Structure, Reactivity, and Electronic Properties of [4]Ferrocenophanes and [4]Ruthenocenophanes Prepared via a Novel Heteroannular Cyclization Reaction

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The reactions of 1,1′-bis((trimethylsilyl)ethynyl)ferrocene and 1,1′-bis((trimethylsilyl)ethynyl)ruthenocene with catalytic quantities of alkali-metal methoxides in methanol directly afforded the highly unsaturated [4]metallocenophanes 1,1′-(1-methoxy-1,3-butadienylene)ferrocene and 1,1′-(1-methoxy-1,3-butadienylene)ruthenocene, respectively, in high yields via a novel desilylation/heteroannular cyclization sequence. Analogously, 1,1′-bis((trimethylsilyl)ethynyl)octamethylferrocene reacted to give 1,1′-(1-methoxy-1,3-butadienylene)octamethylferrocene in high yield. The reactions of ((trimethylsilyl)ethynyl)ferrocene and ((trimethylsilyl)ethynyl)ruthenocene under identical conditions afforded ethynylferrocene and ethynylruthenocene, respectively. Synthetic elaboration of the heteroannular bridge of the cyclization products provided a route to additional [4]metallocenophanes. Treatment of 1,1′-(1-methoxy-1,3-butadienylene)ferrocene with acidic silica gel afforded 1,1′-(4-oxo-1-butenylene)ferrocene. Reaction of 1,1′-(4-oxo-1-butenylene)ferrocene with alane provided 1,1′-(1-butenylene)ferrocene, while reaction with sodium borohydride gave 1,1′-(4-hydroxy-1-butenylene)ferrocene. Dehydration of 1,1′-(4-hydroxy-1-butenylene)ferrocene on activated alumina provided 1,1′-(1,3-butadienylene)ferrocene. Similar synthetic transformations were carried out to yield the analogous series of ruthenocenophanes and octamethylferrocenophanes. Voltammetric half-wave oxidation potentials were measured for all of the metallocenophanes in order to evaluate the electronic effect of the heteroannular bridges. X-ray crystal structure analyses were carried out on 1-1′-(1-methoxy-1,3-butadienylene)ferrocene and 1,1′-(1-methoxy-1,3-butadienylene)ruthenocene. 1,1′-(1-Methoxy-1,3-butadienylene)ferrocene, $C_{15}H_{14}FeO$, crystallized in the orthorhombic space group *Pcnb* with a = 26.997(5) Å, b = 5.981(2) Å, c = 28.962(3) Å, Z = 16, and R = 0.072. 1,1′-(1-Methoxy-1,3-butadienylene)ruthenocene, $C_{15}H_{14}RuO$, crystallized in the monoclinic *C*2/*c* space group with a = 20.590(3) Å, b = 9.023(2) Å, c = 13.940(2) Å, β = 111.296(8)°, Z = 8, and R = 0.021.

Introduction

The preparation of ferrocenophanes and ruthenocenophanes in which the cyclopentadienide (Cp) rings of the parent metallocene are joined by a heteroannular bridge has been the focus of numerous efforts. Ferrocenophanes have been prepared with heteroannular bridges consisting of two,[2–5] three,[6–11] four,[12–15] and five[16,17] contiguous carbon atoms. Heteroannular-bridged ferrocenes containing oxygen, sulfur, silicon, and germanium atoms in the bridge have also been prepared.[18–23] Multibridged ferrocenophanes have been constructed,[24–28] and efforts in this area have culminated with the recent preparation of pentabridged

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superferrocenophane.[29] Ferrocenophanes in which the two ferrocene groups are linked in an annular fashion by bridging chains have also received considerable attention.[12,30-41] Synthetic efforts in the ruthenocenophane family have followed a methodology similar to that pursued in the preparation of ferrocenophanes but have been much more limited in scope.[36,41-45]

One driving force for the preparation of metallocenophanes is their potential to serve as monomers for metal-based polymers.[46] Incorporation of metallocenes into macromolecules is attractive because the metal offers the potential for controlling optical and/or electronic properties of the material.[47-50] Recently, strained [1]ferrocenophanes and [2]ferrocenophanes have been utilized as monomers for thermal ring-opening polymerization reactions.[51-54] A particularly exciting entry to new electronic polymers may be possible using metallocenophanes containing an olefin in the heteroannular bridge. Release of strain from these molecules may drive the ring-opening metathetical polymerization (ROMP)[55,56] reaction, resulting in polymeric products containing metallocenyl groups in the polymer backbone rather than as a side chain. Appropriate choice of the metallocenophane monomer may allow for the preparation of completely conjugated polymeric products with potentially interesting properties.[57-60]

Recently, we reported a novel cyclization reaction of 1,1′-diethynylferrocene that led directly to a [4]ferrocenophane in high yield.[61] The [4]ferrocenophane generated in the reaction yields itself readily to synthetic transformations of the heteroannular bridge. We report here full details of our efforts directed at preparing [4]-ferrocenophanes containing two, three, and four unsaturated centers in the heteroannular bridge and successful extension of this heteroannular cyclization reaction to the preparation of the analogous [4]ruthenocenophanes and to the preparation of a series of methylated [4]ferrocenophanes. We also report the effect of the heteroannular bridge on the structure of these metallocenophanes by X-ray crystallographic studies and the electronic influence of the conjugated bridge by voltammetric examination of the metallocenophanes.

Experimental Section

Ferrocene, bis(triphenylphosphine)palladium(II) chloride, copper(II) acetate hydrate, and 2,3,4,5-tetramethyl-2-cyclopentenone were purchased from Aldrich Chemical Co., ruthenocene was purchased from Strem Chemical Co., and (trimethylsilyl)acetylene (TMSA) was purchased from Farchan Laboratories Inc. Iodoferrocene,[62] 1,1′-diiodoferrocene,[62] iodoruthenocene,[63] 1,1′-diiodoruthenocene,[63] 1,1′-divinylferrocene,[64] and octamethylferrocene[65] were prepared according to literature procedures. Column chromatography was performed over EM Science Kieselgel 60 silica gel (230–400 mesh). Fisher Chemical neutral activity I alumina was employed in dehydration reactions and was activated at 200 °C for at least 24 h prior to use. Diethyl ether, tetrahydrofuran, and benzene were dried via distillation from Na–benzophenone immediately prior to use. ^{1}H and ^{13}C NMR spectra were obtained on Bruker AC-200 or AC-250 instruments. IR spectra were obtained on a Perkin-Elmer 1600 FTIR instrument. Gas chromatography experiments were performed on a Hewlett-Packard 5890A instrument with a polyphenylmethylsiloxane (15 m × 0.53 mm) column using flame-ionization detection. High-resolution mass spectra were obtained in the EI mode at The Ohio State University Chemical Instrumentation Center by use of VG 70–2505 or Kratos MS-30 mass spectrometers. Elemental analyses were performed by either Galbraith Laboratories, Knoxville, TN, or Quantitative Technologies Inc., Bound Brook, NJ.

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X-ray Crystallographic Analysis of 3a. The data collection crystal was cut from the end of a red rod and sealed inside of a glass capillary as a precaution against sublimation in the X-ray beam. Examination of the X-ray pattern with a Rigaku AFC5S diffractometer indicated on orthorhombic crystal system with a systematic absences: $0kl$, $l = 2n + 1$; $h0l$, $h + l = 2n + 1$; $hk0$, $k = 2n + 1$. The space group is uniquely determined as $Pcnb$, which is a nonstandard setting for $Pbcn$. With $Z = 16$ there are two independent molecules in the asymmetric unit. Unit cell constants were determined by a symmetry-restricted least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 20–30° with Mo Kα radiation (λ = 0.710 73 Å). Intensities were measured by the ω-scan method. The intensities of 6 standard reflections measured after every 150 reflections indicated that the crystal remained stable. Data were processed with the TEXSAN[66] package of crystallographic software and corrected for absorption by the analytical method.[67] The data and unit cell were then rearranged to correspond to the standard setting for $Pbcn$. The positions of the two Fe atoms were located by the Patterson method in SHELXS-86.[68] These atoms were then used as a phasing model in DIRDIF,[69] and the remaining nonhydrogen atoms were located on an E-map. Full-matrix least-squares refinements were performed in TEXSAN,[66] the function minimized being $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The hydrogen atoms were included in the model as fixed contributions at calculated positions with C—H = 0.98 Å and β(H) = 1.2[β_{eq}(attached C)]. Methyl hydrogen atoms were idealized to sp^3 geometry on the basis of reasonable positions from a difference electron density map. The final refinement cycle was based on the 2216 intensities with $I > \sigma(I)$ and 307 variables and resulted in agreement factors of $R = 0.072$ and $R_w = 0.050$. The final difference electron density map contained maximum and minimum peak heights of 0.78 and −0.76 e/Å^3. Scattering factors for neutral atoms were used.[70] A final structure factor calculation for the 1640 intensities with $I > 3\sigma(I)$ gave an R factor of 0.044.

X-ray Crystallographic Analysis of 3b. The data collection crystal was cut from a long, pale yellow rod. Examination of the diffraction pattern with a Rigaku AFC5S diffractometer indicated a monoclinic crystal system with systematic absences: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$. Space group possibilities are restricted to Cc or $C2/c$. Unit cell constants were determined by a symmetry-restricted least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 27–30° with Mo Kα radiation (λ = 0.710 73 Å). Intensities were measured by the ω–2θ-scan method. The intensities of 6 standard reflections measured after every 150 reflections indicated that the crystal remained stable. Data were processed with the TEXSAN[66] package of crystallographic software and corrected for absorption by the empirical ψ-scan method.[71] The structure was solved in space group $C2/c$ by the Patterson method. The Ru atom was used as a phasing model in DIRDIF,[69] and the non-hydrogen atoms were located on the E-map. Full-matrix least-squares refinements were performed in TEXSAN,[66] the function minimized being $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. After a cycle of anisotropic refinement all of the hydrogen atoms were located on a difference electron density map. They were included in the model as fixed contributions at their calculated positions with C—H = 0.98 Å and β(H) = 1.2[β_{eq}(attached C)]. Methyl hydrogen atoms were idealized to sp^3 geometry on the basis of their positions in the ΔF map. The final refinement cycle was based on the 2345 intensities with $I > \sigma(I)$ and 154 variables and resulted in agreement factors of $R = 0.021$ and $R_w = 0.027$. The final difference electron density map contained maximum and minimum peak heights of 0.30 and −0.27 e/Å^3. Scattering factors for neutral atoms were used.[70]

General Procedures for Cyclic Voltammetry. Cyclic voltammetry was performed using the standard three-electrode configuration in a one-compartment cell.[72] A platinum working electrode was employed in conjunction with a saturated Ag/AgCl (3.0 M NaCl) reference electrode and a platinum-wire counter electrode. The scan rate was 200 mV/s. Voltammetric measurements were obtained using a Bioanalytical Systems CV-1B cyclic voltammograph, and voltammograms were recorded on a Houston Instruments Omnigraph 2000 chart recorder.

1,1′-Bis((trimethylsilyl)ethynyl)ferrocene (2a). To a deoxygenated solution of 630 mg (1.4 mmol) of 1,1′-diiodoferrocene in 27 mL of diisopropylamine was added 40 mg (0.057 mmol) of $(Ph_3P)_2PdCl_2$, 12 mg (0.060 mmol) of $Cu(OAc)_2{\cdot}H_2O$, and 0.50 mL (0.35 g, 3.5 mmol) of TMSA. The resulting slurry was heated at reflux for 4 h and then cooled to room temperature, diluted with hexane, and filtered through a thin pad of Celite. Solvents were removed from the filtrate in vacuo, and the resulting red oil was dissolved in hexane, washed with 5% aqueous HCl, water, and brine, and then dried over $MgSO_4$ and filtered. Solvent was removed in vacuo, giving an oily, red solid which was flash-chromatographed over silica gel using hexane as the eluant. An orange band eluted which, upon removal of solvent in vacuo, afforded 430 mg (80%) of **2a** as an orange, crystalline solid: mp 60–68 °C; IR (KBr) 3113, 3097, 2956, 2896, 2151, 1455, 1407, 1249, 1042, 1034, 931, 842, 758, 728, 697 cm^{-1}; ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 4.41 (t, J = 2 Hz, 4H), 4.21 (t, J = 2 Hz, 4H), 0.22 (s, 18 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 103.4, 91.2, 73.7, 71.5, 65.9, 0.2. Anal. Calcd for $C_{20}H_{26}FeSi_2$: C, 63.48; H, 6.93. Found: C, 63.18; H, 7.05.

1,1′-Bis((trimethylsilyl)ethynyl)ruthenocene (2b). To a deoxygenated solution of 206 mg (0.427 mmol) of 1,1′-diiodoruthenocene in 10 mL of diisopropylamine was added 15 mg (0.021 mmol) of $(Ph_3P)_2PdCl_2$, 5 mg (0.02 mmol) of $Cu(OAc)_2{\cdot}H_2O$, and 0.20 mL (0.14 g, 1.4 mmol) of TMSA. The resulting slurry was heated at 75 °C for 3.5 h and then cooled to room temperature, diluted with hexane, and filtered through a thin pad of Celite. Solvents were removed from the filtrate in vacuo, and the resulting brown residue was dissolved in ether, washed with 5% aqueous HCl, water, and brine, and then dried over $MgSO_4$ and filtered. Solvent was removed in vacuo, giving a yellow residue which was flash–chromatographed over silica gel, under argon, using hexane as the eluant. A yellow band eluted which, upon removal of solvent in vacuo, afforded 125 mg (69%) of **2b** as a pale yellow crystalline solid: mp 115–116 °C; IR (KBr) 2956, 2899, 2151, 1454, 1249, 1205, 1040, 1023, 926, 855, 819, 759, 722, 702 cm^{-1}; ^{1}H NMR (200.1 MHz, C_6D_6) δ 4.83 (t, J = 2 Hz, 4H), 4.29 (t, J = 2 Hz, 4H), 0.18 (s, 18H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 103.0, 91.5, 75.9, 73.2, 70.5, 0.2. Anal. Calcd for $C_{20}H_{26}Si_2Ru$: C, 56.70; H, 6.19. Found: C, 57.01; H, 6.32.

