

Structural Variations in Hexanuclear Ruthenium Clusters with Thioureato Ligands: Syntheses and Molecular Structures of $[\text{Ru}_6(\text{CO})_{14}(\mu\text{-CO})_2(\mu_4\text{-S})(\mu_3,\eta^2\text{-SCNHPPhNPh})(\mu_3,\eta^2\text{-NPhCNHPh})]$ and $[(\mu\text{-H})_6\text{Ru}_6(\text{CO})_{14}(\mu_3,\eta^2\text{-SCNHPPhNPh})_2]$

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Under thermal conditions, the trinuclear ruthenium cluster $[(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3,\eta^2\text{-SCNHPPhNPh})]$ (**1**) was found to undergo metal framework condensation to hexanuclear ruthenium clusters. The hexanuclear cluster $[\text{Ru}_6(\text{CO})_{14}(\mu_2\text{-CO})_2(\mu_4\text{-S})(\mu_3,\eta^2\text{-SCNHPPhNPh})(\mu_3,\eta^2\text{-NPhCNHPh})]$ (**2**), shown by X-ray crystallography to contain a hexagonal boat arrangement of the six metal atoms, was isolated along with the hexagonal sofa-like cluster $[(\mu_2\text{-H})\text{Ru}_6(\text{CO})_{16}(\mu_5\text{-S})(\mu_3,\eta^2\text{-SCNHPPhNPh})]$ (**3**), reported previously. Crystals of **2** are triclinic, space group $P\bar{1}$, with $a = 12.141(3)$ Å, $b = 12.449(4)$ Å, $c = 19.712(6)$ Å, $\alpha = 90.22(3)^\circ$, $\beta = 99.50(2)^\circ$, $\gamma = 111.61(2)^\circ$, and $Z = 2$. Compound **3** was found to take up molecular hydrogen under mild conditions to give $[(\mu_2\text{-H})_6\text{Ru}_6(\text{CO})_{14}(\mu_3,\eta^2\text{-SCNHPPhNPh})_2]$ (**4**), the X-ray structure analysis of which reveals a hexagonal raft arrangement of the Ru_6 skeleton. Crystals of **4** are triclinic, space group $P\bar{1}$, with $a = 9.799(1)$ Å, $b = 12.594(2)$ Å, $c = 14.466(1)$ Å, $\alpha = 112.45(1)^\circ$, $\beta = 92.71(1)^\circ$, $\gamma = 102.05(1)^\circ$, and $Z = 1$.

Introduction

Interest in hexanuclear transition metal clusters remains strong because of their potential to serve as models for metal surfaces as well as reagents for the preparation of new compounds. The structural motifs displayed by this group of compounds are well documented.¹ The majority of M_6 clusters adopt an octahedral geometry, for which $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ is a typical example.² Many clusters have been isolated whose geometries are derived from standard polyhedra by capping or bridging in order to provide the additional vertices necessary to accommodate all the additional metal atoms. These include the biccapped tetrahedral geometry and the capped square pyramid, as exemplified by $[\text{Os}_6(\text{CO})_{17}(\text{MeCN})]$ and $[\text{Os}_6(\text{CO})_{17}(\mu_4,\eta^2\text{-HCCEt})]$, respectively.³ As opposed to structures created by the addition of vertices, the structures of some hexanuclear clusters can be considered as large polyhedra with missing vertices. This is the case in the edge-bridged diminished pentagonal bipyramid found for $[(\mu_2\text{-H})\text{Ru}_6\text{C}(\text{CO})_{15}(\text{SEt})_3]$.⁴ Further variations are planar raft structures, including both the triangular raft $[(\mu_3\text{-H})\text{Ru}_6(\text{CO})_{15}(\mu_3\text{-S})_3]^-$ ⁵ and the rhombic raft cluster $[(\mu_2\text{-H})_4(\mu_3\text{-H})_2\text{Ru}_6(\text{CO})_{14}(\mu_3,\eta^2\text{-ampy})_2]$.⁶ Distortion of the metal plane of the rhombic raft cluster results in alternative core configurations.

Some of these configurations resemble the various conformers of cyclohexane while others represent structural intermediates between the chair and boat conformations.⁷ Only a few reports have appeared of hexanuclear clusters with geometries analogous to the boat conformer of cyclohexane.⁸

Thioureato ligands appear to be particularly well-suited for structural variations of the Ru_6 metal core. Recently we reported the synthesis of the hexanuclear cluster $[(\mu_2\text{-H})\text{Ru}_6(\text{CO})_{16}(\mu_5\text{-S})(\mu^3,\eta^2\text{-SCNHPPhNPh})]$ (**3**). The X-ray crystal structure analysis revealed an unprecedented sofa-like arrangement of the Ru_6 metal core.^{8d} From a similar reaction, the thermolysis of the trinuclear cluster $[(\mu_2\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3,\eta^2\text{-SCNHPPhNPh})]$ (**1**) in cyclohexane instead of tetrahydrofuran, we were able to isolate a minor product which proved to be $[\text{Ru}_6(\mu_2\text{-CO})_2(\text{CO})_{14}(\mu_4\text{-S})(\mu_3,\eta^2\text{-SCNHPPhNPh})(\mu_3,\eta^2\text{-NPhCNHPh})]$ (**2**), wherein the metal framework presents a hexagonal boatlike arrangement of the six metal atoms. From the reaction of **3** with molecular hydrogen, we obtained the hexanuclear cluster $[(\mu_2\text{-H})_6\text{Ru}_6(\text{CO})_{14}(\mu_3,\eta^2\text{-SCNHPPhNPh})_2]$ (**4**). The X-ray crystal structural analysis shows a raftlike arrangement of the Ru_6 metal core.

