A New Method for the Selective Bridge Functionalization of [2.2]Paracyclophanediene – Indenyl-Annelated [2.2]Paracyclophanedienes and Their Iron Complexes☆

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[2.2]Paracyclophane-1,9-diene (**1**) is readily deprotonated at its vinylic positions with BuLi to give the monolithium derivative **2** and – in the presence of TMEDA – even the 1,9-/1,10-dilithium derivatives 1,9-/1,10-**6**. Reaction of **2** with a variety of electrophiles including benzaldehyde and ethyl formate led to bridge-substituted derivatives **3a–d** (71–89% yields) and **4**, **5** (95 and 91%, respectively). Electrophilic substitution of 1,9-/1,10-**6** with benzaldehyde gave the bis(vinylbenzyl) alcohols 1,9-/1,10-**8** in 39% yield. The vinylbenzyl alcohols **5** and 1,9-/1,10-**8** underwent cyclization upon treatment with zinc(II) chloride in 1,2-dichloroethane to give the indene-annelated [2.2]paracyclophane **9** (72%) and the bis(indene)-annelated compounds *syn*-**11** and *anti*-**11** (39%, ratio 19:1). Both **9** and *syn*-**11**, when treated with $FeCl_2$•$(THF)_2$ after deprotonation with methyllithium in the presence of excess lithium cyclopentadienide gave mixed-ligand ferrocene-type complexes **12** (63%) and *syn*-/*anti*-**16** (46%). The bis(indeno[2.2]paracyclophane-9-ene) complex **13** was obtained from deprotonated **9** in 61% yield and characterized by an X-ray crystal structure analysis.

Introduction

Ever since its first preparation by Farthing et al.[1a] and its popularization by Cram et al.[1b] the [2.2]paracyclophane system has attracted considerable attention especially because of its highly bent benzene rings and its unusually distorted π-electron system[2][3]. The π electrons of the two decks in [2.2]paracyclophane penetrate each other and essentially form a single π-electron system[4]. One may therefore consider [2.2]paracyclophane as a benzene which is extended into the third dimension. The influence of a further extension of the π-electron system along the pronounced molecular axis has been studied especially by Misumi et al.[5] on multilayered paracyclophane hydrocarbons, by Staab et al.[6] on multilayered paracyclophane-derived quinhydrones and by Hopf et al.[7] on multilayered metal complexes of [2.2]paracyclophane derivatives with five-membered rings annelated to the benzene decks. Yet another dimension has been accessed with derivatives of [2.2]paracyclophane-1,9-diene (**1**)[8], in which benzene rings are annelated onto the bridges of the skeleton[9][10]. In this respect, investigations of the radical anions generated from 1:2,9:10-dibenzo[2.2]paracyclophane-1,9-dienes have proven that the two sides of the system can communicate with each other through the orthogonally arranged phane system[11].

We were seeking a deeper insight into the nature and the extent of such electronic interactions through the skeleton with an investigation of multilayered metal complexes derived from [2.2]paracyclophane derivatives with five-membered rings annelated onto the bridges[12]. When exploring various strategies for the construction of bridge-functionalized and bridge-annelated systems[9][10][11][12], we have tested the possiblities of electrophilic substitutions on carbanion equivalents.

The regioselective deprotonation on the bridges of tricarbonylchromium complexes of [2.2]paracyclophane-1,9-diene, which has previously been described by us[13], does in principle open up an access to bridge-substituted derivatives of **1**, yet the overall yields are moderate because of the necessary complexation and decomplexation steps, making this method less attractive for the production of preparatively useful amounts of such compounds. We here describe the direct deprotonation of the hydrocarbon **1**, which is easily prepared in multigram quantities[8b], as a convenient and versatile method to electrophilically introduce functional groups into the bridges of the [2.2]paracyclophane-1,9-diene skeleton.

[+] X-ray crystal structure analyses.

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Electrophilic Substitution at the Bridges of 1

The treatment of [2.2]paracyclophane-1,9-diene (**1**) with 1.5 equivalents of *n*-butyllithium in tetrahydrofuran between −5 and 0°C cleanly led to the anion **2**, which was characterized by its trapping with various electrophiles (see Scheme 1 and Table 1). The ease with which the diene **1** can be deprotonated to **2** indicates a stabilizing influence of the neighboring phane arene on a negatively charged vinylic center. This stabilization ought to be due to the −I effect of the orthogonally arranged arene exerted on the vinylic bridge as well as the partial overlap of the occupied sp^2 orbital on C-1 with the arene π system (see Scheme 1).

To obtain more information about the electronic interaction between the lithiated vinylic center in the bridge and the adjacent phenyl group of the aromatic phane system in **2**, the deprotonation of **1** was effected with solid methyllithium in [D_6]tetrahydrofuran. The ^{1}H-NMR spectrum of the resulting solution of **2** discloses a significant influence of the lithiated center on both phenyl rings. Their protons are significantly more shielded than before deprotonation and their ^{1}H-NMR signals were observed as AB systems at δ = 6.01 (4 H) and 6.21 (4 H). In contrast, the NMR spectrum of **1** shows a single signal for the eight phenyl protons at δ = 6.46. The upfield shift of more than 0.4 ppm for the phenyl proton signals of the ring next to the lithiated center is an indication of the decreasing effective magnetic moment caused by an increasing electron density by a partial charge transfer. In addition, a higher electron density in the phane-arene moiety causes a higher degree of deformation and loss of aromatic character resulting in an upfield shift of the ^{1}H-NMR signals. An interaction between the doubly occupied sp^2 orbital of the lithiated center and the attached phenyl ring is also indicated by the ^{13}C-NMR spectrum of **2**. The ^{13}C signal of the deprotonated carbon atom appears slightly broadened at δ = 123.6. In general, a downfield shift for the ^{13}C signals of negatively charged vinylic carbon atoms compared to those in the corresponding hydrocarbon is expected[14]. However, in **2** the signal for the deprotonated carbon atom is shifted to higher field by 14.3 ppm. This can only be rationalized by assuming a charge transfer into the adjacent phenyl ring which causes a decrease in σ-electron density and therefore an increase of the π-electron density on this carbon atom[15]. Treatment of the NMR sample of the lithiated species **2** with D_2O gave exclusively 1-deuterio[2.2]paracyclophanediene (**3a**) as proven by its ^{1}H-NMR and mass spectrum.

With other electrophiles such as chlorotrimethylsilane, iodine and dimethylformamide, the monosubstitution products **3b**−**d** were obtained in good to very good yields (71−89%). Benzaldehyde reacted with **2** to give α-([2.2]paracyclophane-1,9-dien-1-yl)benzyl alcohol (**4**) (95%), and with ethyl formate bis([2.2]paracyclophane-1,9-dien-1-yl)-methanol (**5**) (89%) was obtained.