1,1′-(1-Methoxy-1,3-butadienylene)ferrocene (3a). A deoxygenated solution of 220 mg (0.58 mmol) of **2a** in 25 mL of methanol cooled to 0 °C was treated with 0.05 mL (0.1 mmol) of a 2.5 M aqueous potassium hydroxide solution. The resulting mixture was stirred at 0 °C for 24 h, warmed to room temperature, and stirred for 8 h and then poured into water. This mixture was extracted with two portions of dichloromethane, and the combined organic extracts were washed with brine, dried over $MgSO_4$, and filtered. Removal of solvent in vacuo gave a red-orange residue which was filtered through

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a plug of silica gel using 1.5% (v/v) triethylamine in hexane as the eluant. Solvents were removed in vacuo from the filtrate, affording 128 mg (85%) of **3a** as an orange oil. Sublimation of this oil at 80–90 °C (0.01 mmHg) onto an ice-cooled probe afforded analytically pure material as a red crystalline solid: mp 63 °C; IR (neat) 3091, 3002, 2952, 2904, 2900, 2828, 1672, 1622, 1478, 1462, 1384, 1346, 1231, 1206, 1141, 1036, 1025, 985, 840, 806, 743 cm^{-1}; ^{1}H NMR (250.1 MHz, CDCl$_3$) δ 6.04 (d, J = 12.4 Hz, 1H), 5.66 (dd, J = 12.4, 7.2 Hz, 1H), 4.76 (d, J = 7.2 Hz, 1H), 4.50 (t, J = 1.8 Hz, 2H), 4.40 (t, J = 1.8 Hz, 2H), 4.22 (t, J = 1.8 Hz, 2H), 4.18 (t, J = 1.8 Hz, 2H), 3.60 (s, 3H); ^{13}C NMR (62.9 MHz, CDCl$_3$) δ 158.9, 126.4, 124.6, 97.4, 80.1, 77.0, 70.1, 69.9, 67.6, 67.4, 54.8; HRMS calcd for $C_{15}H_{14}{}^{56}FeO$ 266.0394, found 266.0402. Anal. Calcd for $C_{15}H_{14}FeO$: C, 67.70; H, 5.30. Found: C, 67.79; H, 5.16.

1,1′-(1-Methoxy-1,3-butadienylene)ruthenocene (3b). A deoxygenated solution of 312 mg (1.00 mmol) of **2b** in 5 mL of ether and 35 mL of methanol at room temperature was treated with 0.2 mL (0.7 mmol) of a 3.4 M aqueous potassium hydroxide solution. The resulting mixture was stirred at room temperature for 3.5 h and then diluted with ether and washed with water. The aqueous layer was extracted with one portion of ether, and the combined organic layers were washed with water and brine and then filtered through MgSO$_4$. Solvents were removed in vacuo, giving a yellow residue which was sublimed at 80 °C (0.01 mmHg) onto an ice-cooled probe, affording 229 mg (74%) of **3b** as a pale yellow crystalline solid: mp 90–97 °C; IR (KBr) 3080, 3007, 2960, 2924, 2853, 1621, 1462, 1261, 1238, 1211, 1130, 1097, 1035, 1026, 861, 805, 729 cm^{-1}; ^{1}H NMR (250.1 MHz, C$_6$D$_6$) δ 6.17 (d, J = 12.8 Hz, 1H), 5.52, (dd, J = 12.8, 8.5 Hz, 1H), 4.76 (t, J = 2 Hz, 2H), 4.65 (d, J = 8.5 Hz, 1H), 4.60–4.59 (m, 6H), 3.15 (s, 3H); ^{13}C NMR (62.9 MHz, C$_6$D$_6$) δ 158.0, 126.8, 122.8, 98.0, 82.7, 79.2, 73.9, 73.9, 69.9, 69.5, 54.4; HRMS calcd for $C_{15}H_{14}{}^{102}RuO$ 312.0082, found 312.0089.

((Trimethylsilyl)ethynyl)ferrocene (5a). To a deoxygenated solution of 189 mg (0.606 mmol) of iodoferrocene in 15 mL of diisopropylamine was added 21 mg (0.030 mmol) of (Ph$_3$P)$_2$PdCl$_2$ and 6 mg (0.03 mmol) of Cu(OAc)$_2$·H$_2$O followed by 0.15 mL (0.10 g, 1.1 mmol) of TMSA. The resulting slurry was heated at reflux for 3.5 h and then cooled to room temperature, diluted with hexane, and filtered through a thin pad of Celite. Solvent was removed from the filtrate in vacuo, and the resulting orange residue was dissolved in hexane, washed with 5% aqueous HCl, water, and brine, and then dried over MgSO$_4$ and filtered. Solvent was removed in vacuo, giving an orange oil which was flash-chromatographed over silica gel using hexane as the eluant. An orange band eluted which, upon removal of solvent in vacuo, afforded 145 mg (85%) of **5a** as an orange crystalline solid: mp 53.5–54.5 °C; IR (KBr) 3101, 3090, 2956, 2897, 2148, 1452, 1411, 1250, 1104, 1025, 1000, 925, 858, 810, 758, 726 cm^{-1}; ^{1}H NMR (200.1 MHz, C$_6$D$_6$) δ 4.40 (t, J = 2 Hz, 2H), 4.03 (s, 5H), 3.83 (t, J = 2 Hz, 2H), 0.24 (s, 9H); ^{13}C NMR (62.9 MHz, CDCl$_3$) δ 104.2, 90.5, 71.7, 70.1, 68.7, 64.9, 0.3. An analytical sample was obtained via sublimation at 50–55 °C (0.01 mmHg) onto an ice-cooled probe. Anal. Calcd for $C_{15}H_{18}FeSi$: C, 63.83; H, 6.43. Found: C, 64.06; H, 6.47.

(Trimethylsilyl)ethynyl)ruthenocene (5b). To a deoxygenated solution of 240 mg (0.67 mmol) of iodoruthenocene in 50 mL of diisopropylamine was added 25 mg (0.040 mmol) of (Ph$_3$P)$_2$PdCl$_2$ and 10 mg (0.050 mmol) of Cu(OAc)$_2$·H$_2$O followed by 1.0 mL (0.70 g, 0.71 mmol) of TMSA. The resulting mixture was heated at 70 °C for 2 h and then cooled to room temperature, diluted with hexane, and filtered through a thin pad of Celite. Solvents were removed from the filtrate in vacuo, and the resulting brown residue was dissolved in hexane and washed with 5% aqueous HCl, water, and brine and then filtered through MgSO$_4$. Solvents were removed in vacuo, giving a yellow oil which was flash-chromatographed over silica gel under argon using hexane as the eluant. A yellow band eluted which, upon removal of solvent in vacuo, afforded 190 mg (86%) of **5b** as a pale yellow crystalline solid: mp 87–90 °C; IR (KBr) 3106, 2952, 2921, 2148, 1454, 1248, 1101, 1024, 998, 923, 861, 810, 761, 722, 699 cm^{-1}; ^{1}H NMR (250.1 MHz, C$_6$D$_6$) δ 4.85 (t, J = 2 Hz, 2H), 4.44 (s, 5H), 4.27 (t, J = 2 Hz, 2H), 0.18 (s, 9H); ^{13}C NMR (62.9 MHz, C$_6$D$_6$) δ 103.9, 90.8, 74.3, 72.2, 70.9, 69.2, 0.2. An analytical sample was obtained via sublimation at 70 °C (0.01 mmHg) onto an ice-cooled probe. Anal. Calcd for $C_{15}H_{18}RuSi$: C, 55.02; H, 5.54. Found: C, 55.31; H, 5.51.

Treatment of 5a with Alkaline Methanol. A deoxygenated solution of 100 mg (0.35 mmol) of **5a** in 10 mL of methanol at room temperature was treated with 0.10 mL (0.070 mmol) of a 0.70 M aqueous potassium hydroxide solution. The resulting solution was stirred at room temperature for 24 h and then diluted with hexane and washed with water. The aqueous layer was extracted with one portion of hexane, and the combined organic layers were washed with water and brine and then dried over MgSO$_4$ and filtered. Solvents were removed in vacuo, giving an orange residue. Sublimation of this residue at 30 °C (0.01 mmHg) onto an ice-cooled probe afforded 70 mg (93%) of ethynylferrocene (**6a**) as a red crystalline solid: mp 48–50 °C (lit.[73] 51–53.5 °C); IR (neat) 3300, 3096, 2924, 2854, 2109, 1462, 1446, 1412, 1266, 1226, 1206, 1106, 1035, 1024, 1002, 916, 821, 739, 646 cm^{-1}; ^{1}H NMR (200.1 MHz, C$_6$D$_6$) δ 4.34 (t, J = 1.7 Hz, 2H), 4.01 (s, 5H), 3.82 (t, J = 1.7 Hz, 2H), 2.47 (s, 1H); ^{13}C NMR (62.9 MHz, CDCl$_3$) δ 82.6, 73.5, 71.8, 70.1, 68.7, 63.9.

Treatment of 5b with Alkaline Methanol. A deoxygenated solution of 114 mg (0.348 mmol) of **5b** in 30 mL of methanol at room temperature was treated with 0.1 mL (0.2 mmol) of a 2.3 M aqueous potassium hydroxide solution. The resulting mixture was stirred under argon at room temperature for 6 h, concentrated to 5 mL in vacuo, and then diluted with ether and washed with water. The aqueous layer was extracted with one portion of ether, and the combined organic layers were washed with two portions of brine, dried over MgSO$_4$, and then filtered. Solvents were removed in vacuo, giving a tan residue. Sublimation of this residue at 60 °C (0.01 mmHg) onto an ice-cooled probe afforded 69 mg (78%) of ethynylruthenocene (**6b**) as a pale yellow crystalline solid: mp 67–70 °C (lit.[74] 73–74 °C); IR (KBr) 3268, 3118, 3102, 2922, 2853, 2104, 1442, 1407, 1221, 1202, 1099, 1026, 996, 906, 812, 656, 620, 519 cm^{-1}; ^{1}H NMR (200.1 MHz, C$_6$D$_6$) δ 4.82 (t, J = 2 Hz, 2H), 4.42 (s, 5H), 4.26 (t, J = 2 Hz, 2H), 2.41 (s, 1H); ^{13}C NMR (62.9 MHz, C$_6$D$_6$) δ 81.6, 74.3, 74.2, 72.1, 70.9, 68.2.

1,1′-(4-Oxo-1-butenylene)ferrocene (8a) via Acetic Acid Hydrolysis of 3a. A deoxygenated solution of 40 mg (0.15 mmol) of **3a**, 0.4 mL of water, and 0.75 mL (0.75 mmol) of 1.0 M aqueous acetic acid in 5 mL of 1,2-dimethoxyethane was heated at reflux for 18 h and then cooled to room temperature, diluted with ether, and washed with saturated aqueous NaHCO$_3$. The aqueous layer was extracted with two portions of ether, and the combined organic layers were washed with water and brine and then dried over MgSO$_4$ and filtered. Solvents were removed in vacuo, giving a yellow-orange solid which was recrystallized from hexane to afford 29 mg (76%) of **8a** as an orange, crystalline solid: mp 124–125 °C; IR (KBr) 3110, 3100, 3018, 2955, 2930, 1652, 1636, 1448, 1373, 1290, 1264, 1079, 1039, 1032, 890, 831, 820, 716 cm^{-1}; ^{1}H NMR (200.1 MHz, C$_6$D$_6$) δ 6.03 (dt, J = 10.9, 7.1 Hz, 1H), 5.77 (dt, J = 10.9, 1.5 Hz, 1H), 4.37 (t, J = 2 Hz, 2H), 4.04 (t, J = 2 Hz, 2H), 3.83 (t, J = 2 Hz, 2H), 3.74 (t, J = 2 Hz, 2H), 2.99 (dd, J = 7.1, 1.5 Hz, 2H); ^{13}C NMR (62.9 MHz, CDCl$_3$) δ 202.5, 132.5, 123.7, 89.5, 79.1, 74.3, 70.5, 70.0, 69.4, 39.0. An analytical sample was obtained via sublimation at 70 °C (0.01 mmHg) onto an ice-cooled probe. Anal. Calcd for $C_{14}H_{12}FeO$: C, 66.70; H, 4.80. Found: C, 67.05; H, 4.94.

1,1′-(4-Oxo-1-butenylene)ferrocene (8a) via Silica Gel/Aqueous Oxalic Acid Hydrolysis of 3a. A well-stirred slurry of 1.0 g of silica gel and 0.10 mL of 10% aqueous oxalic acid in 3.0 mL of methylene chloride at room temperature was

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treated dropwise with a solution of 30 mg (0.11 mmol) of **3a** in 3.0 mL of methylene chloride. The resulting mixture was stirred at room temperature for 75 min and then neutralized via addition of solid $NaHCO_3$ followed by stirring for an additional 5 min. The slurry was filtered through a fritted-glass disk, and the silica gel that collected was thoroughly washed with methylene chloride. Solvent was removed from the filtrate in vacuo, giving a yellow-orange solid which was sublimed at 80 °C (0.01 mmHg) onto an ice-cooled probe, affording 25 mg (90%) of ketone **8a** as a yellow crystalline solid: mp 122–124 °C. Spectral data for this material were identical with those given above.

1,1′-(4-Oxo-1-butenylene)ruthenocene (8b). A deoxygenated solution of 65 mg (0.21 mmol) of **3b** in 2.0 mL of methylene chloride was added to a well-stirred slurry of 1.0 g of silica gel and 0.10 mL of 10% aqueous oxalic acid in 2.0 mL of deoxygenated methylene chloride. The resulting mixture was stirred under argon at room temperature for 2 h and then neutralized via addition of solid $NaHCO_3$ followed by stirring for an additional 5 min. The slurry was filtered through a fritted-glass disk, and the silica gel that collected on the disk was thoroughly washed with methylene chloride. Solvent was removed from the filtrate in vacuo, and the resulting residue was sublimed at 80 °C (0.01 mmHg) onto an ice-cooled probe, affording 54 mg (87%) of **8b** as a pale yellow crystalline solid: mp 147–152 °C; IR (KBr) 3097, 2923, 2853, 1666, 1639, 1446, 1374, 1293, 1250, 1076, 1039, 1031, 810, 707 cm^{-1}; ^1H NMR (200.1 MHz, C_6D_6) δ 6.01 (dt, J = 11, 8 Hz, 1H), 5.77 (dt, J = 11, 1 Hz, 1H), 4.69 (t, J = 2 Hz, 2H), 4.51 (t, J = 2 Hz, 2H), 4.29–4.28 (m, 4H), 2.74 (dd, J = 8, 1 Hz, 2H); ^{13}C NMR (50.3 MHz, C_6D_6) δ 199.0, 134.0, 122.1, 91.1, 82.1, 75.9, 72.4, 72.2, 72.1, 38.4. An analytical sample was obtained via recrystallization from dichloromethane/hexane. Anal. Calcd for $C_{14}H_{12}RuO$: C, 56.56; H, 4.07. Found: C, 56.40; H, 3.98.