Experimental Section

All operations were carried out under nitrogen using standard Schlenk techniques. Solvents were purified, distilled over the appropriate drying agents, and stored under nitrogen prior to use. Preparative thin-layer chromatography was performed on plates coated with Al_2O_3 . Infrared spectra were recorded on a Perkin Elmer FT IR 1720 spectrophotometer using cyclohexane solutions or KBr pellets. ¹H NMR spectra were obtained on a Bruker WM 400 instrument. Elemental analyses were performed by the Mikroelementaranalytisches Laboratorium der Eidgenössischen Technischen Hochschule Zürich.

The compounds $[(\mu_2\text{-H})\text{Ru}_6(\text{CO})_{16}(\mu_5\text{-S})(\mu_3,\eta^2\text{-SCNHPPhNPh})]$ (**3**) and $[(\mu_2\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3,\eta^2\text{-SCNHPPhNPh})]$ (**1**) were prepared according

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Table 1. Data for Crystal Structure Analyses^a

	2	4
molecular formula	C ₄₂ H ₂₂ Cl ₄ N ₄ O ₁₆ Ru ₆ S ₂ ·2CH ₂ Cl ₂	C ₄₀ H ₂₆ N ₄ O ₁₄ Ru ₆ S ₂ ·4(CH ₃) ₂ CO
<i>M</i>	1679.06	1689.50
<i>Z</i>	2	1
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>T</i> /°C	-80	-70
<i>a</i> /Å	12.141(3)	9.799(1)
<i>b</i> /Å	12.449(4)	12.594(2)
<i>c</i> /Å	19.712(6)	14.466(1)
α /deg	90.22(3)	112.45(1)
β /deg	99.50(2)	92.71(1)
γ /deg	111.61(2)	102.05(1)
<i>V</i> /Å ³	2725.1(1)	1597.6(3)
<i>D</i> _c /g cm ⁻³	2.046	1.756
μ (Mo K α)/mm ⁻¹	1.93	2.91
<i>R</i> (<i>R</i> ') ^b	0.045 (0.059)	0.042 (0.048)

^a Details in common: data collected on a Stoe-Siemens AED 2 four-circle diffractometer; graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å. ^b Refinement was by full-matrix least squares with a weighting scheme of the form $w^{-1} = \sigma^2(F_o) + k(F_o^2)$. $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

to published procedures.^{8d,9} Other reagents were purchased from Fluka and used as received.

Isolation of [Ru₆(CO)₁₆(μ_4 -S)(μ_3, η^2 -SCNHPPhNPh)(μ_3, η^2 -NPhC-NPh)] (2). A solution of compound 1 (65 mg, 0.083 mmol) in cyclohexane (25 mL) was prepared in a pressure Schlenk tube (125 cm³). The tube was placed in a preheated 130 °C oil bath, and the contents were stirred for 30 min. Following evaporation of the solvent, the residue was dissolved in dichloromethane and the products were separated by preparative TLC (cyclohexane-dichloromethane, 75:25), which gave 3 (46%) as a red band and 2 as a blue band (5% yield) (in order of elution). Compound 2 was isolated from a dichloromethane-cyclohexane solution; a dichloromethane-pentane solution of 2 at -18 °C produced blue-black, rectangular-rod, X-ray-quality crystals: IR (cyclohexane) (ν_{CO}) 2082 m, 2057 s, 2036 vs, 2005 m, 1976 m, 1854 m, br; IR (KBr) (ν_{NH}) 3343 w, 3304 w, (ν_{CN}) 1558 m, 1498 m; ¹H NMR (CDCl₃, 298 K) δ 7.72-6.41 (m, 20H, C₆H₅), 6.28 (br s, 1H, NH), 6.22 (br s, 1H, NH). Anal. Calcd for C₄₂H₂₂N₄O₁₆Ru₆S₂·CH₂Cl₂·²/₃C₆H₁₂: C, 34.2; H, 1.95; N, 3.40. Found: C, 34.51; H, 2.19; N, 3.47.

Synthesis of [(μ_2 -H)Ru₆(CO)₁₄(μ_3, η^2 -SCNHPPhNPh)₂] (4). A solution of 3 (50 mg, 0.038 mmol) was prepared in an autoclave in CH₂Cl₂ (10 mL). The autoclave was charged with 5 atm of H₂ and the solution stirred for 6 h. After the pressure was released, the solution volume was reduced and the products were separated by preparative TLC (cyclohexane-dichloromethane, 75:25). The fast-moving band contained the previously reported compound [(μ_2 -H)₂Ru₃(CO)₉(μ_3 -S)] (31%).¹⁰ Just below was a band containing the trinuclear complex 1 (25%). Samples of compound 4 for analytical measurements were isolated from a dichloromethane-cyclohexane solution (13%); orange-red, block crystals of 4 could be obtained from acetone-heptane solutions (75:25) at -18 °C. Spectroscopic data for 4: IR (cyclohexane) (ν_{CO}) 2073 m, 2061 vs, 2049 s, 2010 s, 1989 s, br; IR (KBr) (ν_{NH}) 3370 m, (ν_{CN}) 1563 m; ¹H NMR (C₂D₆O, 298 K) δ 8.35 (br s, 1H, NH), 7.66-7.08 (m, 10H, C₆H₅), -12.48 (br s, 1H, μ -H), -13.14 (d(d), *J* = 5.86 (1.86) Hz, 1H, μ -H), -16.05 (m, 1H, μ -H). Anal. Calcd for C₄₀H₂₆N₄O₁₄Ru₆S₂·CH₂Cl₂: C, 31.9; H, 1.93; N, 3.63. Found: C, 31.9; H, 2.08; N, 3.62.

