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1,1′-Dialkynylferrocenes as Substrates for Bidirectional Alkyne Metathesis Reaction

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Dedicated to Professor Dr. Klaus Banert on the occasion of his 60th birthday

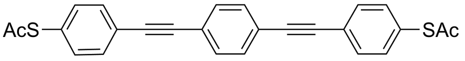
Keywords: Sandwich complexes / Metathesis / Molecular devices / 1,1′-Dialkynylferrocenes / Synthetic methods

In the construction of ferrocene-based molecular wires, alkyne metathesis was investigated as an alternative to palladium-catalyzed coupling reactions for the synthesis of alkynyl ferrocenes. With a Mortreux catalyst system [$Mo(CO)_6$, 4-chloro- or 2-fluorophenol], (1-propynyl)ferrocenes gave the expected homo metathesis products in moderate yields. Because the Mortreux catalyst system is not compatible with 1,1′-dialkynylferrocenes, a nitridomolybdenum catalyst introduced by Fürstner was tested in bidirectional homo and cross-alkyne metathesis reactions. Although the homo alkyne metathesis products were obtained in poor yields, the cross-alkyne metathesis reactions afforded the expected products in good overall yields.

Introduction

The continuing miniaturization of electronic devices demands new techniques to overcome principle physical limitations. Among these, molecular electronics is regarded as a possibility to create electronic devices on the molecular level, which is considered to be the smallest possible.[1,2] In this context molecular wires have been designed, the most popular class of which is oligophenyleneethynylenes (OPEs).[3,4] Typically, molecular wires consist of highly conjugated π systems, such as 1,4-phenylene rings, connected by ethynylene units and are prepared by a building-block principle in repetitive syntheses. OPEs can be prepared by repeated Sonogashira couplings with a very limited number of building blocks.[1,5,6] In addition, they may have end groups – so-called alligator clips – that allow for attachment at gold electrodes or surfaces, for example thioacetyl or nitrile groups.[1,7,8] Compound **1** is an example of an OPE-type molecular wire.

The building principle of OPEs, such as **1**, implies that the structures are rather rigid. They are not prone to adapt their length to the geometrical requirements of a given electrode design. In addition, π–π stacking may occur, so that more than one molecular wire may be involved. To overcome these potential problems, our concept involves replacement of some, but not all, of the 1,4-phenylene units



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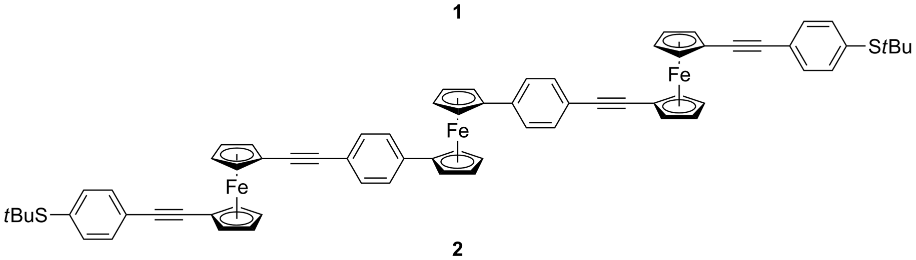

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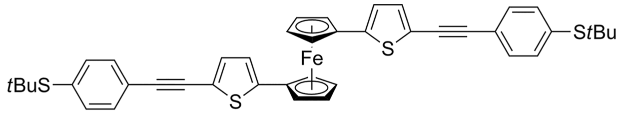

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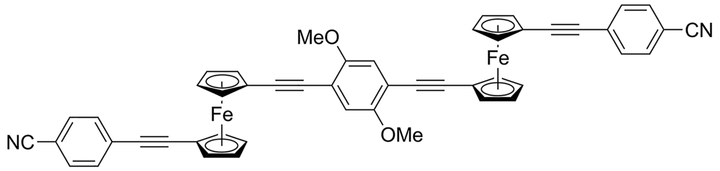

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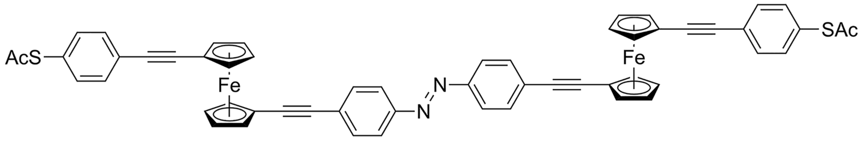

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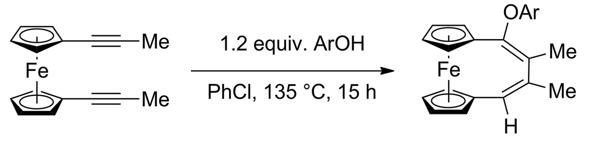
by 1,1′-ferrocenylene ones as in **2**.[9] This renders the compounds three-dimensional, which makes π–π stacking less likely. In addition, the possibility of rotations around the cyclopentadienyl–iron–cyclopentadienyl axis allows for limited conformational flexibility, similar to that of a foldable ruler. Following this concept, we prepared a number of ferrocene-based OPEs with varying structural design in addition to **2**, e.g. **3**–**5**.[9–11] Related contributions have been made by Sita[12,13] and by Long.[14]

As in the case of conventional OPEs, these compounds were prepared predominantly by Sonogashira and related palladium-catalyzed coupling reactions. Although this approach works in many cases, we envisaged alkyne cross metathesis as an alternative route to ferrocene systems connected by triple bonds.[15–23] In a first attempt 1,1′-dialkynylferrocenes such as **6**[24] were treated with a traditional Mortreux catalyst system that consists of hexacarbonylmolybdenum and a phenol in a solvent with a high boiling point such as chlorobenzene. These attempts did not provide the desired coupling products, instead unanticipated transannular coupling of the alkynyl groups was observed, and respective [4]ferrocenophanes **7** were obtained in high yields.[25] Here we report investigations towards bidirectional alkyne metathesis reactions of 1,1′-dialkynylferrocenes with catalysts other than the Mortreux system.



6 **7**

Results and Discussion

Kotora et al. were the first to report alkyne homo metathesis with an alkynylferrocene, namely reaction of (1-propynyl)ferrocene (**8**) with Mortreux catalyst [Mo(CO)$_6$ (10 mol-%), 4-chlorophenol (0.3 equiv.) in toluene, 120 °C, 12 h] to give diferrocenylethyne (**9**) in 40% isolated yield.[26] With some modifications of the reaction conditions [Mo(CO)$_6$ (10 mol-%), 2-fluorophenol (1.0 equiv.) in chlorobenzene, 118 °C, 15 h[27]], we obtained an improved yield of 62%. Next, we were interested in the results of homo metathesis reactions of some building blocks used in the syntheses of ferrocene-based molecular wires, namely propynyl compounds **10**, **12**,[25] and **14**. Alkyne **10** was prepared in 91% yield by reaction of 1-(*tert*-butylsulfanyl)-4-(trimethylsilylethynyl)benzene[28] with methyllithium followed by iodomethane. As another substrate in this context 1′-(4-*tert*-butylsulfanyl)phenyl-substituted ferrocene **14** was prepared from **12** in 33% yield by palladium-catalyzed coupling with 1-(*tert*-butylsulfanyl)-4-iodobenzene.[10] The 4-(*tert*-butylsulfanyl)phenyl substituent is of interest in the context of "alligator clips" in molecular electronics.[1]

The increase in reaction yield observed for **8** was confirmed with the other substrates, which gave symmetric alkynes **11**,[29] **13**, and **15** in satisfactory yields (Table 1). The *tert*-butylsulfanyl substituent in **10** and **14** does not impede catalysis. Compound **15** can be regarded as the first OPE analogue with two ferrocene hinges obtained by alkyne metathesis. The iodo substituents in biferrocene **13** allow for further functionalization.

Bidirectional alkyne metathesis reactions starting from 1,1′-dialkynylferrocenes are highly attractive for the synthesis of extended π systems with ferrocene hinges. Therefore, we envisaged substrates **16** and **17** in addition to **6**.

