Organometallics **1993,** *12,* 1243–1247 1243

Cluster Complexes Containing Polyene Ligands. Synthesis and Structural Characterization of Two Isomers of $Ru_6(CO)_{14}(\mu_6\text{-}C)(\textit{trans}\text{-}1,3,5\text{-}CH_2CHCHCHCHCH_2)$ Containing *trans*-1,3,5-Hexatriene Ligands

Richard D. Adams* and Wengan Wu

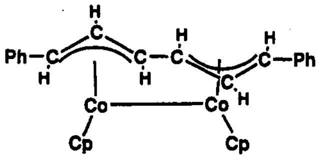
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received December 10, 1992

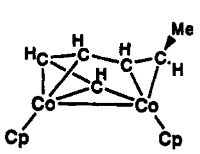
Two carbidohexaruthenium carbonyl cluster complexes, $Ru_6(CO)_{14}(\mu_6\text{-}C)(\mu\text{-}s\text{-}cis,s\text{-}cis\text{-}trans\text{-}1,2\text{-}\eta^2\text{-}4\text{–}6\text{-}\eta^4\text{-}CH_2CHCHCHCHCH_2)$, **2a**, (3%), and $Ru_6(CO)_{14}(\mu_6\text{-}C)(\mu\text{-}s\text{-}trans,s\text{-}cis\text{-}trans\text{-}1,2\text{-}\eta^2\text{-}4\text{–}6\text{-}\eta^4\text{-}CH_2CHCHCHCHCH_2)$, **2b** (19%), containing *trans*-1,3,5-hexatriene ligands in different conformations and the known compound $Ru_6(CO)_{14}(\mu_6\text{-}C)(\eta^6\text{-}C_6H_6)$, **3** (22%), were obtained from the reaction of $Ru_6(CO)_{17}(\mu_6\text{-}C)$ with 1,3,5-hexatriene (a mixture of cis- and trans-isomers) at 155 °C. Compounds **2a** and **2b** were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. The structures of both **2a** and **2b** contain an octahedral cluster of six ruthenium atoms with the carbide ligand located in the center and a bridging *trans*-η^6-hexatriene ligand. The difference between **2a** and **2b** lies in the conformations of the hexatriene ligand. In **2a**, it adopts an *s-cis,s-cis* conformation while, in **2b**, it exhibits an *s*-trans,*s*-cis mode. Crystal data for **2a**: space group $P2_1/n$, $a = 14.794(2)$ Å, $b = 12.290(2)$ Å, $c = 14.927(3)$ Å, $\beta = 92.95(1)°$, $R = 0.033$ for 2078 reflections. For **2b**: space group $P2_1/n$, $a = 14.812\ (2)$ Å, $b = 12.202(2)$ Å, $c = 14.866(2)$ Å, $\beta = 92.06(1)°$, $R = 0.027$ for 2608 reflections.

Introduction

Although there are numerous examples of metal complexes containing η^5-pentadienyl ligands,[1,2] to date, there are only a few examples of complexes that contain conjugated hexatriene ligands.[3] There are no single metal atom complexes that contain a conjugated η^6-hexatriene ligand. In a recent report, Wadepohl described the dicobalt complex **A** containing a 1,6-diphenylhexatriene ligand in which the six carbon atoms were coordinated to the two metal atoms in a 1–3-η^3-4–6-η^3 manner.[4] Vollhardt has shown that the complex CpCo(1–4-η^4-hexatriene) condenses with the elimination of 1 equiv of hexatriene to yield the alkylidenedicobalt complex **B** by the activation of one of the CH bonds on one of the terminal CH_2 groups and transfer of the hydrogen atom to the other CH_2 group to form a methyl group.[5]



A



B

We have recently shown that cluster complexes can support η^5-pentadienyl ligands by using two adjacent metal atoms.[6] In an extension of this work, we have now found that a carbidohexaruthenium cluster can support a bridging η^6-hexatriene ligand by using two metal atoms.

Experimental Section

General Procedures. Reactions were performed under an atmosphere of dry nitrogen. Reagent-grade solvents were dried over molecular sieves and deoxygenated by purging with nitrogen prior to use. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. A Brüker AM-300 FT-NMR spectrometer was used to obtain ^1H NMR spectra. TLC separations were performed by using silica gel (60 Å, f_{254}) on plates (Whatman, 0.25 mm). $Ru_6(CO)_{17}(\mu_6\text{-}C)$ was prepared by previously reported procedures.[7] 1,3,5-Hexatriene was purchased as a mixture of cis- and trans-isomers from Aldrich. A GC-MS analysis showed that this material contains an approximately 50/50 mixture of the two possible geometric isomers. This mixture was purified by vacuum distillation prior to use, but purification did not include a separation of the isomers.