X-ray Crystallography. The crystal data and experimental parameters for compounds 2 and 4 are given in Table 1. Data for 2 were collected at -80 °C while those for 4 were collected at -70 °C. The structures were solved by direct methods (SHELXS);¹¹ all further calculations were carried out using the NRCVAX system.¹² Two

molecules of solvent, CH₂Cl₂, in structure 2 and four molecules of acetone in structure 4 were located from difference maps. Complex neutral atom scattering factors included in NRCVAX are from ref 13. Hydrogen atoms on the phenyl rings of the thioureato ligands of both compounds were placed in calculated positions. The hydride atoms H2R and H3R of 4 were found in the last difference map, at which point their positions were fixed. No correction for absorption or the presence of extinction was made for either structure. For 2 and 4, residual electron density was found exclusively in the vicinity of the Ru atoms and for 2 near the Cl atoms of the solvent molecules. Atomic coordinates and selected bond lengths and angles for 2 are given in Tables 2 and 3 and for 4 in Tables 4 and 5, respectively.

Results and Discussion

From the thermolysis of [(μ_2 -H)Ru₃(CO)₉(μ_3, η^2 -SCNHPPh-NPh)] (1) the primary product is the hexanuclear sofa-like cluster 3 (46%). The hexanuclear boatlike cluster 2 is also obtained from this reaction, but the yield varies inversely with the duration of the reaction: 5 to 3%. If 2 alone is subjected to thermolysis at 130 °C, it is converted to 3 but only in low yield (6%); therefore, it is not certain that 2 is an intermediate in the formation of 3.

Compound 2 has been characterized by X-ray structural analysis, and its molecular structure is presented in Figure 1.¹⁴ Of the six ruthenium atoms comprising the cluster framework, four of them form an approximately square base. Opposite sides of this trapezoid are bridged by the remaining two Ru atoms. Significant deviations from a square geometry occur at the edges bridged by the metal atoms, and large metal-metal bonds are observed [Ru2-Ru4 (3.037(1) Å) and Ru1-Ru5 (3.223(1) Å)]. The remaining Ru-Ru bond lengths fall within the range 2.750(1)-2.916(1) Å. The same sequence of long-short metal bond lengths was observed in the boat clusters cited previously.^{8b-d} The square cluster base is planar within 0.02 Å. Atoms Ru3 and Ru6 lie out of the plane of the square base and form angles with that substructure of 17.27(2) and 19.80(2)°, respectively. The overall result is a metal framework resembling the boat conformer of cyclohexane.

The square base is capped by a μ_4 -sulfur (average Ru-S1 distance 2.469(2) Å). The surface of the cluster opposite the μ_4 -sulfur contains a μ_3, η^2 -diphenylthioureato ligand spanning the triangular substructure composed of atoms Ru2, Ru3, and Ru4. Compared to those of the diethylthioureato cluster analogue,^{8d} the Ru-S2 bonds are slightly longer but the Ru-N2 bond is of the same magnitude (Ru3-N2 2.142(6) Å). The unsaturation at C1 is relieved through formation of a double bond to N2 (N2-C1 1.298(9) Å). On the same side of the cluster, but spanning the second triangular substructure containing atoms Ru1, Ru5, and Ru6, is a μ_3, η^2 -diaminocarbene fragment. Here the Ru-N bonds are identical to those of the previously published diethylthioureato boat cluster (average 2.268(5) Å), while the carbene carbon atom, bound to Ru6, shows a markedly shorter bond to the metal (Ru6-C14 2.044(7) Å). The C-N bond lengths show a lesser degree of sp² character as compared to those of the diethylthioureato ligand (C14-N3 1.324(9) Å, C14-N4 1.399(8) Å), and this is may be responsible for the observed shortening of the Ru6-C14 bond. Bridging carbonyl ligands are found spanning the Ru1-Ru2 bond as well as the Ru4-Ru5 bond and are displaced by ca. 0.94(1) Å below the plane of the four-membered trapezoid

