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Cluster Synthesis. 17. Synthesis and Structural Characterizations of $Ru_5(CO)_{15}(\mu_4\text{-}S)$, $Ru_6(CO)_{18}(\mu_4\text{-}S)$, and $Ru_7(CO)_{21}(\mu_4\text{-}S)$

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When $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) was heated to 68 °C in the presence of $Ru(CO)_5$, the three new higher nuclearity clusters $Ru_5(CO)_{15}(\mu_4\text{-}S)$ (2), $Ru_6(CO)_{15}(\mu\text{-}CO)_3(\mu_4\text{-}S)$ (3), and $Ru_7(CO)_{19}(\mu\text{-}CO)_2(\mu_4\text{-}S)$ (4) were formed. 3 was also made by heating 2 with $Ru(CO)_5$ to 98 °C, and 4 was also made by heating 3 with $Ru(CO)_5$ to 98 °C. 2, 3, and 4 were degraded by treatment with CO (1 atm)/98 °C by the stepwise removal of mononuclear ruthenium carbonyl groupings. Compounds 2, 3, and 4 were characterized structurally by single-crystal X-ray diffraction analyses. For 2: space group $P2_1/c$, $a = 11.896$ (3) Å, $b = 28.956$ (9) Å, $c = 13.009$ (5) Å, $\beta = 90.59$ (2)°, $V = 4481$ (2) Å^3, $Z = 8$, $\rho_{calcd} = 2.84$ g/cm^3. The structure of 2 was solved by direct methods and was refined (4012 reflections) to the final values of the residuals, $R = 0.030$ and $R_{wF} = 0.029$. For 3: space group $P\bar{1}$, $a = 17.505$ (4) Å, $b = 20.303$ (5) Å, $c = 9.047$ (2) Å, $\alpha = 91.43$ (2)°, $\beta = 103.49$ (2)°, $\gamma = 67.20$ (2)°, $V = 2874$ (1) Å^3, $Z = 4$, $\rho_{calcd} = 2.64$ g/cm^3. The structure of 3 was solved by direct methods and was refined (6319 reflections) to the final values of the residuals, $R = 0.037$ and $R_{wF} = 0.041$. For 4: space group $P2_1/n$, $a = 12.485$ (5) Å, $b = 16.821$ (5) Å, $c = 16.208$ (5) Å, $\beta = 104.06$ (3)°, $V = 3302$ (2) Å^3, $Z = 4$, $\rho_{calcd} = 2.67$ g/cm^3. The structure of 4 was solved by direct methods and was refined (2747 reflections) to the final values of residues, $R = 0.048$ and $R_{wF} = 0.048$. Each of the structures of 2, 3, and 4 consists of square-pyramidal cluster of five ruthenium atoms with a quadruply bridging sulfido lignd spanning the square base. Compound 2 contains two symmetry-independent molecules in the crystal, and they are structurally different in the arrangement of their carbonyl ligands. Molecule A contains four bridging carbonyl ligands, one on each edge of the square base of the cluster. Molecule B has three *edge-bridging* carbonyl ligands and one asymmetric triply bridging carbonyl ligand. Compound 3 is similar to molecule A of 2 but has a $Ru(CO)_4$ group in place of one of the bridging CO ligands. Compound 4 is similar to molecule A of 2 but has two $Ru(CO)_4$ groups substituted on opposite edges of the square base for the bridging CO ligands.

Introduction

Much of our recent research has focused on developing procedures for the synthesis of osmium carbonyl clusters that contain sulfido ligands.[1] Due to the relative paucity of high nuclearity carbonyl clusters of ruthenium, we have recently initiated an effort to apply this knowledge to the synthesis of sulfidoruthenium carbonyl clusters.

We have discovered high yield syntheses for the compounds $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) and $Ru_3(CO)_9(\mu_3\text{-}S)_2$ and have found that they are very useful reagents for the preparation of new high nuclearity disulfidoruthenium carbonyl clusters.[3-5] Although some of these new clusters structurally resemble their osmium homologues, there were also examples of significant differences both in the formulas and in the structures of others.

We have now investigated the preparation and structural character of a new series of higher nuclearity ruthenium carbonyl clusters that contain only one sulfido ligand. As with the previous series similarities and differences to the osmium system were observed again. The results of this study are described herein.

Experimental Section

General Information. 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. $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ was prepared as previously reported.[3] $Ru(CO)_5$ was prepared by the reported method.[6] CP grade carbon monoxide was purchased from Linde Co. and was used without further purification.

