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New Soluble Bis[nona-, octa-, and pentamethylferrocenes] as “Molecular Wires” with a Metal-to-Metal Distance of up to 40 Å[#]

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Methylated ferrocenes are useful building blocks for novel materials in molecular electronics with advantageous properties in comparison to normal ferrocene derivatives. The presence of nine, eight, or five methyl substituents leads to (i) a decrease in oxidation potential, (ii) amplified donor capacity with correspondingly increased stability of the ferrocenium salts, and, most significantly, (iii) increased solubility. A modular synthetic approach based on standard Wittig chemistry affords π-conjugated soluble nona-, octa-, and pentamethylated biferrocenes, bridged by up to five vinylene−phenylene subunits. These biferrocenes with spacers are “molecular wires” with a metal-to-metal distance of up to 40 Å and an effective conjugation pathway of up to 50 Å.

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Introduction

In comparison to the well-developed chemistry of ferrocene with its numerous applications[1] in organic synthesis, homogeneous catalysis, and materials science, the analogous chemistry of methylated ferrocene derivatives is limited.[2] Ferrocenes made up of one pentamethylcyclopentadienide (Cp*) and one substituted cyclopentadienide [$(H_3C)_n$Cp-R; $n = 0-4$; R = functional group or bridging ligand] should display favorable properties in terms of increased solubility,[3] lowered oxidation potential, amplified donor capacity, and hence increased stability[3] of the corresponding ferrocenium cations, which could be exploited for improved materials in molecular electronics.[4] Molecular wires[5] are mixed-valence bimetallic compounds with a conjugating bridging ligand that allows electronic communication between the two redox termini (Scheme 1). For example, such systems are known with oligoene bridging ligands between ruthenium pentamine complexes[6] or between simple ferrocenes,[7] where the electronic coupling can be experimentally verified for up to 18 Å separated electrophores.

Scheme 1. Principal Components of Molecular Wires

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[#] Dedicated to Professor K.-E. Schwarzhans on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.

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In this contribution we report on the synthesis of soluble methylated biferrocenes with increased (up to 40Å) metal-to metal distances, using standard Wittig and/or Wittig−Horner olefination procedures.[8] The bridging ligands were selected to be phenylene−vinylene oligomers, which combine chemical stability with good charge conducting properties in comparison to oligoene,[7] oligoyne,[9] and oligophenyleneyne compounds.[10] The number of solubilizing and cation-stabilizing methyl substituents on the metallocenyl termini were systematically varied from 9 to 5 with the anticipation of (i) increasing the solubility with the number of methyl groups attached to the ferrocenyl electrophores and (ii) progressively stabilizing the oxidized ferrocenium species according to the number of electron-donating methyl substituents.

Results and Discussion

(a) General Synthetic Approach. Biferrocenes with olefinic conjugating bridging ligands are most easily prepared by Wittig and/or Wittig−Horner reactions,[8] similar to published results[11] on related oligo(phenylene−vinylenes). The necessary synthons for the stepwise construction of such biferrocenes are thus methylated ferrocene aldehydes, terephthaldialdehyde, and the hydroxymethyl derivatives as the phosphonium progenitors, respectively. Fortunately, in contrast to the normal product distribution of Wittig protocols,[8] the desired (*E*)-vinylferrocenes are favored for the first homologation step, although in general always *E*/*Z*-mixtures are formed.[12] The isomer distribution of the Wittig products of ferrocene aldehydes[13] is strongly influenced by the base used in the preparation of the ylide, and potassium *tert*-butoxide[14] seems to be the base of choice for maximized yields of (*E*)-olefins. The resulting isomer mixtures are usually difficult to separate by chromatography, but sometimes the (*E*)-olefins can be obtained by selective crystallization (see Experimental Section). In addition, according to our own experience, acidic isomerizations[12] to the thermodynamically favored (*E*)-olefins are not applicable for highly methylated ferrocenes. To circumvent these restrictions, Wittig−Horner olefinations utilizing *p*-phenylene bis(phosphonate)[15] as a convenient “bis(ylide)” progenitor are preferable, especially for the construction of the central phenylene−vinylene bridging units in the higher oligomers. (Ferrocenylmethyl)triphenylphosphonium and 1,1′-ferrocenediylbis(methyltriphenylphosphonium) salts[16] are usually synthesized by multistep procedures via the methyl iodides of the corresponding ((dimethylamino)methyl)metallocenes. Since the availability of numerous metallocenyl aldehydes and the alcohols derived thereof has been significantly improved during the recent years,[17] it seemed encouraging to apply a one-pot elimination-substitution sequence according to Hamanaka and Kosuge,[18] which proved to be the most simple and efficient route to the desired ylide progenitors.

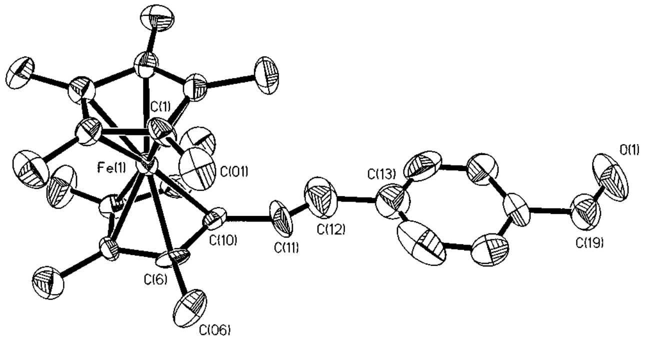

Figure 1. Molecular structure of **4**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. The cyclopentadienyl carbons of ferrocene 1 are C(1)−C(10), and the methyl carbons of ferrocene 1 are C(01)−C(09). Torsion angles: C(12)−C(11)−C(10)−C(9) = −6.0(3.2)°; C(11)−C(12)−C(13)−C(18) = 10.8(3.4)°. Angle of Cp plane [C(6)−C(10)] to phenyl plane [C(13)−C(18)] = 10.5(1.1)°.

(b) Nona- and Octamethylated Ferrocenes (Scheme 2). In this manner, ((octa- and nonamethylferrocenyl)methyl)triphenylphosphonium salts **1a**,**b** and **2** can be obtained in high yield. In addition to their characterization by the usual spectroscopic methods (see Experimental Section), X-ray structure analyses of **1b** and **2** confirm their identity. These two solid-state structures are very similar to the published structure of (ferrocenylmethyl)triphenylphosphonium iodide[16] and present no unexpected features; therefore the details of these crystal structures are included in the Supporting Information only.

Besides these normal (*mono*cationic) phosphonium salts, the stabilizing effect of the methyl substituents allows also the isolation of the green air-stable ((octamethylferroceniumyl)methyl)triphenylphosphonium *di*cation **(1c)**, whose single-crystal structure is included in the Supporting Information. Starting from phosphonium salts **1a,b** and **2** the corresponding ylides afford the “spacered” aldehydes **3** and **4** by reaction with excess terephthaldialdehyde. In accord with NMR analysis the solid-state structures of **3** (Supporting Information) and **4** (Figure 1, Table 1) clearly show an *E*-configuration. Only twinned crystals could be obtained in the case of **4;** however the structure could be solved with correspondingly rather high residuals in the final structure refinement, but the connectivity of the molecule is nevertheless unequivocally determined.

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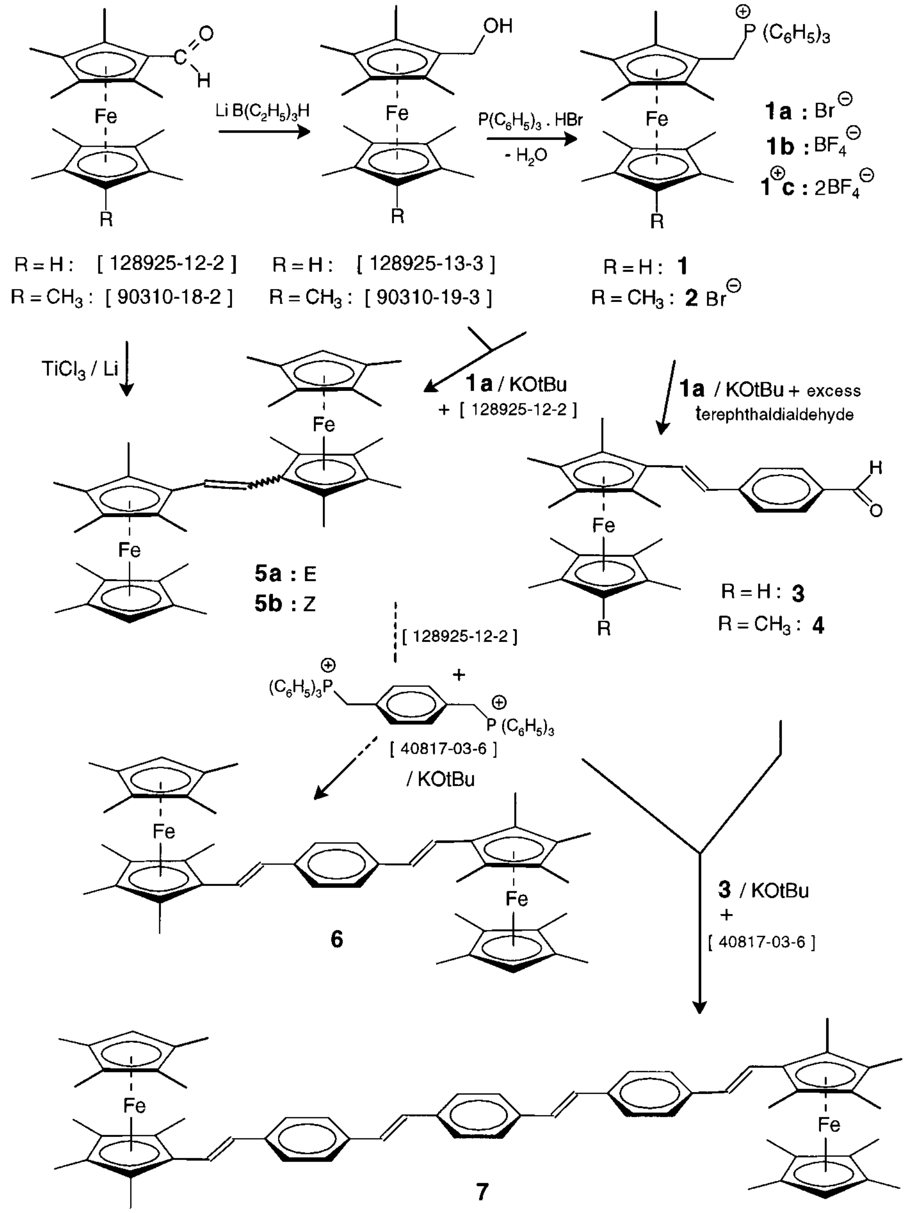
Scheme 2. Synthesis of Compounds 1−7



