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CYCLOPHANES—XXV[1]

[2.2]INDENOPHANES—POTENTIAL BUILDING BLOCKS FOR OLIGOMERIC FERROCENOPHANES

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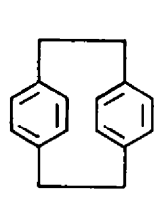
Abstract—The bis-formyl[2.2]paracyclophanes **21–24**, readily obtained by cycloaddition of propiolic aldehyde (**18**) to 1,2,4,5-hexatetraene (**17**), are converted to the indanonophanes **25–28** by Wittig–Horner chain elongation, hydrogenation, saponification and Friedel–Crafts ring closure. Whereas **25–27** may be reduced easily to the [2.2]indenophanes **29–31**, the *pseudo*-geminal diketone **28** affords ether **35** and monoketone **39** on lithium aluminium hydride reduction followed by dehydration. The mechanisms of these processes are discussed. The molecular structures of the mono-iron complexes **6** and **40**, prepared from the anion of **16**, have been determined by X-ray structural analysis.

For more than a century aromatic chemistry has dealt with planar molecular structures.[2] This is obvious for benzene and its countless condensed derivatives.[3] But it is also true for the majority of the non-benzenoid aromatic compounds.[2d,4] In fact, Hückel's rule which initiated the systematic search for these latter aromatics explicitly demands planarity as a prerequisite for "aromatic character".[5] For some time now, however, it has been obvious that aromatic compounds will tolerate considerable deviation from planarity without losing their aromaticity,[6] regardless of whether this is defined by the NMR or chemical reactivity criterion.[7] Modern aromatic chemistry, on the one hand, tries to "bend and batter"[8] benzene rings, and subsequently studies the chemical and physical consequences of this molecular deformation.[9] On the other hand, it uses aromatic units of any type and configuration to construct complex molecular frameworks characterized *inter alia* by π-electron interactions that extend over unusually long distances, molecular cavities, and other novel stereochemical properties. The result of both approaches are three-dimensional aromatic systems.

There exists presently no other group of compounds that illustrates these trends better than the cyclophanes.[10] In fact, the parent compound of the [*m.n*]cyclophanes, [2.2]paracyclophane (**1**) illustrates both alternatives nicely. Hydrocarbon **1** is a three-dimensional aromatic since not only are its *p*-xylylene subunits non-planar,[11] but the molecule as a whole essentially behaves as *one* π-electron system, as has been shown by photoelectron spectroscopy.[12]

Relatively early in cyclophane chemistry the question arose whether the layered structure of **1** could not be extended.[13] Although Longone and Chow prepared the first four-layered cyclophane **2**,[14] Misumi



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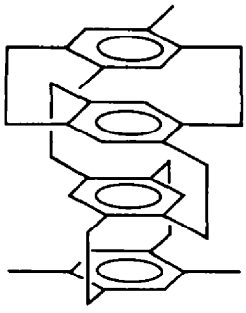

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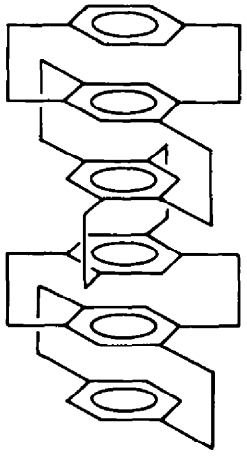

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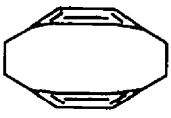

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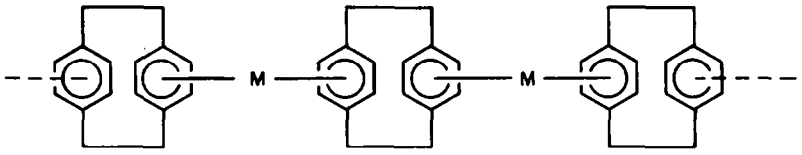
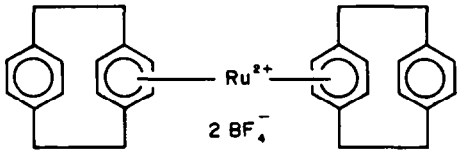
not only made available numerous of these stacked systems, but also studied their chemical and spectroscopic behaviour on a broad scale.[13] The most highly stacked structure Misumi and co-workers could prepare was the sextuple-layered hydrocarbon **3**.[15] Attempts to synthesize still more extended systems by the same preparative method (dimerization of *p*-xylylenes) have so far met with failure.[16] Since the strain energy of the non-substituted triple-layered [2.2]paracyclophane ($E_s = 245.6 \pm 9.8\,kJ\,mol^{-1}$) is already twice the value of **1** ($122.6 \pm 5.4\,kJ\,mol^{-1}$)[17] it appears that molecules like **3** constitute the "natural" upper limit for this particular stacking type.

However, bridging between [2.2]paracyclophane units may be accomplished by means other than ethano bridges. Metal atoms or ions, as well as molecular fragments containing these species, could in principle also serve the purpose of holding benzene rings in parallel and close alignment as illustrated by the general formula **4**.[18] In this manner an oligo- or even polymeric structure could be built up consisting of alternating organic and inorganic elements. If the π-electron delocalization present in the [2.2]paracyclophane subunits of **4** is transmitted by the connecting metal atoms a π-electron system extending over the whole macromolecular framework would result.