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Table 2. Atomic Parameters of Compound **2** with Estimated Standard Deviations in Parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} ^a
Ru1	0.02631(4)	0.37026(5)	0.21175(3)	2.066(21)
Ru2	-0.20085(5)	0.33300(5)	0.11985(3)	2.026(21)
Ru3	-0.40851(5)	0.37838(5)	0.10413(3)	2.134(22)
Ru4	-0.31612(5)	0.36589(5)	0.23982(3)	2.033(21)
Ru5	-0.09737(5)	0.40556(5)	0.33835(3)	2.085(21)
Ru6	0.14776(5)	0.48067(5)	0.33970(3)	2.284(22)
S1	-0.10472(15)	0.47480(14)	0.22288(9)	1.89(7)
S2	-0.31765(14)	0.18408(14)	0.19025(8)	1.80(6)
N1	-0.5252(5)	0.0126(5)	0.1374(3)	2.5(3)
N2	-0.5029(5)	0.1946(5)	0.0998(3)	1.89(23)
N3	0.1038(5)	0.2300(5)	0.3783(3)	2.23(24)
N4	-0.0442(5)	0.2632(4)	0.2992(3)	1.73(24)
C1	-0.4646(6)	0.1258(6)	0.1375(3)	1.9(3)
C2	-0.5202(6)	-0.0611(6)	0.1928(4)	2.3(3)
C3	-0.5261(7)	-0.1709(7)	0.1773(4)	3.2(4)
C4	-0.5300(8)	-0.2463(7)	0.2292(5)	4.0(4)
C5	-0.5290(8)	-0.2112(8)	0.2962(5)	4.2(4)
C6	-0.5202(8)	-0.1009(8)	0.3120(4)	3.8(4)
C7	-0.5162(7)	-0.0234(7)	0.2598(4)	3.2(4)
C8	-0.6180(6)	0.1440(6)	0.0529(3)	2.0(3)
C9	-0.6240(6)	0.0921(7)	-0.0108(4)	2.5(3)
C10	-0.7286(7)	0.0554(7)	-0.0583(4)	3.1(4)
C11	-0.8292(7)	0.0687(8)	-0.0425(4)	3.4(4)
C12	-0.8251(7)	0.1175(8)	0.0218(5)	3.7(4)
C13	-0.7193(7)	0.1534(7)	0.0700(4)	2.7(3)
C14	0.0684(6)	0.3051(6)	0.3426(3)	1.9(3)
C15	0.2175(6)	0.2617(6)	0.4267(4)	2.4(3)
C16	0.3212(7)	0.2761(8)	0.4012(4)	3.4(4)
C17	0.4294(7)	0.3073(9)	0.4472(5)	4.1(4)
C18	0.4331(8)	0.3239(9)	0.5152(5)	4.4(5)
C19	0.3288(8)	0.3067(8)	0.5400(4)	3.8(4)
C20	0.2187(7)	0.2761(7)	0.4949(4)	3.0(4)
C21	-0.1092(6)	0.1399(6)	0.2976(4)	2.2(3)
C22	-0.1695(6)	0.0924(6)	0.3505(4)	2.6(3)
C23	-0.2221(8)	-0.0272(8)	0.3522(5)	3.9(4)
C24	-0.2156(8)	-0.0998(7)	0.3024(5)	3.6(4)
C25	-0.1573(7)	-0.0525(7)	0.2491(5)	3.6(4)
C26	-0.1026(7)	0.0674(6)	0.2465(4)	2.6(3)
C27	0.1199(7)	0.4924(7)	0.1653(4)	2.7(3)
O27	0.1777(5)	0.5663(5)	0.1389(3)	4.0(3)
C28	0.1389(6)	0.2995(6)	0.2121(4)	2.4(3)
O28	0.2021(5)	0.2518(5)	0.2107(3)	3.5(3)
C29	-0.0638(6)	0.2646(6)	0.1189(4)	2.4(3)
O29	-0.0420(5)	0.2079(5)	0.0819(3)	3.4(3)
C30	-0.1312(6)	0.4578(7)	0.0661(4)	2.5(3)
O30	-0.0926(5)	0.5310(5)	0.0332(3)	3.9(3)
C31	-0.2819(6)	0.2398(6)	0.0389(4)	2.4(3)
O31	-0.3267(5)	0.1837(5)	-0.0113(3)	3.1(3)
C32	-0.3099(7)	0.5382(7)	0.1141(4)	2.8(3)
O32	-0.2541(5)	0.6346(5)	0.1177(3)	3.8(3)
C33	-0.5438(6)	0.4113(6)	0.1238(4)	2.6(3)
O33	-0.6182(5)	0.4344(5)	0.1377(3)	4.0(3)
C34	-0.4472(6)	0.3763(6)	0.0057(4)	2.7(3)
O34	-0.4736(6)	0.3726(5)	-0.0526(3)	4.0(3)
C35	-0.3265(6)	0.5071(6)	0.2630(4)	2.6(3)
O35	-0.3379(5)	0.5919(5)	0.2762(3)	3.8(3)
C36	-0.4765(6)	0.2904(6)	0.2484(3)	2.2(3)
O36	-0.5726(4)	0.2406(5)	0.2560(3)	3.2(3)
C37	-0.2769(6)	0.3109(6)	0.3430(4)	2.3(3)
O37	-0.3367(4)	0.2555(5)	0.3795(3)	3.4(3)
C38	-0.0962(6)	0.5506(6)	0.3664(4)	2.6(3)
O38	-0.0976(5)	0.6391(5)	0.3796(3)	3.7(3)
C39	-0.0614(6)	0.3748(6)	0.4317(4)	2.4(3)
O39	-0.0420(5)	0.3573(5)	0.4878(3)	3.3(3)
C40	0.3003(6)	0.4909(6)	0.3199(4)	2.7(3)
O40	0.3896(5)	0.4985(5)	0.3078(3)	3.6(3)
C41	0.1630(7)	0.6374(7)	0.3177(5)	3.3(4)
O41	0.1668(6)	0.7272(5)	0.3053(4)	5.3(4)
C42	0.2049(7)	0.5226(7)	0.4368(4)	2.9(3)
O42	0.2433(5)	0.5489(5)	0.4928(3)	3.8(3)
C1S	0.096(3)	0.8146(18)	0.1622(11)	16.8(24)
C2S	0.7671(19)	0.0351(15)	0.5772(9)	10.9(13)
C11	0.1507(4)	0.9652(3)	0.21041(20)	8.6(3)
C12	0.1113(4)	0.8275(4)	0.08521(21)	9.0(3)
C13	0.7070(5)	0.1109(5)	0.5222(3)	11.7(4)
C14	0.9194(4)	0.0526(4)	0.5686(3)	12.5(3)

^a *B*_{iso} is the mean of the principal axes of the thermal ellipsoid.**Table 3.** Important Bond Lengths (Å) and Angles (deg) of Compound **2**

