Preparation of [4]- and [5]Ferrocenophanes by Ruthenium-Catalyzed Ring-Closing Ene−Yne Metathesis

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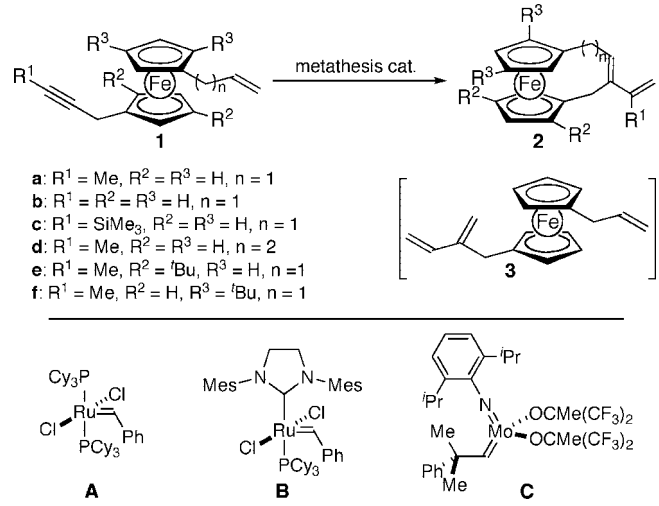
Transannular ring-closing ene−yne metathesis of 1-(ω-alkenyl)-1′-propargylferrocene derivatives affords the corresponding ferrocenophanes in good yields in the presence of the second-generation Grubbs Ru catalyst. The reaction is applicable to the preparation of [4]- and [5]ferrocenophanes. The ferrocenophanes obtained by the present reaction possess a conjugated diene functionality in the bridging side chain, and their further modification is attained via Diels−Alder cycloaddition with tetracyanoethylene or dimethyl acetylenedicarboxylate in a highly diastereoselective fashion.

Since the discovery of the Schrock Mo catalysts[1] and the Grubbs Ru catalysts,[2] olefin metathesis has grown to become a powerful tool in synthetic organic chemistry. These well-defined metathesis catalysts show tolerance to a variety of functional groups and are applicable to the modulation of various organic molecules. Olefin metathesis has proved its usefulness in the modification of organometallic species as well.[3] Recently, Richards,[4] Erker,[5] and our group[6] independently reported the preparation of bridged metallocenes (metallocenophanes; *ansa*-metallocenes) by ruthenium-catalyzed transannular ring-closing metathesis.[7] The transannular RCM route was successfully applied to the preparation of bridged phosphaferrocenes by the use of the Schrock molybdenum catalyst, which was found to be specifically active for the Lewis-basic (η^5-phospholyl)iron(II) substrates.[6b] The RCM process was extended into stereoselective counterparts, and diverse planar-chiral metallocenes were prepared in diastereoselective[6a,d] and enantioselective[6c,d] fashions. In this report, we wish to describe an additional protocol of preparing ferrocenophanes by a transannular metathesis reaction. The substrates for this study are the 1-(ω-alkenyl)-1′-propargylferrocene derivatives **1**. The ring-closing ene−yne metathesis[8] of **1** affords the corresponding ferrocenophanes **2** in good to fair yields in the presence of the second-generation Grubbs Ru catalyst. The ferrocenophanes obtained by the ene−yne metathesis method possess a conjugated diene functionality in the bridging side chain, and their further modification is attained via Diels−Alder cycloaddition with tetracyanoethylene (TCNE) or dimethyl acetylenedicarboxylate (DMAD) in a highly diastereoselective fashion.

Results and Discussion

Preparation of Ferrocenophanes by Ruthenium-Catalyzed Ene−Yne Metathesis. Transformation of 1-allyl-1′-(2-butynyl)ferrocene (**1a**) into the corresponding [4]ferrocenophane **2a** was examined in the presence of 3 mol % of the first-generation Grubbs catalyst **A**[2b] in benzene at 40 °C (Scheme 1; Table 1, entry 1). Although the reaction afforded **2a** as a major product, it was sluggish and the conversion of **1a** was as low as 30% after 6 h. The use of the second-generation Grubbs catalyst **B**[2c]

Scheme 1. Preparation of Ferrocenophanes by Transannular Ring-Closing Ene−Yne Metathesis



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Scheme 2. Isomerization of the [5]Ferrocenophane 2d