1,1′-(4-Hydroxy-1-butenylene)ferrocene (9a). A solution of 26 mg (0.10 mmol) of **8a** in 1 mL of benzene was added to 10 mL of methanol, and this mixture was then treated with 10 mg (0.26 mmol) of sodium borohydride. The resulting mixture was stirred at room temperature for 40 min, and then 5 mL of water was added followed by heating at 65 °C for 5 min. This mixture was added to water and extracted with two portions of methylene chloride. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and then dried over $MgSO_4$ and filtered. Removal of solvent in vacuo gave a yellow residue which was preadsorbed onto silica gel and flash-chromatographed over silica gel using 25% ether/hexane as the eluant. A yellow band eluted which, upon removal of solvent in vacuo, afforded 23 mg (88%) of **9a** as a bright yellow crystalline solid: mp 136–138 °C; IR (KBr) 3350, 3086, 3018, 2926, 1648, 1440, 1270, 1228, 1034, 1002, 841, 816, 745, 701 cm^{-1}; ^1H NMR (200.1 MHz, C_6D_6) δ 6.15, (d, J = 11.3 Hz, 1H), 5.73–5.59 (m, 1H), 4.24–4.22 (m, 1H), 4.07–4.02 (m, 1H), 4.00–3.93 (m, 6H), 3.71–3.69 (m, 1H), 2.87–2.71 (m, 1H), 2.48–2.38 (m, 1H), 1.14 (d, J = 5.3 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 128.4, 127.6, 87.7, 81.3, 69.6, 69.4, 69.1, 69.0, 68.8, 68.5, 68.3, 66.4, 65.6, 35.9. An analytical sample was obtained via recrystallization from dichloromethane/hexane. Anal. Calcd for $C_{14}H_{14}FeO$: C, 66.17; H, 5.55. Found: C, 65.85; H, 5.44.

1,1′-(4-Hydroxy-1-butenylene)ruthenocene (9b). A deoxygenated solution of 94 mg (0.32 mmol) of **8b** in 3 mL of benzene was added to 7 mL of methanol, and this mixture was then treated with 101 mg (2.67 mmol) of sodium borohydride. The resulting mixture was stirred at room temperature for 1.5 h, and then 5 mL of water was added followed by stirring at room temperature for an additional 5 min. The mixture was diluted with ether and washed with water. The aqueous layer was extracted with one portion of ether, and the combined organic layers were washed with water and brine and then dried over $MgSO_4$ and filtered. Removal of solvent in vacuo gave a pale yellow residue which, upon recrystallization from dichloromethane/hexane, afforded 85 mg (89%) of **9b** as a white crystalline solid: mp 127–129 °C; IR (KBr) 3267, 3078, 3010, 2952, 2926, 2854, 1645, 1464, 1439, 1382, 1030, 998, 935, 803, 751, 514, 444 cm^{-1}; ^1H NMR (200.1 MHz, C_6D_6) δ 6.18 (d, J = 11 Hz, 1H), 5.52–5.38 (m, 1 H), 4.67–4.65 (m, 1 H), 4.57–4.54 (m, 1 H), 4.51–4.46 (m, 3 H), 4.42–4.38 (m, 2 H), 4.13–4.12 (m, 1 H), 3.93 (bd, J = 9 Hz, 1 H), 2.55–2.40 (m, 1 H), 2.20–2.09 (m, 1 H), 1.07 (bs, 1 H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 128.1, 127.5, 89.4, 83.0, 72.7, 72.5, 72.2, 72.1, 71.9, 71.7, 71.3, 69.7, 64.7, 37.9; HRMS calcd for $C_{14}H_{14}{}^{102}RuO$ 300.0082, found 300.0085.

1,1′-(1-Butenylene)ferrocene (10a). A solution of 100 mg (0.75 mmol) of anhydrous $AlCl_3$ in 10 mL of dry ether was added to a slurry of 20 mg (0.5 mmol) of $LiAlH_4$ in 10 mL of dry ether. The resulting mixture was stirred at room temperature for 15 min and then treated with a solution of 128 mg (0.508 mmol) of **8a** in 20 mL of dry ether. The mixture was heated at reflux for 2.5 h and then cooled to room temperature and stirred for an additional 14 h. The mixture was quenched with wet ether, washed with water and brine, and then dried over $MgSO_4$ and filtered. Removal of solvent in vacuo gave a yellow-orange solid which was flash-chromatographed over silica gel using hexane as eluant. A yellow band eluted which, upon removal of solvent in vacuo, afforded 100 mg (83%) of **10a** as a bright yellow, crystalline solid: mp 58–60 °C; IR (KBr) 3077, 3008, 2934, 2908, 2862, 2844, 1645, 1444, 1394, 1322, 1228, 1206, 1040, 1027, 851, 810, 746, 719, 521, 489, 474 cm^{-1}; ^1H NMR (250.1 MHz, C_6D_6) δ 6.20 (d, J = 11.3 Hz, 1H), 5.75 (dt, J = 11.3, 8.3 Hz, 1H), 4.03–3.99 (m, 6H), 3.76 (t, J = 1.8 Hz, 2H), 2.24–2.17 (m, 2H), 1.76–1.72 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 131.5, 125.5, 85.3, 80.6, 69.8, 69.3, 68.5, 68.4, 27.7, 21.2. An analytical sample was obtained via sublimation at 50–55 °C (0.01 mmHg) onto an ice-cooled probe. Anal. Calcd for $C_{14}H_{14}Fe$: C, 70.62; H, 5.93. Found: C, 70.70; H, 5.92.

1,1′-(1-Butenylene)ruthenocene (10b). A solution of 22 mg (0.17 mmol) of anhydrous $AlCl_3$ in 5.0 mL of dry ether was added to a slurry of 7 mg (0.2 mmol) of $LiAlH_4$ in 2.0 mL of dry ether. The resulting mixture was stirred at room temperature for 20 min and then treated with a slurry of 33 mg (0.11 mmol) of **8b** in 7.0 mL of ether. The resulting mixture was heated at reflux for 4 h and then cooled to room temperature and quenched with wet ether. The mixture was washed with four portions of water and one portion of brine and then dried over $MgSO_4$ and filtered. Solvent was removed from the filtrate in vacuo, and the resulting yellow residue was sublimed at 60 °C (0.01 mmHg) onto an ice-cooled probe, affording 31 mg (97%) of **10b** as a pale yellow crystalline solid: mp 106–110 °C; IR (KBr) 3075, 3005, 2930, 2899, 2852, 1460, 1438, 1320, 1042, 1024, 843, 802, 751, 720, 622 cm^{-1}; ^1H NMR (200.1 MHz, $CDCl_3$) δ 6.21 (d, J = 11 Hz, 1H), 5.62 (dt, J = 11, 9 Hz, 1H), 4.61 (t, J = 2 Hz, 2H), 4.58 (t, J = 2 Hz, 2H), 4.52 (t, J = 2 Hz, 2H), 4.29 (t, J = 2 Hz, 2H), 2.11–2.01 (m, 2H), 1.82–1.77 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 131.3, 124.5, 86.4, 81.8, 72.7, 72.1, 71.5, 71.2, 29.2, 20.1; HRMS calcd for $C_{14}H_{14}{}^{102}Ru$ 284.0134, found 284.0139.

1,1′-(1,3-Butandienylene)ferrocene (11a). A mixture of 58 mg (0.23 mmol) of **9a** and 430 mg of alumina was added to a sublimation apparatus, and then a fine layer of alumina was added to the top of this mixture. The apparatus was evacuated to 5 mmHg and then partially submerged in an oil bath preheated to 160 °C. The sublimation was maintained for 1.5 h, during which time a red solid was collected on the ice-cooled probe. The solid was recovered and flash-chromatographed over silica gel using hexane as the eluant. An orange band eluted which, upon removal of solvent in vacuo, gave 24 mg (44%) of **11a** as a viscous red oil. Upon standing at room temperature, the oil crystallized, yielding red cubes: mp 49 °C; IR(KBr) 3082, 3007 cm^{-1}; ^1H NMR (200.1 MHz, C_6D_6) δ 6.24–6.13 (m, 2H), 5.45–5.34 (m, 2H), 4.39 (t, J = 2 Hz, 4H), 4.04 (t, J = 2 Hz, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 129.8, 126.8, 78.1, 69.9, 67.9; HRMS calcd for $C_{14}H_{12}{}^{56}Fe$ 236.0288, found 236.0290.

1,1′-(1,3-Butadienylene)ruthenocene (11b). A mixture of 34 mg (0.11 mmol) of **9b** and 1.0 g of activated alumina was added to a sublimation apparatus, and then a thin layer of alumina was added to the top of this mixture. The apparatus was evacuated to 5 mmHg and then partially submerged in an oil bath heated to 190 °C. Sublimation was maintained for 3.5 h, affording 16 mg (51%) of a white crystalline solid: ^{1}H NMR (250.1 MHz, C_6D_6) δ 6.43–6.34 (m, bridge protons **11b**), 6.23 (d, J = 11.2 Hz, vinyl bridge proton **10b**), 5.48 (dt, J = 11.2, 8.5 Hz, vinyl bridge proton **10b**), 5.33–5.24 (m, bridge protons **11b**), 4.61 (t, J = 1.5 Hz, α or β Cp proton **11b**), 4.59 (t, J = 1.5 Hz, α or β Cp proton **11b**), 4.57–4.54 (m, Cp protons **10b**), 4.47 (t, J = 1.6 Hz, Cp protons **10b**), 4.18 (t, J = 1.6 Hz, Cp protons **10b**), 1.86 (m, methylene bridge protons **10b**), 1.60 (m, methylene bridge protons **10b**).

2,3,4,5-Tetramethyl-1-((trimethylsilyl)ethynyl)-2-cyclopenten-1-ol (13). A solution of 4.3 mL (3.0 g, 30 mmol) of TMSA in 55 mL of dry ether cooled to 0 °C was treated dropwise with 14.8 mL (28 mmol) of 1.9 M BuLi in hexanes. The resulting mixture was stirred at 0 °C for 2 h and was then added dropwise over a period of 30 min to a solution of 3.25 g (23.5 mmol) of 2,3,4,5-tetramethyl-2-cyclopentenone (**12**) in 50 mL of dry ether cooled to −78 °C. The resulting mixture was warmed to 0 °C, stirred at this temperature for 1 h, and then warmed to room temperature and stirred for 17 h (overnight). The mixture was quenched with saturated aqueous NH_4Cl, and the aqueous layer was extracted with one portion of ether. The combined organic layers were washed with saturated aqueous $NaHCO_3$, water, and brine and then dried over $MgSO_4$ and filtered. Solvent was removed in vacuo, giving a yellow oil. The oil was flash-chromatographed over silica gel with 10% ether/hexanes as eluant to afford 3.74 g (68%) of **13** as a viscous, pale yellow liquid: IR (NaCl) 3381, 2959, 2930, 2871, 2163, 1681, 1454, 1377, 1250, 1006, 962, 842, 760 cm^{-1}; ^{1}H NMR (250.1 MHz, C_6D_6) δ 2.01–1.96 (m, 1H), 1.79 (s, 1H), 1.77 (bs, 3H), 1.74–1.65 (m, 1H), 1.33 (s, 3H), 1.32 (d, J = 7 Hz, 3H), 0.87 (d, J = 7 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 138.0, 134.5, 106.6, 90.9, 83.4, 53.7, 47.6, 17.3, 14.2, 12.2, 9.8, 0.15; HRMS calcd for $C_{14}H_{24}SiO$ 236.1596, found 236.1579.

Trimethyl((2,3,4,5-tetramethylcyclopentadien-1-yl)ethynyl)silane (14). A solution of 17.2 g (72.7 mmol) of **13** and 1.04 g (5.47 mmol) of *p*-TsOH·H_2O in 1200 mL of dry benzene was heated at reflux for 3.5 h with azeotropic removal of water. The solution was cooled to room temperature and washed with two portions of saturated aqueous $NaHCO_3$, water, and brine and then dried over $MgSO_4$ and filtered. Solvent was removed in vacuo to give a brown liquid which was distilled at reduced pressure to afford 8.42 g (53%) of **14** as a clear, golden liquid: bp 48–50 °C (0.03 mmHg); IR (NaCl) 2962, 2928, 2856, 2131, 1441, 1377, 1248, 865, 842, 759, 697, 665 cm^{-1}; ^{1}H NMR (250.1 MHz, $CDCl_3$) δ 2.84–2.73 (m, 1H), 1.99 (d, J = 2.0 Hz, 3H), 1.85 (bs, 3H), 1.78 (bs, 3H), 1.13 (d, J = 7.6 Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 150.3, 143.4, 134.3, 124.2, 102.4, 99.5, 51.6, 14.3, 13.4, 12.1, 10.7, 0.4; HRMS calcd for $C_{14}H_{22}Si$ 218.1491, found 218.1481.

1,1′-Bis((trimethylsilyl)ethynyl)octamethylferrocene (15). A solution of 6.03 g (27.6 mmol) of **14** in 125 mL of dry THF at room temperature was treated dropwise with 21.0 mL (30.0 mmol) of 1.43 M BuLi in hexanes over a period of 15 min. The resulting solution was heated at reflux for 3 h and then cooled to 0 °C and added dropwise over a period of 1 h to a slurry of 1.97 g (15.5 mmol) of $FeCl_2$ in 125 mL of dry tetrahydrofuran cooled to −78 °C. The resulting dark mixture was warmed to room temperature, stirred for 13 h (overnight), and then washed with saturated aqueous NH_4Cl. The aqueous layer was extracted with one portion of ether, and the combined organic layers were washed with two portions of water and one portion of brine and then dried over $MgSO_4$ and filtered. Solvents were removed in vacuo, giving a brown-orange residue which was flash-chromatographed over silica gel using hexane as the eluant. A broad orange band eluted which, upon removal of solvent in vacuo, afforded 4.0 g (59%) of **15** as an orange, crystalline solid: mp (sealed tube) 142–143 °C; IR (KBr) 2962, 2911, 2144, 1376, 1366, 1248, 1180, 1079, 1033, 864, 841, 759, 698, 679 cm^{-1}; ^{1}H NMR (250.1 MHz, C_6D_6) δ 1.91 (s, 12H), 1.70 (s, 12H), 0.29 (s, 18H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 103.8, 93.6, 82.7, 81.2, 65.4, 9.4, 8.6, 0.3. An analytical sample was prepared via sublimation at 90–100 °C (0.02 mmHg) onto an ice-cooled probe. Anal. Calcd for $C_{28}H_{42}FeSi_2$: C, 68.54; H, 8.63. Found: C, 68.78; H, 8.70.

