Transition-Metal-Promoted Activation of Carbon–Carbon Bonds. A New Synthetic Route to Substituted Ruthenocene Derivatives via Ring Expansion Reactions of 3-Vinyl-1-cyclopropenes

Russell P. Hughes* and David J. Robinson

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

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A new route to substituted ruthenocenes is described. The reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})X]$ (C_8H_{12} = 1,5-cyclooctadiene; X = Cl, Br), $[Ru(\eta^5\text{-}C_9H_7)(\eta^4\text{-}C_8H_{12})Cl]$ (C_9H_7 = indenyl), and $[\{Ru(\eta^5\text{-}C_5Me_5)Cl\}_4]$ with substituted 3-vinyl-1-cyclopropenes (**1**) provides a high-yield route to a range of substituted ruthenocenes, $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5R_5)]$ {**2**, $C_5R_5 = C_5H_2Ph_3$-1,2,3; **3**, $C_5R_5 = C_5H_3Ph_2$-1,2; **4**, $C_5R_5 = C_5H_2Ph_2$-1,2-Me-4; **5**, $C_5R_5 = C_5HMePh_3$-1,2,3}, $[Ru(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_2Ph_3\text{-}1,2,3)]$ (**6**), and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_2Ph_3\text{-}1,2,3)]$ (**7**). No intermediates in these reactions could be detected by ^1H or $^{13}C\{^1H\}$ NMR spectroscopy. The cis-α,-β-disubstituted vinylcyclopropene 1,2,3-triphenyl-3-(*cis*-β-methylvinyl)-1-cyclopropene (**1e**) reacts more rapidly than its trans isomer **1d**, but both yield the same ruthenocene derivative **5**. Treatment of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ with $K[C_5H_2Ph_3$-1,2,3] rapidly gives the expected 1,2,3-triphenylruthenocene derivative **2**, while the reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ or $[\{Ru(\eta^5\text{-}C_5Me_5)Cl\}_4]$ with 1,2,3-triphenylcyclopentadiene proceeds more slowly to yield complexes **5** and **7**, respectively. $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ reacts similarly with cyclopentadiene to give $[Ru(C_5H_5)_2]$.

Introduction

Since its discovery in 1951,[1] the chemistry of ferrocene has attracted much attention and has subsequently developed rapidly.[2] While a number of related metallocenes have been synthesized, their chemistry remains developed to a lesser extent. In particular, the synthesis and investigation of the physical and chemical properties of ruthenocenes have been, to a large extent, limited by the number of suitable precursors and consequently by the number of known derivatives.[3] Indeed, although a few high-yield synthetic procedures have recently been reported,[4,5] there is, to date, no easily adaptable route to highly substituted ruthenocenes.

While 3-vinyl-1-cyclopropenes are known to undergo thermal and photochemical ring expansion reactions, generally yielding cyclopentadienes or indenes,[6] a number of recent studies have focused on the thermal, transition-metal-promoted chemistry of these reactive molecules.[7] In our laboratory, the reactions of coordinatively unsaturated rhodium and iridium phosphine complexes with substituted vinylcyclopropenes have yielded a number of cyclopentadienyl complexes.[8] Intermediate η^4-pentadienediyl and metallacyclohexadiene (η^2-pentadienediyl) complexes of Rh(III) and Ir(III) have also been isolated in these reactions.[8,9] We now wish to report the facile reactions of a range of substituted 3-vinyl-1-cyclopropenes with the reactive ruthenium(II) complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})X]$[10] (X = Cl, Br), $[Ru(\eta^5\text{-}C_9H_7)(\eta^4\text{-}C_8H_{12})Cl]$[11] ($C_9H_7$ = indenyl; C_8H_{12} = 1,5-cyclooctadiene), and $[\{Ru(\eta^5\text{-}C_5Me_5)Cl\}_4]$[12] as a method of preparing substituted ruthenocene derivatives.

Experimental Procedures

All reactions were routinely performed under an inert atmosphere by using standard Schlenk techniques. Solvents were dried, degassed, and distilled under an inert atmosphere immediately prior to use. ^1H NMR spectra and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 and 75 MHz, respectively, by using a Varian XL300 instrument with a probe temperature of 293 K. Mass spectral data were obtained on a Finnigan 4023 mass spectrometer, and microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

The ruthenium complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$,[10] $[Ru(\eta^5\text{-}C_9H_7)(\eta^4\text{-}C_8H_{12})Cl]$[11] ($C_8H_{12}$ = 1,5-cyclooctadiene; C_9H_7 = indenyl), and $[\{Ru(\eta^5\text{-}C_5H_5)Cl\}_4]$[12] were prepared by the literature methods. The reagents 1,2,3-triphenyl-3-vinyl-1-cyclopropene (**1a**),[6,13] 1,2-diphenyl-3-vinyl-1-cyclopropene (**1b**),[6,13] and 1,2,3,4,5-pentamethylcyclopentadiene,[14] were prepared by literature methods. A synthesis of 1,2,3-triphenylcyclopentadiene, which includes some modifications of the literature procedure[15] and full spectroscopic characterization of this molecule, is described below. Dicyclopentadiene was purchased from Aldrich

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and freshly cracked immediately prior to use.