Ru1-Ru2	2.9163(11)	Ru4-C37	2.182(7)
Ru1-Ru6	2.7708(13)	Ru5-Ru6	2.7670(11)
Ru1-Ru5	3.2234(11)	Ru5-S1	2.4365(20)
Ru1-S1	2.4311(18)	Ru5-N4	2.269(5)
Ru1-N4	2.268(5)	Ru5-C37	2.079(7)
Ru1-C29	2.130(7)	Ru6-C14	2.044(7)
Ru2-Ru3	2.7504(10)	S2-C1	1.794(7)
Ru2-Ru4	3.0374(11)	N1-C2	1.437(9)
Ru2-S1	2.5050(20)	N1-C1	1.328(9)
Ru2-S2	2.4712(20)	N2-C1	1.298(9)
Ru2-C29	2.133(7)	N2-C8	1.458(8)
Ru3-Ru4	2.7529(11)	N3-C14	1.324(9)
Ru3-N2	2.142(6)	N3-C15	1.461(8)
Ru4-Ru5	2.8972(11)	N4-C14	1.399(8)
Ru4-S1	2.5021(19)	N4-C21	1.442(9)
Ru4-S2	2.4544(19)		
Ru1-Ru2-Ru3	144.19(3)	Ru4-Ru5-S1	55.14(5)
Ru1-Ru2-S1	52.62(4)	Ru4-Ru3-N2	87.38(15)
Ru1-Ru2-C29	46.80(18)	Ru4-Ru5-N4	99.65(13)
Ru1-Ru2-Ru4	91.47(3)	Ru4-S2-C1	101.73(21)
Ru1-Ru2-S2	92.62(5)	Ru4-Ru5-C37	48.67(20)
Ru1-Ru5-Ru6	54.46(3)	Ru4-C37-Ru5	85.6(3)
Ru1-Ru5-N4	44.72(14)	Ru5-Ru1-Ru6	54.35(3)
Ru1-Ru5-Ru4	88.17(3)	Ru5-Ru1-S1	48.60(5)
Ru1-Ru5-S1	48.46(4)	Ru5-Ru1-N4	44.73(13)
Ru1-Ru5-C37	122.64(19)	Ru5-Ru1-C29	126.06(20)
Ru1-Ru6-C14	67.14(19)	Ru5-Ru4-S1	53.04(5)
Ru1-Ru6-Ru5	71.19(3)	Ru5-Ru4-S2	93.18(5)
Ru1-N4-C14	93.2(4)	Ru5-Ru6-C14	67.06(17)
Ru1-N4-Ru5	90.54(19)	Ru5-N4-C14	92.9(4)
Ru1-C29-Ru2	86.3(3)	Ru6-Ru1-S1	84.12(5)
Ru2-Ru1-Ru5	88.17(3)	Ru6-Ru1-N4	68.03(13)
Ru2-Ru1-Ru6	138.18(3)	Ru6-Ru5-S1	84.10(5)
Ru2-Ru3-Ru4	67.00(3)	Ru6-Ru5-N4	68.09(13)
Ru2-Ru4-Ru3	56.46(3)	Ru6-C14-N3	131.6(5)
Ru2-Ru4-Ru5	92.19(3)	Ru6-C14-N4	110.3(4)
Ru2-Ru4-S1	52.70(5)	S1-Ru1-N4	88.83(14)
Ru2-Ru4-S2	52.18(5)	S1-Ru2-S2	91.64(6)
Ru2-Ru3-N2	86.50(14)	S1-Ru4-S2	92.11(6)
Ru2-S2-Ru4	76.15(6)	S1-Ru5-N4	88.69(14)
Ru3-Ru2-Ru4	56.540(25)	S2-C1-N1	117.0(5)
Ru3-Ru4-Ru5	144.70(3)	S2-C1-N2	118.8(5)
Ru3-Ru2-S1	92.30(5)	N1-C1-N2	124.1(6)
Ru3-Ru4-S1	92.30(5)	N3-C14-N4	118.1(6)
Ru3-N2-C1	123.8(4)	C1-N1-C2	127.7(6)
Ru3-N2-C8	118.2(4)	C1-N2-C8	118.0(6)
Ru4-Ru5-Ru6	138.34(3)	C14-N3-C15	124.1(6)
Ru4-Ru2-S1	52.61(5)		

formed by Ru1, Ru2, Ru4, and Ru5 (planar to within 0.002 Å). Terminal carbonyl ligands complete the coordination sphere of the remaining ruthenium atoms.

A hexanuclear cluster of this type can formally be considered as a bi-edge-bridged square and requires 92 electrons to satisfy its closed-shell requirements.^{1b} Cluster **2** contains a total of 94 electrons, and in order to compensate for the additional electrons, and at the same time satisfy the effective atomic number rule, the Ru1-Ru5 and Ru2-Ru4 bonds are elongated and assigned bond orders of 0.5.

