

Organometallic Fulgides. Part 1. Synthesis and Photochemistry of Ferrocenyl Fulgides [Ferrocenylethylidene(isopropylidene)succinic Anhydrides]

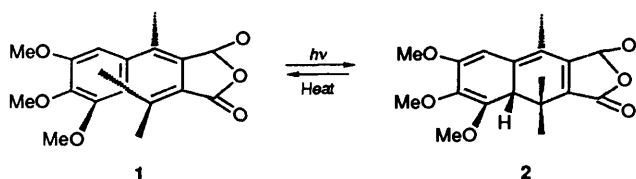
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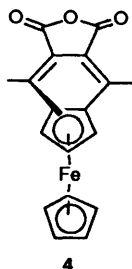
A series of novel ferrocenyl fulgides have been synthesised and their photochemistry examined. *Z/E* Isomerisation of the alkylidene double bond was observed in each case, without the accompanying photochromic ring-closure to the tricyclic dihydronaphthalene derivatives observed with organic fulgides. A π -Hückel MO treatment of a model cyclopentadienylbutadiene fragment was used to explain the lack of desired photochemical ring-closure.

(*E*)-Aralkylidene(alkylidene)succinic anhydrides (fulgides) **1** with electron-releasing substituents on the aryl ring undergo photochemically allowed 6π ring-closure to give highly coloured tricyclic dihydronaphthalene derivatives **2**.¹



Such organic photochromic reactions have not yet been emulated with organometallic systems. Indeed, to explore the possibilities of such novel organometallic systems we decided to synthesise a series of ferrocenyl fulgide derivatives and to examine their chemistry and photochemistry.

Owing to the ready availability of acetylferrocene **3** as a starting material, we began with the synthesis of (*E*)-1-ferrocenylethylidene(isopropylidene)succinic anhydride **4**.



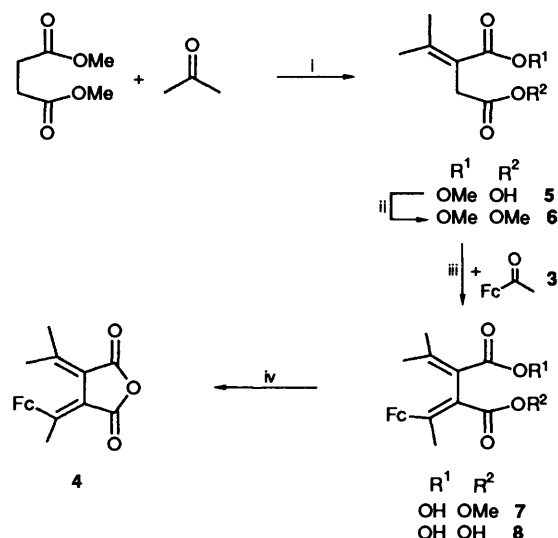
The syntheses of purely organic fulgides are carried out using successive Stobbe condensations between ketones or aldehydes and a succinate diester.¹

Touchard and Dabard² demonstrated that Stobbe condensations can be carried out using acetylferrocene, thus proving the stability of the ferrocene nucleus to the required reaction conditions.

The synthetic route outlined in Scheme 1 was used. The isopropylidene group was introduced first as it was easier to build up stocks of the intermediates.

Acetone was condensed with dimethyl succinate in the presence of potassium *tert*-butoxide using a hybrid of the methods of Johnson³ and Heller.¹

To carry out the second Stobbe condensation, with acetylferrocene, the half ester **5** has to be re-esterified. Initially, the standard Fischer-Speier method of esterification was employed.⁴ However, it was later discovered that these conditions



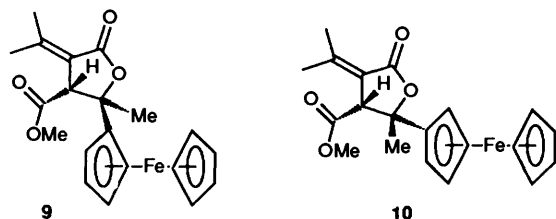
Scheme 1 Synthetic path to (*E*)-1-ferrocenylethylidene(isopropylidene)succinic anhydride. Reagents and conditions: i, Bu^tOK, Bu^tOH, reflux, 2 h; ii, MeOH, 5% (w/v) HCl, 20 °C, 24 h; iii, Bu^tOK, Bu^tOH, reflux, 30 min; iv, 5% (w/v) KOH_{aq}, reflux, 3 h; v, (CF₃CO)₂O, CH₂Cl₂, 0 °C, 1 h.

lead to the polymerisation of the half-ester intermediate.⁵ This problem was alleviated by conducting the reaction at room temperature over 24 h.

Condensation of acetylferrocene with the dimethyl isopropylidenesuccinate **6** yielded, after aqueous work-up, the half-ester **7** as a red oil. Half-ester products of this type are known to be inherently unstable by transesterification,² thus no attempt was made to purify the half-ester and the product was taken directly through to the fulgide **4** instead.

Work by Heller *et al.*⁶ has shown that in sterically hindered systems, the preferred isomer would be expected to have the *E*-configuration, probably due to repulsion between the arene ring and the anhydride carbonyl. The deep purple fulgide **4** was formed as a single isomer, in 37.5% overall yield. The highly shielded position of one of the methyl groups (δ 1.40 compared to δ 2.25 and 2.72 for the others) in the ¹H NMR spectrum of the product, is indicative of an isopropylidene methyl group sitting above the ferrocene ring and thus being shielded by its aromatic ring current. This effect, shown only by *E* fulgides,⁷ permits easy assignment of *E* stereochemistry to this first known example of an organometallic fulgide. It is noteworthy that no trace of the *Z* isomer was detected, which implies that under the highly basic standard reaction conditions, there must be some steric interaction within the five-

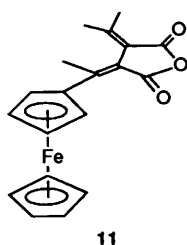
membered cyclic lactone intermediate of the Stobbe reaction, which decreases the amount of the *Z* isomer in the equilibrium mixture. Looking at the lactone intermediates for our compound below, we see that there are two possible conformations, in which the ferrocenyl moiety is either *cis* **9** to or *trans* **10** to the ring methine proton. The *cis* isomer **9** leads to the *E* isomer, whilst the *trans* isomer **10** leads to the *Z* isomer.