Synthesis of 1,2-Diphenyl-3-(α-methylvinyl)-1-cyclopropene (1c) (Based on Modifications of the Methodology of Weinreb[17] and Liebeskind[7c]). (a) *N*-Methoxy-*N*-methyl-1,2-diphenyl-1-cyclopropene-3-carboxamide. 1,2-Diphenyl-1-cyclopropene-3-carboxylic acid chloride was prepared by the literature procedure.[16] To a solution of this acid chloride (2.91 g, 11.4 mmol) in CH_2Cl_2 (30 mL) was added *N*-methyl-*O*-methylhydroxylamine hydrochloride (1.23 g, 12.6 mmol), and the mixture was stirred at 0 °C for 2 h. Pyridine (2.0 g, 25 mmol) was then added, and the mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum, and resultant pale yellow solid was dissolved in a 1:1 mixture of ether and CH_2Cl_2 (50 mL) and washed with brine (1 × 50 mL and 1 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under vacuum to afford spectroscopically pure amide as a white solid (2.80 g, 88%): mp 114–116 °C; ^1H NMR ($CDCl_3$) δ 3.29 (s, 3 H, N*Me*), 3.93 (s, 3 H, NO*Me*), 7.3–7.7 (m, 10 H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 19.7 (N*Me*), 32.8 (*C*H), 61.6 (NO*Me*), 107.0 (Ph*C*=), 128.6, 128.7, 128.9, 129.8 (Ph).

(b) 1,2-Diphenyl-3-acetyl-1-cyclopropene. A solution of *N*-methoxy-*N*-methyl-1,2-diphenyl-1-cyclopropene-3-carboxamide (1.88 g, 6.73 mmol) in THF (40 mL) was cooled to 0 °C and treated dropwise with a solution of methylmagnesium bromide [2.60 mL of a 2.85 M solution in THF; 7.4 mmol; diluted with THF (15 mL)]. The mixture was stirred for 1 h and was then treated with a solution of HCl (30 mL of 5% in ethanol), followed by H_2O (100 mL). Ether (50 mL) was added, and the organic layer was separated. The aqueous layer was washed with a 1:1 mixture of ether/CH_2Cl_2 (2 × 25 mL). The organic layers were combined and evaporated to give the product as a spectroscopically pure white solid (1.42 g, 90%): ^1H NMR ($CDCl_3$) δ 1.85 (s, 3 H, *Me*), 2.95 (s, 1 H, C*H*), 7.46–7.68 (m, 10 H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 24.9 (CH_3), 32.8 (*C*H), 109.7 (Ph*C*=), 126.9, 129.0, 129.6, 129.8 (Ph), 212.2 (*C*=O).

(c) 1,2-Diphenyl-3-(α-methylvinyl)-1-cyclopropene. To a stirred suspension of methyltriphenylphosphonium bromide (1.86 g, 5.2 mmol) in THF (40 mL) was added dropwise butyllithium [2.6 mL of a 1.95 M hexane solution diluted with THF (15 mL)]. To the resultant orange solution was added a solution of 1,2-diphenyl-3-acetyl-1-cyclopropene (1.17 g, 4.9 mmol) in THF (10 mL). After addition was complete, the orange color was discharged to give a white solid suspended in a pale yellow solution. The reaction was quenched with saturated aqueous sodium bicarbonate (100 mL) and extracted with ether (3 × 50 mL). The organic extracts were dried over $MgSO_4$ and evaporated to dryness, and the residue was chromatographed on silica gel. Elution with a 9:1 mixture of petroleum ether/ethyl acetate (250 mL) afforded the product as a pale yellow solid: ^1H NMR ($CDCl_3$) δ 1.47 (s, 3 H, CH_3), 2.88 (s, 1 H, C*H*), 4.85 (s, 1 H, CH_2), 5.08 (s, 1 H, CH_2), 7.35–7.69 (m, 10 H, Ph).