Compounds **16** and **17** were obtained in 90 and 72% yield, respectively, by deprotonation and subsequent methylation of the respective terminal dialkynes. In addition to the consistent spectroscopic data, compound **17** was crystallized from hexane/dichloromethane (3:1) and subjected to a crystal structure analysis.

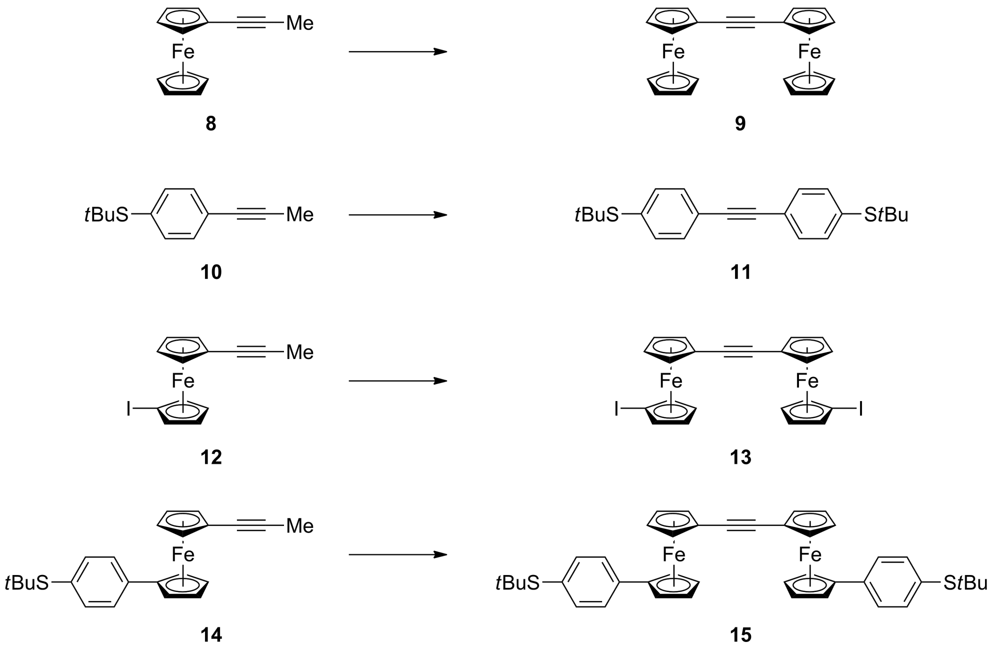
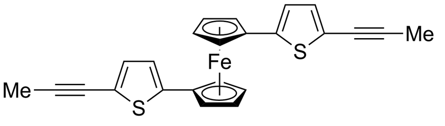


Table 1. Alkyne homo metathesis.

Entry	Starting material	Product	Yield [%][a]	Yield [%][b]
1	**8**	**9**	40[26]	62
2	**10**	**11**[29]	10	36
3	**12**	**13**	20	35
4	**14**	**15**	34	45

[a] Reaction conditions: $Mo(CO)_6$ (10 mol-%), 4-chlorophenol (0.3 equiv.), toluene, 120 °C, 12 h. [b] $Mo(CO)_6$ (10 mol-%), 2-fluorophenol (1.0 equiv.), chlorobenzene, 118–132 °C, 12–15 h.



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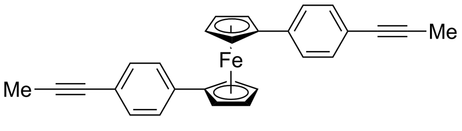

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In the crystal of **17**, two crystallographically independent molecules exist, one of which is shown in Figure 1. Both molecules adopt eclipsed conformations with respect to the cyclopentadienyl–iron–cyclopentadienyl axis and the cyclopentadienyl substituents similar to the conformations observed for some other 1,1′-disubstituted ferrocene derivatives with extended π systems as substituents.[9,31,32] The cyclopentadienyl ligands of the independent molecules show minor deviations from coplanarity (by 3.5 and 2.4°, respectively). The phenyl substituents are slightly twisted out of the planes of the respective cyclopentadienyl rings (by 18.2, 4.7, 5.0, and 7.3°, respectively). The distance between the centers of the phenyl rings are 383.6 pm for the molecule shown in Figure 1 and 361.5 pm for the other one. The conformational differences are likely a result of packing forces. Although the structures of the substituted cyclopentadienyl ligands are similar to one another, they are not identical.

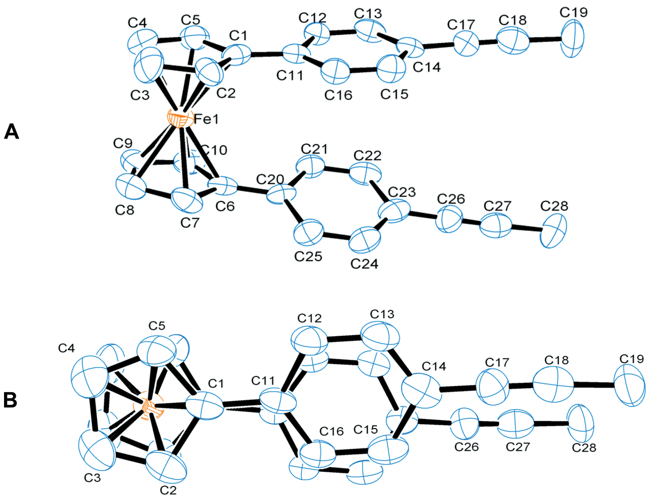
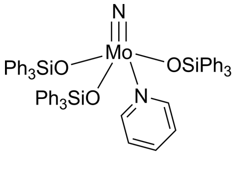


Figure 1. Crystal structure of **17**;[30] A. side view; B. top view. Selected bond lengths [pm] and angles [°]: C1–C2 143.5(7), C1–C5 143.5(7), C1–C11 145.8(7), C2–C3 140.2(8), C3–C4 145.1(9), C4–C5 141.5(9), C6–C7 143.3(8), C6–C10 140.2(7), C6–C20 147.1(7), C7–C8 138.7(8), C8–C9 145.4(9), C9–C10 143.1(8), C17–C18 119.4(8), C26–C27 117.4(8); C14–C17–C18 179.2(6), C17–C18–C19 176.6(6), C23–C26–C27 176.9(7), C26–C27–C28 178.2(7).

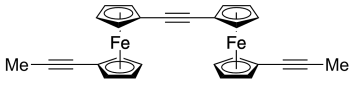
DFT calculations (B3LYP, 6-31G*, Spartan 14) result in a geometry with deviation of the cyclopentadienyl ligands from coplanarity of 0.8° and a twisting of the phenyl rings of 10.2 and 8.7° out of the cyclopentadienyl plane. The HOMO energy of –5.2 eV and the LUMO energy of –1.0 eV result in a HOMO–LUMO gap of 4.2 eV. In contrast to the LUMO, most of those occupied molecular orbitals predominantly located at the 4-(1-propynyl)phenyl substituents show a symmetry that allows for attractive interaction with no nodal plane between substituents (see Supporting Information), which might, in addition to crystal packing effects, be a reason for the observed eclipsed conformation.

Because the Mortreux catalyst system gives [4]ferrocenophanes from 1,1′-dialkynylferrocenes instead of homo metathesis products, nitridomolybdenum complex **18** was tested as an alternative for the alkyne homo metathesis catalyst. Compound **18**, which is prepared from commercially available sodium molybdate, was introduced by Fürstner et al. and has been shown to be tolerant of many functional groups and relatively stable in air for short periods of time.[33]



18

The reaction of 1,1′-dipropynylferrocene (**6**) with **18** (20 mol-%) afforded new triyne **19**. The best yield (29%) was achieved by microwave heating (250 W, 120 °C, 120 min) in toluene. Compound **19** is a promising starting material for subsequent intramolecular homo metathesis and would open access to [2.2]ferrocenophane-1,13-diyne (**20**);[34] however, under the conditions formation of **19** not **20** was observed. Under similar reaction conditions **21** was obtained in 14% yield, and **22** was isolated in only 11% yield. In conclusion, catalyst **18** facilitates the alkyne homo metathesis of 1,1′-dipropynylferrocene (**6**) and of more extended π systems such as diynes **16** or **17** to give ferrocene-based triynes **19**, **21**, and **22**, which are interesting compounds in their own right. However, yields have to be improved by searching for better catalysts.