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As will also be seen in other following structures, the vinylene−phenylene subunit(s) is (are) usually out of plane to the ferrocenyl group and with respect to each other, resulting in a twisted conformation in the solid state with the consequence of crystallographically imposed chirality for these molecules. Therefore the contents of the unit cell correspond to a racemic mixture in these cases. For compound **4** the respective torsion angles are −6.0(3.2) and 10.8(3.4)° (Figure 1). Similar values for successive twisting of vinylene and phenylene segments have recently been published for a purely organic all-*E* oligo(phenylene−vinylene).[11d]

Reaction of the ylide derived from phosphonium salt **1a** with octamethylferrocenyl aldehyde yields an *E*/*Z*-mixture of the symmetrical olefin **5a,b**, whereas the *E*-isomer **5a** can be also obtained more conveniently by a McMurry[19] reaction from the aldehyde, in analogy to other carbonyl ferrocenes.[20]

Figure 2 (see also Table 1) shows the result of an X-ray structure analysis of **5a** which can be compared to the structure of (*E*)-diferrocenylethylene.[21] The overall structural parameters are of course very similar; only the torsion angle between the cyclopentadienyl plane and the double bond is higher in value (23.28° for **5a** and 15.1° for (*E*)-diferrocenylethylene), most likely due to the steric requirements of the methyl substituents.

Bis-olefination of terephthaldialdehyde with 2 equiv of octamethylferrocenyl ylide yields the vinylene−phenylene−vinylene bridged biferrocene **6** in the all-*E* conformation as is evidenced by the observation of the typical *E*-coupling constants of 16 Hz in the ^{1}H NMR spectrum. The solid-state structure (Figure 3, Table 1) confirms this stereochemistry with regard to the double bonds and shows that the vinylene phenylene cyclopentadienyl subunits are twisted in relation to each other with torsion angles of 20.68 and 12.60°, respectively.

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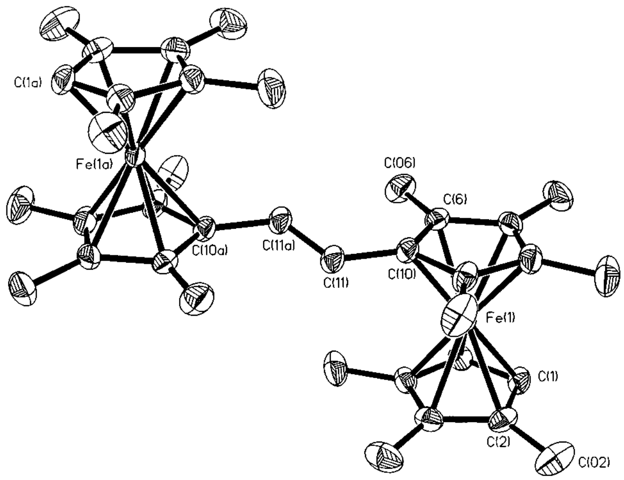

Figure 2. Molecular structure of **5a**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Numbering of the ferrocenyl carbons is analogous to **4**. Distances: Fe(1) to Cp plane [C(6)−C(10)] = 1.656(1) Å; Fe(1) to Cp plane [C(1)−C(5)] = 1.662(1) Å. Angles: Cp plane [C(6)−C(10)] to Cp plane [C(1)−C(5)] = 0.51(0.17)°; C(6)−C(10)−C(11)−C(11a) = −24.90(0.48)°.

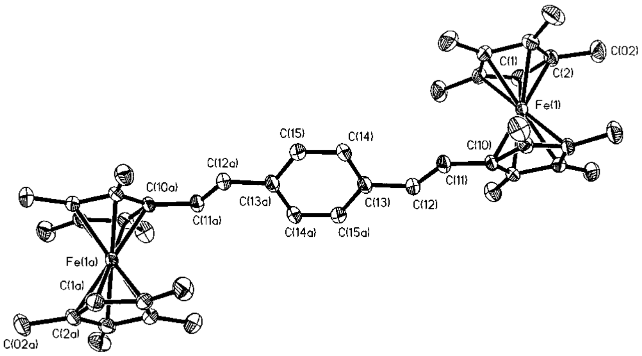

Figure 3. Molecular structure of **6**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Numbering of the ferrocenyl carbons is analogous to **4**. Distances: Fe(1)−Fe(1a) = 13.332(3) Å; Fe(1) to Cp plane [C(6)−C(10)] = 1.653(1) Å; Fe(1) to Cp plane [C(1)−C(5)] = 1.659(1) Å. Angles: Cp plane [C(6)−C(10)] to Cp plane [C(1)−C(5)] = 1.94(23)°; C(12)−C(11)−C(10)−C(6) = 20.68-(49)°; C(11)−C(12)−C(13)−C(14) = 12.6(47)°; Cp plane [C(6)−C(10)] to phenyl plane [C(13)−C(13a)] = 32.18(35)°.

The metal-to-metal distance (through space) equals 13.332(3) Å, and the sum of bond lengths (corresponding to the conjugation pathway from Fe(1) to Fe(1a)) is 16.845 Å. As can be seen from a packing plot (Figure 4), the relatively large angle (32.18°) of the plane of the phenylene ring [C(13)−C(15) and C(13a)−C(15a)] to the plane of the cyclopentadienyl ring [C(6)−C(10)] might be due to steric repulsion by neighboring molecules.

Further elongation of **3** (see Scheme 2) with the bis(ylide) prepared from *p*-xylylene−bis(triphenylphosphonium bromide) gives access to the (vinylene)$_4$−(phenylene)$_3$-bridged biferrocene **7** which precipitates during its formation from the reaction mixture and is insoluble in all common solvents (with the exception of hot toluene). Due to this poor solubility, characterization of **7** is limited to IR and FAB-mass spectroscopy and no NMR-spectroscopic determination of the *E*/*Z* stereochemistry is possible, but the low solubility indicates the existence of **7** as a rigid rod with an all-*E* configuration. Thus within this series of octa- or nonamethylated biferrocenes, despite the anticipated solubilizing properties of 16 or 18 methyl groups, the disappointing low solubility of **7** precludes the synthesis of longer systems.

(c) Pentamethylferrocenes (Scheme 3). By essentially analogous chemistry as described above the corresponding pentamethylated compounds are accessible: Reduction of pentamethylferrocenyl aldehyde[2c] with lithium triethylborohydride affords (hydroxymethyl)pentamethylferrocene **(8)**, which is a progenitor of (pentamethylferrocenyl)methylphosphonium salt and the ylide derived thereof, prepared by the method of Hamanaka and Kosuge.[18] Biferrocenes **9a,b** are obtained as an *E*/*Z*-mixture, from which the *E*-isomer **(9a)** can be separated by selective crystallization.

The X-ray structure of compound **9a** is interesting from a crystallographer's point of view: Only merohedrically twinned crystals were available, but the structure could be solved without problems with good final *R* values (Table 1); there are two independent half-molecules (with an inversion center located in the center of the olefinic bond) in the asymmetric unit. One of the molecules (Figure 5) is regularly ordered, whereas the second molecule (Figure 6) is disordered in a 50:50% ratio with regard to the orientations of the *trans*-olefinic moiety. Interestingly, the very same type of disordering has been published recently for the homologous (*E*)-1,2-bis(pentamethylruthenocenyl)ethylene.[22] The conformation of **9a** in the solid state [angle C(11a)−C(11)−C(10)−C(9) = −7.51°] can be compared to the analogous **5a**, which shows increased torsion due to steric hindrance by the methyl groups of the substituted cyclopentadienyl rings (see above).

Reaction of 2 equiv of pentamethylferrocenyl aldehyde with the bis(ylide) derived from *p*-xylylenebis(triphenylphosphonium bromide) yields the (vinylene)$_2$(phenylene)$_1$ "spacered" biferrocene **10**, which is the system analogous to compound **6**. The gross features of the crystal structures of **10** (Figure 7, Table 1) and **6** (see above) are quite similar, but in the case of **10** smaller torsion angles corresponding to less twisting of the vinylene phenylene cyclopentadienyl subunits [angle C(11)−C(12)−C(13)−C(14) = −1.79°; angle C(12)−C(11)−C(10)−C(9) = −11.37°] are observed, due to less interaction in the solid state by neighboring molecules. In accord with these smaller distortions, the metal-to-metal distance of **10** is slightly shortened to 13.291(2) Å in comparison to 13.332(3) Å in **6**.

Further elongation by similar methods as described for the octa- and nonamethylated compounds gives access to the (vinylene)$_2$(phenylene)$_2$-spacered aldehydes **11a,b**, which are a chiral molecules due to successive twisting of the cyclopentadienyl, vinylene, and phenylene subunits with respect to each other. In the crystalline state (Figure 8, Table 1) a racemic mixture of both enantiomers make up the contents of the unit cell, analogous to the structure of the one vinylene−phenylene unit shorter nonamethylated aldehyde **4**. The helical twisting in **11a** is reflected in torsion angles of −5.75, −2.67, 13.53, and 12.07°, respectively, similar in value to that for compound **4** and to that for a recently published all-*E* oligo(phenylene−vinylene).[11d]

Coupling of the mono(ylide) derived from *p*-xylylenebis(diethylphosphonate) with pentamethylferrocenyl al-

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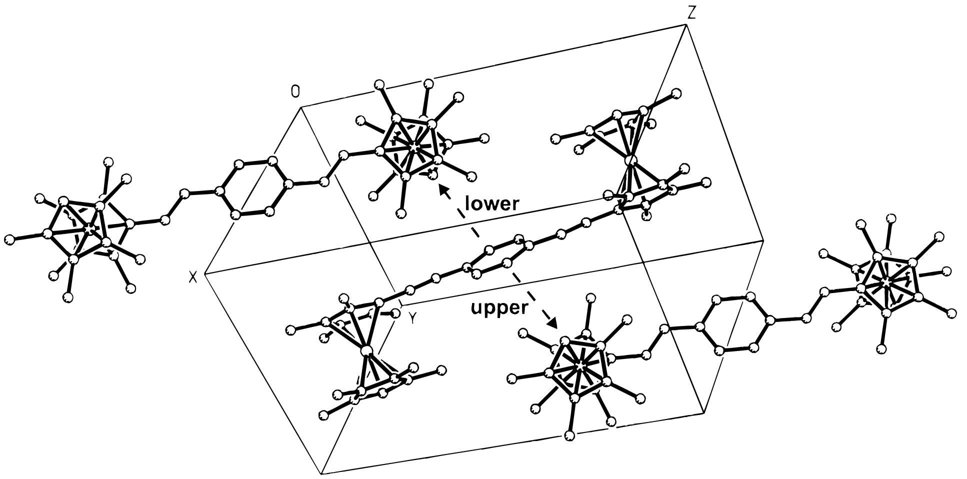

Figure 4. Packing of molecules of **6**.

