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Pentadienyl Ligands in Cluster Complexes. Synthesis and Structural Characterization of $Ru_5(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$ and $Ru_6(CO)_{15}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$

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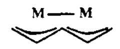
Abstract: The cluster complexes $Ru_5(CO)_{15}(\mu_4\text{-}S)$ (**1**) and $Ru_6(CO)_{18}(\mu_4\text{-}S)$ (**2**) react with *trans*-2-heptene to yield the new complexes $Ru_5(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$ (**3**) and $Ru_6(CO)_{15}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$ (**4**) in the yields 4% and 7%, respectively. Better yields, 26% and 18%, respectively, were obtained by substituting 2,4-heptadiene for the *trans*-2-heptene. Both products were characterized by single-crystal X-ray diffraction analyses. For **3**: space group, $P2_1/n$; $a = 9.556$ (3), $b = 17.878$ (6), $c = 15.642$ (7) Å; $\beta = 98.54$ (3)°; $V = 2642$ (3) Å^3, $Z = 4$. The structure was solved by direct methods and was refined (3373 reflections) to the final residuals $R = 0.026$ and $R_w = 0.027$. The molecule consists of a square-pyramidal cluster of five ruthenium atoms with a quadruply bridging sulfido ligand across the square base. An η^5-1,5-dimethylpentadienyl ligand in an S-conformation bridges two of the metal atoms in the square base, with three carbon atoms bonded to one metal atom and two to the other. A hydride ligand bridges one of the 3-fold faces of the cluster that is adjacent to the pentadienyl ligand. For **4**: space group, $P2_1/n$; $a = 8.311$ (2), $b = 32.479$ (5), $c = 11.491$ (1) Å; $\beta = 99.09$ (1)°; $V = 3063$ (1) Å^3; $Z = 4$. The structure was solved by direct methods and refined (2905 reflections) to the final values of the residuals, $R = 0.030$ and $R_w = 0.030$. The molecule consists of a square-pyramidal cluster of five ruthenium atoms, with a $Ru(CO)_4$ group bridging one edge of the square base, an S-shaped 1,5-dimethylpentadienyl ligand across the basal edge opposite the $Ru(CO)_4$ group, and a sulfido ligand across the square base. The hydride ligand bridges the triangular face that lies opposite of the pentadienyl ligand. The pentadienyl ligands in **3** and **4** were formed by an unusual process that involves the activation of an aliphatic C–H bond in the olefins. Compound **4** was also obtained from **3** in 37% yield by reaction with $Ru(CO)_5$ at 80 °C. Compound **3** was obtained from **4** in 30% yield by treatment with CO at 98 °C.

In recent years major advancements have been made in the preparation and study of metal complexes containing pentadienyl ligands.[1–4] Three types of structures have been observed for the η^5-coordination forms of these ligands. These structures are frequently described as the U, S, and W forms on the basis of their general shapes. Most examples of this ligand are found in mononuclear metal complexes where it adopts the U-structure A. The η^5 S-structure B is rare.[5] This may be due in part to instability caused by an induced nonplanarity of the ligand when all of the carbon atoms are bonded to a single metal atom. The W-structure has been observed, but only in the form of a bridging ligand in the dinuclear nickel complex, $Ni_2(\mu\text{-}C_5H_7)_2$.

A

B



C

We have recently prepared a series of high-nuclearity sulfidoruthenium carbonyl cluster complexes.[8,9] In further investigations of their chemistry, we have carried out reactions of two of these, $Ru_5(CO)_{15}(\mu_4\text{-}S)$ (**1**) and $Ru_6(CO)_{18}(\mu_4\text{-}S)$ (**2**) with two olefins, *trans*-2-heptene and 2,4-heptadiene. Both clusters were found to add the olefins and convert them into a bridging 1,5-dimethylpentadienyl ligand having the S-structural form through processes that must involve the activation of some C–H bonds on the olefins. The results of these studies are described in this report.

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere. Reagent-grade solvents were stored over 4-Å molecular sieves. $Ru_3(CO)_{12}$ was purchased from Strem Chemical Co. and was used as received. *trans*-2-Heptene was purchased from Aldrich Chemical Co. and was used as received. CP-grade carbon monoxide was purchased from Linde Co. and was used without further purification. 2,4-Heptadiene (a mixture of isomers) was purchased from Wiley Organics, Inc., and was used as received. $Ru(CO)_5$ was prepared by a previously reported method.[7] $Ru_5(CO)_{15}(\mu_4\text{-}S)$, **1**, and $Ru_6(CO)_{18}(\mu_4\text{-}S)$, **2**, were prepared as previously reported.[8]