4 (M = connecting element containing a metal or metal ion)

How can this idea be transformed into chemical reality? Whereas Boekelheide and co-workers indeed used metal ions to bind [2.2]paracyclophane moieties together,[19] we prefer to employ the ferrocene unit as the connecting element.[20] The novel metallocenophanes **5**[19] and **6**,[20] which can be regarded as sections of the general macromolecule **4**, may serve as representative examples of the two approaches. For the preparation of **6** [2.2]benzoindenophane is required as a precursor, and we have recently described a general method providing this previously unknown cyclophane ligand.[20,21] Obviously, for the preparation of a polymer, the cyclophane has to possess at least two condensed 5-membered rings. These may be present in an *anti*- or *syn*-arrangement as shown by **7** and **8**, respectively (mixture of isomers, see below). Alternatively, the two 5-membered rings may be annellated to one benzene ring only, as shown in **9**. The related indenophanes **10** and **11** also constitute interesting ligands. It is conceivable that from these latter cyclophanes multi-iron complexes could be prepared that are structurally related to bis(*as*-indacenyliron) (**12**).[22] In this paper we present full experimental details[21] on a general synthesis for the ligand types **7** and **8** as well as the first X-ray structural investigations of two mono-iron ferrocenophanes.[23]



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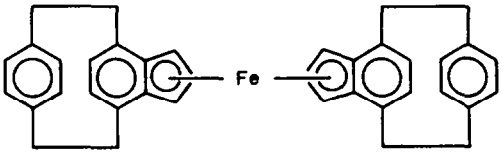

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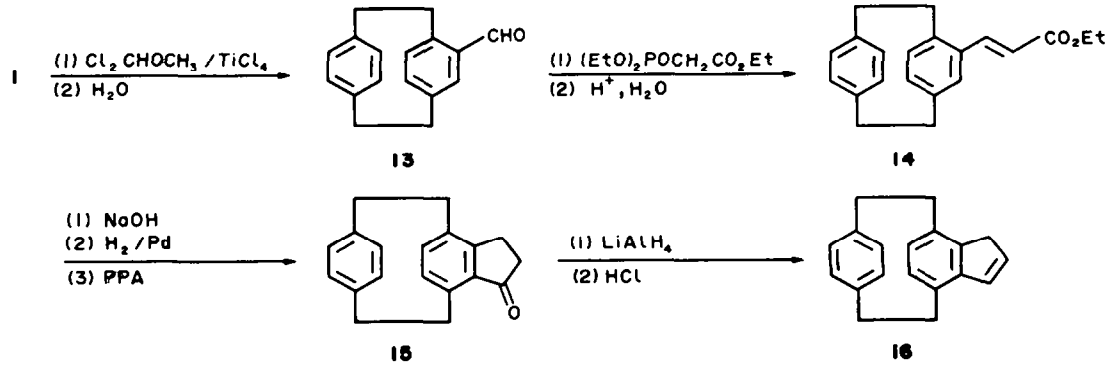
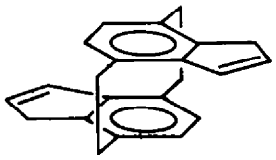
Synthesis

The general method for annellation of a 5-membered ring to the [2.2]paracyclophane system is illustrated in Scheme 1 for the parent hydrocarbon **1**.[20,21] Rieche *et al.*'s formylation[24] of **1** provides the monoaldehyde **13** which is chain-elongated by Wittig–Horner reaction with triethylphosphonoacetate to the *trans*-ester **14**. Saponification, hydrogenation, and Friedel–Crafts ring closure follow, and provide the indanonophane **15**



Scheme 1.



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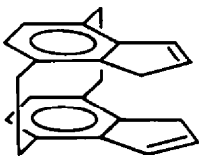

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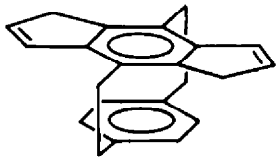

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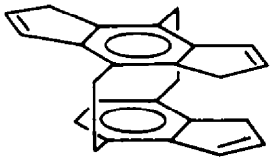

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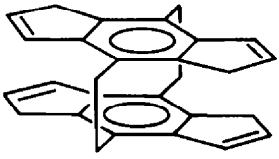

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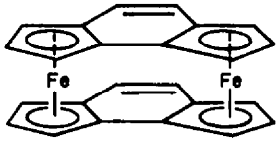

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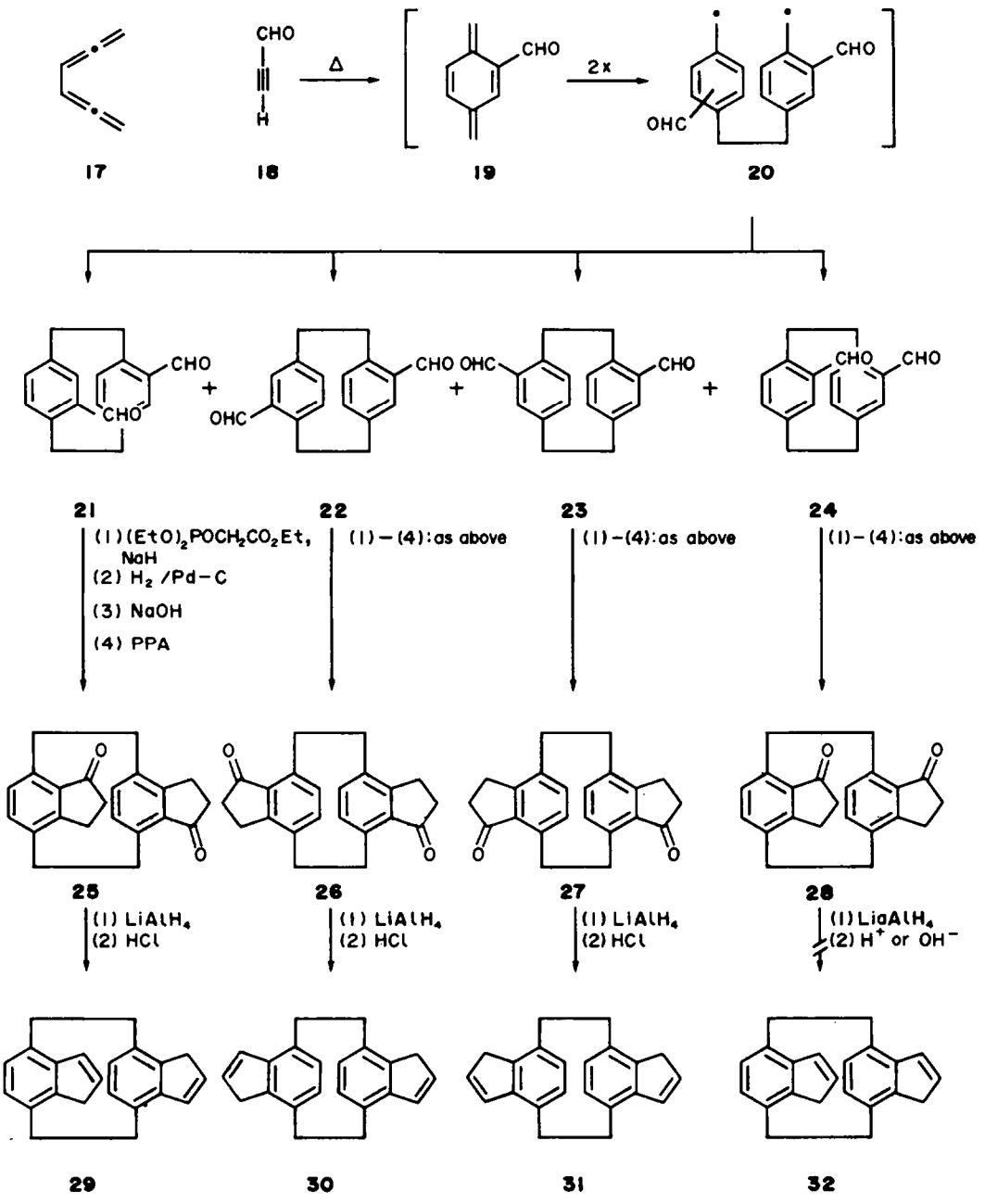
in multi-gram quantities. For the conversion of **15** to the benzoindenophane **16**, lithium aluminium hydride reduction followed by acidic work-up has been found to be the most satisfactory method.[21] Unfortunately, this simple approach cannot be employed to prepare precursors for the doubly-annellated ligands **7**–**9**: the formyl group in **13** deactivates the whole molecule to such an extent that a second formylation (in either ring) cannot be carried out in preparatively acceptable yields.