Synthesis of 1,2,3-Triphenyl-3-(β-methylvinyl)-1-cyclopropene (Mixture of Trans and Cis Isomers 1d and 1e, Respectively). Triphenylcyclopropenyl chloride (4.00 g, 13.2 mmol) was suspended in THF (250 mL) under a dinitrogen atmosphere and cooled to −78 °C. A THF solution (40 mL of approximately 1 M; 40 mmol) of *cis*- and *trans*-1-propenylmagnesium bromide was quickly added by syringe. The mixture was stirred for 30 min at −78 °C and then allowed to come to room temperature overnight. The reaction mixture was quenched with saturated NH_4Cl(aq) and the aqueous layer extracted with diethyl ether. The extract was dried over $MgSO_4$ and the solvent removed to yield a yellow oil. Flash chromatography on silica gel with ethyl acetate/petroleum ether (1:10) yielded a yellow oil that slowly crystallized. Recrystallization from methanol/petroleum ether yielded two crops of white solid (3.38 g, 83%) as a trans–cis mixture of **1d** and **1e** which was not separated. **1d**: ^1H NMR (C_6D_6) δ 1.59 (dd, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz, 3 H, CH_3), 5.77 (dq, $^3J_{H-H}$ = 15 Hz, $^3J_{H-H}$ = 7 Hz, 1 H, *H*C(CH_3)), 6.41 (dq, $^3J_{H-H}$ = 15 Hz, $^4J_{H-H}$ = 2 Hz, 1 H, =C*H*), 7.0–7.7 (phenyl); $^{13}C\{^1H\}$ NMR ($CDCl_3$) 17.9 (s, CH_3), 33.8 (s, *C*(Ph)(vinyl), 116.8 (s, =*C*Ph), 134.5 (s, *C*(H)(CH_3)) (other resonances were not unambiguously assigned). **1e**: ^1H NMR (C_6D_6) δ 1.61 (dd, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz, 3 H, CH_3), 5.66 (dq, $^3J_{H-H}$ = 11 Hz, $^3J_{H-H}$ = 7 Hz, 1 H, *H*C(CH_3)), 6.17 (dq, $^3J_{H-H}$ = 2 Hz, 1 H, =C*H*), 7.0–7.7 (phenyl); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 15.1 (s, CH_3), 32.1 (s, *C*(Ph)(vinyl)), 116.8 (s, =*C*Ph) (other resonances were not unambiguously assigned).

Preparation of [Ru(η⁵-C_5H_5)(η⁵-$C_5H_2Ph_3$-1,2,3)] (2). A solution of [Ru(η⁵-C_5H_5)(η⁴-C_8H_{12})Cl] (0.20 g, 0.65 mmol) in THF (25 mL) was treated with 1,2,3-triphenyl-3-vinyl-1-cyclopropene (0.21 g, 0.72 mmol). The resulting mixture was stirred under an inert atmosphere at room temperature overnight, during which time the orange solution had become a golden yellow color. The solvent was then removed under reduced pressure, and the crude product was extracted with hexanes (4 × 50 mL). Analytically pure compound could be obtained by recrystallization of the crude product from diethyl ether/hexane solutions: yield 0.24 g (0.53 mmol, 81%); ^1H NMR ($CDCl_3$) δ 7.20 (6 H, br m, Ph), 7.16 (9 H, br m, Ph), 5.04 (2 H, s, CH), 4.58 (5 H, s, C_5H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 137.3, 135.6, 132.7, 130.1, 127.4, 127.3, 126.4, 126.2 (Ph), 93.3, 93.2 (*C*Ph), 73.9 (C_5H_5), 71.4 (CH); MS *m/e* (relative abundance) 460 (100), 395 (3), 167 (11); mp 152–153 °C. Anal. Calcd for $C_{28}H_{22}Ru$: C, 73.18; H, 4.83. Found: C, 73.13; H, 4.98.

