the complex to give free carbene which is then trapped by the olefin, which is present in large excess. This would explain why, in each case, the electrophilic olefin (IV) reacts more readily than the nucleophilic olefin (III). It would also indicate why the electrophilic triplet character, which might have been expected for such ferrocenylcarbene systems,[2] is either suppressed or transformed in the present instance.

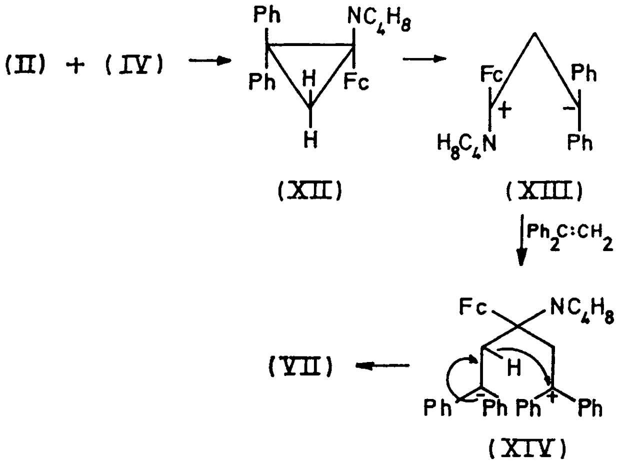
It is reasonable to suggest that both of the ferrocenylcarbene complexes (Ia) and (II) react in a similar manner with the olefins to give the cyclopropanes (Va), and (IX) and (XII) in the first place. However, whereas the cyclopropane ring in (Va) is stable to further reaction under the conditions employed, the cyclopropanes (IX) and (XII) react with a further molecule of olefin under the same conditions of temperature and excess of olefin to give (VI) and (VII).



Scheme 4

The cyclopropane (IX) can be regarded as a β-amino-ester; rupture of the carbon–carbon bond to give an iminium enolate in the formalism of a reverse Mannich reaction is known to occur in such systems. For example, the action of zinc in glacial acetic acid upon the alkaloid catharanthine results in rupture of the C(5)–C(18) bond and the formation of four isomeric methoxycarbonyldihydrocleavamines.[5] Further, the methanolysis and epimerisation of methyl 1-cyano-2,2-diphenylcyclopropanecarboxylate has been shown to proceed by way of a zwitterion (carbocation–carbanion ion pair) rather than a singlet diradical.[6a] A similar type of intermediate in the oxidation of aminocyclopropyl sulphides to give both sulphone acids and oxosulphones has been proposed recently.[6b] It is suggested that such an intermediate will be favoured when both carbocation- and carbanion-stabilising substituents are present on adjacent atoms of a cyclopropane ring. A similar situation exists in structure (IX), which would thus give (X) as the zwitterion intermediate.

The zwitterion (X) might then react with a further molecule of the electrophilic olefin (III), which is present in large excess, at the carbanion site to give (XI). Rearrangement of (XI) by hydride transfer (Scheme 4) would afford the desired final product (VI).



Scheme 5

The application of similar concepts to the conversion of (XII) into (VII) is less straightforward. Opening of the cyclopropane ring of (XII) might give the zwitterion (XIII) if it is assumed that the phenyl substituents are better able to stabilise the carbanion site than the pyrrolidinyl and ferrocenyl substituents, and conversely with respect to the carbocation centre. Such an assumption is supported both by the conversion of 1-morpholino-6,6-diphenylbicyclo[3,1,0]hexane into 2-diphenylmethylcyclopentanone on heating in ethylene glycol at 150° with subsequent acidic hydrolysis,[7a] and by the thermolysis of *exo*-7-chloro-1-morpholino-7-phenylbicyclo[4,1,0]-heptane in pyridine which gives *exo*-7-phenylbicyclo-[3,1,1]heptane-6-one and 2-benzylidenecyclohexanone.[7b] Reaction of (XIII) with a further molecule of the nucleophile olefin (IV), which is present in large excess, might be expected to occur at the carbocation centre in the former, giving (XIV). Rearrangement of (XIV) either directly (as shown) or indirectly could lead to the

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[5] J. P. Kutney, W. J. Cretney, J. R. Hadfield, E. S. Hall, and V. R. Nelson, *J. Amer. Chem. Soc.*, 1970, **92**, 1704.