Reaction of $Ru_6(CO)_{17}(\mu_6\text{-}C)$ with 1,3,5-Hexatriene. A 200-μL amount (2.10 mmol) of 1,3,5-hexatriene (a mixture of the two isomers) was added to a suspension containing 98.0 mg (0.895 mmol) of $Ru_6(CO)_{17}(\mu_6\text{-}C)$ in 10 mL of heptane. The mixture was then sealed in a 25-mL Parr high-pressure reactor. The reactor was heated to 155 °C (oil bath) in 30 min and was kept at this temperature for total of 21 h. After cooling down to 25 °C the solvent was removed under vacuum, and the residue was separated by TLC by using a CH_2Cl_2/hexane (3/7) solvent mixture. This yielded the following in order of elution: 22.3 mg of unreacted 1, 23%; 2.6 mg of red $Ru_6(CO)_{15}(\mu_6\text{-}C)(\mu\text{-}\eta^4\text{-}MeCHCHCHCHMe)$,[8] 3%; 3.2 mg of brown $Ru_6(CO)_{14}(\mu_6\text{-}C)(\mu\text{-}s\text{-}cis,s\text{-}cis\text{-}trans\text{-}1,2\text{-}\eta^2\text{-}4\text{–}6\text{-}\eta^4\text{-}CH_2CHCHCHCHCH_2)$ (**2a**), 3%; 18.7 mg of red-brown $Ru_6(CO)_{14}(\mu_6\text{-}C)(\mu\text{-}s\text{-}trans,s\text{-}cis\text{-}trans\text{-}1,2\text{-}\eta^2\text{-}4\text{–}6\text{-}\eta^4\text{-}CH_2\text{-}$

---

[1] Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255.

[2] Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125.

[3] (a) Powell, P. *J. Organomet. Chem.* **1983**, *244*, 393. (b) Xavier, J.; Theil, M.; Lippincott, E. R. *J. Am. Chem. Soc.* **1961**, *83*, 2403. (c) Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1963**, *46*, 1588. (d) Whitlock, H. W., Jr.; Reich, C.; Woessner, W. D. *J. Am. Chem. Soc.* **1971**, *93*, 2483. (e) Whitlock, H. W., Jr.; Markezich, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 5290. (f) McArdle, P.; Sherlock, H. *J. Chem. Soc., Dalton Trans.* **1978**, 1678.

[4] Wadepohl, H.; Büchner, K.; Pritzkow, H. *Organometallics* **1989**, *8*, 2745.

[5] King, J. A., *Jr.*; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1983**, *105*, 4846.

[6] Adams, R. D.; Babin, J. E.; Tasi, M.; Wolfe, T. A. *J. Am. Chem. Soc.* **1989**, *110*, 7093.

[7] Nicholls, J. M.; Vargas, M. D.; Hriljac, J.; Sailor, M. *Inorg. Syn.* **1989**, *26*, 280.

[8] Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Will, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1190.

0276-7333/93/2312-1243$04.00/0

CHCHCHCHCH$_2$) (**2b**), 19%; and 21.6 mg of deep red Ru$_6$(CO)$_{14}$(μ_6-C)(η^6-C$_6$H$_6$)[9] (**3**), 22%. IR (νCO in CH$_2$Cl$_2$) for **2a**: 2076 (m), 2037 (vs), 1983 (vw), 1951 (vw, br). For **2b**: 2074 (m), 2035 (vs), 1980 (vw), 1953 (vw, br). ^{1}H NMR (δ in CDCl$_3$) for **2a**: 4.70 (m, 2 H, J_{H-H} = 11.4, 7.4, and 4.2 Hz), 4.08 (dd, 2 H, J_{H-H} = 7.4 and 2.1 Hz), 2.23 (d, 2 H, J_{H-H} = 4.2 Hz), 1.63 (dd, 2 H, J_{H-H} = 11.4 and 1.9 Hz). For **2b**: 6.30 (m, 1 H), 4.79 (d, 1 H, J_{H-H} = 7.0 Hz), 4.65 (dd, 1 H, J_{H-H} = 4.6 and 8.6 Hz), 3.05 (d, 1 H, J_{H-H} = 7.0 Hz), 1.93 (dd, 1 H, J_{H-H} = 12.2 and 1.3 Hz), 1.85 (m, 1 H), 1.66 (d, 1 H, J_{H-H} = 8.6 Hz), −1.28 (dd, 1 H, J_{H-H} = 8.9 and 9.0 Hz).

Conversion of 2a to 2b. A 3.8-mg amount of **2a** and 5 mL of heptane were sealed in a Parr high-pressure reactor and then heated to 155 °C for 14 h. After cooling, the solvent was removed by evaporation. Extraction of the black residue with CH$_2$Cl$_2$ solvent followed by chromatography (TLC) yielded 0.6 mg of **2** (16%).

Attempt To Convert 2b to 2a. A 10.0-mg amount of **2b** and 6 mL of heptane were sealed in a Parr high-pressure reactor and then heated to 155 °C for 18 h. The workup was as the same as that described in the previous section. No **2a** was formed and 6.9 mg of **2b** was recovered (69%).

Crystallographic Analysis. Crystals of **2a** suitable for diffraction analysis were grown in a solution of CH$_2$Cl$_2$/hexane (2/1) by slow evaporation of the solvent at 10 °C. Crystals of **2b** were grown by diffusion of hexane solvent into a solution of **2b** in CH$_2$Cl$_2$ at 25 °C. The crystals used for intensity data measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. All structure-solving calculations were performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN program library (version 5.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[10a] Anomalous dispersion corrections were applied to all nonhydrogen atoms.[10b] Lorentz/polarization (*Lp*) and absorption corrections were applied to the data for the structure. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

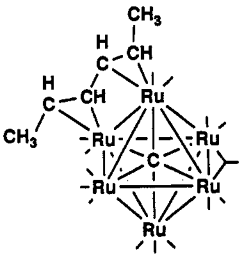
Compounds **2a** and **2b** both crystallized in the monoclinic crystal system in the space group $P2_1/n$ that was identified on the basis of the systematic absences observed during the collection of the intensity data. Both structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The positions of all hydrogen atoms in these structures were calculated by using idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. For **2a**, the carbon atoms of hexatriene were refined isotropically. All other nonhydrogen atoms were refined anisotropically. For **2b**, all nonhydrogen atoms were refined with anisotropic thermal parameters. Crystal data and results of the analyses are listed in Table I.