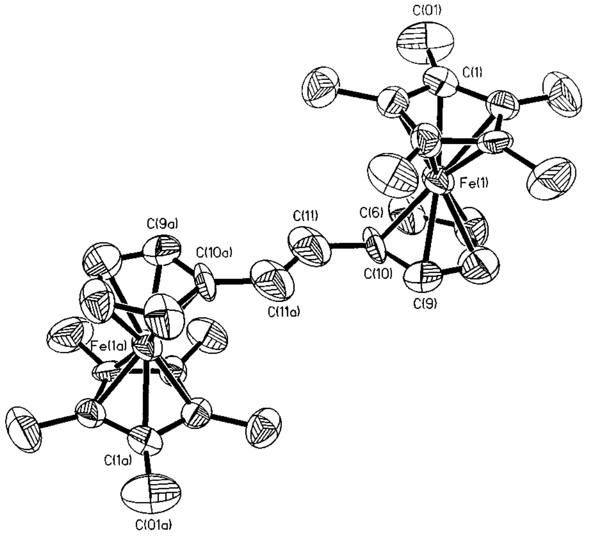

Figure 5. Molecular structure of **9a** (nondisordered molecule A), showing the atom-numbering scheme (hydrogen atoms omitted for clarity). Distances: Fe(1) to Cp plane [C(6)−C(10)] = 1.660(4) Å; Fe(1) to Cp* plane [C(1)−C(5)] = 1.644(4) Å. Angles: Cp plane [C(6)−C(10)] to Cp* plane [C(1)−C(5)] = 0.00(65)°; C(11a)−C(11)−C(10)−C(9) = −7.51(206)°.

dehyde *in situ* and subsequent coupling with **11a** yields (vinylene)$_4$(phenylene)$_3$-spacered biferrocene **12**, which shows good solubility in contrast to the essentially insoluble nonamethylated analogue **7**. The exact stereochemistry with regard to *E* or *Z* configurations of the newly formed double bonds cannot be determined due to the observation of only broad signals with unresolved coupling in the ^{1}H NMR spectrum. Although X-ray-quality crystals have not yet been obtained, **12** represents a soluble biferrocene with a conjugation pathway of 33.6 Å and an estimated metal-to-metal distance of 26.5 Å, assuming (i) an all *E*-configuration with respect to the double bonds, (ii) a trans conformation with respect to the terminal metallocenyl units, and (iii) twist angles of similar values as in the structurally characterized shorter compounds described above.

Reaction of 2 equiv of spacered aldehyde **11a** with the bis(ylide) of *p*-xylylenebis(triphenylphosphonium bromide) [Wittig reaction] or *p*-xylylenebis(diethylphosphonate) [Wittig−Horner reaction] affords α,ω-bis(pentamethylferrocenyl)(vinylene)$_6$(phenylene)$_5$ **(13)** in 59% or 42% yield, respectively, as a red powder with a melting point of 275−80 and 180−185 °C, respectively. Also, in the UV−vis spectra different λ_{max} absorptions (354 and 388 nm) are observed, indicating different stereochemistry of the newly formed double bonds. The Wittig−Horner methodology is known to favor *E*-configurated products,[8] suggesting an all-*E* configuration to the latter product. Similarly to **12**, NMR analysis did not give any conclusive result due to unresolved couplings and X-ray crystallography was not possible until now because the obtained crystals were to small for a single-crystal analysis. Nevertheless, compound **13** is still soluble with good solubility in dichloromethane and THF and constitutes to our knowledge the longest soluble π-conjugated biferrocene prepared so far. Under the same assumptions as stated for **12** (see above), the metal-to-metal distance in **13** can be estimated to approximately 40 Å with a conjugation pathway of 51 Å (Figure 9).

Conclusions and Perspectives. Nona-, octa-, and pentamethylated ferrocenyl aldehydes or methylphosphonium salts are the key synthons for the preparation of soluble, conjugated biferrocenes by standard Wittig and/or Wittig−Horner olefinations with vinylene−phenylene oligomers as bridging ligands between the two redox-active metallocenyl termini. The methyl substituents of the metallocenyl groups are necesssary to ensure increased solubility and enhanced stability of the oxidized species in comparison to nonmethylated spacered biferrocenes. Interestingly, the pentamethylated systems show superior solubility in direct comparison to their higher methylated analogues. These compounds serve as model systems for molecular wires, allowing the examination of the intervalence transfer (up to 40 Å) between the terminal electrophores of the mixed-valence biferrocenes. Such investigations are in progress and will be published elsewhere.

Experimental Section

General Comments. Standard techniques and instrumentation for spectroscopic and physical measurements have been described previously.[23] Tetramethylcyclopentadiene as a starting compound for the synthesis of octamethylferrocene and octamethylferrocene aldehyde was obtained from Raylo Chemicals, Edmonton, Alberta, Canada.

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(23) Lukasser, J.; Angleitner, H.; Schottenberger, H.; Kopacka, H.; Schweiger, M.; Bildstein, B.; Ongania, K.-H.; Wurst, K. *Organometallics* **1995**, *14*, 5566.

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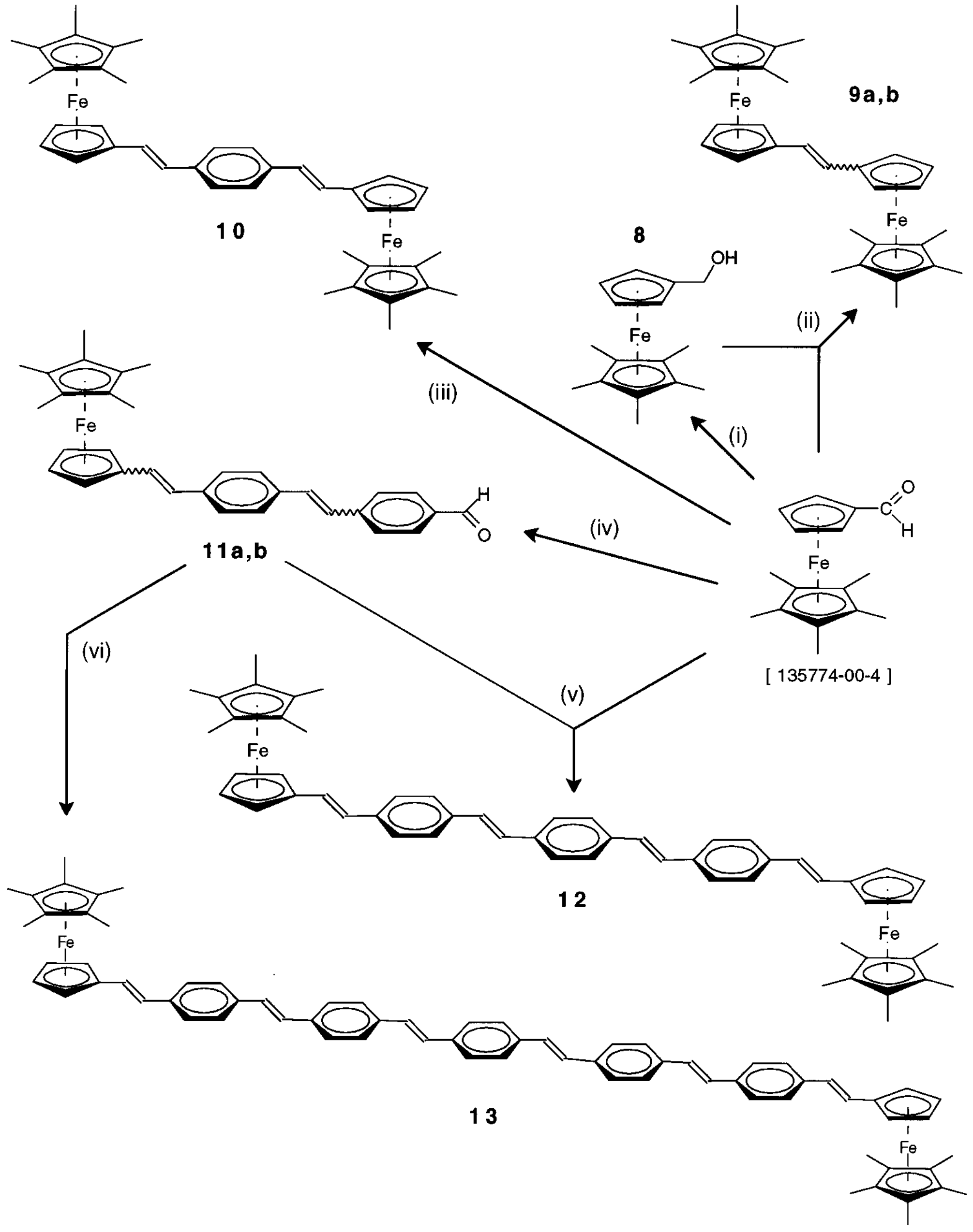
Scheme 3. Synthesis of Compounds 8−13



[a] Legend: (i) $LiB(C_2H_5)_3H$; (ii) $P(C_6H_5)_3{\cdot}HBr/{-}H_2O$; (iii) $(H_5C_6)_3P{=}CHC_6H_4CH{=}P(C_6H_5)_3$; (iv) $(H_5C_6)_3P{=}CHC_6H_4CH{=}O$/*t*-BuOK/$O{=}CHC_6H_4CH{=}O$; (v) $(EtO)_2P(O){=}CHC_6H_4CH_2P(O)(OEt)_2$/*t*-BuOK; (vi) $(EtO)_2P(O){=}CHC_6H_4CH{=}P(O)(OEt)_2$.

