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cis- and *trans*-Diene Coordination in Ruthenium(II) Acetylacetonate Compounds

Richard D. Ernst,* Enrique Melendez, and Lothar Stahl

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Manfred L. Ziegler*[†]

Institut für Anorganische Chemie der Universität, D-6900 Heidelberg 1, West Germany

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Reduction of $Ru(acac)_3$ with zinc in ethanol in the presence of 1,3-dienes leads to the formation of $Ru(\eta^4\text{-diene})(acac)_2$ complexes (diene = 2,3-dimethyl-1,3-butadiene, 2,4-hexadiene, 1,3-cyclohexadiene, 2,4-dimethyl-1,3-pentadiene). Except for the cyclohexadiene compound, these complexes involve unusual η^4-*trans*-diene coordination in the ground state and may be observed in two isomeric forms. In the case of the 2,3-dimethyl-1,3-butadiene complex, small amounts of a third isomeric form may be observed, which appears to involve η^4-*cis*-diene coordination. Single-crystal X-ray structural studies have been carried out for the 2,4-dimethyl-1,3-pentadiene and cyclohexadiene complexes. For the former, the space group is $P2_1/n$, with a = 10.614 (8) Å, b = 13.31 (1) Å, c = 12.93 (1) Å, β = 90.81 (6)°, and V = 1826.5 Å^3 for Z = 4, while, for the latter, the space group is $Pbca$, with a = 11.642 (4) Å, b = 16.162 (6) Å, c = 33.78 (1) Å, and V = 6356.0 Å^3 for Z = 16 (two independent molecules). The former (latter) structures were refined to discrepancy indices of R = 0.037 (0.051) and 0.035 (0.044) for 4015 (4200) reflections having $I > 2\sigma(I)$ ($2.5\sigma(I)$ for the latter).

A number of interesting diene and dienyl compounds of Ru(0) or Ru(II) may be isolated from the reduction of "hydrated ruthenium trichloride" by zinc in ethanol in the presence of various dienes,[1] and this approach has been utilized to prepare open ruthenocenes as well.[2] However, the yields for the open ruthenocene syntheses were observed to range from ca. 30 to 70%, apparently depending on the quality of the starting ruthenium chloride complex. An attempt to make the reaction behave more consistently was therefore made by replacing the ruthenium chloride by $Ru(acac)_3$, which actually had been employed in the first preparations of ruthenocene.[3] Indeed, a cleaner reaction did result, but the product was found to be a $Ru(diene)(acac)_2$ complex. Recently, it has become clear that these compounds involve η^4-*trans*-diene coordination,[4,5] a relatively rare bonding mode that had originally been identified only in earlier metal complexes such as $Zr(C_5H_5)_2(diene)$,[6] $Mo(C_5H_5)(NO)(diene)$,[7] and $Nb(C_6H_5)(diene)_2$[4,8] species. We now report our observations concerning these late-metal 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 NMR solvents were degassed over potassium and stored in glass bulbs under nitrogen. Infrared mulls were prepared in a glovebox with dry, degassed Nujol.

Except for 2,4-dimethyl-1,3-pentadiene, organic dienes were purchased commercially. Triethylphosphine, trimethyl phosphite, 2,4-pentanedione, and hydrated ruthenium trichloride were also obtained commercially. $Ru(acac)_3$ was prepared by a published procedure.[9]

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.[1b] Numbers of carbon atoms associated with given ^{13}C NMR resonances are reported in accord with their assignments but were not precisely integrated. Analytical data were obtained by Desert Analytics and Oneida Research Laboratories.

Bis(acetylacetonato)(η^4-2,4-hexadiene)ruthenium(II), $Ru(\eta^4\text{-}2,4\text{-}C_6H_{10})(C_5H_7O_2)_2$. To a solution of 1.0 g (2.5 mmol) of $Ru(acac)_3$ in 20 mL of ethanol under nitrogen was added 5.7 mL (50 mmol) of 2,4-hexadiene and 4.0 g of activated zinc dust. The reaction mixture was refluxed for 2 h, resulting in an orange-green solution. The solvent was removed in vacuo, and the crude product was extracted with two 40-mL portions of pentane and filtered on a coarse frit. .The light orange solution was concentrated to about 30 mL and cooled to −23 °C for 12 h, precipitating traces of $Zn(acac)_2$ as a byproduct. The orange supernatant liquid was then transferred to a separate flask, reduced in volume to about 10 mL, and cooled to −23 °C for 2 days, yielding an orange, air-stable crystalline product. The yield is about 48–52% based on $Ru(acac)_3$.

Mp (nitrogen-filled, sealed capillary): 94–95 °C. Complete infrared data (Nujol mull): 3078 (w), 1577 (s), 1518 (s), 1266 (m), 1201 (m), 1174 (w), 936 (m), 779 (mw), 756 cm^{-1} (mw). ^1H NMR (benzene-d_6, ambient), isomer I: δ 5.34 (s, 2 H), 3.89 (m, 2 H), 3.56 (m, 2 H), 2.02 (s, 6 H), 1.68 (s, 6 H), 1.64 (d, 6 H, J = 6.2 Hz). ^{13}C NMR (benzene-d_6, ambient), isomer I: δ 186.97 (s, 2 C), 185.06 (s, 2 C), 99.62 (d, 2 C, J = 155.6 Hz), 98.29 (d, 2 C, J = 169.4 Hz), 82.72 (d, 2 C, J = 157.0 Hz), 28.07 (q, 2 C, J = 125.3

[†] Deceased April 30, 1991.

(1) (a) Pertici, P.; Vitulli, G.; Paci, M.; Porri, L. *J. Chem. Soc., Dalton Trans.* **1980**, 1961. (b) Gleiter, R.; Hyla-Kryspin, I.; Ziegler, M. L.; Sergeson, G.; Green, J. C.; Stahl, L.; Ernst, R. D. *Organometallics* **1989**, *8*, 298.

(2) Stahl, L.; Ernst, R. D. *Organometallics* **1983**, *2*, 1229.

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

(4) (a) Melendez, E.; Arif, A. M.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 8703. (b) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255.

(5) (a) An equilibrium between cis-η^4 and trans-η^4 coordination has also been seen for $Ru(diene)(C_5Me_5)(Cl)$ complexes,[5b] and other ruthenium(II) *trans*-diene compounds have subsequently been reported.[5c,d] (b) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843. (c) Benyunes, S. A.; Green, M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268. (d) Benyunes, S. A.; Day, J. P.; Green, M.; Al-Saadoon, A. W.; Waring, T. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1416.

(6) (a) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (b) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723.

(7) Hunter, A. D.; Legzdins, P., Nurse, C. R.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1985**, *107*, 1791.

(8) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008.

(9) Johnson, A.; Everett, G. W., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 1419.

0276-7333/91/2310-3635$02.50/0

Hz), 27.91 (q, 2 C, J = 130.0 Hz), 16.83 (q, 2 C, J = 126.6 Hz). ^{1}H NMR (benzene-d_6, ambient), isomer II: δ 5.07 (s, 2 H), 4.87 (m, 2 H), 3.25 (m, 2 H), 2.08 (s, 6 H), 1.57 (s, 6 H), 1.47 (d, 6 H, J = 6.2 Hz). ^{13}C NMR (benzene-d_6, ambient), isomer II: δ 187.04 (s, 2 C), 185.76 (s, 2 C), 98.53 (d, 2 C, J = 155.0 Hz), 95.73 (d, 2 C, J = 164.2 Hz), 85.35 (d, 2 C, J = 156.3 Hz), 27.72 (q, 2 C, J = 128.6 Hz), 27.47 (q, 2 C, J = 125.8 Hz), 16.92 (q, 2 C, J = 125.9 Hz). MS (FAB) [m/z (relative intensity)]: 107 (11), 136 (38), 153 (12), 154 (28), 179 (12), 180 (30), 181 (30), 183 (10), 294 (10), 297 (43), 298 (57), 299 (68), 300 (100), 302 (66), 379 (27), 380 (36), 381 (45), 382 (71), 384 (37). Anal. Calcd for $C_{16}H_{24}O_4Ru$: C, 50.38; H, 6.34. Found: C, 50.36; H, 6.25.