In a similar manner a THF solution of [Ru(η⁵-C_5H_5)(η⁴-C_8H_{12})Cl], [Ru(η⁵-C_9H_7)(η⁴-C_8H_{12})Cl], or [{Ru(η⁵-C_5Me_5)Cl}₄] was treated with 1.1 molar equiv of 1,2-diphenyl-3-vinyl-1-cyclopropene, 1,2-diphenyl-3-(α-methylvinyl)-1-cyclopropene, or 1,2,3-triphenyl-3-(β-methylvinyl)-1-cyclopropene. A similar workup yielded the respective ruthenocenes. [Ru(η⁵-C_5H_5)(η⁵-$C_5H_3Ph_2$-1,2)] (**3**): yield 93%; ^1H NMR ($CDCl_3$) δ 7.25 (4 H, br m, Ph), 7.09 (6 H, br m, Ph), 4.92 (2 H, d, J = 2 Hz, CH), 4.69 (1 H, t, J = 2 Hz, CH), 4.53 (5 H, s, C_5H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 137.3, 130.2, 127.5, 126.3 (Ph), 87.9 (*C*Ph), 72.9 (2 CH), 72.7 (C_5H_5), 69.5 (CH); MS *m/e* (relative abundance) 384 (100), 167 (8). [Ru(η⁵-C_5H_5)(η⁵-$C_5H_2Ph_2$-1,2-Me-4)] (**4**): yield 87%; ^1H NMR ($CDCl_3$) δ 7.47 (2 H, br m, Ph), 7.37 (4 H, br m, Ph), 7.25 (4 H, br m, Ph), 5.04 (2 H, s, CH), 4.59 (5 H, s, C_5H_5), 2.17 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 137.6, 130.2, 127.4, 126.1 (Ph), 91.2 (*C*Ph), 86.6 (CCH_3), 74.6 (CH), 73.1 (C_5H_5), 15.1 (CH_3); MS, *m/e* (relative abundance) 398 (100), 167 (28); mp 155–157 °C. Anal. Calcd for $C_{23}H_{20}Ru$: C, 69.50; H, 5.07. Found: C, 69.11; H, 4.98. [Ru(η⁵-C_5H_5){η⁵-$C_5H(CH_3)Ph_3$}] (**5**): yield 85%; ^1H NMR ($CDCl_3$) δ 7.24 (3 H, br m, Ph), 7.19 (6 H, br m, Ph), 7.10 (1 H, br m, Ph), 5.07 (1 H, s, CH), 4.55 (5 H, s, C_5H_5), 2.09 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 137.5, 136.1, 136.0, 132.5, 132.1, 130.0, 129.6, 128.8, 128.7, 127.0, 126.0 (Ph), 95.6, 93.6, 86.7 (*C*Ph), 74.3 (CCH_3), 74.2 (C_5H_5), 73.3 (CH), 14.5 (CH_3); MS *m/e* (relative abundance) 474 (100), 409 (2), 167 (25); mp 125–127 °C. Anal. Calcd for $C_{29}H_{24}Ru$: C, 73.55; H, 5.11. Found: C, 73.29; H, 5.07. [Ru(η⁵-C_9H_7)(η⁵-$C_5H_2Ph_3$-1,2,3)] (**6**, C_9H_7 = indenyl): yield 76%; ^1H NMR ($CDCl_3$) δ 7.15 (2 H, m, CH), 7.08 (9 H, br m, Ph), 6.87 (6 H, br m, Ph), 6.81 (2 H, dd, J = 7 Hz, J = 3 Hz, CH), 5.11 (2 H, d, J = 2 Hz, CH), 4.74 (2 H, s, CH), 4.56 (1 H, t, J = 2 Hz, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 136.5, 135.0, 132.2, 129.4, 127.5, 127.2, 126.0, 125.3, 123.7 (Ph, $2CH_{ind}$), 94.3, 93.9 (*C*Ph), 91.1, 70.4 (CH_{ind}), 68.7 (CH); *MS m/e* (relative abundance) 510 (100), 217 (12); mp 166–168 °C. Anal. Calcd for $C_{32}H_{24}Ru$: C, 75.42; H, 4.75. Found: C, 75.54; H, 4.85. [Ru(η⁵-C_5Me_5)(η⁵-$C_5H_2Ph_3$-1,2,3)] (**7**): yield 65%; ^1H NMR ($CDCl_3$) δ 7.48 (2 H, m, Ph), 7.35 (3 H, m, Ph), 7.30 (4 H, br m, Ph), 7.16 (6 H, br m, Ph), 4.72 (2 H, s, CH), 1.79 (15 H, s, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 137.5, 132.9, 130.0, 129.4, 127.9, 127.8, 126.7, 125.9 (Ph), 91.9, 91.0 (*C*Ph), 85.4 (*C*Me), 74.5 (CH), 10.9 (Me); MS *m/e* (relative abundance) 530 (100), 395 (5), 237 (3); mp 108–110 °C. Anal. Calcd for $C_{33}H_{32}Ru$: C, 74.83; H, 6.09. Found: C, 75.02; H, 6.14.

Preparation of 1,2,3-Triphenylcyclopentadiene. (a) 4-Hydroxy-2,3,4-triphenylcyclopent-2-enone. Benzil (21.0 g, 100 mmol) and phenylacetone (26.8 g, 200 mmol) were added to a solution of potassium hydroxide (1.25 g) in ethanol (250 mL), and the golden yellow solution was left stirring under an inert atmosphere at room temperature for 7 days. The crystalline precipitate was then collected by filtration in air and washed with chilled ethanol (2 × 15 mL) and dried under vacuum: yield 23.4 g (72 mmol, 72%); ^1H NMR (acetone-d_6) δ 7.58 (2 H, br m, Ph), 7.35–7.10 (13 H, br m, Ph), 5.44 (1 H, s, OH), 3.14 (1 H, d, J = 18 Hz, CH_2), 3.01 (1 H, d, J = 18 Hz, CH_2); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 204.1 (CO), 170.4, 145.5, 140.6, 134.8, 132.6, 130.7, 130.3,

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129.4, 129.1, 128.7, 128.6, 128.4, 127.6, 125.8 (Ph or *C*Ph), 80.7 {*C*(OH)Ph}, 56.3 (CH_2); IR (CH_2Cl_2) ν(OH) 3581 cm^{-1}, ν(CO) 1713 cm^{-1}; MS *m/e* (relative abundance) 326 (42), 178 (100); mp 164–165 °C.

(b) 2,3,4-Triphenylcyclopent-2-enone. A solution of 4-hydroxy-2,3,4-triphenylcyclopent-2-enone (5.0 g, 15.3 mmol) in glacial acetic acid (30 mL) was treated with hydriodic acid (8.7 g, 32 mmol), and the resulting mixture was refluxed for 5 min. After being cooled to room temperature, the solution was poured into aqueous sodium bisulfite (150 mL) and the product was extracted with diethyl ether (3 × 75 mL). The ether solutions were washed with water (50 mL), aqueous sodium bicarbonate (2 × 50 mL), and finally water (50 mL) and then dried over magnesium sulfate. Solvent removal leaves a pale yellow crystalline product that was washed with diethyl ether (3 mL) and dried under vacuum: yield 3.1 g (10 mmol, 65%); ^1H NMR ($CDCl_3$) δ 7.40–7.15 (15 H, br m, Ph), 4.61 (1 H, dd, J = 7 Hz, J = 2 Hz, C*H*Ph), 3.27 (1 H, dd, J = 19 Hz, J = 7 Hz, CH_2), 2.68 (1 H, dd, J = 19 Hz, J = 2 Hz, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 206.2 (CO), 170.2, 142.1, 140.7, 134.7, 131.7, 129.1, 128.8, 128.6, 128.3, 128.1, 127.9, 127.3, 126.8 (Ph or *C*Ph), 47.1, 45.9 (CH_2 and *C*HPh); IR (CH_2Cl_2) ν(CO) 1701 cm^{-1}; MS *m/e* (relative abundance) 310 (77), 178 (100); mp 138–139 °C.