All chromatographic separations were performed in air on TLC plates (0.25-mm Kieselgel 60 F_{254}, E. Merck, West Germany). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Brüker AM-300 spectrometer operating at 300 MHz. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Preparation of $Ru_5(CO)_{12}(\mu_4\text{-}S)(\mu_3\text{-}H)(\mu\text{-}\eta^5\text{-}1,5\text{-}Me_2C_5H_5)$ (3). (a) From *trans*-2-Heptene. A total of 50 mg (0.052 mmol) of compound **1** and 75 μL (0.54 mmol) of *trans*-2-heptene were added to 100 mL of benzene. This mixture was refluxed for 40 min. During this time, **1** dissolved and the solution turned dark brown. The solvent was removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (v/v, 7/3) solvent mixture yielded 2.2 mg of $Ru_5(CO)_{10}(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_3\text{-}H)(\mu\text{-}\eta^5\text{-}1,5\text{-}Me_2C_5H_5)$ (**3**) 4% as an orange-brown band. IR (ν(CO); hexane): 2078 (s), 2042 (vs), 2026 (m), 2009 (w), 2002 (m), 1997 (m), 1988 (w), 1971 (w), 1860 (m), 1833 (m) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ 5.33 (m, 2 H), 4.66 (m, 1 H), 2.33 (d, 3 H, $J_{H-H} = 5.8$ Hz), 2.08 (m, 1 H), 1.86 (t, 1 H, $J_{H-H} = 11.2$ Hz), 1.37 (d, 3 H, $J_{H-H} = 6.2$ Hz), −14.95 (s, 1 H). Anal. Calcd for $Ru_5SO_{12}C_{19}H_{12}$: C, 23.53; H, 1.25. Found: C, 24.55; H, 1.09.

(b) From 2,4-Heptadiene. A total of 40 mg (0.042 mmol) of compound **1** and 54 μL (0.42 mmol) of 2,4-heptadiene were added to 40 mL of cyclohexane. This mixture was refluxed for 75 min. During this time,

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1 dissolved and the solution turned dark brown. The solvent was removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (v/v, 7/3) solvent mixture yielded 10.7 mg of **3**, 26%.

Preparation of $Ru_6(CO)_{15}(\mu_4\text{-}S)(\mu_3\text{-}H)(\mu\text{-}\eta^5\text{-}1,5\text{-}Me_2C_5H_5)$ (4). (a) From *trans*-2-Heptene. A total of 20 mg (0.0175 mmol) of compound **2** dissolved in 35 mL of *n*-heptane were combined with 20 μL (0.143 mmol) of *trans*-2-heptene. This solution was refluxed for 40 min. The *n*-heptane was removed in vacuo, and the residue was dissolved in a minimal amount of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (v/v, 7/3) solvent mixture yielded 1.4 mg of $Ru_6(CO)_{15}(\mu_4\text{-}S)(\mu_3\text{-}H)(\mu\text{-}\eta^5\text{-}1,5\text{-}Me_2C_5H_5)$ (**4**) 7%, as a red band and 0.8 mg of **3**, 4%. For **4**: IR (ν(CO); CH_2Cl_2): 2110 (m), 2059 (vs), 2033 (v), 2005 (s), 1973 (w), 1953 (w, sh), 1857 (vw, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.26 (m, 1 H), 4.96 (m, 1 H), 3.91 (m, 1 H), 2.43 (m, 1 H), 2.15 (d, 3 H, J_{H-H} = 5.8 Hz), 1.93 (t, 1 H, J_{H-H} = 11.4 Hz), 1.82 (d, 3 H, J_{H-H} = 6.0 Hz), −13.51 (s, 1 H). Anal. Calcd for $Ru_6SO_{15}C_{22}H_{12}$: C, 22.88; H, 1.05. Found: C, 22.55; H, 0.96.

(b) From 2,4-Heptadiene. A total of 40 mg (0.0350 mmol) of **2** were dissolved in 40 mL of cyclohexane and were combined with 45 μL (0.346 mmol) of 2,4-heptadiene. This solution was refluxed for 2.5 h. The cyclohexane was removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (v/v, 7/3) solvent mixture yielded 7.5 mg of **4**, 18%, and 3.3 mg of **3**, 10%.

Reaction of Compound 3 with $Ru(CO)_5$. A total of 11.6 mg (0.0120 mmol) of **3** was dissolved in 10 mL of cyclohexane, and the solution was heated to reflux. A 40-mL cyclohexane solution of $Ru(CO)_5$ (0.122 mmol) was added. The reaction solution was then refluxed for 25 min. The workup as described above yielded 12.8 mg of $Ru_3(CO)_{12}$ as a yellow band, 3.8 mg of compound **4**, 37%, and 3.1 mg of **3**. The yield of **4** was calculated from the amount of **3** that was consumed.

Reaction of 4 with Carbon Monoxide. A total of 11.8 mg (0.0102 mmol) of **4** were dissolved in 15 mL of *n*-heptane. The solution was heated to reflux (98 °C) for 45 min under a carbon monoxide purge. Workup as described above yielded 2.3 mg of a yellow band that contained $Ru_3(CO)_{12}$ and $Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}S)$, 2.7 mg of unreacted **4**, and 2.3 mg of **3**, 30%.

Crystallographic Analyses. Brown crystals of **3** were grown by slow evaporation of solvent from benzene/hexane solutions at 10 °C. Red crystals of **4** were grown by slow evaporation of solvent from benzene/CH_2Cl_2 solutions at 25 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer with graphite-monochromatized Mo Kα radiation. Unit cells were determined from 25 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer, by using the TEXSAN structure solving program library (version 2.0) obtained from the Molecular Structure Corp., College Station, TX. Neutral atom scattering factors were calculated by the standard procedures. Anomalous dispersion corrections were applied to all non-hydrogen atoms. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compound **3** crystallized in the monoclinic crystal system, and the space group, $P2_1/n$, was determined from systematic absences observed during the data collection. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions, including the triply bridging hydride ligand, were also determined from difference Fourier syntheses. All of the hydrogen atom positions were successfully refined with isotropic temperature factors.