X-ray Structure Determinations of 1b,c, 2−4, 5a, 6, 9a, 10a, and 11a. A Siemens P4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 71.073$ pm) was used for data collection. Crystal data, data collection, and refinement parameters of **4**, **5a**, **6**, **9a**, **10**, and **11a** are summarized in Table 1 (for **1b,c**, **2**, and **3**, see Supporting Information). The unit cells were determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Data were measured via ω-scan and corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the ref 24, and an empirical absorption correction[25] was made. The structures were solved by direct methods, SHELXS-86,[26] and refined by a full-matrix least-squares procedure using SHELXL-93.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions. For tables of complete crystallographic data, bond lengths, bond angles, anisotropic thermal parameters, calculated hydrogen atomic coordinates, and final atomic coordinates, see the Supporting Information.

(1′,2,2′,3,3′,4,4′,5-Octamethylferrocenyl)methyl)triphenylphosphonium Bromide (1a) (Protocol According to Ref 18). A mixture of 1-(hydroxymethyl)-1′,2,2′,3,3′,4,4′,5-octamethylferrocene[2i] (1.300 g, 3.96 mmol) [CAS Reg. No. 128925-13-3], triphenylphosphine hydrobromide (1.360 g, 3.96 mmol, 1 mequiv), and 120 mL of toluene was refluxed for 30 min until separation from the eutectic condensate was com-

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(24) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, pp 72−98.

(25) (a) North, A. C. T.; Phillips, D.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351. (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(26) Sheldrick, G. M. *SHELXS-86: Program for Crystal Structure Solutions*; University of Göttingen: Göttingen, Germany, 1986.

(27) Sheldrick, G. M. *SHELXL-93: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

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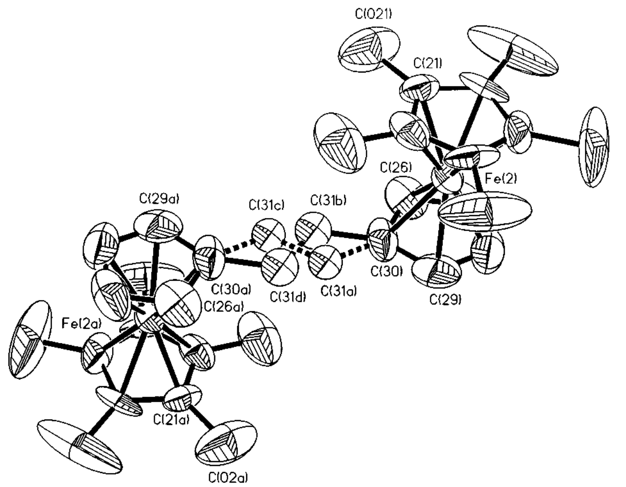

Figure 6. Molecular structure of **9a** (disordered molecule B), showing the two orientations (1:1) of the *E*-olefinic moiety C(30)−C(31a)−C(31c)−C(30a) and C(30)−C(31b)−C(31d)−C(30a), respectively.

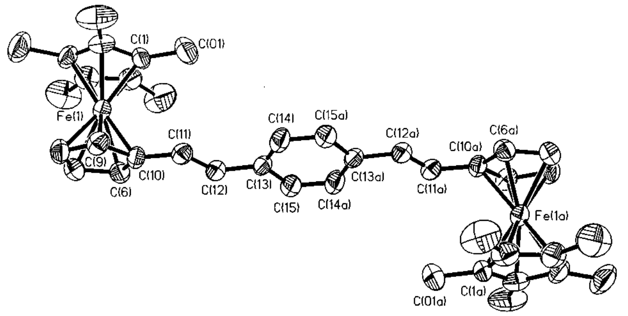

Figure 7. Molecular structure of **10**, showing the atom-numbering scheme (hydrogen atoms are omitted for clarity). Distances: Fe(1)−Fe(1a) = 13.291(2) Å; Fe(1) to Cp plane [C(6)−C(10)] = 1.660(2) Å; Fe(1) to Cp* plane [C(1)−C(5)] = 1.645(2) Å. Angles: Cp plane [C(6)−C(10)] to Cp* plane [C(1)−C(5)] = 2.71(0.33)°; C(12)−C(11)−C(10)−C(9) = −11.37(0.66)°; C(11)−C(12)−C(13)−C(14) = −1.79(0.66)°; Cp plane [C(6)−C(10)] to phenyl plane [C(13)−C(13a)] = 13.73°.

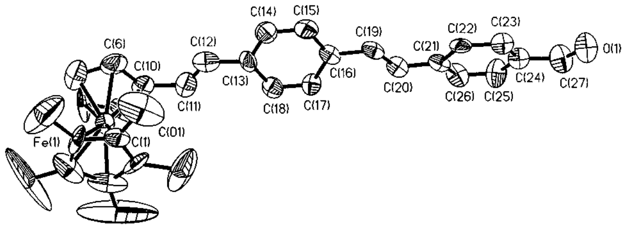

Figure 8. Molecular structure of **11a**, showing the atom-numbering scheme (hydrogen atoms are omitted for clarity). Distances: Fe(1) to Cp plane [C(6)−C(10)] = 1.649(5) Å; Fe(1) to Cp* plane [C(1)−C(5)] = 1.655(5) Å. Angles: Cp plane [C(6)−C(10)] to Cp* plane [C(1)−C(5)] = 1.70(0.96)°; Cp plane [C(6)−C(10)] to phenyl plane [C(13)−C(16)] = 7.28(0.78)°; phenyl plane [C(13)−C(16)] to phenyl plane [C(21)−C(26)] = 26.92(0.50)°; C(12)−C(11)−C(10)−C(6) = −5.75(1.9)°; C(11)−C(12)−C(13)−C(18) = −2.67(1.99)°; C(17)−C(16)−C(19)−C(20) = 13.53(2.11)°; C(19)−C(20)−C(21)−C(22) = 12.07(1.62)°.

plete in a Dean−Stark trap. By cooling, a yellow solid precipitated, which was filtered off and washed with 20 mL of ether and dried. The organic yellow filtrate, which contains some additional product, was reduced in volume (to about 20 mL) and extracted with 70 mL of water. The aqueous layer was washed with 30 mL of ether and re-extracted with CH_2Cl_2. The CH_2Cl_2 layers were combined, and the solvent was evaporated. Yield: 2.264 g (88%) of yellow air-stable microcrystalline solid.

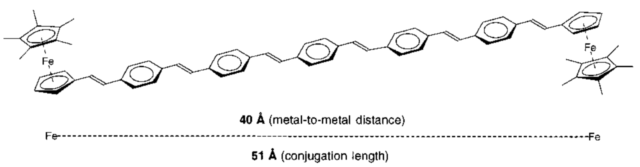

Figure 9. Estimated distances for **13**.

Data for 1a. Mp: 212−214 °C. Anal. Calcd for $C_{37}H_{42}BrFeP$: C, 68.01; H, 6.48. Found: C, 67.81; H, 6.45. MS (FAB): *m*/*z* 573.4 (M^+ of cation, 100%). UV−vis (CH_2Cl_2 [λ_{max} (nm)/log ϵ]): 266/4.03; 273/3.98; 397.0/2.87. IR data (KBr): 3054 w, 2961 m, 2940 m, 2900 m, 2853 m, 1586 m, 1481 m, 1437 s, 1381 m, 1107 s, 1032 m, 997 m, 864 m, 754 vs, 740 vs, 719 m, 713 m, 692 vs, 511 s, 499 s, 472 m, 449 m cm^{-1}. ^1H NMR (CD_3CN): δ 0.61, 1.29 , 2.25 (26H, 3s, CH_3 and CH_2); 3.71 (1H, bs, C−H of Cp); 7.64, 7.68, 7.84, 7.88 (15H, m, C_6H_5). ^{13}C NMR (CD_3CN): δ 8.70, 9.48, 10.65 (CH_3 and CH_2); 130.37, 135.15, 135.57 (C_6H_5).

((1′,2,2′,3,3′,4,4′,5-Octamethylferrocenyl)methyl)triphenylphosphonium Tetrafluoroborate (1b). To a solution of tetrafluoroboric acid (54% in ether) (0.050 g, 0.027 g, 0.30 mmol) in 40 mL of toluene was added a solution of triphenylphosphine (0.080 g, 0.30 mmol) in 40 mL of toluene and a solution of 1-(hydroxymethyl)-1′,2,2′,3,3′,4,4′,5-octamethylferrocene[28] (0.100 g, 0.30 mmol) [128925-13-3] in 30 mL of toluene. The mixture was refluxed for 10 min, until the separation from a eutectic condensate was complete in a Dean−Stark trap. TLC (silica/ether) showed no remaining starting material. By cooling, a yellow solid precipitated, which was filtered off and dried. Yield: 0.184 g (91.5%) of yellow air-stable microcrystalline solid.

Data for 1b. Mp: 248−249 °C. Anal. Calcd for $C_{37}H_{42}BF_4FeP$: C, 67.30; H, 6.41. Found: C, 67.23; H, 6.39. MS (FAB): *m*/*z* 573.2 (M^+ of cation, 100%). HR-MS (FAB): *m*/*z* 573.23266 (M^+ of cation; exact mass calcd for $C_{37}H_{42}FeP$, 573.2327). IR data (KBr): 3064 w, 2965 m, 2944 m, 2902 m, 1588 m, 1485 s, 1441 vs, 1381 s, 1111 vs (b), 997 s, 752 s, 739 s, 719 s, 692 vs, 519 s, 509 s, 497 s, 470 m, 451 m cm^{-1}. Single crystals were obtained from dichloromethane/acetone (v:v = 1:1) (Supporting Information, Figure 10).

