Half-Open Ruthenocenes Derived from $[Ru(C_5Me_5)Cl]_4$: Syntheses, Characterizations, and Solid-State Structures

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A variety of half-open ruthenocenes of the general formula $Ru(C_5Me_5)(Pdl)$ have been prepared from $[Ru(C_5Me_5)Cl]_4$. For C_5H_7 or alkylated or arylated pentadienyl groups (1-, 2-, or 3-C_6H_9; 2,3-C_7H_{11}; 2,4-C_7H_{11}; 1,5-$(C_6H_5)_2C_5H_5$), their introductions were brought about by using their potassium salts. For the oxo dienyl analogues 2,4-OC_6H_9 or 3,5-OC_6H_9, the respective enone or enal could be utilized, which underwent deprotonation upon coordination in the presence of K_2CO_3. With HPdl = 2,4-$(CF_3)_2C_5H_6$, coordination is accompanied by the spontaneous elimination of HCl, yielding $Ru(C_5Me_5)[2,4\text{-}(CF_3)_2C_5H_5]$. A similar reaction led to $Ru(C_5Me_4Et)[2,4\text{-}(CF_3)_2C_5H_5]$. In addition to various spectroscopic studies, structural studies were carried out on the Pdl = 3-C_6H_9 and 3,5-OC_6H_9 complexes, as well as for $Ru(C_5Me_4Et)[2,4\text{-}(CF_3)_2C_5H_5]$. For the Pdl = 3-$C_6H_9$ complex, the space group is $P2_1/m$ with a = 7.598 (1) Å, b = 13.246 (2) Å, c = 7.526 (1) Å, β = 96.429 (4)°, and V = 752.7 Å^3 for Z = 2. For the oxo dienyl compound, the space group is $P2_12_12_1$, with a = 10.651 (2) Å, b = 11.925 (1) Å, c = 11.987 (2) Å, and V = 1522.4 Å^3 for Z = 4. For the 2,4-$(CF_3)_2C_5H_5$ compound, the space group is $Cmc2_1$ with a = 15.324 (3) Å, b = 8.785 (2) Å, c = 13.726 (2) Å, and V = 1847.8 Å^3 for Z = 4. The structures were refined to respective R (and R_w) values of 0.026 (0.030), 0.034 (0.035), and 0.028 (0.031).

One of the goals of our research efforts has been to gain an understanding of the relationship between pentadienyl and cyclopentadienyl ligands.[1] While the bis(pentadienyl)metal (open metallocene) compounds might seem like reasonable species to compare to metallocenes for such a purpose, their differences with regard to steric, symmetry, and spin environments severely complicate such efforts. However, if one deals instead with half-open metallocenes, in which one open and one closed ligand are present, these differences are eliminated, and more fruitful comparisons may be made. Ideally, one would like to be able to incorporate as wide a variety of pentadienyl ligands as possible, and therefore a versatile starting material would be most desirable, particularly if it would allow for the incorporation of highly modified dienyl ligands whose anions were not stable. We have therefore investigated the use of $[Ru(C_5Me_5)Cl]_4$ as such a starting material and have found that a wide variety of substituent patterns is indeed tolerable. Herein we report our initial studies on these compounds.

Experimental Section

All hydrocarbon, aromatic, and ethereal solvents were thoroughly dried and deoxygenated by distillation under nitrogen from Na/K benzophenone ketyl immediately before use. Deuterated benzene was degassed over potassium and stored in a glass bulb under nitrogen. Infrared mulls were prepared in a glovebox with dry, degassed Nujol. All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen or in a glovebox. Solvents and solutions were added by glass syringes with stainless steel needles or by a pressure-equalizing addition funnel. Spectroscopic studies were carried out as previously described.[2] Analytical data were obtained by Beller Laboratories and Oneida Research Laboratories. $[Ru(C_5Me_5)Cl]_4$, $[Ru(C_5Me_5)OCH_3]_2$, $[Ru(C_5Me_4Et)Cl]_4$, potassium pentadienides, and 2,4-$(CF_3)_2$-1,3-C_5H_6 (provided by Dr. T. Newbound) were prepared by literature procedures.[3-5]

(1) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255.
(2) Newbound, T. D.; Stahl, L.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1990**, *9*, 2962.
(3) (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698. (b) Kölle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383. (c) Kölle, U.; Kossakowski, J.; Klaff, N.; Wesemann, L.; Englert, U.; Heberich, G. E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 690.

Half-Open Ruthenocenes RuCp*Pdl (Pdl = C_5H_7, 1-, 2-, or 3-C_6H_9, 2,3-C_7H_{11}, 2,4-C_7H_{11}). A solution of 1.00 g of $[Cp^*RuCl]_4$ (3.68 mmol of Ru) in 30 mL of THF was cooled to −78 °C under nitrogen. A solution of the desired potassium pentadienide (3.68 mmol) in 30 mL of THF was then slowly added dropwise. The resulting red-brown solution was stirred at −78 °C for 30 min, slowly warmed to room temperature, and then stirred for an additional 4 h. The solvent was removed in vacuo, and the red oily residue was extracted with 3 × 25 mL of pentane and filtered through Celite. The red filtrate was pumped dry to give a dark red oil, which was sublimed at ca. 60–80 °C under vacuum (20% yield). Better yields (ca. 30%) were obtained if the crude red solution was filtered through alumina (florisil for the 2,3-C_7H_{11} compound), followed by concentration of the yellow filtrate and cooling to −50 °C to give the yellow crystalline product. Single crystals could be obtained by sublimation of the desired compound at ca. 60–80 °C. This procedure may also be carried out using $[Ru(C_5Me_5)OCH_3]_2$ in an entirely analogous fashion.

Spectral and Analytical Data. $Ru(C_5Me_5)(C_5H_7)$. Mp (nitrogen-filled, sealed capillary): 74.0–74.5 °C. Anal. Calcd for $C_{15}H_{22}Ru$: C, 59.38; H, 7.31. Found: C, 59.23; H, 7.14. ^1H NMR (benzene-d_6, ambient): δ 4.82 (t, 1 H, H-3, J = 6.1 Hz), 4.02 (m, 2 H, H-2,4), 2.30 (d, 2 H, H_x-1,5, J = 8.1 Hz), 1.72 (s, 15 H, C_5Me_5), 0.32 (d, 2 H, H_n-1,5, J = 8.1 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 92.1 (d, C-3, J = 159 Hz), 90.5 (s, C_5Me_5), 83.2 (d, C-2,4, J = 153 Hz), 44.0 (t, C-1,5, J = 156 Hz), 11.1 (q, C_5Me_5, J = 128 Hz).

$Ru(C_5Me_5)(1\text{-}C_6H_9)$. Mp (nitrogen-filled, sealed capillary): 68.5–69 °C. Anal. Calcd for $C_{16}H_{24}Ru$: C, 60.54; H, 7.62. Found: C, 60.38; H, 7.61. ^1H NMR (benzene-d_6, ambient): δ 4.71 (d, 1 H, H-3, J = 6.0 Hz), 3.98 (t, 1 H, H-4, J = 6.0 Hz), 3.82 (q, 1 H, H-2, J = 9.0, 6.0 Hz), 2.25 (d, 1 H, H_x-5, J = 7.7 Hz), 1.70 (s, 15 H, C_5Me_5), 1.47 (s, 3 H, CH_3), 0.65 (m, 1 H, H_n-5), 0.30 (d, 1 H, H_n-1, J = 9.0 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 89.3 (d, C-3, J = 155 Hz), 89.1 (s, C_5Me_5), 86.9 (d, C-2, J = 155 Hz), 82.7 (d, C-4, J = 155 Hz), 52.6 (d, C-1, J = 153 Hz), 44.1 (t, C-5, J = 156 Hz), 20.4 (q, 3 H, CH_3, J = 122 Hz), 10.5 (q, C_5Me_5), J = 125 Hz).