In the first round, attempted twofold deprotonation with an excess base and/or longer reaction times was not successful. But after addition of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA)[16], the dilithium derivative **6** could be generated and trapped with chlorotrimethylsilane as well as benzaldehyde to give the products 1,9-/1,10-**7** (34%) and 1,9-/1,10-**8** (39% yield), respectively; the ^{1}H-NMR spectrum of the mixture after independent synthesis of both authentic isomers[8b] proved the ratio to be 64:36. Apparently, the 1,9-dilithium derivative is formed preferentially, and its slightly higher stability must be due to the slightly smaller Coulomb repulsion in 1,9-**6**. In contrast, the deprotonation/silylation of the tricarbonylchromium complex of **1** yields 1,9-/1,10-**7** in a ratio of 38:62 with a preference for the 1,10 isomer.

Scheme 1. Deprotonation of [2.2]paracyclophanediene **1** and trapping of the resulting lithiated species with electrophiles (for conditions see Table 1)

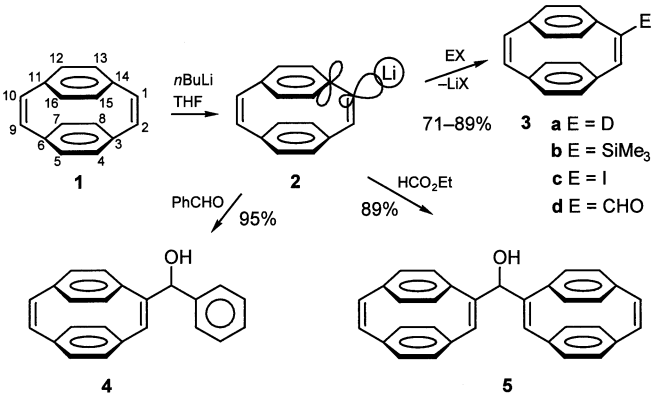
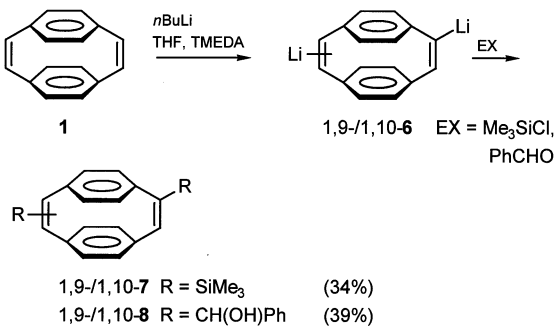


Table 1. Reactions of 1-lithio[2.2]paracyclophane-1,9-diene (**2**) with various electrophiles (see Scheme 1)

Electrophile	Conditions Temp./Time	Product	Yield [%]
$ClSiMe_3$	−78→20°C	**3b**	89
I_2	−78→20°C	**3c**	71
Me_2NCHO	−78→0°C	**3d**	71
PhCHO	−78→20°C/15 min	**4**	95
HCO_2Et	0°C/15 min	**5**	89

Scheme 2



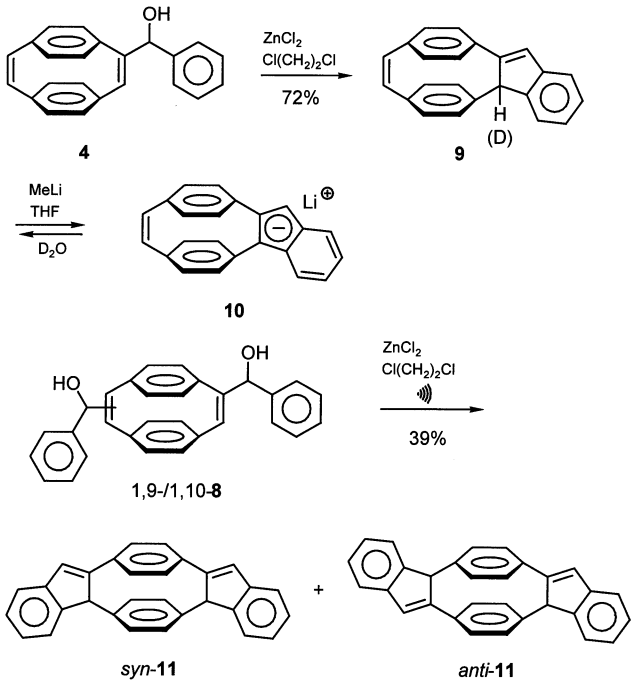
This difference corroborates the previously made suggestion that the tricarbonylchromium group by its electron-withdrawing effect stabilizes more efficiently the immediately adjacent carbanionic centers[13].

Five-Membered Ring Annelation and Formation of Iron Complexes

In order to achieve five-membered ring annelation, the mono(α-hydroxybenzyl)-substituted **4** and the bis(α-hydroxybenzyl) derivatives 1,9-/1,10-**8** were treated with the weak Lewis acid zinc chloride. Compound **4** thus gave in a relatively clean reaction the indenyl-annelated [2.2]paracyclophane-9-ene **9** in up to 72% yield. This strikingly simple procedure applied to the twofold ring closure in 1,10-**8** and 1,9-**8** led to a mixture of *syn*-**11** and *anti*-**11** (ratio 19:1), in 39% yield. The vast predominance of the *syn* isomer *syn*-**11** probably has to do with the poor solubility of *anti*-**11**, due to which most of latter was lost during the work-up procedure.

According to MNDO[17] calculations, the skeletal geometries of the isomers *syn*-**11** and *anti*-**11** should be detectably different, in that only the *anti* isomer *anti*-**11** should have an undistorted [2.2]paracyclophane skeleton, while that of the *syn* isomer *syn*-**11** should be slightly twisted due to its two sp^2-hybridized bridgehead carbon atoms being 1,10-positioned. This is expressed in a slightly lower heat of formation [ΔH_f(*syn*-**11**) = 183.2 versus ΔH_f(*anti*-**11**) = 185.3 kcal/mol].