Models of these two isomers clearly show that in the *trans* case **10**, the intermediate is much more hindered than in the *cis* case **9**, with strong steric interactions, particularly between the lower ring of the ferrocenyl moiety and the methyl ester on the adjacent carbon. This is not so in the *cis* case **9** which will thus, be the favoured intermediate. Formation of a single isomer is in accord with earlier work by Touchard and Dabard on acetyl- and benzoyl-ferrocenes.²

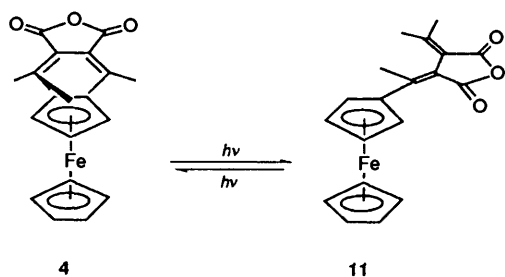
Photolysis of (*E*)-1-ferrocenylethylidene(isopropylidene)succinic anhydride **4** in [²H₆]benzene (Heller *et al.*¹ used toluene with organic fulgides) with a 125 W medium-pressure mercury vapour lamp through a Pyrex filter gave a photostationary state in 6.5 h. The product ratios (1:3) remained constant despite prolonged irradiation (> 125 h) and did not alter substantially even when a low-pressure lamp or a quartz filter were used.

Repetition of this photolysis on a larger scale enabled separation (silica gel chromatography) and identification of the photoproduct as (*Z*)-1-ferrocenylethylidene(isopropylidene)succinic anhydride **11**.



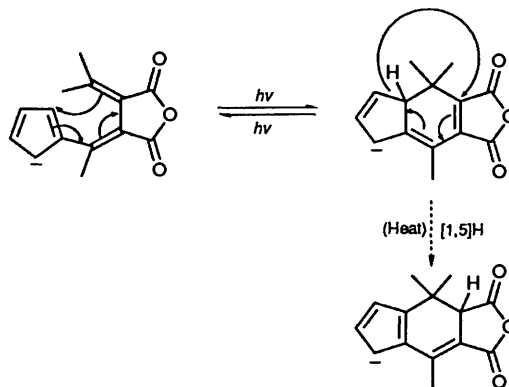
When the purified *Z* isomer **11** was photolysed in an NMR tube under the same conditions as the *E* isomer **4**, the ¹H NMR spectrum showed the same photostationary equilibrium state being attained. Thus, the photochemistry of the ferrocenylethylidene(isopropylidene)fulgides **4** and **11** may be defined as a simple *E/Z* isomerisation.

The *Z* isomer was found to have UV absorptions at slightly



longer wavelengths than the *E* isomer due to better conjugation in the almost planar *Z* configuration of the fulgide.

It had been hoped that the ferrocenyl fulgide **4** would have undergone a similar photochromic ring closure to that of Heller's fulgides^{8,9} as shown in Scheme 2 below. However,



Scheme 2 The expected ring-closure and possible [1,5] hydride shift of (*E*)-ferrocenylfulgides (N.B. For greater clarity, the metal and lower ring of the ferrocenyl unit have been omitted and a Kekulé type structure for the cyclopentadienyl-ring has been adopted.)

there was no evidence for the formation of ring-closed products, not even those re-aromatized by hydrogen migration.

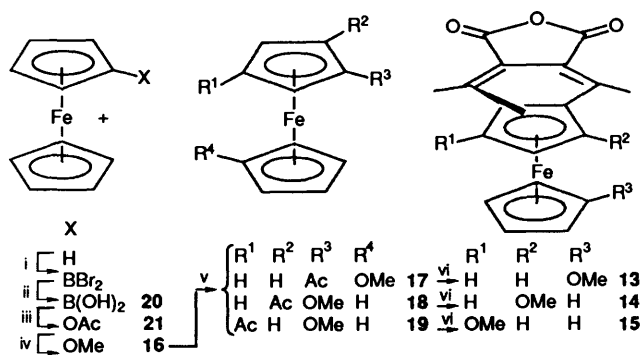
It was evident from the absence of photodecomposition that there had been no charge transfer to solvent (CTTS) transitions and since the olefinic units are not directly bonded to the metal, the *E/Z* isomerism is most likely to be the result of an intraligand charge transfer (ILCT) transition. Indeed, this type of *E/Z* isomerisation is found in the uncomplexed fulgides and the occurrence of such activity in the ferrocenylfulgides **4** and **11** shows that the presence of the metal atom does not completely corrupt the photochemistry of the organic ligand.

However, unlike the isomerisation, the electrocyclic ring-closure normally seen in simple organic fulgides appears not to occur in the case of the ferrocenylfulgide **4**. The questions that therefore arise are: (i) how has the iron atom prevented the ring-closure, and (ii) can this effect be circumvented?

The pericyclic reaction with the ferrocenylfulgide would not only involve loss of aromaticity, as with phenylfulgides,¹ but would also contravene the 18 electron rule.¹⁰ Since the presence of electron-releasing groups on the aromatic ring reduces the energy barrier to ring-closure with simple organic fulgides,^{8,9,11,12} it was wondered if a similar effect could occur, even temporarily, with the ferrocenylfulgides.

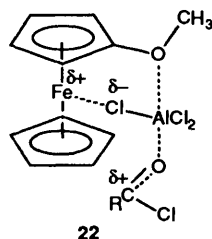
It was apparent from the literature (*e.g.* refs. 8, 9, 11 and 12) that the most suitable substituent was probably the methoxy group; therefore, the three 1-(methoxyferrocenyl)ethylidene(isopropylidene)succinic anhydrides **13–15** were synthesised from methoxyferrocene **16**.^{13,14} Acetylation of the methoxyferrocene **16** to give 1'-acetylmethoxyferrocene **17**, 2-acetylmethoxyferrocene **18** or 3-acetylmethoxyferrocene **19**,¹⁵ would be followed by elaboration to the desired fulgides **13–15** respectively, using the same route as for the original ferrocenylfulgide **4** (see Schemes 3 and 1).

While most workers seemed to have synthesised ferrocenylboronic acid **20** *via* lithiation,¹⁴ a careful search of the literature revealed that the apparently simpler route of Epton, Marr and Rodgers¹⁶ used a method (previously described in a German paper)¹⁷ in which the ferrocene was allowed to react directly with boron tribromide. It was discovered that, although not mentioned in the publication by Epton *et al.*;¹⁶ that the order of addition of the two reactants is crucial; the ferrocene must be added to the boron tribromide as a carbon disulfide solution, and not (more logically) *vice versa*, to achieve yields of > 30%.