The reaction of **3** with hydrogen under relatively mild conditions results in the formation of the 92-electron cluster [(μ₂-H)₆Ru₆(CO)₁₄(μ₃,η²-SCNHPNP)₂] (**4**). Since the known cluster [(μ₂-H)₂Ru₃(CO)₉(μ₃-S)]¹⁰ is also formed in this reaction, it can be assumed that upon hydrogenation the hexanuclear framework of **3** breaks down to [(μ₂-H)₂Ru₃(CO)₉(μ₃-S)] and it is this unsaturated 46-electron trinuclear fragment which dimerizes to give **4**. Such oligomerizations to relieve unsaturation have been observed previously.¹⁵ Alternatively, the intermediate trinuclear species may pick up CO with subsequent H₂ elimination to form **1**, also found in the reaction mixture. That formation of **4** in reactions of the trinuclear cluster **1** with

Table 4. Atomic Parameters for Compound **4** with Estimated Standard Deviations in Parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} ^a
Ru1	0.49654(6)	0.02996(5)	0.15119(5)	1.86(3)
Ru2	0.28281(6)	0.02641(5)	0.00857(5)	1.82(3)
Ru3	0.24630(6)	0.07121(5)	0.22030(5)	1.91(3)
S1	0.48343(19)	0.18946(16)	0.10111(15)	1.99(8)
N1	0.4801(7)	0.4086(5)	0.2249(5)	2.5(3)
N2	0.3353(6)	0.2553(5)	0.2559(5)	2.1(3)
C1	0.4250(8)	0.2927(6)	0.2051(5)	1.9(3)
C2	0.2870(8)	0.3428(7)	0.3360(6)	2.3(4)
C3	0.3520(9)	0.3813(7)	0.4346(6)	2.9(4)
C4	0.3038(10)	0.4647(9)	0.5127(7)	4.3(5)
C5	0.1916(11)	0.5066(9)	0.4900(8)	4.4(5)
C6	0.1289(9)	0.4653(7)	0.3934(8)	3.7(5)
C7	0.1739(9)	0.3833(7)	0.3162(7)	3.0(4)
C8	0.5948(8)	0.4545(7)	0.1832(6)	2.6(4)
C9	0.7245(9)	0.4274(8)	0.1924(7)	3.3(5)
C10	0.8338(10)	0.4740(9)	0.1511(9)	5.1(6)
C11	0.8210(13)	0.5502(10)	0.1078(11)	6.2(7)
C12	0.6931(14)	0.5810(10)	0.1019(10)	6.1(8)
C13	0.5792(10)	0.5311(8)	0.1391(8)	4.0(6)
C14	0.4864(8)	-0.1084(8)	0.1715(7)	2.9(4)
O14	0.4852(7)	-0.1927(6)	0.1834(6)	4.9(4)
O15	0.6072(8)	0.1253(8)	0.2743(7)	2.7(4)
O16	0.6725(7)	0.1886(6)	0.3526(5)	4.5(4)
O17	0.1370(6)	0.1678(6)	-0.0728(5)	4.2(4)
C16	0.1892(8)	0.1144(7)	-0.0410(6)	2.5(4)
C17	0.1516(8)	-0.1184(7)	-0.0592(6)	2.5(4)
O17	0.0726(6)	-0.2077(5)	-0.1017(5)	3.9(3)
C18	0.1817(8)	-0.0953(8)	0.1755(6)	2.4(4)
O18	0.1421(6)	-0.1942(5)	0.1467(5)	3.7(4)
C19	0.3235(8)	0.0845(7)	0.3487(7)	2.6(4)
O19	0.3645(7)	0.0893(6)	0.4262(5)	4.2(4)
C20	0.0639(9)	0.0990(7)	0.2578(6)	2.7(4)
O20	-0.0429(6)	0.1101(6)	0.2789(5)	3.8(4)
C1S	0.6548(9)	0.3219(7)	0.6698(7)	3.1(4)
O1S	0.5687(7)	0.3692(5)	0.6491(5)	3.8(3)
C2S	0.6585(11)	0.2000(9)	0.6021(8)	4.7(6)
C3S	0.7619(11)	0.3836(8)	0.7616(8)	4.4(5)
C4S	0.0727(14)	0.1418(11)	0.6158(9)	5.7(7)
O4S	-0.0371(9)	0.0905(9)	0.6288(8)	7.8(7)
C5S	0.0841(16)	0.2283(13)	0.5704(13)	8.9(11)
C6S	0.2087(13)	0.1163(14)	0.6460(10)	7.8(10)
H2R	0.209(9)	0.048(8)	0.108(7)	4.6(24)
H3R	0.644(8)	-0.003(7)	0.081(6)	3.7(20)

^a *B*_{iso} is the mean of the principal axes of the thermal ellipsoid.

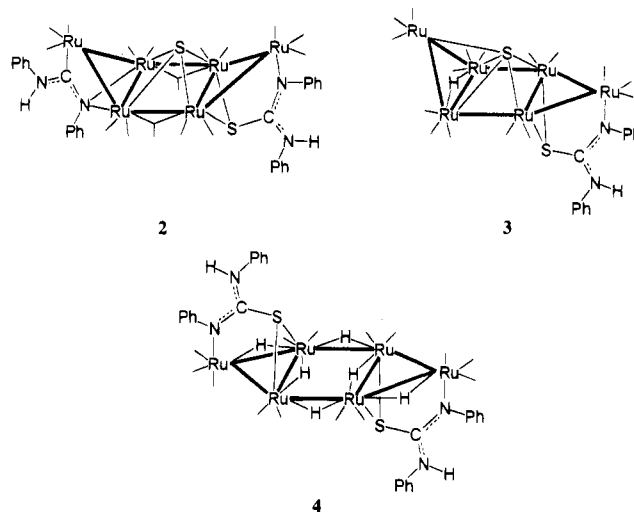
molecular hydrogen does not occur implies a carbon monoxide deficient intermediate not accessible from **1**.