Bis(acetylacetonato)(η^4-2,3-dimethyl-1,3-butadiene)ruthenium(II), Ru(η^4-2,3-C_6H_{10})($C_5H_7O_2$)$_2$. This air-stable orange crystalline compound is isolated in an analogous manner as described for Ru(2,4-C_6H_{10})($C_5H_7O_2$)$_2$, substituting 2,4-hexadiene by 2,3-dimethyl-1,3-butadiene. The yield is 55% (0.52 g) based on Ru(acac)$_3$.

Mp (nitrogen-filled, sealed capillary): ca. 90 °C. Complete infrared data (Nujol mull): 3080 (w), 1578 (s), 1518 (s), 1401 (m), 1267 (m), 1200 (m), 935 (m), 777 (m), 754 cm^{-1} (m). ^{1}H NMR (benzene-d_6, ambient), isomer I: δ 5.39 (s, 2 H), 3.59 (s, 2 H), 3.46 (s, 2 H), 1.99 (s, 6 H), 1.76 (s, 6 H), 1.38 (s, 6 H). ^{13}C NMR (benzene-d_6, ambient), isomer I: δ 186.97 (s, 2 C), 185.39 (s, 2 C), 105.62 (s, 2 C), 99.29 (d, 2 C, J = 154.3 Hz), 64.02 (t, 2 C, J = 154.7 Hz), 28.07 (q, 2 C, J = 126.5 Hz), 27.45 (q, 2 C, J = 126.6 Hz), 15.87 (q, 2 C), J = 127.7 Hz). ^{1}H NMR (benzene-d_6, ambient), isomer II: δ 5.09 (s, 2 H), 4.30 (s, 2 H), 3.64 (s, 2 H), 1.94 (s, 6 H), 1.64 (s, 6 H), 1.09 (s, 6 H). ^{13}C NMR (benzene-d_6, ambient), isomer II: δ 186.7 (s, 2 C), 186.40 (s, 2 C), 104.82 (s, 2 C), 98.83 (d, 2 C, J = 154.3 Hz), 66.10 (t, 2 C, J = 156.3 Hz), 27.52 (q, 2 C, J = 126.9 Hz), 27.24 (q, 2 C, J = 126.0 Hz), 16.48 (q, 2 C, J = 130.0 Hz). MS (FAB) [m/z (relative intensity)]: 136 (13), 283 (16), 285 (11), 297 (40), 298 (43), 299 (49), 300 (100), 302 (55), 380 (14), 381 (12), 382 (46), 384 (11). Anal. Calcd for $C_{16}H_{24}O_4Ru$: C, 50.38; H, 6.34. Found: C, 50.42; H, 6.02.

Bis(acetylacetonato)(η^4-1,3-cyclohexadiene)ruthenium(II), Ru(1,3-C_6H_8)($C_5H_7O_2$)$_2$. To an (absolute) ethanolic solution of 1.0 g (2.5 mmol) of tris(acetylacetonato)ruthenium(III), Ru(acac)$_3$, was added 0.20 mL (2.6 mmol) of 1,3-cyclohexadiene and 0.20 g (3.0 mmol) of activated zinc dust. The reaction mixture was refluxed for 2 h until an orange-brown color developed. The solvent was removed in vacuo, and the crude product was extracted with two 50-mL portions of pentane and filtered on a coarse frit. The solution was concentrated to about 20 mL and cooled to −23 °C for 24 h, yielding a brown-red, air-stable solid (Ru(η^4-1,3-C_6H_8)(acac)$_2$) and a light yellow solid (Ru(η^6-C_6H_6)(η^4-C_6H_8)).[1a] The two products can be separated physically and recrystallized. The yield is 20% (0.19 g) based on Ru(acac)$_3$.

Mp (nitrogen-filled, sealed capillary): 99–100 °C. Complete infrared data (Nujol mull): 3070 (w), 1580 (s), 1521 (s), 1266 (m), 1203 (m), 1174 (w), 932 (m), 779 (mw), 755 cm^{-1} (mw). ^{1}H NMR (benzene-d_6, ambient): δ 5.48 (s, 1 H), 5.06 (s, 1 H), 5.01 (m, 1 H), 4.76 (m, 1 H), 4.41 (m, 1 H), 4.31 (m, 1 H), 1.96 (s, 3 H), 1.95 (s, 3 H), 1.89 (s, 3 H), 1.78 (s, 3 H), 1.45 (m, 1 H), 1.13 (m, 2 H), 0.52 (m, 1 H). ^{13}C NMR (benzene-d_6, ambient): δ 187.68 (s, 1 C), 186.97 (s, 1 C), 186.66 (s, 1 C), 185.42 (s, 1 C), 99.84 (d, 1 C, J = 156.9 Hz), 98.90 (d, 1 C, J = 157.7 Hz), 89.29 (d, 1 C, J = 172.5 Hz), 87.80 (d, 1 C, J = 170.2 Hz), 75.22 (d, 1 C, J = 155.5 Hz), 74.30 (d, 1 C, J = 157.7 Hz), 27.91 (q, 1 C, J = 126.5 Hz), 27.12 (q, 1 C, J = 126.9 Hz), 26.17 (q, 1 C, J = 126.5 Hz), 26.12 (q, 1 C, J = 126.2 Hz), 21.81 (t, 1 C, J = 123.5 Hz), 20.16 (t, 1 C, J = 122.9 Hz). MS (FAB) [m/z (relative intensity)]: 136 (10), 154 (12), 277 (11), 278 (34), 280 (29), 281 (40), 297 (42), 298 (42), 299 (55), 300 (100), 302 (50), 380 (9). Anal. Calcd for $C_{16}H_{22}O_4Ru$: C, 50.65; H, 5.84. Found: C, 50.61; H, 5.84.

Bis(acetylacetonato)(η^4-2,4-dimethyl-1,3-pentadiene)ruthenium(II), Ru(η^4-2,4-C_7H_{12})($C_5H_7O_2$)$_2$. In a 250-mL three-necked flask equipped with nitrogen inlet, reflux condenser, and magnetic spinning bar, 1.20 g (3.01 mmol) of Ru(acac)$_3$ was dissolved in 50 mL of absolute ethanol. To this solution was added by syringe 10 mL (approximately 82 mmol) of degassed 2,4-dimethylpentadiene and 4.0 g of activated (3 N HCl) zinc powder. The reaction mixture was then refluxed for 3 h, during which the initially deep red solution became orange-yellow. Removal of all liquids in vacuo yielded a sticky orange mass, which was extracted with two 25-mL portions of hexanes. The ensuing orange solution was filtered over a coarse frit and then kept in a −20 °C freezer for 48 h. The large crop of colorless crystals (Zn(acac)$_2$) was separated from the orange solution and discarded, and the solution was concentrated to 30 mL. After 5 days at −20 °C, 0.920 g (2.25 mmol) of bar-shaped orange crystals could be isolated. Yield: 75%.

Mp: 99–100 °C. ^{1}H NMR (benzene-d_6, ambient): major isomer, δ 5.33 (s, 1 H), 5.32 (s, 1 H), 3.77 (s, 1 H), 2.98 (s, 1 H), 2.80 (s, 1 H), 2.06 (s, 3 H), 1.97 (s, 3 H), 1.77 (s, 3 H), 1.74 (s, 3 H), 1.70 (two s, 6 H), 1.46 (s, 3 H); minor isomer (ca. 15% intensity[10]), δ 5.22 (s, 1 H), 5.05 (s, 1 H), 3.99 (s, 1 H), 3.85 (s, 1 H), 1.94 (s, 3 H), 1.92 (s, 3 H), 1.65 (s, 3 H), 1.57 (s, 3 H), 1.46 (s, 3 H), 1.32 (s, 3 H). MS (EI) [m/z (relative intensity)]: 39 (18), 41 (23), 43 (78), 53 (11), 81 (23), 85 (13), 96 (14), 216 (12), 260 (17), 262 (12), 294 (19), 296 (10), 297 (41), 298 (44), 299 (57), 300 (100), 301 (11), 302 (57), 396 (18), 398 (11). Anal. Calcd for $C_{17}H_{26}O_4Ru$: C, 51.63; H, 6.63. Found: C, 51.90; H, 6.65.