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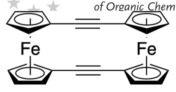

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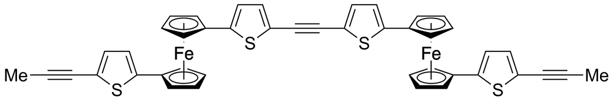

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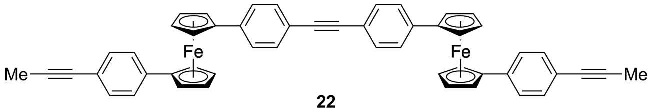

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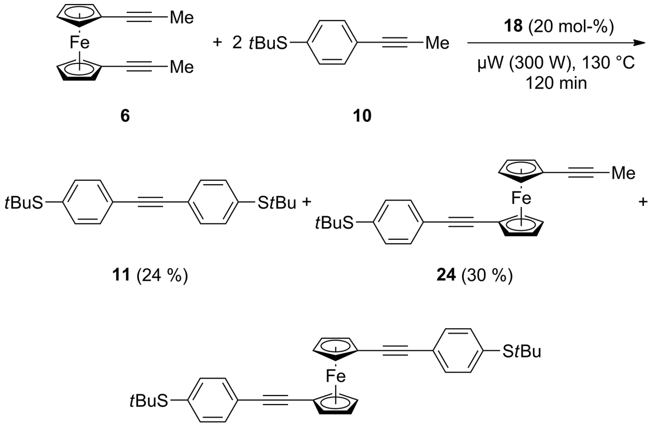
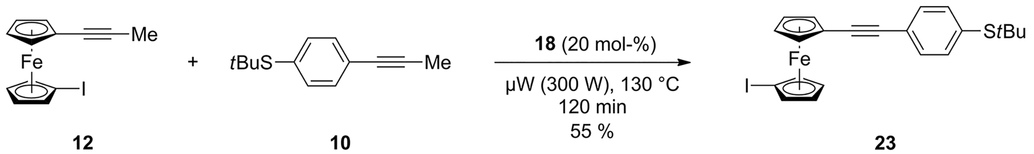
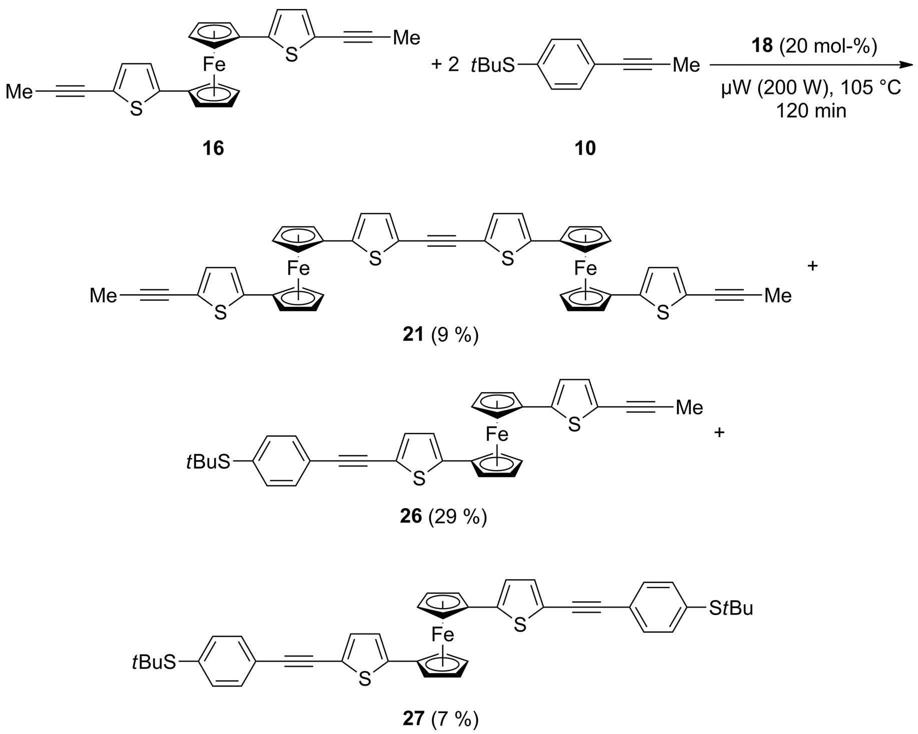
Next, we turned our attention to the possibility of alkyne cross metathesis. Stepnicka, Kotora et al. reported alkyne cross metathesis of (1-propynyl)ferrocene (**8**) and methylated alkynes in 27–80% yield with Mortreux catalyst,[35] which is not suitable for 1,1′-dialkynylferrocenes.[25] Mono- and 1,1′-dialkynyl ferrocenes **6**, **12**, **16**, and **17** were treated with 1-*tert*-butyl-4-propynylbenzene (**10**; 2 equiv.) in the presence of catalyst **18**.

The cross metathesis of iodoalkynylferrocene **12** with 1 equiv. of alkyne **10** was tested. In the presence of catalyst **18** (20 mol-%) and by microwave heating at 130 °C for 120 min a 55% yield of metathesis product **23** was achieved, which indicates that the catalyst is compatible with the iodo as well as with the sulfanyl substituents. The yield is comparable to alkyne cross metatheses, which Stepnicka and Kotora et al. reported with Mortreux catalyst.[35] Compound **23** has been prepared by a Sonogashira coupling of 1-ethynyl-1′-iodoferrocene with 1-(*tert*-butylsulfanyl)-4-iodobenzene in 95% yield.[10,36] Encouraged by this result twofold cross metathesis reactions were tried with the mentioned diynes.





12 **10** **23**



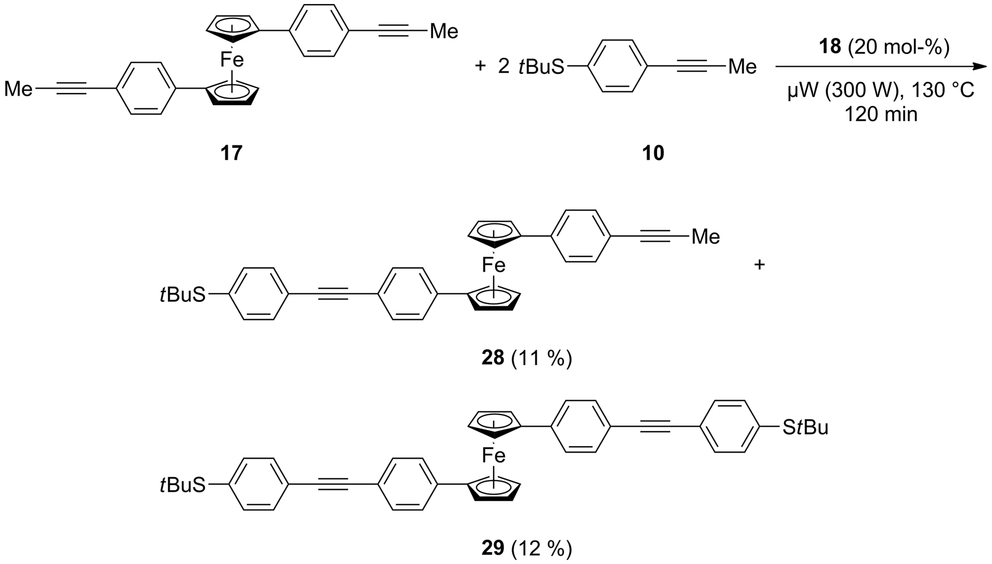
16

10

21 (9 %)

26 (29 %)

27 (7 %)



17

10

28 (11 %)

29 (12 %)

The reaction of **6** with 2 equiv. of **10** resulted in a mixture of homo metathesis product **11** (24%), single cross metathesis product **24** (30%), and double cross metathesis product **25** (36%) with a high overall yield of 90%. In addition, some starting material **10** was isolated. No homo metathesis product **19** of diyne **6** was observed. This result indicates a preference for cross versus homo alkyne metathesis.