Scheme 3



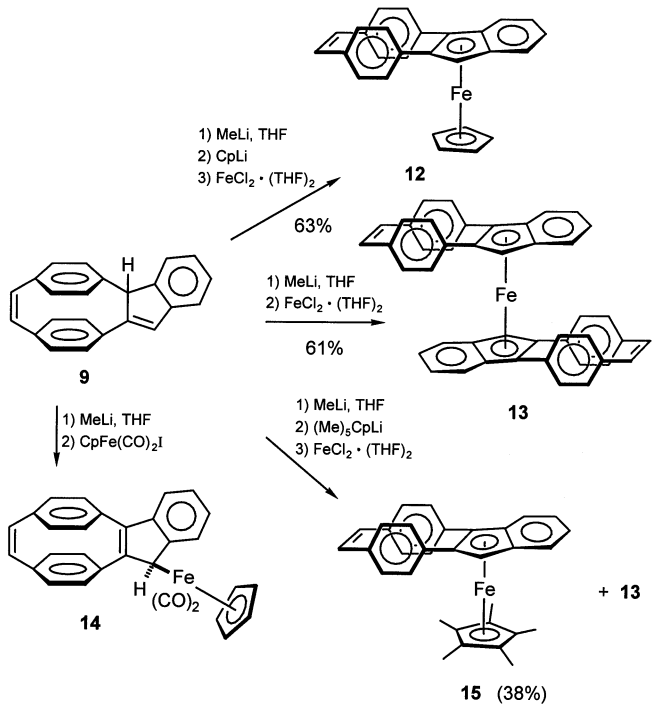
In order to probe the feasibility of the mono- and bis(indenyl)-annelated [2.2]paracyclophanes **9** and *syn*-/*anti*-**11**, respectively, as ligands in transition-metal complexes, the ease of their deprotonation was tested first. Treatment of **9** with methyllithium in [D_8]THF led to a deep red solution, in which the anion **10** could be detected by NMR spectroscopy.

Trapping of the anion **10** in the presence of an excess of lithium cyclopentadienide with iron(II) chloride−tetrahydrofuran complex [$FeCl_2$·$(THF)_2$], led to the mixed-ligand ferrocene-type complex **12** as an air-stable pink solid in 63% yield. The analogous transformation in the presence of lithium pentamethylcyclopentadienide surprisingly yielded a mixture of the bisindenyl complex **13** and the mixed ligand complex **15** from which the latter could be isolated by crystallization as a red-violet solid (38%). Apparently, **15** with its sterically demanding pentamethylcyclopentadiene ligand is formed far less easily than **12**, so that **10** in spite of a ten-fold excess of pentamethylcyclopentadienide can compete successfully. In contrast to **12**, complex **15** is far more sensitive towards oxygen in spite of the better shielding of the metal center.

Upon treatment of only **10** with $FeCl_2$·$(THF)_2$, the bisbenzoferrocene[18] resembling complex **13** was obtained in 61% yield. The latter is a green solid, less air-stable than **12**, yet in crystalline form can be handled in air. The facile formation of **13** documents the relatively good ligand properties of **10** in spite of its reasonably high steric demand.

In their ^{1}H- and ^{13}C-NMR spectra, all these ferrocene-type complexes with indene-annelated [2.2]paracyclophane ligands show typical coordination shifts of the signals, but also influences due to the anisotropies of the respective opposite ligands.

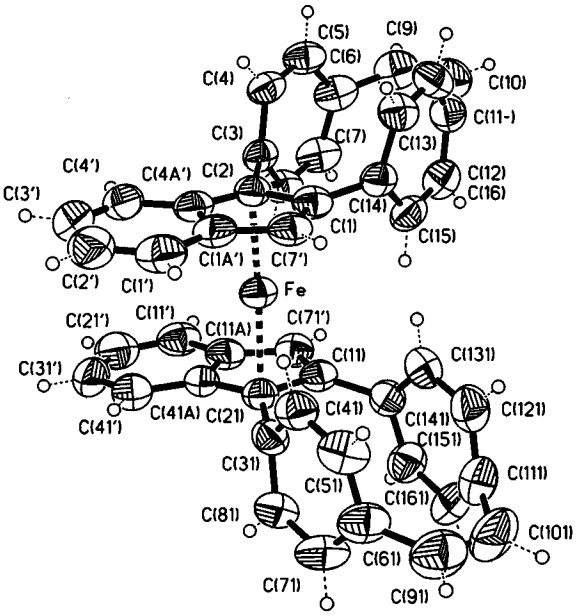
Scheme 4



The X-ray crystal structure analysis of **13** (Figure 1) shows the two [2.2]paracyclophane moieties of the ligands at a dihedral angle (with respect to the Cp−Fe−Cp axis) of almost 90° with respect to each other which enforces a partial overlap of the phenyl rings of the annelated indene systems. As a result of this overlap the planes of the five- and six-membered rings are slightly bent towards each other with an interplanar angle of 4°. The mean distance

between the coordinated carbon atoms and the iron center is comparable to that in ferrocene (209 pm)[19]. The repulsion between the centers of high electron density, namely the aromatic [2.2]paracyclophane system and the metal-ligand coordination sphere causes a bending of the annelated phane moieties by 12° out of the expected sp^2 planarity away from the complexed iron center. Except for a slight elongation of the annelated-bridge C−C bond to 146 pm, the overall geometries of the paracyclophane units in **13** are almost unchanged compared to that in **1**[20].

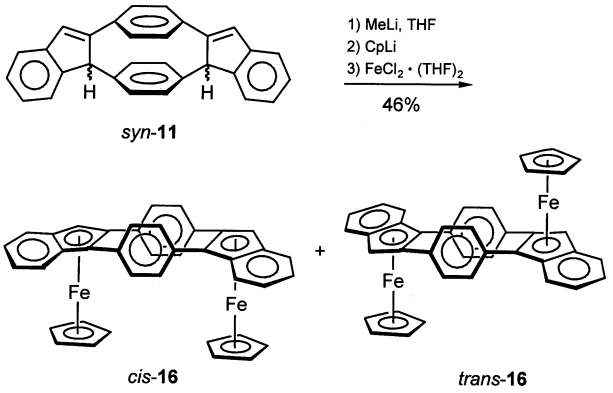
Figure 1. Structure of complex **13** in the crystal[21]



The η^5 coordination of the ligand **10** as realized in complexes **12**, **13**, **15** is not the only type observed. When a solution of **10** was treated with dicarbonylcyclopentadienyliron iodide [$CpFe(CO)_2I$], an extremely air-sensitive, bright yellow solid was obtained. On the basis of its IR, ^{1}H-NMR and MS data this complex contained an η^1-coordinated ligand **10** as in structure **14**. The EI mass spectrum showed a parent peak at *m/z* 582 which corresponds to a dimer of the ligand, and a second dominant peak at *m/z* 291 corresponding to the free ligand **10**. Apparently, the η^1 complex **14** is rather labile and therefore decomposes in the hot inlet of the mass spectrometer, the occurrence of the intense peak at 582 indicates that one may actually use this thermal decomposition of **14** to prepare a dimeric ligand of the type **9**.