Bis(acetylacetonato)bis(triethylphosphine)ruthenium(II), Ru(PEt$_3$)$_2$($C_5H_7O_2$)$_2$. To a solution of 0.50 g (1.3 mmol) of Ru(C_6H_{10})($C_5H_7O_2$)$_2$ (C_6H_{10} = 2,4-hexadiene, 2,3-dimethyl-1,3-butadiene) in 20 mL of toluene under nitrogen was added 0.75 mL (5.2 mmol) of PEt$_3$. The reaction mixture was stirred for 2 h at 25 °C, and the solvent was removed in vacuo. The product was extracted with pentane and cooled to −23 °C, yielding a brown crystalline product (0.61 g, 87% yield).

Mp (nitrogen-filled, sealed capillary): 154 °C dec. Complete infrared data (Nujol mull): 3075 (w), 1565 (s), 1510 (s), 1400 (w), 1255 (m), 1195 (m), 928 (m), 765 (ms), 755 (ms), 700 (mw), 658 (m), 625 (ms), 612 cm^{-1} (w). ^{1}H NMR (benzene-d_6, ambient): δ 5.06 (s, 2 H), 1.53 (br, 30 H), 0.88 (m, 12 H). ^{13}C NMR (benzene-d_6, ambient): δ 184.27 (s, 4 C), 99.19 (d, 2 C, J = 152.1 Hz), 27.27 (q, 4 C, J = 126.6 Hz), 14.12 (t, 6 C, J = 126.1 Hz), 7.07 (q, 6 C, J = 126.6 Hz). Anal. Calcd for $C_{22}H_{44}O_4P_2Ru$: C, 49.33; H, 8.27. Found: C, 49.48; H, 8.32.

Bis(acetylacetonato)bis(trimethyl phosphite)ruthenium(II), Ru[P(OMe)$_3$]$_2$($C_5H_7O_2$)$_2$. To a magnetically stirred solution of 0.50 g (1.3 mmol) of Ru(C_6H_{10})($C_5H_7O_2$)$_2$ (C_6H_{10} = 2,4-hexadiene, 2,3-dimethyl-1,3-butadiene) in 20 mL of toluene at 25 °C under nitrogen was added 0.62 mL (5.2 mmol) of trimethyl phosphite. After the mixture was stirred for 2 h, the solvent was removed in vacuo and the product was extracted with hexane and filtered on a coarse frit. The solution volume was then reduced to about 10 mL, and the product was isolated, by cooling to −78 °C, as a bright-orange crystalline solid (0.61 g, 86% yield).

Mp (nitrogen-filled, sealed capillary): 133–135 °C dec. Complete infrared data (Nujol mull): 3080 (w), 1581 (s), 1571 (s), 1405 (mw), 1262 (s), 1197 (mw), 930 (m), 797 (s), 781 (s), 637 cm^{-1} (m). ^{1}H NMR (benzene-d_6, ambient): δ 5.26 (s, 2 H), 3.62 (t, 18 H, J = 3.9 Hz), 1.83 (s, 12 H). Resonances for the cis isomer: δ 5.36 (s, 2 H), ca. 3.62 (18 H), 1.98 (s, 6 H), 1.77 (s, 6 H). ^{13}C NMR (benzene-d_6, ambient): δ 186.27 (s, 4 C), 99.87 (d, 2 C, J = 156.9 Hz), 50.49 (q, 6 C, J = 145.0 Hz), 27.27 (q, 4 C, J = 125.4 Hz). Anal. Calcd for $C_{16}H_{32}P_2O_{10}Ru$: C, 35.10; H, 5.89. Found: C, 35.05; H, 6.09.

X-ray Diffraction Studies. The crystallographic studies for the Ru(diene)(acac)$_2$ complexes (diene = 2,4-C_7H_{12}, 1,3-C_6H_8) were carried out on Siemens-Stoe AED II and Syntex R3 diffractometers, respectively. Negligible decays in diffraction intensities were observed for the two compounds. The ruthenium atom positions were deduced from Patterson syntheses, after which the remaining non-hydrogen atoms were located by successive Fourier maps and least-squares refinements. Hydrogen atoms were placed in idealized positions by using the SHELXTL program HFIX. A single thermal parameter was refined for the hydrogen atoms of the *trans*-diene structure (0.098 (2)), while in the *cis*-diene structure the thermal parameters were fixed at ca. 1.15 times those of the

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(10) (a) All of the peaks for the minor isomer could not be located with certainty due to their being obscured somewhat by the major isomer. Even weaker peaks were observed (vide infra), perhaps due to the presence of one or two other minor isomers (ca. 1–3% intensity). Some of these peaks were located below 1 ppm, characteristic of the endo protons of one or more cis isomers.[10b] (b) Marks, T. J. In *The Organic Chemistry of Iron*; Koerner von Gustorf, E. A., Grevels, F.-W., Eds.; Academic Press: New York, 1978; Vol. 1.

Table I. Summary of the Diffraction Studies for $Ru(2,4\text{-}C_7H_{12})(acac)_2$ (I) and $Ru(1,3\text{-}C_6H_8)(acac)_2$ (II)

	I	II
formula	$RuC_{17}H_{26}O_4$	$RuC_{16}H_{22}O_4$
mol wt	395.46	381.43
space group	$P2_1/n$	$Pbca$
lattice constants		
a, Å	10.614 (8)	11.642 (4)
b, Å	13.31 (1)	16.162 (6)
c, Å	12.93 (1)	33.78 (1)
β, deg	90.81 (6)	90
V, Å^3	1826.5	6356.0
Z	4	16
d(calc), g/cm^3	1.43	1.58
λ	0.71073	0.71073
temp, °C	20	20
cryst shape	irregular	nearly cubic
cryst size, mm	0.46 × 0.53 × 0.68	0.35 × 0.35 × 0.35
linear abs coeff, cm^{-1}	8.54	9.8
scan type	Ω	Ω
scan speed, deg/min	2–4	2–4
abs treatment	ψ scan	ψ scan
transm factors	0.466–0.521	0.83–1.00
2θ limits, deg	3–70	3–60
min hkl	0,0,–21	0,0,0
max hkl	17,21,21	17,23,48
no. of unique obsd data	4015 (2σ)	4200 (2.5σ)
no. of variables	218	403
$R(F)$	0.037	0.051
$R_w(F)$	0.035	0.044
max diff Fourrier peak, e/Å^3	0.39	0.72

attached carbon atoms. Other pertinent data collection and structural refinement parameters are provided in Table I.

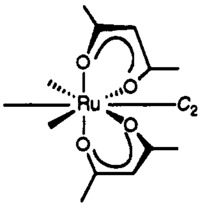
Results

The reduction of Ru(acac)$_3$ by zinc in ethanol in the presence of various dienes leads to Ru(diene)(acac)$_2$ complexes (eq 1), which exhibit some resistance to air oxidation

$$Ru(acac)_3 + \text{diene} \xrightarrow{\text{Zn, EtOH}} Ru(\text{diene})(acac)_2 \quad (1)$$

diene = 2,4-hexadiene, 2,3-dimethylbutadiene,
2,4-dimethyl-1,3-pentadiene, 1,3-cyclohexadiene

in the solid state but are more sensitive in solution. For these diamagnetic complexes, an 18-electron configuration could be attained from η^4-diene and η^2-acac coordination. One could therefore envision the coordination geometry to be pseudooctahedral, with the Ru(acac)$_2$ moiety possessing C_2 symmetry, as in I. Coordination of a diene ligand in the cis form, which had previously been the only observed mode for later transition metals,[5] would therefore remove the C_2 symmetry, leaving no nontrivial symmetry possible for the molecule. For the 1,3-C_6H_8 (C_6H_8 = cyclohexadiene) complex, this is indeed observed, as both ^{1}H and ^{13}C NMR spectroscopy revealed no symmetry elements in the molecule.