The reaction of diyne **16** with **10** (2 equiv.) under somewhat milder reaction conditions afforded single and double cross metathesis products **26** and **27**[9] in 29 and 7% yield, respectively, in addition to 9% of homo metathesis product **21**, which indicates a preference for mono cross metathesis under these conditions.

The reaction of **17** with **10** (2 equiv.) afforded cross metathesis products **28** and **29** in 11 and 12% yield, respectively. Here one must take into account that **29** is the product of a bidirectional reaction that gives an average yield of 35% per metathesis step.

Conclusions

The results indicate that alkyne cross metathesis may be used as a tool for the bidirectional extension of 1,1′-dialkynylferrocenes as building blocks for molecular wires. Iodo and *tert*-butylsulfanyl substituents are compatible with Mortreux catalyst systems as well as with nitridomolybdenum catalyst **18**, which can compete with the Mortreux catalyst system. Investigations with other catalysts introduced by Fürstner et al. and by Tamm et al. are under investigation in our laboratory.[37,38] Remarkably, the yields of the bidirectional double reaction are comparable or even higher than those of the single reactions. However, so far the yields obtained are not comparable to those of palladium-catalyzed coupling reactions that lead to related products.

Experimental Section

General: All reactions were performed by using Schlenk techniques with nitrogen or argon as the inert gas. All glassware was heated at < 0.1 mbar with a heat gun prior to use to remove any oxygen or water. Tetrahydrofuran (THF) and toluene were dried with sodium/potassium alloy/benzophenone and distilled. Pentane and dichloromethane were dried with CaH_2 and distilled. Starting materials were either commercially acquired or were prepared according to published procedures. Ferrocene was obtained as a donation from Innospec Deutschland GmbH. ^{1}H and ^{13}C NMR spectra were obtained with Bruker AVS 200 (^{1}H: 200 MHz) and AVS 400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) instruments. Chemical shifts are referenced to $\delta_{TMS} = 0$ ppm or to residual solvent signals. Primary, secondary, tertiary and quaternary carbon atom signals were identified as such by APT and DEPT techniques. In some cases signal assignments were based on 2D NMR spectra (HMC, HMBC). IR spectra were obtained with Perkin–Elmer instruments FT-IR 580 and 1170 by using ATR techniques. Signal characteristics are abbreviated as s (strong), m (medium), w (weak), and br (broad). Mass spectra were obtained with a Micromass LCT instrument with lockspray source and direct injection and with a Q-TOF premier LC-MS/MS instrument with an Ionsabre APCI source (25 µA, 350 °C). In all cases dichloromethane was used as the solvent. Analytical TLC was performed with Merck 60F-254 silica gel thin layer plates. Column chromatography was performed with J. T. Baker silica gel (60 µm) as the stationary phase by using the flash chromatography method.[39] Elemental analyses were obtained with an Elementar Vario EL instrument. Reactions under microwave irradiation (µW) were performed with a CEM Discover™ Labmate reactor under nitrogen ("open vessel") in a 100 mL reaction flask by using ChemDriver™ software. The temperature was monitored by means of an IR sensor. Some reactions were performed by using the PowerMax™ method.

Diferrocenylethyne (9): (a) Ref.[26] (b) Hexacarbonylmolybdenum (26 mg, 0.1 mmol, 10 mol-%) and 2-fluorophenol (112 mg, 1.0 mmol) were added to (1-propynyl)ferrocene[24] (**8**; 224 mg, 1.0 mmol) in chlorobenzene (20 mL) and heated at 118 °C (oil-bath temperature) for 15 h. After solvent removal under reduced pressure, the crude product was purified by column chromatography (30 × 2 cm, hexane/dichloromethane, 4:1) to give **9** (122 mg, 0.3 mmol, 62 %), identified by ^{1}H NMR spectroscopy.[26]

1-(*tert*-Butylsulfanyl)-4-(1-propynyl)benzene (10): At –78 °C MeLi (1.6 M in diethyl ether, 2.5 mL, 3.9 mmol) was added dropwise to 1-(*tert*-butylsulfanyl)-4-(trimethylsilylethynyl)benzene[28] (0.69 g, 2.6 mmol) in THF (30 mL), and the mixture was stirred at 25 °C for 20 h. After addition of iodomethane (0.3 mL, 5.3 mmol) at –78 °C, the solution was stirred at 25 °C for 5 h. Water (20 mL) was added, and, after stirring for 5 min, the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The collected organic layers were washed with brine (20 mL) and dried with $MgSO_4$. After solvent removal under reduced pressure, the residue was purified by column chromatography (30 × 3 cm, petroleum ether/dichloromethane, 4:1) to give **10** (0.49 g, 2.4 mmol, 91 %) as a white solid, which was recrystallized from hexane/dichloromethane (3:1). Colorless crystals (m.p. 82.0–83.5 °C). IR (ATR): $\tilde{\nu}$ = 3041 (w), 2960 (m), 2921 (m), 2855 (m), 2251 (w) 1692 (w), 1590 (w), 1486 (s), 1470 (m), 1363 (s), 1169 (m), 1151 (s), 845 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.30 [s, 9 H, $C(CH_3)_3$], 2.08 (s, 3 H, $CCCH_3$), 7.35 + 7.46 (AA′BB′, 4 H, C_6H_4) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 4.4 ($CC\mathit{C}H_3$), 30.9 [$C(\mathit{C}H_3)_3$], 46.2 [$\mathit{C}(CH_3)_3$], 79.2 ($C\equiv C$), 87.5 ($C\equiv C$), 124.5 ($C_{Ar}C$), 131.4 ($C_{Ar}H$), 132.2 ($C_{Ar}S$), 137.2 ($C_{Ar}H$) ppm. MS (70 eV): *m*/*z* (%) = 204 (26) [M$^+$], 149 (15), 148 (100) [M$^+$ – C_4H_8], 147 (31), 115 (32), 57 (27) [*t*Bu$^+$]. HRMS: calcd. for $C_{13}H_{16}S$ 204.0973; found 204.0974. $C_{13}H_{16}S$ (204.3): calcd. C 76.41, H 7.89; found C 76.45, H 7.67.

Bis[(4-*tert*-butylsulfanyl)phenyl]ethyne (11):[29] (a) Hexacarbonylmolybdenum (26 mg, 0.1 mmol, 10 mol-%) and 4-chlorophenol (38 mg, 0.3 mmol) were added to 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**10**; 204 mg, 1.0 mmol) in toluene (10 mL), and the solution was heated at 120 °C for 12 h. After solvent removal under reduced pressure, the mixture was separated by column chromatography (20 × 2 cm, petroleum ether/dichloromethane, 4:1). I. **10** (129 mg, 0.6 mmol, 60 %). II. **11** (21 mg, 0.05 mmol, 10 %), orange crystals (m.p. 128.4–130.1 °C). (b) After addition of $Mo(CO)_6$ (13 mg, 0.05 mmol, 5 mol-%) and 2-fluorophenol (112 mg, 1.0 mmol) to 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**10**; 0.20 g, 1.0 mmol) in chlorobenzene (20 mL), the solution was heated at reflux (oil-bath temperature 132 °C) for 4 h. After cooling to 25 °C and solvent removal under reduced pressure, the residue was purified by column chromatography (30 × 3 cm, petroleum ether/dichloromethane, 4:1) to give **11** (63 mg, 0.2 mmol, 36 %) as colorless shiny crystals (m.p. 113.5–115.0 °C). Identified by comparison of the analytical data (IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, and MS) with literature data.[29]