[6] (*a*) E. W. Yankee and D. J. Cram, *J. Amer. Chem. Soc.*, 1970, **92**, 6328, 6329, 6331; (*b*) R. H. Rynbrandt and F. E. Dutton, *Tetrahedron Letters*, 1972, 1937.

[7] (*a*) I. G. Bolesov, S. A. Gladyr, A. S. Koz'min, and R. Y. Levina, *Zhur. org. Khim.*, 1970, **6**, 2431; (*b*) U. K. Pandit and S. A. G. de Graaf, *J.C.S. Chem. Comm.*, 1972, 659.

final product (VIII). We have no evidence for intramolecular as distinct from intermolecular hydride transfer in this rearrangement. Experiments with molecular models suggest that ring closure of (XIV) [and also that of (XI)] to give a cyclopentane product is prevented by steric factors.

It appears that the complex (II) has a greater affinity than (Ia) for the nucleophilic olefin (IV) and there is evidence to suggest that this order is inverted with respect to the electrophilic olefin (III). This may be taken as further evidence against the participation of a free carbene species in these reactions and in favour of a bimolecular transition state of some kind, since ^{13}C n.m.r. spectra of these and other carbene complexes have shown that the carbene carbon atom in (Ia) has appreciably greater sp^2 character than that in (II).[8]

These results emphasise the differences which have been observed in the thermal decomposition and chemical reactions of compounds similar to (Ia) and (II). Thus the main product of the thermal decomposition of (Ib) is αα′-dimethoxystilbene (both *cis*- and *trans*-isomers)[9] whereas, in the case of [$(CO)_5CrC(NMe_2)Ph$] αα′-bisdimethylaminobibenzyl is formed and stabilised as the complex [*cis*-$(PhCH{\cdot}NMe_2)_2Cr(CO)_4$].[10] Also compound (Ib) reacts much more rapidly with organometallic hydrides of group IV (R_3MH; M = Si, Ge, or Sn, R = alkyl or aryl) to give the benzyl derivative [$R_3MCH(OMe)Ph$] than does the pyrrolidinylcarbene complex [$(CO)_5CrC(NC_4H_8)Ph$] to give [$R_3MCH(NC_4H_8)Ph$].[11]

EXPERIMENTAL

The ferrocenylcarbene complexes (Ia) and (II) were prepared as described earlier.[3] Dimethyl fumarate (IV) was prepared from fumaric acid. 1,1-Diphenylethylene (Light) (III) was used without further purification. Spectra (i.r., n.m.r., and mass) were measured as described earlier. All manipulations and preparations were carried out in an atmosphere of oxygen-free nitrogen. All solvents were dried and purified and then purged at reflux with nitrogen immediately before use.

[Ferrocenyl(methoxy)carbene]pentacarbonylchromium (Ia) *with Dimethyl Fumarate* (III).—The complex (Ia) (0·395 g, 0·95 mmol) and the diester (III) (2 g, 14 mmol) were heated in a Schlenk tube at 136 ± 2° for 0·75 h. Hexacarbonylchromium and excess of olefin, both of which sublimed on to the sides of the tube, were removed by heating in high vacuum (60° and 0·1 mmHg), leaving a brown oil. Chromatography of this oil on alumina (grade III; 15 × 2 cm column; benzene) gave one orange band, affording a brown oil. Crystallisation from hexane–ether (3 : 1 v/v) gave brown-orange crystals of *dimethyl* 3-*ferrocenyl*-3-*methoxycyclopropane*-1,2-*dicarboxylate* (Va) [0·175 g, 0·47 mmol; 50% based on (I)], m.p. 90—91° (Found: C, 58·1; H, 5·4; Fe, 15·1. $C_{18}H_{20}FeO_5$ requires C, 58·1; H, 5·4; Fe, 15·0%), δ ($CDCl_3$) 2·92 (2H, q, J_{AB} 7·5 Hz, CH), 3·58 (3H, s, CO_2Me), 3·63 (3H, s, CO_2Me), 3·78 (3H, s, OMe), 4·22 (5H, s, C_5H_5), and 4·19 (4H, m, C_5H_4) p.p.m., *m/e* 372 (91%, M^+), 341 (13), 313 (74), 307 (21), 298 (100), 213 (26), 185 (33), 133 (56), 129 (46), and 121 (102), $\nu_{max.}$ (CS_2, $CHCl_3$) 3095w, 3020w, 2985w, 2945w, 2830w, 1736vs, 1446m, 1340m, 1320s, 1272s, 1240m, 1220w, 1190m, 1165s, 1120m, 1105m, 1062m, 1035m, 1025m, 1000w, 930vw, 902w, 870w, 830wsh, 820m, 810wsh, 760w, and 690w cm^{-1}.