$Ru(C_5Me_5)(2\text{-}C_6H_9)$. Mp (nitrogen-filled, sealed capillary): 85.0–85.5 °C. Anal. Calcd for $C_{16}H_{24}Ru$: C, 60.54; H, 7.62. Found: C, 60.13; H, 7.47. ^1H NMR (benzene-d_6, ambient): δ 4.79 (d, 1 H, H-3, J = 5.5 Hz), 3.97 (m, 1 H, H-4), 2.25 (dd, 1 H, H_x-5, J = 8.0, 2.3 Hz), 2.20 (d, 1 H, H_x-1, J = 2.3 Hz), 1.73 (s, 3 H, CH_3), 1.70 (s, 15 H, C_5Me_5), 0.45 (dd, 1 H, H_n-5, J = 8.5, 2.3 Hz), 0.17

(4) Wilson, D. R.; Stahl, L.; Ernst, R. D. *Organomet. Synth.* **1986**, *3*, 136.
(5) Newbound, T. D.; Ernst, R. D. *J. Organomet. Chem.* **1986**, *316*, 213.

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(d, 1 H, H_n-1, J = 2.3 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 92.9 (s, C-2), 92.2 (d, C-3, J = 150 Hz), 90.1 (s, C_5Me_5), 82.3 (d, C-4, J = 162 Hz), 44.6 (t, C-1,5, J = 154 Hz), 25.7 (q, CH_3, J = 128.0 Hz), 11.1 (q, C_5Me_5), J = 127 Hz).

$Ru(C_5Me_5)(3\text{-}C_6H_9)$. Mp (nitrogen-filled, sealed capillary): 86.0–87.0 °C. Anal. Calcd for $C_{16}H_{24}Ru$: C, 60.54; H, 7.62. Found: C, 60.59; H, 7.58. ^1H NMR (benzene-d_6, ambient): δ 3.88 (t, 2 H, H-2,4, J = 8.2 Hz), 2.30 (dd, 2 H, H_x-1,5, J = 8.2, 2.3 Hz), 1.79 (s, 3 H, CH_3), 1.70 (s, 15 H, C_5Me_5), 0.38 (dd, 2 H, H_n-1,5, J = 8.2, 2.3 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 100.9 (s, C-3), 90.2 (s, C_5Me_5), 83.7 (d, C-2,4, J = 158 Hz), 44.3 (dd, C-1,5, J = 162, 147 Hz), 22.3 (q, CH_3, J = 126 Hz), 10.9 (q, C_5Me_5, J = 127 Hz).

$Ru(C_5Me_5)(2,3\text{-}C_7H_{11})$. Mp (nitrogen-filled, sealed capillary): 117–118 °C. Anal. Calcd for $C_{17}H_{26}Ru$: C, 61.60; H, 7.91. Found: C, 62.96; H, 8.35. ^1H NMR (benzene-d_6, ambient): δ 3.89 (t, 1 H, H-4, J = 8.5 Hz), 2.60 (dd, 1 H, H_x-5, J = 8.5, 2.8 Hz), 2.24 (d, 1 H, H_x-1, J = 2.5 Hz), 1.80 (s, 3 H, CH_3), 1.68 (s, 15 H, C_5Me_5), 1.43 (s, 3 H, CH_3), 0.60 (dd, 1 H, H_n-5, J = 8.5, 2.7 Hz), 0.03 (d, 1 H, H_n-1, J = 2.5 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 99.4 (s, C-2), 89.9 (s, C-3), 89.4 (s, C_5Me_5), 84.3 (d, C-4, J = 163 Hz), 46.6 (dd, C-1,5, J = 162, 146 Hz), 45.2 (ddd, C-1,5, J = 164, 147, 4 Hz), 23.1 (q, CH_3, J = 126 Hz), 19.6 (q, CH_3, J = 126 Hz), 10.5 (q, C_5Me_5, J = 126 Hz).

$Ru(C_5Me_5)(2,4\text{-}C_7H_{11})$. Mp (nitrogen-filled, sealed capillary): 117–119 °C. Anal. Calcd for $C_{17}H_{26}Ru$: C, 61.60; H, 7.91. Found: C, 61.36; H, 8.04. ^1H NMR (benzene-d_6, ambient): δ 4.78 (s, H-3), 2.16 (s, 2 H, H_x-1,5), 1.73 (s, 3 H, CH_3), 1.68 (s, 15 H, C_5Me_5), 0.36 (s, H_n-1,5). ^{13}C NMR (benzene-d_6, ambient): δ 92.3 (s, C-2,4), 91.5 (d, C-3, J = 155 Hz), 89.6 (s, C_5Me_5), 45.0 (t, C-1,5, J = 154 Hz), 25.9 (q, CH_3, J = 127 Hz), 10.9 (q, C_5Me_5, J = 124 Hz).

(Pentamethylcyclopentadienyl)(1,5-diphenylpentadienyl)ruthenium(II), $Ru(C_5Me_5)[1,5\text{-}(C_6H_5)_2C_5H_5]$. A solution of 0.56 g of Cp*RuCl (2.06 mmol of Ru) in 30 mL of THF was cooled to −78 °C. A solution of 0.53 g (2.06 mmol) of the potassium salt of the 1,5-diphenylpentadienyl anion in 20 mL of THF was slowly added. The resulting purple solution was stirred at −78 °C for 30 min and thereafter slowly warmed to room temperature. The red solution was stirred for an additional 3 h, and the solvent was removed in vacuo. The crude product was extracted with 3 × 25 mL of hexane, and the solution was cooled to −50 °C, yielding a yellow air-stable crystalline compound (60% yield). Mp (nitrogen-filled, sealed capillary): 225–230 °C dec. Anal. Calcd for $C_{27}H_{30}Ru$: C, 71.18; H, 6.64. Found: C, 69.41; H, 6.85. ^1H NMR (benzene-d_6, ambient): δ 7.18 and 7.13 (m, 10 H, Ph), 4.95 (dd, 2 H, H-2,4, J = 8.9, 5.8 Hz), 4.79 (t, 1 H, H-3, J = 5.8 Hz), 2.28 (d, 2 H, H_n-1,5, J = 8.9 Hz), 1.19 (s, 15 H, C_5Me_5). ^{13}C NMR (benzene-d_6, ambient): δ 143.5 (s, Ph), 128.5 (d, Ph, J = 159 Hz), 125.5 (d, Ph, J = 159 Hz), 123.8 (d, Ph, J = 159 Hz), 89.4 (s, C_5Me_5), 85.8 (d, C-3, J = 163 Hz), 81.8 (d, C-2,4, J = 159 Hz), 60.4 (d, C-1,5, J = 163 Hz), 9.7 (q, C_5Me_5, J = 127 Hz).

(Pentamethylcyclopentadienyl)[2,4-bis(trifluoromethyl)pentadienyl]ruthenium(II), $Ru(C_5Me_5)[2,4\text{-}(CF_3)_2C_5H_5]$. A THF solution (25 mL) containing 1.10 g (4.05 mmol) of Cp*RuCl and 0.91 g (4.45 mmol) of 2,4-bis(trifluoromethyl)-1,3-pentadiene was stirred at room temperature for 24 h, resulting in a color change from dark brown-red to green. The solvent was then removed in vacuo, the green residue was extracted with 3 × 25 mL of pentane, and the solution was filtered through Celite. The dark green filtrate was pumped dry to give a green solid, which was sublimed at ca. 40 °C under vacuum. The yellow crystalline, air-stable product was isolated in yields of 25–35%. An analogous procedure may be utilized to prepare $Ru(C_5Me_4Et)(2,4\text{-}(CF_3)_2C_5H_5)$.