Scheme 3 Synthetic route to the methoxyferrocenylfulgides 13–15. Reagents and conditions: i, BBr_3 , CS_2 , reflux, 24 h; ii, NaOH , 0°C ; iii, $\text{Cu}(\text{OAc})_2$, $\text{EtOH}-\text{H}_2\text{O}$ (3:2), 50°C , 60 min; iv, Me_2SO_4 , NaOH (50%), MeOH , reflux, 2 h; v, Et_2AlCl , MeCOCl , CH_2Cl_2 ; vi, several steps (as in Scheme 1).

The Friedel–Crafts acetylation of ferrocene proceeds smoothly.¹⁸ However, McVey, Morrison and Pauson's¹⁵ claim to the synthesis of 2- and 3-acetylmethoxyferrocenes 18 and 19, using aluminium chloride as catalyst was based solely on IR evidence and appears to be erroneous. We showed that aluminium chloride-catalysed Friedel–Crafts acetylation of methoxyferrocene 16 gave 1'-acetyl(methoxy)ferrocene 17 as the sole product, possibly due to the formation of an intermediate 22 which involves coordination of the Perrier complex to the methoxy group. This would have the effect of withdrawing electron density from the methoxycyclopentadienyl ring, and thus deactivating it. Uncomplexed aluminium chloride would have the same effect when co-ordinated to the methoxy group. Weaker Lewis acids such as zinc chloride and iron(III) chloride were found to be unable to promote any reaction at all. Eventually, the bulky Lewis acid diethylaluminium chloride (based on an adaptation of a literature method using ethylaluminium dichloride)¹⁹ was found to give a mixture of all three isomers 17–19.



The (*E*)-1-[1'-, (*E*)-1-(2- or (*E*)-1-(3-methoxyferrocenyl)ethylidene]isopropylidene succinic anhydrides 13–15 were obtained as purple, slightly unstable compounds each of which on photolysis in [$^2\text{H}_6$]benzene gave only the corresponding *Z*

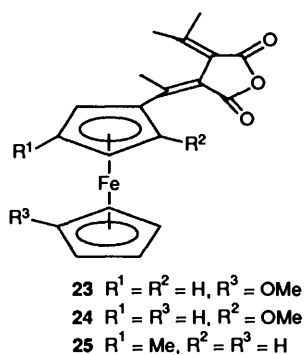


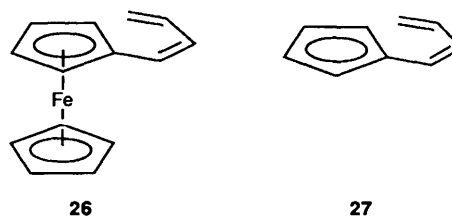
Table 1 Electronic absorption maxima data for ferrocenylfulgides

Fulgide	$\lambda_{\text{max}}/\text{nm}$
(<i>E</i>)-Ferrocenyl- 4	230, 336, 498
(<i>Z</i>)-Ferrocenyl- 11	235, 341, 516
(<i>E</i>)-1'-Methoxyferrocenyl- 13	238, 346, 510
(<i>Z</i>)-1'-Methoxyferrocenyl- 23	233, 342, 518
(<i>E</i>)-2-Methoxyferrocenyl- 14	236, 336, 502
(<i>E</i>)-3-Methoxyferrocenyl- 15	259, 351, 502

isomers 23–25; there was no evidence of ring-closure on prolonged irradiation. This was somewhat surprising as the methoxy group, depending on the substitution pattern of the ring (see Table 1), does have the desired electron-releasing effect on the chromophores of some of the molecules: this was shown by the bathochromic shift in their UV absorbances.

We have seen the photochemistry of all the ferrocene-based fulgides to be that of *E/Z* isomerisation. This naturally raised the question of why, even when bearing highly electron-donating substituents, none of these novel organometallic fulgides showed ring-closure analogues to that of the organic fulgides. In order to account for this difference, the approximate π -Hückel MO method²⁰ was employed.

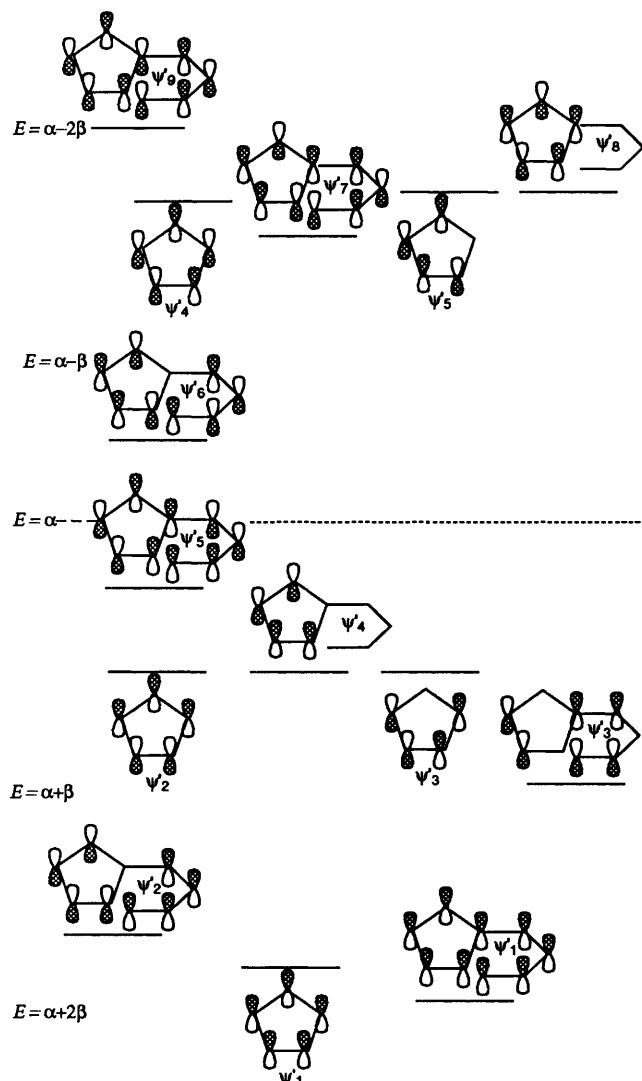
In the fulgide-type electrocyclic ring-closures, the part of the molecule involved in the pericyclic reaction can be regarded, in frontier orbital (FO) terms as a triene system. In order to assess whether or not the ring-closure is symmetry allowed (under Woodward–Hoffmann rules), the FO's of the ferrocenylfulgide must be examined which, in turn, leads to a requirement for a MO diagram of the fulgide. Quantum mechanical calculation of the full MO diagram of 4 is feasible but was regarded as too cumbersome, so a simpler system, ferrocenylbutadiene 26 was adopted as a realistic model of the fulgide 4. A π -Hückel calculation²⁰ for the cyclopentadienylbutadiene fragment 27 of



the molecule yielded a set of nine MO's. The five cyclopentadienyl ion MO's were also 'constructed' for comparative purposes. The energy level diagrams for these two fragments were then interleaved (Scheme 4) to show the relative energy ordering of the orbitals.