1,1′-(1-Methoxy-1,3-butadienylene)octamethylferrocene (16). To 30 mL of deoxygenated methanol at room temperature was added 0.103 g (4.48 mmol) of Na wire under a gentle flow of argon. Upon complete consumption of the Na, 0.313 g (0.641 mmol) of solid **15** was added to the solution in one portion. The resulting slurry was stirred at room temperature for 24 h; then the solvent was removed in vacuo, giving a red-orange residue which was transferred to a sublimation apparatus. Direct sublimation of the residue at 85–90 °C (0.01 mmHg) onto an ice-cooled probe afforded 0.212 g (88%) of **16** as a red-orange solid: IR (KBr) 2996, 2964, 2944, 2904, 1615, 1447, 1376, 1203, 1186, 1151, 1122, 1063, 1030, 994, 723 cm^{-1}; ^{1}H NMR (250.1 MHz, C_6D_6) δ 6.03 (d, J = 12.6 Hz, 1H), 5.80 (dd, J = 12.6, 8.4 Hz, 1H), 5.02 (d, J = 8.4 Hz, 1H), 3.19 (s, 3H), 2.00 (s, 6H), 1.97 (s, 6H), 1.62 (s, 12H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 160.3, 127.8, 123.5, 100.6, 81.2, 80.7, 78.8, 77.3, 76.9, 75.5, 54.1, 10.3, 10.2, 9.5, 9.4. Anal. Calcd for $C_{23}H_{30}FeO$: C, 73.02; H, 7.99. Found: C, 73.34; H, 8.15.

1,1′-(4-Oxo-1-butenylene)octamethylferrocene (17). A well-stirred slurry of 20.1 g of silica gel and 2.0 mL of 10% aqueous oxalic acid in 50 mL of dichloromethane at room temperature was treated dropwise with a solution of 2.34 g (6.18 mmol) of **16** in 20 mL of dichloromethane. The resulting mixture was stirred at room temperature for 24 h and was then neutralized by the addition of 0.50 g of solid $NaHCO_3$ followed by stirring for an additional 15 min. The slurry was filtered through a fritted-glass disk, and the silica gel that collected was washed thoroughly with ether. Solvent was removed in vacuo from the filtrate, giving an orange solid which was preadsorbed onto silica gel and flash-chromatographed over silica gel using 20% ether/hexane as eluant. A dark orange band eluted which, upon removal of solvent in vacuo, afforded 2.03 g (90%) of **17** as an orange, powdery solid: IR (KBr) 3007, 2970, 2946, 2905, 1659, 1632, 1478, 1421, 1394, 1374, 1283, 1246, 1029, 1004, 853, 729, 695, 478, 468 cm^{-1}; ^{1}H NMR (200.1 MHz, C_6D_6) δ 6.16 (dt, J = 10.8, 7.2 Hz, 1H), 5.72 (dt, J = 10.8, 1.5 Hz, 1H), 3.25 (dd, J = 7.2, 1.5 Hz, 2H), 1.74 (s, 6H), 1.49 (s, 6H), 1.41 (s, 6H), 1.37 (s, 6H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 203.7, 132.6, 124.2, 84.3, 83.9, 81.7, 80.3, 79.6, 74.9, 43.2, 10.4, 9.5, 9.4, 9.3. An analytical sample was prepared via sublimation at 90–92 °C (0.005 mmHg) onto an ice-cooled probe. Anal. Calcd for $C_{22}H_{28}FeO$: C, 72.53; H, 7.75. Found: C, 72.61; H, 7.77.

1,1′-(4-Hydroxy-1-butenylene)octamethylferrocene (18). A deoxygenated solution of 1.53 g (4.20 mmol) of **17** in 90 mL of methanol/ether (5:4) at room temperature was treated with 0.21 g (5.6 mmol) of solid $NaBH_4$. The mixture was stirred at room temperature for 20 h and then quenched via addition of 10 mL of 0.5 N aqueous HCl followed by stirring for an additional 15 min. The resulting solution was washed with saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with one portion of ether. The combined organic layers were washed with water and brine and then dried over $MgSO_4$ and filtered. Solvent was removed in vacuo, giving a yellow solid which was preadsorbed onto silica gel and flash-chromatographed over silica gel using 30% ether/hexane as eluant. A broad yellow band eluted which, upon removal of solvent in vacuo, afforded 1.45 g (94%) of **18** as a bright yellow crystalline solid: IR (KBr) 3355, 3003, 2967, 2942, 2901, 1638, 1475, 1445, 1377, 1312, 1199, 1029, 921, 844, 738, 710 cm^{-1}; ^{1}H NMR (500.1 MHz, C_6D_6) δ 6.06–6.04 (m, 1H), 5.88–5.82 (m, 1H), 4.09–4.07 (m, 1H), 2.93–2.87 (m, 1H), 2.61–2.56 (m, 1H), 1.83 (s, 3H), 1.64 (s, 3H), 1.56 (s, 3H), 1.54 (s, 3H), 1.52 (s, 6H), 1.51 (s, 3H), 1.47 (s, 3H), 0.96 (d, J = 2 Hz, 1H): ^{13}C NMR (62.9 MHz, THF-d_8) δ 130.7, 128.2, 81.0, 80.71, 80.67, 80.5, 80.4, 80.1, 79.6, 79.5, 78.8, 77.9, 65.4, 38.2, 10.7, 10.4, 10.1, 10.0, 9.9, 9.8, 9.6, 9.4; HRMS calcd for $C_{22}H_{30}{}^{56}FeO$ 366.1646, found 366.1662.

1,1′-(1-Butenylene)octamethylferrocene (19). A solution of 95 mg (0.071 mmol) of $AlCl_3$ in 10 mL of dry ether was added to a slurry of 18 mg (0.47 mmol) of $LiAlH_4$ in 10 mL of ether. The resulting mixture was stirred at room temperature for 15 min and then treated dropwise with a solution of 145 mg (0.398 mmol) of **17** in 20 mL of dry ether. The mixture was heated at reflux for 1.5 h and then cooled to room temperature and quenched with wet ether. The resulting mixture was washed with two portions of saturated aqueous NH_4Cl, two portions of water, and one portion of brine and then dried over $MgSO_4$ and filtered. Solvent was removed in vacuo, giving a yellow solid which was sublimed at 90–95 °C (0.004 mmHg) onto an ice-cooled probe to afford 132 mg (95%) of **19** as a bright yellow, crystalline solid: IR (KBr) 2999, 2966, 2940, 2899, 1477, 1447, 1432, 1376, 1030, 1007, 736, 694, 474, 456 cm^{-1}; ^1H NMR (200.1 MHz, C_6D_6) δ 6.19 (d, J = 11.5 Hz, 1H), 5.80 (dt, J = 11.5, 8.2 Hz, 1H), 2.30–2.20 (m, 2H), 1.78–1.72 (m, 2H), 1.61 (s, 12H), 1.59 (s, 6H), 1.50 (s, 6H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 130.1, 127.0, 80.5, 79.8, 79.7, 79.1, 79.0, 75.8, 28.4, 17.7, 10.3, 9.8, 9.3. Anal. Calcd for $C_{22}H_{30}Fe$: C, 75.43; H, 8.63. Found: C, 75.62; H, 8.61.

1,1′-(1,3-Butadienylene)octamethylferrocene (20). A solution of 1.14 g (3.11 mmol) of **18** and 0.063 g (0.33 mmol) of p-TsOH·H_2O in 400 mL of dry benzene was heated at reflux for 3.5 h with azeotropic removal of water. The solution was cooled to room temperature and washed with two portions of saturated aqueous $NaHCO_3$, two portions of water, and one portion of brine and then dried over $MgSO_4$ and filtered. Solvent was removed in vacuo, giving a red-orange, powdery solid which was flash-chromatographed over silica gel using 5% ether/hexane as eluant. A narrow red band eluted which, upon removal of solvent in vacuo, afforded 0.937 g (87%) of **20** as a red crystalline solid: IR (KBr) 2996, 2960, 2902, 2854, 1614, 1446, 1376, 1028, 821, 709, 609, 454 cm^{-1}; ^1H NMR (200.1 MHz, C_6D_6) δ 6.34–6.22 (m, 2H), 5.67–5.54 (m, 2H), 2.05 (s, 12H), 1.63 (s, 12H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 130.4, 127.6, 80.5, 76.8, 75.8, 10.2, 9.5. An analytical sample was prepared via sublimation at 85–90 °C (0.005 mmHg) onto an ice-cooled probe. Anal. Calcd for $C_{22}H_{28}Fe$: C, 75.86; H, 8.10. Found: C, 76.26; H, 8.23.

Results and Discussion

1. Preparation of 1,1′-Bis((trimethylsilyl)ethynyl)metallocenes and Their Cyclization to [4]-Metallocenophanes. The coupling reaction[75–77] between 1,1′-diiodoferrocene (**1a**) and excess (trimethylsilyl)acetylene (TMSA) catalyzed by 4–5 mol % of $(Ph_3P)_2PdCl_2$ and 4–5 mol % of $Cu(OAc)_2·H_2O$ in refluxing diisopropylamine gives 1,1′-bis((trimethylsilyl)ethynyl)ferrocene (**2a**) in 80% yield after flash-chromatographic purification over silica gel (Scheme 1).[61] In a similar fashion, the coupling reaction of 1,1′-diiodoruthenocene (**1b**) and excess TMSA gives 1,1′-bis((trimethylsilyl)ethynyl)ruthenocene (**2b**) as a pale yellow crystalline solid in 69% yield after flash-chromatographic purification over silica gel under argon.

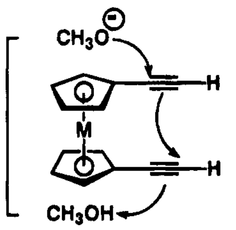
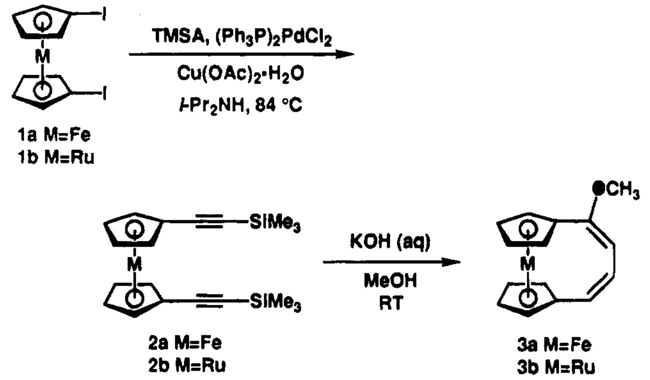


Figure 1. Methoxide attack and cyclization to [4]metallocenophanes.

Scheme 1



Treatment of a deoxygenated solution of **2a** in methanol with aqueous potassium hydroxide at room temperature gives 1,1′-(1-methoxy-1,3-butadienylene)ferrocene (**3a**) as the only detectable product in isolated yields from 75 to 90% (Scheme 1).[61] The ruthenocene analog reacts in a fashion analogous to that described for **2a**. Treatment of a deoxygenated solution of **2b** in methanol with aqueous potassium hydroxide followed by stirring at room temperature for 3.5 h resulted in smooth cyclization to 1,1′-(1-methoxy-1,3-butadienylene)ruthenocene (**3b**) as the only detectable product (Scheme 1). Vacuum sublimation of the crude product gave **3b** as a pale yellow crystalline solid in 74% yield. A reaction pathway consistent with these results involves sequential desilylation[78,79] of **2a,b** to yield an intermediate 1,1′-diethynylmetallocene, which then suffers methoxide attack at an ethynyl carbon α to the Cp ring followed by cyclization onto the β-carbon of the ethynyl group on the opposing Cp ring (Figure 1). Abstraction of a proton from methanol gives the [4]-metallocenophane and regenerates methoxide.[61] A catalytic quantity of hydroxide is generally employed when the reaction is performed. Use of stoichiometric or excess quantities of hydroxide reduces the reaction times from approximately 12 h to less than 1 h. Performing the reaction of 0 °C has no effect on the yield of the reaction, although the reaction time is accordingly longer. Interestingly, we have not detected any ferrocenophane cyclization products when ethanol, 2-propanol, and 2-methyl-2-propanol were employed as solvents. In each case with these solvents, desilylation of **2a** to 1-ethynyl-1′-((trimethylsilyl)ethynyl)ferrocene was observed by gas-chromatographic (GC) analyses. This compound was then consumed, yielding a brown, insoluble material and no products which were detectable by GC analysis or isolable via chromatographic separation.

The ease with which the heteroannular bridge is formed with both of these metallocenes is somewhat surprising, given that the Cp—Cp′ separation is ferrocene is 3.32 Å[80] while in ruthenocene it is 3.68 Å.[81]

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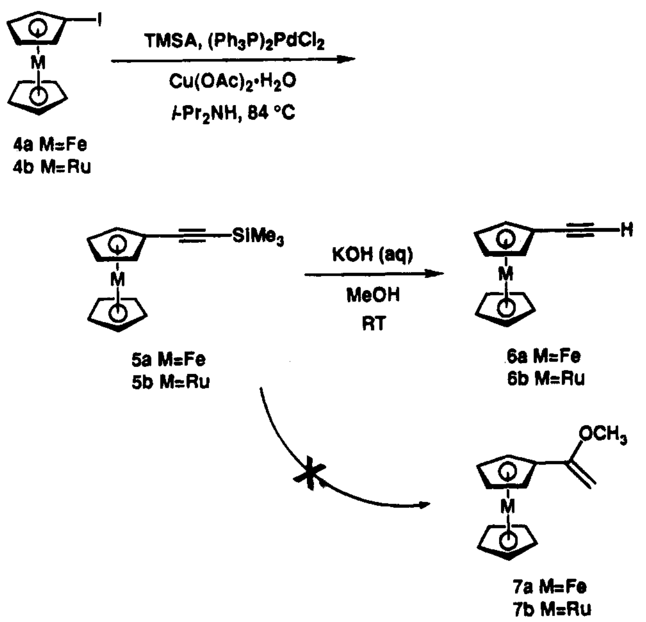
Scheme 2



The greater Cp—Cp′ separation of the ruthenocene system has been suggested as the reason for the dramatically more forcing conditions required for the heteroannular cyclization of β-ruthenocenylpropionic acid relative to β-ferrocenylpropionic acid.[42] An alternative explanation for the lower cyclization reactivity of β-ruthenocenylpropionic acid is the reduced electrophilic substitution reactivity of ruthenocene relative to ferrocene.[42] Both the ferrocene and ruthenocene systems reported herein yield efficient production of [4]-metallocenophanes under the same reaction conditions with approximately the same rate of reaction. It is likely that because these cyclizations do not rely on the electrophilic substitution reactivity of the metallocenes, we did not observe a substantial difference in cyclization reactivity of the metallocenes.