((1′,2,2′,3,3′,4,4′,5-Octamethylferroceniumyl)methyl)triphenylphosphonium Bis(tetrafluoroborate) (1c). A 5 mg (0.0075 mmol) amount of **1b** was dissolved in 5 mL of a mixture (v:v = 1:1) of dichloromethane and acetone; under stirring, 3 drops of a 54% solution of tetrafluoroboric acid in ether and 5 drops of a 30% solution of H_2O_2 in water were added, and the mixture changed color to green. Upon standing the product crystallized and was isolated by filtration (2 mg, 35.4% yield) as dark green air-stable crystals.

Data for 1c. Mp: 285−290 °C. Anal. Calcd for $C_{37}H_{42}B_2F_8FeP$: C, 59.48; H, 5.67. Found: due to only 2 mg of material available, no analysis was possible. MS (FAB): not observed, 286.6 ($M^+/2$ of bis(cation)). UV−vis (CH_2Cl_2 [λ_{max} (nm)/log ϵ]): 276.0/4.24; 317.0/4.05. IR data (KBr): 3424 m (b), 2963 w, 2923 w, 2853 w, 1655 w, 1638 w, 1470 w, 1459 w, 1437 m, 1391 m, 1109 s, 1090 s, 1038 s, 758 m, 744 m, 721 m, 694 m, 515 w, 493 w cm^{-1}. Single crystals were obtained from dichloromethane/acetone (v:v = 1:1) (Supporting Information, Figure 11).

((Nonamethylferrocenyl)methyl)triphenylphosphonium Bromide (2) (Procedure According to the Method of Refs 18 and 28). To a cold solution (−50 °C) of formylnonamethylferrocene[2h,i] (0.634 g, 1.86 mmol) [90310-18-2] in 25 mL of anhydrous THF was added by syringe 2.05 mL of a 1 M solution of lithium triethylborohydride in THF (0.217 g, 2.05 mmol). The color of the solution immediately changed

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[28] Elsner, O. Diploma Thesis, Innsbruck, 1995; p 114.

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from deep red to dark yellow. The mixture was allowed to warm to ambient temperature and was stirred further for 90 min at room temperature. TLC (silica/*n*-hexane/ether = 1:1) showed no remaining starting material. After the THF was removed in vacuo the residue was extracted with 30 mL of water and 50 mL of ether, the combined etheral layers were washed with 80 mL of water, the ether was evaporated, the remaining crude solid product was dissolved in 100 mL of toluene, and triphenylphosphine hydrobromide (0.639 g, 1.86 mmol, 1 mequiv) was added in one portion. The mixture was refluxed for 15 min until the separation from eutectic condensate was complete in a Dean−Stark trap. By cooling, a yellow solid precipitated, which was filtered off, washed with 20 mL ether, and dried, affording 0.829 g (66.7%) of **2** as a yellow air-stable microcrystalline solid.

Data for 2. Mp: 228−233 °C, dec. Anal. Calcd for $C_{38}H_{44}BrFeP$: C, 68.38; H, 6.64. Found: C, 68.15; H, 6.62. MS (FAB): *m/z* 588 (M^+ of cation, 11%), 325.3 ($M^+ - P(C_6H_5)_3$, 100%). UV−vis (CH_2Cl_2 [λ_{max} (nm)/log ϵ]): 266.5/4.07; 273.5/4.04. IR data (KBr): 3052 w, 2967 m, 2940 m, 2900 m, 2861 m, 1481 m, 1437 vs, 1379 m, 1107 vs, 1032 m, 995 m, 754 s, 735 vs, 719 m, 690 s, 511 m, 501 s, 493 m cm^{-1}. Single crystals were obtained from CH_3CN (Supporting Information, Figure 12).

4-[2-(1′,2,2′,3,3′,4,4′,5-Octamethylferrocenyl)ethenyl]benzaldehyde (3). A Schlenk vessel was charged with ((1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)methyl)triphenylphosphonium bromide **(1a)** (1.00 g, 1.53 mmol) and 15 mL of anhydrous THF, the resulting suspension was cooled to −40 °C, potassium *tert*-butoxide (0.189 g, 1.68 mmol, 1.1 mequiv) was added in one portion, and the red suspension was stirred for 10 min in an ice/water bath. Subsequently, terephthalaldehyde (0.821 g, 6.12 mmol, 4 mequiv) was added, and the deep purple solution was allowed to warm to room temperature during 1 h. At this point TLC (silica/CH_2Cl_2/*n*-hexane = 2:1) showed no further reaction. The solvent was removed in vacuo, the residue was washed with 35 mL of saturated ammonium chloride solution and extracted with 50 mL ether, the combined organic layers were dried with Na_2SO_4, solvents were evaporated, and the crude product was purified by column chromatography (silica/CH_2Cl_2/*n*-hexane = 2:1), yielding 0.336 g (51.3%) of **3** as a purple air-stable solid.

Data for 3. Mp: 93−95 °C. Anal. Calcd for $C_{27}H_{33}FeO$: C, 75.52; H, 7.75. Found: C, 75.55; H, 7.75. MS (EI, 70 eV): *m/z* 428.5 (M^+, 100%). HR-MS (FAB): *m/z* 429.18804 (M^+; exact mass calcd for $C_{27}H_{33}FeO$, 429.18808). UV−vis (CH_2Cl_2 [λ_{max} (nm)/log ϵ]): 360.5/4.36; 530.0/3.64. IR data (KBr): 3040 w, 2961 w, 2900 w, 1697 vs, 1593 m, 1564 m, 1308 m, 1213 m, 1165 s, 1030 m, 962 s, 860 s, 843 m, 821 vs, 798 m, 787 s, 501 s, 468 s, 459 s, 451 s cm^{-1}. ^1H NMR (CD_3CN): δ 1.62, 1.66, 1.81, 1.97 (12H, each signal: 3H, s, CH_3 of Cp); 2.21 (12H, s, 4 × CH_3 of Cp); 3.31 (1H, s, CH of Cp); 6.77 (1H, d, $^3J_{trans}(^1H-^1H) = 16$ Hz, CH=CH); 7.14 (1H, d, $^3J_{trans}(^1H-^1H) = 16$ Hz, CH=CH); 7.66, 7.82 (4H, m, C_6H_4); 9.92 (1H, s, CH=O). ^{13}C NMR (CD_3CN): δ 9.52, 10.09, 11.39 (8 × CH_3); 72.39 (CH of Cp); 77.72, 80.75, 81.66, 83.57 (Cp); 125.1, 126.5, 131.1, 133.3 (C_6H_4 and CH=CH); 192.8 (CH=O). Single crystals were obtained from CH_2Cl_2 (Supporting Information, Figure 13).

4-[2-(Nonamethylferrocenyl)ethenyl]benzaldehyde (4). In analogy to the synthesis of **3**, compound **4** was prepared by starting from ((nonamethylferrocenyl)methyl)triphenylphosphonium bromide **(2)** (0.300 g, 0.45 mmol), resulting in 0.118 g (59.3% yield) of 4-[2-(nonamethylferrocenyl)ethenyl]benzaldehyde **(4)** as air-stable purple flakes.

Data for 4. Mp: 174−175 °C. Anal. Calcd for $C_{28}H_{35}FeO$: C, 75.84; H, 7.96. Found: C, 75.87; H, 7.98. MS (EI, 70 eV): *m/z* 442 (M^+, 100%). HR-MS (FAB): *m/z* 443.203749 (M^+; exact mass calcd for $C_{28}H_{35}FeO$, 443.203727). UV−vis (CH_2Cl_2 [λ_{max} (nm)/log ϵ]): 365.5/4.35; 539.0/3.64. IR data (KBr): 2965 w, 2948 w, 2903 w, 2857 w, 1694 m, 1626 w, 1598 vs, 1562 w, 1377 w, 1215 w, 1165 m, 1028 w, 820 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.67 (15H, s, 5 × CH_3 of unsubst. Cp); 1.78 (6H, s, 2 × CH_3 of subst. Cp); 1.95 (6H, s, 2 × CH_3 of subst. Cp); 6.70 (1H, d, $^3J_{trans}(^1H-^1H) = 16$ Hz, CH=CH); 7.03 (1H, d, $^3J_{trans}(^1H-^1H) = 16$ Hz, CH=CH); 7.56, 7.82 (4H, m, C_6H_4); 9.96 (1H, s, CH=O). ^{13}C NMR ($CDCl_3$): δ 9.30, 10.60 (9 × CH_3); 79.46, 79.73, 82.37 (Cp); 124.29, 125.34, 130.39, 132.15, 134.05, 145.09 (C_6H_4 and CH=CH); 191.46 (CH=O). Single crystals were obtained from CH_2Cl_2 (Table 1, Figure 1, Supporting Information).

1,2-Bis(1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)ethene (5a,b). Method A (Wittig Reaction). A suspension of ((1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)methyl)triphenylphosphonium bromide **(1a)** (0.350 g, 0.54 mmol) in 15 mL of anhydrous THF in a Schlenk vessel was cooled to −40 °C and converted to the corresponding ylide in the usual manner (see above) with 0.066 g (0.59 mmol, 1.1 mequiv) of potassium *tert*-butoxide. The red mixture was stirred for 5 min with the cooling bath removed, and 0.192 g (0.59 mmol, 1.1 mequiv) of formyl-1′,2,2′,3,3′,4, 4′,5-octamethylferrocene [CAS No. 128925-12-2] was added. The mixture was stirred at room temperature for 30 min and refluxed for a further 150 min. The THF was removed in vacuo, and the crude product was purified by column chromatography (silica, CH_2Cl_2/*n*-hexane = 2:1), yielding 0.067 g of **5a,b** (20.2% or 37.5% based on recovered starting material) as a red air-stable solid, consisting of a 1:3 mixture of *trans* **(5a)** and *cis* **(5b)** according to NMR analysis.