$Ru(C_5Me_5)[2,4\text{-}(CF_3)_2C_5H_5]$. Mp (nitrogen-filled, sealed capillary): 120–121 °C. Anal. Calcd for $C_{17}H_{20}F_6Ru$: C, 46.36; H, 4.58. Found: C, 45.70; H, 4.63. ^1H NMR (benzene-d_6, ambient): δ 6.00 (s, 1 H, H-3), 2.54 (d, 2 H, H_x-1,5, J = 3.4 Hz), 1.53 (s, 15 H, C_5Me_5), 0.02 (d, 2 H, H_n-1,5, J = 3.4 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 128 (q, CF_3, J(CF) = 274 Hz), 94.7 (s, C_5Me_5), 85.9 (d, C-3, J(CH) = 155 Hz), 84.9 (q, C-2,4, J(CF) = 33 Hz), 38.1 (dt, C-1,5, J(CH) = 160 Hz, J(CF) = 16.5 Hz), 10.1 (q, C_5Me_5, J(CH) = 127 Hz).

$Ru(C_5Me_4Et)[2,4\text{-}(CF_3)_2C_5H_5]$. Mp (nitrogen-filled, sealed capillary): 69–70 °C. Anal. Calcd for $C_{18}H_{22}F_6Ru$: C, 47.68; H, 4.89. Found: C, 47.77; H, 4.92. ^1H NMR (benzene-d_6, ambient): δ 6.02 (s, 1 H, H-3), 2.54 (d, 2 H, H_x-1,5, J = 3.4 Hz), 2.02 (q, 2 H, CH_2, J = 7.6 Hz), 1.55 (s, 6 H, C_5Me_4Et), 1.52 (s, 6 H, C_5Me_4Et), 0.81 (t, 3 H, CH_3, J = 7.6 Hz), 0.03 (d, 2 H, H_n-1,5, J = 3.4 Hz). ^{13}C NMR (benzene-d_6, ambient): δ 128.1 (q, CF_3, J(CF) = 275 Hz), 99.6, 95.3 and 94.0 (s, C_5Me_4Et), 86.0 (d, C-3, J(CH) = 153 Hz), 84.9 (q, C-2,4, J(CF) = 22 Hz), 37.9 (dt, C-1,5, J(CH) = 157 Hz, J(CF) = 15 Hz), 18.9 (t, CH_2, J(CH) = 128 Hz), 15.2 (q, CH_3, J(CH) = 126 Hz), 10.0 and 9.8 (q, C_5Me_4Et, J(CH) = 128 Hz).

Half-Open Ruthenocenes $Ru(C_5Me_5)(Odl)$ (Odl = 2,4-OC_6H_9, 3,5-OC_6H_9). A THF solution (25 mL) containing 0.32 g (1.2 mmol) of (pentamethylcyclopentadienyl)ruthenium(II) chloride, 0.19 g (1.4 mmol) of potassium carbonate, and 0.14 g (1.4 mmol) of mesityl oxide or 2-methyl-2-pentenal was stirred at room temperature for 1 h. After the mixture was refluxed at 80–90 °C for 6 h, the solvent was removed in vacuo. The orange residue was extracted with 3 × 25 mL of pentane, and the mixture was filtered through Celite. The dark red-orange filtrate was concentrated and cooled to −60 °C, resulting in the formation of yellow-orange air-stable crystals (ca. 65% yield). Single crystals were obtained by sublimation of the product at ca. 60°C.

$Ru(C_5Me_5)(2,4\text{-}OC_6H_9)$. Mp (nitrogen-filled, sealed capillary): 93–94 °C. Anal. Calcd for $C_{16}H_{23}ORu$: C, 57.64; H, 7.26. Found: C, 57.63; H, 7.15. ^1H NMR (benzene-d_6, ambient): δ 4.68 (s, 1 H, H-3), 3.25 (s, 1 H, H-5), 2.28 (s, 1 H, H-5′), 1.96 (s, 3 H, CH_3), 1.59 (15 H, C_5Me_5), 1.48 (s, 3 H, CH_3). ^{13}C NMR (benzene-d_6, ambient): δ 101.2 (s, C_5Me_5), 87.1 (s, C-2,4), 84.0 (d, C-3, J = 160 Hz), 54.9 (t, C-1,5, J = 160 Hz), 25.2 (q, CH_3, J = 122 Hz), 23.3 (q, CH_3, J = 127 Hz), 10.7 (q, C_5Me_5, J = 127 Hz).

$Ru(C_5Me_5)(3,5\text{-}OC_6H_9)$. Mp (nitrogen-filled, sealed capillary): 103–104 °C. Anal. Calcd for $C_{16}H_{24}ORu$: C, 57.64; H, 7.26. Found: C, 57.76; H, 7.24. ^1H NMR (benzene-d_6, ambient): δ 6.72 (d, 1 H, H-2, J = 1.8 Hz), 4.14 (d, 1 H, H-4, J = 9.8 Hz), 2.82 (q, 1 H, H-5, J = 9.8, 6.4 Hz), 1.67 (d, 3 H, CH_3, J = 6.4 Hz), 1.63 (s, 3 H, CH_3), 1.56 (s, 15 H, C_5Me_5). ^{13}C NMR (benzene-d_6, ambient): δ 123.6 (d, C-2, J = 179 (Hz), 94.8 (d, C-4, J = 155 Hz), 92.9 (s, C-3), 87.7 (s, C_5Me_5), 65.6 (d, C-5, J = 164 Hz), 19.5 (q, CH_3, J = 125 Hz), 17.0 (q, CH_3, J = 123 Hz), 10.3 (q, C_5Me_5, J = 127 Hz).

X-ray Structural Studies. Single crystals of the compounds studied herein were obtained by slow sublimation (ca. 20 °C for the fluoro-substituted complex; 60 °C for the others). Data were collected using a Nicolet-Siemens P$\bar{1}$ autodiffractometer with accompanying software. All calculations employed the Enraf-Nonius SDP programs. Background levels were estimated with the program CARESS.[6] Direct methods were used to locate at least the ruthenium atom locations, after which the remaining non-hydrogen atoms were located from difference Fourier maps. Subsequent least-squares refinements of positional and thermal parameters involved the minimization of the function $\{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. Once the structures were nearly refined to convergence, attempts were made to locate hydrogen atoms from additional difference Fourier maps, and these atoms were then placed in idealized positions, while those which could not be located were placed in calculated positions. A "decay" correction of 16% had to be applied for the fluorine-containing compound, as a result of its continual slow sublimation even at room temperature. For $RuC_{16}H_{24}O$, an attempt was made to distinguish between the two possible polar forms, but the differences were negligible. Other pertinent parameters relating to the data collection are given in Table I.

Results and Discussion

Half-open ruthenocenes of the general composition $Ru(C_5Me_5)(Pdl)$ may readily be prepared by conventional means (eq 1) or from $[Ru(C_5Me_5)OCH_3]_2$. The species

$$\tfrac{1}{4}[Ru(C_5Me_5)Cl]_4 + KPdl \rightarrow Ru(C_5Me_5)(Pdl) \quad (1)$$

$$Pdl = C_5H_7,\ 1\text{-},\ 2\text{-},\ \text{or}\ 3\text{-}C_6H_9,\ 2,3\text{-}C_7H_{11},\ 2,4\text{-}C_7H_{11},\ 1,5\text{-}(C_6H_5)_2C_5H_5$$

$Ru(C_5Me_5)(2,4\text{-}C_7H_{11})$ has also been obtained by other

(6) Packett, D. L.; Jensen, C. M.; Cowan, R. L.; Strouse, C. E.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 3578.