Compound **4** also crystallized in the monoclinic crystal system, and the space group, $P2_1/n$, was determined from systematic absences observed in the data. Metal atom positions were determined by direct methods (MITHRIL). All other non-hydrogen atoms were located in subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The location of the triply bridging hydride ligand was determined from a difference Fourier map, and its position was successfully refined. All other hydrogen atoms were calculated by assuming idealized geometries. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Error analyses for both structures were calculated from the inverse matrix obtained on the final cycle of refinement. See supplementary material for the tables of structure factor amplitudes, positional parameters, and values of the anisotropic thermal parameters.

Table I. Crystallographic Data for the Structural Analyses for Compounds **3** and **4**

compd	**3**	**4**
formula	$Ru_5SO_{12}C_{19}H_{12}$	$Ru_6SO_{15}C_{22}H_{12}$
temp (±3 °C), °C	23	
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	9.556 (3)	8.311 (2)
b, Å	17.878 (6)	32.479 (5)
c, Å	15.642 (7)	11.491 (1)
α, deg	90.0	90.0
β, deg	98.54 (3)	99.09 (1)
γ, deg	90.0	90.0
V, Å^3	2642 (3)	3063 (1)
M_r	969.7	1154.8
Z	4	4
ρ_{calcd}, g/cc	2.44	2.50
(A) Measurement of Intensity Data		
radiation	Mo Kα (0.71069 Å)	
monochromator	graphite	
detector aperture, mm		
horizontal	2.0	
vertical	2.0	
cryst faces	101, $\bar{1}0\bar{1}$, 010, $0\bar{1}0$; 001, $00\bar{1}$, $\bar{1}01$, $10\bar{1}$	010, $0\bar{1}0$, $01\bar{1}$; $0\bar{1}1$, 100, $\bar{1}00$
cryst size, mm	0.13 × 0.28 × 0.16	0.07 × 0.14 × 0.30
cryst orientn		
lattice direction	[102]	[100]
deg from Φ-axis	5.2	8.8
reflctns measd	$h,k,\pm l$	$h,k,\pm l$
max 2θ, deg	48	45
scan type	moving crystal–stationary counter	
ω-scan width (A + 0.347 tan θ), deg	A = 1.10	
bkgd (time at each end of scan)	1/4 scan time	
ω-scan rate,[a] deg/min	4.0	
data used ($F^2 \geq 3.0\sigma(F^2)$)	3373	2905
(B) Treatment of Data		
absorpn corrn	analytical	
coeff, cm^{-1}	28.57	29.46
transmissn coeff		
max	0.719	0.833
min	0.631	0.647
P-factor	0.02	0.02
final residuals		
R_F	0.026	0.030
R_{wF}	0.027	0.030
goodness of fit	1.34	1.35
largest shift/error value of final cycle	0.10	0.09
largest peak in final diff Fourier, e$^-$/Å^3	0.40	0.24
no. of variables	382	401

[a] Rigaku software uses a multiple-scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to the first scan, etc. A maximum of three scans was permitted per reflection.

Results and Discussion

The reactions of **1** and **2** with *trans*-2-heptene yielded the new cluster complexes $Ru_5(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$ (**3**) 4%, and $Ru_6(CO)_{15}(\mu_4\text{-}S)$ $(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$ (**4**) 7%, respectively in low yields. A small amount of **3** was also obtained from the preparation of **4**. The yields of **3** and **4** were improved considerably, 26% and 18%, respectively, by using 2,4-heptadiene as the precursor to the pentadienyl ligand. Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses.

An ORTEP drawing of the molecular structure of **3** is shown in Figure 1. Intramolecular bond distances and angles are listed in Tables II and III, respectively. The molecule consists of a square-pyramidal cluster of five ruthenium atoms, with a quadruply bridging sulfido ligand spanning the square base. This portion of the molecule is very similar to that of its parent **1**.[8] Compound **1** was found to exist in two isomeric forms in the solid

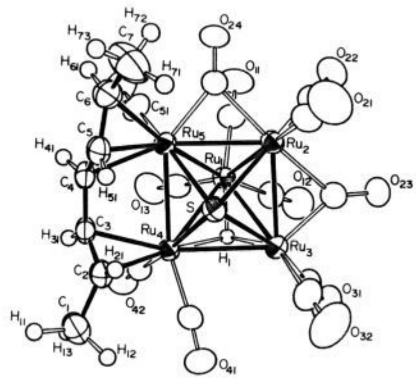


Figure 1. ORTEP diagram of $Ru_5(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$, **3**, showing 50% probability thermal motion ellipsoids.