Method B (McMurry Reaction). A suspension of 5.254 g (14.2 mmol) of $TiCl_3\cdot 3THF$ in 40 mL of DME (dimethoxyethane) was reduced with 325 mg (46.9 mmol) of lithium powder by immersing the reaction vessel in an ultrasonic cleaning bath at room temperature for 30 min. To the resulting black suspension of low-valent titanium was added 300 mg (0.920 mmol) of formyl-1′,2,2′,3,3′,4, 4′,5-octamethylferrocene [CAS No. 128925-12-2], and sonication was continued for an additional $^1/_2$ h. Workup: DME was removed in vacuo, the mixture was poured into water, the organic material was extracted with three portions of ether, and the combined organic layers were washed with water and dried with Na_2SO_4. After removal of solvents, the crude product mixture was purified by chromatography as described above, yielding 0.164 g (28.7%) of a mixture of *trans* **(5a)** and *cis* **(5b)** according to NMR analysis. Fractional crystallization from *n*-hexane afforded 69 mg (12.1% yield) of large single crystals of *trans*-**(5a)**.

Data for 5a,b. MS (EI, 70 eV): *m/z* 620.5 (M^+, 100%); 312 $(CH_3)_8FcCH_2$, 97%). IR data (KBr): 3056 w, 2905 w, 2716 w, 1628 w, 1449 m, 1427 m, 1375 m, 1261 m, 1084 m, 1028 m, 955 m, 858 m, 820 s, 802 s, 694 m, 507 m, 464 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.43, 1.56, 1.60, 1.63, 1.67, 1.69, 1.72, 1.74, 1.81, 1.86, 1.98 (CH_3); 3.30 (s, CH of Cp); 6.68, 6.85, 7.33, 7.42 (CH=CH). ^{13}C NMR ($CDCl_3$): δ 9.06, 9.28, 9.66, 9.75, 9.83, 10.93, 11.02, 11.08, 11.15 (8 × CH_3); 71.28, 79.20, 79.48, 80.60, 80.75, 81.74 (Cp); 125.63, 126.38, 126.47, 128.47, 128.62, 133.48, 133.87 (CH of the *E* and *Z* double bonds).

Data for 5a. Mp: 219−220 °C. Anal. Calcd for $C_{38}H_{52}Fe_2$: C, 73.55; H, 8.45. Found: C, 73.54; H, 8.43. MS (EI, 70 eV): *m/z* 620.5 (M^+, 100%). UV−vis (CH_2Cl_2 [λ_{max} (nm)/log ϵ]): 318.0/4.23; 461.5/3.26. IR data (KBr): 3060 w, 2965 s, 2944 m, 2859 s, 2714 m, 1630 w, 1476 w, 1458 m, 1439 m, 1374 s, 1261 w, 1111 m, 1080 w, 1028 s, 966 m, 818 m, 515 w, 482 w, 449 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.60, 1.63, 1.69, 1.79 (CH_3); 3.30 (s, CH of Cp); 6.24 (2H, s(br), CH=CH). ^{13}C NMR (CD_2Cl_2): δ 9.36, 9.91, 11.25 (CH_3); 71.76, 78.48, 80.85, 81.02, 81.51, 81.72 (Cp); 125.42 (CH=CH). Single crystals were obtained from *n*-hexane (Table 1, Figure 2; Supporting Information).

1,4-Bis[2-(1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)ethenyl]benzene (6). Similarly to the synthesis of compounds **5a,b**, ((1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)methyl)triphenylphosphonium bromide **(1a)** (0.250 g, 0.383 mmol) was converted

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Table 1. Crystal and Structure Refinement for Data for 4, 5a, 6, 9a, 10, and 11a

	4	**5a**	**6**
mol formula	$C_{28}H_{34}FeO$	$C_{40}H_{50}Fe_2$	$C_{46}H_{58}Fe_2$
fw	442.40	642.50	722.62
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (pm)	1425.0(5)	956.5(3)	995.4(2)
b (pm)	1114.9(5)	1241.5(3)	1176.2(2)
c (pm)	1497.4(12)	1414.3(3)	1659.7(4)
α (deg)	90	90	90
β (deg)	104.58(4)	106.11(2)	102.90(2)
γ (deg)	90	90	90
V (nm^3)	2.302(2)	1.6135(7)	1.8941(7)
Z	4	2	2
temp (K)	213(2)	213(2)	223(2)
d(calcd) (Mg/m^3)	1.276	1.322	1.267
abs coeff (mm^{-1})	0.672	0.926	0.797
F(000)	944	684	772
color, habit	red platelet	red column	red prism
cryst size (mm)	0.38 × 0.32 × 0.19	0.85 × 0.3 × 0.2	0.6 × 0.3 × 0.11
θ range for data collcn (deg)	3.35−20.50	3.20−24.99	3.06−24.00
index ranges	$0 \leq h \leq 14$	$0 \leq h \leq 11$	$-1 \leq h \leq 10$
	$-1 \leq k \leq 11$	$-1 \leq k \leq 14$	$-1 \leq k \leq 12$
	$-14 \leq l \leq 15$	$-16 \leq l \leq 16$	$-18 \leq l \leq 18$
no. of rflns collcd	2286	3295	3803
no. of indep rflns	2015 ($R_{int} = 0.0426$)	2824 ($R_{int} = 0.0217$)	2880 ($R_{int} = 0.0251$)
no. of rflns with $I > 2\sigma(I)$	1587	2412	2315
abs cor	none	ψ-scan	ψ-scan
max and min transm		0.643 and 0.589	0.925 and 0.808
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parms	1962/0/270	2818/0/189	2880/0/333
goodness-of-fit on F^2	1.115	1.042	1.038
final R indices [$I > 2\sigma(I)$	$R_1 = 0.1106$	$R_1 = 0.0334$	$R_1 = 0.0354$
	$wR_2 = 0.2940$	$wR_2 = 0.0782$	$wR_2 = 0.0815$
R indices (all data)	$R_1 = 0.1445$	$R_1 = 0.0444$	$R_1 = 0.0519$
	$wR_2 = 0.4003$	$wR_2 = 0.0883$	$wR_2 = 0.0897$
largest diff peak and hole (e·nm^{-3})	1590 and −657	294 and −403	244 and −234

	9a	**10**	**11a**
mol formula	$C_{32}H_{40}Fe_2$	$C_{40}H_{46}Fe_2$	$C_{32}H_{32}FeO$
fw	536.34	638.47	488.43
cryst system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
a (pm)	1759.0(6)	831.6(2)	838.9(4)
b (pm)	1085.6(3)	937.7(2)	883.3(6)
c (pm)	1673.0(3)	1239.9(2)	1795.9(9)
α (deg)	90	98.86(1)	90
β (deg)	118.32(2)	108.86(1)	101.24(3)
γ (deg)	90	107.41(1)	90
V (nm^3)	2.8123(13)	0.8387(3)	1.3052(13)
Z	4	1	2
temp (K)	208(2)	213(2)	213(2)
d(calcd) (Mg/m^3)	1.267	1.264	1.243
abs coeff (mm^{-1})	1.049	0.891	0.599
F(000)	1136	338	516
color, habit	red platelet	red platelet	red platelet
cryst size (nm)	0.55 × 0.55 × 0.12	0.5 × 0.25 × 0.09	0.3 × 0.3 × 0.05
θ range for data collcn (deg)	3.07−21.00	3.19−23.00	2.31−18.50
index ranges	$-17 \leq h \leq 6$	$-1 \leq h \leq 8$	$-1 \leq h \leq 7$
	$-10 \leq k \leq 1$	$-9 \leq k \leq 9$	$-16 \leq l \leq 15$
	$-12 \leq k \leq 14$	$-13 \leq l \leq 13$	$-16 \leq l \leq 15$
no. of rflns collcd	3113	2843	2100
no. of indep rflns	2635 ($R_{int} = 0.0194$)	2284 ($R_{int} = 0.0243$)	1767 ($R_{int} = 0.0287$)
no. of rflns with $I > 2\sigma(I)$	2198	1838	1430
abs cor	none	ψ-scan	ψ-scan
max and min transm		0.861 and 0.750	0.926 and 0.862
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parms	2635/0/321	2284/0/195	1767/1/312
goodness-of-fit on F^2	1.069	1.044	1.090
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0511$	$R_1 = 0.0434$	$R_1 = 0.0466$
	$wR_2 = 0.1131$	$wR_2 = 0.968$	$wR_2 = 0.0933$
R indices (all data)	$R_1 = 0.0679$	$R_1 = 0.0613$	$R_1 = 0.0702$
	$wR_2 = 0.1222$	$wR_2 = 0.1061$	$wR_2 = 0.1035$
largest diff peak and hole (e·nm^{-3})	373 and −428	352 and −261	246 and −203

with 0.047 g (0.420 mmol, 1.1 mequiv) of potassium *tert*-butoxide to the corresponding ylide and olefinated with 0.026 g (0.191 mmol, 0.5 mequiv) of terephthalaldehyde. After the usual workup (see above) and chromatography (silica, CH_2Cl_2/*n*-hexane = 2:1) 0.075 g (54.4%) of **6** was obtained as an air-stable, orange-red microcrystalline solid.

Data for (6). Mp: 158−161 °C. Anal. Calcd for $C_{46}H_{58}Fe_2$: C, 76.45; H, 8.09. Found: C, 76.53; H, 8.06. MS (EI, 70

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eV): *m/z* 722.5 (M^+, 100%). HR-MS (FAB): *m/z* 722.32348 (M^+; exact mass calcd for $C_{46}H_{58}Fe_2$, 722.32372). UV−vis (CH_2Cl_2 [λ_{max} (nm)/log ϵ]): 362/4.29; 490/3.60. IR data (KBr): 3056 w, 2963 w, 2902 w, 1626 w, 1468 w, 1447 w, 1427 w, 1373 m, 1261 m, 1095 m, 1028 s, 955 m, 858 m, 820 vs, 800 vs, 505 m, 460 vs, 445 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.52, 1.65, 1.70, 1.80, 1.96 (48H, 5 × s, 16 × CH_3); 3.29 (2H, s, CH of Cp); 6.65 (2H, d, $^3J_{trans}(^1H-^1H) = 16$ Hz, CH=CH); 6.85 (2H, d, $^3J_{trans}(^1H-^1H) = 16$ Hz, CH=CH); 7.40 (4H, s, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 8.44, 8.83, 9.31, 9.44, 9.88, 10.65, 11.13, 11.18 (16 × CH_3); 71.47, 79.37, 80.82, 80.96, 81.94 (Cp); 125.68, 126.47, 126.51 (C_6H_4 and CH=CH). Single crystals were obtained from acetone (Table 1, Figures 3 and 4; Supporting Information).