*[Ferrocenyl(pyrrolidin-*1*-yl)carbene]pentacarbonylchromium* (II) *with Dimethyl Fumarate*.—The complex (II) (0·42 g, 0·92 mmol) and the diester (III) (5·0 g, 35 mmol) were treated as in the previous experiment (1·5 h heating). Similar chromatographic separation of the black residue followed by repeated t.l.c. (silica 5%; benzene) gave, as a brown oil, *dimethyl* 5-*[ferrocenyl(pyrrolidin-*1*-yl)methyl]*-3,4-*bismethoxycarbonylhex*-2-*enedioate* (VI) (0·17 g, 0·30 mmol, 32%) (Found: C, 58·3; H, 6·0; Fe, 9·9; N, 2·8. $C_{27}H_{33}FeNO_8$ requires C, 58·4; H, 5·9; Fe, 10·1; N, 2·5%), δ ($CDCl_3$) 1·75 (4H, m, pyrrolidine β-CH_2), 2·50 (1H, dd, *J* 5·5 Hz, 5-H), 2·59 (1H, d, *J* 8·5 Hz, 4-H), 2·81 (1H, d, *J* 7·5 Hz, H_A), 3·14 (4H, m, pyrrolidine α-CH_2), 3·59 (6H, s, CO_2Me), 3·65 (6H, m, CO_2Me), 4·11 (5H, s, C_5H_5), 4·25 (4H, m, C_5H_4), and 5·88 (1H, s, 2-H) p.p.m., *m/e* 555 [100% (Found: 555·161. $C_{27}H_{33}FeNO_8$ requires 555·156)], 524 (48), 496 (20), 472 (11), 412 [20 (Found: 412·124. $C_{21}H_{26}FeNO_4$ requires 412·119)], 398 (26), 358 (45), 298 (52), 286 [18 (Found: 286·076. $C_{12}H_{14}O_8$ requires 286·069)], 269 (81), 198 (95), 185 (37), 144 (56), and 121 (142), $\nu_{max.}$ (CS_2,$CHCl_3$) 3095w, 3005w, 2995w, 2945s, 2920m, 2850m, 1740vs, 1650w, 1430w, 1337w, 1270m, 1180s, 1165s, 1125m, 1105m, 1045m, 1020m, 1002m, 835w, 820m, 795w, 720w, and 675m cm^{-1}.

*[Ferrocenyl(pyrrolidin-*1*-yl)carbene]pentacarbonylchromium* (II) *with Dimethyl Fumarate and Pyridine*.—The complex (II) (0·28 g, 0·61 mmol) and the diester (III) (2 g, 14 mmol) were refluxed in pyridine (4 ml) for 2·5 h. The colour of the solution gradually changed from red to brown. The pyridine and excess of olefin were removed by distillation (80° and 0·2 mmHg), leaving a dark brown oil. The benzene-soluble extracts of this oil were chromatographed on alumina (grade III; 15 × 2 cm column; benzene). A small amount of complex (II) [0·01 g, 0·024 mmol, 4% (identified by its i.r. spectrum and m.p.)] was followed by an orange band which gave a brown oil on removal of the solvent. This oil was identical (i.r. and n.m.r.) with the compound (VI) obtained in the thermal reaction (0·15 g, 0·27 mmol; 44%) (Found: C, 58·0; H, 6·2; N, 2·7. Calc. for $C_{27}H_{33}FeNO_8$: C, 58·4; H, 5·9; N, 2·5%).