On the other hand, we described several years ago a general method for the preparation of multifunctionalized [2.2]paracyclophanes involving the addition of activated triple-bond dienophiles to 1,2,4,5-hexatetraene (**17**).[25] If this conjugated bisallene is reacted with propiolic aldehyde (**18**, benzene, 65°) the required dialdehydes **21**–**24** are indeed produced in satisfactory yield (46%, ratio 1:1.5:1.5:1). The most reasonable mechanism for this one-pot [2.2]paracyclophane synthesis is also shown in Scheme 2: Diels–Alder addition between **17** and **18** initially provides the cycloadduct **19** which subsequently dimerizes to the isomeric dialdehydes via diradical **20**.[26]

Although time-consuming, the four aldehydes may be separated by a combination of recrystallization and chromatography, **21** and **22** being the two most readily obtainable in pure form. When these two isomers are subjected to the four-step sequence described for the monoaldehyde **13**, the two ketones **25** and **26** are isolated. As above, lithium aluminium hydride reduction and acid-catalyzed dehydration leads to the indenophanes **29** and **30**, respectively.[21] One representative of either the *anti*- or *syn*-series, **7** or **8**, is hence available. Nevertheless, it seemed desirable to prepare the whole set of diketones **25**–**28** as well as the derived indenes **29**–**32**. Of course, during the anion formation required for complexation the isomeric purity within the two types of ligands will be lost.

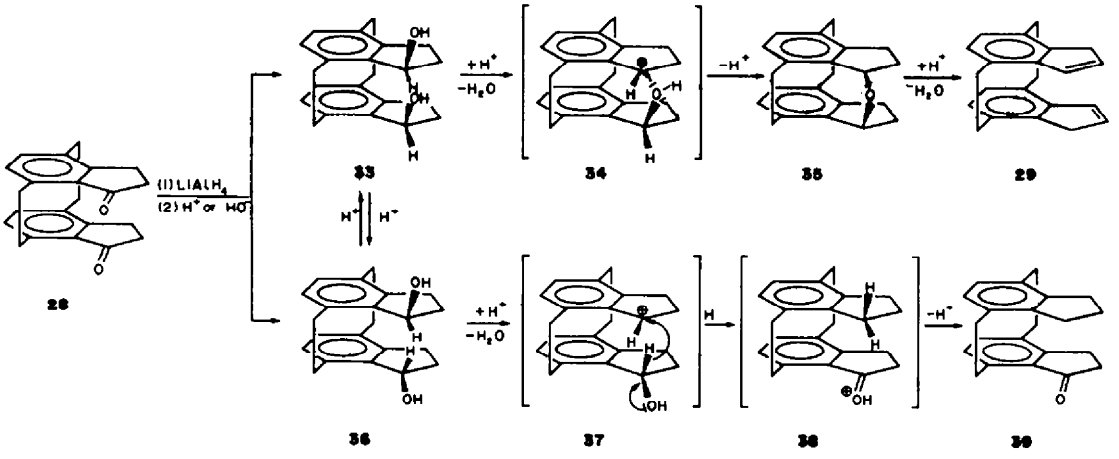
Rather than separating **23** from its accompanying **22** by repeated column chromatography (or even HPLC), we took a fraction enriched in these two isomers and prepared a mixture of the diketones **26** and **27** by the now routine four-step sequence. To our satisfaction simple column chromatography (methylene chloride, silica gel) at this relatively late stage provided both indanonophanes in analytically pure form. The origin of this clean separation most likely derives from pronounced polarity differences between the two isomers. For the rigid diketones **26** and **27** these should be larger than for any of their precursors. As expected, the reduction of **27** to **31** posed no difficulties. The same was true for the preparation of **28** from the so-called *pseudo*-geminal[27] dialdehyde **24** (Experimental). On the other hand, we have so far been unable to convert **28** to the *syn*-isomer **32**, with its face-to-face oriented double bonds. Depending on the work-up conditions (Experimental) the lithium aluminium hydride reduction of **28** leads to mixtures of **29** and the *mono*ketone **39** (Scheme 3). For example, if 4 N HCl is employed for hydrolysis the product mixture consists of **29** and **39** in a ratio of 1:3. When the acid strength is increased to 6 N only **39** is obtained. If, however, a basic hydrolysis is carried out (15% aqueous sodium hydroxide solution) two primary products, **33** and **36**, may be isolated with the former predominating (ratio 2.7:1). Careful interpretation of the ^{1}H- and ^{13}C-NMR spectra (including 2D-NMR spectroscopy)† allows the *exo,endo*-structure **33** to be assigned to the major, and

† We thank Doz. Dr L. Ernst (Gesellschaft für Biotechnologische Forschung, Braunschweig-Stöckheim) for these NMR spectra and their interpretation.