All chromatographic separations were carried out in air. IR spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (1) with $Ru(CO)_5$. a. Preparation of $Ru_5(CO)_{15}(\mu_4\text{-}S)$ (2). $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (30 mg, 0.049 mmol) was added to a solution of $Ru(CO)_5$ (0.147 mmol) in 100 mL of hexane, and the reaction solution was heated to reflux under a continuous purge with CO for 10 min. During this time, the yellow solution turned brown. The solution was concentrated and chromatographed on a Florisil column. Hexane solvent eluted a yellow band containing 7.6 mg of $Ru_3(CO)_{12}$. A hexane/CH_2Cl_2 (9/1) solvent mixture, eluted a light brown band (29.4 mg) of $Ru_5(CO)_{15}(\mu_4\text{-}S)$ (2), 62%. Finally, a dark brown band was eluted with hexane/CH_2Cl_2 (85/15) and yielded 5.2 mg of $Ru_6(CO)_{18}(\mu_4\text{-}S)$ (3) 9%. For 2: IR (ν(CO), cm^{-1}, in CH_2Cl_2 2063 (vs), 2043 (m, sh), 2028 (w, sh), 1992 (vw), 1893 (vw, sh), 1872 (w), 1782 (vvw); IR (ν(CO), cm^{-1}, in a KBr pellet) 2062 (vs), 2045 (m), 2037 (m), 2027 (m), 2006 (w), 1996 (vw), 1984 (vw), 1977 (vw), 1902 (vw), 1892 (w), 1878 (w), 1865 (w), 1840 (w), 1779 (vw). Anal. Calcd for $Ru_5SO_{15}C_{15}$: C, 18.81. Found: C, 18.37.

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Table I. Crystallographic Data for X-ray Diffraction Studies

	2	3	4
(A) Crystal Data			
formula	$Ru_5SO_{15}C_{15}$	$Ru_6SO_{18}C_{18}$	$Ru_7SO_{21}C_{21}$
temp (±3 °C)	23 °C	23 °C	23 °C
space group	$P2_1/c$, No. 14	$P\bar{1}$, No. 2	$P2_1/n$, No. 14
a (Å)	11.896 (3)	17.505 (4)	12.485 (5)
b (Å)	28.956 (9)	20.303 (5)	16.821 (5)
c (Å)	13.009 (5)	9.047 (2)	16.208 (5)
α (deg)	90	91.43 (2)	90
β (deg)	90.59 (2)	103.49 (2)	104.06 (3)
γ (deg)	90	67.20 (2)	90
V (Å^3)	4481 (2)	2874 (1)	3302 (2)
M_r	957.6	1142.7	1327.7
Z	8	4	4
ρ_{calcd} (g/cm^3)	2.84	2.64	2.67
(B) Measurement of Intensity Data			
radiatn		Mo Kα	
monochromator		graphite	
detector aperture (mm)			
horizontal		4.0	
vertical		4.0	
cryst faces	101, $\bar{1}0\bar{1}$, 010 $0\bar{1}0$, $11\bar{1}$, $\bar{1}\bar{1}1$	100, $\bar{1}00$, $\bar{1}\bar{2}0$, 001 120, 111, $0\bar{1}2$, 011, $22\bar{1}$	$10\bar{1}$, $\bar{1}01$, $0\bar{1}0$ 010, $\bar{1}0\bar{1}$, $1\bar{2}1$, 011
cryst size (mm)	0.14 × 0.23 × 0.32	0.15 × 0.13 × 0.20	0.08 × 0.19 × 0.37
cryst orientatn			
lattice directn	[101]	$[10\bar{2}]$	[102]
deg from ϕ axis	6.0	6.9	1.6
reflctns measd	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$
max 2θ (deg)	45	46	45
scan type		moving crystal–stationary counter	
ω-scan width: A = (A + 0.347 tan θ)	1.1	1.1	1.1
bkgd (count time at end of each scan)		$^1/_4$ scan time	
ω-scan rate^a (deg/min)	4.0	4.0	4.0
no. of reflectns measd	6370	8385	4773
data used ($F^2 \geq 3.0\sigma(F^2)$)	4012	6319	2747
(C) Treatment of Data			
absorptn correctn	none	applied	none
coeff (cm^{-1})	33.8	31.5	31.8
transmissn coeff			
max		0.71	
min		0.63	
P factor	0.02	0.02	0.02
final residuals			
R_F	0.030	0.037	0.048
R_{wF}	0.029	0.041	0.048
esd of unit wt observn	1.16	2.04	1.68
largest shift/error value of final cycle	0.01	0.21	0.01
largest peak in final diff Fourier (e/Å^3)	0.68	1.62	1.37

[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.