In addition to these mononuclear iron complex **12**−**15** from **9**, a dinuclear iron complex could also be prepared from the bisindenyl-annelated [2.2]paracyclophanediene *syn*-**11**. Treatment of *syn*-**11** with two equivalents of methyllithium and trapping of the resulting dianion in the presence of an excess of lithium cyclopentadienide with $FeCl_2{\cdot}(THF)_2$ gave a mixture of the *cis*- and *trans*-isomeric complexes *cis*/*trans*-**16** (ratio 1:1) in 46% yield. The relatively poorly soluble isomers *cis*- and *trans*-**16** could not be separated, but characterized as a mixture by NMR spectroscopy.

Scheme 5



Since the indene moiety in **9** with its annelated [2.2]paracyclophane system is electronically different from the parent indene, it would certainly be interesting to see whether **9** as a ligand in catalytically active complexes might have a positive influence on their properties and activities.

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Experimental Section

General: ^{1}H NMR: Bruker AW250 (250 MHz), WM270 (270 MHz), WM400 (400 MHz); δ (ppm) = 0 for tetramethylsilane, 2.04 for [D_5]acetone, 2.49 for [D_5]DMSO, 3.30 for [D_3]methanol, 5.32 for $CDHCl_2$, 7.15 for C_6D_5H, 7.24 for $CHCl_3$. Characterization of signal multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, mc = centrosymmetric multiplet. − ^{13}C NMR: Bruker AW250 (62.9 MHz), WM270 (67.9 MHz), δ = 77.0 for $CDCl_3$, 128.0 for C_6D_6. Assignments of ^{13}C signals were supported by applying the DEPT puls sequence (DEPT = distortionless enhancement by polarization transfer), results are reported as follows: + = primary or tertiary, − = secondary, C_{quat} = quaternary C atom. − IR: Perkin Elmer 297, 399. − MS: Varian MAT CH7 with Varian Aerograph 1740, Varian MAT 311 A (high resolution). − Column chromatography: Merck silica gel 60, (70−230 mesh). − TLC: Merck silica gel 60 F_{254} on aluminum foil. Detection under UV light of 254 nm.

General Procedure for Generation of 1-Lithio[2.2]paracyclophane-1,9-diene (**2**) *(GP 1)*: *n*-Butyllithium in hexane was added to a solution of [2.2]paracyclophane-1,9-diene (**1**) in tetrahydrofuran (THF) at −78°C. The reaction mixture was warmed to 0°C and stirred at this temp. for the given time, by which the solution had turned dark green indicating the formation of **2**.

1-Lithio[2.2]paracyclophane-1,9-diene (**2**) *and 1-Deuterio-[2.2]paracyclophane-1,9-diene* (**3a**): 15.0 mg (0.073 mmol) of **1** was dissolved in 0.7 ml of [D_8]THF in a 5-mm NMR tube. To this solution was added 2.0 mg (0.09 mmol) of solid methyllithium [obtained from an ether solution by evaporating the solvent under reduced pressure (10^{-3} Torr) at 0°C] under argon. After 2 h at 0°C and 5 h at room temp., the NMR signal of **1** had disappeared, and

a dark green solution of **2** had formed. – ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 6.06 (AB system, $^3J_{AB}$ = 7.8, 4 H, phane-arene-H), 6.21 (AB system, $^3J_{AB}$ = 7.3, 4 H, phane-arene-H), 7.03 [s, 2 H, 9(10)-H], 7.25 (bs, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, [D$_8$]THF): δ = 123.57 (broad, C_{quat}), 129.01 (C_{quat}), 130.30 (+), 130.40 (+), 131.55 (+), 136.72 (C_{quat}), 137.81 (+), 138.06 (+), 138.78 (+), 141.34 (C_{quat}). To this NMR solution, kept at 0°C, two drops of D_2O were added, the solution dried with $MgSO_4$, and the solvent evaporated under reduced pressure. Analysis by NMR and mass spectrometry showed the exclusive formation of **3a**. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.46 (s, 8 H, phane-arene-H), 7.21 [s, 3 H, 2(9,10)-H]. – MS (70 eV); *m/z* (%): 205 (100) [M$^+$].

1-Trimethylsilyl[2.2]paracyclophane-1,9-diene (**3b**): 250 mg (1.23 mmol) of **1**, 20 ml of THF, and 1 ml (1.5 mmol) of 1.5 M *n*BuLi were allowed to react for 1 h according to *GP 1*. The solution was cooled to −78°C, 0.50 ml (3.94 mmol) of chlorotrimethylsilane (TMSCl) was added, and the mixture was allowed to warm up to room temp. After evaporation of the solvent, the remaining solid was purified by column chromatography on 60 g of silica gel (25 × 3 cm, light petroleum ether 60−70). Fraction I (R_f = 0.32, hexane): 270 mg (80%) of **3b**. Fraction II: 40 mg of **3b** with some impurities. Fraction II was again purified by column chromatography on 60 g of silica gel (25 × 3 cm, light petroleum ether 60−70) resulting in additional 30 mg (9%) of **3b**. Overall yield 300 mg (89%) of **3b** as colorless crystals, m.p. 101°C (ethanol). – IR (KBr): ṽ = 3050 cm^{-1}, 3000, 2950, 1580, 1425, 1290, 1245 ($SiCH_3$), 975, 940, 870, 825 (CSi), 715, 710, 680, 620. – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.24 (s, 9 H, $SiCH_3$), 6.32 (d, ^3J = 8.0 Hz, 2 H, arene-H), 6.45 (m, 6 H, arene-H), 7.18 [s, 2 H, 9(10)-H], 7.36 (s, 1 H, 2-H). – $C_{19}H_{20}Si$ (276.5): calcd. C 82.55, H 7.29; found C 82.41, H 7.33.

1-Iodo[2.2]paracyclophane-1,9-diene (**3c**): 200 mg (0.98 mmol) of **1**, 10 ml of THF, and 0.85 ml (1.28 mmol) of 1.5 M *n*BuLi were allowed to react for 1 h according to *GP 1*. The solution was cooled to −78°C, 450 mg (1.77 mmol) of iodine was added, and the mixture was allowed to warm up to room temp. Excess iodine was removed by extracting the reaction mixture with 10 ml of saturated $NaHSO_3$ solution, and the organic layer was dried with $MgSO_4$. After evaporating the solvent, the remaining solid was purified by column chromatography on 22 g of silica gel (22 × 1.5 cm, CH_2Cl_2/light petroleum ether 60−70, 1:6) resulting in 230 mg (71%) of **3c** (R_f = 0.52), m.p. 126°C. – IR (KBr): ṽ = 2995 cm^{-1}, 1575, 1475, 1295, 1260, 1145, 1095, 935, 910, 850, 815, 805, 715, 705, 685, 535. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.50 [s, 4 H, 4(5,7,8)-H], 6.53 and 6.59 [AB system, $^3J_{AB}$ = 8.6 Hz, 4 H, 12(13,15,16)-H], 7.17 [AB system, $^3J_{AB}$ = 10.6 Hz, 2 H, 9(10)-H], 7.75 (s, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 97.21 (C-1), 129.38, 130.34, 131.03, 131.08 [C-4(5,7,8,12,13,15,16)], 136.80, 136.91 [C-9(10)], 130.87, 138.29, 138.75, 139.17 [C-3(6,11,14)], 145.73 (C-2). – MS (70 eV); *m/z* (%): 330 (30) [M$^+$], 202 (100) [M$^+$ − HI]. – $C_{16}H_{11}I$ (330.2): calcd. C 58.21, H 3.36, I 38.43; found C 58.36, H 3.28, I 37.12.