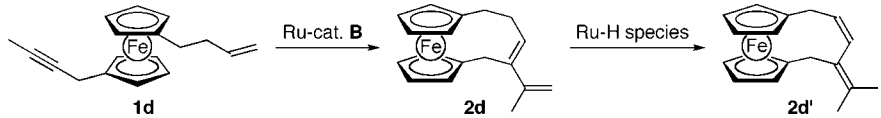

Table 1. Ruthenium-Catalyzed Ene−Yne Metathesis of 1[a]

entry	substrate **1**	cat. (amt (%))	conditions	yield of **2** (%)[b]
1	**1a**	**A** (3)	40 °C, 6 h, in C_6H_6	31 (**2a**),[d]
2	**1a**	**B** (3)	40 °C, 6 h, in C_6H_6	79 (**2a**)
3	**1a**	**B** (3)	40 °C, 12 h, in CH_2Cl_2	74 (**2a**)
4	**1a**	**C** (5)	50 °C, 15 h, in C_6H_6	0
5	**1b**	**B** (10)	50 °C, 24 h, in CH_2Cl_2	NR
6[e]	**1b**	**B** (10)	23 °C, 10 h, in CH_2Cl_2	15 (**2b**),[f]
7	**1c**	**B** (10)	60 °C, 24 h, in C_6H_6	NR
8[g]	**1d**	**B** (10)	60 °C, 24 h, in C_6H_6	81 (**2d**)
9	**1e**	**B** (3)	40 °C, 12 h, in C_6H_6	84 (**2e**)
10	**1f**	**B** (3)	40 °C, 12 h, in C_6H_6	70 (**2f**)

[a] The reaction was carried out in the given solvent under Ar with an initial concentration of **1** at 0.1 mol/L unless otherwise noted. [b] Isolated yields unless otherwise noted. [c] Determined by ^{1}H NMR. [d] Incomplete reactions. [e] Under an ethylene atmosphere (1 atm). [f] 17% of **3** was also formed. [g] With an initial concentration of **1d** at 0.01 mol/L in the presence of a catalytic amount of benzophenone (10 mol % to **1d**).

in place of **A** dramatically accelerated the reaction. Thus, a mixture of **1a** (83.4 mg, 300 μmol) and **B** (7.6 mg, 9.0 μmol; 3 mol %) was dissolved in C_6H_6 (3.0 mL) and the solution was stirred at 40 °C. The substrate **2a** was completely consumed within 6 h, and 66 mg of **3a** (79% yield) was isolated as a yellow-orange crystalline solid by silica gel column chromatography (entry 2). Benzene and CH_2Cl_2 are solvents which have been frequently used for Ru-catalyzed metathesis reactions,[2,8] and both of them were found to be good solvents for the present reaction as well. The Schrock Mo catalyst **C** was not effective for the ene−yne metathesis reaction.[9,10] Although the ene−yne ferrocene **1a** was completely consumed in the presence of **C** (5 mol %), a poorly characterized oligomeric mixture was obtained and **2a** was not detected by GC and NMR analyses (entry 4). The ^{1}H and ^{13}C NMR spectra of the undesired oligomers showed the presence of terminal olefins and the absence of alkyne moieties, implying that the Mo complex **C** oligomerized **1a** at the alkynyl substituent while keeping the olefinic moiety intact.[10]

The reaction is quite sensitive to a substituent at the alkynyl terminus. The substrate with an unsubstituted propargyl group (**1b**) is inert for the reaction under Ar (entry 5). As reported for ene−yne metathesis of terminal alkynyl substrates,[11] the reaction took place under an ethylene atmosphere and the cyclized product **2b** was obtained in 15% yield together with 17% of **3**, which was a product from intermolecular ene−yne metathesis between **2b** and ethylene, and 32% of recovered **1b** (entry 6). The low yield of **2b** is ascribed to the formation of undesirable cross-metathesized oligomers, because **2b** possesses a reactive monosubstituted vinyl pendant group. The substrate **1c**, which has a $SiMe_3$ group at the alkynyl terminus, was inert even at higher temperature (60 °C) with higher catalyst loading (10 mol %, entry 7).

In the reaction of **1d**, which has a longer alkenyl side chain, the intramolecular ring-closing ene−yne metathesis and intermolecular processes are competing to lower the yield. To avoid the latter undesirable processes, high-dilution conditions at higher temperature (60 °C) were required. Under these harsh conditions, however, isomerization of the initially formed [5]ferrocenophane **2d** took place to a certain extent, and thus **2d** was contaminated with the inseparable isomeric **2d′** (ca. 15%; Scheme 2). The isomerization was possibly promoted by a Ru−hydride species derived by decomposition of the Grubbs catalyst,[12] and the side reaction was hampered by an addition of catalytic benzophenone (10 mol % to **1d**) as reported recently.[13] Under the optimized conditions, **2d** was obtained in 81% yield in a pure form (entry 8). The present ring-closing ene−yne metathesis route was also applicable to the ferrocenyl substrates with a polysubstituted η^5-cyclopentadienide such as **1e**,**f**, and the corresponding [4]ferrocenophanes **2e**,**f** were obtained in 84% and 70% yields, respectively (entries 9 and 10).