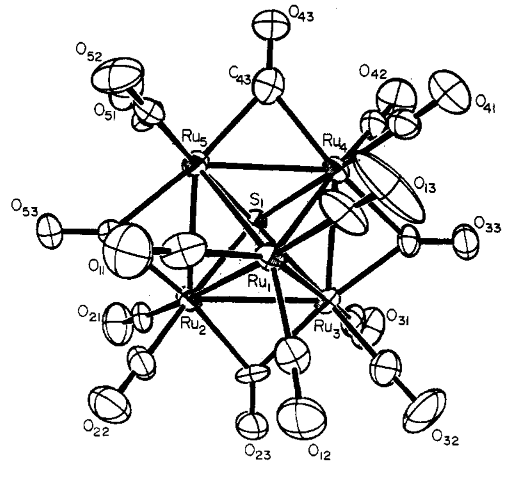

Figure 1. An ORTEP diagram of $Ru_5(CO)_{11}(\mu\text{-}CO)_4(\mu_4\text{-}S)$ (**2A**) showing 50% probability thermal ellipsoids.

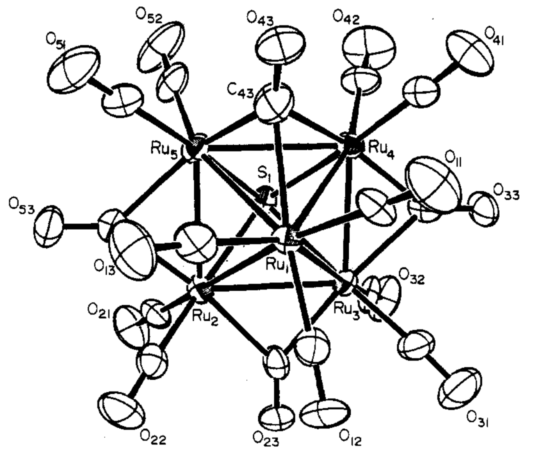

Figure 2. An ORTEP diagram of $Ru_5(CO)_{11}(\mu\text{-}CO)_3(\mu_3\text{-}CO)(\mu_4\text{-}S)$ (**2B**) showing 50% probability thermal ellipsoids.

Table II. Positional Parameters and B(eq) for $Ru_5(CO)_{15}(\mu_4\text{-}S)$ (2)