Scheme 2.

the *exo,exo*-configuration **36** to the minor isomer. An *endo,endo*-diol could not be detected among the reduction products; with both hydroxyl groups pointing towards the "interior" of the molecule it would presumably be a highly congested molecule. On standing in deuteriochloroform **33** is slowly converted to the bridged ether **35**. This, in turn, on treatment with dilute 2 N HCl is transformed to the *syn*-[2.2]indenophane **29**. An interpretation of these findings is presented in Scheme 3. The ether formation most likely involves the thermodynamically less stable *exo,endo*-alcohol. Protonation of its more accessible *exo*-OH group and subsequent loss of water leads to the cation **34** in which the *endo*-OH function is in perfect orientation for bridging (**34** → **35**). If, on the other hand, the *exo,exo*-diol **36** is protonated, cation **37** results. Its inwardly pointing hydrogen substituent undergoes a hydride shift providing the protonated ketone **38**. Deprotonation to **39** concludes the process. Since this product becomes the only one under strongly acidic conditions it must be concluded that an acid-catalyzed equilibration exists between **33** and **36** or intermediates derived therefrom favouring the (presumably) sterically less hindered *exo,exo*-series. For both ether formation (**33** → **35**) and disproportionation (**36** → **39**) there is ample precedent in the phane literature,[28] making the suggested reaction scheme even more reasonable. Unclear at present, however, is the formation of **29** from **35**. Conceivably, **32**, once formed, is unstable under the acidic conditions, and isomerizes to **29**. Molecular



Scheme 3.

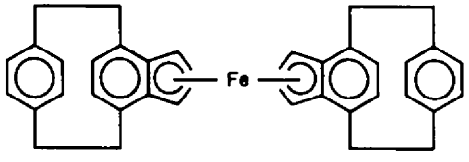
models indicate that steric interactions between the 5-membered rings in **29** are less pronounced than in **32**. To solve this interesting mechanistic phenomenon a reduction of **28** has to be devised avoiding rearrangement reactions at any stage.

X-Ray analysis

As mentioned above, the ferrocenophane **6** was the first representative of this novel group of metallocenophanes we could prepare.[20] In the meantime we have not only synthesized the mono-iron complex **40** for comparison,[21] but also obtained crystals of high enough quality of these two compounds (Experimental) to perform an X-ray structural investigation.

the distances between the cyclopentadienyl rings are 333 and 334 pm, respectively. Distinct deviations from the geometry observed in **1** arise from the formation of a condensed ring system. Whereas the bonds formed by the bridgehead atoms of the outer rings are very similar to the values found in **1**, corresponding parameters in the inner 6-membered rings are significantly different (in the direction of the cyclopentadienyl ring 143.0 and 142.6–143.4 respectively, in the other direction 135.6 and 134.9–135.7 pm).

The bond lengths between the non-bridgehead atoms 2–3 and 5–6 in the outer ring (136.5–137.3 pm in **40**, 137.5–138.1 pm in **6**) are also similar to the value found in **1** (138.7 pm), whereas distinctly longer bond



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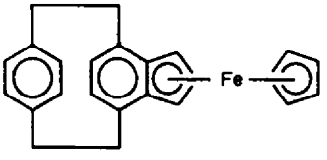

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Molecular structures of **6** *and* **40**

The typical distortion of standard bonding parameters which is normally found in [2.2]paracyclophanes[30] can also be observed in complexes **6** and **40**. As an example the aromatic rings are apparently not planar but show a boat-conformation instead, in which the bridgehead atoms 1 and 4 are about 15 pm off the plane.

In the bridge, the bond between the sp^3-carbon atoms (156.6 pm in **40**, 156.8–157.7 pm in **6**, cf. 159.3 pm in **1**)[11] is distinctly longer than the normal value of 154 pm. Despite this increase in bond length and a widening of the bond angles at the bridge atoms to 112.0–113.4° (C_{arom}—C_{sp}—C_{sp}) in both compounds very short non-bonding distances between the ring atoms of the 6-membered rings are found which are caused by the shortness of the bridge. The distance between the bridgehead atoms is only 274.1–276.9 pm, that between the other ring atoms is 300.4–309.8 pm (compared to 278 and 309 pm, respectively in **1**).[11] In comparison, the ideal packing distance of aromatic rings is near 340 pm; lengths are observed in the inner rings. This is especially obvious for the common bond between the 5- and 6-membered ring (144.2 pm in **40**, 143.4–143.9 pm in **6**), but is also true for the opposite bond (141.3, 140.9–141.2 pm).

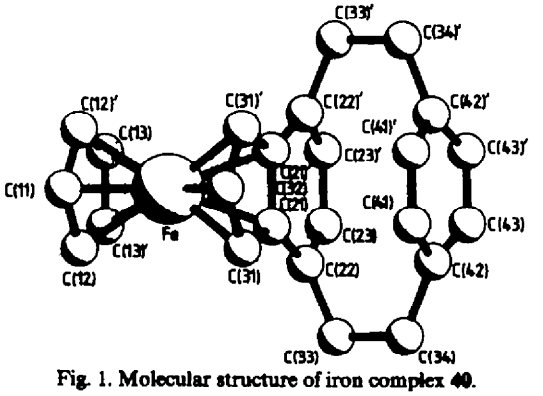

Fig. 1. Molecular structure of iron complex **40**.