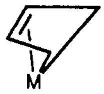
I

Table II. Positional Parameters for the Non-Hydrogen Atoms of $Ru(1,3\text{-}C_6H_8)(acac)_2$

atom	x	y	z
Ru1	0.0816 (1)	0.2543 (1)	0.0210 (1)
Ru2	0.5700 (1)	0.0230 (1)	0.7702 (1)
O1	–0.0155 (4)	0.1905 (3)	0.0630 (1)
O2	0.1816 (4)	0.1505 (3)	0.0148 (1)
O3	0.2008 (4)	0.2725 (3)	0.0659 (1)
O4	–0.0140 (4)	0.3516 (3)	0.0436 (1)
O5	0.6837 (4)	0.1194 (2)	0.7623 (1)
O6	0.4824 (4)	0.0965 (3)	0.8103 (1)
O7	0.6912 (4)	–0.0054 (3)	0.8133 (1)
O8	0.4618 (4)	–0.0643 (3)	0.7953 (1)
C1	–0.0179 (6)	0.1117 (4)	0.0668 (2)
C2	–0.1061 (6)	0.0792 (5)	0.0950 (2)
C3	0.0553 (6)	0.0560 (4)	0.0473 (2)
C4	0.1527 (5)	0.0779 (4)	0.0267 (2)
C5	0.2384 (7)	0.0117 (4)	0.0153 (3)
C6	0.1973 (5)	0.3268 (4)	0.0928 (2)
C7	0.2962 (6)	0.3292 (5)	0.1211 (2)
C8	0.1095 (5)	0.3839 (4)	0.0979 (2)
C9	0.0108 (6)	0.3925 (4)	0.0750 (2)
C10	–0.0786 (7)	0.4557 (4)	0.0866 (2)
C11	–0.0174 (6)	0.2901 (4)	–0.0291 (2)
C12	0.0003 (6)	0.2061 (4)	–0.0344 (2)
C13	0.0960 (5)	0.1727 (4)	–0.0602 (2)
C14	0.2052 (6)	0.2244 (4)	–0.0566 (2)
C15	0.1908 (6)	0.2972 (4)	–0.0296 (2)
C16	0.0860 (6)	0.3394 (4)	–0.0265 (2)
C21	0.6689 (6)	0.1931 (4)	0.7749 (2)
C22	0.7645 (6)	0.2515 (4)	0.7638 (2)
C23	0.5771 (6)	0.2223 (4)	0.7970 (2)
C24	0.4923 (5)	0.1748 (4)	0.8138 (2)
C25	0.4059 (6)	0.2157 (5)	0.8410 (2)
C26	0.6818 (5)	–0.0606 (4)	0.8403 (2)
C27	0.7869 (6)	–0.0740 (5)	0.8652 (2)
C28	0.5838 (6)	–0.1069 (4)	0.8471 (2)
C29	0.4822 (6)	–0.1058 (4)	0.8261 (2)
C30	0.3818 (7)	–0.1571 (5)	0.8402 (2)
C31	0.4650 (5)	–0.0103 (4)	0.7215 (2)
C32	0.5618 (5)	–0.0652 (4)	0.7238 (2)
C33	0.6712 (5)	–0.0300 (4)	0.7200 (2)
C34	0.6908 (6)	0.0396 (4)	0.6911 (2)
C35	0.5866 (6)	0.0972 (4)	0.6881 (2)
C36	0.4898 (6)	0.0730 (4)	0.7152 (2)

The expected structure for the Ru(1,3-C_6H_8)(acac)$_2$ compound was confirmed by a single-crystal X-ray diffraction study (Figure 1; Tables II and III). Two independent molecules were found present in the unit cell, each existing as a pair of enantiomers and exhibiting essentially identical structures. In fact, their inner coordination spheres, defined by the Ru(diene)O$_4$ fragments, exhibit essentially C_s symmetry; i.e., the C_2 symmetry of the Ru(acac)$_2$ fragment does not significantly affect the C_s symmetry of the Ru(diene) fragment. Thus, the four Ru–C(external) bond distances are essentially equal at 2.236 (3) Å, while the Ru–C(internal) bond distances are essentially equal at 2.120 (3) Å.[11] Similarly, the external C–C bonds of the diene units are essentially equal at 1.395 (5) Å, compared to the average 1.441 (7) Å distance for the internal bonds. The short–long–short bond alternation is typical of η^4-*cis*-diene (IIa) as opposed to enediyl (IIb) coordination. The pseudo-mirror-plane symmetry carries over to the acac coordination, in that the Ru1–O1,3 and Ru2–O6,7 bond distances are essentially equal to 2.078 (2) Å. The Ru1–O4 and Ru2–O8 distances are not significantly different, averaging 2.074 (3) Å. However, some shortening seems to take place for the Ru1–O2 and Ru2–O5 bonds, which average 2.056 (3) Å in length. This

IIa



IIb

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[11] Standard deviations for average values of bonding parameters reflect the uncertainties in the average values but not necessarily the distributions of individual values.

Table III. Pertinent Bond Distances (Å) and Angles (deg) for Ru(1,3-C_6H_8)(acac)$_2$

Bond Distances

Ru1–O1	2.085 (4)	Ru1–O2	2.052 (4)	Ru1–O3	2.076 (4)	Ru1–O4	2.073 (4)
Ru2–O5	2.061 (4)	Ru2–O6	2.071 (4)	Ru2–O7	2.081 (4)	Ru2–O8	2.074 (4)
Ru1–C11	2.128 (6)	Ru1–C12	2.238 (7)	Ru1–C15	2.242 (7)	Ru1–C16	2.115 (6)
Ru2–C31	2.117 (7)	Ru2–C32	2.121 (6)	Ru2–C33	2.235 (6)	Ru2–C36	2.230 (7)
O1–C1	1.281 (8)	O2–C4	1.285 (8)	O3–C6	1.263 (8)	O4–C9	1.282 (7)
O5–C21	1.277 (7)	O6–C24	1.277 (8)	O7–C26	1.280 (8)	O8–C29	1.261 (8)
C1–C3	1.403 (9)	C3–C4	1.377 (9)	C6–C8	1.388 (9)	C8–C9	1.393 (9)
C21–C23	1.387 (9)	C23–C24	1.372 (9)	C26–C28	1.383 (10)	C28–C29	1.379 (10)
C1–C2	1.496 (10)	C4–C5	1.513 (10)	C6–C7	1.497 (10)	C9–C10	1.511 (10)
C21–C22	1.506 (10)	C24–C25	1.514 (10)	C26–C27	1.501 (10)	C29–C30	1.510 (10)
C12–C13	1.515 (9)	C14–C15	1.498 (10)	C33–C34	1.506 (9)	C35–C36	1.504 (10)
C13–C14	1.526 (9)	C34–C35	1.533 (10)	C11–C16	1.446 (10)	C31–C32	1.436 (9)
C11–C12	1.385 (10)	C15–C16	1.401 (10)	C31–C36	1.394 (10)	C32–C33	1.401 (9)

Bond Angles

O1–Ru1–O2	88.5 (2)	O1–Ru1–O3	86.3 (2)	O5–Ru2–O7	79.7 (2)
O3–Ru1–O4	89.0 (2)	O1–Ru1–O4	80.4 (2)	O5–Ru2–O8	163.1 (2)
O5–Ru2–O6	88.1 (2)	O2–Ru1–O3	79.2 (2)	O6–Ru2–O7	90.1 (2)
O7–Ru2–O8	88.5 (2)	O2–Ru1–O4	164.3 (2)	O6–Ru2–O8	79.8 (2)
C11–C12–C13	122.3 (6)	C12–C13–C14	111.8 (6)	C13–C14–C15	112.7 (5)
C14–C15–C16	121.6 (6)	C15–C16–C11	117.0 (6)	C16–C11–C12	115.0 (6)
C31–C32–C33	117.2 (6)	C32–C33–C34	120.0 (5)	C33–C34–C35	112.2 (5)
C34–C35–C36	113.2 (6)	C35–C36–C31	120.0 (6)	C36–C31–C32	116.2 (6)
Ru1–O1–C1	124.8 (4)	Ru1–O2–C4	124.4 (4)	Ru1–O3–C6	127.0 (4)
Ru1–O4–C9	125.1 (4)	Ru2–O5–C21	125.2 (4)	Ru2–O6–C24	125.7 (4)
Ru2–O7–C26	126.5 (4)	Ru2–O8–C29	125.9 (4)	O1–C1–C2	115.3 (6)
O1–C1–C3	125.3 (6)	O2–C4–C3	127.5 (6)	O2–C4–C5	113.2 (6)
O3–C6–C7	116.9 (6)	O3–C6–C8	125.1 (6)	O4–C9–C8	126.5 (6)
O4–C9–C10	114.1 (6)	O5–C21–C22	113.8 (5)	O5–C21–C23	126.9 (6)
O6–C24–C23	125.6 (6)	O6–C24–C25	115.4 (6)	O7–C26–C27	115.5 (6)
O6–C26–C28	124.5 (6)	O8–C29–C28	126.4 (6)	O8–C29–C30	114.0 (6)
C1–C3–C4	124.9 (6)	C6–C8–C9	127.1 (6)	C21–C23–C24	125.9 (6)
C26–C28–C29	127.9 (6)	C3–C1–C2	119.3 (6)	C3–C4–C5	119.3 (6)
C8–C6–C7	118.0 (6)	C8–C9–C10	119.4 (6)	C23–C21–C22	119.4 (6)
C23–C24–C25	119.0 (6)	C28–C26–C27	120.1 (6)	C28–C29–C30	119.7 (6)