atom	x	y	z	B(eq), Å^2	atom	x	y	z	B(eq), Å^2
Ru1A	0.626446 (67)	0.142227 (31)	0.549114 (60)	2.08 (4)	Ru1B	1.112184 (68)	0.358585 (30)	0.424450 (59)	1.98 (4)
Ru2A	0.857001 (66)	0.142706 (30)	0.515350 (60)	1.99 (4)	Ru2B	1.349653 (67)	0.358181 (31)	0.459730 (60)	2.11 (4)
Ru3A	0.713395 (70)	0.173519 (29)	0.359618 (61)	2.02 (4)	Ru3B	1.210328 (68)	0.324425 (30)	0.613281 (61)	1.92 (4)
Ru4A	0.600464 (68)	0.090711 (30)	0.363509 (61)	2.08 (4)	Ru4B	1.089111 (69)	0.405107 (30)	0.614193 (61)	2.03 (4)
Ru5A	0.742684 (72)	0.058662 (30)	0.515388 (62)	2.14 (4)	Ru5B	1.232973 (73)	0.440867 (29)	0.457707 (61)	2.21 (4)
S1A	0.80497 (21)	0.098786 (88)	0.36406 (18)	2.0 (1)	S1B	1.29242 (21)	0.401103 (90)	0.61182 (18)	2.1 (1)
O11A	0.65037 (78)	0.12272 (33)	0.77670 (63)	5.4 (5)	O11B	0.85818 (70)	0.34767 (33)	0.42076 (64)	5.1 (5)
O12A	0.61811 (74)	0.24310 (33)	0.60879 (65)	4.9 (5)	O12B	1.13581 (71)	0.25638 (28)	0.37482 (65)	4.5 (5)
O13A	0.37402 (74)	0.13513 (46)	0.56939 (78)	8.5 (7)	O13B	1.14337 (72)	0.37902 (33)	0.19657 (60)	5.1 (5)
O21A	1.10922 (67)	0.13485 (33)	0.46903 (61)	4.8 (5)	O21B	1.60208 (68)	0.35958 (35)	0.50999 (61)	4.9 (5)
O22A	0.87769 (71)	0.19843 (30)	0.70967 (63)	4.4 (5)	O22B	1.38100 (73)	0.30450 (30)	0.26371 (63)	4.7 (5)
O23A	0.89212 (67)	0.24135 (28)	0.44139 (58)	3.8 (4)	O23B	1.38468 (67)	0.25771 (27)	0.52834 (61)	3.9 (4)
O31A	0.81803 (71)	0.19843 (31)	0.15225 (64)	4.8 (5)	O31B	1.09627 (79)	0.23128 (32)	0.61473 (67)	5.3 (5)
O32A	0.59610 (85)	0.26659 (33)	0.36946 (73)	6.1 (6)	O32B	1.31719 (72)	0.30393 (31)	0.82142 (62)	4.9 (5)
O33A	0.51164 (60)	0.16519 (27)	0.21705 (57)	3.4 (4)	O33B	1.01703 (63)	0.33288 (26)	0.76633 (56)	3.6 (4)
O41A	0.34794 (69)	0.08145 (30)	0.37878 (59)	4.2 (5)	O41B	0.83732 (70)	0.41528 (31)	0.61106 (57)	4.3 (5)
O42A	0.57699 (78)	0.04154 (31)	0.15707 (66)	5.2 (5)	O42B	1.09730 (88)	0.47375 (35)	0.78909 (70)	6.5 (6)
O43A	0.58164 (68)	−0.01282 (29)	0.42043 (62)	4.2 (5)	O43B	0.98139 (68)	0.45747 (28)	0.42140 (59)	4.1 (4)
O51A	0.88765 (80)	−0.02547 (33)	0.47070 (66)	5.4 (5)	O51B	1.18559 (78)	0.49258 (30)	0.26146 (65)	5.0 (5)
O52A	0.64109 (72)	0.01612 (28)	0.70619 (60)	4.3 (4)	O52B	1.31371 (95)	0.52900 (32)	0.55925 (67)	6.6 (6)
O53A	0.91587 (70)	0.07495 (28)	0.68872 (61)	4.3 (4)	O53B	1.43030 (77)	0.43200 (31)	0.30941 (73)	6.0 (5)
C11A	0.64273 (96)	0.12819 (39)	0.69223 (94)	3.4 (6)	C11B	0.95255 (93)	0.35121 (40)	0.42401 (77)	2.8 (6)
C12A	0.62044 (89)	0.20558 (44)	0.58213 (82)	2.9 (6)	C12B	1.12976 (88)	0.29435 (44)	0.39910 (86)	3.1 (6)
C13A	0.4670 (11)	0.13655 (48)	0.55786 (90)	4.5 (7)	C13B	1.12846 (90)	0.37247 (40)	0.28231 (90)	3.2 (6)
C21A	1.01744 (87)	0.13905 (38)	0.48663 (73)	2.5 (5)	C21B	1.50918 (98)	0.35907 (40)	0.49323 (76)	2.9 (6)
C22A	0.87085 (89)	0.17784 (41)	0.63612 (84)	2.9 (6)	C22B	1.36852 (83)	0.32526 (39)	0.33604 (85)	2.7 (5)
C23A	0.85117 (90)	0.20651 (36)	0.44062 (76)	2.4 (5)	C23B	1.34099 (91)	0.29260 (42)	0.53392 (74)	2.7 (6)
C31A	0.78276 (88)	0.19029 (40)	0.22883 (95)	3.2 (6)	C31B	1.13560 (98)	0.26743 (42)	0.61433 (88)	3.3 (6)
C32A	0.64131 (92)	0.23171 (44)	0.36709 (84)	3.2 (6)	C32B	1.28043 (84)	0.31123 (38)	0.74273 (89)	2.9 (6)
C33A	0.57428 (79)	0.15206 (37)	0.27943 (76)	2.3 (5)	C33B	1.07163 (90)	0.34908 (38)	0.70151 (75)	2.6 (5)
C41A	0.44238 (97)	0.08559 ((37)	0.37525 (78)	2.6 (5)	C41B	0.9333 (10)	0.41072 (38)	0.61198 (72)	2.5 (5)
C42A	0.59076 (90)	0.05988 (40)	0.23211 (92)	3.1 (6)	C42B	1.0940 (10)	0.44947 (41)	0.72238 (92)	3.7 (6)
C43A	0.61903 (90)	0.02451 (43)	0.43153 (82)	2.9 (6)	C43B	1.0578 (11)	0.43598 (44)	0.45413 (92)	4.1 (7)
C51A	0.8390 (10)	0.00564 (41)	0.48922 (84)	3.2 (6)	C51B	1.20237 (94)	0.47361 (39)	0.33449 (91)	3.2 (6)
C52A	0.67742 (84)	0.03211 (36)	0.63618 (83)	2.4 (5)	C52B	1.2833 (10)	0.49631 (44)	0.51980 (80)	3.5 (6)
C53A	0.86901 (87)	0.08588 (35)	0.61505 (82)	2.5 (5)	C53B	1.3758 (10)	0.41719 (40)	0.37407 (90)	3.5 (6)