Bis(1′-iodoferrocenyl)ethyne (13): (a) Hexacarbonylmolybdenum (26 mg, 0.1 mmol, 10 mol-%) and 4-chlorophenol (40 mg, 0.3 mmol) were added to 1-iodo-1′-(1-propynyl)ferrocene[25] (**12**; 350 mg, 1.0 mmol) in 1,4-dimethylbenzene (10 mL), and the solution was heated at 120 °C for 10 h. After solvent removal, the residue was taken up with dichloromethane (20 mL), and the solution was washed with aq. NaOH (1 M, 10 mL), brine (20 mL), and dried with $MgSO_4$. After solvent removal under reduced pressure, the mixture was separated by column chromatography (30 × 3 cm, petroleum ether/dichloromethane, 4:1). I. **12** (57 mg, 0.2 mmol, 16 %). II. **13** (31 mg, 0.05 mmol, 10 %), orange crystals (m.p. 128.4–130.1 °C). (b) Hexacarbonylmolybdenum (26 mg, 0.1 mmol, 10 mol-%) and 2-fluorophenol (112 mg, 0.1 mmol) were added to 1-iodo-1′-(1-propynyl)ferrocene[25] (**12**; 350 mg, 1.0 mmol) in chlorobenzene (10 mL), and the mixture was heated at 132 °C for 15 h. After solvent removal under reduced pressure, the residue was purified by column chromatography (30 × 3 cm, petroleum ether/dichloromethane, 4:1) to give **13** (113 mg, 0.2 mmol, 35 %) as orange crystals (m.p. 128.4–130.1 °C). IR (ATR): $\tilde{\nu}$ = 3101 (m), 2918 (m), 2849 (m), 2216 (w), 1631 (w), 1500 (w), 1403 (m), 1378 (m), 1347 (s), 1287 (m), 1202 (m), 1138 (m), 1057 (m), 1043 (m), 0128 (m), 1010 (s), 935 (s), 861 (s), 833 (s), 803 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 4.24 (m, 4 H, H$_{\mathrm{Cp}}$), 4.44 (m, 4 H, H$_{\mathrm{Cp}}$) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 40.9 (CI), 68.2 (C_{Cp}C), 71.0 (C$_{\mathrm{Cp}}$H), 71.8 (C$_{\mathrm{Cp}}$H), 74.1 (C$_{\mathrm{Cp}}$H), 76.4 (C$_{\mathrm{Cp}}$H), 84.0 (C$_{\mathrm{Cp}}$*C*C) ppm. MS (70 eV): *m/z* (%) = 647 (11) [M + 1]$^+$, 646 (100) [M$^+$], 644 (11), 350 (10), 336 (11), 290 (14), 288 (14), 216 (14), 215 (26), 189 (10), 85 (14), 83 (16), 71 (12), 57 (23), 56 (13) [Fe$^+$]. HRMS: calcd. for $C_{22}H_{16}Fe_2I_2$ 645.8040; found 645.8045. $C_{22}H_{16}Fe_2I_2$ (645.8): calcd. C 40.91, H 2.50; found C 41.49, H 2.79.

1-(4-*tert*-Butylsulfanylphenyl)-1′-(1-propynyl)ferrocene (14): At –78 °C butyllithium (1.6 м in hexane, 1.4 mL, 2.2 mmol) was slowly added dropwise to 1-iodo-1′-(1-propynyl)ferrocene (**12**; 0.70 g, 2.0 mmol) in THF (30 mL), and the mixture was stirred at –78 °C for 1 h. At 0 °C zinc chloride (0.33 g, 2.4 mmol) in THF (10 mL) was added. The solution was stirred at 0 °C for 30 min, then at 25 °C for 1 h. 1-(*tert*-Butylsulfanyl)-4-iodobenzene[10,28] (0.64 g, 2.2 mmol) and Pd^0 catalyst (5 mol-%) were added at 0 °C [the Pd^0 catalyst was prepared in situ: at 0 °C diisobutylaluminium hydride (20% in toluene, 0.2 mL, 0.2 mmol) was added to Pd(PPh$_3$)$_2$Cl$_2$ (75 mg, 0.1 mmol) in THF (5 mL), and the mixture was stirred for 10 min]. The solution was stirred at 85 °C for 15 h. After cooling to 25 °C, aq. NaOH (1 м, 10 mL) was added, and the mixture was stirred for 5 min. The aqueous layer was separated and extracted with dichloromethane (3× 30 mL). The collected organic layers were washed with brine (30 mL) and then dried with MgSO$_4$. After solvent removal under reduced pressure, the residue was purified by column chromatography (30×3 cm, petroleum ether/dichloromethane, 4:1) to give **14** (254 mg, 0.7 mmol, 33%) as a dark red solid (m.p. 86.1–87.8 °C). IR (ATR): ṽ = 3068 (w), 2966 (m), 2911 (m), 2856 (m), 2359 (w), 1596 (s), 1508 (m), 1468 (m), 1455 (m), 1362 (s), 1166 (s), 1103 (m), 1036 (s), 1016 (s), 886 (s), 831 (s), 814 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.30 [s, 9 H, SC(CH$_3$)$_3$], 1.83 (s, 3 H, CCCH$_3$), 4.02 (m, 2 H, H$_{\mathrm{Cp}}$), 4.18 (m, 2 H, H$_{\mathrm{Cp}}$), 4.37 (m, 2 H, H$_{\mathrm{Cp}}$), 4.64 (m, 2 H, H$_{\mathrm{Cp}}$), 7.44 (m, 4 H, C$_6$H$_4$) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 4.4 (CC*C*H$_3$), 31.0 [SC(*C*H$_3$)$_3$], 45.9 [S*C*(CH$_3$)$_3$], 68.0 (C$_{\mathrm{Cp}}$H), 69.7 (C$_{\mathrm{Cp}}$H), 70.9 (C$_{\mathrm{Cp}}$H), 72.5 (C$_{\mathrm{Cp}}$H), 76.2 (C_{Cp}C), 77.2 (C_{Cp}C), 82.4 (C≡C), 85.4 (C≡C), 126.2 (C$_{\mathrm{Ar}}$H), 129.8 (C_{Ar}C), 137.4 (C$_{\mathrm{Ar}}$H), 138.8 (C$_{\mathrm{Ar}}$S) ppm. MS (70 eV): *m/z* (%) = 389 (22) [M + 1]$^+$, 388 (100) [M$^+$], 333 (24), 332 (100) [M$^+$ – C$_4$H$_8$], 331 (8), 330 (8), 298 (9), 171 (8), 139 (12), 57 (45), 56 (10) [Fe$^+$]. HRMS: calcd. for $C_{23}H_{24}FeS$ 388.0948; found 388.0951. $C_{23}H_{24}FeS$ (388.4): calcd. C 71.13, H 6.23; found C 70.99, H 6.48.

Bis[1′-(4-*tert*-butylsulfanylphenyl)ferrocenyl]ethyne (15): After addition of hexacarbonylmolybdenum (6 mg, 0.03 mmol, 10 mol-%) and 4-chlorophenol (10 mg, 0.08 mmol) to 1-(4-*tert*-butylsulfanylphenyl)-1′-(1-propynyl)ferrocene (**14**, 97 mg, 0.3 mmol) in toluene (10 mL), the solution was heated at reflux (oil-bath temperature 120 °C) for 20 h. After cooling to 25 °C, aq. NaOH (1 м, 10 mL) was added, and the mixture was stirred for 5 min. After extraction with dichloromethane (3× 10 mL), the collected organic layers were washed with brine (10 mL) and dried with MgSO$_4$. After solvent removal under reduced pressure, the residue was purified by column chromatography (30×3 cm, petroleum ether/dichloromethane, 2:1) to give **15** (31 mg, 0.04 mmol, 34%) as an orange solid (m.p. 198.2–200.1 °C). IR (ATR): ṽ = 3068 (w), 2954 (s), 2920 (s), 2853 (s), 2162 (w), 1597 (m), 1509 (m), 1449 (m), 1409 (w), 1364 (s), 1278 (m), 1167 (s), 1103 (m), 1049 (m), 1039 (s), 936 (s), 885 (s), 831 (s), 808 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.30 (s, 18 H, CH$_3$), 4.10 (m, 4 H, H$_{\mathrm{Cp}}$), 4.23 (m, 4 H, H$_{\mathrm{Cp}}$), 4.40 (m, 4 H, H$_{\mathrm{Cp}}$), 4.64 (m, 4 H, H$_{\mathrm{Cp}}$), 7.46 (m, 8 H, C$_6$H$_4$) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 31.0 (*C*H$_3$), 45.9 [*C*(CH$_3$)$_3$], 67.1 (C$_{\mathrm{Cp}}$C), 68.5 (C$_{\mathrm{Cp}}$H), 70.4 (C$_{\mathrm{Cp}}$H), 71.3 (C$_{\mathrm{Cp}}$H), 72.8 (C_{Cp}H), 84.0 (C_{Cp}H), 85.5 (C$_{\mathrm{Cp}}$*C*CC$_{\mathrm{Cp}}$), 126.2 (C_{Ar}H), 130.0 (C_{Ar}C), 137.5 (C_{Ar}H), 139.2 (C$_{\mathrm{Ar}}$S) ppm. MS (70 eV): *m/z* (%) = 725 (7), 724 (23), 723 (52) [M + 1]$^+$, 722 (100) [M$^+$], 721 (6), 720 (13), 666 (8), 610 (11), 608 (6), 438 (7), 437 (21), 436 (50), 434 (8), 305 (11), 57 (20). HRMS: calcd. for $C_{42}H_{42}Fe_2S_2$ 722.1427; found 722.1774.