Single crystals of **2a** suitable for X-ray analysis were grown from a cold pentane solution. The crystal structure is shown in Figure 1, along with selected bond lengths and angles (see the Supporting Information for details). The two η^5-cyclopentadienyl moieties are nearly eclipsed. Because of the C_4 bridge, the ferrocene core is slightly distorted; the dihedral angle between the two cyclopentadienyl ligands is 5.04°, which is within the range of those found in the analogous [4]ferrocenophanes.[6a] The butadiene unit in the bridging moiety possesses an s-trans conformation. Due to conjugation between the C(2)−C(3) and the C(5)−C(6) double bonds, the C(3)−C(2)−C(5)−C(6) dihedral angle is 10.61° and the C(2)−C(5) bond is somewhat shorter (1.481(3) Å) compared to typical C−C single bonds.

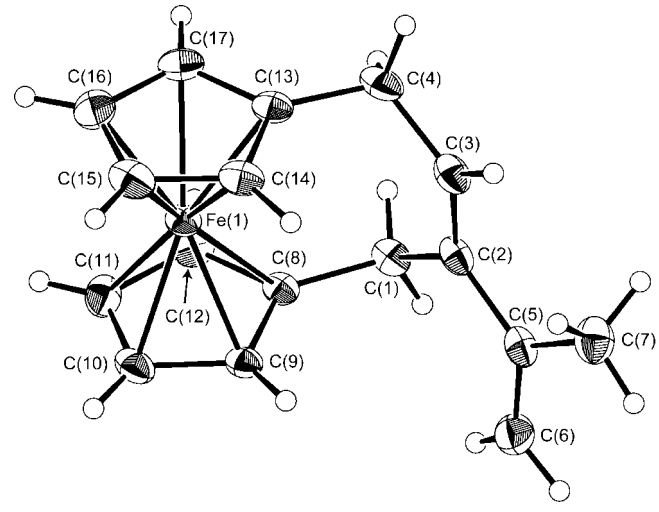

Figure 1. ORTEP drawing of **2a** with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): C(1)−C(2) = 1.521(3), C(2) -C(3) = 1.347(3), C(3)−C(4) = 1.498(4), C(2) -C(5) = 1.481(3),C(5)−C(6)=1.329(3),C(5)−C(7)=1.507(3);C(1)−C(2)−C(3) = 119.7(2), C(1)−C(2)−C(5) = 118.91(19), C(3)−C(2)−C(5) = 121.4(2), C(2)−C(3)−C(4) = 125.6(2), C(6)−C(5)−C(7) = 118.9(3).

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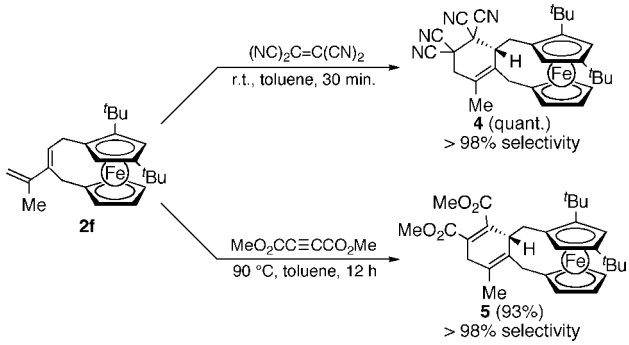
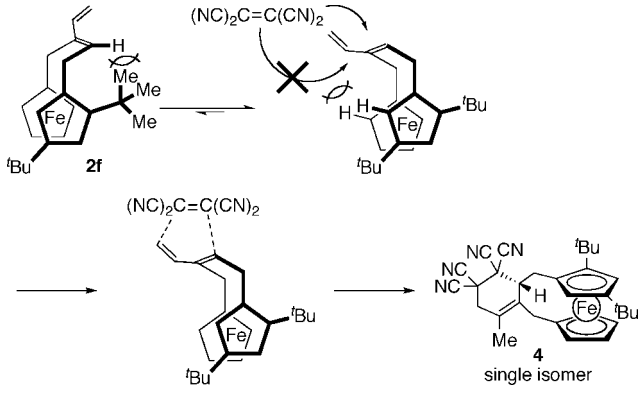
Scheme 3. Diastereoselective Diels−Alder Cycloaddition of the Planar-Chiral [4]Ferrocenophane 2f with Dienophiles



Scheme 4. Plausible Stereochemical Pathway of Diastereoselective Diels−Alder Cycloaddition