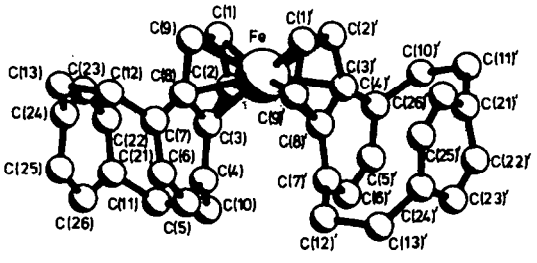

Fig. 2. Molecular structure of iron complex **6**.

In the ferrocene part of the molecule structural changes can be found which are caused by the cyclophane part; e.g. in both molecules the cyclopentadienyl rings are in an eclipsed position (mean torsion angle of the planes in: **40**, 0° (symmetry); **6**, 1.2°),[31] whereas they are staggered in unsubstituted ferrocene.[31] The substituents of the cyclopentadienyl rings in **6** are not directly opposed to each other but are rotated in such a way (73.2°; 360 : 5 = 72°) that non-equivalent carbon atoms are opposed (Fig. 2). This arrangement is certainly sterically more favourable. Any especially short non-bonding distances between the two ligand groups at the iron atom are not found in the present conformation.

In both compounds the position of the iron atom is not directly above the centre of the substituted cyclopentadienyl rings but is displaced away from the 6-membered rings. The mean bond distance between the iron and the carbon atoms in the substituted cyclopentadienyl rings is slightly longer (205.9 pm in **40**, 204.7 pm in **6**) than in the unsubstituted ring (203.9 pm in **40**); the comparable value in unsubstituted ferrocene is 205.8 pm.[32]

EXPERIMENTAL

General. NMR spectra ($CDCl_3$/int. TMS) were recorded on a Varian EM-360, Bruker WH 90, and Bruker WM 400 spectrometer, respectively; IR spectra on a Beckman Acculab 4 and a Beckman IR-4240 spectrometer; UV spectra on a Beckman 5230, and mass spectra on a MAT CH7 instrument. M.ps were taken on a Kofler apparatus and are uncorrected. For the X-ray work the data were collected at room temp on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo-K radiation (71.69 pm) in the $\theta-2\theta$ mode in the range $3° \leqslant 2\theta \leqslant 50°$ at a scan speed between 2.93 and 29.30° min^{-1} depending on the intensity of the reflection.

Preparation of **26** *and* **27** *from a mixture of* **22** *and* **23**

(a) *Preparation of dialdehydes* **21–24**. A 1 M soln of **17**[35] in 400 ml benzene and *ca* 400 ml ether is placed in a 2 l 3-necked flask equipped with a Vigreux column, distillation bridge, reflux condenser and dropping funnel. The temp is raised to 40°, and while the ether slowly begins to distill, an ethereal soln of 80 g (1.48 mol) propinal (**18**)[36] is added during 1 h. The temp is increased to 65°, and the mixture stirred at this temp overnight. The solvent is removed by rotatory evaporation and the oily residue extracted carefully with boiling MeOH. From the hot soln **22** begins to crystallize (7.8 g), and from the mother liquor 53.4 g of a mixture containing all four dialdehydes **21–24** is obtained (total yield 46%). Analytically pure samples of these compounds may be obtained by recrystallization–chromatography; their structural proof rests on chemical and spectroscopic evidence as will be reported elsewhere.[38]

(b) *Preparation of the saturated diacids.* 3.33 g (0.11 mol) NaH (from a paraffin suspension by washing with THF) is placed under N_2 in a 1 l 3-necked flask equipped with magnetic stirrer, reflux condenser, dropping funnel and septum, and covered with 90 ml abs THF. To the cooled (0°) suspension 13.32 g (0.06 mol) triethylphosphonoacetate is added with a syringe at such a rate that the H_2 evolution does not become too vigorous. After 15 min 7.4 g (0.028 mol) of a mixture of **22** and **23** in 370 ml THF is added within 30 min, and the mixture refluxed for 45 min. Hydrolysis (300 ml sat NH_4Cl aq), phase separation, and solvent removal provides 11.4 g (100%) of the isomeric *unsaturated esters* which may be used without further purification. Hydrogenation of a 13.35 g (0.034 mol) sample (5 g Pd/C, normal pressure, room temp, 20 h) furnishes 12.2 g (88%) of the isomeric *saturated diesters*. When these are refluxed in 50 ml EtOH and 550 ml 2 N NaOH for 16 h 10.4 g (98%) of the free *acids* are isolated.