Table I. X-ray Data Collection Parameters for $Ru(C_5Me_5)(3\text{-}C_6H_9)$ (A), $Ru(C_5Me_5)(3,5\text{-}OC_6H_9)$ (B), and $Ru(C_5Me_4Et)[2,4\text{-}(CF_3)_2C_5H_5]$ (C)

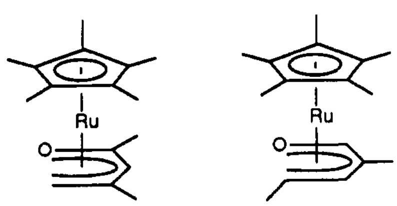
	A	B	C
formula	$RuC_{16}H_{24}$	$RuC_{16}H_{24}O$	$RuC_{18}H_{22}F_6$
mol wt	317.44	333.44	453.44
space group	$P2_1/m$	$P2_12_12_1$	$Cmc2_1$
a, Å	7.598 (1)	10.651 (2)	15.324 (3)
b, Å	13.246 (2)	11.925 (1)	8.785 (2)
c, Å	7.526 (1)	11.987 (2)	13.726 (2)
β, deg	96.429 (4)	90	90
V, Å^3	752.68	1522.4	1847.8
Z	2	4	4
d_{calc}, g/cm^3	1.40	1.46	1.63
λ	0.71073	0.71073	0.71073
temp, °C	16	16	16
cryst size, mm	0.30 × 0.28 × 0.20	0.24 × 0.22 × 0.19	0.30 × 0.15 × 0.11
linear abs coeff, cm^{-1}	10.01	9.98	8.85
scan type	θ–2θ	θ–2θ	θ–2θ
scan speed, deg/min	3	3	3
abs treatment	ψ scan	ψ scan	ψ scan
transm factors (rel)	0.926–0.999	0.880–0.999	0.617–1.00
scan range, deg	−1.3, +1.6	1 + 0.35 tan θ	±1
2θ limits, deg	1–50	4–50	2–48
min *hkl*	0,0,−8	−12,0,0	0,0,0
max *hkl*	9,15,8	0,14,14	17,10,15
no. of unique obsd data	1389	1247	739
no. of variables	86	163	121
$R(F)$	0.026	0.034	0.028
$R_w(F)$	0.030	0.035	0.031
max diff Fourier peak, e/Å^3	0.42	0.41	0.38

routes,[7] which may or may not be extendable to the other Pdl groups we have employed. For at least some of the more electronegative oxopentadienyl analogues, it is possible to prepare related metal complexes via presumed $Ru(C_5Me_5)(Cl)(\eta^4$-enal or enone) intermediates, which lose HCl in the presence of a mild base in hot THF (eqs 2 and 3). Although spectroscopic studies on these latter yellow

$$\tfrac{1}{4}[Ru(C_5Me_5)Cl]_4 + (CH_3)_2CCHC(O)CH_3 \xrightarrow{K_2CO_3,\ THF,\ \Delta} Ru(C_5Me_5)(2,4\text{-}OC_6H_9) \quad (2)$$

$$\tfrac{1}{4}[Ru(C_5Me_5)Cl]_4 + CH_3CH_2CH_2CH(CH_3)C(O)H \xrightarrow{K_2CO_3,\ THF,\ \Delta} Ru(C_5Me_5)(3,5\text{-}OC_6H_9) \quad (3)$$

compounds are in accord with the respective expected η^5-oxopentadienyl structures I and II, the utilization of less



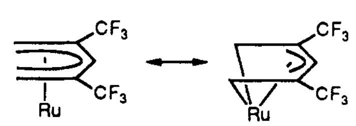
I II

substituted enals or enones yields instead deeply colored products of entirely different constitutions which are currently under investigation.[8] Interestingly, we have found that a similar route may be used to prepare $Ru(2,4\text{-}OC_6H_9)_2$, which has recently been described by others as well.[9] Other η^5-oxo dienyl complexes have been known for some time[10] but had been prepared inadvertently.[1] More recently, additional examples of oxo dienyl complexes have been prepared by more rationale routes.[11]

While earlier indirect attempts to introduce a $2,4\text{-}(CF_3)_2C_5H_5$ ligand into a metal complex failed,[5] treatment of $[Ru(C_5Me_5)Cl]_4$ with 2,4-bis(trifluoromethyl)-1,3-pentadiene led spontaneously to $Ru(C_5Me_5)[2,4\text{-}(CF_3)_2C_5H_5]$ (eq 4). Thus, although the CF_3 groups do not reside

$$\tfrac{1}{4}[Ru(C_5Me_4R)Cl]_4 + 2,4\text{-}(CF_3)_2\text{-}1,3\text{-}C_5H_6 \xrightarrow[R\ =\ CH_3,\ C_2H_5]{THF} Ru(C_5Me_4R)[2,4\text{-}(CF_3)_2C_5H_5] + HCl \quad (4)$$

directly on the formally charged carbon atoms, they still exert a significantly strong enough inductive effect to lead to spontaneous elimination of HCl from the presumed $Ru(C_5Me_4R)(Cl)(\eta^4$-diene) intermediate. As will also be seen from the structural studies, the presence of the CF_3 substituents leads to significantly different behavior relative to the foregoing compounds. In particular, while all these half-open ruthenocenes are air stable as solids, only the CF_3-substituted ones retain air stability in the solution phase. This might be a consequence of the possible participation of a Ru(IV) species of a trianionic dienyl ligand (IV), the general form of which had been earlier proposed[12]



III IV

(7) (a) Cox, D. N.; Roulet, R. *J. Chem. Soc., Chem. Commun.* **1989**, *111*, 175. (b) Kreindlin, A. Z.; Petrovskii, P. V.; Rybinskaya, M. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1987**, 1772.

(8) (a) These species are carbonyl complexes, possessing additional ligands such as alkynes. The appropriate fragments have been abstracted from the respective organic molecules.[9a] A conversion of a OCH_3 to a CO ligand in the $Ru(C_5Me_5)$ coordination sphere has also been observed recently.[8b] $Ru(C_5Me_5)$ might thus be considered to be significantly "carboxophilic". (b) Kang, B.-S.; Koelle, U.; Thewalt, U. *Organometallics* **1991**, *10*, 2569.

(9) (a) Trakarnpruk, W.; Ernst, R. D. Unpublished results. (b) Schmidt, T.; Goddard, R. *J. Chem. Soc., Chem. Commun.* **1991**, 1427.

(10) (a) Bannister, W. D.; Green, M.; Haszeldine, R. N. *J. Chem. Soc. A* **1966**, 194. (b) Green, M.; Hancock, R. I. *Ibid.* **1968**, 109. (c) Bennett, R. L.; Bruce, M. I. *Aust. J. Chem.* **1975**, *28*, 1141. (d) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *134*, 319. (e) Baudry, D.; Daran, J. C.; Dromzee, Y.; Ephritikhine, M.; Felkin, H.; Jeannin, Y.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1983**, 813.

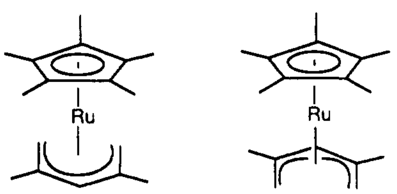
(11) (a) Cheng, M.-H.; Wu, Y.-J.; Wang, S.-L.; Liu, R.-S. *J. Organomet. Chem.* **1989**, *373*, 119. (b) Cheng, M.-H.; Cheng, C.-Y.; Wang, S.-L.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1990**, *9*, 1853. (c) Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Ibid.* **1991**, *10*, 19.