Diastereoselective Diels−Alder Reaction of Planar-Chiral [4]Ferrocenophane with Dienophiles. The ferrocenophane **2** obtained by the ene−yne metathesis possesses a conjugated diene moiety in the bridging sidearm, and thus it undergoes Diels−Alder cycloaddition with an appropriate dienophile. A reaction of the planar-chiral **2f** (racemic) with tetracyanoethylene (TCNE) was complete within 30 min at room temperature to give the cyclized product **4** quantitatively (Scheme 3, top). The cycloaddition was highly stereoselective, and one of the two possible diastereomers was obtained exclusively (>98% selectivity determined by ^{1}H NMR). The structure of **4** was unambiguously determined by a single-crystal X-ray analysis, and the ORTEP drawing is depicted in Figure 2. The fused six-membered carbocycle adds an extra distortion in **4**. The dihedral angle between the two cyclopentadienyl planes in **4** is 5.91°, while their relative orientation remains eclipsed (see the Supporting Information for details).

A reaction between **2f** and dimethyl acetylenedicarboxylate (DMAD) was slower and needed prolonged reaction time at higher temperature (90 °C). Despite these harsh conditions, diastereoselectivity of the cycloaddition was still excellent and the product **5**, which was isolated in 93% yield, was obtained as a single isomer (the stereochemistry of **5** shown in Scheme 3 was deduced from the X-ray structure of **4**).

A plausible stereochemical pathway for the diastereoselective formation of **4** is shown in Scheme 4. The bridging diene moiety takes the anti conformation ("anti" with respect to the neighboring ^{t}Bu group) due to steric repulsion with the ^{t}Bu group. In the anti conformer, the re face of the dienic moiety is pointing to open space, while the si face is blocked by the ortho hydrogens. Thus, the dienophile approaches the re face of **2f** to form **4** with excellent diastereoselectivity.

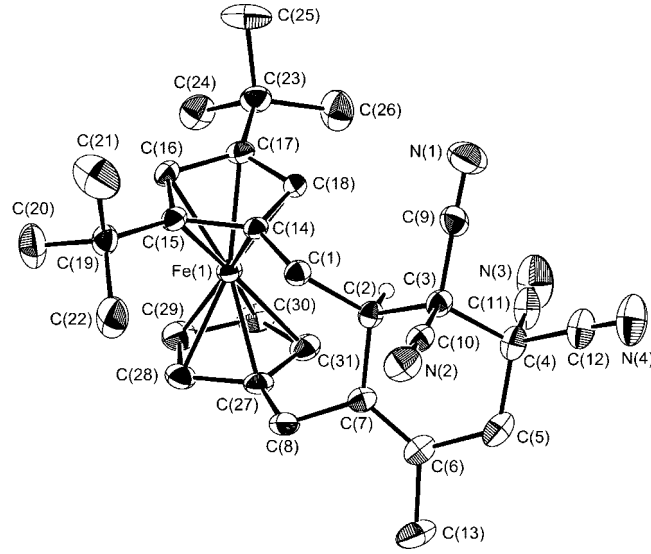


Figure 2. ORTEP drawing of **4** with 30% thermal ellipsoids. All hydrogen atoms except that on C(2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−C(2) = 1.554(4), C(2)−C(3) = 1.563(4), C(2)−C(7) = 1.530(4), C(3)−C(4) = 1.570(4),C(6)−C(7)=1.333(4),C(7)−C(8)=1.514(4);C(1)−C(2)−C(3) = 110.0(2), C(2)−C(7)−C(6) = 122.6(3), C(2)−C(7)−C(8) = 116.3(3), C(6)−C(7)−C(8) = 121.1(3), C(5)−C(6)−C(7) = 123.7(3), C(5)−C(6)−C(13) = 110.9(3).

Conclusions

In summary, we have developed an efficient method of converting a variety of 1-(ω-alkenyl)-1′-propargylferrocene derivatives into the corresponding ferrocenophanes by ruthenium-catalyzed ring-closing ene−yne metathesis. A planar-chiral ferrocenophane obtained by the present method was applied to the Diels−Alder cycloaddition with TCNE or DMAD and showed excellent diastereoselectivity.

Experimental Section

General Considerations. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 100 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. Tetrahydrofuran and benzene were distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. Sodium cyclopentadienide,[14] $C_5H_4{}^tBu_2$,[15] 4-iodo-2-butyne,[16] allylcyclopentadiene,[17] (3-butenyl)cyclopentadiene,[18] C_5H_3(allyl)$^tBu_2$,[6c] (3-(trimethylsilyl)-2-propynyl)cyclopentadiene,[19] $(Cy_3P)_2Cl_2Ru(=CHPh)$,[2b] and $(H_2IMes)(Cy_3P)Cl_2Ru(=CHPh)$[20] were prepared according to the reported methods. All other chemicals were obtained from commercial sources.