Table III. Selected Intramolecular Distances (Å) for Molecule A, $Ru_5(CO)_{11}(\mu\text{-}CO)_4(\mu_4\text{-}S)$ (2A), in the Crystal of $Ru_5(CO)_{15}(\mu_4\text{-}S)$

atom	atom	dist	atom	atom	dist
Ru1A	C12A	1.89 (1)	Ru3A	C23A	2.16 (1)
Ru1A	C13A	1.91 (1)	Ru3A	S1A	2.424 (3)
Ru1A	C11A	1.91 (1)	Ru3A	Ru4A	2.749 (2)
Ru1A	Ru2A	2.782 (1)	Ru4A	C41A	1.89 (1)
Ru1A	Ru5A	2.824 (2)	Ru4A	C42A	1.93 (1)
Ru1A	Ru3A	2.832 (2)	Ru4A	C33A	2.11 (1)
Ru1A	Ru4A	2.852 (2)	Ru4A	C43A	2.12 (1)
Ru2A	C22A	1.88 (1)	Ru4A	S1A	2.444 (3)
Ru2A	C21A	1.95 (1)	Ru4A	Ru5A	2.750 (1)
Ru2A	C23A	2.09 (1)	Ru5A	C52A	1.92 (1)
Ru2A	C53A	2.10 (1)	Ru5A	C51A	1.95 (1)
Ru2A	S1A	2.418 (3)	Ru5A	C43A	2.07 (1)
Ru2A	Ru3A	2.784 (1)	Ru5A	C53A	2.13 (1)
Ru2A	Ru5A	2.787 (2)	Ru5A	S1A	2.409 (3)
Ru3A	C32A	1.89 (1)	O	C_{av}	1.13 (1)
Ru3A	C31A	1.96 (1)	Ru1A···C43A		3.74 (1)
Ru3A	C33A	2.04 (1)			

b. Preparation of $Ru_6(CO)_{18}(\mu_4\text{-}S)$ (3) and $Ru_7(CO)_{21}(\mu_4\text{-}S)$ (4). 1 (46 mg 0.075 mmol) was added to a solution of $Ru(CO)_5$ (0.75 mmol) in 200 mL of heptane. This solution was heated to reflux under continuous purge with carbon monoxide for 15 min. During this time, the yellow solution turned dark brown. Separation as described above yielded 78 mg of $Ru_3(CO)_{12}$, 6 mg of 2 (8%), and 47 mg of 3 (55%). Hexane/CH_2Cl_2 (7/3) eluted a violet band, compound 4, 23 mg, 23%. For 3: IR (ν(CO), cm^{-1} in hexane) 2118 (w), 2078 (s), 2058 (vs), 2041 (m), 2028 (w), 2015 (vw), 1879 (w), 1858 (w), 1844 (vw). Anal. Calcd for $Ru_6SO_{18}C_{18}$: C, 18.91. Found: C, 19.03. For 4: IR (ν(CO), cm^{-1} in CH_2Cl_2) 2104 (vs), 2060 (vs), 2044 (vs), 2026 (w), 2015 (w), 1983 (vw), 1835 (vw, br). Anal. Calcd for $Ru_7SO_{21}C_{21}$: C, 18.99. Found: C, 19.07.

Reaction of 2 with $Ru(CO)_5$. 2 (15 mg, 0.016 mmol) and $Ru(CO)_5$ (0.16 mmol) in 60 mL of heptane were heated to 98 °C for 20 min. The products were separated by column chromatography on Florisil (see previous section) and yielded 19.8 mg of $Ru_3(CO)_{12}$, 13.6 mg of 3 (76%), and 2.5 mg of 4 (12%).

Reaction of Compound 3 with $Ru(CO)_5$. 3 (7.5 mg, 0.0066 mmol) and $Ru(CO)_5$ (0.132 mmol) in 60 mL of heptane were heated to 98 °C under a slow purge with CO for 25 min. Workup yielded 7.4 mg of 4 (88%).

Reaction of 4 with CO. 4 (20 mg, 0.015 mmol) in 25 mL of heptane was heated to 98 °C for 2 h under a continuous purge with CO. The products were separated on Florisil column as described above and yielded 1.7 mg of $Ru_3(CO)_{12}$, 1.3 mg of 2 (11%), 8.2 mg of 3 (60%), and 4.1 mg of unreacted 4. (Yields are based on the amount of 4 consumed).