Table I. Crystal Data for Compounds 2a and 2b

	2a	2b
formula	Ru$_6$O$_{14}$C$_{21}$H$_8$	Ru$_6$O$_{14}$C$_{21}$H$_8$
formula weight	1090.70	1090.70
crystal system	monoclinic	monoclinic
lattice parameters		
a (Å)	14.794(2)	14.812(2)
b (Å)	12.290(2)	12.202(2)
c (Å)	14.927(3)	14.866(2)
β (deg)	92.95(1)	92.06(1)
V (Å^3)	2710(1)	2685(1)
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z value	4	4
ρ (g/cm^3)	2.67	2.70
μ(Mo Kα) (cm^{-1})	32.66	32.97
temperature (°C)	20	20
2θ_{max} (deg)	40.0	42.0
no. of observations	2078	2608
no. of variables	340	370
goodness of fit	1.95	1.91
largest peak in final diff map (e/Å^3)	1.22	0.83
absorption correction	empirical	empirical
residuals: *R*, R_w	0.033, 0.037	0.027, 0.032

Results and Discussion

The reaction of Ru$_6$(CO)$_{17}$(μ_6-C), **1**, with a mixture of *cis*- and *trans*-1,3,5-hexatriene in heptane solvent at 155 °C yielded three products: Ru$_6$(CO)$_{14}$(μ_6-C)(*s-cis,s-cis-trans*-1,2-η^2-4–6-η^4-CH$_2$CHCHCHCHCH$_2$), **2a** (3%), Ru$_6$(CO)$_{14}$(μ_6-C)(*s-trans,s-cis-trans*-1,2-η^2-4–6-η^4-CH$_2$CHCHCHCHCH$_2$), **2b** (19%), and the known compound Ru$_6$(CO)$_{14}$(μ_6-C)(η^6-C$_6$H$_6$), **3** (22%).[9] The known compound Ru$_6$(CO)$_{15}$(μ_6-C)(μ-η^4-*trans*-MeCHCHCHCHMe),[8] **4** was also obtained in trace amounts (3% yield). We suspect that the **4** was produced by the reaction of some trace organic impurities in the hexatriene and not from a reaction involving 1,3,5-hexatriene, but this has not been confirmed.



(4)

Except for the positions of the absorptions (with differences no greater than 2–3 cm^{-1}), the IR spectra of compounds **2a** and **2b** are virtually identical; however, the ^{1}H NMR spectra are complex and show completely different patterns; see below. Single-crystal X-ray diffraction analyses were then performed on both complexes to determine the structural differences between them.

An ORTEP diagram of the molecular structure of **2a** is shown in Figure 1. Final atomic parameters are listed in Table II. Selected interatomic bond distances and angles are listed in Tables III and IV. Like its parent compound **1**, compound **2a** contains an octahedral cluster of six ruthenium atoms with the carbido carbon located in the center of the octahedron. The Ru–Ru bond distances range from 2.827(1) to 3.013(1) Å and are very similar to those found in **1**, 2.827(5)–3.034(5) Å.[11] The Ru–C (carbide) bond distances, 2.03(1)–2.07(1) Å in **2a** and 2.05 Å (av) in **1** are also very similar. The complex contains fourteen carbonyl ligands. Two of these, C(23)–O(23) and C(33)–O(33), are bridging ligands across the two short Ru–Ru bonds, Ru(1)–Ru(2) and Ru(1)–Ru(3). The hexatriene ligand bridges the Ru(1)–Ru(4) edge of the cluster with four carbon atoms bonded to Ru(1) and two bonded to

---

(9) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2606.

(10) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, (a) Table 2.2B, p 99–101. (b) Table 2.3.1, p 149–150.

(11) A. Sirigu, M. Bianchi, and E. Benedetti *J. Chem. Soc., Chem. Commun.*, **1969**, 596.

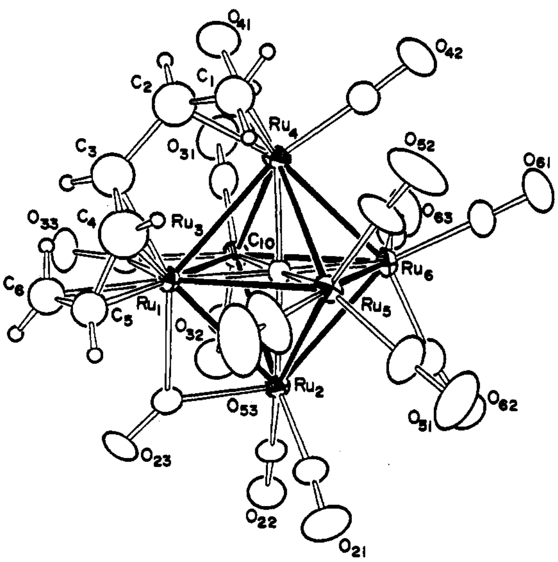


Figure 1. An ORTEP drawing of $Ru_6(CO)_{14}(\mu_6\text{-}C)(\mu\text{-}s\text{-}cis,s\text{-}cis\text{-}trans\text{-}1,2\text{-}\eta^2\text{-}4\text{–}6\text{-}\eta^4\text{-}CH_2CHCHCHCHCH_2)$, **2a**, showing 50% probability thermal ellipsoids.