The vinyl ether group in **3a** or **3b** is extremely labile to hydrolysis on silica gel, alumina, and Florisil. Purification of **3a** was readily effected by the addition of 1−2% triethylamine to the chromatography eluant, alleviating hydrolysis and allowing for isolation of the vinyl ether product in high yield. The isolation of the ruthenocenophane vinyl ether product **3b** is most easily accomplished by direct sublimation of the crude reaction material. All of the ferrocenophanes prepared in this study are stable to air and moisture as solids and in solution. However, while stable to moisture and oxygen as solids and to moisture in solution, the analogous ruthenocenophanes are only moderately stable in solution in the presence of oxygen.

2. Preparation and Reactions of ((Trimethylsilyl)ethynyl)metallocenes. Mono((trimethylsilyl)ethynyl)metallocenes can also be readily prepared. The coupling reaction of iodoferrocene (**4a**) and TMSA catalyzed by $(Ph_3P)_2PdCl_2$ and $Cu(OAc)_2{\cdot}H_2O$ in refluxing diisopropylamine gives ((trimethylsilyl)ethynyl)ferrocene (**5a**; Scheme 2). This compound is isolated as an orange crystalline solid in 85% yield after flash-chromatographic purification over silica gel. Similarly, the reaction of iodoruthenocene (**4b**) under reaction conditions identical with those for the preparation of **5a** yields ((trimethylsilyl)ethynyl)ruthenocene (**5b**) in 86% yield. Purification of this material by vaccum sublimation gave analytically pure **5b** as a pale yellow crystalline solid.

In contrast to the results obtained on treatment of the bis((trimethylsilyl)ethynyl)metallocenes **2a,b** with alkaline methanol, reactions of the ((trimethylsilyl)ethynyl)metallocenes **5a,b** with potassium hydroxide in methanol at room temperature result in the simple desilylation of the alkynes to give **6a,b** in 93% and 78% isolated yield, respectively (Scheme 2). A product that might be expected on the basis of the reaction of the bis((trimethylsilyl)ethynyl)metallocenes would be the vinyl ethers **7a,b**. However, no products were isolated or observed consistent with nucleophilic attack on the alkyne. Because of the high yields of these reactions, the mild reaction conditions, and straightforward experimental protocol, the sequence consisting of the coupling reaction of TMSA with the desired iodometallocene followed by desilylation of the resulting product provides an attractive alternative to the published preparations of the ethynylmetallocenes **6a,b**.[73,74]

3. Synthetic Elaboration of the Heteroannular Bridge of [4]Metallocenophanes. The heteroannular bridge of **3a,b** contains both a vinyl ether and an olefin, which serve as convenient handles for the synthetic manipulation of the bridging unit. In a preliminary report we described the hydrolysis of the vinyl ether group in **3a** to the corresponding ketone and the subsequent reduction of the ketone to the methylene group.[61] We report here further chemistry of the heteroannular bridge and, in particular, the preparation of additional structurally interesting [4]metallocenophanes containing four unsaturated carbon centers in the heteroannular bridge.

Previously, we effected hydrolysis of the vinyl ether group in **3a** by reaction with aqueous acetic acid in refluxing 1,2-dimethoxyethane for 18 h to give 1,1′-(4-oxo-1-butenylene)ferrocene (**8a**) in 76% yield after recrystallization from hexane.[61] Because the vinyl ether group in **3a** is susceptibile to hydrolysis on silica gel, we have subsequently employed a procedure published by Conia for hydrolysis of ketals on acidic silica gel to efficiently effect the hydrolysis of this group.[82] Thus, addition of **3a** to a methylene chloride slurry of silica gel containing 10% aqueous oxalic acid followed by stirring at room temperature for 1.25 h gave ketone **8a** as the only observable product. Neutralization of the reaction solution, filtration, removal of solvent, and vacuum sublimation of the crude product gave **8a** in 90% yield as a yellow-orange crystalline solid (Scheme 3). Analogous treatment of **3b** gave 1,1′-(4-oxo-1-butenylene)ruthenocene (**8b**) in 87% yield as a pale yellow crystalline solid after vacuum sublimation of the crude product.

Reduction of the ketone group in **8a** with $NaBH_4$ in methanol at room temperature gave 1,1′-(4-hydroxy-1-butenylene)ferrocene (**9a**) as a bright yellow crystalline solid in 88% yield after flash chromatographic purification over silica gel (Scheme 3). Reduction of the ketone group in **8b** with $NaBH_4$ in methanol at room temperature gave 1,1′-(4-hydroxy-1-butenylene)ruthenocene (**9b**) as a white crystalline solid in 89% yield after recrystallization from ether/hexane. Complete reduction of the ketone group in **8a** to the methylene was accomplished with $AlCl_3/LiAlH_4$[83,84] in refluxing ether to

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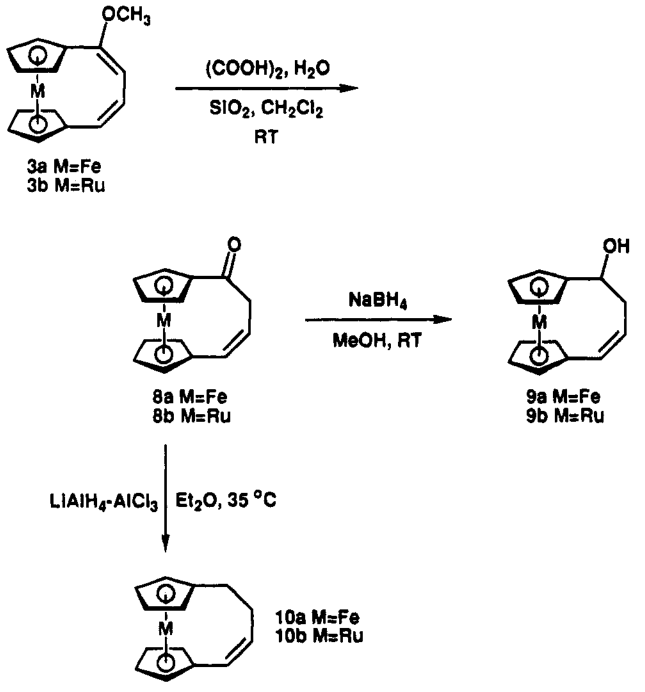
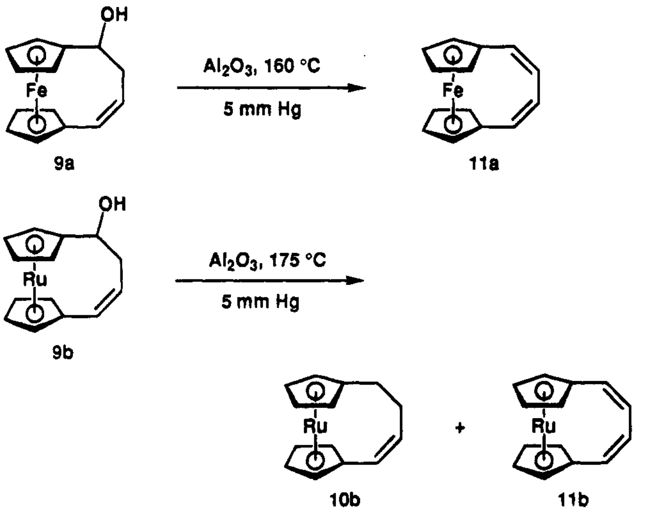
[82] Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63−65.

Scheme 3



Scheme 4



give 1,1′-(1-butenylene)ferrocene (**10a**) as a bright yellow crystalline solid in 83% isolated yield after flash-chromatographic purification over silica gel. Similarly, 1,1′-(1-butenylene)ruthenocene (**10b**) was obtained in nearly quantitative yield as a pale yellow crystalline solid by treatment of **8b** with $AlCl_3/LiAlH_4$ in refluxing ether followed by direct sublimation of the crude product.

We have investigated a variety of procedures for the preparation of the unsaturated [4]ferrocenophane 1,1′-(1,3-butadienylene)ferrocene (**11a**; Scheme 4). Dehydration of **9a** with a catalytic quantity of *p*-toluenesulfonic acid in refluxing benzene under Dean–Stark conditions gave only a trace amount of **11a**. Attempts to convert the hydroxyl group in **9a** to a better leaving group via reaction with *p*-toluenesulfonyl chloride and methanesulfonyl chloride also proved unsuccessful. However, we found that the dehydration of **9a** via a procedure similar to that published by Rausch for the preparation of vinylmetallocenes works quite well (Scheme 4).[64] Thus, heating a mixture of activated neutral alumina and **9a** at 160 °C (5 mmHg) led to a sublimation of **11a** and a trace amount of unreacted **9a**. Flash-chromatographic purification of this mixture over silica gel gave **11a** as a low-melting, red crystalline solid in 44% yield (Scheme 4). Unlike the structurally related 1,1′-divnylferrocene, which is unstable to air both in solution and as a solid,[64] we find **11a** to be quite stable to air as a solid and in solution.

Likewise, several attempts to prepare 1,1′-(1,3-butadienylene)ruthenocene (**11b**) via conventional dehydration procedures proved unsuccessful. When the alumina dehydration reaction was carried out with **9b** at 175 °C (5 mmHg), we found an inseparable 1.1:1 mixture of monoene **10b** and diene **11b** (Scheme 4), as indicated by ^1H NMR analysis.

4. Preparation of a Series of Methylated Ferrocenophanes. In order to further examine the scope of the heteroannular cyclization reaction and as part of an effort directed at the preparation of metallocenophanes with interesting structural and electronic properties, we prepared the methylated ferrocene derivative 1,1′-bis(trimethylsilyl)ethynyl)octamethylferrocene (**15**; Scheme 5). We found that this ferrocene could be conveniently accessed via preparation of trimethyl[(2,3,4,5-tetramethylcyclopentadien-1-yl)ethynyl]silane (**14**) followed by metallation of this cyclopentadiene and reaction with $FeCl_2$. Attempts to prepare the analogous ruthenocene proved unsuccessful. Thus, lithiation of excess TMSA with BuLi at 0 °C followed by dropwise addition of the resulting solution to a THF solution of 2,3,4,5-tetramethyl-2-cyclopentenone (**12**) at −78 °C gave crude 2,3,4,5-tetramethyl-1-((trimethylsilyl)ethynyl)-2-cyclopenten-1-ol (**13**) in quantitative yield as a mixture of cis and trans isomers. Attempted distillation of this compound at reduced pressure resulted in decomposition, but flash chromatographic purification over silica gel led to recovery of **13** in 68% yield as a clear, pale yellow liquid. When a dilute benzene solution of **13** was heated at reflux with 7.5 mol % of p-$TsOH{\cdot}H_2O$ for 3.5 h with azeotropic removal of water, distillation of the crude product at reduced pressure afforded **14** as a clear, golden liquid in 53% yield. ^1H and ^{13}C NMR analysis show that **14** is generated as a mixture of double-bond isomers. Treatment of a THF solution of **14** with excess BuLi followed by heating at reflux for 3 h and then dropwise addition of the resulting solution to a THF slurry of $^1/_2$ equiv of $FeCl_2$, cooled to −78 °C, gave crude ferrocene **15** as a brown-orange residue. Flash-chromatographic purification of this residue over silica gel afforded a 59% yield of **15** as an orange crystalline solid.

Not surprisingly, we found that the desilylation/cyclization of **15** to 1,1′-(1-methoxy-1,3-butadienylene)octamethylferrocene (**16**) requires a reaction time considerably longer than for the analogous transformations of non-methylated derivatives **2a,b** (Scheme 6). Although this conversion can be achieved with the use of a catalytic quantity of sodium methoxide, the extremely long reaction times required render the catalytic route inconvenient. These more forcing conditions are likely necessary due to steric congestion imposed by the methyl groups in **15**, although electronic effects of the methyl groups cannot be ruled out.

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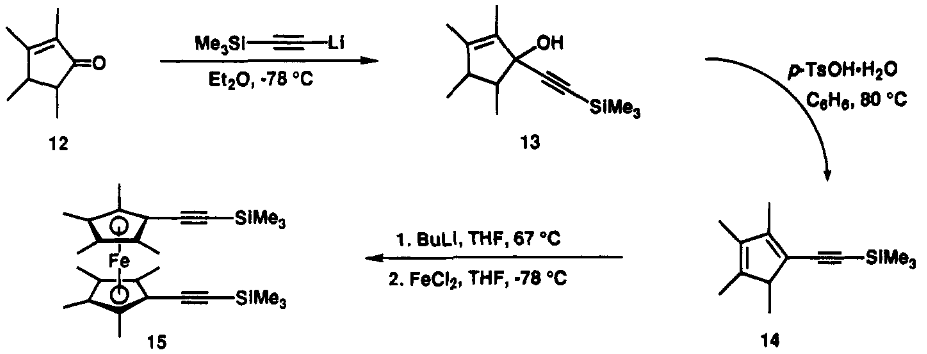
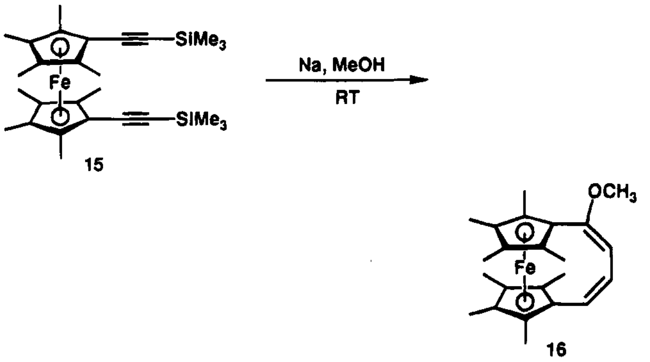
Scheme 5



Scheme 6



Upon addition of **15** to a deoxygenated solution of 7 equiv of sodium methoxide in methanol, desilylation and the heteroannular cyclization proceeded smoothly at room temperature over a period of 24 h to give **16** as the only detectable product (Scheme 6). In order to prepare **16** in an anhydrous environment, thereby preventing hydrolysis of the sensitive vinyl ether group, sodium methoxide was generated via addition of sodium to deoxygenated methanol prior to addition of **16**. This approach also allowed for the anhydrous purification of crude **16** by removal of solvent followed by direct sublimation of the crude residue, giving analytically pure **16** as a red-orange crystalline solid in 88% yield.