(c) 1,2,3-Triphenylcyclopentadiene. A solution of 2,3,4-triphenylcyclopentenone (2.3 g, 7.4 mmol) in dioxane (80 mL) was treated with a solution of sodium borohydride (2.4 g, 63 mmol) in water (25 mL), and the mixture was stirred at room temperature for 3 days. The mixture was reduced on a rotary evaporator to approximately 10 mL and poured into water (100 mL). The crude product was then extracted into diethyl ether (3 × 100 mL), and the solution was dried over magnesium sulfate and reduced to a yellow oil. The crude mixture of cyclopentenols was taken up in ethanol and under an inert atmosphere was treated with concentrated HCl (6 mL), added in a dropwise manner. The reaction mixture was then refluxed for 1 h and allowed to cool to room temperature. The white precipitate was collected by filtration and washed with chilled diethyl ether (5 mL); the crude product was then dried under vacuum: yield 1.45 g (5.1 mmol, 70%); ^1H NMR ($CDCl_3$) δ 7.25 (3 H, br m, Ph), 7.19 (6 H, br m, Ph), 7.09 (3 H, br m, Ph), 6.56 (1 H, t, J = 2 Hz, CH), 3.65 (2 H, d, J = 2 Hz, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 149.4, 142.5, 141.9, 136.9, 136.7, 136.5, 129.9, 129.4, 128.2, 128.1, 128.0, 127.8, 126.8, 126.7, 126.3 (Ph, *C*Ph or CH), 43.4 (CH_2); mp 161–162 °C.

Reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ and $[\{Ru(\eta^5\text{-}C_5Me_5)Cl\}_4]$ with 1,2,3-Triphenylcyclopentadiene. A solution of the respective ruthenium complex (0.1 g) in THF (15 mL) was treated with 1.1 equiv of 1,2,3-triphenylcyclopentadiene and stirred at room temperature. Periodically, the reaction solvent was removed and the reaction mixture was taken up in $CDCl_3$, to allow the progress of the reaction to be monitored by ^1H NMR spectroscopy. Complexes **2** and **7** were formed cleanly and identified by their ^1H NMR spectra. Isolated yields of these complexes ranged from 70 to 80%.

Reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ with Potassium 1,2,3-Triphenylcyclopentadienide. A solution of potassium 1,2,3-triphenylcyclopentadienide was prepared in a standard manner from a THF solution of 1,2,3-triphenylcyclopentadiene and a sodium/potassium alloy.[5] A solution of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ (0.06 g, 0.2 mmol) in THF (10 mL) was treated with 1.1 equiv of $K[C_5H_2Ph_3\text{-}1,2,3]$ in THF. The reaction mixture was stirred at room temperature for 5 h. Following solvent removal, the crude product could be extracted into hexanes or diethyl ether and the pure compound was obtained by recrystallization from these solvents (0.07 g, 75%). The spectroscopic properties of the product were identical with those described above for **2**.

Results and Discussion

Wilkinson's synthesis of ruthenocene[18] from $[Ru(acac)_3]$ and $(C_5H_5)MgBr$ provided the first, albeit low yield, route to the ruthenium analogue of the known ferrocene. Since then a wide range of synthetic routes have been developed, which with varying degrees of success, have provided an entry into the chemistry of bis(cyclopentadienyl)ruthenium complexes. While only low yields of ruthenocene are obtained from the ligand exchange reaction (involving ferrocene and anhydrous $RuCl_3$),[19] reasonable yields may be obtained from the reaction of (cyclopentadienyl)sodium with ruthenium trichloride–ruthenium metal mixtures[20] or $[Ru(DMSO)_4Cl_2]$.[21] However, the most convenient and large scale route to the parent ruthenocene complex $[Ru(\eta^5\text{-}C_5H_5)_2]$ reported to date involves the direct reaction of a refluxing ethanolic ruthenium trichloride solution with cyclopentadiene using zinc as a mild reducing agent.[4] More recently the reactions of the polymeric ruthenium compound $[\{Ru(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ with (cyclopentadienyl)thallium or the (cyclopentadienyl)tin reagents, $[Sn\text{-}n\text{-}Bu_3(C_5R_5)]$ (R = H, Me) have provided a high-yield route to both ruthenocene and decamethylruthenocene, and treatment of the labile (cyclooctadiene)ruthenium complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ with appropriate cyclopentadienyl anions is an adaptable route to a range of mixed-ligand ruthenocenes.[5]