Table II. Positional Parameters and *B*(eq) Values for $Ru_6C(CO)_{14}$(*trans*-C_6H_8), 2a

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru(1)	0.23269(06)	0.57594(08)	0.99225(06)	3.08(5)
Ru(2)	0.31249(06)	0.70376(08)	0.86016(06)	3.16(5)
Ru(3)	0.12044(07)	0.72451(08)	0.89273(07)	3.45(5)
Ru(4)	0.16895(07)	0.76817(09)	1.08159(07)	3.95(5)
Ru(5)	0.35845(07)	0.76123(09)	1.04297(06)	3.91(5)
Ru(6)	0.23968(07)	0.90134(08)	0.94064(07)	3.76(5)
O(21)	0.5098(07)	0.6911(12)	0.8231(08)	9.3(8)
O(22)	0.2791(06)	0.7004(08)	0.6585(06)	6.2(5)
O(23)	0.3255(08)	0.4603(08)	0.8402(06)	7.4(6)
O(31)	–0.0770(07)	0.7841(10)	0.8882(09)	9.5(8)
O(32)	0.0827(07)	0.7108(10)	0.6929(07)	7.7(7)
O(33)	0.0552(07)	0.4937(08)	0.9012(07)	6.9(6)
O(41)	–0.0353(09)	0.7683(11)	1.0850(09)	10.6(9)
O(42)	0.1595(08)	0.9846(10)	1.1756(07)	8.7(7)
O(51)	0.5157(10)	0.8858(14)	0.9744(11)	15(1)
O(52)	0.3783(09)	0.8892(12)	1.2148(09)	13(1)
O(53)	0.4658(12)	0.5815(14)	1.1058(14)	16(1)
O(61)	0.2835(08)	1.1129(09)	1.0407(07)	8.1(7)
O(62)	0.3607(09)	0.9702(09)	0.7930(08)	9.2(8)
O(63)	0.0729(07)	1.0029(08)	0.8444(08)	8.2(7)
C(1)	0.1985(12)	0.6924(15)	1.2247(11)	8.5(5)
C(2)	0.1435(13)	0.6255(17)	1.1812(13)	10.2(5)
C(3)	0.1680(14)	0.5211(17)	1.1174(13)	10.2(5)
C(4)	0.2656(16)	0.495(02)	1.1170(16)	13.1(7)
C(5)	0.2983(10)	0.4281(13)	1.0444(10)	7.0(4)
C(6)	0.2197(11)	0.3975(13)	1.0018(10)	7.4(4)
C(10)	0.2406(07)	0.7394(09)	0.9693(07)	3.0(5)
C(21)	0.4362(10)	0.7002(12)	0.8380(09)	5.2(8)
C(22)	0.2898(08)	0.7038(10)	0.7348(08)	4.1(7)
C(23)	0.3055(09)	0.5404(12)	0.8744(08)	4.7(7)
C(31)	–0.0021(11)	0.7604(11)	0.8929(11)	6.3(9)
C(32)	0.0992(09)	0.7151(12)	0.7687(10)	5.5(8)
C(33)	0.1069(09)	0.5627(11)	0.9160(08)	4.5(7)
C(41)	0.0433(10)	0.7668(14)	1.0801(11)	7(1)
C(42)	0.1641(11)	0.9018(14)	1.1370(10)	7(1)
C(51)	0.4567(12)	0.8353(16)	0.9995(11)	9(1)
C(52)	0.3679(11)	0.8396(14)	1.1504(11)	8(1)
C(53)	0.4274(16)	0.6428(17)	1.0829(17)	12(1)
C(61)	0.2681(10)	1.0344(12)	1.0024(10)	5.5(8)
C(62)	0.3160(11)	0.9341(12)	0.8476(10)	6.0(9)
C(63)	0.1327(10)	0.9565(11)	0.8790(09)	5.3(8)

Table III. Intramolecular Distances for 2a[a]

Ru(1)–Ru(2)	2.827(1)	Ru(3)–C(33)	2.03(1)
Ru(1)–Ru(3)	2.836(1)	Ru(4)–Ru(5)	2.892(2)
Ru(1)–Ru(4)	2.895(1)	Ru(4)–Ru(6)	2.903(2)
Ru(1)–Ru(5)	3.013(1)	Ru(4)–C(1)	2.35(2)
Ru(1)–C(3)	2.25(2)	Ru(4)–C(2)	2.34(2)
Ru(1)–C(4)	2.15(2)	Ru(4)–C(10)	2.06(1)
Ru(1)–C(5)	2.18(2)	Ru(4)–C(41)	1.86(2)
Ru(1)–C(6)	2.21(2)	Ru(4)–C(42)	1.84(2)
Ru(1)–C(10)	2.04(1)	Ru(5)–Ru(6)	2.848(2)
Ru(1)–C(23)	2.15(1)	Ru(5)–C(10)	2.03(1)
Ru(1)–C(33)	2.14(1)	Ru(5)–C(51)	1.86(2)
Ru(2)–Ru(3)	2.918(2)	Ru(5)–C(52)	1.87(2)
Ru(2)–Ru(5)	2.866(1)	Ru(5)–C(53)	1.86(2)
Ru(2)–Ru(6)	2.938(1)	Ru(6)–C(10)	2.04(1)
Ru(2)–C(10)	2.04(1)	Ru(6)–C(61)	1.91(2)
Ru(2)–C(21)	1.88(2)	Ru(6)–C(62)	1.88(2)
Ru(2)–C(22)	1.88(1)	Ru(6)–C(63)	1.91(2)
Ru(2)–C(23)	2.02(1)	C(1)–C(2)	1.31(2)
Ru(3)–Ru(4)	2.923(2)	C(2)–C(3)	1.65(3)
Ru(3)–Ru(6)	2.866(1)	C(3)–C(4)	1.48(3)
Ru(3)–C(10)	2.07(1)	C(4)–C(5)	1.46(2)
Ru(3)–C(31)	1.87(2)	C(5)–C(6)	1.35(2)
Ru(3)–C(32)	1.87(1)	O–C(av)	1.14(2)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