(c) *Friedel–Crafts acylation to* **26** *and* **27**. In a 2 l 3-necked flask equipped with mechanical stirrer and reflux condenser 720 g P_2O_5 is carefully added at 0° under N_2 to 360 ml phosphoric acid (89%). After stirring at 110° for 3 h the mixture is homogeneous, and 10.4 g (0.029 mol) of the saturated diacids are added in small portions within 15 min. To complete the cyclization the mixture is stirred for 2 h at 100°. Hydrolysis with 2 l ice–water provides a light brown residue which is dissolved in 300 ml $CHCl_3$. The organic soln is carefully washed with water, sat $NaHCO_3$ aq, and dried over Na_2SO_4. The crystalline residue (6.95 g, 74%) obtained after solvent evaporation is separated by column chromatography on silica gel (CH_2Cl_2). Fraction 1: 1.2 g of **26**, colourless plates, m.p. 281°; IR (KBr): ν 2930 (w), 1692 (vs), 1565 (m), 1440 (w), 1245 (w), 1150 (m), 872 (m), 831 (m), 720 cm^{-1} (w); UV (EtOH): λ_{max} 335 (sh, ε 1200), 317 (3400), 261 (15,000), 220 nm (29,500); MS: *m/e* (%) 316 (41, M^+), 158 (100), 129 (54), 115 (44); ^{1}H-NMR: δ 6.59 (d, J = 7.5 Hz, 2H, Ar—H), 6.46 (d, J = 7.5 Hz, 2H, Ar—H), 4.25–4.10 (m, 2H, —CH_2—), 3.30–2.45 (m, 14H, —CH_2CH_2—); ^{13}C-NMR: δ 207.19 (s), 156.80 (s), 139.89 (s), 138.35 (s), 137.50 (s), 135.35 (d), 128.39 (d), 36.01 (t), 30.04 (t), 29.35 (t), 24.63 (t). (Found: C, 83.34; H, 6.51%. Calc: C, 83.52; H, 6.37%.) Fraction 2: 2.35 g of a mixture of **26** and **27**. Fraction 3: 3.4 g of **27**, colourless plates, m.p. 308°; IR (KBr): ν 3000 (w), 2935 (w), 1687 (vs), 1565 (m), 1486 (w), 1258 (m), 868 (m), 612 cm^{-1} (w); UV (EtOH): λ_{max} 334 (ε 1900), 276 (7100), 221 nm (30,300); MS: *m/e* (%) 316 (58), 158 (100), 129 (52), 115 (49); ^{1}H-NMR: δ 6.74 (d, J = 7.5 Hz, 2H, Ar—H), 6.34 (d, J = 7.5 Hz, 2H, Ar—H), 4.15–4.00 (m, 2H, —CH_2—), 3.7–2.2 (m, 14H, —CH_2CH_2—); ^{13}C-NMR: δ 206.90 (s), 156.50 (s), 141.11 (s), 138.34 (s), 136.49 (s), 138.34 (d), 136.49 (d), 35.91 (t), 30.01 (t), 29.80 (t), 24.81 (t). (Found: C, 83.39; H, 6.21%. Calc: C, 83.52; H, 6.37%.)

$LiAlH_4$ *Reduction of diketone* **27** *to* **31**. To a soln of 1.5 g (1.6 mmol) **27** in 110 ml abs THF is added under ice cooling and N_2 1.2 g (0.032 mol) $LiAlH_4$, and the mixture refluxed for 2 h. After cooling with an ice–salt bath excess hydride is carefully destroyed with a few ml of water, 145 ml 6 N HCl is added, followed by 40 ml $CHCl_3$. The dehydration mixture is stirred at room temp until the intermediate diols have disappeared completely (TLC control). The organic layer is separated, neutralized, and the solvent removed by rotatory evaporation. The residue is purified by chromatography on silica gel (CCl_4): 1.11 g (83%) **31**, colourless plates, m.p. 235° (dec.); IR (KBr): ν 3055 (w), 2930 (w), 2895 (m), 2830 (m), 2855 (s), 1475 (m), 1382 (s), 1140 (w), 1100 (m), 948 (m), 905 (s), 755 (s), 705 (s), 695 cm^{-1} (s); UV (EtOH): λ_{max} 277 (ε 4900), 265 (13,800), 257 (14,200), 230 (22,300), 221 nm (sh, 21,400); MS: *m/e* (%) 284 (90, M^+), 142 (100), 115 (59); ^{1}H-NMR: δ 6.80 (m, 2H, —CH=), 6.49 (m, 2H, —CH=), 6.15 (ps-s, 4H, Ar—H), 3.12 and 2.96 (m, 2 × 2H, —CH_2CH=), 3.30–2.70 (m, 8H, —CH_2CH_2—); ^{13}C-NMR: δ 146.32 (s), 144.11 (s), 134.26 (s), 131.89 (s), 132.60 (d), 132.04 (d), 126.77 (d), 125.59 (d), 39.13 (t), 31.79 (t), 30.91 (t). (Found: C, 92.87; H, 7.06%. Calc: C, 92.91; H, 7.09%.)

Preparation of diketone **28**

(a) *Wittig–Horner reaction of* **24**. To a suspension of 0.63 g (15.7 mmol) NaH in 100 ml THF, prepared as described above, is added with a syringe 2.53 g (13.1 mmol) triethylphosphono-

acetate at 0° under N_2. When the H_2 evolution has subsided (15 min) 1.4 g (5.3 mmol) **24** in 250 ml THF is added within 30 min. To complete the reaction, the mixture is refluxed for 1 h; 200 ml sat NH_4Cl aq is added, the organic layer separated, carefully washed with brine, and dried. The raw diester obtained after solvent removal (1.85 g, 86%) is pure enough for the subsequent step. For analytical purposes a sample is purified by column chromatography (aluminium oxide, toluene): colourless plates, m.p. 123°; IR (KBr): ν 2980 (w), 2930 (w), 1705 (s), 1630 (s), 1362 (m), 1310 (s), 1222 (m), 1175 (s), 1158 (s), 1032 (m), 972 cm^{-1} (m); UV (EtOH): λ_{max} 346 (sh, ε 3700), 322 (sh, 7400), 289 (35,400), 233 (sh, 18,100), 221 nm (26,300); MS: *m/e* (%) 404 (32, M^+), 201 (58), 157 (55), 129 (100); ^{1}H-NMR: δ 7.68 (d, J = 16.0 Hz, 2H, —CH=), 6.71 (ps-s, 2H, Ar—H), 6.54 (ps-s, 4H, Ar—H), 6.07 (d, J = 16.0 Hz, 2H, —CH=), 4.20 (q, J = 7.0 Hz, 4H, $—CH_2—$), 3.8–3.4 (m, 2H, $—CH_2—$), 3.3–2.9 (m, 2H, $—CH_2—$), 3.08 (ps-s, 4H, $—CH_2CH_2—$), 1.32 (t, J = 7.0 Hz, 6H, CH_3); ^{13}C-NMR: δ 166.69 (s), 141.84 (d), 139.90 (s), 139.82 (s), 134.75 (s), 135.14 (d), 134.61 (d), 130.67 (d), 118.60 (d), 60.24 (t), 34.95 (t), 32.76 (t), 14.29 (t). (Found: C, 77.29; H, 6.91%. Calc: C, 72.20; H, 6.98%.)