1,1′-Bis{2-[5-(1-propynyl)]thiophenyl}ferrocene (16): At –78 °C BuLi (1.6 м in hexane, 3.5 mL, 5.5 mmol) was added dropwise to 1,1′-bis[2-(4-ethynyl)thiophenyl]ferrocene[9] (1.00 g, 2.5 mmol) in THF (40 mL), and the mixture was stirred for 1 h. After addition of iodomethane (1.3 mL, 20.1 mmol) at –78 °C, the solution was stirred at 25 °C for 2 h. Water (20 mL) was added, and the mixture was stirred for 5 min. The aqueous layer was extracted with dichloromethane (3× 30 mL). The collected organic layers were washed with brine (30 mL) and dried with MgSO$_4$. After solvent removal under reduced pressure, the residue was purified by column chromatography (30×3 cm, silica gel deactivated with 5% triethylamine, petroleum ether/dichloromethane, 4:1) to give **16** (769 mg, 1.8 mmol, 72%) as a red solid (m.p. 118.5–120.0 °C). IR (ATR): ṽ = 3081 (w), 2908 (w), 2843 (m), 2340 (w), 2189 (w), 1427 (m), 1029 (s), 973 (m), 929 (m), 865 (m), 811 (s), 784 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 2.09 (s, 6 H, CH$_3$), 4.21 (m, 4 H, H$_{\mathrm{Cp}}$), 4.41 (m, 4 H, H$_{\mathrm{Cp}}$), 6.66 (d, ^3J = 3.8 Hz, 2 H, SCCH), 6.88 (d, ^3J = 3.8 Hz, 2 H, SCCH) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 4.8 (CH$_3$), 68.5 (C$_{\mathrm{Cp}}$H), 70.8 (C$_{\mathrm{Cp}}$H), 73.4 (C_{Cp}C), 80.8 (C≡C), 90.0 (C≡C), 121.4 (C_{Ar}C), 122.1 (C$_{\mathrm{Ar}}$H), 131.5 (C$_{\mathrm{Ar}}$H), 142.3 (C_{Ar}C) ppm. MS (70 eV): *m/z* (%) = 428 (14), 427 (29) [M + 1]$^+$, 426 (100) [M$^+$], 424 (6), 185 (13), 184 (7), 152 (10), 57 (7), 56 (7) [Fe$^+$]. HRMS: calcd. for $C_{24}H_{18}FeS_2$ 426.0199; found 426.0201. $C_{24}H_{18}FeS_2$ (426.4): calcd. C 67.61, H 4.26; found C 67.58, H 4.39.

1,1′-Bis[4-(1-propynyl)phenyl]ferrocene (17): At –78 °C BuLi (1.6 м in hexane, 3.3 mL, 5.3 mmol) was added dropwise to 1,1′-bis(4-ethynylphenyl)ferrocene[9] (924 mg, 2.4 mmol) in THF (50 mL). After stirring for 1 h, iodomethane (1.2 mL, 19.0 mmol) was added at –78 °C, and the mixture was stirred at 25 °C for 3 h. Water (30 mL) was added, and the mixture was stirred for 5 min. The aqueous layer was extracted with dichloromethane (3× 30 mL), and the collected organic layers were washed with brine and dried with MgSO$_4$. After solvent removal under reduced pressure, the residue was purified by column chromatography (30×3 cm, petroleum ether/dichloromethane, 3:1) to give **17** (894 mg, 2.2 mmol, 90%) as a red solid (m.p. 186.7–188.3 °C). IR (ATR): ṽ = 3084 (w), 2914 (w), 2850 (m), 2243 (w), 1605 (w), 1523 (s), 1454 (m), 1415 (w), 1279 (m), 1106 (m), 1084 (m), 1032 (s), 888 (s), 848 (m), 832 (s), 810 (s), 728 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 2.08 (s, 6 H, CH$_3$), 4.22 (m, 4 H, H$_{\mathrm{Cp}}$), 4.41 (m, 4 H, H$_{\mathrm{Cp}}$), 7.18 (m, 4 H, C$_6$H$_4$), 7.23 (m, 4 H, C$_6$H$_4$) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 4.4 (CH$_3$), 68.0 (C$_{\mathrm{Cp}}$H), 70.7 (C$_{\mathrm{Cp}}$H), 80.0 (C_{Cp}C), 85.2 (C≡C), 85.7 (C≡C), 121.3 (H$_3$CCC*C*CH), 125.6 (H$_3$CCCCCH*C*H), 131.4 (H$_3$CCCC*C*H), 137.6 (C$_{\mathrm{Cp}}$*C*CH) ppm. MS (70 eV): *m/z* (%) = 416 (9), 415 (48) [M + 1]$^+$, 414 (100) [M$^+$], 413 (6), 412 (11), 179 (29), 178 (17), 152 (11), 57 (9), 56 (7) [Fe$^+$]. HRMS: calcd. for $C_{28}H_{22}Fe$ 414.1071; found 414.1072. $C_{28}H_{22}Fe$ (414.3): calcd. C 81.17, H 5.35; found C 80.96, H 5.35.

Crystal Structure Analysis of 17:[30] Single crystals of **17** were obtained by crystallization from hexane/dichloromethane (1:3). $C_{28}H_{16}Fe$, red needles, M_r = 408.26 g mol^{-1}, crystal system monoclinic, space group *P*21/*n*, a = 12.8480(1), b = 7.4634(1), c = 43.1025(4) Å, β = 98.095(1), V = 4091.91(7) Å^3, Z = 8, $\rho_{\mathrm{calcd.}}$ = 1.325 g cm^{-3}, μ = 5.968 mm^{-1}, crystal size 0.25×0.16×0.08 mm; F(000) = 1680, Bruker KAPPA APEX II diffractometer, T = 213 K, Cu-K_α radiation (λ = 1.54187 Å), 3.48° ≤ θ ≤ 65.78°, reflections collected/unique 23274/6884, R(int) = 0.065; index ranges –15

$\leq h \leq 15$, $-4 \leq k \leq 8$, $-49 \leq l \leq 50$, parameter/restraints 523/0, structure solution and refinement with SHELXS-97 or SHELXL-97 (Sheldrick, 1997), respectively,[40] refinement method full-matrix least squares, no absorption correction, goodness-of-fit on F^2 = 1.038, R = 0.0912 [$I > 2\sigma(I)$], wR = 0.2890 (all data), final difference electron densities 1.585 and –0.759 e Å^{-3}. Positions of the methyl hydrogen atoms were not determined.