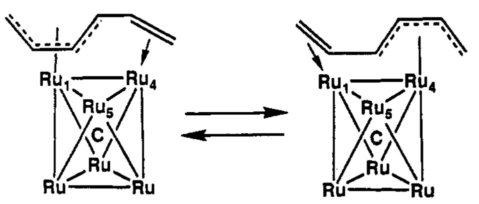
Table IV. Intramolecular Bond Angles for 2a[a]

Ru(2)–Ru(1)–Ru(4)	91.46(4)	Ru(1)–C(10)–Ru(3)	87.2(4)
Ru(3)–Ru(1)–Ru(5)	88.98(4)	Ru(1)–C(10)–Ru(4)	89.8(4)
Ru(1)–Ru(2)–Ru(6)	89.95(4)	Ru(1)–C(10)–Ru(5)	95.4(4)
Ru(3)–Ru(2)–Ru(5)	90.29(4)	Ru(2)–C(10)–Ru(3)	90.5(4)
Ru(1)–Ru(3)–Ru(6)	91.22(4)	Ru(2)–C(10)–Ru(5)	89.5(4)
Ru(2)–Ru(3)–Ru(4)	89.08(4)	Ru(2)–C(10)–Ru(6)	92.3(4)
Ru(1)–Ru(4)–Ru(6)	89.32(4)	Ru(3)–C(10)–Ru(4)	90.1(4)
Ru(3)–Ru(4)–Ru(5)	89.70(4)	Ru(3)–C(10)–Ru(6)	88.5(4)
Ru(1)–Ru(5)–Ru(6)	88.07(4)	Ru(4)–C(10)–Ru(5)	90.0(4)
Ru(2)–Ru(5)–Ru(4)	90.70(4)	Ru(4)–C(10)–Ru(6)	90.3(4)
Ru(2)–Ru(6)–Ru(4)	89.07(4)	Ru(5)–C(10)–Ru(6)	88.9(4)
Ru(3)–Ru(6)–Ru(5)	91.73(4)	Ru(1)–C(23)–O(23)	133(1)
C(1)–C(2)–C(3)	129(2)	Ru(2)–C(23)–O(23)	142(1)
C(2)–C(3)–C(4)	115(2)	Ru(1)–C(33)–O(33)	135(1)
C(3)–C(4)–C(5)	119(2)	Ru(3)–C(33)–O(33)	139(1)
C(4)–C(5)–C(6)	101(2)	Ru–C(av)–O	176(2)
Ru(1)–C(10)–Ru(2)	87.7(4)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Ru(4). It exhibits an *s*-cis,*s*-cis conformation at the 2,3 and 4,5 carbon–carbon bonds. The Ru–C bond distances between the cluster and the hexatriene ligand, Ru(1)–C(3) = 2.25(2) Å, Ru(1)–C(4) = 2.15(2) Å, Ru(1)–C(5) = 2.18(2) Å, Ru(1)–C(6) = 2.21(2) Å, Ru(4)–C(1) = 2.35(2) Å, and Ru(4)–C(2) = 2.34(2) Å, span a fairly wide range, but none are unusual for π-coordinated ligands. Similar Ru–C bond distances were also observed in the related carbidoruthenium cluster complex 4 that contains an *s*-trans-η^4-coordinated diene grouping.[8] The C–C bond distances along the π-bonded chain span a considerable range, C(1)–C(2) = 1.35(2) Å, C(2)–C(3) = 1.65(3) Å, C(3)–C(4) = 1.48(2) Å, C(4)–C(5) = 1.46(2) Å, and C(5)–C(6) = 1.35(2) Å. Except for the distance between the atoms C(3) and C(4) these distances are in accord with the long and short alternation that is expected for the 1,3,5-hexatriene molecule. The anomalous length of the C(2)–C(3) bond may be due to some small unresolvable disorder in the positions of the carbon atoms of the hexatriene ligand. The carbon atoms did not yield positive thermal parameters in refinement attempts using anisotropic thermal parameters and were thus refined with isotropic thermal parameters only. The ligand is probably best described as a combination of an η^4-diene coordinated to Ru(1) and an η^2-monoene coordinated to Ru(4). The increased length of the C(3)–C(4) bond and short length of the C(4)–C(5) bond suggests that some π-delocalization between the C(3)–C(4) bond and the neighboring C(4)–C(5) bond has occurred in the η^4-diene group coordinated to Ru(1). The six carbon atoms are not coplanar and deviate from the