In order for an electrocyclic ring-closure to take place, an intra-ligand electronic event must occur. Placing the required 16 electrons (6 for cyclopentadienyl and 10 for cyclopentadienylbutadiene) into the diagram (Scheme 4), the LUMO is clearly ψ'_6 . However, an electronic transition into ψ'_6 from ψ'_5 (an ILCT) could not bring about ring-closure, since despite the apparently correct symmetry of ψ'_6 , it lacks the required lobe on carbon 1. This missing lobe prevents any electrocyclic processes from occurring, thus preventing the pericyclic ring-closure. It is also clear that, by the requirements of the Woodward–Hoffmann rules,²¹ none of the remaining orbitals (all of which lie above the $E = \alpha\text{-}\beta$ level) are of suitable symmetry for a photochemical ring-closure.

Some of the molecular orbitals (ψ'_4 , ψ'_8) have zero amplitudes for the lobes on carbon 1 because of the artificial reflection symmetry introduced by the severe approximations of the π -Hückel method. However, in the case of ψ'_6 (and also ψ'_2) the zero amplitude is associated with the accidental



Scheme 4 The relative energy ordering of the cyclopentadienyl and cyclopentadienylbutadiene MO's.

degeneracy of some of the π -Hückel energy levels of cyclopentadienyl and butadiene. The amplitude is not zero in calculations when a side-chain of different length, or when a benzene rather than a cyclopentadienyl ring, is employed.

The symmetry of the butadienyl portion of ψ'_6 , on the other hand, does allow for *E/Z* isomerisation. This would be brought about by an electronic transition to ψ'_6 from the ψ'_5 orbital.

It is pleasing to note that the quantitative MO calculations obtained for the cyclopentadienylbutadiene fragment and the conclusions to be drawn from them are consistent with the experimental observations.

Experimental

General.—All reactions involving the synthesis or use of metal complexes were carried out under nitrogen or argon unless otherwise stated. All reagents were freshly purchased and used without further refinement. Petroleum refers to the redistilled 60–80 °C boiling fraction, unless otherwise stated, and the hexane used was the hexane fraction of petroleum. All reaction solvents were dried over an appropriate desiccant, distilled and stored under nitrogen.

The ^1H NMR spectra were obtained on Perkin-Elmer R12 (60 MHz), Hitachi R1200 (60 MHz) and Bruker WM250 (250 MHz) spectrometers. The UV-VIS and FTIR spectra were recorded using Perkin-Elmer Lambda 3 and Mattson Polaris

Icon Spectrometers respectively. GC-Mass spectra were obtained on a Perkin-Elmer 8500 Gas Chromatograph with an ITD Ion Trap Detector. Microanalyses were carried out as a service by the University of Manchester. M.p.s were found using a Gallenkamp m.p. apparatus and are uncorrected. Hanovia 125 W medium and low-pressure mercury vapour immersion lamps were used (as specified) for the photolyses, in conjunction with a Spectrophysics microphotolysis apparatus for some NMR tube scale work.

Methyl Isopropylidenesuccinate 5.—A modification of the methods originally published by Heller¹ and Johnson³ was used. Acetone (29 g, 0.5 mol) and dimethyl succinate (91.34 g, 0.625 mol) in *tert*-butyl alcohol (75 cm³) were added to a stirred suspension of potassium *tert*-butoxide (62.79 g, 0.56 mol) in *tert*-butyl alcohol, the addition causing immediate development of a yellow colour. The mixture was heated under reflux for *ca.* 2 h and, after cooling, evaporation under reduced pressure gave a viscous oil. The resultant yellow-brown mass was then dissolved in an excess of aqueous sodium hydroxide (2 mol dm⁻³) and washed with diethyl ether until the extracts became colourless. The half-ester was then liberated by acidification with hydrochloric acid (6 mol dm⁻³) and extracted with dichloromethane (4 \times 150 cm³). The combined extracts were dried (Na₂SO₄) and the dichloromethane removed under reduced pressure to give the title compound **5** (61.63 g, 68.6%). Yields were in the range 60–80%; $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 60 \text{ MHz})$ 1.88 (3 H, s, isopropylidene CH₂ trans to C=O), 2.15 (3 H, s, isopropylidene CH₃ *cis* to C=O), 3.42 (2 H, s, CH₂), 3.72 (3 H, s, OCH₃) and 9.38 (1 H, s, CO₂H).

Dimethyl Isopropylidenesuccinate 6.—A chilled (<0 °C) solution of the ester **5** (5.4 g, 28 mmol) in anhydrous methanol (100 cm³) was treated with sufficient dry hydrogen chloride gas to give a 5% (w/w) hydrogen chloride solution. The reaction mixture was then stirred at room temperature for 24 h before removal of the excess of methanol under reduced pressure. The residue was poured onto an ice-water slurry and the ester was extracted with ether (4 \times 20 cm³). The combined ether extracts were washed with 10% aqueous sodium hydrogen carbonate and dried (Na₂SO₄). Some starting material (0.67 g, 13.6%) was recovered from the alkaline washings by acidification with hydrochloric acid (6 mol dm⁻³) and extraction with dichloromethane. Removal of the ether from the dried organic phase afforded the title compound (4.23 g, 90.5% based on starting material consumed). The crude product was purified by distillation (101 °C, 15 mmHg); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 60 \text{ MHz})$ 1.80 (3 H, s, isopropylidene CH₃ trans C=O), 2.80 (3 H, s, isopropylidene CH₃ *cis* to C=O), 3.33 (2 H, s, CH₂) and 3.65 (2 \times 3 H, s, 2 \times OCH₃).