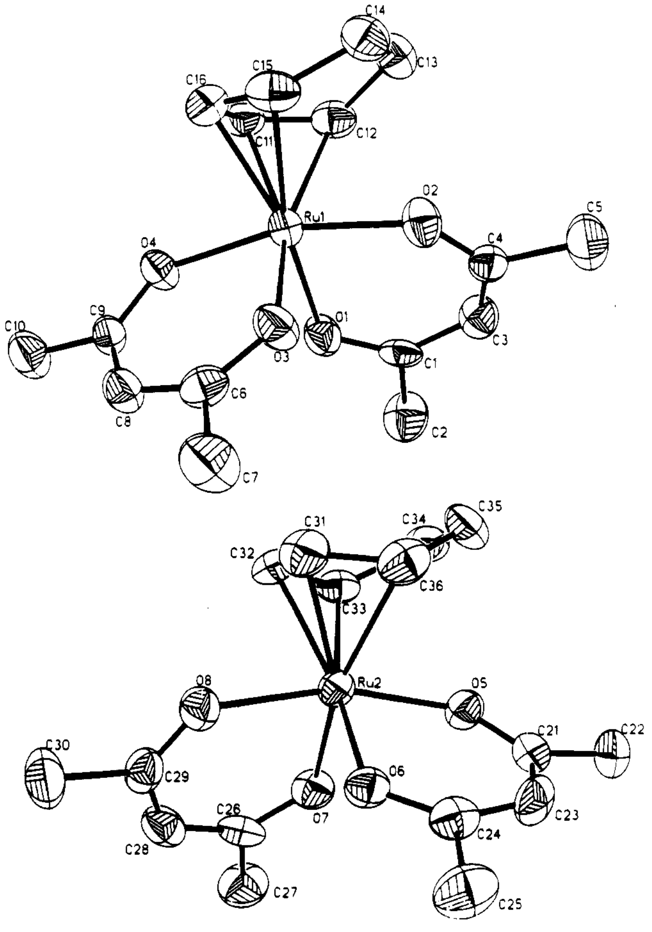
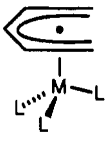
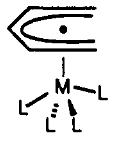


Figure 1. Perspective views and numbering schemes for the two independent molecules of Ru(C_6H_8)(acac)$_2$.

shortening, although small in magnitude, is reminiscent of shortenings observed for M(dienyl)L_3 and M(dienyl)L_4 complexes,[12] e.g., III and IV. In such cases, the ligand



III



IV

positioned under the open edge of the dienyl group is seen to move up toward the open edge, apparently to allow for better utilization of otherwise unused metal orbital density, and this results in slightly to somewhat shorter (presumably stronger) bonds for that ligand. In addition to the observed bond shortening, the oxygen atoms (O2 and O5) located under the open diene edge also have tilted toward the diene plane, as they are situated an average of 1.780 Å below this plane, compared to 2.324 Å for O4 and O8 (cf., 1.762 Å for Ru1,2, 3.260 Å for O1,6 and 3.218 Å for O3,7).

Other ligand-related parameters are not unusual. The delocalized C–C and C–O bond distances for the acac ligands average 1.385 (4) and 1.276 (3) Å, respectively, while the C–CH_3 bond distances average 1.506 (4) Å. The O–Ru–O angles fall in three categories. the O–Ru–O(trans) angles average 163.7 (2)°, the intraligand (chelating) values average 88.5 (1)°, and the interligand values range from 79.2 to 90.1°.

Somewhat different behavior is exhibited by the noncyclic diene complexes. In particular, for the complexes

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[12] (a) Newbound, T. D.; Stahl, L.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1990**, *9*, 2962. Waldman, T. E.; Rheingold, A. L.; Ernst, R. D. *J. Organomet. Chem.* **1991**, *401*, 331.

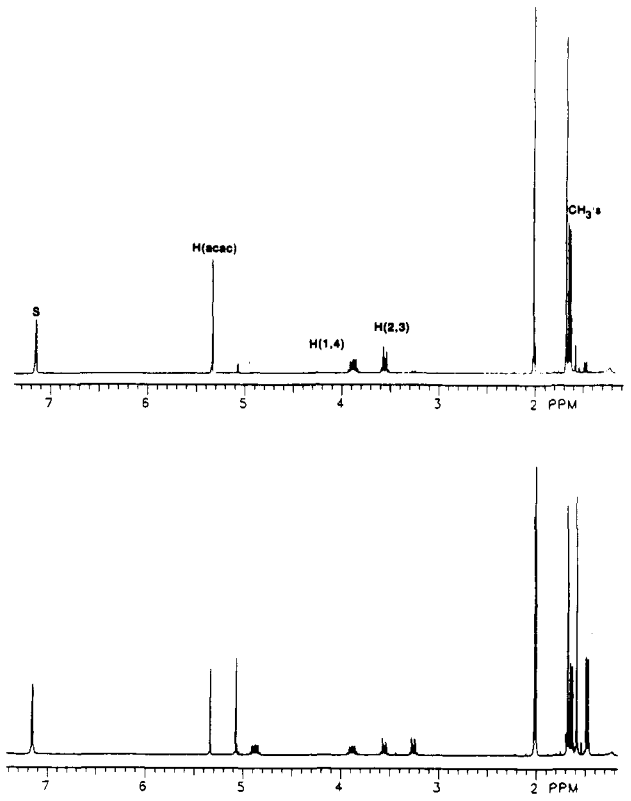
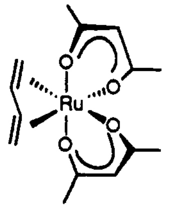
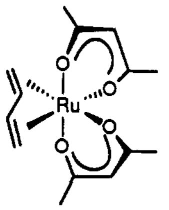


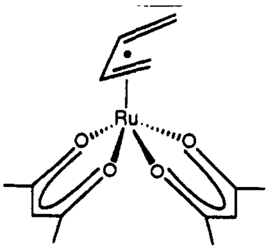
Figure 2. ^{1}H NMR spectrum (C_6D_6) of Ru(2,4-hexadiene)(acac)$_2$: (bottom) mixture of isomers; (top) enriched in one isomer.

of 2,4-hexadiene and 2,3-dimethyl-1,3-butadiene, ^{1}H and ^{13}C NMR spectroscopy indicate that two diastereomeric isomers are present for each (see Figure 2); quite notably, the spectra for the individual isomers are symmetric, with a total of six resonances for the ^{1}H NMR spectra of each. For this to occur in an octahedral environment (I), the dienes would have to conform to the C_2 symmetry of the Ru(acac)$_2$ fragment, necessitating η^4-*trans*-diene coordination and leading to the possibility of isomer formation through binding of the two enantiofaces of the dienes shown as





An alternative to this would be a trigonal-prismatic coordination geometry with η^4-cis diene coordination (V), but

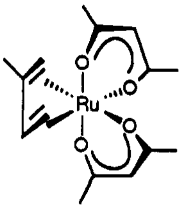


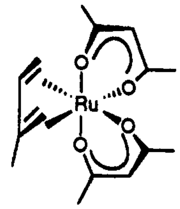
V

in this case the molecule is superimposable on its mirror image, and hence only one trigonal-prismatic cis isomer would be possible. Furthermore, an additional resonance would be expected for both the ^{1}H and ^{13}C NMR spectra, although coincidental overlaps could be invoked. However, the similarities of the splitting patterns for the two isomers of Ru(2,4-hexadiene)(acac)$_2$ (Figure 2) strongly indicate that two *trans*-diene isomers are present rather than a combination of trans and cis forms.