(3-Butynyl)cyclopentadienes. C_5H_5(2-butynyl) and C_5H_3(2-butynyl)$^tBu_2$ were prepared from 4-iodo-2-butyne and Cp·Na or $(C_5H_3$-1,3-$^tBu_2)$·Li, which were generated from $C_5H_4{}^tBu_2$ and ^{n}BuLi in THF, and purified by vacuum distillation prior to use. These cyclopentadiene derivatives were obtained as mixtures of double-bond regioisomers and were thus characterized by GC and LR-MS analyses.

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1-(ω-Alkenyl)-1′-(propargyl)ferrocene Derivatives (1). A typical procedure is given for the synthesis of **1a**. To a THF (10 mL) suspension of $FeCl_2$ (1.08 g, 8.52 mmol) was added a THF (25 mL) solution of $[C_5H_4(allyl)]\cdot Na$ and $[C_5H_4(2\text{-butynyl})]\cdot Na$ (prepared from $C_5H_5(allyl)$ (910 mg, 8.57 mmol), $C_5H_5(2\text{-butynyl})$ (1.20 g, 8.56 mmol), and NaH (415 mg, 17.3 mmol) in THF) at room temperature, and the mixture was stirred at 50 °C for 8 h. The mixture was diluted with hexane and filtered through a pad of Celite. After removal of the solvent, the remaining dark red oil was purified by column chromatography on silica gel (with 8/2 hexane/C_6H_6) and subsequent vacuum transfer gave **1a** as a dark red oil. The reaction conditions were not optimized. The characterization data of **1a**,**c**−**f** are listed below.

1-Allyl-1′-(2-butynyl)ferrocene (1a). Yield: 36%. ^{1}H NMR (C_6D_6): δ 1.59 (t, J = 2.7 Hz, 3H), 3.03 (dt, J = 6.6 and 1.5 Hz, 2H), 3.13 (q, J = 2.7 Hz, 2H), 3.94−3.95 (m, 2H), 3.99−4.00 (m, 2H), 4.02−4.03 (m, 2H), 4.09−4.10 (m, 2H), 4.97−5.07 (m, 2H), 5.99 (ddt, J = 17.0, 10.0, and 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 3.4, 19.7, 33.9, 68.3, 68.7, 68.9, 69.3, 76.2, 78.0, 85.8, 87.5, 115.0, 138.1. Anal. Calcd for $C_{17}H_{18}Fe$: C, 73.40; H, 6.52. Found: C, 73.40; H, 6.56. HRMS: *m*/*z* calcd for $C_{17}H_{18}Fe$ 278.0758, found 278.0751.

1-Allyl-1′-(3-(trimethylsilyl)-2-propynyl)ferrocene (1c). Yield: 20%. ^{1}H NMR (C_6D_6): δ 0.25 (s, 9H), 3.05 (dt, J = 6.5 and 1.3 Hz, 2H), 3.14 (s, 2H), 3.92−3.93 (m, 2H), 4.02−4.03 (m, 2H), 4.05−4.06 (m, 2H), 4.08−4.09 (m, 2H), 4.98−5.07 (m, 2H), 5.98 (ddt, J = 17.0, 10.1, and 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 0.3, 20.8, 33.9, 68.5, 68.80, 68.82, 69.4, 84.3, 85.3, 87.5, 105.8, 115.1, 138.1. Anal. Calcd for $C_{19}H_{24}FeSi$: C, 67.85; H, 7.19. Found: C, 68.12; H, 7.19. HRMS: *m*/*z* calcd for $C_{19}H_{24}FeSi$ 336.0997, found 336.1007.

1-(3-Butenyl)-1′-(2-butynyl)ferrocene (1d). Yield: 36%. ^{1}H NMR (C_6D_6): δ 1.61 (t, J = 2.6 Hz, 3H), 2.20−2.25 (m, 2H), 2.37−2.41 (m, 2H), 3.13 (q, J = 2.6 Hz, 2H), 3.92−3.93 (m, 2H), 3.97−3.98 (m, 2H), 4.00−4.01 (m, 2H), 4.07−4.08 (m, 2H), 4.97−5.07 (m, 2H), 5.99 (ddt, J = 17.2, 10.5, and 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 3.5, 19.7, 29.4, 36.0, 68.3, 68.5, 68.9, 69.3, 76.2, 78.0, 85.7, 89.1, 114.7, 138.9. Anal. Calcd for $C_{18}H_{20}Fe$: C, 73.99; H, 6.90. Found: C, 73.95; H, 7.04. HRMS: *m*/*z* calcd for $C_{18}H_{20}Fe$ 292.0913, found 292.0916.