Table II. Intramolecular Distances for $Ru_5(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$, **3**

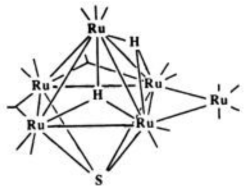
Ru1–H1	1.73 (4)	Ru5–C51	1.861 (7)
Ru1–C11	1.878 (7)	Ru5–C24	2.037 (6)
Ru1–C12	1.894 (6)	Ru5–C5	2.227 (6)
Ru1–C13	1.901 (8)	Ru5–C4	2.227 (6)
Ru1–Ru5	2.794 (1)	Ru5–C6	2.401 (6)
Ru1–Ru2	2.821 (1)	Ru5–S	2.437 (2)
Ru1–Ru4	2.927 (1)	O11–C11	1.144 (7)
Ru1–Ru3	2.973 (1)	O12–C12	1.127 (7)
Ru2–C22	1.883 (6)	O13–C13	1.155 (8)
Ru2–C21	1.922 (7)	O21–C21	1.126 (7)
Ru2–C24	2.118 (6)	O22–C22	1.142 (7)
Ru2–C23	2.146 (6)	O23–C23	1.158 (7)
Ru2–S	2.465 (2)	O24–C24	1.159 (7)
Ru2–Ru3	2.761 (1)	O31–C31	1.133 (7)
Ru2–Ru5	2.766 (1)	O32–C32	1.135 (8)
Ru3–C32	1.861 (7)	O41–C41	1.149 (7)
Ru3–C31	1.891 (7)	O42–C42	1.140 (7)
Ru3–C23	1.998 (6)	O51–C51	1.140 (7)
Ru3–S	2.424 (2)	C1–C2	1.500 (9)
Ru3–Ru4	2.861 (1)	C2–C3	1.403 (8)
Ru4–C41	1.874 (6)	C3–C4	1.448 (8)
Ru4–C42	1.876 (6)	C4–C5	1.426 (8)
Ru4–C2	2.244 (6)	C5–C6	1.374 (9)
Ru4–C3	2.293 (6)	C6–C7	1.49 (1)
Ru4–S	2.449 (2)		
Ru4–Ru5	2.866 (1)		

Table III. Intramolecular Bond Angles for $Ru_5(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$, **3**[a]

C11–Ru1–Ru5	88.6 (2)	C3–Ru4–Ru3	150.5 (2)
C11–Ru1–Ru2	82.6 (2)	C3–Ru4–Ru5	71.6 (1)
C11–Ru1–Ru4	147.4 (2)	C3–Ru4–Ru1	118.5 (2)
C11–Ru1–Ru3	134.8 (2)	S–Ru4–Ru3	53.66 (4)
C12–Ru1–Ru5	165.0 (2)	S–Ru4–Ru5	53.90 (4)
C12–Ru1–Ru2	106.0 (2)	S–Ru4–Ru1	80.71 (4)
C12–Ru1–Ru4	122.3 (2)	Ru3–Ru4–Ru5	87.63 (2)
C12–Ru1–Ru3	83.4 (2)	Ru3–Ru4–Ru1	61.81 (3)
C13–Ru1–Ru5	98.3 (2)	Ru5–Ru4–Ru1	57.66 (2)
C13–Ru1–Ru2	156.6 (2)	C51–Ru5–Ru2	120.8 (2)
C13–Ru1–Ru4	84.4 (2)	C51–Ru5–Ru1	84.8 (2)
C13–Ru1–Ru3	133.2 (2)	C51–Ru5–Ru4	116.0 (2)
Ru5–Ru1–Ru2	59.02 (3)	C24–Ru5–Ru2	49.5 (2)
Ru5–Ru1–Ru4	60.08 (3)	C24–Ru5–Ru1	90.9 (2)
Ru5–Ru1–Ru3	86.81 (3)	C24–Ru5–Ru4	139.7 (2)
Ru2–Ru1–Ru4	87.93 (3)	C5–Ru5–C4	37.3 (2)
Ru2–Ru1–Ru3	56.85 (3)	C5–Ru5–C6	34.3 (2)
Ru4–Ru1–Ru3	58.01 (3)	C5–Ru5–Ru2	127.7 (2)
C22–Ru2–Ru3	122.4 (2)	C5–Ru5–Ru1	154.4 (2)
C22–Ru2–Ru5	122.2 (2)	C5–Ru5–Ru4	92.5 (2)
C22–Ru2–Ru1	92.2 (2)	C4–Ru5–C6	63.6 (2)
C21–Ru2–Ru3	112.4 (2)	C4–Ru5–Ru2	152.8 (2)
C21–Ru2–Ru5	115.7 (2)	C4–Ru5–Ru1	122.4 (2)
C21–Ru2–Ru1	173.8 (2)	C4–Ru5–Ru4	71.7 (2)
C24–Ru2–Ru3	138.7 (2)	C6–Ru5–Ru2	117.4 (2)
C24–Ru2–Ru5	47.0 (2)	C6–Ru5–Ru1	170.9 (2)
C24–Ru2–Ru1	88.5 (2)	C6–Ru5–Ru4	126.7 (2)
C23–Ru2–Ru3	46.0 (2)	S–Ru5–Ru2	56.13 (4)
C23–Ru2–Ru5	136.8 (2)	S–Ru5–Ru1	83.70 (5)
C23–Ru2–Ru1	88.6 (2)	S–Ru5–Ru4	54.27 (3)
S–Ru2–Ru3	54.93 (4)	Ru2–Ru5–Ru1	60.98 (3)
S–Ru2–Ru5	55.18 (4)	Ru2–Ru5–Ru4	90.24 (2)
S–Ru2–Ru1	82.63 (5)	Ru1–Ru5–Ru4	62.26 (2)
Ru3–Ru2–Ru5	91.68 (2)	Ru3–S–Ru5	109.28 (6)
Ru3–Ru2–Ru1	64.36 (3)	Ru3–S–Ru4	71.90 (5)
Ru5–Ru2–Ru1	60.00 (3)	Ru3–S–Ru2	68.76 (5)
C32–Ru3–Ru2	117.0 (2)	Ru5–S–Ru4	71.83 (5)
C32–Ru3–Ru4	114.2 (2)	Ru5–S–Ru2	68.69 (5)
C32–Ru3–Ru1	171.7 (2)	Ru4–S–Ru2	108.63 (6)
C31–Ru3–Ru2	134.4 (2)	C3–C2–C1	121.1 (6)
C31–Ru3–Ru4	114.6 (2)	C3–C2–Ru4	73.9 (3)
C31–Ru3–Ru1	100.0 (2)	C1–C2–Ru4	119.4 (4)
C23–Ru3–Ru2	50.6 (2)	C2–C3–C4	127.4 (6)
C23–Ru3–Ru4	139.8 (2)	C2–C3–Ru4	70.1 (3)
C23–Ru3–Ru1	87.3 (2)	C4–C3–Ru4	105.9 (4)
S–Ru3–Ru2	56.31 (4)	C5–C4–C3	125.0 (6)
S–Ru3–Ru4	54.45 (4)	C5–C4–Ru5	71.3 (3)
S–Ru3–Ru1	80.14 (5)	C3–C4–Ru5	110.7 (4)
Ru2–Ru3–Ru4	90.43 (2)	C6–C5–C4	121.6 (6)
Ru2–Ru3–Ru1	58.80 (2)	C6–C5–Ru5	79.8 (4)
Ru4–Ru3–Ru1	60.18 (3)	C4–C5–Ru5	71.3 (3)
C41–Ru4–Ru3	72.7 (2)	C5–C6–C7	120.7 (8)
C41–Ru4–Ru5	150.0 (2)	C5–C6–Ru5	65.9 (3)
C41–Ru4–Ru1	125.4 (2)	C7–C6–Ru5	122.4 (6)
C42–Ru4–Ru3	125.9 (2)	Ru3–C23–Ru2	83.5 (2)
C42–Ru4–Ru5	119.9 (2)	Ru5–C24–Ru2	83.4 (2)
C42–Ru4–Ru1	93.0 (2)	O23–C23–Ru3	141.1 (5)
C2–Ru4–C3	36.0 (2)	O23–C23–Ru2	135.4 (5)
C2–Ru4–Ru3	130.0 (2)	O24–C24–Ru5	140.6 (5)
C2–Ru4–Ru5	93.9 (2)	O24C24–Ru2	135.9 (5)
C2–Ru4–Ru1	150.7 (2)	O–C–Ru(av)	177.7 (6)