It is notable that the relative ratios for a given two isomers may vary considerably from one reaction to another, which demonstrates that any interconversion process must be slow. As the products are prepared at higher temperatures, at which appropriate equilibria should be established (vide infra), it would appear that these variations are related to the differing solubilities of the two isomers, which may lead to different degrees of precipitation during the crystallizations used for isolation. This possibility was examined by variable-temperature ^{1}H NMR spectroscopy for the 2,3-dimethylbutadiene complex (Figure 3). A sample enriched in one isomer was prepared by separation of the two types of single crystals, and thereafter was dissolved in toluene-d_8 at −78 °C. A spectrum at −78 °C does indeed indicate that one isomer predominates (the *minor* isomer of the original mixture), although the six resonances arising from the other isomer are also present to the extent of perhaps a 10% abundance. Little change in the spectrum is observed up until room temperature, at which some equilibration is noticeable over the course of several hours. By 85 °C, the equilibrium appears to be established, and more resonances appear, some of which are visible even at lower temperatures. From an examination of an expanded spectrum, 12 new resonances may be identified, whose general locations are reasonably similar to those of the η^4-*trans*-diene isomers, and this new species may be identified as the η^4-cis isomer. When the sample is cooled to room temperature, these new peaks slowly diminish and after 5 days have only retained about half their earlier intensity at 85 °C. These data thus establish that there is a thermodynamic preference exhibited by the Ru(acac)$_2$ fragment for η^4-*trans*-diene coordination (to *either* diene enantioface).

For the 2,4-dimethyl-1,3-pentadiene complex, the lack of C_2 symmetry in the free *trans*-diene, and the presence of a methyl substituent on an internal diene carbon atom, render spectroscopic methods less reliable for determining the mode of diene coordination. However, NMR spectroscopic data seem to indicate the presence of one dominant isomer (see Experimental Section), although as many as three minor isomers may also have been present. Whereas the complexes of symmetric dienes may exist in three isomeric forms (two trans and one cis, ignoring enantiomers), complexes of unsymmetric dienes may exist as four diastereomers, two of which involve cis coordination shown as





A structural study of Ru(2,4-C_7H_{12})(acac)$_2$ (Figures 4 and 5; Tables IV and V) clearly reveals the presence of the expected η^4-*trans*-diene ligand in a pseudooctahedral coordination sphere. Despite the different mode of diene coordination, the bonding parameters for the Ru(acac)$_2$ fragment are changed only slightly. Thus, the Ru–O distances average 2.058 (3) Å, relative to 2.072 (3) Å in the C_6H_8 structure. The (trans) O1–Ru–O3 angle of 171.7 (1)° is somewhat larger than the value of 163.7 (2)° in the C_6H_8 complex, as in the latter O2 may be seen to experience

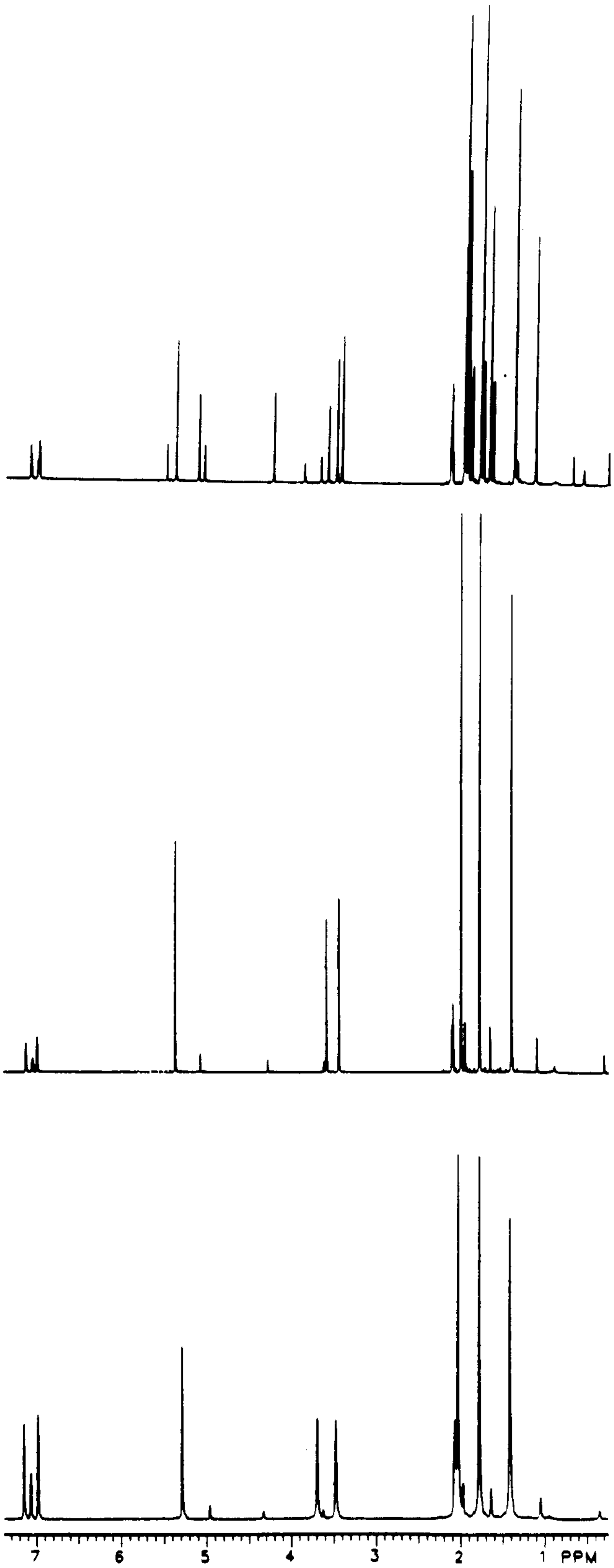


Figure 3. Variable-temperature ^1H NMR spectra of Ru(2,3-dimethylbutadiene)(acac)$_2$. The spectra were recorded at -78 °C (bottom), -15 °C and 85 °C (top) in toluene-d_8.

closer contacts with the external carbon atoms of the diene ligand (particularly due to its being oriented up near the diene plane, vide supra), while O4 experiences close contacts with the internal carbon atoms (Figure 4). In addition, the two chelating O-Ru-O angles average 92.6°, indicating an expansion relative to the C_6H_8 complex (88.5 (1)°). The interligand O-Ru-O(cis) angles average 81.9° (82.6° for the C_6H_8 compound). Overall, then, it appears that diene-acac repulsions are relieved for *trans*-diene

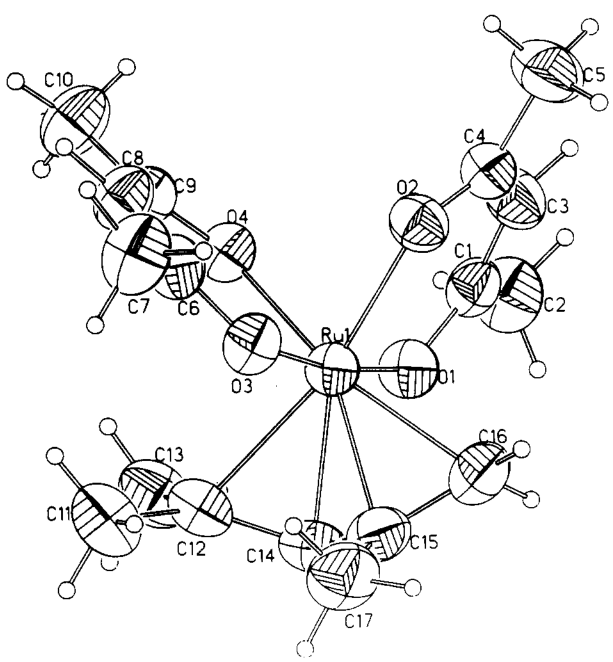


Figure 4. Perspective view and numbering scheme for Ru(2,4-dimethyl-1,3-pentadiene)(acac)$_2$.