1-Formyl[2.2]paracyclophane-1,9-diene (**3d**): 160 mg (0.78 mmol) of **1**, 10 ml of THF, and 0.65 ml (0.97 mmol) of 1.5 M *n*BuLi were allowed to react for 1 h according to *GP 1*. The solution was cooled to −78°C, 1.0 ml (13 mmol) of dimethylformamide was added and the mixture allowed to warm up to 0°C. 10 ml of saturated NH_4Cl solution was added, and the mixture stirred for a short time. After separation, the organic layer was dried with $MgSO_4$, the solvent was evaporated under reduced pressure, and the remaining solid purified by column chromatography on 20 g of silica gel (20 × 1.5 cm, CH_2Cl_2/light petroleum ether 30−50, 2:1) resulting in 129 mg (71%) of **3d** (R_f = 0.35). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.55 [m, 8 H, 4(5,7,8,12,13,15,16)-H], 7.23 [s, 2 H, 9(10)-H], 8.09 (s, 1 H, 2-H), 9.89 (s, 1 H, formyl-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 128.98 (+), 131.12 (+), 131.19 (+), 131.35 (C_{quat}), 135.59 (+), 136.74 (C_{quat}), 137.19 (+), 138.62 (C_{quat}), 138.88 (C_{quat}), 152.85 (C_{quat}), 154.95 (+), 170.60 (+), 190.96 (+, CO). – MS (70 eV); *m/z* (%): 232 (100) [M$^+$], 203 (72) [M$^+$ − CHO]. – $C_{17}H_{12}O$ (232.3): calcd. C 87.90, H 5.21; found C 86.78, H 5.44. – HR-MS: 232.0886 ($C_{17}H_{12}O$, M$^+$; calcd. 232.0888).

1-(1′-Hydroxy-1′-phenylmethyl)[2.2]paracyclophane-1,9-diene (**4**): 500 mg (2.45 mmol) of **1**, 25 ml of THF, and 2 ml (3 mmol) of 1.5 M *n*BuLi were allowed to react for 1 h according to *GP 1*. The solution was cooled to −78°C, 0.40 ml (3.95 mmol) of benzaldehyde was added, the mixture allowed to warm up to 0°C and stirred for an additional 15 min. Subsequently, 20 ml of saturated NH_4Cl solution and 20 ml of diethyl ether were added, and the mixture was stirred for a short time. After separation, the organic layer was dried with $MgSO_4$, the solvent evaporated under reduced pressure, the remaining material adsorbed on 3 g of silica gel and purified by column chromatography on 30 g of silica gel (12 × 3 cm, first CH_2Cl_2/light petroleum ether 30−50, 1:1, then CH_2Cl_2). Fraction I: 50 mg of benzaldehyde. Fraction II (R_f = 0.33, CH_2Cl_2): 720 mg (95%) of **4**, m.p. 104°C. – IR (KBr): ṽ = 3250 cm^{-1} (OH), 3000, 2950, 1580, 1480, 1450, 1280, 1190, 1080, 1000, 930, 710, 700, 680. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.36 (d, ^3J = 4.0 Hz, 1 H, OH), 5.67 (d, ^3J = 4.0 Hz, 1 H, C*H*OH), 6.16 (m, 2 H, phane-arene-H), 6.28−6.64 (m, 6 H, phane-arene-H), 7.16 [s, 2 H, 9(10)-H], 7.21−7.64 (m, 6 H, 2-H and phenyl-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 77.07 (+) (COH), 126.85 (+), 127.83 (+), 128.32 (+), 130.08 (+), 130.65 (+), 130.68 (+), 130.75 (+), 130.78 (+), 130.82 (+), 130.85 (+), 132.01 (+), 132.64 (+), 136.68 (C_{quat}), 136.79 (+), 136.89 (+), 137.40 (C_{quat}), 137.92 (C_{quat}), 138.29 (C_{quat}), 141.37 (C_{quat}), 152.13 (C_{quat}). – MS (70 eV); *m/z* (%): 310 (100) [M$^+$], 202 [M$^+$ − C_7H_7 − OH]. – $C_{23}H_{18}O$ (310.4): calcd. C 89.00, H 5.85; found C 89.37, H 6.03.

Bis([2.2]paracyclophane-1,9-dien-1-yl)methanol (**5**): 1.0 g (4.9 mmol) of **1**, 60 ml of THF, and 2.13 ml (4.9 mmol) of 2.3 M *n*BuLi were allowed to react for 1 h according to *GP 1*. To this solution was added 0.2 ml of ethyl formate by use of a syringe pump within 30 min. The reaction mixture was stirred for an additional 15 min, and then 20 ml of saturated NH_4Cl solution was added. The organic layer was extracted with two portions of H_2O, dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. After washing the remaining solid three times each with 40 ml of pentane, 953 mg (89%) of **5** (R_f = 0.25, CH_2Cl_2/light petroleum ether 60−70, 2:1) was obtained, m.p. 267°C. – IR (KBr): ṽ = 3570 cm^{-1}, 3000, 1580, 1485, 1370, 1095, 1075, 990, 935, 894, 815, 795, 725, 700, 685, 660, 520. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.44 (d, ^3J = 6.2 Hz, 1 H, OH), 5.56 (dd, ^3J = 6.2, ^4J = 1.2 Hz, 1 H, C*H*OH), 6.46−6.80 (m, 16 H, phane-arene-H), 7.16 [s, 2 H, 2(2′)-H], 7.24 [s, 4 H, 9(9′,10,10′)-H]. – MS (70 eV); *m/z* (%): 436 (20) [M$^+$]. – HR-MS: 436.1818 ($C_{33}H_{24}O$, M$^+$; calcd. 436.1826).

1,9-/1,10-Dilithio[2.2]paracyclophane-1,9-diene (**6**). – *General Procedure 2 (GP 2):* *n*BuLi in *n*-hexane was added at −78°C to a suspension of [2.2]paracyclophane-1,9-diene (**1**) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) in diethyl ether. The reaction mixture was allowed to warm up to room temp. and stirred for the stated time.