*[Ferrocenyl(pyrrolidin-*1*-yl)carbene]pentacarbonylchromium* (II) *with* 1,1-*Diphenylethylene*.—The complex (II) (1·2 g, 2·6 mmol) and the olefin (IV) (3 g, 17 mmol) were placed in a Schlenk tube (25 × 4 cm). The system was rigorously deoxygenated. The reactants were stirred together in the absence of light for 3·5 h in an oil-bath maintained at 136 ± 2°. Hexacarbonylchromium (0·2 g, 0·9 mmol, 35%) sublimed on to the walls of the vessel. The products were isolated from the residual brown oil by chromatography (alumina grade III; 50 × 2 cm column).

Fraction A (*benzene*). T.l.c. [silica (5%); benzene–hexane (4 : 1 v/v)] showed that this fraction contained four compounds including unchanged (II) and excess (IV). It was therefore chromatographed once more (alumina grade III; 10 × 5 cm column; hexane) until the eluate showed no further u.v. absorption due to (IV). Olefin

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[8] J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1972, **2419**.

[9] E. O. Fischer, B. Heckl, K. H. Dötz, J. Müller, and H. Werner, *J. Organometallic Chem.*, 1969, **16**, P29.

[10] J. A. Connor and J. P. Lloyd, *J. Chem. Soc.* (*A*), 1970, 3237.

[11] J. A. Connor, P. D. Rose, and R. M. Turner, *J. Organometallic.*, in the press ; see also J. A. Connor and P. D. Rose, *J. Organometallic Chem.*, 1970, **24**, C.45.

(IV) (1·7 g, 9·4 mmol, corresponding to 57%) was thus recovered. The three components remaining were eluted as one band with benzene, giving a red-yellow oil. Washing with cold hexane (20 ml) resulted in the separation of unchanged complex (II) as an almost insoluble red solid (0·12 g, 10% recovery).

The hexane solution which now contained two components, showed metal carbonyl vibrations at 2053w and 1919s cm^{-1}. Evaporation *in vacuo* left an oil which, on treatment with methanol, gave a yellow powder. This was twice recrystallised from cold pentane to give brown crystals of 3-*ferrocenyl*-1,1,5,5-*tetraphenyl*-3-(*pyrrolidin*-1-*yl*)-*pent*-1-*ene* (VII) (0·1 g, 0·16 mmol, 7%), m.p. 152—153° (Found: C, 82·0; H, 6·7; Fe, 8·9; N, 2·1. $C_{43}H_{41}FeN$ requires C, 82·3; H, 6·5; Fe, 8·9; N, 2·2%), δ (CCl_4) 1·72 (4H, m, pyrrolidine β-CH_2), 2·86 (4H, m, pyrrolidine α-CH_2), 3·58 (2H, d, *J* 8 Hz, CH_2), 3·80 (4H, m, C_5H_4), 4·00 (5H, s, C_5H_5), 4·48 (1H, t, *J* 7·5 Hz, 5-H), 5·82 (1H, s, 2-H), and 7·20 (20H, m, Ph) p.p.m., *m/e* 627 [37% (Found: 627·262, $C_{43}H_{41}FeN$ requires 627·259)], 560 (2), 446 [100 (Found: 446·151, $C_{29}H_{28}FeN$ requires 446·156)], 378 (47), 314 (15), 249 (12), 212 (54), 181 (13), 178 (16), 167 (45), 152 (15), and 121 (28), $\nu_{max.}$ (CS_2,$CHCl_3$) 3095w, 3090w, 3060m, 3025m, 2985s, 2960s, 2950m, 2920w, 1600m, 1490m, 1448m, 1368w, 1125w, 1108s, 1058w, 1042w, 1032w, 1002m, 830w, 818m, 762m, 750m, 730w, and 652s cm^{-1}.

Fraction B (benzene–ether, 10 : 1 v/v) afforded a brown oil. Sublimation at 70° and 0·1 mmHg gave ferrocenecarbaldehyde [0·01 g, 0·05 mmol, 2% based on (II)], identical (m.p. and i.r.) with an authentic sample.[12] The residual brown oil was twice crystallised from hexane–ether (4 : 1 v/v) giving brown plates of 3,3-*diphenylpropionylferrocene* [0·1 g, 0·25 mmol, 10% based on (II)], m.p. 173—174°, identified by comparison (m.p., i.r., n.m.r., and mass spectra) with a sample prepared by independent synthesis. Addition of methanol to the column afforded a further fraction which gave a brown tarry material (*ca.* 0·1 g); it was not characterised.