Treatment of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ (C_8H_{12} = 1,5-cyclooctadiene) with 1 molar equiv of 1,2,3-triphenyl-3-vinyl-1-cyclopropene (**1a**) in THF rapidly affords a pale yellow solution from which the substituted ruthenocene $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_2Ph_3\text{-}1,2,3)]$ (**2**) can be isolated in high yield. Complex **2** and all other new compounds reported in this paper were characterized by analytical and spectroscopic methods. The ^1H NMR spectrum of **2** contains multiplet resonances at δ 7.20 and 7.16 characteristic of phenyl groups and two sharp singlets at δ 5.04 (2 H) and 4.58 (5 H) assignable to the protons on the substituted and unsubstituted cyclopentadienyl rings, respectively. Similarly, the $^{13}C\{^1H\}$ NMR spectrum contains resonances typical of phenyl groups and resonances at δ 93.3, 93.2, 71.4, and 73.9 associated with the carbon atoms of the same cyclopentadienyl rings. No intermediates could be observed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopic monitoring of the reaction in $CDCl_3$ at room temperature. While the ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with the proposed structure, they are not unambiguous, since complex **2** could conceivably contain a 1,2,4-triphenylcyclopentadienyl ring.

In order to determine unambiguously the substitution pattern on the triphenylcyclopentadienyl ring in **2**, a solution of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ was treated with $K[C_5H_2Ph_3\text{-}1,2,3]$, prepared by deprotonation of 1,2,3-triphenylcyclopentadiene. This diene was prepared by a modification of the literature procedure (see Experimental Section). The reaction proceeded rapidly and yielded a ruthenocene with ^1H and $^{13}C\{^1H\}$ NMR spectra identical with those obtained for **2**. Interestingly, **2** can also be prepared from the direct reaction of 1,2,3-triphenylcyclopentadiene with $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ (see below).

When $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ was treated with 1,2-diphenyl-3-vinyl-1-cyclopropene (**1b**), the 1,2-diphenylruthenocene **3** was obtained cleanly. The ^1H NMR spectrum of **3** exhibited a triplet at δ 4.69 and a doublet at δ 4.92 (J = 2 Hz) establishing clearly the 1,2-substitution pattern. On treatment of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ with 1,2-diphenyl-3-(α-methylvinyl)-1-cyclopropene (**1c**), a significantly slower reaction than that observed with **1a** or **1b** ensued and ultimately afforded the symmetrically substituted ruthenocene **4**. Similarly $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ was allowed to react with a mixture of *cis*- and

(18) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6146.

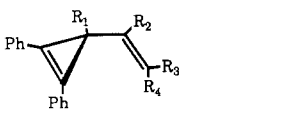
(19) Gauthier, G. J. *J. Chem. Soc. D* **1969**, 690.

(20) Bublitz, D. E.; Kleinberg, J. *Org. Synth.* **1961**, *41*, 96.

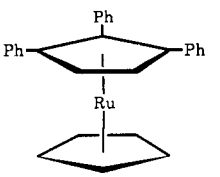
(21) Ritchie, G. L. D.; Cooper, M. K.; Calvert, R. L.; Dennis, G. R.; Phillips, L.; Vrbancich, J. *J. Am. Chem. Soc.* **1983**, *105*, 5215.

trans-1,2,3-triphenyl-3-(β-methylvinyl)-1-cyclopropene (**1d** and **1e**). Monitoring this reaction by ^1H NMR spectroscopy clearly showed that both isomers reacted more slowly than did **1a** or **1b**; however, the cis isomer reacted significantly faster than the trans isomer and only one product (**5**) was obtained. There was no spectral evidence for the interconversion of the isomers **1d** and **1e** under the reaction conditions. The ^1H NMR spectrum of **5** contains aromatic multiplet resonances and three singlets at δ 5.07 (1 H), 4.55 (5 H), and 2.09 (3 H) which are readily assigned to the sole proton on the substituted cyclopentadienyl ring, the unsubstituted cyclopentadienyl ring protons, and the methyl group, respectively. Mass spectral data for complexes **2**–**5** were also obtained and confirmed the predicted molecular ion; interestingly these spectra contained a major fragmentation peak for the mono(cyclopentadienyl)ruthenium fragment $\{Ru(\eta^5\text{-}C_5H_5)\}^+$ but either a very small or nondetectable peak for the analogous derivatized fragment $\{Ru(\eta^5\text{-}C_5R_5)\}^+$ (C_5R_5 = substituted cyclopentadienyl ring).

This general reaction pattern is also observed with other ruthenium starting materials. The indenyl analogue $[Ru(\eta^5\text{-}C_9H_7)(\eta^4\text{-}C_8H_{12})Cl]$ also reacted swiftly with **1a** to afford the analogous complex **6**. The tetranuclear ruthenium(II) cluster $[\{Ru(\eta^5\text{-}C_5Me_5)Cl\}_4]$ is known to be a reactive species, providing a ready source of the unsaturated 14-electron $\{Ru(\eta^5\text{-}C_5Me_5)Cl\}$ fragment.[12] In the presence of **1a**, a rapid reaction occurs to yield the ruthenocene derivative **7**. Monitoring this reaction by ^1H NMR spectroscopy established the rapid formation of **7** and other minor unidentified species, which disappear over a period of several hours leaving **7** as the sole product.