Bis(trimethylsilyl)[2.2]paracyclophane-1,9-diene (1,9-/1,10-**7**)[8b]: 100 mg (0.49 mmol) of **1**, 10 ml of diethyl ether, 2 ml of TMEDA, and 2 ml (3 mmol) of 1.5 M *n*BuLi were allowed to react for 3 h according to *GP 2*. The solution was cooled to −78°C and 1.0 ml

(7.91 mmol) of chlorotrimethylsilane was added. After allowing the reaction mixture to warm up to room temp., 10 ml of water was added. The organic layer was extracted with 10 ml of water, dried with $MgSO_4$, and after addition of 1 g of silica gel the solvent was evaporated under reduced pressure. The remaining solid was purified by column chromatography on 20 g of silica gel (20 × 1.5 cm, light petroleum ether 60−70). Fraction I (R_f = 0.41): 45 mg (26%) of 1,9-/1,10-**7**. Fraction II (R_f = 0.41 and 0.34): 60 mg of 1,9-/1,10-**7** and 1-trimethylsilyl[2.2]paracyclophane-1,9-diene (**3b**). Fraction III (R_f = 0.34): 20 mg (15%) of **3b**. Fraction II was again purified under the same conditions to yield 14 mg (8%) of 1,9-/1,10-**7** and 20 mg (15%) of **3b**. Total yield 59 mg (34%) of 1,9-/1,10-**7** and 40 mg (30%) of **3b**. The spectroscopic data of 1,9-**7** and 1,10-**7** were identical with those of authentic samples prepared from 1,9- and 1,10-dibromo[2.2]paracyclophanediene as reported previously[8b].

1,9- and 1,10-Bis(1-hydroxy-1-phenylmethyl)[2.2]paracyclophane-1,9-diene (1,9-**8** and 1,10-**8**): 500 mg (2.45 mmol) of **1**, 5 ml of TMEDA, 30 ml of diethyl ether, and 10 ml (15 mmol) of 1.5 M *n*BuLi were allowed to react for 4.5 h according to *GP 2*. Then 2 ml (19.8 mmol) of benzaldehyde was added at −78°C. The reaction mixture was allowed to warm up to room temp., stirred for an additional 15 min and 10 ml of saturated NH_4Cl solution was added. The organic layer was extracted with 10 ml of H_2O, dried with $MgSO_4$, and after having added 5 g of silica gel, the solvent was evaporated under reduced pressure. The remaining solid was purified by column chromatography on 60 g of silica gel (25 × 3 cm, CH_2Cl_2/diethyl ether, 20:1) to yield 400 mg (39%) of 1,9-**8**/1,10-**8** in a ratio of 64:36 (R_f = 0.31). Isomerically pure 1,9-**8** was obtained by threefold recrystallization from toluene/heptane, m.p. 202°C. − IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (OH), 3040, 2980, 1620, 1520, 1480, 1435, 1155, 1070, 1000, 920, 820, 710. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.24 (d, ^3J = 4.2 Hz, 2 H, OH), 5.62 (d, ^3J = 4.2 Hz, 2 H, C*H*OH), 6.01−6.24 (m, 4 H, phane-arene-H), 6.26−6.35 (m, 4 H, phane-arene-H), 7.10−7.60 [m, 12 H, phenyl-H and 2(10)-H]. − ^{1}H NMR (400 MHz, [D_6]acetone): δ = 4.81 (d, ^3J = 4.0 Hz, 2 H, OH), 5.60 (m, 2 H, C*H*OH), 6.02−6.13 (m, 4 H, phane-arene-H), 6.26−6.41 (m, 4 H, phane-arene-H), 7.16−7.37 [m, 8 H, phenyl-H and 2(10)-H], 7.42−7.53 (m, 4 H, phenyl-H). − MS (70 eV); *m/z* (%): 416 (59) [M^+].

1:2-(2,3-Indeno)[2.2]paracyclophane-9-ene (**9**): A mixture of 200 mg (0.65 mmol) of **4** and 200 mg of zinc(II) chloride in 100 ml of 1,2-dichloroethane was stirred at room temp. under exclusion of light for 2 d. After filtration, the reaction mixture was extracted twice each with 20 ml of saturated $NaHCO_3$ solution and once with 20 ml of H_2O, dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The remaining material was purified by column chromatography on 10 g of silica gel (light petroleum ether 60−80) to yield 136 mg (72%) of **9** (R_f = 0.62, light petroleum ether 60−80/CH_2Cl_2, 1:1). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.61 (s, 1 H, 2-H), 5.89 (AB system, δ_A = 6.07, δ_B = 5.7, ^3J = 8 Hz, 2 H, phane-arene-H), 6.45 (AB system, δ_A = 6.54, δ_B = 6.36, ^3J = 8 Hz, 2 H, phane-arene-H), 6.76 (AB system, δ_A = 6.84, δ_B = 6.68, ^3J = 8 Hz, 2 H, phane-arene-H), 6.95 (s, 1 H, indene-olefinic-H), 6.96 (AB system, δ_A = 7.14, δ_B = 6.78, ^3J = 8 Hz, 2 H, phane-arene-H), 7.20 [s, 2 H, 9(10)-H], 7.34 (t, 1 H, arene-H), 7.52 (dd, 2 H, arene-H), 7.58 (t, 1 H, arene-H). − ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ = 63.78, 121.73, 122.71, 124.43, 125.08, 127.58, 129.64, 130.25, 131.18, 131.87, 133.03, 133.70, 134.23, 136.30, 137.19, 137.61, 137.90, 138.32, 140.47, 145.87, 148.46, 158.99. − MS (70 eV); *m/z* (%): 293/292 (24/100) [M^+], 289 (54). − $C_{23}H_{16}$ (292.4): calcd. C 94.48, H 5.52; found C 94.19, H 5.68.

syn-1:2,9:10-Bis(2,3-indeno)[2.2]paracyclophane (*syn*-**11**): A mixture of 493 mg (1.18 mmol) of 1,10-bis(1-hydroxy-1-phenylmethyl)[2.2]paracyclophane-1,9-diene (1,10-**8**) and 620 mg of zinc(II) chloride in 1000 ml of 1,2-dichloroethane was sonicated at room temp. under exclusion of light for 3 d. After filtration, the reaction mixture was extracted twice, each with 100 ml of saturated $NaHCO_3$ solution and once with 100 ml of H_2O, dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The remaining material was purified by column chromatography on 30 g of silica gel (light petroleum ether 60−80/CH_2Cl_2, 3:1) to yield 175 mg (39%) of *syn*-**11** (R_f = 0.32, light petroleum ether 60−80/CH_2Cl_2, 1:1). − IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1}, 2923, 2867, 1699, 1601, 1486, 1154, 889, 868. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.77 [s, 2 H, 2(9)-H], 5.54 (s, 2 H, phane-arene-H), 6.58 (s, 2 H, phane-arene-H), 6.99 (bs, 2 H, olefin-H), 7.02 (s, 2 H, phane-arene-H), 7.18−7.21 (m, 2 H, arene-H), 7.34 (m, 4 H, arene-H and phane-arene-H), 7.5 (m, 4 H, arene-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 62.88 (+), 121.43 (+), 122.90 (+), 123.95 (+), 124.91 (+), 127.32 (+), 132.19 (+), 132.27 (+), 132.39 (+), 135.29 (C_{quat}), 139.03 (C_{quat}), 145.10 (C_{quat}), 147.82 (C_{quat}), 157.36 (C_{quat}). − MS (70 eV); *m/z* (%): 380 (100) [M^+], 363 (15), 350 (10). − HR-MS: 380.1567 ($C_{30}H_{20}$ M^+; calcd. 380.1565).