Synthetic manipulation of the heteroannular bridge of **16** provides access to additional methylated ferrocenophanes, and we have observed reactivity similar to that exhibited by the non-methylated metallocenophanes. One difference, however, is that most synthetic transformations of the methylated ferrocenophanes require reaction times considerably longer than for analogous transformations of the non-methylated metallocenophanes. Thus, hydrolysis of the vinyl ether group in **16** was smoothly effected via addition of **16** to a methylene chloride slurry of silica gel containing 10% aqueous oxalic acid followed by vigorous stirring at room temperature for 24 h (Scheme 7). Flash-chromatographic purification of the crude product over silica gel gave 1,1′-(4-oxo-1-butenylene)octamethylferrocene (**17**) in 90% yield as a powdery orange solid. Reduction of the ketone group in **17** via treatment with sodium borohydride in ether/methanol required 20 h at room temperature. Although sublimation of the crude product resulted in slow decomposition of the compound, flash chromatographic purification of the crude material over silica gel afforded a 94% yield of 1,1′-(4-hydroxy-1-butenylene)octamethylferrocene (**18**) as a bright yellow crystalline solid. Complete reduction of the ketone group in **17** to the methylene group was accomplished via treatment with excess $LiAlH_4/AlCl_3$ in refluxing ether for 1.5 h, affording 1,1′-(1-butenylene)octamethylferrocene (**19**). Although **19** was found to be oxidized rapidly on silica gel, even under argon, direct vacuum sublimation of the crude product gave a 95% yield of analytically pure material as a bright yellow crystalline solid.

In contrast to the acid-catalyzed dehydration reactions of the analogous non-methylated alcohols **9a**,**b**, which suffered poor recovery of the desired dienes, alcohol **18** was successfully dehydrated via treatment with a catalytic quantity of p-TsOH·H_2O in refluxing benzene. Thus, heating a dilute benzene solution of **18** and 11 mol % of p-TsOH·H_2O at reflux for 3.5 h with azeotropic removal of water afforded 1,1′-(1,3-butadienylene)octamethylferrocene (**20**) as a red crystalline solid in 87% yield after flash-chromatographic purification of the crude product over silica gel.

5. X-ray Crystallographic Studies of Unsaturated [4]Metallocenophanes: Structures of 3a,b. X-ray crystal structures have been determined for a number of ferrocenophanes[27-29,51,53,85-87] and several ruthenocenophanes.[88,89] In order to examine the structural effects of the highly unsaturated heteroannular bridges contained in the metallocenophanes prepared in this study, especially with regard to structural features indicative of strain, an X-ray crystallographic study was undertaken. Ferrocenophane **3a** and ruthenocenophane **3b** were chosen for analysis in order to determine the structural effect of increasing the Cp—Cp′ separation while maintaining the same highly unsaturated bridging unit. Crystals of **3a**,**b** suitable for X-ray analysis were obtained from ethanol and hexane solutions of the respective compounds at −10 °C. Table 1 lists the parameters of the data collection for **3a**,**b**.

X-ray analysis found two independent molecules in the unit cell for **3a**. Table 2 contains selected bond lengths and bond angles for **3a**, Table 3 contains positional parameters and β(eq) values for **3a**, and Figure 2 shows two ORTEP views of this ferrocenophane (molecule B). The Cp(1) rings (atoms C(1) to C(5)) are planar to ±0.01 and ±0.005 Å, while the Cp(2) rings (atoms C(6) to C(10)) are each planar to ±0.006 Å for these two independent molecules. The conformation of

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Scheme 7

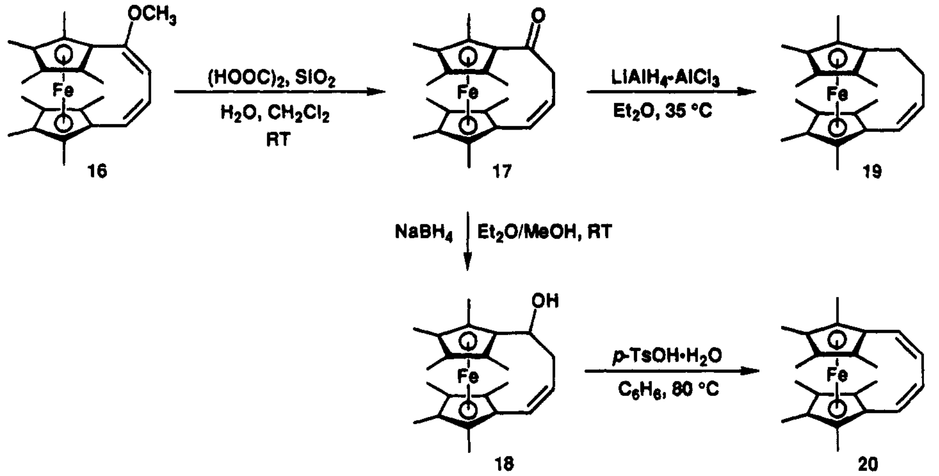

Table 1. Experimental Data for Crystallographic Analyses of 3a,b

	3a	3b
formula	$C_{15}H_{14}FeO$	$C_{15}H_{14}RuO$
fw	266.12	311.35
space group	*Pcnb* (nonstd for *Pbcn*)	*C2/c*
cell dimens		
a, Å	26.997(5)	20.590(3)
b, Å	5.981(2)	9.023(2)
c, Å	28.962(3)	13.940(2)
β, deg		111.296(8)
V, Å^3	4677(4)	2413.0(6)
Z	16	8
density (calc), g/cm^3	1.51	1.71
cryst size, mm	0.04 × 0.27 × 0.46	0.15 × 0.15 × 0.46
radiation (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
monochromator	graphite	graphite
linear abs coeff, cm^{-1}	12.65	12.53
transmissn factors	0.71−0.93	0.90−1.00
temp, °C	23	23
2*θ* limits, deg	$4 \leq 2\theta \leq 55$	$4 \leq 2\theta \leq 55$
scan speed, deg/min in *ω*	4	4
max scans/rfln	4	4
bkgd time/scan time	0.5	0.5
scan range in *ω*, deg	$(1.00 + 0.35 \tan \theta)$	$(1.35 + 0.35 \tan \theta)$
data collected	$+h,+k,+l$ $(4° \leq 2\theta \leq 55°)$; $+h,+k,-l$ $(4° \leq 2\theta \leq 30°)$	$+h,+k,\pm l$
no. unique data	6130, 2216 with $F_o^2 > \sigma(R_o^2)$	2958, 2345 with $F_o^2 > \sigma(F_o^2)$
final no. of variables	307	154
$R(F)^a$	0.072	0.021
$R_w(F)^b$	0.050	0.027
error in observn of unit wt	1.23	1.16

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, with $w = 1/\sigma^2(F_o)$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 3a (Molecules A and B)

	Bond Lengths		
Fe(1)−C(1A)	2.006(7)	Fe(2)−C(1B)	1.997(7)
Fe(1)−C(2A)	2.021(8)	Fe(2)−C(2B)	2.019(8)
Fe(1)−C(3A)	2.028(8)	Fe(2)−C(3B)	2.048(8)
Fe(1)−C(4A)	2.054(8)	Fe(2)−C(4B)	2.073(7)
Fe(1)−C(5A)	2.033(7)	Fe(2)−C(5B)	2.032(7)
Fe(1)−C(6A)	2.015(7)	Fe(2)−C(6B)	2.012(7)
Fe(1)−C(7A)	2.025(7)	Fe(2)−C(7B)	2.047(8)
Fe(1)−C(8A)	2.048(7)	Fe(2)−C(8B)	2.065(8)
Fe(1)−C(9A)	2.043(8)	Fe(2)−C(9B)	2.042(9)
Fe(1)−C(10A)	2.036(9)	Fe(2)−C(10B)	2.013(8)
O(1A)−C(11A)	1.386(8)	O(1B)−C(11B)	1.364(9)
O(1A)−C(15A)	1.416(10)	O(1B)−C(15B)	1.424(9)
C(1A)−C(2A)	1.429(11)	C(1B)−C(2B)	1.430(11)
C(1A)−C(5A)	1.420(10)	C(1B)−C(5B)	1.427(9)
C(1A)−C(11A)	1.474(11)	C(1B)−C(11B)	1.467(10)
C(2A)−C(3A)	1.419(11)	C(2B)−C(3B)	1.408(9)
C(3A)−C(4A)	1.399(11)	C(3B)−C(4B)	1.395(12)
C(4A)−C(5A)	1.403(10)	C(4B)−C(5B)	1.410(10)
C(6A)−C(7A)	1.408(10)	C(6B)−C(7B)	1.410(10)
C(6A)−C(10A)	1.424(10)	C(6B)−C(10B)	1.416(11)
C(6A)−C(14A)	1.472(10)	C(6B)−C(14B)	1.481(11)
C(7A)−C(8)A	1.400(11)	C(7B)−C(8B)	1.414(11)
C(8A)−C(9A)	1.411(12)	C(8B)-C(9B)	1.403(12)
C(9A)−C(10A)	1.413(11)	C(9B)−C(10B)	1.412(10)
C(11A)−C(12A)	1.332(10)	C(11B)−C(12B)	1.351(10)
C(12A)−C(13A)	1.470(10)	C(12B)−C(13B)	1.468(11)
C(13A)−C(14A)	1.335(10)	C(13B)−C(14B)	1.328(11)
Fe(1)−RC(1A)	1.633(8)	Fe(2)-RC(1B)	1.640(8)
Fe(1)−RC(2A)	1.641(8)	Fe(2)−RC(2B)	1.645(8)
	Bond Angles		
C(11A)−O(1A)−C(15A)	119.7(7)	C(11B)−O(1B)−C(15B)	118.7(7)
C(2A)−C(1A)−C(5A)	106.8(8)	C(2B)−C(1B)−C(5B)	106.9(7)
C(2A)−C(1A)−C(11A)	127.2(8)	C(2B)−C(1B)−C(11B)	126.9(8)
C(5A)−C(1A)−C(11A)	125.9(9)	C(5B)−C(1B)−C(11B)	126.1(8)
C(1A)−C(2A)−C(3A)	107.4(8)	C(1B)−C(2B)−C(3B)	107.4(8)
C(2A)−C(3A)−C(4A)	108.8(8)	C(2B)−C(3B)−C(4B)	109.6(8)
C(3A)−C(4A)−C(5A)	107.9(8)	C(3B)−C(4B)−C(5B)	107.7(7)
C(1A)−C(5A)−C(4A)	109.0(8)	C(1B)−C(5B)−C(4B)	108.5(7)
C(7A)−C(6A)−C(10A)	107.2(7)	C(7B)−C(6B)−C(10B)	107.6(8)
C(7A)−C(6A)−C(14A)	126.0(8)	C(7B)−C(6B)−C(14B)	124(1)
C(10A)−C(6A)−C(14A)	126.7(8)	C(10B)−C(6B)−C(14B)	128.0(8)
C(6A)−C(7A)−C(8A)	109.3(8)	C(6B)−C(7B)−C(8B)	108.7(8)
C(7A)−C(8A)−C(9A)	107.4(8)	C(7B)−C(8B)−C(9B)	107.3(8)
C(8A)−C(9A)−C(10A)	108.6(8)	C(8B)−C(9B)−C(10B)	109(1)
C(6A)−C(10A)−C(9A)	107.5(8)	C(6B)−C(10B)−C(9B)	107.6(8)
O(1A)−C(11A)−C(1A)	107.3(7)	O(1B)−C(11B)−C(1B)	109.1(7)
O(1A)−C(11A)−C(12A)	123.0(8)	O(1B)−C(11B)−C(12B)	123.8(8)

the Cp rings can be described by the mean twist angle between the Cp rings, defined as the mean torsion angle of type C(*n*)−RC(1)−RC(2)−C(*n* + 5), where RC(1) is the ring centroid for the Cp(1) ring and RC(2) is the ring centroid for the Cp(2) ring.[90] Mean twist angles of 36.4 and 43.1° are observed for the two independent molecules in the unit cell of **3a**, indicating that the Cp rings of this ferrocenophane are staggered. The iron−RC(1) distances average 1.637 Å for the two independent molecules, while the iron−RC(2) distances average 1.643 Å. These distances are similar to those observed for α-keto-1,1′-trimethyleneferrocene[86] and 1,1′-(tetramethylethylene)ferrocene[85] but are slightly shorter than the distance found in ferrocene.[80] The unsaturated heteroannular bridge imposes ring tilt in **3a**, as evidenced by dihedral angles between the Cp rings of 7.16 and 11.07° found for the two independent molecules. These dihedral angle values are comparable to the value of 8.8° observed for α-keto-1,1′-trimethyleneferrocene[86] but are considerably smaller than the value of 23.2°