Scheme I



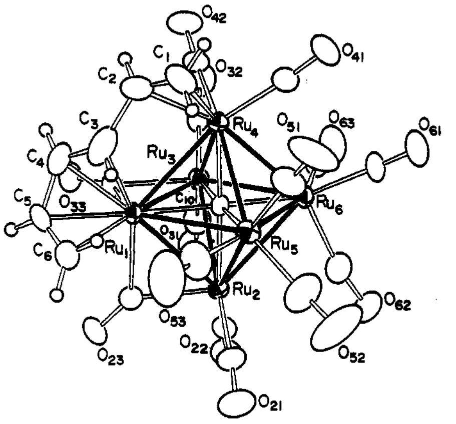


Figure 2. An ORTEP diagram of $Ru_6(CO)_{14}(\mu_6\text{-}C)(\mu\text{-}s\text{-}trans,s\text{-}cis\text{-}trans\text{-}1,2\text{-}\eta^2\text{-}4\text{-}6\text{-}\eta^4\text{-}CH_2CHCHCHCHCH_2)$, **2a**, showing 50% probability thermal ellipsoids.

mean plane as follows: C(1), +0.13 Å; C(2), −0.02 Å; C(3), −0.16 Å; C(4), −0.25 Å; C(5), +0.03 Å; and C(6), +0.14 Å. The ^1H NMR spectrum of **2a** at 25 °C shows only four resonances, each of intensity two: 4.70 (m, 2 H, J_{H-H} = 11.4, 7.4, and 4.2 Hz), 4.08 (dd, 2 H, J_{H-H} = 7.4 and 2.1 Hz), 2.23 (d, 2 H, J_{H-H} = 4.2 Hz), 1.63 (dd, 2 H, J_{H-H} = 11.4 and 1.9 Hz). This simple spectrum is not consistent with the solid-state structure, but it could be explained as an averaged spectrum in which the eight protons are averaged in pairs. This could occur by a shifting of the hexatriene ligand from the 1,2-η^2-4–6-η^4-mode found in **2a** to an energetically equivalent isomer having a 1–4-η^4-5,6-η^2-coordination; see Scheme I. This process would generate a C_2 time-averaged molecular geometry. It is anticipated that the required rearrangements of the carbonyl ligands could occur with a minimum of difficulty. The existence of such a dynamical rearrangement was supported by a low-temperature ^1H NMR study taken in CD_2Cl_2 solvent. At lower temperatures, the resonances at 4.70, 2.23, and 1.63 ppm are broadened and have collapsed into the baseline at −91 °C. The resonance at 4.08 ppm broadens slightly and the couplings disappear, but this resonance does not collapse into the baseline. We were unable to record spectra at lower temperatures and thus could not obtain spectra of the complex in the slow exchange region.

Table V. Positional Parameters and B(eq) Values for $Ru_6C(CO)_{14}$(*trans*-C_6H_8), 2b

atom	x	y	z	B(eq), Å^2
Ru(1)	0.50827(04)	0.42896(05)	0.76674(04)	2.86(3)
Ru(2)	0.64055(04)	0.29797(05)	0.68927(04)	2.90(3)
Ru(3)	0.60203(05)	0.27456(05)	0.87877(04)	3.10(3)
Ru(4)	0.41207(04)	0.23741(05)	0.82688(04)	3.22(3)
Ru(5)	0.45732(05)	0.24135(05)	0.63875(04)	3.52(3)
Ru(6)	0.55395(05)	0.09950(05)	0.75848(04)	3.25(3)
O(21)	0.6787(06)	0.3258(07)	0.4941(05)	7.9(5)
O(22)	0.8430(05)	0.2890(05)	0.7206(05)	5.9(4)
O(23)	0.6757(04)	0.5418(05)	0.6927(05)	6.1(4)
O(31)	0.8028(05)	0.2862(06)	0.9137(05)	7.0(4)
O(32)	0.6049(06)	0.2119(06)	1.0763(05)	7.9(5)
O(33)	0.5995(04)	0.5103(05)	0.9399(04)	5.3(3)
O(41)	0.3195(05)	0.0167(05)	0.8394(05)	6.8(4)
O(42)	0.4048(06)	0.2393(06)	1.0297(05)	7.5(5)
O(51)	0.2864(06)	0.1083(08)	0.6192(06)	10.8(6)
O(52)	0.5278(07)	0.1268(10)	0.4754(06)	14.5(8)
O(53)	0.3838(09)	0.4243(08)	0.5295(07)	13.9(8)
O(61)	0.4537(05)	−0.1145(06)	0.7192(05)	7.3(4)
O(62)	0.6985(05)	0.0269(06)	0.6322(05)	7.5(4)
O(63)	0.6493(05)	−0.0028(05)	0.9232(05)	7.1(4)
C(1)	0.2651(08)	0.3032(09)	0.8030(08)	7.1(7)
C(2)	0.3125(08)	0.3797(10)	0.8463(08)	7.2(7)
C(3)	0.3622(08)	0.4674(10)	0.7918(09)	8.6(8)
C(4)	0.4207(08)	0.5442(08)	0.8337(07)	6.2(6)
C(5)	0.4786(07)	0.6034(06)	0.7759(07)	5.5(5)
C(6)	0.4705(07)	0.5772(07)	0.6869(07)	5.4(5)
C(10)	0.5280(05)	0.2639(05)	0.7586(05)	2.8(4)
C(21)	0.6626(06)	0.3118(08)	0.5679(06)	4.7(5)
C(22)	0.7666(06)	0.2893(06)	0.7105(06)	3.8(4)
C(23)	0.6337(06)	0.4632(07)	0.7065(06)	4.1(4)
C(31)	0.7254(07)	0.2822(07)	0.8990(06)	4.8(5)
C(32)	0.6006(07)	0.2374(07)	1.0010(07)	5.0(5)
C(33)	0.5825(05)	0.4396(07)	0.8910(05)	3.4(4)
C(41)	0.3587(06)	0.0995(08)	0.8331(06)	4.5(5)
C(42)	0.4124(07)	0.2407(07)	0.9540(07)	4.9(5)
C(51)	0.3515(08)	0.1579(09)	0.6296(06)	6.2(6)
C(52)	0.5050(08)	0.1703(11)	0.5376(08)	8.4(8)
C(53)	0.4113(10)	0.3588(10)	0.5721(08)	7.9(7)
C(61)	0.4917(06)	−0.0353(07)	0.7325(06)	4.9(5)
C(62)	0.6468(07)	0.0646(08)	0.6793(07)	5.6(6)
C(63)	0.6141(06)	0.0445(07)	0.8656(07)	4.6(5)