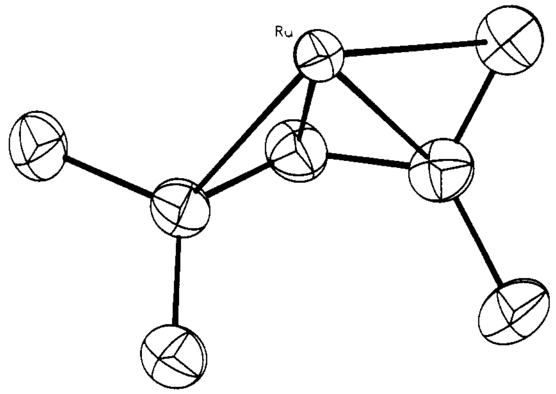


Figure 5. View of the η^4-*trans*-diene bonding in Ru(2,4-dimethyl-1,3-pentadiene)(acac)$_2$.

Table IV. Positional Parameters for the Non-Hydrogen Atoms of Ru(2,4-C_7H_{12})(acac)$_2$

atom	*x*	*y*	*z*
Ru1	0.17861 (2)	0.20791 (2)	0.39475 (2)
O1	0.01745 (17)	0.28945 (14)	0.42054 (13)
O2	0.08622 (16)	0.10546 (13)	0.30059 (13)
O3	0.33133 (16)	0.12676 (13)	0.34678 (13)
O4	0.17852 (16)	0.29468 (13)	0.26288 (13)
C1	−0.0861 (2)	0.2700 (2)	0.3734 (2)
C2	−0.1889 (3)	0.3465 (2)	0.3919 (3)
C3	−0.1128 (3)	0.1876 (2)	0.3120 (2)
C4	−0.0307 (3)	0.1119 (2)	0.2802 (2)
C5	−0.0819 (3)	0.0277 (3)	0.2152 (2)
C6	0.3785 (2)	0.1369 (2)	0.2574 (2)
C7	0.4820 (3)	0.0623 (2)	0.2334 (3)
C8	0.3486 (2)	0.2096 (2)	0.1830 (2)
C9	0.2562 (2)	0.2839 (2)	0.1895 (2)
C10	0.2446 (3)	0.3614 (2)	0.1042 (2)
C11	0.4468 (3)	0.3048 (2)	0.4462 (3)
C12	0.3090 (3)	0.3265 (2)	0.4672 (2)
C13	0.2694 (3)	0.4328 (2)	0.4413 (2)
C14	0.2338 (3)	0.2733 (2)	0.5367 (2)
C15	0.2382 (3)	0.1645 (2)	0.5476 (2)
C16	0.1209 (3)	0.1204 (2)	0.5300 (2)
C17	0.3541 (3)	0.1016 (3)	0.5705 (2)

Table V. Pertinent Bond Distances (Å) and Angles (deg) for $Ru(2,4-C_7H_{12})(acac)_2$

Bond Distances

Ru1–O1	2.057 (2)	Ru1–O2	2.066 (2)	Ru1–O3	2.051 (2)	Ru1–O4	2.059 (2)
Ru1–C12	2.291 (3)	Ru1–C14	2.107 (3)	Ru1–C15	2.146 (3)	Ru1–C16	2.196 (3)
O1–C1	1.276 (3)	O2–C4	1.267 (3)	O3–C6	1.272 (3)	O4–C9	1.274 (3)
C1–C3	1.381 (4)	C3–C4	1.397 (4)	C6–C8	1.397 (4)	C8–C9	1.397 (4)
C1–C2	1.514 (4)	C4–C5	1.499 (4)	C6–C7	1.516 (4)	C9–C10	1.513 (4)
C11–C12	1.519 (4)	C12–C14	1.402 (4)	C14–C15	1.457 (4)	C15–C16	1.392 (4)
C12–C13	1.511 (4)	C15–C17	1.513 (5)				

Bond Angles

O1–Ru1–O2	93.1 (1)	O1–Ru1–O3	171.7 (1)	O2–Ru1–O3	81.1 (1)
O3–Ru1–O4	92.1 (1)	O1–Ru1–O4	81.2 (1)	O2–Ru1–O4	83.5 (1)
C11–C12–C14	125.2 (3)	Ru1–O1–C1	121.9 (2)	Ru1–O3–C6	122.8 (2)
C12–C14–C15	123.1 (3)	Ru1–O2–C4	122.2 (2)	Ru1–O4–C9	124.1 (2)
C14–C15–C16	112.1 (3)	C3–C1–O1	127.2 (3)	C8–C6–O3	127.6 (3)
C11–C12–C13	113.8 (3)	C3–C4–O2	126.9 (3)	C8–C9–O4	125.9 (2)
C13–C12–C14	117.1 (3)	C2–C1–C3	118.9 (2)	C7–C6–C8	118.0 (3)
C14–C15–C17	126.4 (3)	C2–C1–O1	113.9 (2)	C7–C6–O3	114.3 (2)
C16–C15–C17	121.4 (3)	C5–C4–C3	118.7 (3)	C10–C9–C8	119.3 (2)
C1–C3–C4	128.2 (3)	C5–C4–O2	114.3 (3)	C10–C9–O4	114.8 (2)
C6–C8–C9	127.0 (2)				

coordination, allowing the acac ligands to open up somewhat. Other acac ligand parameters are similar to those of the C_6H_8 analogue. Thus, the C–CH_3, C–O, and delocalized C–C bond distances average 1.510 (3), 1.272 (2), and 1.393 (3) Å, respectively.

The diene coordination is naturally of greatest interest. First, as observed in all other η^4-bound *trans*-diene complexes,[6,7] the diene fragment is decidedly nonplanar, in this case the torsion angle being 122.6°, indicating a twist of 57.4° from planarity. The substitution pattern for this diene is such that the two internal carbon atoms differ (0 vs 1 methyl group) as do also the external ones (0 vs 2 methyl groups). In each case, the presence of the extra substituents leads to a longer Ru–C distance, 2.146 (3) vs 2.107 (3) and 2.291 (3) vs 2.196 (3) Å, respectively, each methyl group adding ca. 0.04–0.05 Å to the given bond length. It can be noted that in a structure of a related $Ru^{II}(\eta^4$-*cis*-2,4-$C_7H_{12})$ complex, $Ru(2,4-C_7H_{11})(\eta^4-2,4-C_7H_{12})(CO)^+$, a similar pattern of Ru–C distances is observed (2.414 (7), 2.205 (6), 2.236 (6), 2.248 (7) Å).[12a] The general pattern exhibited for both C_7H_{12} compounds, with longer Ru–C(external) bonds, is similar to that seen for the C_6H_8 complex (vide supra) and for other examples of η^4-*trans*-diene coordination.[6,7] The diene C–C bonds adopt a short–long–short pattern (1.397 (3) vs 1.457 (4) Å) as was also the case for the C_6H_8 complex. One can note that the Ru–C distances in the trans complex (2.291 (3), 2.107 (3), 2.146 (3), 2.196 (3) Å) seem slightly longer overall than the values for the C_6H_8 complex (2.236 (3), 2.120 (3), 2.120 (3), 2.236 (3) Å), perhaps a reflection of the greater steric crowding brought about by the three methyl substitutents. One might well expect that this trend would be reversed for a less substituted complex, leading to both shorter Ru–C and Ru–O (vide supra) bonds for the trans coordination, which would be consistent with the thermodynamic preference for η^4-trans coordination.

The diene ligands in these complexes may be readily replaced with phosphine or phosphite ligands (eq 2).

$$Ru(diene)(acac)_2 + 2L \rightarrow Ru(L)_2(acac)_2 \quad (2)$$

diene = 2,4-hexadiene, 2,3-dimethylbutadiene;
$L = PEt_3, P(OMe)_3$

While ^1H NMR spectroscopy indicates that both the cis and trans isomers are present in the initial reaction mixtures, the isolated crystalline products tend to contain predominantly the trans isomer, probably as a result of a lower degree of solubility. Not only might the cis isomer remain in solution during purification but the expected lower solubility of the trans form could lead to further conversion of the cis to the trans form as the latter crystallizes should the equilibrium between them be sufficiently rapidly established.