1-Allyl-1′-(2-butynyl)-2,4-di-*tert*-butylferrocene (1e). Yield: 26%. ^{1}H NMR (C_6D_6): δ 1.21 (s, 9H), 1.30 (s, 9H), 1.60 (t, J = 2.6 Hz, 3H), 3.14−3.30 (m, 4H), 3.83 (d, J = 1.8 Hz, 1H), 3.84 (d, J = 1.8 Hz, 1H), 3.89−3.91 (m, 1H), 4.00−4.02 (m, 1H), 4.07−4.08 (m, 1H), 4.19−4.20 (m, 1H), 4.98−5.06 (m, 2H), 5.90−6.00 (m, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 3.5, 19.6, 30.6, 31.7, 32.1, 32.2, 34.6, 64.1, 68.4, 68.6, 68.9, 69.4, 70.6, 76.4, 78.2, 82.4, 85.5, 97.2, 99.2, 115.0, 138.9. Anal. Calcd for $C_{25}H_{34}Fe$: C, 76.92; H, 8.78. Found: C, 76.71; H, 9.04. HRMS: *m*/*z* calcd for $C_{25}H_{34}Fe$ 390.2010, found 390.2009.

1-Allyl-1′-(2-butynyl)-2′,4′-di-*tert*-butylferrocene (1f). Yield: 16%. ^{1}H NMR (C_6D_6): δ 1.18 (s, 9H), 1.31 (s, 9H), 1.54 (t, J = 2.6 Hz, 3H), 3.11 (d, J = 6.4 Hz, 2H), 3.26 (dq, J = 18.0 and 2.6 Hz, 1H), 3.38 (dq, J = 18.0 and 2.6 Hz, 1H), 3.78−3.79 (m, 2H), 3.88−3.89 (m, 1H), 4.01−4.02 (m, 1H), 4.04−4.05 (m, 1H), 4.08−4.09 (m, 1H), 4.96−5.05 (m, 2H), 5.92−6.02 (m, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 3.5, 20.8, 30.6, 31.8, 31.9, 32.1, 34.0, 64.2, 68.76, 68.82, 69.0, 69.9, 71.2, 76.4, 78.7, 80.4, 86.8, 96.8, 98.8, 114.8, 138.7. Anal. Calcd for $C_{25}H_{34}Fe$: C, 76.92; H, 8.78. Found: C, 77.04; H, 8.91. HRMS: *m*/*z* calcd for $C_{25}H_{34}Fe$ 390.2010, found 390.2008.

1-Allyl-1′-propargylferrocene (1b). A mixture of **1c** (825 mg, 2.45 mmol) and K_2CO_3 (ca. 100 mg, 724 μmol) was suspended in MeOH (ca. 10 mL) and the suspension stirred for 2 h at 45 °C. The mixture was partitioned between hexane and H_2O, and the organic solution was dried over $MgSO_4$. After removal of the solvent, the remaining dark red oil was purified by column chromatography on silica gel (with 95/5 hexane/Et_2O) and subsequent vacuum transfer gave **1b** as a dark red oil. Yield: 600 mg (93%). ^{1}H NMR (C_6D_6): δ 1.85 (t, J = 2.7 Hz, 1H), 3.00 (d, J = 6.6 Hz, 2H), 3.02 (d, J = 2.7 Hz, 2H), 3.91−3.92 (m, 2H), 3.97−3.98 (m, 2H), 4.00−4.01 (m, 2H), 4.04−4.05 (m, 2H), 4.97−5.06 (m, 2H), 5.96 (ddt, J = 17.0, 10.1, and 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 19.4, 33.9, 68.5, 68.7, 68.8, 69.3, 69.4, 82.6, 84.1, 87.5, 115.1, 138.0. Anal. Calcd for $C_{16}H_{16}Fe$: C, 72.75; H, 6.11. Found: C, 72.94; H, 6.09. HRMS: *m*/*z* calcd for $C_{16}H_{16}Fe$ 264.0601, found 264.0602.

Ruthenium-Catalyzed Ring-Closing Ene−Yne Metathesis of 1. The reaction conditions and the results are summarized in Table 1. A typical procedure is given for the preparation of 1,1′-(2-propen-2-ylbut-2-en-1,4-diyl)ferrocene (**2a**) (entry 1, Table 1): a mixture of **1a** (83.4 mg, 300 μmol) and the Ru catalyst **B** (7.6 mg, 9.0 μmol, 3 mol %) was dissolved in C_6H_6 (3 mL), and the solution was stirred at 40 °C for 6 h. The solvent was removed under reduced pressure, and the brown residue was chromatographed on silica gel with hexane to give **2a** as a yellow crystalline solid. Yield: 66.0 mg (237 μmol, 79%). The characterization data of the ene−yne metathesis products are listed below.