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

state that differ in the arrangement of the carbonyl ligands. One isomer contained four bridging carbonyl ligands about the edges of the square base. The other isomer contained three edge-bridging carbonyl ligands and one triply bridging carbonyl ligand. The Ru–Ru distances in **3** are very similar to those of both isomers of **1**. The shortest Ru–Ru bonds are those in the square base of the cluster that are bridged by carbonyl ligands, Ru2–Ru3 = 2.761 (1) Å and Ru2–Ru5 = 2.766 (1) Å. As in **1** the distances to the apical atom Ru1 are generally longer than those in the square base, but two of these, Ru1–Ru3 = 2.973 (1) Å and Ru(1)–Ru4 = 2.927 (1) Å, are exceptional. The unusual lengths of these can be attributed to the presence of a triply bridging hydride ligand H1 that was located and refined and was found to bridge the Ru1, Ru3, Ru4 triangular face of the cluster. The Ru–H distances of 1.73 (4), 1.89 (5), and 1.93 (5) Å are similar to those found in the complex $Ru_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}H)_2$, **5**.[10] The tendency of bridging hydride ligands to produce lengthening effects on metal–metal bonds is well-known,[11] although there are only a few structural studies that have demonstrated this effect for triply bridging hydride ligands.[10,11b,12] The hydride ligand in **3** exhibits a characteristic high-field NMR shift, −14.95 ppm, similar to those of the hydride ligands in **5**.



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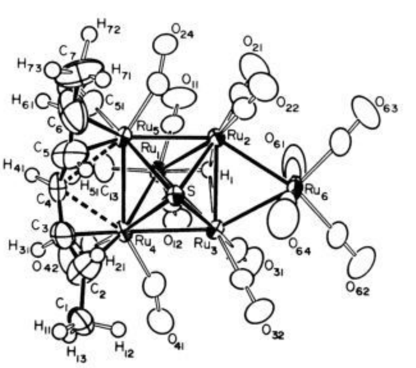


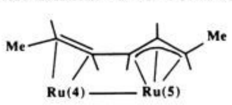
Figure 2. ORTEP diagram of $Ru_6(CO)_{15}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$, **4**, showing 50% probability thermal motion ellipsoids.