η^5-Cyclopentadienyl{1:2-(1-3a-η,7a-η-indenido)[2.2]paracyclophane-9-ene}iron (**12**): To a solution of 200 mg (0.68 mmol) of **9** and 450 mg (6.8 mmol) of cyclopentadiene in 20 ml of THF was added dropwise 5.65 ml (9.0 mmol) of a 1.6 M solution of methyllithium in diethyl ether at 0°C. After 1 h, this solution was transferred via a steel capillary to a suspension of 1.1 g (4.0 mmol) of $FeCl_2{\cdot}(THF)_2$[15] in 60 ml of THF. The reaction mixture was stirred first for 20 min at room temp. and then for 18 h under reflux. The solvent was evaporated under reduced pressure, and the remaining solid was purified by flash chromatography on 10 g of deoxygenated florisil (20 × 1 cm, light petroleum ether 60−80, R_f = 0.1). After recrystallization from hexane/CH_2Cl_2 (20:1), 177 mg (63%) of **12** was obtained. − IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 2870, 1638, 1494, 1359, 1107, 881, 823, 768, 741, 725, 708, 673, 651, 608, 591. − ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 4.03 (s, 5 H, Cp-H), 5.26 (s, 1 H, indene-H), 6.21 (dd, 1 H, phane-arene-H), 6.35 (m, 3 H, phane-arene-H), 6.61 (dd, 1 H, phane-arene-H), 6.72 (dd, 1 H, phane-arene-H), 7.07 (m, 3 H, phane-arene-H and indene-arene-H), 7.24 [bs, 2 H, 9(10)-H], 7.56 (m, 1 H, indene-arene-H), 7.72 (m, 2 H, indene-arene-H). − ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ = 60.81 (+), 70.51 (+), 85.81 (C_{quat}), 86.34 (C_{quat}), 90.71 (C_{quat}), 99.19 (C_{quat}), 124.52 (+), 124.65 (+), 129.07 (+), 130.03 (+), 130.16 (+), 130.28 (+), 131.29 (+), 131.56 (+), 132.52 (+), 133.69 (+), 134.03 (+), 134.08 (+), 135.10 (C_{quat}), 135.63 (C_{quat}), 137.40 (+), 137.46 (+), 139.16 (C_{quat}), 139.44 (C_{quat}). − MS (70 eV); *m/z* (%): 413/412 (39/100) [M^+], 292 (24), 289 (31). − HR-MS: 412.0912 ($C_{28}H_{20}Fe$ M^+; calcd. 412.0914).

{1:2-(1-3a-η,7a-η-Indenido)[2.2]paracyclophane-9-ene}(η^5-pentamethylcyclopentadienyl)iron (**15**): To a solution of 100 mg (0.34 mmol) of **9** and 466 mg (3.43 mmol) of pentamethylcyclopentadiene in 10 ml of THF was added dropwise 2.8 ml (4.5 mmol) of a 1.6 M solution of methyllithium in diethyl ether at 0°C. After 1 h, this solution was transferred dropwise via a steel capillary into a suspension of 500 mg (1.8 mmol) of $FeCl_2{\cdot}(THF)_2$ in 50 ml of THF. The reaction mixture was initially stirred for 20 min at room temp. and than for 18 h under reflux. The solvent was evaporated under reduced pressure, and the remaining solid was purified by flash chromatography on 10 g of deoxygenated florisil (20 × 1 cm, first light petroleum ether 60−80, then CH_2Cl_2) resulting in a solution of a mixture of **13** and **15**, from which **15** was separated by crystallization from hexane/CH_2Cl_2 at −23°C. After evaporating

the solvent under reduced pressure, 64 mg (38%) of **15** (R_f = 0.09, light petroleum ether 60−80) was obtained as a red solid. − IR (KBr): $\tilde{\nu}$ = 3001 cm^{-1}, 1586, 1495, 1358, 1097, 901, 880, 847, 797, 740 (s), 724 (s), 672 (s), 649, 608, 590, 518, 455. − ^1H NMR (250 MHz, CD_2Cl_2): δ = 1.74 (s, 15 H, CH_3), 4.59 (s, 1 H, indene-H), 6.12 (dd, 2 H, phane-arene-H), 6.29 (m, 2 H, phane-arene-H), 6.67 (dd, 2 H, phane-arene-H), 7.1−7.4 (m, 6 H, phane-arene-, olefin- and indene-arene-H), 7.61 (m, 2 H, indene-arene-H). − ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ = 10.45 (+), 62.87 (+), 78.36 (C_{quat}), 85.96 (C_{quat}), 88.95 (C_{quat}), 90.24 (C_{quat}), 101.38 (C_{quat}), 124.52 (+), 125.20 (+), 127.28 (+), 127.65 (+), 130.04 (+), 130.20 (+), 130.97 (+), 131.18 (+), 131.42 (+), 131.95 (+), 132.43 (+), 134.16 (+), 134.24 (+), 136.44 (C_{quat}), 136.99 (C_{quat}), 137.56 (+), 138.95 (C_{quat}), 139.21 (C_{quat}). − HR-MS: 482.1690 ($C_{30}H_{30}Fe$, M^+; calcd. 482.1697).