General Procedure (GP): Catalyst **18**[33] (50 mg, 0.05 mmol, 20 mol-%) was dissolved in toluene (10 mL). After addition of the starting material(s), the flask was subjected to microwave irradiation (Open Vessel). After cooling to 25 °C, the solution was filtered through a 3 cm layer of silica gel and washed with dichloromethane. After solvent removal under reduced pressure, the residue was purified by column chromatography (30 × 3 cm, silica gel deactivated with 5% triethylamine, petroleum ether/dichloromethane, 2:1).

Bis[1′-(1-propynyl)ferrocenyl]ethyne (19): GP, 1,1′-bis(1-propynyl)ferrocene (**6**; 66 mg, 0.3 mmol), µW (250 W), 120 °C, 30 min RAMP, 120 min HOLD. Compound **19** (17 mg, 0.04 mmol, 29%) was obtained as a red solid (m.p. 181.0–182.5 °C). IR (ATR): $\tilde{\nu}$ = 3099 (w), 2966 (m), 2919 (s), 2850 (m), 2232 (w), 1719 (w), 1494 (m), 1463 (m), 1265 (m), 1202 (m), 1057 (m), 1043 (m), 1026 (s), 982 (m), 935 (s), 873 (m), 848 (s), 822 (s), 735 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.91 (s, 6 H, CH$_3$), 4.21 (m, 4 H, H$_{\mathrm{Cp}}$), 4.24 (m, 4 H, H$_{\mathrm{Cp}}$), 4.37 (m, 4 H, H$_{\mathrm{Cp}}$), 4.45 (m, 4 H, H$_{\mathrm{Cp}}$) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 4.5 (CH$_3$), 67.5 (C*C*CH$_3$), 68.0 (C_{Cp}C), 70.4 (C$_{\mathrm{Cp}}$H), 70.5 (C$_{\mathrm{Cp}}$H), 72.6 (C$_{\mathrm{Cp}}$H), 72.7 (C$_{\mathrm{Cp}}$H), 76.4 (C_{Cp}C), 82.6 (*C*CCH$_3$), 83.8 (C≡C) ppm. MS (70 eV): *m*/*z* (%) = 471 (37) [M + 1]$^+$, 470 (100) [M$^+$], 468 (14), 235 (8), 86 (10), 84 (14), 81 (9), 57 (11), 56 (16) [Fe$^+$]. HRMS: calcd. for $C_{28}H_{22}Fe_2$ 470.0420; found 470.0417. $C_{28}H_{22}Fe_2$ (470.2): calcd. C 71.53, H 4.72; found C 71.53, H 5.15.

Bis{2-[5-(1′-{2-[5-(1-propynyl)]thiophenyl}ferrocenyl)]thiophenyl}-ethyne (21): .GP, 1,1′-bis{2-[4-(1-propynyl)]thiophenyl}ferrocene (**16**; 106 mg, 0.3 mmol), µW (200 W), 105 °C, 30 min RAMP, 120 min HOLD. Compound **21** (14 mg, 0.02 mmol, 14%) was obtained as a red solid (m.p. 172.2–173.6 °C). IR (ATR): $\tilde{\nu}$ = 3081 (w), 2959 (m), 2919 (m), 2851 (m), 2189 (w), 1753 (w), 1543 (w), 1428 (m), 1202 (m), 1044 (m), 1030 (s), 958 (s), 851 (m), 797 (s), 743 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 2.08 (s, 6 H, CH$_3$), 4.24 (m, 8 H, H$_{\mathrm{Cp}}$), 4.44 (m, 8 H, H$_{\mathrm{Cp}}$), 6.68 (d, ^3J = 3.8 Hz, 2 H, SCCH), 6.73 (d, ^3J = 3.8 Hz, 2 H, SCCH), 6.89 (d, ^3J = 3.8 Hz, 2 H, SCCH), 7.04 (d, ^3J = 3.8 Hz, 2 H, SCCH) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 4.7 (CH$_3$), 68.5 (C$_{\mathrm{Cp}}$H), 68.6 (C$_{\mathrm{Cp}}$H), 70.8 (C$_{\mathrm{Cp}}$H), 71.0 (C$_{\mathrm{Cp}}$H), 73.4 (C$_{\mathrm{Cp}}$C), 80.6 (C$_{\mathrm{Cp}}$C), 81.0 (C≡C), 87.1 (C≡C), 90.2 (C≡C), 120.3 (C_{Ar}C), 121.5 (C_{Ar}C), 122.2 (C_{Ar}H), 122.5 (C_{Ar}H), 131.5 (C_{Ar}H), 132.6 (C_{Ar}H), 142.1 (C_{Ar}C), 144.2 (C_{Ar}C) ppm. MS (70 eV): *m*/*z* (%) = 577 (31), 576 (76), 520 (26), 388 (34), 330 (34), 186 (29), 185 (24), 111 (22), 97 (36), 95 (26), 85 (28), 83 (38), 81 (26), 71 (40), 69 (43), 57 (100), 56 (46), 55 (53). HRMS: calcd. for $C_{44}H_{30}Fe_2S_4$ 797.9929; found 797.9911. $C_{44}H_{30}Fe_2S_4$ (798.7): calcd. C 66.17, H 3.79; found C 66.73, H 4.58.

Bis(4-{1′-[4-(1-propynyl)phenyl]ferrocenyl}phenyl)ethyne (22): GP, 1,1′-bis[4-(1-propynyl)phenyl]ferrocene (**17**; 103 mg, 0.3 mmol), µW (200 W), 130 °C, 30 min RAMP, 120 min HOLD. Compound **22** (11 mg, 0.01 mmol, 11%) was obtained as an orange solid (m.p. 258.0 °C, dec.). IR (ATR): $\tilde{\nu}$ = 3104 (w), 2921 (m), 2850 (m), 2223 (w), 1910 (w), 1604 (w), 1524 (s), 1454 (m), 1280 (m), 1108 (m), 1084 (m), 1033 (s), 880 (s), 848 (s), 838 (s), 818 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 2.04 (s, 6 H, CH$_3$), 4.25 (m, 8 H, H$_{\mathrm{Cp}}$), 4.45 (m, 8 H, H$_{\mathrm{Cp}}$), 7.25 (m, 8 H, H$_{\mathrm{Ar}}$), 7.38 (m, 8 H, H$_{\mathrm{Ar}}$) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 4.4 (CH$_3$), 68.0 (C$_{\mathrm{Cp}}$H), 68.1 (C$_{\mathrm{Cp}}$H), 69.5 (C$_{\mathrm{Cp}}$H), 69.6 (C$_{\mathrm{Cp}}$H), 70.7 (C_{Cp}C), 70.8 (C_{Cp}C), 85.1 (C≡C), 85.4 (C≡C), 90.2 (C≡C), 120.7 (C_{Ar}C), 120.8 (C_{Ar}C), 125.6 (C_{Ar}C), 125.7 (C$_{\mathrm{Ar}}$H), 125.9 (C$_{\mathrm{Ar}}$H), 131.4 (C$_{\mathrm{Ar}}$H), 131.5 (C$_{\mathrm{Ar}}$H), 138.9 (C_{Ar}C) ppm. MS (70 eV): *m*/*z* (%) = 776 (18), 775 (57) [M + 1]$^+$, 774 (100) [M$^+$], 772 (13), 388 (14), 387 (39), 386 (6), 179 (6), 178 (5), 84 (8). HRMS calcd. for $C_{52}H_{38}Fe_2$ 774.1672; found 4774.1677. $C_{52}H_{38}Fe_2$ (774.6): calcd. C 80.63, H 4.95; found C 81.09, H 4.98.