Table II. Positional Parameters for the Non-Hydrogen Atoms of $Ru(C_5Me_5)(3\text{-}C_6H_9)$

atom	x	y	z
Ru	0.44145 (4)	0.25	0.23016 (4)
C1	0.5788 (5)	0.3531 (4)	0.0704 (6)
C2	0.6707 (5)	0.3427 (3)	0.2373 (6)
C3	0.7251 (6)	0.25	0.3210 (7)
C4	0.8122 (8)	0.25	0.5069 (9)
C5	0.1571 (6)	0.25	0.1531 (6)
C6	0.2015 (4)	0.3358 (3)	0.2609 (5)
C7	0.2728 (4)	0.1970 (2)	0.4329 (4)
C8	0.0596 (8)	0.25	−0.0291 (8)
C9	0.1621 (7)	0.4418 (4)	0.1993 (8)
C10	0.3278 (6)	0.1290 (3)	0.5885 (6)

but would not generally be considered of any significance in the absence of some stabilizing influence. As will be seen subsequently, a structural study does indeed provide support for such a contribution. Additionally, these species are far more volatile than the other complexes (see Experimental Section), a not uncommon influence of CF_3 substituents.[13]

In addition to analytical and mass spectral data, ^1H and ^{13}C spectroscopic data are also in accord with the presence of the expected η^5-Pdl ligands (U conformation) in all of the above complexes. For those possessing symmetric pentadienyl ligands (C_5H_7, 3-C_6H_9, 2,4-C_7H_{11}, 1,5-$(C_6H_5)_2C_5H_5$, 2,4-$(CF_3)_2C_5H_5$), the spectra are simplified, such that a virtual vertical mirror plane passes through the complex, as in V or VI, although the ground states might actually lie somewhere in between, and the observed symmetry would simply be the result of rapid C_5Me_5 ligand rotation.



V VI

The spectral shifts of the simple (alkylated or arylated) pentadienyl complexes are reasonably similar to those in related compounds. For the Pdl = 1,5-$(C_6H_5)_2C_5H_5$ compound, the H(1,5)-endo proton resonances lie significantly downfield those of the other simple pentadienyl complexes, while, for the Pdl = 2,4-$(CF_3)_2C_5H_5$ complexes, the H(3) resonances experience large downfield shifts. Even more dramatic shifts are observed for the oxopentadienyl complexes, however. Thus, for $Ru(C_5Me_5)(3,5\text{-}OC_6H_9)$, the resonance for the proton attached to C2 (adjacent to O) is found far downfield, at ca. 6.72 ppm, while the H(5)-endo resonance is found at 2.82 ppm. For comparison, the respective resonances for $Ru(C_5Me_5)(3\text{-}C_6H_9)$ occur at 3.88 and 0.38 ppm.

Structural Results and Discussion

The structure of $Ru(C_5Me_5)(3\text{-}C_6H_9)$ (Tables II and III) will first be considered as a typical example of a half-open ruthenocene. From Figure 1, the molecule may be seen to have imposed mirror plane symmetry, such that an ideally perfectly staggered (V), as opposed to eclipsed (VI), conformation is adopted. Interestingly, the related $Ru(C_5H_5)(2,4\text{-}C_7H_{11})$ was also found to possess mirror plane symmetry,[14] but an ideally eclipsed conformation appeared to be adopted, although large thermal parameters for the cyclopentadienyl carbon atoms might reflect instead the presence of two slightly staggered forms. In fact, the solid-state conformation of $Cr(C_5Me_5)(C_5H_7)$ was found to be slightly staggered (by ca. 6°).[15] In the present situation, however, the adoption of a staggered conformation is reasonable in that interligand methyl group repulsions are minimized.

Table III. Bond Distances (Å) and Angles (deg) for $Ru(C_5Me_5)(3\text{-}C_6H_9)$

Bond Distances			
Ru–C1	2.164 (2)	C3–C4	1.479 (4)
Ru–C2	2.126 (2)	C5–C6	1.415 (2)
Ru–C3	2.187 (2)	C5–C8	1.484 (4)
Ru–C5	2.174 (2)	C6–C7	1.414 (2)
Ru–C6	2.182 (2)	C6–C9	1.499 (3)
Ru–C7	2.214 (1)	C7–C7′	1.405 (3)
C1–C2	1.374 (3)	C7–C10	1.499 (2)
C2–C3	1.420 (3)		
Bond Angles			
C1–C2–C3	125.9 (2)	C5–C6–C9	123.3 (2)
C2–C3–C2′	119.6 (2)	C7–C6–C9	127.8 (2)
C2–C3–C4	119.8 (1)	C6–C7–C7′	107.8 (1)
C6–C5–C6′	106.8 (2)	C6–C7–C10	125.2 (2)
C6–C5–C8	126.3 (1)	C7′–C7–C10	126.9 (1)
C5–C5–C7	108.7 (2)		

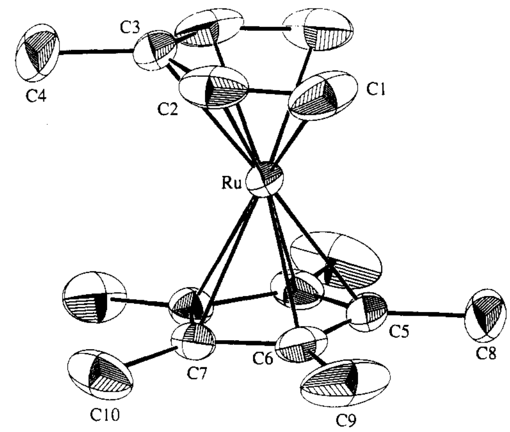


Figure 1. Perspective view of $Ru(C_5Me_5)(3\text{-}C_6H_9)$, which lies on a crystallographic mirror plane.

The two ligands are each reasonably planar, the maximum deviations for the metal-bound atoms being 0.001 and 0.025 Å for the cyclic and acyclic ligand, respectively. Although the Ru–C distances for the two ligands are similar (vide infra), the metal atom is located closer to the acyclic group, 1.567 vs 1.834 Å. Such a situation is to be expected for a wider, open ligand,[1] and leads to significantly greater steric demands (e.g., cone angle)[16] than for C_5Me_5. As is generally observed, the ligand substituents do not lie in the above planes. For the C_5Me_5 ligand, the deviations range from 0.067 Å for C(10) to 0.160 Å for C(8), corresponding to tilts of 2.6–6.2° away from the metal.[17] For the 3-C_6H_9 ligand, the methyl group lies 0.108 Å out of the plane, corresponding to a tilt of 4.2° toward the metal. Such tilts are typical of large ligands which try to

(12) Coates, G. E.; Green, M. L. H.; Powell, P.; Wade, K. *Principles of Organometallic Chemistry*; Methuen: London, 1971; p 198.
(13) Elguero, J.; Yranzo, G. I.; Laynez, J.; Jiménez, P.; Menéndez, M.; Catalán, J.; de Paz, J. L. G.; Anvia, F.; Taft, R. W. *J. Org. Chem.* **1991**, *56*, 3942.
(14) Gleiter, R.; Hyla-Kryspin, I.; Ziegler, M. L.; Sergeson, G.; Green, J. C.; Stahl, L.; Ernst, R. D. *Organometallics* **1989**, *8*, 298.
(15) Freeman, J. W.; Hallinan, N. C.; Arif, A. M.; Gedridge, R. W.; Ernst, R. D.; Basolo, F. *J. Am. Chem. Soc.* **1991**, *113*, 6509.
(16) Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673.
(17) The sine of the tilt angle is taken as the deviation from the plane divided by the bond distance from the substituent to its attached dienyl atom.

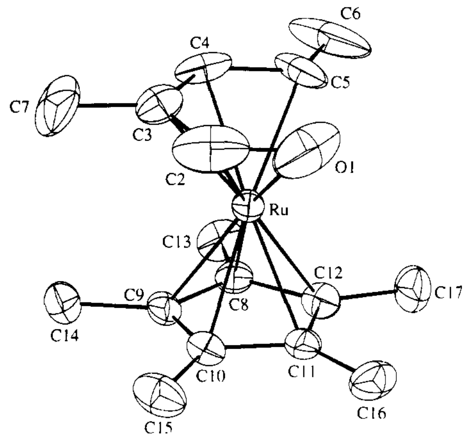


Figure 2. Perspective view and numbering scheme for Ru(C_5Me_5)(3,5-OC_6H_9).

improve the metal–ligand overlap by pointing the p orbitals more toward the metal center.[18] The analogous tilts for the hydrogen atoms are also not unusual (see supplementary material). An angle of 8.0 (5)° exists between the ligand planes.