(b) *Hydrogenation of the* trans*-diester.* 13.7 g (0.034 mol) of the diester is dissolved in 300 ml EtOAc, and 5 g Pd (10% on C) is added. The hydrogenation is complete after 2 h at normal pressure and 30°. The catalyst is filtered off, and the solvent removed: 12.3 g (89%) of the *saturated diester*: colourless oil, b.p. 160° (10^{-3} Torr); IR (film): ν 2980 (m), 2935 (m), 2860 (w), 1735 (vs), 1595 (w), 1182 (m), 1040 cm^{-1} (w); UV (EtOH): λ_{max} 245 (ε 3600), 228 (18,100), 207 nm (11,400); MS: *m/e* (%) 408 (93, M^+), 362 (86), 317 (66), 204 (81), 160 (100), 131 (96), 115 (76); ^{1}H-NMR: δ 6.36 (ps-s, 4H, Ar—H), 6.18 (ps-s, 2H, Ar—H), 4.00 (q, J = 7.0 Hz, 4H, $—CH_2—$), 3.6–2.0 (m, 16H, $—CH_2CH_2—$), 1.11 (t, J = 7.0 Hz, 6H, CH_3). (Found: C, 76.37; H, 7.96%. Calc: C, 76.44; H, 7.90%.)

(c) *Saponification of the saturated diester.* 12.3 g (0.03 mol) of the diester is refluxed in 500 ml 2 N NaOH and 50 ml EtOH for 16 h. The hot soln is filtered and neutralized carefully with conc HCl. On cooling, the diacid (8.78 g, 83%) crystallizes, colourless needles, m.p. 191°; IR (KBr): ν 3700–2300 (m-s), 2925 (m), 1710 (s), 1590 (w), 1410 (w), 1205 (w), 885 cm^{-1} (w); UV (EtOH): λ_{max} 242 (sh, ε 3500), 226 (17,300), 212 nm (sh, 11,700); MS: *m/e* (%) 352 (76, M^+), 334 (75), 316 (54), 306 (61), 177 (100), 176 (99), 157 (72), 146 (80), 130 (83), 175 (71); ^{1}H-NMR: δ 10.8 (s, 2H, CO_2H), 6.8–6.1 (m, 6H, Ar—H), 3.5–2.3 (m, 16H, $—CH_2CH_2—$). (Found: C, 74.98; H, 6.86%. Calc: C, 74.99; H, 6.85%.)

(d) *Friedel–Crafts acylation to* **28**. Polyphosphoric acid is prepared from 600 g P_2O_5 and 300 ml phosphoric acid (89%) as described above. At 110° 8.5 g (0.024 mol) of the saturated diacid is added in small portions while the mixture slowly turns brown–red. After 3 h the temp is lowered to 70°, and the highly viscous soln poured into 1.5 l of ice–water. Stirring is continued until all the polyphosphoric acid has dissolved, and after an additional dilution with water (2 l), the fine ppt is collected on a Büchner funnel. The raw diketone is dissolved in $CHCl_3$ (300 ml), and the soln neutralized and washed thoroughly with water. The brown residue obtained after solvent evaporation is purified by column chromatography (silica gel, CH_2Cl_2–EtOAc, 10:1): 6.0 g (79%) **28**, colourless plates, m.p. 267–269° (dec); IR (KBr): ν 2925 (w), 2855 (w), 1700 (vs), 1685 (s), 1565 (m), 1482 (m), 1455 (m), 1265 (w), 1247 (m), 720 cm^{-1} (m); UV (EtOH): λ_{max} 317 (ε 3300), 261 (12,700), 219 nm (37,600); MS: *m/e* (%) 316 (80, M^+), 158 (100), 129 (72), 115 (78); ^{1}H-NMR: δ 6.70 (d, J = 7.5 Hz, 2H, Ar—H), 6.63 (d, J = 7.5 Hz, 2H, Ar—H), 4.5–4.2 (m, 2H), 3.5–3.1 (m, 4H) and 3.1–2.8 (m, 2H, ethano bridges), 3.2–2.3 (m, 8H, 5-membered ring); ^{13}C-NMR: δ 205.03 (s), 154.31 (s), 140.74 (s), 136.55 (s), 136.47 (s), 138.75 (d), 134.72 (d), 36.12 (t), 30.53 (t), 30.15 (t), 14.37 (t). (Found: C, 83.31; H, 6.34%. Calc: C, 83.52; H, 6.37%.)

$LiAlH_4$ *Reduction of diketone* **28**

(a) *Acidic work-up.* A soln of 1 g (3.3 mmol) **27** and 2 g (0.053 mol) $LiAlH_4$ in 120 ml abs THF is refluxed for 6 h, cooled to room temp, and, after destruction of excess hydride with 2 ml water, stirred for 15 min with 6 N HCl. Work-up and chromatography on aluminium oxide (toluene) provides 0.6 g (63%) of **39**, colourless plates, m.p. 227–228° (dec); IR (KBr): ν 2950 (w), 2850 (w), 1680 (vs), 1482 (w), 1450 (w), 1062 (m), 720 cm^{-1} (w); UV (EtOH): λ_{max} 325 (sh, ε 1700), 290 (3300), 244 (sh, 8400) 217 nm (27,200); MS: *m/e* (%) 302 (32, M^+), 158 (3), 144 (100), 129 (33); ^{1}H-NMR: δ 6.73 (d, J = 7.0 Hz, 1H, Ar—H), 6.54 (d, 1H, Ar—H), 6.45 and 6.43 (2d, J = 8.0 Hz, 2H, Ar—H), 4.4–4.2 (m, 1H, —CH—bridge), 3.4–2.3 (m, 15H, $—CH_2CH_2—$), 2.0–1.5 (m, 2H, central $—CH_2—$ of sat ring); ^{13}C-NMR: δ 207.57 (s), 154.67 (s), 144.53 (s), 140.24 (s), 136.57 (s), 136.09 (s), 135.21 (s), 139.14 (d), 134.71 (d), 132.47 (d), 131.40 (d), 36.50 (t), 32.40 (t), 31.99 (t), 31.84 (t), 31.69 (t), 30.18 (t), 29.26 (t), 24.50 (t), 23.38 (t). (Found: C, 85.89; H, 7.49%. Calc: C, 87.38; H, 7.33%.) When the same experiment is carried out with 4 N HCl a product mixture consisting of 23% **38** and 8% **28** is obtained.