Table IV. Intramolecular Distances for $Ru_6(CO)_{15}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$, **4**[a]

Ru1–H1	1.76 (8)	Ru4–C41	1.89 (1)
Ru1–C13	1.87 (1)	Ru4–C3	2.18 (1)
Ru1–C12	1.90 (1)	Ru4–C2	2.28 (1)
Ru1–C11	1.90 (1)	Ru4–C4	2.58 (1)
Ru1–Ru4	2.789 (1)	Ru4–S	2.467 (2)
Ru1–Ru5	2.797 (1)	Ru4–Ru5	2.900 (1)
Ru1–Ru3	2.948 (1)	Ru5–C51	1.86 (1)
Ru1–Ru2	2.977 (1)	Ru5–C24	1.89 (1)
Ru2–H1	1.81 (8)	Ru5–C5	2.20 (1)
Ru2–C22	1.84 (1)	Ru5–C6	2.32 (1)
Ru2–C21	1.87 (1)	Ru5–C4	2.47 (1)
Ru2–C24	2.40 (1)	Ru5–S	2.478 (2)
Ru2–S	2.426 (2)	Ru6–C62	1.91 (1)
Ru2–Ru6	2.758 (1)	Ru6–C63	1.92 (1)
Ru2–Ru5	2.781 (1)	Ru6–C61	1.93 (1)
Ru2–Ru3	2.848 (1)	Ru6–C64	1.95 (1)
Ru3–H1	2.04 (8)	O–C(av)	1.14 (1)
Ru3–C31	1.84 (1)	C1–C2	1.48 (2)
Ru3–C32	1.87 (1)	C2–C3	1.18 (1)
Ru3–S	2.446 (2)	C3–C4	1.38 (1)
Ru3–Ru6	2.761 (1)	C4–C5	1.44 (2)
Ru3–Ru4	2.818 (1)	C5–C6	1.20 (2)
Ru4–C42	1.85 (1)	C6–C7	1.39 (2)

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

The η^5-1,5-dimethylpentadienyl bridges the Ru4–Ru5 basal edge of the cluster. It contains the S-conformation B with two carbon atoms bonded to Ru4, Ru4–C2 = 2.244 (6) Å and Ru4–C3 = 2.293 (6) Å, and three carbon atoms bonded to Ru5, Ru5–C4 = 2.227 (6) Å, Ru5–C5 = 2.227 (6) Å, and Ru5–C6 = 2.401 (6) Å. The long Ru4···C4 distance of 3.029 (6) Å indicates a lack of significant bonding between these atoms. One could view the coordination of the ligand in a form that could be described as a combination of olefin and allyl groups attached to Ru4 and Ru5, respectively, D, but the similar C–C bond lengths suggest that there is a significant amount of electron delocalization and π-unsaturation throughout the entire length of the π-bonded chain. The π-bonded chain is not perfectly planar but is slightly twisted such that the dihedral angle between the C2, C3, C4 and the C4, C5, C6 planes is 15°. Both methyl groups at the termini of the chain adopt syn conformations. Compound **3** contains bridging carbonyl ligands on the Ru2–Ru3 and Ru2–Ru5 basal edges of the cluster. The other carbonyl ligands are of a terminal type. The apical metal atom of the cluster contains three terminal CO ligands. It is believed to be significant that the arrangement of this $Ru(CO)_3$ group has one CO ligand (C11–O11) positioned trans to the bridging hydride ligand.



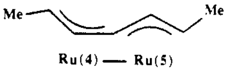
D

Table V. Intramolecular Bond Angles for $Ru_6(CO)_{15}(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$, **4**[a]