The bond lengths within the ligands are also reasonable. The internal pentadienyl bond (C2–C3) is clearly longer than the external (C1–C2) one, 1.420 (3) vs 1.374 (3) Å, pointing to a contribution from resonance hybrid VII. For comparison, the delocalized C–C bonds around the C_5Me_5 ring average 1.413 (2) Å.

VII

The metal–carbon bonding is naturally of primary interest. The Ru–C bonds for the open ligand average 2.153 (1) Å, somewhat shorter than the 2.193 (1) Å average for the C_5Me_5 ligand. Such shorter bonds for the open dienyl ligands seem normal, reflecting its lower π stabilization relative to an aromatic counterpart such as C_5H_5 or C_5Me_5, which then have less to gain from additional bonding.[1] It should be noted, however, that the bonding within each ligand is not entirely symmetric. Thus, for the 3-C_6H_9 ligand, the bonds to the formally uncharged (C2) atoms are shortest, which is understandable in that the methyl substitution at C3 leads to a smaller C2–C3–C2′ angle relative to the C1–C2–C3 angle (119.6 (2) vs 125.9 (2)°).[18c] A difference in M–C(C_5Me_5) bond lengths is less common, however, and in this case the bond to C5 is shortest while those to C7 are longest.

It is also interesting to compare these structural parameters to those of Ru(C_5H_5)(2,4-C_7H_{11}),[14] for which the average Ru–C distances for the open and closed dienyl ligands were found to be 2.168 (3) and 2.178 (3) Å, respectively. It would seem in Ru(C_5Me_5)(3-C_6H_9) that the Ru–(3-C_6H_9) bonding has improved at the expense of the Ru–C_5Me_5 bonding. As the pentadienyl ligands generally seem to function as the better acceptors in these types of compounds,[1] the greater donating ability of C_5Me_5 relative to C_5H_5 has probably enhanced the Ru–(3-C_6H_9) bonding, while the increased steric crowding leads to the longer Ru–C(C_5Me_5) bonds.

The structure of Ru(C_5Me_5)(3,5-OC_6H_9) was undertaken to provide a representative picture of the bonding in an

(18) (a) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148. (b) Haaland, A. *Acc. Chem. Res.* **1979**, *12*, 415. (c) Ernst, R. D. *Struct. Bonding (Berlin)* **1984**, *57*, 1.

Table IV. Positional Parameters for the Non-Hydrogen Atoms of Ru(C_5Me_5)(3,5-OC_6H_9)

atom	*x*	*y*	*z*
Ru	0.09466 (5)	−0.00783 (5)	−0.05587 (5)
O1	0.1664 (9)	0.0836 (8)	−0.1984 (7)
C2	0.2618 (11)	0.0178 (12)	−0.1519 (9)
C3	0.2956 (7)	0.0291 (8)	−0.0404 (7)
C4	0.2242 (9)	0.1010 (8)	0.0294 (7)
C5	0.1200 (9)	0.1677 (7)	−0.0112 (11)
C6	0.0492 (13)	0.2256 (8)	0.0837 (15)
C7	0.3961 (10)	−0.0447 (11)	0.0075 (11)
C8	−0.0326 (7)	−0.0833 (6)	0.0616 (7)
C9	0.0557 (7)	−0.1662 (6)	0.0241 (7)
C10	0.0423 (8)	−0.1804 (6)	−0.0923 (7)
C11	−0.0567 (8)	−0.1072 (6)	−0.1287 (7)
C12	−0.1032 (8)	−0.0473 (6)	−0.0356 (7)
C13	−0.0593 (8)	−0.0516 (8)	0.1795 (7)
C14	0.1424 (9)	−0.2315 (8)	0.1009 (9)
C15	0.1081 (11)	−0.2633 (8)	−0.1649 (9)
C16	−0.1034 (11)	−0.0978 (8)	−0.2455 (8)
C17	−0.2118 (8)	0.0310 (8)	−0.0347 (9)

Table V. Bond Distances (Å) and Angles (deg) for Ru(C_5Me_5)(3,5-OC_6H_9)

Bond Distances			
Ru–O1	2.166 (7)	C3–C7	1.500 (12)
Ru–C2	2.142 (9)	C4–C5	1.450 (13)
Ru–C3	2.193 (7)	C5–C6	1.530 (15)
Ru–C4	2.153 (7)	C8–C9	1.437 (10)
Ru–C5	2.178 (7)	C8–C12	1.452 (10)
Ru–C8	2.151 (7)	C8–C13	1.490 (10)
Ru–C9	2.158 (7)	C9–C10	1.412 (10)
Ru–C10	2.176 (7)	C9–C14	1.519 (11)
Ru–C11	2.183 (7)	C10–C11	1.436 (10)
Ru–C12	2.173 (8)	C10–C15	1.492 (11)
O1–C2	1.400 (16)	C11–C12	1.414 (10)
C2–C3	1.392 (14)	C11–C16	1.490 (10)
C3–C4	1.420 (12)	C12–C17	1.486 (10)
Bond Angles			
O1–C2–C3	121.1 (11)	C10–C9–C14	126.8 (7)
C2–C3–C4	119.1 (10)	C9–C10–C11	107.5 (7)
C2–C3–C7	119.7 (11)	C9–C10–C15	127.4 (8)
C4–C3–C7	120.8 (9)	C11–C10–C15	124.8 (7)
C3–C4–C5	122.9 (8)	C10–C11–C12	109.0 (6)
C4–C5–C6	112.0 (10)	C10–C11–C16	125.2 (7)
C9–C8–C12	107.0 (6)	C12–C11–C16	125.9 (7)
C9–C8–C13	126.6 (7)	C8–C12–C17	125.6 (7)
C12–C8–C13	126.0 (6)	C11–C12–C17	126.6 (7)
C8–C9–C10	109.0 (7)	C8–C12–C11	107.6 (6)
C8–C9–C14	124.1 (7)		

oxo dienyl analogue. With its "unsymmetric" methyl substitution pattern (cf., the 2,4-OC_6H_9 complex) it should be less prone to potential disorders which might lead to apparent mirror plane symmetry, which is often found in structures of these types.[19] A perspective view of the structure may be seen in Figure 2, and important bonding parameters are presented in Tables IV and V.

As is normal, the five metal-bound carbon atoms for the C_5Me_5 ligand are more nearly planar than those on the open ligand, the maximum deviations being 0.005 and 0.032 Å. An angle of 3.5° exists between the ligand planes. The relative conformation defined by the two ligands seems determined primarily by the need to stagger the C6 methyl group between those of C13 and C17. As C6 is located on a terminal pentadienyl carbon atom, it tends to bend significantly more toward the metal atom than would an internally located substituent, e.g., C7. In fact,

(19) Structural determinations were also carried out for the Pdl = 1-C_6H_9 and 2-C_6H_9 compounds, but in each case the results were poor due to pseudo mirror plane symmetry. For the 1-C_6H_9 complex, a = 10.694, b = 11.559, and c = 12.036 Å, while for the 2-C_6H_9 complexes, a = 10.333 (1), b = 11.968 (2), and c = 11.914 (2) Å.