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Table 3. Positional Parameters and β(eq) Values (Å^2) for 3a (Molecules A and B)

atom	x	y	z	β(eq)^a
Fe(1)	0.08711(4)	0.1397(2)	0.14382(3)	2.46(5)
O(1A)	0.1686(2)	−0.128(1)	0.2504(2)	4.0(3)
C(1A)	0.1272(3)	0.114(2)	0.2019(2)	2.9(4)
C(2A)	0.1267(3)	0.340(2)	0.1862(2)	3.1(4)
C(3A)	0.0765(4)	0.410(2)	0.1848(3)	3.8(5)
C(4A)	0.0465(3)	0.235(2)	0.2004(3)	3.3(4)
C(5A)	0.0773(3)	0.054(1)	0.2111(2)	2.8(4)
C(6A)	0.1329(3)	0.051(1)	0.0920(2)	2.2(4)
C(7A)	0.1011(3)	0.223(1)	0.0773(2)	3.1(4)
C(8A)	0.0519(3)	0.152(2)	0.0812(3)	3.9(5)
C(9A)	0.0527(3)	−0.069(2)	0.0982(3)	3.7(5)
C(10A)	0.1025(3)	−0.134(2)	0.1046(2)	3.2(4)
C(11A)	0.1707(3)	−0.034(1)	0.2067(3)	3.0(4)
C(12A)	0.2069(3)	−0.0781(1)	0.1768(3)	3.2(4)
C(13A)	0.2163(3)	0.006(2)	0.1298(3)	3.3(4)
C(14A)	0.1873(3)	0.062(1)	0.0944(3)	3.3(4)
C(15A)	0.2057(4)	−0.280(2)	0.2646(3)	4.9(5)
Fe(2)	0.12870(4)	0.3664(2)	0.45592(3)	2.46(5)
O(1B)	0.0451(2)	0.591(1)	0.3515(2)	4.1(3)
C(1B)	0.0750(3)	0.358(2)	0.4086(2)	2.4(3)
C(2B)	0.0852(3)	0.137(1)	0.4247(2)	2.6(3)
C(3B)	0.0759(3)	0.134(2)	0.4726(2)	2.9(4)
C(4B)	0.0595(3)	0.344(2)	0.4867(2)	2.9(4)
C(5B)	0.0587(3)	0.484(1)	0.4475(3)	2.5(4)
C(6B)	0.1923(3)	0.356(2)	0.4198(3)	2.9(4)
C(7B)	0.1999(3)	0.254(2)	0.4630(3)	3.6(5)
C(8B)	0.1895(3)	0.411(2)	0.4982(3)	3.6(5)
C(9B)	0.1764(3)	0.612(2)	0.4764(3)	3.9(5)
C(10B)	0.1779(3)	0.580(1)	0.4281(3)	3.0(5)
C(11B)	0.0821(3)	0.443(1)	0.3616(3)	3.2(4)
C(12B)	0.1191(3)	0.391(2)	0.3321(2)	3.5(4)
C(13B)	0.1634(4)	0.253(2)	0.3395(3)	3.9(5)
C(14B)	0.1942(3)	0.236(2)	0.3750(3)	3.8(5)
C(15B)	0.0491(4)	0.723(2)	0.3107(3)	5.6(6)

^{a} $\beta(\mathrm{eq}) = (8\pi^2/3)\sum_i \sum_j U_{ij}a^*_i a^*_j a_i \cdot a_j$.

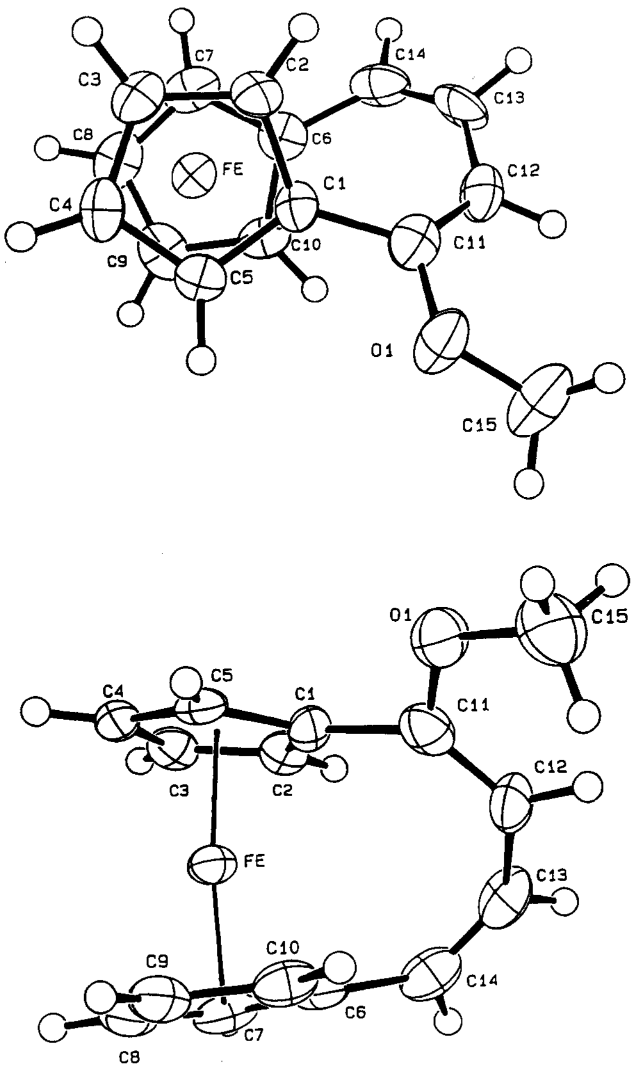

Figure 2. Top (above) and side (below) ORTEP views of **3a** (molecule B) with crystallographic numbering scheme. Non-hydrogen atoms are represented by 50% probability thermal ellipsoids. Hydrogen atoms are drawn with an artificial radius.

observed for 1,1′-(tetramethylethylene)ferrocene.[85] The presence of ring tilt in **3a** is significant, since ring tilt has been suggested to be an indication of strain in ferrocenophanes.[87] The orientation of this ring tilt can be determined via analysis of iron–ring-carbon distances. The iron–ipso-carbon distances average 2.011 and 2.005 Å for the two independent molecules, while the iron–α-carbon distances average 2.029 and 2.028 Å and the iron–β-carbon distances average 2.043 and 2.057 Å, indicating that the Cp–Cp′ separation is smallest at the heteroannular bridge. Strain in metallocenophanes is also related to deviation of the exocyclic bridge bonds from the planes of the Cp rings,[87] and modest deviation of this type is found in **3a**. In this ferrocenophane, bridge atom C(11) lies slightly below (average of 0.071 Å for the two molecules of the unit cell) the plane of Cp(1), while bridge atom C(14) lies slightly above (average of 0.092 Å for the two molecules of the unit cell) the plane of Cp(2).

Table 4 gives selected bond lengths and bond angles for **3b**, Table 5 contains positional parameters and β(eq) values for **3b**, and Figure 3 shows two ORTEP views of this ruthenocenophane. The Cp(1) ring is planar to ±0.01 Å, while Cp(2) is planar to ±0.008 Å. The mean twist angle between the Cp rings is 0.4°, indicating that, like those of crystalline ruthenocene,[81] the Cp rings of **3b** are eclipsed. The ruthenium–RC(1) and ruthenium–RC(2) distances are 1.798 and 1.802 Å, respectively. Accordingly, these distances are longer than those observed for **3a** and are comparable to those observed for 1,1′-trimethyleneruthenocene[88] but slightly shorter than the values observed for ruthenocene[81] and for 1,1′-tetramethyleneruthenocene.[88] Ring tilt is also observed in **3b**, which exhibits a dihedral angle between the Cp rings of 7.73°. This value falls between the values of 14.3 and 1.7° reported for 1,1′-trimethyleneruthenocene and 1,1′-tetramethyleneruthenocene.[88] Ruthenium–ipso-carbon distances average 2.134 Å, while ruthenium–α-carbon and ruthenium–β-carbon distances average 2.166 and 2.189 Å, respectively, indicating that, as in the case of **3a**, the Cp–Cp′ distance is smallest at the heteroannular bridge. Modest deviation of the exocyclic bridge bonds from the planes of the Cp rings is also observed for **3b**. In contrast to the structure of **3a**, however, bridge atom C(11) of **3b** lies slightly *above* (0.12 Å) the plane of Cp(1) and bridge atom C(14) lies slightly *below* (0.084 Å) the plane of Cp(2).

A most striking structural feature of these compounds is the bond angle distortion in their heteroannular bridges. Table 6 gives the bridge bond angles and bridge torsion angles for **3a,b**. Like ring tilt, bond angle distortion in the heteroannular bridge has been suggested to be indicative of strain in ferrocenophanes.[87] These bond angle data reveal that metallocenophanes **3a,b** exhibit considerable expansion of their bridge bond angles from the ideal angle of 120°. The interior pair of angles, C(11)–C(12)–C(13) and C(12)–C(13)–C(14), are distorted to a greater extent than the exterior pair of angles, C(1)–C(11)–C(12) and C(13)–C(14)–C(6), for

Table 4. Bond Lengths (Å) and Bond Angles (deg) for 3b

Bond Lengths			
Ru—C(1)	2.129(2)	C(2)—C(3)	1.428(3)
Ru—C(2)	2.167(2)	C(3)—C(4)	1.417(4)
Ru—C(3)	2.194(2)	C(4)—C(5)	1.427(3)
Ru—C(4)	2.190(2)	C(6)—C(7)	1.425(4)
Ru—C(5)	2.168(2)	C(6)—C(10)	1.419(4)
Ru—C(6)	2.139(2)	C(6)—C(14)	1.470(4)
Ru—C(7)	2.174(3)	C(7)—C(8)	1.413(4)
Ru—C(8)	2.191(3)	C(8)—C(9)	1.413(5)
Ru—C(9)	2.182(3)	C(9)—C(10)	1.424(4)
Ru—C(10)	2.156(3)	C(11)—C(12)	1.346(4)
O—C(11)	1.372(3)	C(12)—C(13)	1.471(4)
O—C(15)	1.430(3)	C(13)—C(14)	1.330(4)
C(1)—C(2)	1.437(3)	Ru—RC(1)	1.798(3)
C(1)—C(5)	1.430(3)	Ru—RC(2)	1.802(3)
C(1)—C(11)	1.476(3)		

Bond Angles			
C(11)—O—C(15)	118.9(2)	C(7)—C(6)—C(14)	124.5(3)
C(2)—C(1)—C(5)	107.6(2)	C(10)—C(6)—C(14)	127.8(3)
C(2)—C(1)—C(11)	125.7(2)	C(6)—C(7)—C(8)	108.4(3)
C(5)—C(1)—C(11)	126.1(2)	C(7)—C(8)—C(9)	108.1(3)
C(1)—C(2)—C(3)	107.9(2)	C(8)—C(9)—C(10)	108.1(3)
C(2)—C(3)—C(4)	108.1(2)	C(6)—C(10)—C(9)	108.0(3)
C(3)—C(4)—C(5)	108.5(2)	O—C(11)—C(1)	106.9(2)
C(1)—C(5)—C(4)	108.8(2)	O—C(11)—C(12)	121.9(2)
C(7)—C(6)—C(10)	107.4(2)		

Table 5. Positional Parameters and β(eq) Values (Å^2) for 3b

atom	x	y	z	β(eq)^a
Ru	0.40593(1)	0.34024(2)	0.05967(1)	2.396(8)
O	0.2835(1)	0.2730(2)	0.2546(1)	3.78(7)
C(1)	0.3455(1)	0.3436(2)	0.1553(2)	2.49(7)
C(2)	0.4075(1)	0.4292(2)	0.2049(2)	2.63(8)
C(3)	0.4071(1)	0.5507(2)	0.1391(2)	3.10(9)
C(4)	0.3451(1)	0.5424(3)	0.0508(2)	3.41(1)
C(5)	0.3063(1)	0.4161(3)	0.0608(2)	2.99(9)
C(6)	0.4260(1)	0.1121(3)	0.0392(2)	3.2(1)
C(7)	0.4914(1)	0.1864(3)	0.0815(2)	3.6(1)
C(8)	0.4942(2)	0.2969(3)	0.0113(3)	4.2(1)
C(9)	0.4316(2)	0.2904(3)	−0.0755(2)	4.5(1)
C(10)	0.3895(2)	0.1755(3)	−0.0589(2)	3.9(1)
C(11)	0.3221(1)	0.2164(3)	0.2010(2)	2.67(8)
C(12)	0.3335(1)	0.0700(3)	0.1976(2)	3.2(1)
C(13)	0.3705(2)	−0.0274(3)	0.1500(2)	4.3(1)
C(14)	0.4055(2)	−0.0161(3)	0.0867(3)	4.4(1)
C(15)	0.2562(2)	0.1736(3)	0.3103(3)	5.2(1)

^{a} $\beta(\mathrm{eq}) = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i a_j$.

each compound. Bridge bond angles found for **3b** are considerably greater than those found for **3a**, most likely in order to accommodate the increased Cp—Cp′ separation in the ruthenocenophane relative to the ferrocenophane while maintaining eclipsed Cp rings. On the basis of this bond angle distortion, it is reasonable to conclude that the heteroannular bridge units in **3a,b** are sources of considerable strain.

Twist in the heteroannular bridge of **3a** is revealed by analysis of the torsion angle data given in Table 6. While showing nearly negligible C(1)—C(11)—C(12)—C(13) and C(12)—C(13)—C(14)—C(6) torsion angles, **3a** exhibits a considerable C(11)—C(12)—C(13)—C(14) torsion angle, indicative of twist in the bridge of this ferrocenophane. In striking contrast, all three bridge torsion angles in **3b** are negligible. This unusual and interesting structural feature is nicely illustrated by the ORTEP views of Figure 3.

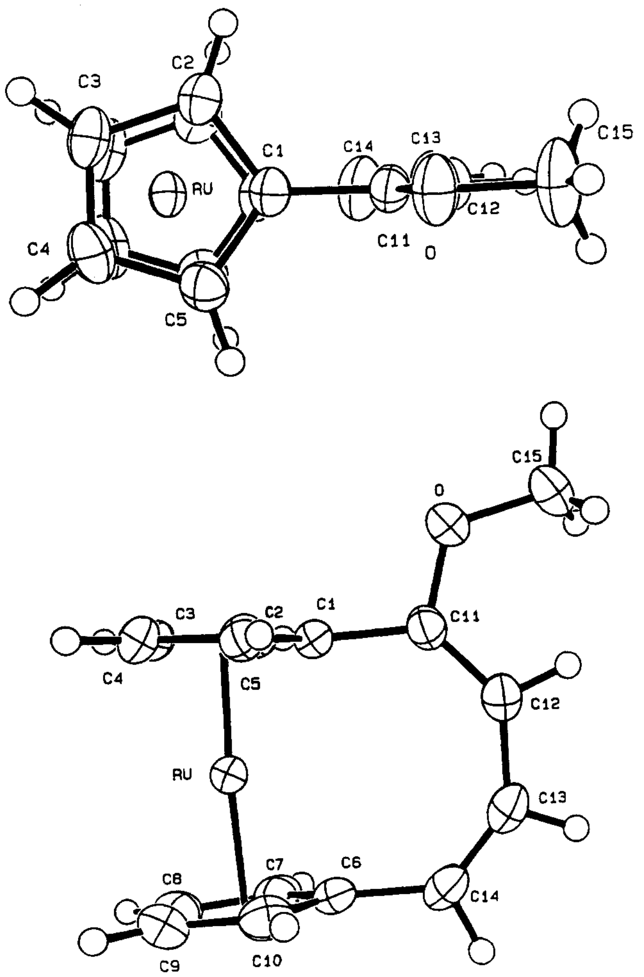

Figure 3. Top (above) and side (below) ORTEP views of **3b** with crystallographic numbering scheme. Non-hydrogen atoms are represented as 50% probability thermal ellipsoids. Hydrogen atoms are drawn with an artificial radius.