(b) *Basic work-up.* To a soln of 0.5 g (1.6 mmol) **27** in 60 ml abs THF is added at 0° 1 g (0.026 mol) $LiAlH_4$, and the mixture is refluxed for 2 h. After excess hydride has been destroyed by the addition of 1 ml water, 1 ml 15% NaOH aq is added followed by another 3 ml portion of water. The white ppt is removed by filtration and carefully washed with THF. The combined organic layers are dried (Na_2SO_4), the solvent is evaporated, and the residue (0.47 g, 92%) chromatographed on silica gel ($CHCl_3$–EtOH, 98:2): 0.13 g **36** (colourless plates, m.p. 238–240°) and 0.34 g **33**. The latter diol was always contaminated by varying amounts of the ether **35** (see below). *Spectral data of* **36**: IR (KBr): ν 3220 (s), 3000 (w), 2915 (s), 2850 (s), 1480 (m), 1432 (m), 1295 (m), 1240 (m), 1152 (m), 1072 (s), 1048 (s), 1025 (m), 965 (m), 905 cm^{-1} (w); UV (EtOH): λ_{max} 293 (ε 800), 248 (sh, 4700), 232 (17,600), 212 nm (13,000); ^{1}H-NMR: δ 6.55 (ps-s, 4H, Ar—H), 5.05 (ps-t, 2H, —CH—O), 3.8–2.0 (m, 16H, $—CH_2CH_2—$), 3.05 (s, 2H, OH); ^{13}C-NMR: δ 141.57 (s), 139.29 (s), 137.27 (s), 135.49 (s), 134.27 (d), 134.00 (d), 77.05 (d), 35.32 (t), 31.87 (t), 31.53 (t), 28.43 (t). ^{1}H-NMR spectrum of **33**: δ 6.61 (d, J = 7.5 Hz, 1H, Ar—H), 5.56 (d, J = 7.5 Hz, 1H, Ar—H), 6.50 (d, 1H, Ar—H), 6.43 (d, 1H, Ar—H), 5.77 (ps-t, 1H, —CH—O), 5.15 (ps-t, 1H, —CH—O), 3.70–1.50 (m, 18H, $—CH_2CH_2—$ and OH).

Formation of ether **35** *from* **33**. A soln of 30 mg (0.09 mmol) **33** in 0.4 ml $CDCl_3$ is kept for 24 h at room temp: quantitative conversion to **35** (NMR analysis). Solvent removal provides 25 mg (92%) **35**, m.p. > 190° (dec); IR (KBr): ν 3025 (w), 2930 (s), 2900 (s), 2850 (m), 1480 (s), 1038 (s), 1020 (m), 978 (m), 940 (m), 900 cm^{-1} (m); UV (EtOH): λ_{max} 277 (sh, ε 800), 248 (sh, 3100), 232 (20,100), 210 nm (950); MS: *m/e* (%) 302 (86, M^+), 284 (100), 269 (69), 159 (46), 142 (98), 129 (78), 117 (67); ^{1}H-NMR: δ 6.41 (d, J = 7.5 Hz, 2H, Ar—H), 6.35 (d, 2H, Ar—H), 5.69 (ps.d, J = 8.0 Hz, 2H, —CH—O), 3.6–2.1 (m, 16H, $—CH_2CH_2—$); ^{13}C-NMR: δ 145.08 (s), 138.53 (s), 138.08 (s), 136.31 (s), 134.57 (d), 132.88 (d), 82.28 (d), 32.53 (t), 31.86 (t), 31.79 (t), 31.57 (t); high resolution MS: found 302.1671 ± 2 ppm, calc 302.16706.

Dehydration of **35** to **29**. 55 mg (0.182 mmol) **35** in 7 ml $CHCl_3$ and 10 ml 3 N HCl is stirred for 5 h at room temp. The organic layer is washed thoroughly with water, dried over $MgSO_4$, and the solvent removed by rotatory evaporation. Chromatography on silica gel (CH_2Cl_2) affords 10 mg (19%) **29**, identified by spectral comparison with an authentic sample.[21]

X-Ray analysis. Crystals of **40**, obtained by high vacuum sublimation at 10^{-3} Torr and 150°, have orthorhombic symmetry, space group *Pnma*. The unit cell, which has the parameters a = 2333.72(10), b = 943.03(6), c = 766.60(4) pm, contains four molecules yielding a calculated density of 1.355 g cm^{-3}. The data were corrected for Lorentz, polarization, and absorption effects (μ = 0.881 mm^{-1}). The structure was solved by Patterson and difference Fourier syntheses. The refinement using 1333 out of 1574 measured independent reflections ($I \geq 1.25\ \sigma(I)$) converged at R = 0.039 (R_w = 0.038). The hydrogen atom positions were refined together with isotropic temp factors. A final difference map displayed no electron density higher than 0.39 e $Å^{-3}$.

Crystals of **6**, obtained by recrystallization from

cyclohexane, have orthorhombic symmetry, space group *Pbca*. The unit cell which has the parameters $a = 1293.44(5)$, $b = 2134.88(9)$, $c = 1952.48(6)$ pm, contains eight molecules yielding a calculated density of 1.346 g cm^{-3}. The data collection, data reduction (μ for MoK$_\alpha$ 0.564 mm^{-1}) and structure solution were performed as described above for **40**. The refinement using 3462 out of 4764 measured independent reflections ($I \geq 1.25\ \sigma\ (I)$) converged at $R = 0.054$ ($R_w = 0.045$). The hydrogen atom positions were refined together with isotropic temperature factors. A final difference map displayed no electron density higher than 0.32 e Å^{-3}. The program SHELX-76[35] and our own programs were used. Complex atom scattering factors[36] were employed.

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