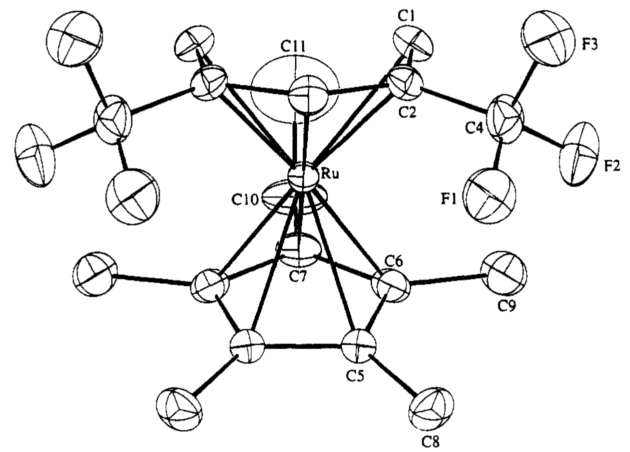
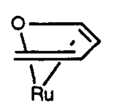


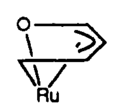
Figure 3. Perspective view of $Ru(C_5Me_4Et)[2,4-(CF_3)_2C_5H_5]$, which possesses crystallographically imposed mirror plane symmetry. For purposes of clarity, C3 has not been labeled.

the relative deformations experienced by these two groups are 0.212 vs 0.074 Å, or 8.0 vs 2.8° (both toward Ru), which accounts for the positioning of C7 in a nearly eclipsing orientation.[20] For comparison, the C_5Me_5 substituents bend away from the metal atom by 0.027–0.145 Å. The ruthenium atoms are again closer to the open rather than the closed ligand plane, 1.629 vs 1.795 Å, although the difference is not so large as before, both as a result of geometric and bonding factors. A comparison of the backbone C–C–C angles reveals the oxo dienyl ligand to be smaller than the $3-C_6H_9$ ligand, which means for comparable metal–ligand bond distances the metal atom will be located further from the ligand plane. As the C_5Me_5 ligand is not so flexible, a closer approach to the metal atom reflects shorter M–C bonds relative to $Ru(C_5Me_5)(3-C_6H_9)$. This could easily be a consequence of the apparent weaker bonding of the oxo dienyl relative to the $3-C_6H_9$ ligand (vide infra), which then results in stronger $M-C_5Me_5$ bonding for the oxo dienyl compound.

Although the ligand-related parameters are not particularly well determined, a few features are still apparent. While one might have expected an alternation (l–s–l–s) (l = long; s = short) in the ligand framework from the contribution of resonance hybrid VIII,[18c] the actual trend



VIII



IX

observed, l–s–s–l, seems more in line with IX, which would entail a Ru(IV) complex, although the distortion is slight (see, however, the following structure description). This

(20) (a) Despite the staggered location of C6, it appears that it is still engaged in repulsive interactions with C13 and C17, as such terminal substituents more commonly are observed to tilt ca. 15–20° below the open dienyl ligand plane.[1,18c] In fact, the C6 to C13 and C17 nonbonded contact distances are 3.685 (15) and 3.889 (16) Å, respectively, less than the 4.0-Å sum of the van der Waals radii of two methyl groups.[22] For comparison, the C7- -C14 distance is 3.677 (15) Å. Notably, for $Ru(C_5Me_5)(3-C_6H_9)$, the C4- -C10 nonbonded contact distance is 4.123 (7) Å, greater than the van der Waals' separation, so it is possible that an attractive interaction actually might slightly increase the tilt of C4 (vide supra). In contrast, for the eclipsed $Cr(C_5Me_5)(3-C_6H_9)(CO)^+$, the methyl group on the $3-C_6H_9$ ligand is tilted 6.1° away from the metal,[20b] due to a CH_3- -CH_3 contact of only 3.240 (12) Å. For $Fe(2,3,4-C_8H_{13})_2$, a CH_3- -CH_3 contact distance of 3.546 (10) Å involving the $3-CH_3$ substituent leads to a tilt of 3.2° away from the meal.[20c] (b) Freeman, J. W.; Arif, A. M.; Ernst, R. D. Unpublished results. (c) Han, J.-C.; Hutchinson, J. P.; Erst, R. D. *J. Organomet. Chem.* **1987**, *321*, 389.

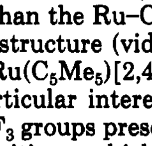
Table VI. Positional Parameters for the Non-Hydrogen Atoms of $Ru(C_5Me_4Et)[2,4-(CF_3)_2C_5H_5]$

atom	x	y	z
Ru	0.0	0.11797 (7)	0.0
F1	−0.1467 (4)	0.4360 (7)	0.0609 (5)
F2	−0.2239 (3)	0.2414 (8)	0.0533 (5)
F3	−0.1948 (4)	0.3358 (8)	0.1918 (5)
C1	−0.0902 (5)	0.0425 (9)	0.1129 (6)
C2	−0.0807 (5)	0.2052 (9)	0.1158 (6)
C3	0.0	0.2767 (14)	0.1212 (9)
C4	−0.1613 (6)	0.3041 (12)	0.1047 (7)
C5	−0.0461 (5)	0.1925 (8)	−0.1498 (5)
C6	−0.0746 (5)	0.0457 (9)	−0.1270 (5)
C7	0.0	−0.0500 (12)	−0.1156 (8)
C8	−0.1037 (6)	0.3256 (10)	−0.1784 (7)
C9	−0.1683 (6)	−0.0082 (13)	−0.1288 (7)
C10	0.0	−0.2233 (14)	−0.1066 (10)
C11	0.0	−0.2827 (14)	−0.0143 (19)

Table VII. Bond Distances (Å) and Angles (deg) for $Ru(C_5Me_4Et)[2,4-(CF_3)_2C_5H_5]$

Bond Distances			
Ru–C1	2.179 (6)	C2–C3	1.388 (6)
Ru–C2	2.154 (5)	C2–C4	1.518 (7)
Ru–C3	2.171 (7)	C5–C5′	1.413 (10)
Ru–C5	2.271 (5)	C5–C6	1.397 (11)
Ru–C6	2.180 (7)	C5–C8	1.517 (7)
Ru–C7	2.167 (7)	C6–C7	1.428 (9)
F1–C4	1.325 (7)	C6–C9	1.511 (9)
F2–C4	1.311 (7)	C7–C10	1.527 (9)
F3–C4	1.330 (7)	C10–C11	1.370 (20)
C1–C2	1.437 (12)		
Bond Angles			
C1–C2–C3	122.8 (6)	F3–C4–C2	110.1 (6)
C1–C2–C4	118.9 (5)	C5′–C5–C6	108.2 (4)
C3–C2–C4	118.2 (6)	C5′–C5–C8	125.6 (3)
C2–C3–C2′	125.8 (8)	C6–C5–C8	126.0 (5)
F1–C4–F2	104.3 (6)	C7–C6–C9	125.3 (7)
F1–C4–F3	106.9 (5)	C5–C6–C7	108.5 (6)
F1–C4–C2	114.1 (5)	C5–C6–C9	125.6 (7)
F2–C4–F3	106.9 (5)	C6–C7–C6′	106.4 (8)
F2–C4–C2	114.2 (5)	C6–C7–C10	126.6 (4)

may point to a similar possibility for an acac or hexafluoroacac ligand, for which a trianionic hybrid such as X



X

would seem quite reasonable.[21] Nonetheless, the bonding of the oxo dienyl ligand does not seem particularly impressive. Especially considering the smaller size of an oxygen relative to a carbon atom,[22] the Ru– (oxo dienyl) bonds seem longer than the $Ru-C(3-C_6H_9)$ bonds in the $Ru(C_5Me_5)(3-C_6H_9)$ structure (vide supra).

The structure of $Ru(C_5Me_5)[2,4-(CF_3)_2C_5H_5]$ was considered to be of particular interest in that it has electron-withdrawing CF_3 groups present in the formally uncharged 2- and 4-positions, which could be expected to participate the most in the M → L back-bonding interactions. While data were readily collected for this com-

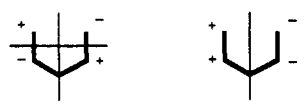
(21) It might well be that the acac or F_6-acac ligand will be quite effective in stabilizing formally very low oxidation states as a result of the accessibility of the trianionic resonance form. However, it can also be noted that in $Ru(C_5Me_5)(acac)$, η^2-acac coordination is present, yielding a 16-electron complex,[3c] even though η^5-acac (dioxo dienyl) coordination would lead to an 18-electron species. Taken together with the fact that the oxo dienyl coordination in $Ru(C_5Me_5)(3,5-OC_6H_9)$ does not seem very impressive, this might suggest that η^5-acac coordination would experience difficulties of one sort or another.