Discussion

While $Ru(diene)(acac)_2$ complexes have been known since 1970, they employed rigid dienes such as 1,5-cyclooctadiene and norbornadiene.[13] With the utilization of acyclic dienes such as 2,4-hexadiene or 2,3-dimethylbutadiene, it now appears that the $Ru(acac)_2$ fragment has a general thermodynamic preference for η^4-*trans*-1,3-diene coordination as opposed to the more normal η^4-*cis*-1,3-diene coordination.[14] Although thermodynamically this preference may be slight, these appear to be the first examples of such coordination involving a late transition metal.[4,5] Molecular orbital studies have indicated that the η^4-*trans*-diene coordination is favored when the diene → metal donor interaction dominates,[15] and given the potential for the late transition metals to engage in backbonding interactions, it is not surprising that the present compounds involve a positive (divalent) oxidation state. It should therefore be expected that other examples of trans coordination for late transition metals could be found and perhaps even predicted.

It has been observed that related η^4-*trans*- and η^4-*cis*-diene complexes of the early transition metals tend to differ greatly electronically and structurally, the former involving more diene character (IIa), while the latter employs more enediyl character (IIb) in order that the metal may attain a higher formal oxidation state.[4,6,7] In contrast, the structures for $Ru(cis-C_6H_8)(acac)_2$ and $Ru(trans-2,4-C_7H_{12})(acac)_2$ reveal very similar Ru–C and C–C bonding patterns (IIa, vide supra), which is reasonable given that there is no overwhelming stabilization of the Ru(IV) oxidation state. Thus, the *cis*-diene complexes of the early transition metals appear to be unique in their great propensity to support enediyl coordination, and the apparent inability of the trans form to adopt enediyl coordination may be explained either by steric or electronic arguments.[16,17]

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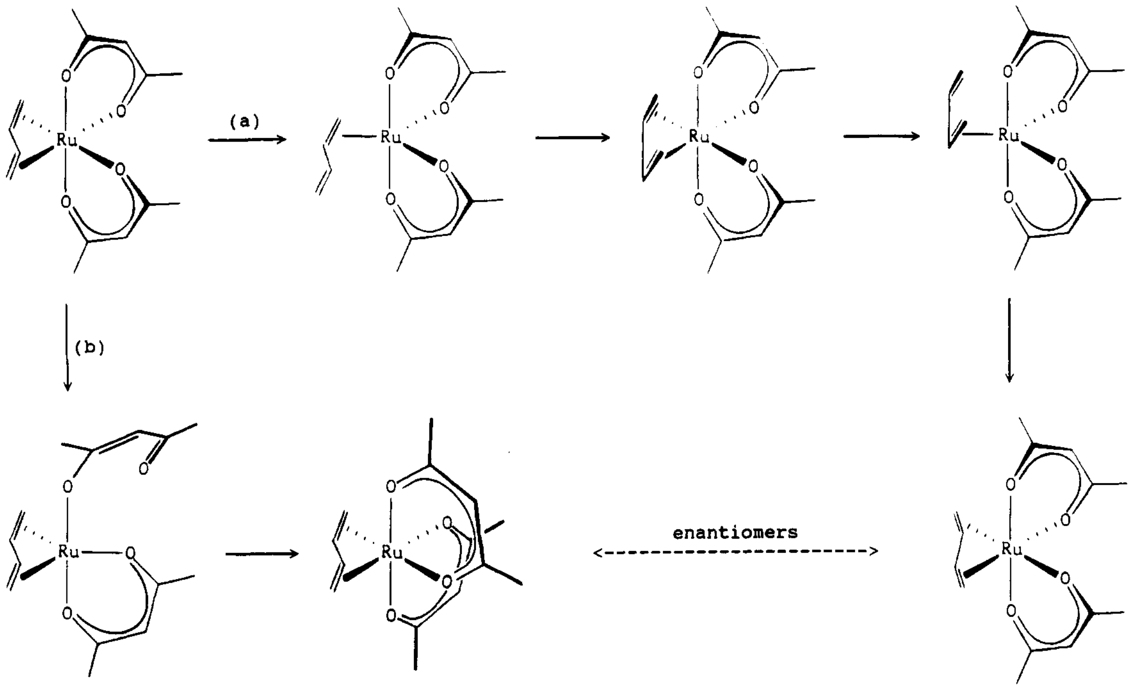
(13) (a) Potvin, C.; Pannetier, G. *J. Less-Common Met.* **1970**, *22*, 91. (b) Potvin, C.; Manoli, J. M.; Dereigne, A.; Pannetier, G. *Ibid.* **1971**, *25*, 373. (c) Powell, P. *J. Organomet. Chem.* **1974**, *65*, 89.

(14) (a) The $\eta^{2,2'}$ coordination of *trans*-dienes to dimetallic centers is also known.[14b] (b) Guggolz, E.; Oberdorfer, F.; Ziegler, M. L. *Z. Naturforsch.* **1981**, *36B*, 1060.

(15) Hunter, A. D.; Legzdins, P.; Einstein, F. W. B.; Willis, A. C.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1986**, *108*, 3843.

Scheme I



The observed interconversions involving the cis and two trans isomers of Ru(2,3-dimethylbutadiene)(acac)$_2$ require further mention. While the cis $\rightleftarrows$ trans interconversions must necessarily involve a change from $\eta^4 \rightarrow \eta^2$ diene coordination in the transition state, the interconversion between the two trans forms could take place either through a diene slip pathway ($\eta^4 \rightarrow \eta^2$) or, alternatively, through an $\eta^2 \rightarrow \eta^1$ change in acac coordination[18] (see Scheme Ia,b). Qualitatively it is not at all clear that the trans $\rightleftarrows$ trans′ equilibrium is established before the trans $\rightleftarrows$ cis equilibrium (Figure 3), and therefore, it is not possible at this time to make a clear choice between parts a and b of Scheme I for the former equilibrium.[19] The fact that phosphine and phosphite ligands do readily replace the diene ligands at room temperature (vide supra), however, would seem to favor path Ia. It is also notable that results of kinetic studies of the isomerizations of unsymmetrical ruthenium(III) β-diketonate complexes have been interpreted in terms of a M–O bond-breaking process.[18b] These processes were readily observable at temperatures around and above 90 °C, which does leave open the possibility, although considered less likely, that Ru–O bond breakage processes for the Ru(diene)(acac)$_2$ complexes might be competitive with the Ru(η^4-diene) → Ru(η^2-diene) transformations.

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Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom parameters, and least-squares-plane information (4 pages); tables of structure factors (49 pages). Ordering information is given on any current masthead page.

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(16) (a) It can be noted that in mono(olefin) complexes, the four substituents tend to bend back significantly away from the metal center,[16b] whereas *trans*-enediyl coordination would require that at least the two substituent carbon centers bound to the metal be bent toward the metal center 9cf., Figures 4 and 5). Additionally, enediyl ligands are formally dianions, and the observation that *trans*-diene coordination should involve primarily L → M interactions[15] would seem to exclude *trans*-enediyl coordination. Hence, the *trans*-enediyl coordination may experience geometric as well as electronic problems. (b) Ittel, S. D.; Ibers, J. A. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic: London, 1976; Vol. 14, p 33.

(17) (a) Enediyl coordination in late-metal complexes can be stabilized by appropriate electronic effects.[17b] (b) Churchill, M. R.; Mason, R. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic: London, 1967, Vol. 5, p 93.

(18) (a) Trigonal twists without metal–ligand bond breakage could also be implicated for the trans $\rightleftarrows$ trans′ interconversion but in related situations have been concluded to be insignificant.[18b] (b) Hoshino, Y.; Takahashi, R.; Shimizu, K.; Satô, G. P.; Aoki, K. *Inorg. Chem.* **1990**, *29*, 4816.

(19) While a small amount of the second trans isomer can be seen in the spectrum at −78 °C (Figure 3), its relative abundance at −15 °C does not seem to have changed any, indicating that it was present at the time of initial sample preparation. Likewise, although some of the cis isomer peaks are more evident at −15 °C than at −78 °C, this appears to be due primarily to the greater line broadening in the latter spectrum.