The ZORTEP¹⁶ plot of cluster **4** (see Figure 2) shows a basal raft structure defined by six ruthenium atoms. Two equivalent triangular ruthenium units, related by an inversion center, are held together by relatively long metal-metal bonds (Ru1-Ru2a 3.22(1) Å). Unsaturation at Ru1 and Ru2 (and necessarily Ru1a and Ru2a) requires these bonds. These same metal-metal bonds are bridged by hydride ligands (H3R and H3Ra) which lie toward the exterior of the metal ring. The six-membered metal ring formed by Ru1-Ru3 and Ru1a-Ru3a is planar to within 0.02(1) Å. Within experimental error, H3R and H3Ra lie in this plane. Bridging hydrides span the Ru2-Ru3 and Ru2a-Ru3a bonds (H2R and H2Ra, respectively) and are located on the periphery of the metal skeleton. Presumably these hydrides contribute to the lengthening of the Ru2-Ru3 and Ru2a-Ru3a bonds (2.95(1) Å) as compared to the same bond in the trinuclear complex **1** (2.77(1) Å) which contains no

Table 5. Selected Bond Lengths (Å) and Angles (deg) of Compound **4**

Ru1-Ru2	2.8507(9)	Ru1-Ru2 ^a	3.2218(9)
Ru1-Ru3	2.7657(9)	Ru1-S1	2.4056(20)
Ru1-H3R	1.83(8)	Ru2-Ru3	2.9489(9)
Ru2-S1	2.4165(20)	Ru2-H2R	1.59(9)
Ru2-H3R ^a	1.48(8)	Ru3-N2	2.145(6)
Ru3-H2R	1.55(9)	S1-C1	1.784(8)
N2-C1	1.299(9)	N2-C2	1.441(10)
N1-C1	1.357(9)	N1-C8	1.422(10)
Ru1-Ru2-Ru1 ^a	86.034(24)	Ru1-Ru2-Ru3	56.934(22)
Ru1-Ru2-S1	53.58(5)	Ru1-Ru3-Ru2	59.744(23)
Ru1-Ru3-N2	87.14(16)	Ru1-S1-C1	104.39(24)
Ru1-S1-Ru2	72.48(6)	Ru1 ^a -Ru3-Ru3	142.97(3)
Ru1-H3R-Ru2 ^a	154(5)	Ru2-Ru1-Ru3	63.322(23)
Ru1 ^a -Ru2-S1	80.27(5)	Ru2-H2R-Ru3	139(6)
Ru2-Ru1-Ru2 ^a	93.97(3)	Ru2 ^a -Ru1-S1	84.96(5)
Ru2-Ru1-S1	53.94(5)	Ru2-Ru3-N2	87.32(17)
Ru2-S1-C1	107.88(24)	Ru3-Ru1-S1	81.57(5)
Ru2 ^a -Ru1-Ru3	157.29(3)	Ru3-Ru2-S1	77.64(5)
Ru3-N2-C1	123.5(5)	Ru3-N2-C2	118.8(4)
S1-C1-N2	120.2(5)	S1-C1-N1	115.3(5)
N2-C1-N1	124.5(7)	C1-N1-C8	126.4(6)
C1-N2-C2	117.6(6)		

^a Symmetry operator: 1 - *x*, -*y*, -*z*.

Chart 1. Schematic Representation of the Hexanuclear Clusters **2-4**

bridging hydride at this position. The Ru1-Ru3 bond in the triangular substructure is of the same magnitude as its analogue in complex **1** (Ru1-Ru3 2.77(1) Å), while Ru1-Ru2 is longer (2.85(1) Å). The hexanuclear raft cluster of Cabeza et al.^{6b} contains slightly longer metal-metal bonds between the two triangular subunits and μ_3 -hydrides positioned so as to connect the two trinuclear units.

Bonded in a centrosymmetric fashion to each triangular end of the complex are two μ_3, η^2 -diphenylthioureato ligands, one above and one below the metal plane. Atom N2, terminally bound to Ru3, shows bonds typical of this arrangement (Ru3-N2 2.14(1) Å) as does the bridging S (average Ru-S 2.41(1) Å). Double-bond character is retained between C1 and N2 (1.30(1) Å). The coordination sphere of each ruthenium atom is completed by terminal carbonyl ligands.

As seen in Figure 2, this structure represents an unsaturated 90-electron cluster. However ¹H NMR spectra for complex **4** suggest two bridging hydrides in addition to the four located crystallographically. The two spectroscopically identified hydrides (H1R and H1Ra) are believed to bridge the Ru1-Ru2 and Ru1a-Ru2a bonds. The hydride region of the ¹H NMR spectrum for **4** is displayed in Figure 3 and shows three hydride

(15) (a) Adams, R. D.; Babin, J. E.; Wolfe, T. A. *Polyhedron* **1989**, *8*, 1123. (b) Adams, R. D.; Manig, D.; Segmüller, B. E. *Organometallics* **1983**, *2*, 149.

(16) Johnson, C. K. *ORTEP*; Oak Ridge National Laboratory: Oak Ridge, TN. Modified for PC: Zsolnai, L.; Pritzkow, H. *ZORTEP*; University of Heidelberg: Heidelberg, Germany, 1994.