1,4-Bis{2-[4-(2-(1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)-ethenyl)phenyl]ethenyl}benzene (7). *p*-Xylylenebis(triphenylphosphonium bromide) (0.167 g, 0.21 mmol) [CAS Reg. No. 40817-03-6] was converted to the corresponding bis(ylide) with potassium *tert*-butoxide (0.050 g, 0.45 mmol, 2.1 mequiv) in THF and was allowed to react with 2 equiv of 4-[2-(1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)ethenyl]benzaldehyde **(3)** (0.200 g, 0.47 mmol, 2.2 mequiv) for 2 h at room temperature and for additional 15 min at reflux temperature. During the course of the reaction the product precipitated as a red solid. After cooling to ambient temperature 30 mL of ether was added and the precipitate was filtered off, washed with one portion of ether, water, and acetone, and dried in vacuo, yielding 0.040 g (20.4%) of **7** as an air-stable red solid.

Data for 7. Mp: 200−205 °C, dec. Anal. Calcd for $C_{62}H_{70}Fe_2$: C, 80.34; H, 7.61. Found: C, 80.40; H, 7.58. MS (FAB): *m/z* 926.5 (M^+, 3%); 307 $(CH_3)_8Fc$, 100%). UV−vis (CH_2Cl_2 [λ_{max} (nm)/log ϵ]): 400.5/4.87; 503.0/4.12. IR data (KBr): 3023 m, 2965 m, 2944 m, 2902 m, 2859 m, 1626 s, 1595 s, 1516 s, 1425 m, 1377 m, 1109 m, 1080 m, 1030 s, 960 vs, 854 m, 825 s, 547 s, 466 s cm^{-1}. Due to insolubility in all common solvents, no NMR analysis was possible.

1,2,3,4,5-Pentamethyl-1′-(hydroxymethyl)ferrocene (8). A solution of 820 mg (2.9 mmol) of 1,2,3,4,5-pentamethyl-1′-formylferrocene in 30 mL of THF was cooled to 0 °C, and 4.4 mL of a 1.0 M THF solution of lithium triethylborohydride (4.4 mmol) was added. After the solution was stirred for 5 min the cooling bath was removed, and stirring was continued for a further 60 min. Aqueous workup and chromatography (aluminum oxide, *n*-hexane/ether (v/v = 1/1) as eluent) afforded 700 mg (2.5 mmol, 86.2% yield) of 1,2,3,4,5-pentamethyl-1′-(hydroxymethyl)ferrocene **(8)** as yellow crystals.

Data for 8. Mp: 90−92 °C. Anal. Calcd for $C_{16}H_{22}FeO$: C, 67.15; H, 7.75. Found: C, 66.88; H, 7.72. MS (EI, 70 eV): *m/z* 286 (M^+, 98%); 270 ($M^+ - OH$, 23%); 256 ($M^+ - CH_2OH$, 38%). IR data (KBr): 3664−3269 m, br; 2900 m, 1478 m, 1382 s, 1038 s, 814 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.65 (15H, s, CH_3); 3.72 (5H, br m, subst. Cp and OH); 4.20 (2H, s, CH_2). ^{13}C NMR (CD_2Cl_2): δ 10.4 (CH_3); 59.9 (CH_2); 71.0, 73.0 (Cp); 79.9 (C_1' of subst. Cp); 80.4 (Cp*).

1,2-Bis(1,2,3,4,5-pentamethylferrocen-1′-yl)ethylene ("(α,ω-bis(pentamethylferrocenyl)[vinylene]") (9a,b). In a Schlenk vessel 200 mg (0.7 mmol) of 1,2,3,4,5-pentamethyl-1′-(hydroxymethyl)ferrocene **(8)** was dissolved in 20 mL of dry dichloromethane, and the contents were cooled to −80 °C. To the stirred solution was added 0.22 mL (1.6 mmol) of a 54% etheral solution of tetrafluoroboric acid, causing immediate change in color from orange to intense red, indicative of formation of the corresponding (pentamethylferrocenyl)methylium tetrafluoroborate. The mixture was stirred for a further 10 min at a temperature of −80 °C, and 184 mg (0.7 mmol) of triphenylphosphine was added; the cooling bath was removed, and stirring was continued for 1 h, during which time the color changed from red to brownish yellow. Solvents and volatile materials were removed in vacuo, the residue was triturated four times with 20 mL portions of diethyl ether, and the resulting green ((1,2,3,4,5-pentamethylferrocen-1′-yl)methyl)-triphenylphosphonium tetrafluoroborate was dried in vacuo, yielding 340 mg (0.56 mmol, 78.6%) of green, solid material. Mp: 85−90 °C. MS (FAB): *m/z* 531.29 (M^+ of cation, 100%). IR (KBr): 3058 m, 2964 m, 2906 m, 1629 w, 1588 w, 1482 m, 1385 m, 1111 s, 1061 s, 1040 s, 998 s, 920 m, 745 s cm^{-1}. No NMR spectra could be obtained, probably due to paramagnetic impurities, but the phosphonium salt is sufficiently pure for the following step:

((Pentamethylferrocenyl)methyl)phosphonium tetrafluoroborate (108 mg, 0.17 mmol) was converted to the correspondig ylide with 19 mg (0.17 mmol) of potassium *tert*-butoxide in THF. Addition of 48 mg (0.17 mmol) of 1,2,3,4,5-pentamethyl-1′-formylferrocene and aqueous workup and chromatography (silica, *n*-hexane) yielded a red oil, consisting of *trans*-1,2-bis-(1,2,3,4,5-pentamethylferrocen-1′-yl)ethylene **(9a)** and *cis*-1,2-bis-(1,2,3,4,5-pentamethylferrocen-1′-yl)ethylene **(9b)**, respectively. From this mixture, crystallization afforded red crystals (35 mg, 0.065 mmol, 38.4% yield) of the *trans*-isomer **(9a)**: Mp 210 °C.

Data for the Mixture of 9a and 9b. Anal. Calcd for $C_{32}H_{40}Fe_2$: C, 71.66; H, 7.52. Found: C, 71.59; H, 7.54. MS (EI, 70 eV): *m/z* 536.5 (M^+, 59%); 404.5 ($M^+ - Cp^*$, 44%). HR-MS (FAB): *m/z* 536.18280 (M^+; exact mass calcd for $C_{32}H_{40}Fe_2$, 536.18288). UV−vis (THF [λ_{max} (nm)/log ϵ]): 453.0/2.99; 460.0/2.99. IR data (KBr): 3081 m, 2964 s, 2946 s, 2904 s, 2858 s, 1623 w, 1476 s, 1453 s, 1428 m, 1380 s, 1262 m, 1071 s, 1032 s, 951 m, 851 m cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.82−1.87 (30H, 3s, CH_3); 3.46−3.80 (8H, 6m, subst. Cp); 6.02, 6.12 (2H, 2s, CH=CH). ^{13}C NMR ($CDCl_3$): δ 11.0−11.1 (CH_3); 69.1−80.1 (Cp and Cp*); 123.3, 124.3 (CH=CH). Single crystals of **9a** were obtained from *n*-hexane (Table 1, Figures 5 and 6; Supporting Information).

1,4-Bis(1,2,3,4,5-pentamethylferrocen-1′-yl-ethenyl)-benzene ("(α,ω-Bis(pentamethylferrocenyl)[(vinylene)$_2$-(phenylene)]") (10). A 126 mg (0.33 mmol) amount of *p*-xylylenebis(diethylphosphonate) [CAS Reg. No. 4546-04-7],[15] dissolved in 30 mL THF, was converted to the corresponding bis(ylide) by addition of 79 mg (0.7 mmol) of potassium *tert*-butoxide at a temperature of −80 °C and subsequent warming to room temperature under efficient stirring. The resulting orange solution was cooled to −80 °C, and 200 mg (0.7 mmol) of 1,2,3,4,5-pentamethy-1′-formylferrocene was added. The cooling bath was removed, and the mixture was stirred for 6 h. Aqueous workup and chromatography (silica, ether/*n*-hexane (v/v = 1/1) as eluent) afforded 155 mg (0.24 mmol, 72.7% yield) of *trans,trans*-1,4-bis((1,2,3,4,5-pentamethylferrocen-1′-yl)ethenyl)benzene **(10)** as red crystals.

Data for 10. Mp: 199−203 °C. Anal. Calcd for $C_{40}H_{46}Fe_2$: C, 75.25; H, 7.26. Found: C, 75.18; H, 7.29. MS (EI, 70 eV): *m/z* 638.5 (M^+, 100%); 448.5 ($M^+ - FeCp^*$, 19%). HR-MS (FAB): *m/z* 638.23864 (M^+; exact mass calcd for $C_{40}H_{46}Fe_2$, 638.22982). UV−vis (THF [λ_{max} (nm)/log ϵ]): 358/4.57; 481/3.97. IR data (KBr): 2964 s, 2906 s, 2856 s, 1630 m, 1513 m, 1474 m, 1459 m, 1380 m, 1262 m, 1096 m, 1071 m, 1032 s, 953 s, 861 m cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.83 (30H, s, CH_3); 3.88 (4H, m, subst. Cp); 3.94 (4H, subst. Cp); 6.56, 6.72 (each signal: 2H, d, $^3J_{trans}(^1H-^1H) = 15.9$ Hz, CH=CH); 7.42 (4H, s, C_6H_4). ^{13}C NMR (CD_2Cl_2): δ 11.1 (CH_3); 69.8, 73.8 (Cp); 81.3 (Cp*); 83.8 (C_1 of subst. Cp); 125.2, 126.1, 126.7, 137.0 (CH=CH and (C_6H_4). Single crystals were obtained from CH_2Cl_2/EtOH (Table 1, Figure 7; Supporting Information).