1-Ferrocenylethylidene(isopropylidene)succinic Acid 8.—A *tert*-butyl alcohol (60 cm³) solution of acetylferrocene (5 g, 22 mmol) and dimethyl isopropylidenesuccinate **6** (5.21 g, 27 mmol) was added to a chilled (0–5 °C) stirred suspension of potassium *tert*-butoxide (12.77 g, 25 mmol) in *tert*-butyl alcohol at a rate sufficient to prevent solidification of the *tert*-butyl alcohol in the suspension. The solution immediately turned red and was heated under reflux for 15 min on completion of the addition. After cooling, the *tert*-butyl alcohol was removed under reduced pressure to give a dark oil residue, which was dissolved in an excess of aqueous sodium hydroxide (2 mol dm⁻³) and washed with ether until the washings were virtually colourless. The half-ester was liberated by acidification with hydrochloric acid (6 mol dm⁻³) and extracted with dichloromethane (5 \times 50 cm³ aliquots). The combined organic phases were dried (Na₂SO₄) and evaporated under reduced pressure to yield the half-ester **7** as a red oil. Owing to its propensity for

transesterification, the half ester **7** was immediately taken through to the diacid and subsequently to the anhydride at which stage purification is easiest. The red oil was thus dissolved in aqueous potassium hydroxide (5% w/v; 150 cm³) and heated under reflux for 3 h. After cooling, the solution was washed with ether (2 × 50 cm³), acidified, extracted, dried and evaporated under reduced pressure as before to give the crude title compound **8** (4.85 g, 60.1% based on acetylferrocene consumed). A small amount of the diacid was crystallised from dichloromethane–petroleum to give deep red microcrystals, m.p. 120 °C (decomp.) (Found: C, 61.9; H, 5.7. C₁₉H₂₀FeO₄ requires C, 61.98; H, 5.47%); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 250 \text{ MHz})$ 1.47 (3 H, s, isopropylidene CH₃ *trans* to C=O), 1.99 (3 H, s, isopropylidene CH₃ *cis* to C=O), 2.41 (3 H, s, ferrocenylethylidene CH₃), 4.14 (5 H, s, Cp ring protons), 4.31 (4 H, s, Cp ring protons) and 11.96 (2 H, s, 2 × CO₂H).

(*E*)-1-Ferrocenylethylidene(isopropylidene)succinic Anhydride **4**.—The crude diacid **8** (4.72 g, 13 mmol) was dissolved in dichloromethane (200 cm³) to give a dark orange–red solution which was cooled in an ice–salt–water slush. Upon addition of trifluoroacetic anhydride (2 cm³) dissolved in dichloromethane (20 cm³), the solution turned deep purple. After being stirred at room temperature for 3 h, the mixture was poured onto an ice–water slush. The product was extracted with ether until the extracts were colourless, and the combined organic phases were washed with 10% aqueous sodium hydrogen carbonate, again until the washings were colourless. The ether solution was dried (Na₂SO₄) and evaporated to dryness under reduced pressure to give a dark purple oil, which afforded the title compound **4** as deep purple crystals (2.87 g, 64%), m.p. 158–160 °C (Found: C, 65.5; H, 5.2. C₁₉H₁₈FeO₃ requires C, 65.17; H, 5.18%); $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 1803 and 1753 (acid anhydride), 1585 (C=C), 1231 (acid anhydride), 1132 (Cp ring deformation), 1003 (Cp CH in-plane bending) and 862 and 827 (Cp CH out-of-plane bending); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 230, 336 and 398 ($\log_{10}\epsilon$ 4.18, 4.08 and 3.38); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 250 \text{ MHz})$ 1.38 (3 H, s, isopropylidene CH₃ *trans* to C=O), 2.22 (3 H, s, isopropylidene CH₃ *cis* to C=O), 2.68 (3 H, s, ferrocenylethylidene CH₃), 4.18 (5 H, s, Cp'), 4.43 (2 H, t, Cp 3-H and 4-H) and 4.49 (2 H, t, Cp 2-H and 5-H).

Photolysis of the Anhydride **4**.—The fulgide **4** (250 mg) was dissolved in benzene (140 cm³) and the solution irradiated for 40 h using a medium-pressure Hg lamp and Pyrex filter. The solvent was removed under reduced pressure and the purple oil purified by chromatography on preparative TLC plates (Kieselgel 60 PF₂₅₄, 1 mm; petroleum–dichloromethane, 4:1). The (*E*)-ferrocenylfulgide **4** was recovered as the higher *R*_f band, whilst the darker purple, lower *R*_f band consisted of (*Z*)-1-ferrocenylethylideneisopropylidene succinic anhydride **11**, which yielded dark purple crystals at –20 °C from methanol–petroleum (b.p. 30–40 °C) plus a trace of water to induce crystallisation, m.p. 137–139 °C (Found: C, 65.1; H, 5.3. C₁₉H₁₈FeO₃ requires C, 65.17; H, 5.18%); $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2, \text{solution})/\text{cm}^{-1}$ 1422 (Cp C–C stretch), 1262 (C–O stretch); 1132 (weak, Cp' ring CH bend) and 896 (Cp ring CH bend); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 235, 341 and 516 ($\log_{10}\epsilon$ 3.92, 3.94 and 3.28); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 250 \text{ MHz})$ 2.04 (3 H, s, isopropylidene CH₃ *trans* to C=O), 2.23 (3 H, s, ferrocenylethylidene CH₃), 2.39 (3 H, s, isopropylidene CH₃ *cis* to C=O), 4.19 (5 H, s, Cp'), 4.58 (2 H, s, Cp ring 3-H and 4-H) and 4.87 (2 H, s, Cp ring 2-H and 5-H).

Similar results to the above were also obtained on photolysis with a low-pressure lamp and with quartz apparatus.

Ferrocenylboronic Acid **23**.—The boronic acid **23** was prepared using a modified version of the method of Epton, Marr

and Rodgers.¹⁶ The ferrocene (5 g, 27 mmol) must be added as a carbon disulfide solution (50 cm³) to a stirred solution of boron tribromide (10.27 g, 41 mmol) in carbon disulfide (50 cm³) in order to achieve yields > 30%. It is essential that the reactants be added in this order as the reverse order of addition seems to either inhibit formation of, or even destroy the product. In its pure form ferrocenylboronic acid **23** appears as golden flake-like crystals, m.p. > 50 °C (decomp.); $\delta_{\text{H}}([\text{C}^2\text{H}_6]\text{acetone}, 60 \text{ MHz})$ 4.17 (5 H, s, Cp'), (2 H, t, 3-H and 4-H Cp ring) 4.39, 4.52 (2 H, t, 2-H and 5-Cp ring) and 6.48 [2 H, s, B(OH)₂].