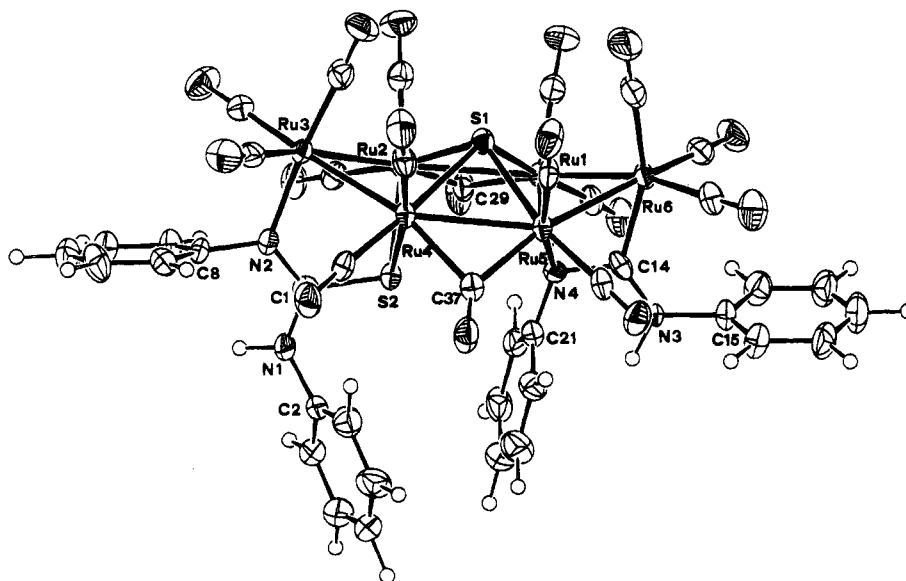


Figure 1. ORTEP plot (ellipsoids at 50% probability level)¹⁴ of $[\text{Ru}_6(\mu_2\text{-CO})_2(\text{CO})_{14}(\mu_4\text{-S})(\mu_3, \eta^2\text{-SCNHPPhNPh})(\mu_3, \eta^2\text{-NPhCNHPPh})]$ (**2**).

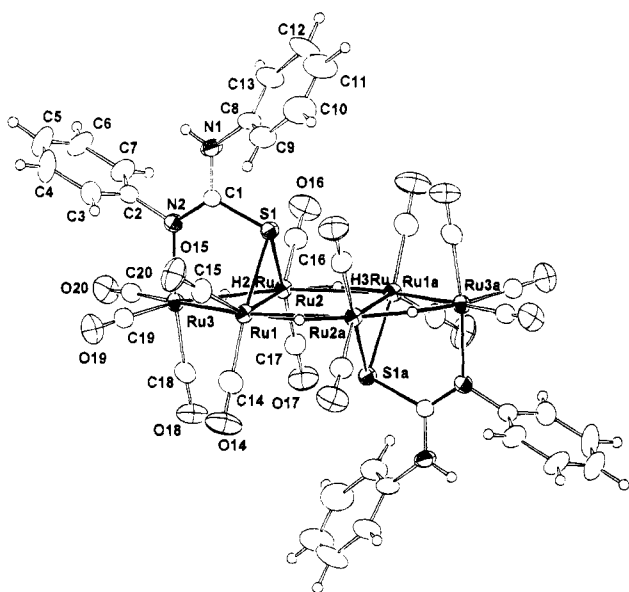


Figure 2. ZORTEP plot¹⁶ (ellipsoids at 50% probability level) of $[(\mu_2\text{-H})_6\text{Ru}_6(\text{CO})_{14}(\mu_3, \eta^2\text{-SCNHPPhNPh})_2]$ (**4**).

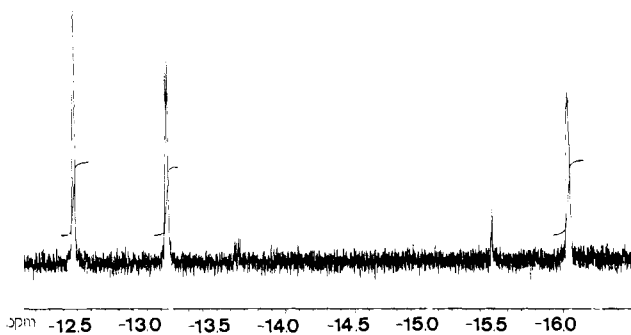


Figure 3. ^1H NMR (CDCl_3) of the hydride region of compound **4**; H3R at -12.48 , H2R at -13.14 , and H1R at -16.05 ppm.

resonances which are assigned as follows: the upfield multiplet at -16.05 ppm is assigned to the hydride(s) H1R (H1Ra), the doublet of doublets at -13.14 ppm is assigned to H2R (H2Ra),

and the multiplet (appearing as a broad singlet) at -12.48 ppm results from H3R (H3Ra). COSY spectra indicate mutual coupling between all three protons. To clarify the nature of these interactions, decoupling experiments were carried out. Most significantly, decoupling at the -12.48 ppm signal (H3R, H3Ra) results in doublets for the two remaining hydride signals at -13.14 and -16.05 ppm, each doublet displaying the same coupling constant of 5.86 Hz. The fine splitting generating the doublet at -13.14 ppm with the smaller coupling constant ($J = 1.66$ Hz) must therefore result from coupling to protons H3R (H3Ra), while the larger J value of 5.86 Hz arises from coupling to H1R (H1Ra). The larger coupling constant produced by the H1R protons, as well as the upfield shift in their signal, suggests a different chemical environment compared to that of the H2R and H3R protons. Given the postulated positions of the H1R protons, that is in the interior of the ruthenium framework where anisotropy due to the surrounding metal atoms would be large, these effects might be expected. The location of these hydrides is further implied by the elongation of the metal–metal bonds in question (Ru1–Ru2 2.92(1) Å). The addition of these two hydride ligands to the structure results in a total of 92 electrons, as predicted for this type of cluster.

Conclusion

The two hexanuclear clusters reported here (**2** and **4**), as well as the hexanuclear cluster which preceded them (**3**), reflect the structural flexibility inherent in metal clusters of medium nuclearity and their tendency to adopt an arrangement which most appropriately accommodates the multisite-bonded ligands present.

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Supporting Information Available: For compounds **2** and **4**, tables of data collection details, complete fractional atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, least-squares planes, and complete tables of bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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