1 a. R_1 = Ph; R_2, R_3, R_4 = H
b. R_1, R_2, R_3, R_4 = H
c. R_2 = Me; R_1, R_3, R_4 = H
d. R_1 = Ph; R_3 = Me; R_2, R_4 = H
e. R_1 = Ph; R_4 = Me; R_2, R_3 = H



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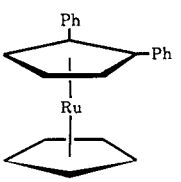

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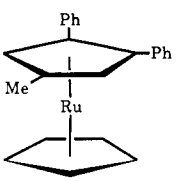

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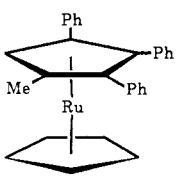

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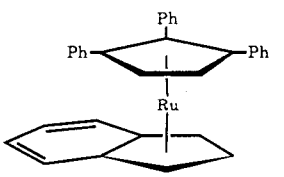

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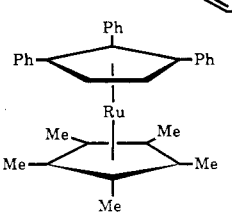
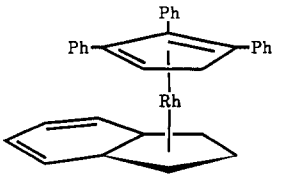


7

Although we have been unsuccessful in observing intermediate species in these ruthenium reactions, previously reported rhodium chemistry of vinylcyclopropenes points to the probable stepwise mechanism of ruthenocene formation. Reaction of $[Rh(\eta^5\text{-}C_9H_7)(\eta^2\text{-}C_2H_4)_2]$ with **1a** affords the η^4-triphenylcyclopentadiene complex **8**,[7a] while reactions of **1a** with "$RhClP_2$" fragments (P = PMe_3, P^iPr_3) yield the (cyclopentadienyl)hydridorhodium complexes **9**, via intermediate ring-opened pentadienediyl complexes **10** and **11**.[8,9] In these latter systems, formation of the five-membered ring is clearly a stepwise process involving initial binding of the vinylcyclopropene and opening of the cyclopropene ring prior to formation of the cyclopentadiene or cyclopentadienyl hydrido complex.



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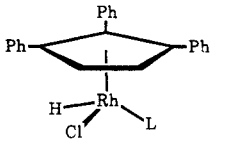
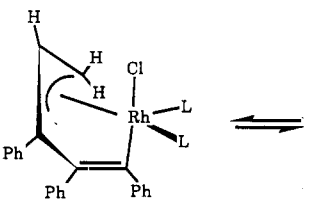


9 L = PMe_3, P^iPr_3



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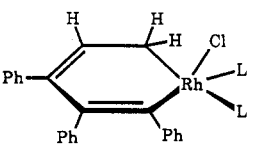
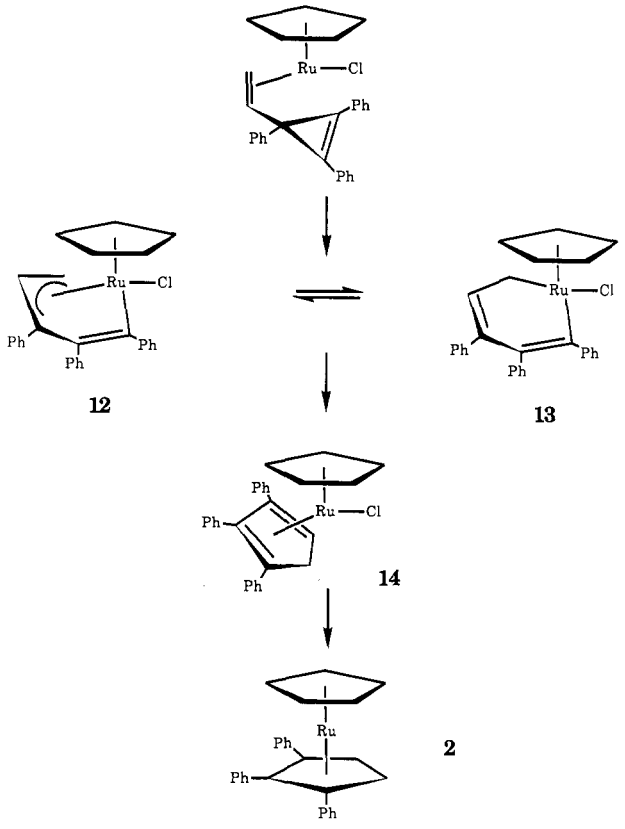