H1–Ru1–Ru4	97 (2)	C41–Ru4–Ru1	108.1 (3)
H1–Ru1–Ru5	90 (2)	C41–Ru4–Ru3	61.2 (3)
H1–Ru1–Ru3	43 (3)	C41–Ru4–Ru5	149.6 (3)
H1–Ru1–Ru2	34 (2)	C3–Ru4–C2	30.7 (4)
C13–Ru1–Ru4	81.7 (3)	C3–Ru4–Ru1	135.2 (3)
C13–Ru1–Ru5	82.3 (3)	C3–Ru4–Ru3	145.2 (4)
C13–Ru1–Ru3	138.8 (3)	C3–Ru4–Ru5	83.2 (3)
C13–Ru1–Ru2	138.4 (3)	C2–Ru4–Ru1	162.3 (4)
C12–Ru1–Ru4	102.5 (3)	C2–Ru4–Ru3	122.0 (4)
C12–Ru1–Ru5	164.8 (3)	C2–Ru4–Ru5	103.5 (4)
C12–Ru1–Ru3	85.5 (3)	S–Ru4–Ru1	82.58 (6)
C12–Ru1–Ru2	128.7 (3)	S–Ru4–Ru3	54.64 (5)
C11–Ru1–Ru4	164.1 (3)	S–Ru4–Ru5	54.28 (5)
C11–Ru1–Ru5	101.9 (3)	Ru1–Ru4–Ru3	63.45 (3)
C11–Ru1–Ru3	127.7 (3)	Ru1–Ru4–Ru5	58.87 (3)
C11–Ru1–Ru2	85.6 (3)	Ru3–Ru4–Ru5	89.22 (3)
Ru4–Ru1–Ru5	62.56 (3)	C51–Ru5–Ru2	120.9 (3)
Ru4–Ru1–Ru3	58.77 (3)	C51–Ru5–Ru1	85.5 (3)
Ru4–Ru1–Ru2	88.01 (3)	C51–Ru5–Ru4	117.3 (3)
Ru5–Ru1–Ru3	88.66 (3)	C24–Ru5–Ru2	58.2 (3)
Ru5–Ru1–Ru2	57.48 (3)	C24–Ru5–Ru1	104.9 (4)
Ru3–Ru1–Ru2	57.46 (2)	C24–Ru5–Ru4	147.7 (3)
H1–Ru2–Ru6	80 (2)	C5–Ru5–C6	30.6 (4)
H1–Ru2–Ru5	90 (2)	C5–Ru5–Ru2	133.9 (5)
H1–Ru2–Ru3	46 (2)	C5–Ru5–Ru1	140.0 (4)
H1–Ru2–Ru1	33 (2)	C5–Ru5–Ru4	83.8 (4)
C22–Ru2–Ru6	81.9 (3)	C6–Ru5–Ru2	128.5 (4)
C22–Ru2–Ru5	107.1 (3)	C6–Ru5–Ru1	166.6 (3)
C22–Ru2–Ru3	125.5 (3)	C6–Ru5–Ru4	114.4 (4)
C22–Ru2–Ru1	165.1 (3)	S–Ru5–Ru2	54.58 (5)
C21–Ru2–Ru6	94.1 (3)	S–Ru5–Ru1	82.20 (6)
C21–Ru2–Ru5	118.3 (3)	S–Ru5–Ru4	53.91 (5)
C21–Ru2–Ru3	126.7 (3)	Ru2–Ru5–Ru1	64.50 (3)
C21–Ru2–Ru1	96.5 (3)	Ru2–Ru5–Ru4	89.71 (3)
C24–Ru2–Ru6	160.3 (3)	Ru1–Ru5–Ru4	58.58 (3)
C24–Ru2–Ru5	41.9 (3)	C62–Ru6–Ru2	163.6 (3)
C24–Ru2–Ru3	132.9 (3)	C62–Ru6–Ru3	101.8 (3)
C24–Ru2–Ru1	87.9 (3)	C63–Ru6–Ru2	99.8 (3)
S–Ru2–Ru6	90.94 (5)	C63–Ru6–Ru3	161.8 (3)
S–Ru2–Ru5	56.36 (5)	C61–Ru6–Ru2	85.1 (3)
S–Ru2–Ru3	54.55 (5)	C61–Ru6–Ru3	85.6 (3)
S–Ru2–Ru1	79.38 (6)	C64–Ru6–Ru2	88.4 (3)
Ru6–Ru2–Ru5	145.96 (3)	C64–Ru6–Ru3	86.7 (3)
Ru6–Ru2–Ru3	58.99 (3)	Ru2–Ru6–Ru3	62.13 (2)
Ru6–Ru2–Ru1	111.24 (3)	Ru2–S–Ru3	71.55 (6)
Ru5–Ru2–Ru3	91.04 (3)	Ru2–S–Ru4	109.97 (8)
Ru5–Ru2–Ru1	58.02 (3)	Ru2–S–Ru5	69.06 (6)
Ru3–Ru2–Ru1	60.77 (2)	Ru3–S–Ru4	70.02 (6)
C31–Ru3–Ru6	94.2 (3)	Ru3–S–Ru5	109.30 (8)
C31–Ru3–Ru4	119.3 (3)	Ru4–S–Ru5	71.81 (6)
C31–Ru3–Ru2	125.8 (3)	C3–C2–C1	143 (2)
C31–Ru3–Ru1	94.9 (3)	C3–C2–Ru4	70.2 (7)
C32–Ru3–Ru6	82.1 (3)	C1–C2–Ru4	125.0 (9)
C32–Ru3–Ru4	108.6 (3)	C2–C3–C4	150 (2)
C32–Ru3–Ru2	127.4 (3)	C2–C3–Ru4	79.1 (7)
C32–Ru3–Ru1	165.4 (3)	C4–C3–Ru4	89.8 (6)
S–Ru3–Ru6	90.44 (6)	C3–C4–C5	120 (1)
S–Ru3–Ru4	55.35 (5)	C6–C5–C4	142 (2)
S–Ru3–Ru2	53.90 (5)	C6–C5–Ru5	80 (1)
S–Ru3–Ru1	79.66 (5)	C4–C5–Ru5	82.5 (6)
Ru6–Ru3–Ru4	144.56 (3)	C5–C6–C7	144 (2)
Ru6–Ru3–Ru2	58.87 (3)	C5–C6–Ru5	69.5 (8)
Ru6–Ru3–Ru1	111.99 (3)	C7–C6–Ru5	129 (1)
Ru4–Ru3–Ru2	90.02 (3)	Ru5–C24–Ru2	79.9 (4)
Ru4–Ru3–Ru1	57.78 (2)	Ru1–H1–Ru2	113 (4)
Ru2–Ru3–Ru1	61.77 (3)	O24–C24–Ru5	157 (1)
C42–Ru4–Ru1	88.5 (3)	O24–C24–Ru2	123.8 (9)
C42–Ru4–Ru3	123.0 (3)	O41–C41–Ru4	159 (1)
C42–Ru4–Ru5	118.5 (3)	O–C–Ru(av)	177 (1)