Reaction of 3 with CO. 3 (20 mg, 0.0175 mmol) in 25 mL of heptane was heated to 98 °C for 2 h under a purge with CO. The workup yielded 1.9 mg of $Ru_3(CO)_{12}$, 6.0 mg of 2 (50%), 5.8 mg of unreacted 3, 0.6 mg of 1 (8%), and 1.5 mg of 4 (18%). (Yields are based on the amount of 3 consumed.)

Reaction of 2 with CO. 2 (15 mg, 0.0157 mmol) in 25 mL of heptane was heated to 98 °C for 1 h under a slow purge with CO. The workup yielded 1.4 mg of $Ru_3(CO)_{12}$, 4.1 mg of unreacted 2, 4.4 mg of 1 (63%), 1.8 mg of 3 (28%), and 0.4 mg of 4 (5%). (Yields are based on the amount of 2 consumed.)

Crystallographic Analyses. Dark gray crystals of 2 were grown at 25 °C by slow evaporation of solvent from a solution in a CH_2Cl_2/benzene solvent mixture. Dark brown crystals of 3 were grown by cooling a solution in a hexane/CH_2Cl_2 (5/1) solvent mixture to −20 °C. Black crystals of 4 were grown by slow evaporation of solvent from a benzene solution at 25 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the AFC6 automatic

Table IV. Intramolecular Bond Angles (deg) for $Ru_5(CO)_{11}(\mu\text{-}CO)_4(\mu_4\text{-}S)$ (2A)