1,1′-(2-Propen-2-ylbut-2-ene-1,4-diyl)ferrocene (2a). ^{1}H NMR (C_6D_6): δ 1.90 (d, J = 0.7 Hz, 3H), 2.82 (d, J = 8.2 Hz, 2H), 3.15 (s, 2H), 3.88−3.89 (m, 2H), 3.97−3.99 (m, 6H), 4.96 (q, J = 0.7 Hz, 1H), 5.17 (s, 1H), 5.93 (t, J = 8.2 Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.2, 25.4, 25.5, 68.0, 68.2, 68.7, 69.0, 86.3, 88.3, 112.2, 126.6, 142.3, 144.6. Anal. Calcd for $C_{17}H_{18}Fe$: C, 73.40; H, 6.52. Found: C, 73.31; H, 6.58. HRMS: *m*/*z* calcd for $C_{17}H_{18}Fe$ 278.0758, found 278.0761.

1,1′-(2-Vinylbut-2-ene-1,4-diyl)ferrocene (2b). ^{1}H NMR ($CDCl_3$): δ 2.99 (d, J = 8.2 Hz, 2H), 3.19 (s, 2H), 4.00−4.01 (m, 6H), 4.04−4.05 (m, 2H), 5.03 (d, J = 10.7 Hz, 1H), 5.27 (d, J = 17.4 Hz, 1H), 6.04 (t, J = 8.2 Hz, 1H), 6.54 (dd, J = 17.4 and 10.7 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.2, 24.9, 67.5, 67.7, 68.2, 68.6, 86.0, 88.3, 111.3, 131.2, 140.8, 141.1. HRMS: *m*/*z* calcd for $C_{16}H_{16}Fe$ 264.0601, found 264.0599.

1,1′-(2-Propen-2-ylpent-2-ene-1,5-diyl)ferrocene (2d). ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 3H), 2.29−2.32 (m, 2H), 2.55−2.60 (m, 2H), 3.31 (s, 2H), 3.92 (br, 2H), 4.00 (br, 2H), 4.03 (br, 2H), 4.09 (br, 2H), 4.98 (s, 1H), 5.05 (s, 1H), 5.80 (t, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.3, 26.6, 26.8, 29.5, 66.6, 66.8, 67.8, 69.7, 89.9, 90.5, 112.1, 129.7, 139.4, 144.1. HRMS: *m*/*z* calcd for $C_{18}H_{20}Fe$ 292.0913, found 292.0909.

2,4-Di-*tert*-butyl-1,1′-(3-propen-2-ylbut-2-ene-1,4-diyl)ferrocene (2e). ^{1}H NMR (C_6D_6): δ 1.18 (s, 9H), 1.31 (s, 9H), 1.92 (d, J = 0.9 Hz, 3H), 2.80 (dd, J = 14.4 and 8.2 Hz, 1H), 3.12 (d, 15.2 Hz, 1H), 3.32 (d, J = 15.2 Hz, 1H), 3.37 (dd, J = 14.4 and 7.9 Hz, 1H), 3.71 (d, J = 1.8 Hz, 1H), 3.90 (d, J = 1.8 Hz, 1H), 3.99−4.00 (m, 1H), 4.01−4.02 (m, 1H), 4.03−4.05 (m, 1H), 4.14−4.16 (m, 1H), 4.97 (q, J = 0.9 Hz, 1H), 5.21 (s, 1H), 6.01 (t, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.2, 25.1, 25.2, 30.3, 31.4, 32.1, 32.6, 63.3, 66.0, 67.0, 67.2, 70.1, 70.7, 82.3, 84.9, 98.4, 100.0, 111.7, 127.0, 141.5, 144.5. Anal. Calcd for $C_{25}H_{34}Fe$: C, 76.92; H, 8.78. Found: C, 76.78; H, 8.92. HRMS: *m*/*z* calcd for $C_{25}H_{34}Fe$ 390.2010, found 390.2007.

2,4-Di-*tert*-butyl-1,1′-(2-propen-2-ylbut-2-ene-1,4-diyl)ferrocene (2f). ^{1}H NMR ($CDCl_3$): δ 1.12 (s, 9H), 1.33 (s, 9H), 2.01 (s, 3H), 2.96 (dd, J = 14.6 and 8.2 Hz, 1H), 3.02 (dd, 14.6 and 8.2 Hz, 1H), 3.13 (d, J = 15.1 Hz, 1H), 3.61 (d, J = 15.1 Hz, 1H),

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3.65 (d, $J = 1.7$ Hz, 1H), 3.78 (s, 1H), 3.80 (d, $J = 1.7$ Hz, 1H), 3.96 (s, 1H), 3.99 (s, 1H), 4.18 (s, 1H), 4.99 (s, 1H), 5.18 (s, 1H), 6.09 (t, $J = 8.2$ Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.2, 25.2, 25.5, 30.3, 31.4, 32.2, 32.6, 63.8, 65.8, 66.1, 67.0, 70.8, 70.9, 80.5, 87.0, 97.6, 99.6, 112.1, 126.4, 142.8, 144.3. Anal. Calcd for $C_{25}H_{34}Fe$: C, 76.92; H, 8.78. Found: C, 76.67; H, 8.87. HRMS: *m*/*z* calcd for $C_{25}H_{34}Fe$ 390.2010, found 390.2021.