Cross Metathesis Reaction with 10 and 12: GP, 1-iodo-1′-(1-propynyl)ferrocene[25] (**12**; 88 mg, 0.3 mmol) and 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene[29] (**10**; 51 mg, 0.3 mmol), µW (300 W), 130 °C, 30 min RAMP, 120 min HOLD. 1-{[4-(*tert*-Butylsulfanyl)-phenyl]ethynyl}-1′-iodoferrocene (**23**; 69 mg, 0.1 mmol, 55%) was obtained as a dark red solid, identified by ^{1}H NMR spectroscopy.[10,36]

Cross Metathesis Reaction with 6 and 10: GP, 1,1′-bis(1-propynyl)-ferrocene[24] (**6**; 66 mg, 0.25 mmol) and 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**10**; 102 mg, 0.5 mmol), µW (300 W), 130 °C, 30 min RAMP, 120 min HOLD. The product mixture was separated by column chromatography (30 × 2 cm, petroleum ether/dichloromethane, 2:1 to 1:1). I. **10** (22 mg, 0.10 mmol, 20%). II. **11**[29] (21 mg, 0.06 mmol, 24%), identified by ^{1}H NMR spectroscopy. III. **24**[25] (30 mg, 0.07 mmol, 30%), identified by ^{1}H NMR spectroscopy. IV. **25**[25] (50 mg, 0.09 mmol, 36%), identified by ^{1}H NMR spectroscopy.

Cross Metathesis Reaction with 10 and 16: GP, 1,1′-bis{2-[5-(1-propynyl)]thiophenyl}ferrocene (**16**; 106 mg, 0.25 mmol) and 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**6**; 102 mg, 0.50 mmol), µW (200 W), 110 °C, 30 min RAMP, 120 min HOLD. The product mixture was separated by column chromatography (30 × 2 cm, petroleum ether/dichloromethane, 3:1 to 2:1). I. 1-{5-[2-(4-*tert*-Butylsulfanylphenyl)ethynyl]-2-thiophenyl}-1′-[5-(1-propynyl)-2-thiophenyl]ferrocene (**26**) (42 mg, 0.07 mmol, 29%), orange solid (m.p. 111.5–113.1 °C). II. **21** (9 mg, 0.01 mmol, 9%). III. **27**[9](13 mg, 0.02 mmol, 7%), identified by ^{1}H NMR spectroscopy. **26:** IR (ATR): $\tilde{\nu}$ = 3081 (w), 2958 (w), 2920 (w), 2852 (w), 2189 (m), 1588 (w), 1469 (m), 1427 (m), 1363 (m), 1214 (m), 1167 (m), 1030 (m), 1014 (w), 973 (m), 838 (m), 811 (s), 770 (s), 730 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.31 [s, 9 H, C(C*H*$_3$)$_3$], 2.05 (s, 3 H, CCC*H*$_3$), 4.24 (m, 4 H, H$_{\mathrm{Cp}}$), 4.44 (m, 4 H, H$_{\mathrm{Cp}}$), 6.66 (d, J = 3.8 Hz, 1 H, arom. H), 6.73 (d, J = 3.8 Hz, 1 H, arom. H), 6.88 (d, J = 3.8 Hz, 1 H, C≡CCSCCH), 7.05 (d, J = 3.8 Hz, 1 H, C≡CCSCCHC*H*), 7.50 (m, 4 H, H$_{\mathrm{Ar}}$) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 4.7 (CC*C*H$_3$), 31.0 [C(*C*H$_3$)$_3$], 46.4 [*C*(CH$_3$)$_3$], 68.5 (C_{Cp}H), 68.6 (C_{Cp}H), 70.7 (C$_{\mathrm{Cp}}$H), 70.9 (C_{Cp}H), 73.4 (C_{Cp}C), 80.5 (C_{Cp}C), 81.0 (C≡C), 85.0 (C≡C), 90.1 (C≡C), 92.7 (C≡C), 120.1 (C_{Ar}C or C_{Tp}C), 121.5 (C_{Ar}C or C_{Tp}C), 122.2 (C_{Ar}H or C_{Tp}H), 122.4 (C_{Ar}H or C_{Tp}H), 123.6 (C_{Ar}C or C_{Tp}C), 131.1 (C_{Ar}H or C_{Tp}H), 131.5 (C_{Ar}H or C_{Tp}H), 132.8 (C_{Ar}H or C_{Tp}H), 133.1 (C_{Ar}C or C_{Tp}C), 137.2 (C_{Ar}H or C_{Tp}H), 142.0 (C_{Ar}C or C_{Tp}C), 144.3 (C_{Ar}C or C_{Tp}C) ppm. MS (70 eV): *m*/*z* (%) = 578 (22), 577 (41) [M + 1]$^+$, 576 (100) [M$^+$], 521 (14), 520 (38), 57 (27). HRMS: calcd. for $C_{33}H_{28}FeS_3$ 576.0703; found 576.0699. $C_{33}H_{28}FeS_3$ (576.1): calcd. C 68.74, H 4.89; found C 69.05, H 5.20.

Cross Metathesis Reaction with 10 and 17: GP, 1,1′-bis[4-(1-propynyl)phenyl]ferrocene (**17**; 104 mg, 0.3 mmol) and 1-(*tert*-butylsulfanyl)-4-(1-propynyl)benzene (**10**; 102 mg, 0.5 mmol), µW (300 W), 130 °C, 30 min RAMP, 120 min HOLD. The product mixture was separated by column chromatography (30 × 2 cm, petroleum ether/dichloromethane, 3:1 to 2:1). I. 1-{4-[2-(4-*tert*-Butylsulfanylphenyl)ethynyl]phenyl}-1′-[4-(1-propynyl)phenyl]ferrocene (**28**; 16 mg, 0.03 mmol, 11%). II. 1,1′-Bis{4-[2-(4-*tert*-butylsulfanylphenyl)ethynyl]phenyl}ferrocene (**29**;[9] 21 mg, 0.03 mmol, 12%), identified by ^{1}H NMR spectroscopy. **28:** IR (ATR): $\tilde{\nu}$ = 3095 (w), 2946 (s), 2921 (s), 2852 (s), 2216 (w), 1588 (w), 1524 (m), 1454 (s), 1260 (s), 1165 (m), 1082 (s), 1033 (s), 1016 (s), 878 (m), 824 (s), 811 (s), 797 (s), 784 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.31 [s, 9 H, C(C*H*$_3$)$_3$], 2.02 (s, 3 H, C*H*$_3$), 4.25 (m, 4 H, H$_{\text{Cp}}$), 4.45 (m, 4 H, H$_{\text{Cp}}$), 7.16 (m, 2 H, H$_{\text{Ar}}$), 7.22 (m, 4 H, H$_{\text{Ar}}$), 7.34 (m, 2 H, H$_{\text{Ar}}$) 7.53 (m, 4 H, H$_{\text{Ar}}$) ppm. ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 4.4 (*C*H$_3$), 31.0 [C(*C*H$_3$)$_3$], 46.4 [*C*(CH$_3$)$_3$], 67.9 (*C*$_{\text{Cp}}$H), 68.0 (*C*$_{\text{Cp}}$H), 70.6 (*C*$_{\text{Cp}}$H), 70.8 (*C*$_{\text{Cp}}$H), 80.0 (C≡C), 85.0 (*C*$_{\text{Cp}}$C), 85.4 (*C*$_{\text{Cp}}$C), 85.8 (C≡C), 88.9 (C≡C), 91.4 (C≡C), 120.1 (*C*$_{\text{Ar}}$C), 121.3 (*C*$_{\text{Ar}}$C), 124.0 (*C*$_{\text{Ar}}$C), 125.6 (*C*$_{\text{Ar}}$H), 125.7 (*C*$_{\text{Ar}}$H), 131.4 (*C*$_{\text{Ar}}$H), 131.5 (*C*$_{\text{Ar}}$H), 131.6 (*C*$_{\text{Ar}}$H), 133.0 (*C*$_{\text{Ar}}$C), 137.2 (*C*$_{\text{Ar}}$H) 137.3 (*C*$_{\text{Ar}}$C or C$_{\text{Ar}}$S), 138.6 (*C*$_{\text{Ar}}$C or C$_{\text{Ar}}$S) ppm. MS (70 eV): *m*/*z* (%) = 566 (17), 564 (43) [M + 1]$^+$, 564 (100) [M$^+$], 509 (13), 508 (34), 57 (33). HRMS: calcd. for $C_{37}H_{32}FeS$ 564.1574; found 564.1570. $C_{37}H_{32}FeS$ (564.6): calcd. C 78.72, H 5.71; found C 78.22, H 5.95.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra of all new compounds.

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