Table VI. Intramolecular Distances for 2b[a]

Ru(1)–Ru(2)	2.8075(9)	Ru(3)–C(33)	2.044(8)
Ru(1)–Ru(3)	2.8435(9)	Ru(4)–Ru(5)	2.900(1)
Ru(1)–Ru(4)	2.8954(9)	Ru(4)–Ru(6)	2.9043(9)
Ru(1)–Ru(5)	3.0540(9)	Ru(4)–C(1)	2.33(1)
Ru(1)–C(3)	2.26(1)	Ru(4)–C(2)	2.30(1)
Ru(1)–C(4)	2.18(1)	Ru(4)–C(10)	2.051(7)
Ru(1)–C(5)	2.178(8)	Ru(4)–C(41)	1.86(1)
Ru(1)–C(6)	2.224(9)	Ru(4)–C(42)	1.89(1)
Ru(1)–C(10)	2.039(7)	Ru(5)–Ru(6)	2.8336(9)
Ru(1)–C(23)	2.133(9)	Ru(5)–C(10)	2.053(7)
Ru(1)–C(33)	2.119(8)	Ru(5)–C(51)	1.87(1)
Ru(2)–Ru(3)	2.9084(9)	Ru(5)–C(52)	1.89(1)
Ru(2)–Ru(5)	2.874(1)	Ru(5)–C(53)	1.86(1)
Ru(2)–Ru(6)	2.9434(9)	Ru(6)–C(10)	2.043(7)
Ru(2)–C(10)	2.035(7)	Ru(6)–C(61)	1.918(9)
Ru(2)–C(21)	1.85(1)	Ru(6)–C(62)	1.89(1)
Ru(2)–C(22)	1.885(9)	Ru(6)–C(63)	1.92(1)
Ru(2)–C(23)	2.035(9)	C(1)–C(2)	1.32(2)
Ru(3)–Ru(4)	2.926(1)	C(2)–C(3)	1.55(2)
Ru(3)–Ru(6)	2.8594(9)	C(3)–C(4)	1.41(1)
Ru(3)–C(10)	2.066(7)	C(4)–C(5)	1.43(1)
Ru(3)–C(31)	1.84(1)	C(5)–C(6)	1.36(1)
Ru(3)–C(32)	1.87(1)	O–C(av)	1.15(1)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

An ORTEP drawing of the molecular structure of **2b** is shown in Figure 2. Final atomic parameters are listed in Table V. Selected interatomic bond distances and angles are listed in Tables VI and VII. The structure of compound **2b** is almost same as that of **2a**, but differs in the conformation of the hexatriene ligand. In **2b** it has adopted an *s*-trans,*s*-cis conformation. Once again, it bridges the two metal atoms through a combination of an η^4-diene grouping coordinated to Ru(1) and an η^2-monoene grouping coordinated to Ru(4). The C–C bond distance pattern is similar to that found in **2a**: C(1)–C(2) = 1.32(2) Å, C(2)–C(3) = 1.55(2) Å, C(3)–C(4) = 1.41(1) Å, C(4)–C(5) = 1.43(1) Å, and C(5)–C(6) = 1.36(1) Å. The ligand is much closer to planar than that found in **2a**. The deviation from the least-squares plane passing through them is as follows: C(1), +0.04 Å; C(2), +0.06 Å; C(3), −0.16 Å; C(4), −0.02 Å; C(5), +0.06 Å; and C(6), 0.00 Å. The ^1H NMR spectrum for **2b** shows eight resonances, 6.30 (m, 1 H), 4.79 (d, 1 H, J_{H-H} = 7.0 Hz), 4.65 (dd, 1 H, J_{H-H} = 4.6 and

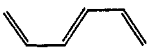
Table VII. Intramolecular Bond Angles for 2b[a]