4-(2-(1,2,3,4,5-Pentamethylferrocen-1′-yl)ethenyl)-4′-formylstilbene ("Pentamethylferrocenyl[(vinylene)$_2$-(phenylene)$_2$] Aldehyde") (11a,b). To a suspension of 3 g (3.8 mmol) of *p*-xylylenebis(triphenylphosphonium bromide) [CAS Reg. No. 40817-03-6] in 50 mL of THF at a temperature of −30 °C was added 430 mg (3.8 mmol) of potassium *tert*-butoxide, and the mixture was stirred for 0.5 h at −30 °C. The cooling bath was removed, and stirring was continued for 45 min, during which time the color of the solution gradually changed to orange, indicative of formation of the mono(ylide). The mixture was coooled to −30 °C, 700 mg (2.5 mmol) of 1,2,3,4,5-pentamethyl-1′-formylferrocene was added, and further stirring for 2 h afforded the *mono*-olefination product in

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solution. The mixture was once again cooled to −30 °C, and with 430 mg (3.8 mmol) of potassium *tert*-butoxide the second phosphonium group was converted to the ylide, which was olefinated with 510 mg (3.8 mmol) of terephthalaldehyde in a similar manner as described above. After the mixture was stirred overnight, aqueous workup and chromatography (silica, ether/hexane (v/v = 1/2) as eluent) produced three products. The first orange fraction yielded 250 mg of a mixture of **10** and 4-(2-(1,2,3,4,5-pentamethylferrocen-1′-yl)ethenyl)-4′-methylstilbene methylferrocene, and the second and third red fractions were different isomers (700 mg, 1.43 mmol, 57.3% yield of *trans*/*trans*-isomer **(11a)** and 240 mg, 0.49 mmol, 19.6% yield of *cis*/*trans*-isomer **(11b)**) of the desired aldehyde:

Data for 11a. Red crystals formed. Mp: 220 °C, dec. Anal. Calcd for $C_{32}H_{32}FeO$: C, 78.69; H, 6.60. Found: C, 78.65; H, 6.56. MS (EI, 70 eV): *m/z* 488.5 (M^+, 100%); 353.5 ($M^+ - Cp^*$, 63%). HR-MS (FAB): *m/z* 488.17828 (M^+; exact mass calcd for $C_{32}H_{32}Fe_2$, 488.18026). IR data (KBr): 2966 w, 2906 m, 2856 w, 2746 w, 1698 s, 1690 s, 1659 s, 1598 s, 1383 m, 1034 m, 824 s cm^{-1}. ^1H NMR (acetone-d_6): δ 1.82 (15H, s, CH_3); 3.87−4.28 (4H, m, subst. Cp); 6.64−7.93 (12H, m, olefinic and aromatic H); 9.71, 10.01 (1H, 2s, CHO). ^{13}C NMR (acetone-d_6): δ 11.0 (CH_3); 70.3−77.9 (Cp and Cp*); 125.1−132.7 (olefinic and aromatic C); 192.1 (CHO). Single crystals were obtained from *n*-hexane (Table 1, Figure 8; Supporting Information).

Data for 11b. A red oil formed. Mp: not available. MS (FAB): *m/z* 489 (M^+, 23%); 461.6 ($M^+ - CHO$, 15%); 281.2 ($M^+ - CH{=}CHC_6H_4CHO$, 97%). IR data (KBr): 2962 w, 2927 w, 2860 w, 1729 s, 1702 s, 1602 s, 1382 m, 1119 s, 1040 s, 807 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.81 (15H, s, CH_3); 3.84−4.32 (4H, m, subst. Cp); 6.54−7.72 (12H, m, olefinic and aromatic H); 9.93, 9.95 (1H, 2s, CHO). ^{13}C NMR ($CDCl_3$): δ 11.0 (CH_3); 68.2−76.2 (Cp and Cp*); 126.1−131.9 (olefinic and aromatic C); not observed, CHO.

α,*ω*-Bis(pentamethylferrocenyl)[(vinylene)$_4$(phenylene)$_3$] (12). A 57 mg (0.15 mmol) amount of *p*-xylylenebis(diethylphosphonate) [CAS Reg. No. 4546-04-7],[15] dissolved in 20 mL of THF, was converted to the corresponding mono(ylide) by addition of 17 mg (0.15 mmol) of potassium *tert*-butoxide at a temperature of −80 °C and subsequent warming to room temperature under efficient stirring. The resulting orange solution was cooled to −80 °C, 56 mg (0.15 mmol) of 1,2,3,4,5-pentamethyl-1′-formylferrocene was added, and the mixture was refluxed for 3 h to complete the mono-olefination. After cooling of the mixture to −80 °C a second portion of 17 mg (0.15 mmol) of potassium *tert*-butoxide was added and the mixture was allowed to warm to room temperature. The so formed dark solution of the ylide was olefinated by addition of 73 mg (0.15 mmol) of 4-(2-(1,2,3,4,5-pentamethylferrocen-1′-yl)ethenyl)-4′-formylstilbene **(11a)** at a temperature of −80 °C and subsequent refluxing for 12 h. Aqueous workup and chromatography (silica, ether/*n*-hexane (v/v = 1/1)) afforded 50 mg (0.06 mmol, 40% yield) of **12** as red crystals.

Data for 12. Mp: 185−190 °C. Anal. Calcd for $C_{56}H_{58}Fe_2$: C, 79.81; H, 6.94. Found: C, 80.06; H, 6.97. MS (FAB): *m/z* 843.1 (M^+, 16%); 652.3 ($M^+ - FeCp^*$, 10%). HR-MS (FAB): *m/z* 842.32238 (M^+; exact mass calcd for $C_{56}H_{58}Fe_2$, 842.32373). UV−vis (THF [λ_{max} (nm)/log ϵ]): 359/4.38; 481/3.73. IR data (KBr): 2964 m, 2925 m, 1630 w, 1262 s, 1100 s, 1028 s, 861 m, 803 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.84 (30H, s, CH_3); 3.86 (4H, m, subst. Cp); 3.92 (4H, subst. Cp); 6.53−6.76 (8H, m, CH=CH); 7.41 (12H, s, C_6H_4). ^{13}C NMR (CD_2Cl_2): δ 11.1 (CH_3); 69.8, 73.7 (Cp); 81.3 (Cp*); 83.8 (C_1 of subst. Cp); 125.2−126.7 (CH=CH and C_6H_4).

α,*ω*-Bis(pentamethylferrocenyl)[(vinylene)$_6$(phenylene)$_5$] (13). Method A (Wittig Reaction). A 100 mg (0.125 mmol) amount of *p*-xylylenebis(triphenylphosphonium bromide) was converted to the corresponding bis(ylide) by deprotonation with 31 mg (0.25 mmol) of potassium *tert*-butoxide in a similar manner as described above. Addition of 120 mg (0.25 mmol) of 4-(2-(1,2,3,4,5-pentamethylferrocen-1′-yl)ethenyl)-4′-formylstilbene ("pentamethylferrocenyl[(ene)$_2$(phenylene)$_2$]aldehyde") **(11a)** at a temperature of −80 °C and stirring overnight gave a red solution. Aqueous workup and chromatography (silica, dichloromethane/hexane (v/v = 1/2)) yielded 46 mg (0.05 mmol, 59%) α,*ω*-bis(pentamethylferrocenyl)[(ene)$_6$(phenylene)$_5$] **(13)** as the first fraction, and 40 mg of unreacted pentamethylferrocenyl[(ene)$_2$(phenylene)$_2$] aldehyde **(11a)** as the second fraction.

Method B (Wittig−Horner Reaction). A 57 mg (0.15 mmol) amount of *p*-xylylenebis(diethylphosphonate)[15] was converted to the corresponding bis(ylide) by deprotonation with 35 mg (0.31 mmol) of potassium *tert*-butoxide in a similar manner as described above. Addition of 150 mg (0.31 mmol) of 4-(2-(1,2,3,4,5-pentamethylferrocen-1′-yl)ethenyl)-4′-formylstilbene ("pentamethylferrocenyl[(ene)$_2$(phenylene)$_2$] aldehyde") **(11a)** at a temperature of −80 °C and subsequent refluxing for 5 days gave a red solution. Aqueous workup and chromatography (silica, dichloromethane/hexane (v/v = 1/2)) yielded 50 mg (0.05 mmol, 42%) of α,*ω*-bis(pentamethylferrocenyl)[(ene)$_6$(phenylene)$_5$] **(13)** as the first fraction and 35 mg of unreacted pentamethylferrocenyl[(ene)$_2$(phenylene)$_2$] aldehyde **(11a)** as the second fraction.

Data for 13. A red powder formed. Mp: 275−280 °C (product of method A); mp 180−185 °C (product of method B). Anal. Calcd for $C_{72}H_{70}Fe_2$: C, 82.59; H, 6.74. Found: C, 82.67; H, 6.81. MS (FAB): *m/z* 1046.7 (M^+, 12%); 842.5 ($M^+ - FeCp^* - Me$, 77%); 780.5 ($M^+ - CHCpFeCp^*$, 15%); 576.2 ($M^+ - C_6H_4\text{-}CH{=}CHCpFeCp^*$, 100%). HR-MS (FAB): *m/z* 1046.43908 (M^+; exact mass calcd for $C_{72}H_{70}Fe_2$, 1046.41815). UV−vis for product of method B (THF [λ_{max} (nm)/log ϵ]): 387.5/4.82; 500/shoulder. IR data (KBr): 3020 w, 2964 s, 2923 s, 2854 s, 1630 m, 1515 m, 1459 m, 1380 m, 1262 s, 1098 s, 1030 s, 807 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.84 (30H, s, CH_3); 3.86 (4H, m, subst. Cp); 3.92 (4H, subst. Cp); 6.53−6.76 (8H, m, CH=CH); 7.41 (12H, s, C_6H_4). ^{13}C NMR (CD_2Cl_2): δ 11.1 (CH_3); 69.8, 73.7 (Cp); 81.3 (Cp*); 83.8 (C1 of subst. Cp); 125.2−126.7 (CH=CH and C_6H_4).

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Supporting Information Available: Tables of crystal data and structure refinement details, anisotropic thermal parameters, fractional atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms, all bond lengths and angles, and fractional atomic coordinates for the hydrogen atoms for **1a,b**, **2**−**4**, **5a**, **6**, **9a**, **10**, and **11a** and ORTEP diagrams for **1b,c**, **2**, and **3** (Figures 10−13) (76 pages). Ordering information is given on any current masthead page. The authors have deposited atomic coordinates for structures **1b,c**, **2**−**4**, **5a**, **6**, **9a**, **10**, and **11a** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, CB2 1EW, U.K.

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