1-Allyl-1′-(2-methylene-3-butenyl)ferrocene (3). ^1H NMR ($CDCl_3$): δ 3.09 (br d, $J = 6.8$ Hz, 2H), 3.27 (br s, 2H), 4.00−4.01 (m, 2H), 4.04−4.05 (m, 6H), 4.83 (br s, 1H), 4.98−5.09 (m, 4H), 5.30 (d, $J = 17.6$, 1H), 5.99 (ddt, $J = 17.1$, 10.2, and 6.7 Hz, 1H), 6.41 (dd, $J = 17.6$ and 6.7 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.8, 33.7, 68.0, 68.2, 68.7, 69.8, 86.1, 87.2, 113.4, 115.1, 116.7, 137.6, 138.8, 146.3. HRMS: *m*/*z* calcd for $C_{18}H_{20}Fe$ 292.0913, found 292.0913.

Diels−Alder Reaction of 2f with TCNE (Preparation of 4). A mixture of **2f** (52.0 mg, 133 μmol) and TCNE (20.5 mg, 160 μmol) was dissolved in toluene (1 mL) and the solution stirred for 30 min at room temperature. After removal of the solvent, the residue was purified by preparative TLC (with 75/25 hexane/EtOAc) to give the cycloaddition product **4** quantitatively. ^1H NMR ($CDCl_3$): δ 1.18 (s, 9H), 1.30 (s, 9H), 1.87 (s, 3H), 2.83 (d, $J =$ 15.6 Hz, 1H), 3.02 (d, 18.1 Hz, 1H), 3.14−3.25 (m, 3H), 3.72 (d, $J = 16.8$ Hz, 1H), 3.79 (br d, $J = 7.1$ Hz, 1H), 3.85−3.86 (m, 2H), 3.95 (d, $J = 1.7$ Hz, 1H), 4.06−4.07 (m, 1H), 4.18−4.19 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.7, 27.6, 27.7, 30.2, 31.3, 32.2, 32.4, 38.2, 38.8, 43.8, 45.6, 64.8, 65.2, 66.8, 69.2, 69.4, 71.0, 74.7, 79.5, 99.1, 102.5, 109.8, 111.1, 111.2, 111.9, 124.1, 128.4. Anal. Calcd for $C_{31}H_{34}N_4Fe$: C, 71.81; H, 6.61; N, 10.81. Found: C, 72.07; H, 6.69; N, 10.86. HRMS: *m*/*z* calcd for $C_{31}H_{34}N_4Fe$ 518.2131, found 518.2140.

Diels−Alder Reaction of 2f with DMAD (Preparation of 5). A mixture of **2f** (83.0 mg, 213 μmol) and DMAD (36.3 mg, 255 μmol) was dissolved in toluene (2 mL) and the solution stirred for 12 h at 90 °C. After removal of the solvent, the residue was purified by preparative TLC (with 80/20 hexane/EtOAc) to give the cycloaddition product **5** in 93% yield (105 mg). ^1H NMR ($CDCl_3$): δ 1.19 (s, 9H), 1.21 (s, 9H), 1,83 (s, 3H), 2.68−2.70 (m, 2H), 2.84 (d, $J = 14.7$ Hz, 1H), 2.99 (d, $J = 21.4$ Hz, 1H), 3.15 (d, $J = 21.4$ Hz, 1H), 3.39−3.42 (m, 1H), 3.69 (d, $J = 14.7$ Hz, 1H), 3.80 (s, 3H), 3.82 (br s, 4H), 4.04 (br s, 1H), 4.06 (br s, 2H), 4.10 (br s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.4, 30.5, 31.66, 31.74, 32.0, 33.8, 34.6, 35.5, 44.3, 52.3, 52.5, 64.4, 64.7, 68.0, 69.4, 69.7, 70.2, 79.7, 83.7, 96.9, 99.0, 127.9, 132.5, 133.4, 142.0, 167.9, 168.5. HRMS: *m*/*z* calcd for $C_{31}H_{40}O_4Fe$ 532.2274, found 532.2269.

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Supporting Information Available: Figures giving ^1H and ^{13}C NMR spectra for all new compounds and CIF files giving crystallographic data for **2a** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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