Table 6. Bridge Bond Angles (deg) and Bridge Torsion Angles (deg) for 3a (Molecules A and B) and 3b

angle	3a(A)	3a(B)	3b
Bond Angles			
C(1)—C(11)—C(12)	129.8(8)	127.0(8)	131.3(2)
C(11)—C(12)—C(13)	131.4(8)	129.9(8)	136.8(2)
C(12)—C(13)—C(14)	134.1(7)	131.7(8)	138.4(2)
C(13)—C(14)—C(6)	127.6(7)	128.3(8)	132.3(2)
Torsion Angles			
C(1)—C(11)—C(12)—C(13)	0.8(16)	5.5(16)	1.2(6)
C(11)—C(12)—C(13)—C(14)	35.1(18)	40.3(17)	4.0(7)
C(12)—C(13)—C(14)—C(6)	1.7(18)	0.4(17)	4.1(7)

Table 7. Dihedral Angles (deg) between Selected Planes in 3a (Molecules A and B) and 3b

atoms defining plane 1	atoms defining plane 2	dihedral angle between planes 1 and 2		
		3a(A)	3a(B)	3b
Cp(1)	C(1),C(11),C(12)	130.11	38.26	87.62
Cp(1)	C(11),C(12),C(13)	130.61	53.96	88.48
Cp(1)	C(12),C(13),C(14)	128.68	94.20	88.70
Cp(2)	C(6),C(14),C(13)	131.01	138.75	90.41
Cp(2)	C(12),C(13),C(14)	49.97	82.43	86.67
Cp(2)	C(11),C(12),C(13)	53.48	122.52	86.98

A perpendicular orientation of the planar heteroannular bridge in **3b** relative to the Cp rings of the ruthenocenyl group is revealed in the ORTEP views of Figure 3. This novel structural relationship is further illustrated by the data in Table 7, which give dihedral angles between selected planes in **3a,b**. In these metallocenophanes, the planes defined by atoms C(1), C(11), C(12) and C(6), C(14), C(13) represent the bridge olefins adjacent to the Cp(1) rings and Cp(2) rings, respectively. For **3b**, as can be seen from the near-90° dihedral angles found in entries **1** and **4** of Table 7, these olefins are perpendicular to the adjacent Cp rings of the ruthenocenyl group. Conversely, the analogous dihedral angles for **3a** deviate significantly from 90°, indicating that the bridge olefins of this ferrocenophane are skewed with respect to the adjacent Cp rings of the ferrocenyl group. Furthermore, dihedral angles between all other planes in the bridge of **3b** and the Cp rings of the ruthenocenyl group are approximately 90°, while this is clearly not the case for **3a**.

6. Cyclic Voltammetry Analysis of [4]Ferrocenophanes and [4]Ruthenocenophanes. Ferrocenes generally undergo reversible one-electron electrochemical oxidation–reduction cycles, and these compounds have been the subject of numerous electrochemical studies.[91–101] Ruthenocenes have also been the subject of electrochemical studies,[98–104] but unlike ferrocenes, these compounds frequently undergo irreversible electrochemical oxidations. For both of these metallocenes, studies indicate that electron-donating groups facilitate oxidation, thus lowering the half-wave oxidation potential ($E_{1/2}$) of the substituted compound, while electron-withdrawing substituents increase the $E_{1/2}$ of the substituted compound.[99,105] In the case of metallocenophanes, interpretation of $E_{1/2}$ data is not straightforward, since geometrical constraints may reduce conjugation between the Cp rings and unsaturated heteroannular bridges, thereby preventing transmission of electronic effects to the iron atom.[94] Furthermore, the heteroannular bridge often imposes a ring-tilt distortion on the molecule, not present in the simple metallocene, which may affect the electrochemical behavior of the metallocenophane. For instance, Gorton et al. report the $E_{1/2}$ of 1,1′-dimethylferrocene to be 0.23 V vs SCE, while that of 1,1′-ethyleneferrocene under identical conditions is 0.18 V.[94] Gorton et al. attribute this significant decrease in $E_{1/2}$ to ring-tilt distortion in the latter compound, as the Cp rings in the analogous 1,1′-(tetramethylethylene)ferrocene are tilted by 23° from planarity and a similar distortion is expected to exist in 1,1′-ethyleneferrocene.

The redox behavior of [4]ferrocenophanes has received only limited attention, and we are not aware of any published electrochemical studies of ruthenocenophanes. A particularly interesting aspect of the metallocenophanes that we have prepared is the effect of the conjugated heteroannular bridge on their redox behavior. Contained in Table 8 are our $E_{1/2}$ values for ferrocenophanes **3a** and **8a–11a**, methylated ferrocenophanes **16–20**, and ruthenocenophanes **3b** and **8b–10b** measured under identical conditions and reported vs Ag/AgCl in 3.0 M NaCl (SSCE). Also included are $E_{1/2}$ values measured for reference compounds ferrocene, octamethylferrocene, and ruthenocene and model compound 1,1′-divinylferrocene. The $E_{1/2}$ values of the nonmethylated ferrocenophanes were referenced against ferrocene, the methylated ferrocenophane values were referenced against octamethylferrocene, and the ruthenocenophane values were referenced against ruthenocene. All ferrocenophanes exhibited reversible redox processes, while 1,1′-divinylferrocene and all ruthenocenophanes exhibited irreversible oxidations.

Table 8. Cyclic Voltammetric Half-Wave Oxidation Potentials for [4]Ferrocenophanes, [4]Ruthenocenophanes, and Model Compounds

compd	$E_{1/2}$[a] (mV vs SSCE)	$\Delta E_{1/2}$[b] (mV)
Cp_2Fe	370	
3a	460	90
8a	660	290
9a	380	10
10a	330	−40
11a	400	30
1,1′-divinylferrocene	380	10
$(Me_4Cp)_2Fe$	−30	
16	60	90
17	220	250
18	0	30
19	−60	−30
20	20	50
Cp_2Ru	800	
3b	590	−210
8b	1040	240
9b	760	−40
10b	760	−40

[a] Evaluated by single-sweep cyclic voltammetry at 23 °C in acetonitrile solutions which were 1.0×10^{-3} M in substrate and 0.20 M in $NaClO_4$. Reported $E_{1/2}$ values represent the average of at least three independent analyses. All ferrocenophane $E_{1/2}$ values were within ±10 mV of the reported values, while ruthenocenophane $E_{1/2}$ values were within ±30 mV. [b] $\Delta E_{1/2} = E_{1/2}(\text{compound}) - E_{1/2}(\text{reference})$. For ferrocenophanes **3a** and **8a–11a** the reference was ferrocene. For ferrocenophanes **16–20** the reference was octamethylferrocene. For ruthenocenophanes **3b** and **8b–10b** the reference was ruthenocene.

Comparison of the $\Delta E_{1/2}$ values found for the methylated ferrocenophanes (referenced against octamethylferrocene) with those found to the non-methylated series (referenced against ferrocene) is revealing. While the methylated derivatives each exhibit a negative shift in $E_{1/2}$ of ca. 400 mV relative to their nonmethylated analog due to the electron-releasing effects of the methyl groups, the same trends in $\Delta E_{1/2}$ are found for the two series. The highest $E_{1/2}$ value among the non-methylated ferrocenophanes was exhibited by ketone **8a**, with an $E_{1/2}$ value of 660 mV vs SSCE. The resulting $\Delta E_{1/2}$ value of 290 mV, similar to that found for acetylferrocene in previous studies,[92,99] is consistent with the carbonyl group in **8a** being in strong conjugation with the adjacent Cp ring. The highest $E_{1/2}$ value found in the methylated series was exhibited by ketone **17**, which showed an $E_{1/2}$ value of 220 mV vs SSCE corresponding to a $\Delta E_{1/2}$ value of 250 mV. The somewhat lower $\Delta E_{1/2}$ value found for **17**, relative to **8a**, may suggest that carbonyl conjugation and the adjacent Cp ring is weaker in **17** than in **8a**, possibly due to increased steric hindrance imposed by the methyl groups about the

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heteroannular bridge in the former compound. The methylene group adjacent to the carbonyl group in **8a** and **17** may provide the heteroannular bridge with sufficient *conformational flexibility to allow for carbonyl* conjugation with the Cp ring.

The heteroannular bridges in ferrocenophanes **10a** and **19** each contain an olefin, conjugated with a Cp ring, and two saturated centers which should provide conformational flexibility. Previous studies have found vinyl groups to be modestly electron-withdrawing and alkyl groups to be electron-releasing.[99] Accordingly, the $E_{1/2}$ values of **10a** and **19** are consistent with electronic interactions of the vinyl groups and electron-releasing effects of alkyl substitution, resulting in net negative $\Delta E_{1/2}$ values for these compounds. In contrast, small positive $\Delta E_{1/2}$ values were found for the structurally similar ferrocenophanes **9a** and **18**. The higher $E_{1/2}$ values found for alcohols **9a** and **18** are consistent with similar increases observed for α-oxygenated ferrocenes, relative to their non-oxygenated analogs, which have been attributed to the electronegativity of the oxygenated substituent.[94,99] The low $E_{1/2}$ value found for **19** is consistent with the oxidation sensitivity of this compound on silica gel that we have observed, while alcohol **18**, for which we have found a slightly higher $E_{1/2}$ value, does not suffer oxidation on silica gel.

Particularly interesting compounds in this study were ferrocenophanes **3a**, **11a**, **16**, and **20**, for which geometrical constraints should affect conjugation of the highly unsaturated heteroannular bridge with the Cp rings. Recall also that X-ray crystal structure analysis found an average ring tilt of 9.12° for the two molecules in the unit cell of **3a**. Because of these factors, we expected that the effect of the heteroannular bridge in these compounds would be distinct electronically from the effect of conjugated vinyl groups in the 1,1′-divinylferrocene model. The small $\Delta E_{1/2}$ value of +10 mV found for 1,1′-divinylferrocene indicates that, as expected, the vinyl substituents in this compound serve as modest electron-withdrawing groups. Ferrocenophanes **3a** and **16** each exhibited $E_{1/2}$ values of 90 mV, while $\Delta E_{1/2}$ values of 30 and 50 mV were found for ferrocenophanes **11a**, and **20**, respectively. As expected, the greater values of $\Delta E_{1/2}$ found for **3a** and **16**, relative to **11a** and **20**, is consistent with α-substitution of the bridge with electronegative methoxy groups in the former compounds. Although the $\Delta E_{1/2}$ values of these unsaturated ferrocenophanes are greater than that found for the model 1,1′-divinylferrocene, the effect of ring tilt on the redox behavior of the ferrocenophanes is difficult to assess.

Under the conditions of this study, ruthenocene and ruthenocenophanes **3b** and **8b**–**10b** exhibited irreversible electrochemical oxidations. The large positive $\Delta E_{1/2}$ value found for ruthenocenophane **8b** and the small negative values found for ruthenocenophanes **9b** and **10b** are consistent with the values found for the analogous ferrocenophanes. In striking contrast to the 90 mV values found for ferrocenophanes **3a** and **16**, an $\Delta E_{1/2}$ value of −210 mV was found for ruthenocenophane **3b**. The large negative value of $\Delta E_{1/2}$ found for **3b** indicates that the 1-methoxy-1,3-butadienyl heteroannular bridge in this ruthenocenophane acts as a strong electron-donating group, in contrast to its moderate electron-withdrawing effect in ferrocenophanes **3a** and **16**. This result was unexpected, since the chemical reactivity of **3b** was quite similar to that observed for both **3a** and **16** and the stability of **3b** was not noted to differ from that observed for ruthenocene or any other ruthenocenophane in this study. The low $E_{1/2}$ value was, however, reproducible, and the presence of new compounds in the samples after voltammetric analysis could not be detected by GC analysis.

A possible explanation for the unexpected electronic effect exhibited by the bridge unit in **3b** may lie in the unusual geometry of this ruthenocenophane, although Cp ring tilt, found to be less severe in **3b** than in **3a**, is not a likely contributor. As discussed above, the heteroannular bridge in **3b** is planar and the bridge olefins are oriented perpendicular to the adjacent Cp rings of the ruthenocenyl moiety. Conversely, the bridge in **3a** was found to be twisted and dihedral angles between the Cp rings and adjacent bridge olefins deviated significantly from 90°. When the 1-methoxy-1,3-butadienyl bridge adopts a planar geometry with a perpendicular orientation to the adjacent Cp rings, its electronic effect, which would otherwise be expected to be electron-withdrawing, becomes that of a strong electron donor.

Conclusions

We have developed a novel and general heteroannular cyclization reaction of ethynyl-substituted ferrocenes and ruthenocenes which affords high yields of [4]-metallocenophane products. Additionally, we have demonstrated two synthetic routes to the bis((trimethylsilyl)ethynyl)metallocene cyclization precursors. The vinyl ether group contained in the heteroannular bridge of the metallocenophane cyclization products provides a convenient handle for synthetic elaboration of the bridge units. Structural and electronic properties of the metallocenophanes were manipulated via simple synthetic transformations of the bridge unit.

X-ray crystal structure studies of the metallocenophanes containing four unsaturated centers in the heteroannular bridge revealed modest tilting of the Cp rings, modest deviation of the exocyclic bridge bonds from the planes of the Cp rings, and bond angle expansion in the bridge, indicative of strain in these compounds. Greater bond angle expansion found in the bridge of ruthenocenophane **3b**, relative to **3a**, suggests that the ruthenocenophanes are more strained than the analogous ferrocenophanes. Preparation of strained metallocenophanes is significant, since release of this strain might drive new and potentially useful reactions of these compounds such as ROMP.

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Supplementary Material Available: Side and top ORTEP views of **3a** (molecule A) and tables of bond angles, bond lengths, least-squares planes, torsion angles, calculated positional parameters for hydrogen atoms, and anisotropic displacement parameters for **3a,b** (23 pages). Ordering information is given on any current masthead page.

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