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C12A	Ru1A	Ru2A	94.1 (3)	C31A	Ru3A	Ru2A	116.8 (3)	C43A	Ru5A	Ru1A	98.3 (3)
C12A	Ru1A	Ru5A	152.7 (3)	C31A	Ru3A	Ru1A	174.8 (3)	C53A	Ru5A	Ru4A	137.7 (3)
C12A	Ru1A	Ru3A	84.4 (3)	C33A	Ru3A	Ru4A	49.5 (3)	C53A	Ru5A	Ru2A	48.3 (3)
C12A	Ru1A	Ru4A	134.2 (3)	C33A	Ru3A	Ru2A	139.6 (3)	C53A	Ru5A	Ru1A	86.1 (3)
C13A	Ru1A	Ru2A	172.7 (4)	C33A	Ru3A	Ru1A	92.6 (3)	S1A	Ru5A	Ru4A	56.09 (7)
C13A	Ru1A	Ru5A	115.1 (4)	C23A	Ru3A	Ru4A	138.1 (3)	S1A	Ru5A	Ru2A	54.89 (7)
C13A	Ru1A	Ru3A	116.8 (4)	C23A	Ru3A	Ru2A	48.0 (3)	S1A	Ru5A	Ru1A	82.47 (7)
C13A	Ru1A	Ru4A	84.6 (3)	C23A	Ru3A	Ru1A	89.9 (3)	Ru4A	Ru5A	Ru2A	90.09 (4)
C11A	Ru1A	Ru2A	93.7 (3)	S1A	Ru3A	Ru4A	55.97 (7)	Ru4A	Ru5A	Ru1A	61.54 (4)
C11A	Ru1A	Ru5A	85.7 (3)	S1A	Ru3A	Ru2A	54.82 (7)	Ru2A	Ru5A	Ru1A	59.44 (4)
C11A	Ru1A	Ru3A	151.7 (3)	S1A	Ru3A	Ru1A	82.06 (7)	Ru5A	S1A	Ru2A	70.53 (7)
C11A	Ru1A	Ru4A	136.2 (3)	Ru4A	Ru3A	Ru2A	90.19 (4)	Ru5A	S1A	Ru3A	107.9 (1)
Ru2A	Ru1A	Ru5A	59.62 (4)	Ru4A	Ru3A	Ru1A	61.45 (4)	Ru5A	S1A	Ru4A	69.02 (8)
Ru2A	Ru1A	Ru3A	59.44 (3)	Ru2A	Ru3A	Ru1A	59.39 (4)	Ru2A	S1A	Ru3A	70.19 (8)
Ru2A	Ru1A	Ru4A	88.12 (4)	C41A	Ru4A	Ru3A	123.7 (3)	Ru2A	S1A	Ru4A	107.4 (1)
Ru5A	Ru1A	Ru3A	87.42 (4)	C41A	Ru4A	Ru5A	121.3 (3)	Ru3A	S1A	Ru4A	68.76 (8)
Ru5A	Ru1A	Ru4A	57.94 (4)	C41A	Ru4A	Ru1A	94.1 (3)	O11A	C11A	Ru1A	176 (1)
Ru3A	Ru1A	Ru4A	57.84 (4)	C42A	Ru4A	Ru5A	120.7 (3)	O12A	C12A	Ru1A	175 (1)
C22A	Ru2A	Ru1A	87.0 (3)	C42A	Ru4A	Ru1A	175.0 (3)	O13A	C13A	Ru1A	175 (1)
C22A	Ru2A	Ru3A	118.9 (3)	C33A	Ru4A	Ru3A	47.5 (3)	O21A	C21A	Ru2A	177 (1)
C22A	Ru2A	Ru5A	120.8 (3)	C33A	Ru4A	Ru5A	138.1 (3)	O22A	C22A	Ru2A	179 (1)
C21A	Ru2A	Ru1A	176.1 (3)	C33A	Ru4A	Ru1A	90.7 (3)	O23A	C23A	Ru2A	141 (1)
C21A	Ru2A	Ru3A	118.2 (3)	C43A	Ru4A	Ru3A	138.3 (3)	O23A	C23A	Ru3A	136.8 (9)
C21A	Ru2A	Ru5A	115.5 (3)	C43A	Ru4A	Ru5A	48.3 (3)	Ru2A	C23A	Ru3A	81.8 (4)
C23A	Ru2A	Ru1A	92.8 (3)	C43A	Ru4A	Ru1A	96.3 (3)	O31A	C31A	Ru3A	176 (1)
C23A	Ru2A	Ru3A	50.2 (3)	S1A	Ru4A	Ru3A	55.27 (7)	O32A	C32A	Ru3A	178 (1)
C23A	Ru2A	Ru5A	139.3 (3)	S1A	Ru4A	Ru5A	54.89 (6)	O33A	C33A	Ru3A	140.2 (9)
C53A	Ru2A	Ru1A	87.7 (3)	S1A	Ru4A	Ru1A	81.29 (7)	O33A	C33A	Ru4A	136.9 (8)
C53A	Ru2A	Ru3A	137.6 (3)	Ru3A	Ru4A	Ru5A	90.61 (4)	Ru3A	C33A	Ru4A	82.9 (4)
C53A	Ru2A	Ru5A	49.1 (3)	Ru3A	Ru4A	Ru1A	60.71 (4)	O41A	C41A	Ru4A	177 (1)
S1A	Ru2A	Ru1A	83.20 (7)	Ru5A	Ru4A	Ru1A	60.52 (4)	O42A	C42A	Ru4A	175 (1)
S1A	Ru2A	Ru3A	55.00 (7)	C52A	Ru5A	Ru4A	118.2 (3)	O43A	C43A	Ru5A	140 (1)
S1A	Ru2A	Ru5A	54.58 (7)	C52A	Ru5A	Ru2A	123.4 (3)	O43A	C43A	Ru4A	138 (1)
Ru1A	Ru2A	Ru3A	61.17 (4)	C52A	Ru5A	Ru1A	90.8 (3)	Ru5A	C43A	Ru4A	81.9 (5)
Ru1A	Ru2A	Ru5A	60.94 (4)	C51A	Ru5A	Ru4A	120.0 (3)	O51A	C51A	Ru5A	175 (1)
Ru3A	Ru2A	Ru5A	89.10 (4)	C51A	Ru5A	Ru2A	113.6 (4)	O52A	C52A	Ru5A	179 (1)
C32A	Ru3A	Ru4A	123.6 (3)	C51A	Ru5A	Ru1A	173.0 (3)	O53A	C53A	Ru2A	139.6 (8)
C32A	Ru3A	Ru2A	121.5 (3)	C43A	Ru5A	Ru4A	49.8 (3)	O53A	C53A	Ru5A	137.8 (8)
C32A	Ru3A	Ru1A	94.0 (3)	C43A	Ru5A	Ru2A	139.4 (3)	Ru2A	C53A	Ru5A	82.5 (4)
C31A	Ru3A	Ru4A	116.2 (3)								

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 (ν 2.0) obtained from Molecular Structure Corp., College Station, TX. Neutral atom scattering factors were obtained from the standard sources.[7] Anamolous dispersion corrections were applied to all non-hydrogen atoms. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_0| - |F_c|)^2$, where $w = 1/\sigma(F)^2, \sigma(F) = (F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o)^2]^{1/2}/Lp$.

For **2**, the monoclinic space group $P2_1/c$ was established from systematic absences observed in the data. The crystal contains two independent molecules in the asymmetric unit. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All atoms were refined with anisotropic thermal parameters.