1'-Acetyl(methoxy)ferrocene **17**.—(This reaction was originally reported¹⁶ to produce a mixture of 2-acetyl- and 3-acetyl-methoxyferrocenes **18** and **19**).

Acetyl chloride (0.714 cm³, 0.01 mol) was stirred for 2 h (care being taken to exclude moisture) with an excess of freshly ground aluminium chloride (8 g) in dichloromethane (40 cm³). The insoluble aluminium chloride was then filtered off, and the resulting solution of the Perrier complex added over *ca.* 40 min to a stirred solution of methoxyferrocene (2 g, 9.26 mmol) in the same solvent (35 cm³) at 0 °C. After completion of the addition, stirring was maintained for a further 5–10 min, when the dark purple reaction mixture was poured (with vigorous stirring) onto an ice–water slush containing a few drops of titanium(III) chloride. The orange organic phase was separated and the aqueous phase extracted once with dichloromethane (20 cm³). The combined dichloromethane phases were dried (Na₂O₄) and evaporated under reduced pressure, and decomposition products were removed on a short column (Kieselgel 60; dichloromethane). The resultant red oil was further purified by chromatography on a preparative TLC plate [Kieselgel 60 PF₂₅₄, 1 mm; petroleum (b.p. 30–40 °C)–dichloromethane—the proportion of dichloromethane being progressively increased from 0 to 50%, and the plates being run several times to achieve good separation]. The first orange band was acetylferrocene (*ca.* 0.02 g). The next two major bands were ferrocene (0.07 g) and methoxyferrocene **16** (0.2 g). The 1'-acetyl(methoxy)ferrocene **17** formed the fourth major band (0.06 g, 2.5%); $\nu_{\text{max}}(\text{CCl}_4, \text{solution})/\text{cm}^{-1}$ 3099 (med., Cp CH stretch), 1668 (C=O), 1499, 1453 and 1428 (Cp C=C) and 1276 and 1061 (ester C–O); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 250 \text{ MHz})$ 2.25 (3 H, s, acetyl CH₃), 3.45 (3 H, s, OCH₃), 3.72 (2 H, t, 2'-H and 5'-H Cp' ring), 3.99 (2 H, t, 3'-H and 4'-H Cp' ring), 4.39 (2 H, t, 2-H and 5-H Cp ring) and 4.68 (2 H, t, 3-H and 4-H Cp ring). (*N.B.* The occurrence of two sets of triplets in the ¹H NMR spectrum proves that acetylation took place on the unsubstituted ring, a result that contrasts with that reported by the previous workers.)¹⁶

(*E*)-1'-Methoxyferrocenyl(ethylidene)isopropylidene succinic Acid.—Following a similar method to that used for acid **8**, 1'-acetyl(methoxy)ferrocene **17** (0.72 g, 2.79 mmol) was condensed with dimethyl isopropylidene succinate **6** (0.72 g, 2.79 mmol) in the presence of potassium *tert*-butoxide (0.35 g, 3.07 mmol). The reaction mixture was heated under reflux for 6 days, the reaction being monitored by TLC. During this time, following an initial lack of reaction, two further portions (0.5 g) of potassium *tert*-butoxide were added along with the ester **6** (0.5 g). The reaction mixture was worked up to give the half-ester as a red oil. This was dissolved in an excess of 5% aqueous potassium hydroxide and the solution heated under reflux for 3 h; it was then left at room temperature overnight (12 h). The basic solution was washed with ether and the diacid, liberated by acidification with hydrochloric acid (6 mol dm⁻³), was extracted with dichloromethane (50 cm³ aliquots) until the extracts were colourless. The organic extracts were combined, dried (Na₂SO₄) and evaporated under reduced pressure to afford the title compound as a dark red oil.

Since this was a diacid, it was taken straight through to the anhydride without further refinement, purification being more easily achieved at the latter stage.

(E)-1-(1'-Methoxyferrocenyl)ethylidene(isopropylidene)succinic Anhydride **13**.—The diacid from the previous stage was dissolved in dichloromethane (25 cm³) and the solution cooled (ice-salt bath). Trifluoroacetic anhydride (4 cm³, 30 mmol) in dichloromethane (10 cm³) was then added to it with stirring. After being stirred for 3 h at room temperature, the deep purple reaction solution was worked up (*cf.* ferrocenylethylideneisopropylidene fulgide **4**) to yield a dark purple oil, which was partially purified on a short column (Kieselgel 60; dichloromethane). The purified purple oil was then chromatographed on preparative TLC plates (Kieselgel 60 PF₂₅₄, 1 mm; petroleum (b.p. 30–40 °C)–dichloromethane—the proportion of the latter being increased from 0 to 70% over several elutions). The two bands present were so close in *R_f* that complete separation proved impossible. Approximately half of the lower *R_f* band could be cut from the plate, whilst the upper half was completely covered by the overlapping upper band which, although not identified, was later shown not to be the *Z* isomer, as the latter was of lower *R_f* than the *E* isomer.

The lower *R_f* band cut from the plate yielded a purple oil which, in turn, afforded the title compound **20** (22 mg, 2.1% based on acetylferrocene consumed) as purple needles at –20 °C from methanol–petroleum (b.p. 30–40 °C) plus a few drops of water to induce crystallisation, m.p. 86.5–88.5 °C; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 238, 346 and 510 ($\log_{10}\epsilon$ 4.04, 4.00 and 3.26); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 250 \text{ MHz})$ 1.22 (3 H, s, isopropylidene CH₃ *trans* to C=O), 2.24 (3 H, s, isopropylidene CH₃ *cis* to C=O), 2.71 (3 H, s, ethylidene CH₃), 3.56 (3 H, s, OCH₃), 3.87 (2 H, t, 2-H and 5-H Cp' ring), 4.13 (2 H, t, 3-H and 4-H Cp' ring) and 4.53 (4 H, s, Cp).