11

The reactive ruthenium complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ is known to undergo dehydrohalogenation reactions and promote the dehydrogenation of cyclic polyolefinic hydrocarbons under mild reaction conditions.[22] It seems likely that the mechanism of the ruthenium reactions described herein involves formation of an η^4-cyclopentadiene complex (e.g. $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_3Ph_3\text{-}1,2,3)Cl]$) and subsequent rapid dehydrohalogenation to yield the ruthenocene derivative. In order to determine the feasibility of this hypothesis, $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ was treated with cyclopentadiene and the reaction was monitored by ^1H NMR spectroscopy. The reaction proceeded rapidly at room temperature, and after 4 h only ruthenocene and free cyclooctadiene were present. Following solvent and cyclooctadiene removal under reduced pressure, the characterization of the product was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.[23] In a similar reaction **2** was obtained directly from $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$ and 1,2,3-triphenylcyclopentadiene; however, this reaction required over 11 days at room temperature to reach completion. Interestingly at no stage in this reaction could any intermediate species be detected by ^1H or $^{13}C\{^1H\}$ NMR spectroscopy. Thus the expected initial product $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_3\text{-}1,2,3)Cl]$, if formed, undergoes rapid dehydrohalogenation, and the slowness of the reaction is merely a reflection of the kinetics of binding of the hindered cyclopentadiene to ruthenium in this system. That competition between cyclooctadiene and the triphenylcyclopentadiene for coordination sites on ruthenium in this latter reaction is responsible for the slow rate of product formation is illustrated by the facility of the corresponding reaction using the "bare" complex $[\{Ru(\eta^5\text{-}C_5Me_5)Cl\}_4]$ with 1,2,3-triphenylcyclopentadiene, which

(22) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1986**, 1102.
(23) (a) Rausch, M. D.; Mark, V. J. *Org. Chem.* **1963**, *28*, 3225. (b) Crecely, R. W.; Crecely, K. M.; Goldstein, J. H. *Inorg. Chem.* **1969**, *8*, 252.

Scheme I



yields **7** in a much faster reaction which is complete in less than **5** h.

We feel that the chemistry outlined in this paper can adequately be described by the mechanism shown in Scheme I. Initial binding of Ru to the exocyclic olefin rather than the cyclopropene double bond presumably accounts for the experimental observation that the reaction rate is faster for unsubstituted vinyl groups (i.e. **1a** and **1b**) and that the cis compound **1e** reacts faster than its trans isomer **1d**. By analogy to the rhodium chemistry outlined above, cyclopropene ring opening would give intermediates **12** (and **13**), and ring closure followed by dehydrohalogenation of an intermediate cyclopentadiene complex **14** would afford the final ruthenocene products.

In summary, this chemistry affords a new route to substituted ruthenocenes by an overall metal-promoted 1,3-sigmatropic rearrangement of vinylcyclopropenes, followed by dehydrohalogenation. Notably, the sequence of metal-promoted C–C cleavage and formation reactions to give the five-membered ring system occurs under very mild thermal conditions compared to those required (180 °C) to isomerize free **1a** to give 1,2,3-triphenylcyclopentadiene.[6d]

Acknowledgment. We are grateful to the National Science Foundation, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support. A loan of ruthenium trichloride from Matthey-Bishop is also gratefully acknowledged. We thank Dr. Paul Fagan for a preprint of ref 12 and Dr. James Egan and Mr. Robert Roussey for experimental assistance in the preparation of compounds **1c–e**.

Registry No. **1a**, 62747-62-0; **1b**, 62937-82-0; **1c**, 119009-84-6; **1d**, 119009-85-7; **1e**, 119009-86-8; **2**, 119071-14-6; **3**, 119071-15-7; **4**, 119071-16-8; **5**, 119071-17-9; **6**, 119108-42-8; **7**, 119071-18-0; **8**, 110790-45-9; $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$, 97913-63-8; $[Ru(\eta^5\text{-}C_9H_7)(\eta^4\text{-}C_8H_{12})Cl]$, 119108-43-9; $[\{(\eta^5\text{-}C_5Me_5)Cl\}_4]$, 113860-07-4; $[Ru(C_5H_5)_2]$, 1287-13-4; 1,2-diphenyl-1-cyclopropene-3-carboxylic acid chloride, 6415-58-3; *N*-methyl-*O*-methylhyeroxylamine hydrochloride, 6638-79-5; *N*-methoxy-*N*-1,2-diphenyl-1-cyclopropane-3-carboxamide, 119009-87-9; 1,2-diphenyl-3-acetyl-1-cyclopropene, 4400-53-7; triphenylcyclopropenyl chloride, 23147-73-1; *cis*-1-propenylmagnesium bromide, 13154-14-8; *trans*-1-propenylmagnesium bromide, 13154-15-9; 4-hydroxy-2,3,4-triphenylcyclopent-2-enone, 28742-18-9; benzil, 134-81-6; phenylacetone, 103-79-7; 2,3,4-triphenylcyclopent-2-enone, 4970-80-3; 1,2,3-triphenylcyclopentadiene, 108535-09-7; potassium 1,2,3-triphenylcyclopentadiene, 119009-88-0; cyclopentadiene, 542-92-7.