Ru(2)-Ru(1)-Ru(4)	91.46(3)	Ru(1)-C(10)-Ru(4)	90.1(3)
Ru(1)-Ru(2)-Ru(6)	90.32(3)	Ru(1)-C(10)-Ru(5)	96.6(3)
Ru(3)-Ru(2)-Ru(5)	90.76(3)	Ru(2)-C(10)-Ru(3)	90.3(3)
Ru(1)-Ru(3)-Ru(6)	91.33(3)	Ru(2)-C(10)-Ru(5)	89.4(3)
Ru(2)-Ru(3)-Ru(4)	88.86(3)	Ru(2)-C(10)-Ru(6)	92.4(3)
Ru(1)-Ru(4)-Ru(6)	89.39(3)	Ru(3)-C(10)-Ru(4)	90.6(3)
Ru(3)-Ru(4)-Ru(5)	89.91(3)	Ru(3)-C(10)-Ru(6)	88.2(3)
Ru(2)-Ru(5)-Ru(4)	90.04(3)	Ru(4)-C(10)-Ru(5)	89.9(3)
Ru(2)-Ru(6)-Ru(4)	88.60(3)	Ru(4)-C(10)-Ru(6)	90.4(3)
Ru(3)-Ru(6)-Ru(5)	92.60(3)	Ru(5)-C(10)-Ru(6)	87.5(3)
C(1)-C(2)-C(3)	119(1)	Ru(1)-C(23)-O(23)	135.5(7)
C(2)-C(3)-C(4)	122(1)	Ru(2)-C(23)-O(23)	139.8(7)
C(3)-C(4)-C(5)	116(1)	Ru(1)-C(33)-O(33)	133.8(6)
C(4)-C(5)-C(6)	116(1)	Ru(3)-C(33)-O(33)	140.0(7)
Ru(1)-C(10)-Ru(2)	87.1(3)	Ru-C(av)-O	175(1)
Ru(1)-C(10)-Ru(3)	87.7(3)		

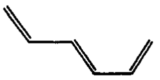
[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

8.6 Hz), 3.05 (d, 1 H, J_{H-H} = 7.0 Hz), 1.93 (dd, 1 H, J_{H-H} = 12.2 and 1.3 Hz), 1.85 (m, 1 H), 1.66 (d, 1 H, J_{H-H} = 8.6 Hz), 1.28 (dd, 1 H, J_{H-H} = 8.9 and 9.0 Hz), which is consistent with the structure found in the solid state. Compounds **2a** and **2b** both contain 86 electrons and obey the polyhedral skeletal electron pair counting theory.[12]

There are three possible planar isomers of *trans*-1,3,5-hexatriene, *s*-cis,*s*-cis, *s*-trans,*s*-cis, and *s*-trans,*s*-trans, that



s-cis,s-cis

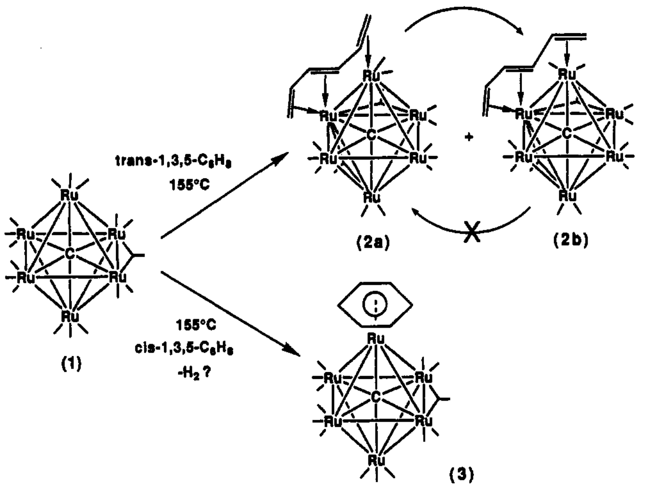


s-trans,s-cis

s-trans,s-trans

are formed from different conformations produced by rotations about the C–C single bonds. Our results show that *trans*-1,3,5-hexatriene can coordinate effectively to clusters by bridging two metal atoms through a combination of an η^4-diene and η^2-monoene modes by using both the *s*-cis,cis, *s*-trans,cis conformations.

Scheme II



The results of this study are summarized in Scheme II. In **2a** the *trans*-hexatriene ligand has an *s*-cis,*s*-cis conformation while in **2b** it has an *s*-trans,*s*-cis mode. Attempts to convert **2b** to **2a** were unsuccessful, but at 155 °C some **2b** was obtained from **2a** (16%). This may help to account for the low yield of **2a** in the reaction. No complexes containing the *cis*-1,3,5-hexatriene ligand were obtained, but the benzene complex **3** was obtained. We suspect that the benzene complex **3** was obtained indirectly from the reaction of **1** with the *cis*-1,3,5-hexatriene present in the 1,3,5-hexatriene reagent. It is likely that the *cis*-1,3,5-hexatriene would have been converted initially to cyclohexadiene, a reaction that is known to occur thermally under the conditions that were used,[13] and that the cyclohexadiene then reacted with **1** to yield the **3**. We have shown in an independent study that cyclohexadiene will react with **1** to yield the benzene complex **3** under these conditions.[14] Similar transformations of cyclohexadiene to benzene complexes have been reported by Braga et al.[15]

Acknowledgment. These studies were supported by the National Science Foundation under Grant No. CHE-8919786. We would like to thank Mr. John H. Yamamoto for assistance in recording the variable-temperature NMR spectra.

Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

OM920789P

---

[12] D. M. P. Mingos and A. S. May in *The Chemistry of Metal Cluster Complexes*, D. F. Shriver, H. D. Kaesz, R. D. Adams, Eds; VCH Publishers, Inc.: New York, 1990; Chapter 2.

[13] Lewis, K. E.; Steiner, H. *J. Chem. Soc.* **1964**, 3080.

[14] Adams, R. D.; Wu, W. *Polyhedron* **1992**, *11*, 2123.

[15] Braga, D.; Grepioni, F.; Righi, S.; Dyson, P. J.; Johnson, B. F. G.; Bailey, P. J.; Lewis, J. *Organometallics* **1992**, *11*, 4042.