(22) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

pound, however, three independent molecular fragments (or half-fragments) were present in the unit cell,[23] and insufficient data could be obtained for an acceptable structure solution. Hence, resort was made to the C_5Me_4Et counterpart, which did lead to a successful structure determination. The structure of this compound is presented in Figure 3, with pertinent bonding parameters being listed in Tables VI and VII.

The molecule was found to lie on a crystallographic mirror plane and to adopt a perfectly staggered, rather than eclipsed, orientation. This leads to the CF_3 groups being located near, although not truly eclipsing, the C8 atoms, and the fluorine atoms appear to adopt orientations which minimize the C8- -CF_3 interactions. The C_2H_5 group has also managed to fit in a convenient niche, near the open edge of the other dienyl ligand.[24] A relatively large interplanar angle of 15.4° is present, again perhaps due to the C8- -CF_3 interactions (vide infra).

The CF_3 groups can indeed be seen to exert significant influences on the bonding in the complex. First, one sees that the external C–C bond in the open ligand is clearly longer than the internal bond, 1.437 (12) vs 1.388 (6) Å. A somewhat similar, but less clear, difference seemed present in the oxo dienyl structure (vide supra). Such a situation is exactly the opposite of the expected[18c] and can be explained by invoking a trianionic resonance form for the dienyl ligand (IV). Alternatively, this pattern could be explained through greater population of the π^* molecular orbital XI, as a result of the enhanced back-bonding



XI XII

interactions, perhaps accompanied by a depletion of electron density in the π molecular orbital XII. A second geometric observation regarding methyl substituents on a pentadienyl skeleton is that they are commonly observed to bend out of the ligand plane toward the metal atom, apparently in order to improve overlap between the metal and ligand orbitals.[18] This tendency can also be seen to carry over to the electronegative CF_3 substituents, which lie 0.211 Å, or 8.0°, beneath the open ligand plane, despite their resulting proximity to C8.[25] One can note that, in a dimetallic analogue of $Ru(C_5Me_5)(2,4\text{-}C_7H_{11})$, the open ligand methyl groups are found to tilt 9.0° toward the metal.[26] For comparison, the tilts for C8, C9, and C10 are 4.9, 4.3, and 8.8°, respectively, in the opposite direction. Finally, methyl substituents generally bring about a contraction of the framework C–C–C angle about their attached atoms.[18c] In this case, the CF_3 substituents also seem to lead to a contraction (∠C1–C2–C3 = 122.8 (6)° vs ∠C2–C3–C2′ = 125.8 (8)°), but the actual magnitude is obscured by the statistical uncertainties.[27]

The Ru–C bond lengths also are of interest. The Ru–C distances for the open ligand are clearly shorter than those for the C_5Me_4Et ligand, averaging 2.167 (4) vs 2.214 (4) Å, but appear at least slightly longer than those for the $3\text{-}C_6H_9$ ligand in $Ru(C_5Me_5)(3\text{-}C_6H_9)$, probably due to the additional steric demands of the two CF_3 groups. Most likely the steric hindrance leads to the Ru–C5 distance (2.271 (5) Å) being about 0.1 Å longer than the Ru–C6 and Ru–C7 distances, and indeed C5 lies significantly further from the open dienyl plane than C6 or C7 (3.66 vs 3.28 and 3.09 Å, respectively). Although the structural evidence for enhanced Ru–Pdl bonding in this complex is not overwhelming, it may well be that this is in part a consequence that there is no overriding tendency for Ru(II) to become Ru(IV). It could easily be anticipated that other metal systems for which the higher oxidation state is particularly favorable will exhibit even more dramatic structural and chemical behaviors.

The $Ru(C_5Me_5)$(Pdl) class of compounds has proven capable of supporting a rich variety of pentadienyl ligands. Already it is becoming clear that the pentadienyl skeleton and the metal–pentadienyl bonding are keenly affected by the presence and location of the pentadienyl substituents and/or framework heteroatoms, and a much greater understanding of the electronic natures of pentadienyl ligands should ultimately be gained. Additional efforts in this regard are currently underway.

Note Added in Proof. We have recently learned of the independent syntheses of a number of the compounds reported herein, and of other interesting relatives, by Prof. Dr. Albrecht Salzer and his group.

Acknowledgment. R.D.E. thanks the National Science Foundation for generous support of this work. We are also grateful to Dr. Tim Newbound for providing the sample of $2,4\text{-}(CF_3)_2\text{-}1,3\text{-}C_5H_6$.

Registry No. $Ru(C_5Me_5)(C_5H_7)$, 139407-22-0; $Ru(C_5Me_5)(1\text{-}C_6H_9)$, 139375-85-2; $Ru(C_5Me_5)(2\text{-}C_6H_9)$, 139375-86-3; $Ru(C_5Me_5)(3\text{-}C_6H_9)$, 139375-87-4; $Ru(C_5Me_5)(2,3\text{-}C_7H_{11})$, 139375-88-5; $Ru(C_5Me_5)(2,4\text{-}C_7H_{11})$, 115557-91-0; $Ru(C_5Me_5)[1,5\text{-}(C_6H_5)_2C_5H_5]$, 139375-89-6; $Ru(C_5Me_5)[2,4\text{-}(CF_3)_2C_5H_5]$, 139375-90-9; $Ru(C_5Me_4Et)[2,4\text{-}(CF_3)_2C_5H_5]$, 139375-91-0; $Ru(C_5Me_5)(2,4\text{-}OC_6H_9)$, 139375-92-1; $Ru(C_5Me_5)(3,5\text{-}OC_6H_9)$, 139575-93-2; $[Ru(C_5Me_5)Cl]_4$, 113860-07-4; $[Ru(C_5Me_4Et)Cl]_4$, 139110-38-6; $[Ru(C_5Me_5)OCH_3]_2$, 120883-04-7; Cp*RuCl, 121334-82-5; C_5H_7K, 51391-25-4; $1\text{-}C_6H_9K$, 74206-01-2; $2\text{-}C_6H_9K$, 74205-99-5; $3\text{-}C_6H_9K$, 74206-00-1; $2,3\text{-}C_7H_{11}K$, 118398-23-5; $2,4\text{-}C_7H_{11}K$, 74205-98-4; $1,5\text{-}(C_6H_5)_2C_5H_5K$, 77132-13-9; 2,4-bis(trifluoromethyl)-1,3-pentadiene, 110625-01-9; mesityl oxide, 141-79-7; 2-methyl-2-pentenal, 623-36-9.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, least-squares plane data, and IR and mass spectral data (14 pages); tables of structure factors (13 pages). Ordering information is given on any current masthead page.

(23) The unit cell for $Ru(C_5Me_5)[2,4\text{-}(CF_3)_2C_5H_5]$ is monoclinic, with a = 22.271, b = 13.634, and c = 8.852 Å and β = 97.58° for Z = 3 (apparent space group $P2_1$ or $P2_1/m$).

(24) The apparent shortness of the C10–C11 bond and the large thermal parameters for these atoms indicate that the ethyl group does not actually lie entirely in the mirror plane but probably adopts at least two orientations which have become averaged out in the observed structure.

(25) The C8- -F1 and C8- -F2 nonbonded contact separations are 3.488 (12) and 3.749 (11) Å, respectively, compared to a CH_3- -F van der Waals separation of 3.47 Å.

(26) Weng, W.-Q.; Kunze, K.; Arif, A. M.; Ernst, R. D. *Organometallics* **1991**, *10*, 3643.

(27) One might look to the C1- -C5 nonbonded contact separations for a general indication of ligand contraction. The value for this compound is 2.763 (15) Å, which may be compared to the values of 2.790 (10) and 2.700 (28) Å for $Ru(C_5H_5)(2,4\text{-}C_7H_{11})$[14] and a dimetallic analogue of $Ru(C_5Me_5)(2,4\text{-}C_7H_{11})$,[26] respectively. Unfortunately, the magnitudes of the statistical uncertainties do not allow for a definitive conclusion to be reached.