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

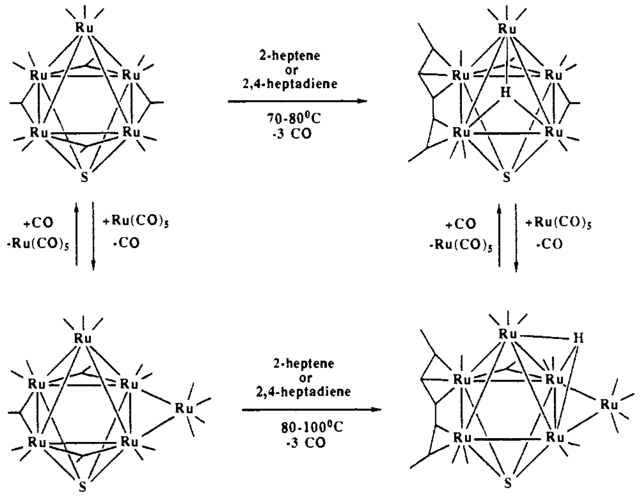
An ORTEP drawing of the molecular structure of **4** is shown in Figure 2. Interatomic distances and angles are listed in Tables IV and V. The gross structure of **4** is very similar to that of **3**. It consists of a square-pyramidal cluster of five ruthenium atoms with a quadruply bridging sulfido ligand on the square base. It differs from **3** in that the bridging CO group along the Ru2–Ru3 bond has been replaced with a bridging $Ru(CO)_4$ group. The cluster is thus very similar to **5** and its parent carbonyl complex **2**. The metal–metal bonding in **4** is similar to that in **3** with the following exceptions: (1) The Ru2–Ru3 bond in **4** is 0.09 Å longer than that in **3**. This could be due to the replacement of the bridging CO ligand in **3** with the bridging $Ru(CO)_4$ group. (2) The Ru1–Ru2 bond in **4** (2.977 (1) Å) is 0.15 Å longer than that in **3**, and the Ru1–Ru4 bond (2.789 (1) Å) and Ru3–Ru4 bond (2.818 (1) Å) in **4** are significantly shorter 0.14 and 0.04 Å, respectively, than the corresponding bonds in **3**. All of these effects could be explained by distortions caused by the different location of the bridging hydride ligand (located and refined) in **4** compared to that in **3**. In **4** the hydride ligand H1 (^{1}H NMR δ −13.51) was found to bridge the Ru1, Ru2, Ru3 triangular face, Ru1–H1 = 1.76 (8) Å, Ru2–H1 = 1.81 (8) Å, and Ru3–H1 = 2.04 (8) Å. On the basis of the Ru–H distances it appears to be an unsymmetrical bridge, but this is uncertain in view of the relatively large estimated standard deviations. An η^5-1,5-dimethylpentadienyl ligand bridges the Ru4–Ru5 edge of the cluster and possesses an S-conformation as in **3**. Overall, the pentadienyl ligand in **4** is shifted closer to Ru4 than it is in **3**. This is apparent from a comparison of the Ru–C distances to C4. In **4** Ru4–C4 = 2.58 (1) Å and Ru5–C4 = 2.47 (1) Å, while in **3** Ru4–C4 = 3.029 (6) Å and Ru5–C4 = 2.227 (6) Å. The bonding could be represented as shown in structure E. The final results show two of the carbon–carbon bond distances in the pentadienyl ligand to be anomalously short, C2–C3 = 1.18 (1) Å and C5–C6 = 1.20 (2) Å. These distances seem to be much too short to be true, and an explanation for these unusual values was considered. It was observed that the crystallographic thermal parameters of atoms C2, C3, C5, and C6 in **4** were significantly larger (range B(eq) = 6.3–8.7 Å^2 than those of the corresponding atoms in **3** (range B(eq) = 3.1–4.3 Å^2). It is believed that the larger values in **4** are due to a small unresolved solid-state disorder in the position of these atoms. The center of thermal ellipsoid is thus an average value of the true positions, and all C–C distances associated with these atoms will be subject to error that exceeds the estimated standard deviation values that were derived from the least-squares refinement. Compound **4** contains two semibridging carbonyl ligands C24–O24 and C41–O41. All the others are terminal ligands. Interestingly, the $Ru(CO)_3$ group of the apex of the square pyramid has adopted a rotational conformation that orients one of the CO ligands into a position trans to the triply bridging hydride ligand.



E

When treated with CO under 1 atm of pressure at 98 °C, the edge-bridging $Ru(CO)_4$ group in **4** was removed and **4** was converted to **3** in 30% yield (see Scheme I). This process is partially reversible. Treatment of **3** with $Ru(CO)_5$ at 80 °C produced **4** in 37% yield. A similar relationship was observed between **1** and **2**.[8]

Scheme I



The only previous report of the preparation of a complex containing acyclic η^5-pentadienyl ligands in one step from an olefin precursor was for the complex $Ni_2(\mu\text{-}C_5H_7)_2$.[6,13,14] This complex contains two metal atoms, but since it was made from mononuclear nickel reagents, the metal nuclearity of the intermediates, when the olefin (1,4-pentadiene) was transformed into the pentadienyl ligand, is not known. Since the conversion of olefins into pentadienyl ligands requires the activation of one or more aliphatic C–H bonds, this process may be easier in polynuclear metal complexes where the olefin can be coordinated to one metal atom and undergo C–H activation at a neighbor.[16] Thus, transition-metal cluster compounds may, in general, prove to be an excellent class of compounds for the formation of complexes containing pentadienyl ligands directly from olefins. However, the higher yields of **3** and **4** obtained from the 2,4-heptadiene are probably due to the fact that fewer C–H bond activation steps are required to convert this olefin into the pentadienyl ligand.

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Supplementary Material Available: Tables of positional parameters and anisotropic thermal parameters (9 pages); listings of observed and calculated structure factor amplitudes for both structural analyses (43 pages). Ordering information is given on any current masthead page.

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