Bis[1:2-(1-3a-η,7a-η-indenido)[2.2]paracyclophan-9-enyl]iron (**13**): To a solution of 300 mg (1.03 mmol) of **9** in 20 ml of THF was added dropwise 0.73 ml (1.17 mmol) of a 1.6 M solution of methyllithium in diethyl ether at 0°C. After 1 h, this solution was transferred dropwise via a steel capillary into a suspension of 380 mg (1.4 mmol) of $FeCl_2 \cdot (THF)_2$[15] in 50 ml of THF. The reaction mixture was stirred for 24 h, and the solvent evaporated under reduced pressure. The remaining solid was purified by flash chromatography on 10 g of deoxygenated florisil (20 × 1 cm, first hexane, then CH_2Cl_2) resulting in 202 mg (61%) of **13** as a green solid. − ^1H NMR (400 MHz, CD_2Cl_2): δ = 5.96 (s, 2 H, indene-H), 6.19−6.48 (m, 10 H, phane-arene-H), 6.62 (d, 2 H, phane-arene-H), 6.88 (d, 2 H, phane-arene-H), 7.01 (m, 4 H, phane-arene and indene-arene-H), 7.25 [dd, 4 H, 9(10)-H], 7.53 (dd, 2 H, arene-H), 7.72 (m, 2 H, arene-H), 8.25 (d, 2 H, arene-H). − ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ = 60.77 (+), 84.20 (C_{quat}), 85.96 (C_{quat}), 89.86 (C_{quat}), 96.96 (C_{quat}), 120.53 (+), 124.28 (+), 124.88 (+), 129.08 (+), 130.20 (+), 130.58 (+), 131.59 (+), 131.80 (+), 133.45 (+), 133.66 (+), 133.73 (+), 134.45 (+), 134.97 (C_{quat}), 135.32 (C_{quat}), 137.43 (+), 137.50 (+), 139.54 (C_{quat}), 139.68 (C_{quat}). − MS (70 eV); *m/z* (%): 639/638 (63/100) [M^+], 582 (21), 292 (20), 291 (22), 290 (11). − HR-MS: 638.1700 ($C_{46}H_{30}Fe$, M^+; calcd. 638.1697).

X-ray Crystal Structure Analysis of Complex **13**[21]: Crystals were obtained from CH_2Cl_2. The data of a crystal of size 0.60 × 0.50 × 0.50 mm were recorded with a STOE AED4 four-circle diffractometer. Orthorhombic space group *Pbca*, *Z* = 8, unit cell dimensions *a* = 128.1(10), *b* = 197.9(2), *c* = 245.7(4) pm, $\rho_{calcd.}$ = 1.36 $Mg \cdot m^{-3}$, 3190 observed reflections with 2θ < 45°, Mo-K_α, R_w = 5.2%.

Dicarbonyl(η⁵-cyclopentadienyl){1:2-(1-η¹-Indenido)[2.2]paracyclophan-9-ene}iron (**14**): To a solution of 100 mg (0.34 mmol) of **9** in 10 ml of THF was added at 0°C 0.24 ml (0.38 mmol) of a 1.6 M solution of methyllithium in diethyl ether. The mixture was stirred at ambient temp. for 1 h, and then transferred dropwise via a steel capillary into a solution of 123 mg (0.4 mmol) of dicarbonyl(cyclopentadienyl)iron iodide in 8 ml of THF. After the mixture had been stirred at ambient temp. for 24 h, it was concentrated to dryness under reduced pressure, and the residue was quickly chromatographed on 10 g of deoxygenated florisil (column 20 × 1 cm, eluting with *n*-hexane). The solution was concentrated to dryness, and the residue recrystallized from *n*-hexane to yield 40 mg (25%) of **14** as a bright yellow, air-sensitive solid. − IR (KBr): $\tilde{\nu}$ = 3004 cm^{-1}, 2924, 2008 (s, CO), 1956 (s, CO), 1582, 1459, 1379, 1261, 1098, 1017, 933, 877, 796, 767, 753, 726, 715, 664, 626. − ^1H NMR (250 MHz, CD_2Cl_2): δ = 4.04 (s, 1 H, 3′-H), 4.41 (s, 5 H, Cp-H), 6.34−6.81 (m, 8 H, phane-arene-H), 7.18−7.22 (m, 2 H, indene-arene-H), 7.24 [s, 2 H, 9(10)-H], 7.43 and 7.68 (mc, 1 H each, indene-arene-H). − MS (70 eV); *m/z* (%): 582 (100) dimer of ligand], 291 (68) [ligand].

cis-Bis(η⁵-cyclopentadienyl){μ-syn-1:2,9:10-Bis(2,3-indenido)-[2.2]paracyclophane}diiron (*cis*-**16**) *and trans-Bis(η⁵-cyclopentadienyl){μ-syn-1:2,9:10-Bis(2,3-indenido)[2.2]paracyclophane}-diiron* (*trans*-**16**): To a solution of 100 mg (0.26 mmol) of *syn*-**11** and 156 mg (2.36 mmol) of cyclopentadiene in 25 ml of THF was added dropwise 2.7 ml (4.3 mmol) of a 1.6 M solution of methyllithium in diethyl ether at 0°C. After 1 h, this solution was transferred dropwise via a steel capillary into a suspension of 588 mg (2.2 mmol) of $FeCl_2 \cdot (THF)_2$[15] in 25 ml of THF. The reaction mixture was stirred first for 20 min at room temp. and then for 18 h under reflux. The solvent was evaporated under reduced pressure, and the remaining solid was purified by flash chromatography on 10 g of deoxygenated florisil (20 × 1 cm, light petroleum ether 60−80, then CH_2Cl_2). After evaporation of the solvent under reduced pressure, the remaining solid was washed three times each with 5 ml of pentane to yield 76 mg (46%) of *cis*/*trans*-**16**. − ^1H NMR (250 MHz, $CDCl_3$): δ = 4.04 (s, 10 H, Cp-H), 4.11 (s, 10 H, Cp-H), 5.24 (s, 2 H, indene-H), 5.26 (s, 2 H, indene-H), 6.11 (bs, 2 H, phane-arene-H), 6.31 (bs, 2 H, phane-arene-H), 6.36 (d, 2 H, phane-arene-H), 6.62 (d, 2 H, phane-arene-H), 7.09 (m, 8 H, phane-arene-H and indene-arene-H), 7.27 (s, 2 H, phane-arene-H), 7.63 (m, 12 H, indene-arene-H), 7.93 (bs, 2 H, phane-arene-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 60.39 (+), 60.61 (+), 69.80 (+), 69.71 (+), 85.50 (C_{quat}), 85.62 (C_{quat}), 85.92 (C_{quat}), 86.18 (C_{quat}), 90.10 (C_{quat}), 98.42 (C_{quat}), 98.52 (C_{quat}), 124.21 (+), 124.35 (+), 128.67 (+), 129.62 (+), 129.67 (+), 131.67 (+), 132.42 (+), 132.83 (+), 133.27 (+), 133.49 (+), 133.92 (+), 135.52 (C_{quat}), 135.61 (C_{quat}), 135.84 (C_{quat}). − HR-MS: 620.0885 ($C_{40}H_{28}Fe_2$, M^+; calcd. 620.0890).

☆ Dedicated to Professor *Ronald N. Warrener* on the occasion of his 65th birthday.

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[21] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101362. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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