Hydrogenation of the Olefin (VII).—Compound (VII) (0·035 g, 0·056 mmol) in methanol solution (15 ml) containing platinum oxide (5%) (Adams catalyst) was shaken with hydrogen at S.T.P. (uptake 1 mol. equiv. in 7·5 h). The yellow crystals deposited gave yellow prisms of 3-*ferrocenyl*-1,1,5,5-*tetraphenyl*-3-(*pyrrolidin*-1-*yl*)*pentane* (VIII) (0·02 g, 0·032 mmol, 57%), m.p. 174—175° (from ether–methanol) (Found: C, 81·9; H, 6·5; N, 2·3. $C_{43}H_{43}FeN$ requires C, 82·2; H, 6·8; N, 2·2%), δ (CCl_4) 1·64 (4H, m, pyrrolidine β-CH_2), 2·80 (4H, m, pyrrolidine α-CH_2), 3·62 (4H, d, *J* 7·8 Hz, CH_2), 3·76 (4H, m, C_5H_4), 3·96 (5H, s, C_5H_5), 4·40 (2H, t, *J* 7·0 Hz, CH), and 7·18 (20H, m, Ph) p.p.m., *m/e* 629 [18% (Found: 629·286, $C_{43}H_{43}FeN$ requires 629·274)], 448 [62 (Found: 448·177. $C_{29}H_{30}FeN$ requires 448·171)], 378 (100), 251 (23), and 181 (36), $\nu_{max.}$ (CS_2,$CHCl_3$) 3095w, 3090m, 3060m, 3025m, 2950m, 2920s, 2850m, 2820w, 1490m, 1445m, 1362w, 1230w, 1121w, 1104s, 1053w, 1040w, 1029m, 998m, 905w, 835w, 828m, 815m, 760w, 746m, 735m, and 700s cm^{-1}.

3,3-*Diphenylpropionylferrocene*.—The reaction of cinnamic acid with benzene in the presence of aluminium chloride gave 3,3-diphenylpropionic acid,[13] m.p. 153—154°, δ ($CDCl_3$) 3·05 (2H, d, *J* 8 Hz, CH_2), 4·50 (1H, t, *J* 8 Hz, CH), 7·16 (10H, s, Ph), and 10·75 (1H, s, CO_2H) p.p.m., M^+ 225. Chlorination of the acid gave 3,3-diphenylpropionyl chloride,[14] b.p. 123—124° at 0·5 mmHg, m.p. 52—53°, δ ($CDCl_3$) 3·52 (2H, d, *J* 8 Hz, CH_2), 4·53 (1H, t, *J* 8 Hz, CH), and 7·18 (10H, s, Ph) p.p.m. Treatment of this with ferrocene in the presence of aluminium chloride[15] gave 3,3-*diphenylpropionylferrocene* (46%), m.p. 174—175° (Found: C, 75·9; H, 5·5; Fe, 14·0. $C_{25}H_{22}FeO$ requires C, 76·1; H, 5·6; Fe, 14·2%), δ ($CDCl_3$) 3·42 (2H, d, *J* 7·0 Hz, CH_2), 3·94 (5H, s, C_5H_5), 4·44 (2H, t, ferrocene H-3 and H-4), 4·73 (2H, t, ferrocene H-2 and H-5), 4·85 (1H, t, *J* 7·5 Hz, CH), and 7·26 (10H, m, Ph) p.p.m., *m/e* 394 (100%, M^+), 199 (15), 167 (30), 165 (17), 129 (22), 121 (21), 56 (7), $\nu_{max.}$ ($CHCl_3$, CS_2) 3095w, 3080w, 3060m, 3025m, 1675vs, 1600m, 1492m, 1450s, 1410w, 1380m, 1265m, 1222m, 1110s, 1087w, 1070s, 1026m, 1002m, 895m, 835m,sh, 820s, 792w, 748m, 722m, and 700s cm^{-1}.

We thank Professor C. W. Rees and Drs. T. L. Gilchrist and G. R. Knox for comments and a referee who pointed out ref. 6*a* to us. We also thank the S.R.C. for a Studentship (to J. P. L.).

[2/1501 *Received, 27th June,* 1972]

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