Photolysis of the Anhydride 13.—Because only very small quantities of this crystalline anhydride were obtained the photolysis was only carried out on an NMR tube scale. A [²H₆]benzene (0.4 cm³) solution of the fulgide **13** (12.8 mg) in a quartz NMR tube was irradiated with a medium-pressure lamp for 24 h, the ¹H NMR spectrum indicating attainment of a photostationary state at that time. The NMR solution was chromatographed on a preparative TLC plate [Kieselgel 60 PF₂₅₄, 1 mm; petroleum (b.p. 40–60 °C) followed by petroleum (b.p. 40–60 °C)–dichloromethane, 3:1, once the separation was well established] giving two bands that were cut from the plate and extracted with acetone (AnalaR). The higher *R_f* band was the unchanged *E* isomer, whilst the lower *R_f* purple band was found to be (*Z*)-1-(1'-methoxyferrocenyl)ethylideneisopropylidene succinic anhydride **23** (2.6 mg, 20%); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 233, 342 and 518; $\delta_{\text{H}}(\text{C}_6^2\text{H}_6, 250 \text{ MHz})$ 1.42 (3 H, s, isopropylidene CH₃ *trans* to C=O), 1.74 (3 H, s, ethylidene CH₃), 2.16 (3 H, s, isopropylidene CH₃ *cis* to C=O), 3.21 (3 H, s, OCH₃), 3.63 (2 H, t, 2'-H and 5'-H Cp' ring), 3.89 (2 H, t, 3'-H and 4'-H Cp' ring), 4.36 (2 H, t, 3-H and 4-H Cp ring) and (2 H, t, 2-H and 5-H Cp ring).

2- and 3-Acetylmethoxyferrocenes 18 and 19.—Diethylaluminium chloride (1.0 mol dm⁻³ in hexanes; 89 cm³) was added to a chloromethane solution (75 cm³) of acetyl chloride (31.8 cm³, 0.45 mol) with stirring at 0 °C, care being taken to exclude moisture. This acetylation mixture was added dropwise to a chilled (<0 °C) stirred solution of the methoxyferrocene **16** (19.24 g, 89 mmol) in dichloromethane (100 cm³) over 15 min, after which time the dark purple solution was left at room temperature for 2 h. The reaction mixture was then poured into an ice-water slush, containing a few drops of titanium(III)

chloride, with vigorous stirring. The organic layer, which returned to a dark orange colour, was separated, and the aqueous phase re-extracted with fresh dichloromethane (50 cm³). The combined organic extracts were dried (Na₂SO₄) and evaporated to dryness under reduced pressure. The unchanged methoxyferrocene **16** was removed on a short column (Sorbisil Colpack; dichloromethane) and the product mixture then separated on a flash column (Sorbisil Colpack; petroleum–diethyl ether, 3:1) into three orange bands. The second band consisted of 1'-acetyl(methoxy)ferrocene **17** (2.61 g, 11.34%), whilst the 2-acetyl(methoxy)ferrocene **18** was eluted as the first of the orange bands and the 3-acetyl(methoxy)ferrocene **19** as the third.

The 2-acetyl(methoxy)ferrocene **18** was obtained as orange needles (0.63 g, 2.74%) from petroleum–ether–dichloromethane at –20 °C, m.p. 75.1–76.1 °C (Found: C, 60.5; H, 5.45. C₁₃H₁₄FeO₂ requires C, 60.5; H, 5.47%); $\nu_{\max}(\text{C}^2\text{HCl}_3, \text{solution})/\text{cm}^{-1}$ 1658 (acetyl C=O), 1485, 1449 and 1420 (Cp C=C), 1236 and 1051 (ester C–O) and 825 (Cp CH out-of-plane bending); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 250 \text{ MHz})$ 2.49 (3 H, s, acetyl CH₃), 3.76 (3 H, s, OCH₃), 4.16 (1 H, t, 4-H Cp ring), 4.20 (5 H, s, Cp'), 4.34 (1 H, m, 3-H Cp ring) and 4.55 (1 H, m, 5-H Cp ring).

The 3-acetyl(methoxy)ferrocene **19** crystallised from petroleum–ether–dichloromethane at –20 °C (0.85 g, 3.70%), m.p. 55.9–56.9 °C (Found: C, 60.6; H, 5.5. C₁₃H₁₄FeO₂ requires C, 60.5; H, 5.47%); $\nu_{\max}(\text{C}^2\text{HCl}_3, \text{solution})/\text{cm}^{-1}$ 1658 (acetyl C=O), 1500, 1466 and 1418 (Cp C=C) 1216 and 1025 (ester C–O) and 825 (Cp CH out-of-plane bending); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 250 \text{ MHz})$ 2.32 (3 H, s, acetyl CH₃), 3.67 (3 H, s, OCH₃), 4.22 (5 H, s, Cp'), 4.47 (1 H, m, 4-H Cp), 4.52 (1 H, m, 2-H Cp ring) and 4.68 (1 H, t, 5-H Cp ring).

(E)-1-(3-Methoxyferrocenyl)ethylideneisopropylidene succinic Acid.—By the usual method, 3-acetyl(methoxy)ferrocene **19** (0.25 g, 0.969 mmol) and dimethyl isopropylidene succinate **6** (0.23 g, 1.21 mmol) were condensed in the presence of potassium *tert*-butoxide (0.122 g, 1.09 mmol). During the 6 h period of reflux, more isopropylidene succinate **6** (0.1 g) was added, along with extra potassium *tert*-butoxide (0.1 g). Work-up gave the half-ester as a red oil that was dissolved in 5% aqueous potassium hydroxide (40 cm³) and heated under reflux for 3 h. After storage overnight (12 h), the saponified mixture was washed with ether (50 cm³) acidified with hydrochloric acid (6 mol dm⁻³) and repeatedly extracted with dichloromethane (75 cm³ aliquots) until the washings became colourless. The combined organic phases were dried (Na₂SO₄) and evaporated under reduced pressure to give the diacid as a red oil. Since purification at this stage would have been wasteful (in terms of product) and time consuming, the diacid was taken straight through to the anhydride **15**, which is easier to purify.

(E)-1-(3-Methoxyferrocenyl)ethylidene(isopropylidene)succinic Anhydride **15**.—The diacid from the previous stage was dissolved in dichloromethane (25 cm³) and converted into the title anhydride in the usual manner using trifluoroacetic anhydride (1.5 cm³) in dichloromethane (5 cm³). After work-up, small amounts of impurity were removed on a short column (Sorbisil Colpack; petroleum–chloroform, 2:1). Recrystallisation from petroleum–dichloromethane gave the title compound **15** (0.16 g, 43.4%—based on acetylmethoxyferrocene **19** consumed) as a purple microcrystalline solid, m.p. 133–134.6 °C (Found: C, 62.1; H, 5.2. C₂₀H₂₀FeO₄ requires C, 63.18; H, 5.30%); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 259, 351 and 502 ($\log_{10}\epsilon$ 4.21, 4.11 and 3.46); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 250 \text{ MHz})$ 1.46 (3 H, s, isopropylidene CH₃ *trans* to C=O), 2.23 (3 H, s, isopropylidene CH₃ *cis* to C=O), 2.61 (3 H, s, ethylidene CH₃), 3.64 (3 H, s, OCH₃), 4.21 (5 H, s, Cp') and 4.39 (three overlapping 1 H, m, 2-H, 4-H and 5-H Cp ring).

Photolysis of (E)-1-(3-Methoxyferrocenyl)ethylidene(isopropylidene)succinic Anhydride 15.—The fulgide **15** (65 mg) was dissolved in [²H₆]benzene in an NMR tube to enable the reaction to be followed by ¹H NMR spectroscopy. The solution was irradiated using a medium-pressure Hg lamp, and a ¹H NMR spectrum was recorded every hour. After 9 h a small amount (*ca.* 10% by NMR integral) of the (*Z*)-1-(3-methoxyferrocenyl)ethylidene fulgide **25** was clearly present. No further change was noted on prolonged irradiation; $\delta_{\text{H}}(\text{C}_6^2\text{H}_6, 250 \text{ MHz})$ 1.33 (3 H, s, isopropylidene CH₃ *trans* to C=O), 2.1 (3 H, s, ethylidene CH₃), 3.25 (3 H, s, OCH₃), 3.98 (5 H, s, Cp' ring), and 4.25, 4.50 and 4.75 (2-H, 4-H and 5-H, 3 × m, Cp ring).

(E)-1-(2-Methoxyferrocenyl)ethylidene(isopropylidene)succinic Acid.—Following the standard procedure, the ferrocene **18** (0.25 g, 0.969 mmol) and the ester **6** (0.23 g, 1.21 mmol) were dissolved in *tert*-butyl alcohol (25 cm³) and condensed in the presence of potassium *tert*-butoxide (0.122 g, 1.09 mmol). During the 6 h of heating under reflux, a further quantity of potassium *tert*-butoxide (0.25 g, 2.2 mmol) was added. Work-up was carried out once the reaction mixture had cooled. The half-ester produced was dissolved in an excess of 5% aqueous potassium hydroxide, heated under reflux for 3 h and then left overnight (*ca.* 12 h) at room temperature. As before, the reaction mixture was washed with ether (50 cm³), acidified with hydrochloric acid (6 mol dm⁻³), extracted with dichloromethane (2 × 50 cm³), and the combined organic phases were dried (Na₂SO₄) and evaporated under reduced pressure to give the title diacid as a red oil. As before, the diacid was then taken straight through to the anhydride.

(E)-1-(2-Methoxyferrocenyl)ethylidene(isopropylidene)succinic Anhydride 14.—A dichloromethane solution (25 cm³) of the diacid from the previous stage was chilled in an ice-methanol slush and treated with trifluoroacetic anhydride (1.5 cm³) in dichloromethane (5 cm³). After 2 h at room temperature the solution was worked up by the standard method. The resultant purple oil was purified on a short column (Sorbisil Colpack; petroleum–chloroform, 2:1) and recrystallised from petroleum–dichloromethane at –20 °C to afford purple microcrystals of the title compound **14** [0.14 g, 38.0% based on the ferrocene **18** consumed], m.p. 132–133 °C (Found: C, 62.1; H, 5.3. C₂₀H₂₀FeO₄ requires C, 63.17; H, 5.3%); $\delta_{\text{H}}(\text{C}^2\text{HCl}_3, 250 \text{ MHz})$ 1.30 (3 H, s, isopropylidene CH₃ *trans* to C=O), 2.19 (3 H, s, isopropylidene CH₃ *cis* to C=O), 2.81 (3 H, s, ferrocenylethyl-

idene CH₃), 3.70 (3 H, s, CH₃O), 3.87 (1 H, m, 3-H Cp ring), 4.04 (1 H, m, 5-H Cp ring), 4.22 (5 H, s, Cp'), 4.31 (4-H, Cp ring).

Acknowledgements

The authors thank the British Technology Group for financial support of Stephen P. Saberi. One of us (D. E. P.) acknowledges a helpful conversation with Dr. J. M. Maud.

References

- H. G. Heller and M. Szweczyk, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1487.
- P. Touchard and R. Dabard, *Bull. Soc. Chim., Fr.*, 1975, **11–12**(2), 2567.
- W. S. Johnson, A. Goldman and W. P. Schneider, *J. Am. Chem. Soc.*, 1945, **67**, 1357.
- E. I. Vogel, *Textbook of Practical Organic Chemistry*, 5th edn., Longman Scientific and Technical, 1989.
- C. S. Marvel and T. H. Shepherd, *J. Org. Chem.*, 1959, **24**, 599.
- R. J. Hart and H. G. Heller, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1321.
- e.g.* H. G. Heller and R. E. Megitt, *J. Chem. Soc., Perkin Trans. 1*, 1974, 923.
- H. G. Heller, B.P. 1271655 (1972).
- H. G. Heller, B.P. 1442628 (1976).
- K. F. Purcell and J. C. Kotz, *Inorganic Chemistry*, Holt-Saunders, 1977.
- The Plessey Company PLC, Eur. Pat. Appl., 0239376 (1987); The Plessey Company PLC, B.P. Appl., 22082714 (1989).
- H. G. Heller, B.P., 1464603 (1977); The Plessey Company PLC, Eur. Pat. Appl., 0190016 (1968).
- D. W. Slocum, B. P. Koonsvitsky and C. R. Ernest, *J. Organomet. Chem.*, 1972, **38**, 125.
- A. N. Nesmeyanov, V. A. Sazanova and V. N. Drozd, *Chem. Ber.*, 1960, **93**, 2717.
- S. McVey, I. G. Morrison and P. L. Pauson, *J. Chem. Soc. C*, 1967, 1843.
- R. Epton, G. Marr and G. K. Rodgers, *J. Organomet. Chem.*, 1978, **150**, 93.
- W. Ruf, M. Fueller and W. Siebert, *J. Organomet. Chem.*, 1974, **64**, C45.
- G. E. Coates, *Organo-Metallic Chemistry*, 2nd edn., Methuen, 1960.
- J. C. D. Brand and W. Snedden, *Trans. Faraday Soc.*, 1957, **53**, 894.
- C. A. Coulson, B. O'Leary and R. B. Mallion, *Hückel Theory for Organic Chemists*, Academic Press, London, 1978.
- R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**(11), 781.

Paper 3/00245D

Received 14th January 1993

Accepted 21st January 1993