Compound **3** crystallizes in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Two independent molecules were also found in the asymmetric crystal unit of **3**. The positions of the metal atoms were determined by direct methods. All other atom positions were obtained by subsequent difference Fourier syntheses. All atoms heavier than oxygen were refined with anisotropic thermal parameters.

Table V. Selected Intramolecular Distances (Å) for Molecule B, $Ru_5(CO)_{11}(\mu\text{-}CO)_3(\mu_3\text{-}CO)(\mu_4\text{-}S)$ (2B), in the Crystal of $Ru_5(CO)_{15}(\mu_4\text{-}S)$

atom	atom	dist	atom	atom	dist
Ru1B	C12B	1.90 (1)	Ru3B	C23B	2.09 (1)
Ru1B	C13B	1.90 (1)	Ru3B	C33B	2.14 (1)
Ru1B	C11B	1.91 (1)	Ru3B	S1B	2.425 (3)
Ru1B	C43B	2.37 (1)	Ru3B	Ru4B	2.746 (2)
Ru1B	Ru5B	2.813 (2)	Ru4B	C41B	1.86 (1)
Ru1B	Ru4B	2.828 (2)	Ru4B	C42B	1.91 (1)
Ru1B	Ru2B	2.857 (1)	Ru4B	C33B	1.99 (1)
Ru1B	Ru3B	2.884 (2)	Ru4B	C43B	2.29 (1)
Ru2B	C22B	1.89 (1)	Ru4B	S1B	2.422 (3)
Ru2B	C21B	1.94 (1)	Ru4B	Ru5B	2.866 (2)
Ru2B	C53B	2.07 (1)	Ru5B	C52B	1.89 (1)
Ru2B	C23B	2.13 (1)	Ru5B	C51B	1.89 (1)
Ru2B	S1B	2.440 (3)	Ru5B	C43B	2.09 (1)
Ru2B	Ru5B	2.768 (2)	Ru5B	C53B	2.14 (1)
Ru2B	Ru3B	2.786 (1)	Ru5B	S1B	2.412 (3)
Ru3B	C31B	1.87 (1)	O	C_{av}	1.14 (1)
Ru3B	C32B	1.91 (1)			

Compound **4** crystallizes in the monoclinic crystal system. The space group $P2_1/n$ (a variant of $P2_1/c$) was determined by the absences observed in the data. The structure was solved by a combination of direct methods and difference Fourier techniques. All atoms larger than oxygen were refined with anisotropic thermal parameters. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure.

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

Table VI. Intramolecular Bond Angles (deg) for $Ru_5(CO)_{11}(\mu\text{-}CO)_3(\mu_3\text{-}CO)(\mu_4\text{-}S)$ (2B)

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C12B	Ru1B	Ru5B	143.0 (3)	C31B	Ru3B	Ru1B	96.9 (3)	C43B	Ru5B	Ru4B	52.3 (3)
C12B	Ru1B	Ru4B	129.0 (3)	C32B	Ru3B	Ru4B	113.0 (4)	C53B	Ru5B	Ru2B	47.7 (3)
C12B	Ru1B	Ru2B	85.0 (3)	C32B	Ru3B	Ru2B	116.4 (3)	C53B	Ru5B	Ru1B	93.3 (3)
C12B	Ru1B	Ru3B	76.6 (3)	C32B	Ru3B	Ru1B	171.4 (3)	C53B	Ru5B	Ru4B	136.7 (3)
C13B	Ru1B	Ru5B	85.0 (3)	C23B	Ru3B	Ru4B	140.5 (3)	S1B	Ru5B	Ru2B	55.68 (7)
C13B	Ru1B	Ru4B	139.4 (3)	C23B	Ru3B	Ru2B	49.4 (3)	S1B	Ru5B	Ru1B	82.44 (7)
C13B	Ru1B	Ru2B	92.7 (3)	C23B	Ru3B	Ru1B	91.6 (3)	S1B	Ru5B	Ru4B	53.80 (7)
C13B	Ru1B	Ru3B	148.8 (3)	C33B	Ru3B	Ru4B	46.1 (3)	Ru2B	Ru5B	Ru1B	61.59 (4)
C11B	Ru1B	Ru5B	126.9 (3)	C33B	Ru3B	Ru2B	137.3 (3)	Ru2B	Ru5B	Ru4B	89.08 (4)
C11B	Ru1B	Ru4B	87.1 (3)	C33B	Ru3B	Ru1B	92.0 (3)	Ru1B	Ru5B	Ru4B	59.72 (4)
C11B	Ru1B	Ru2B	168.8 (3)	S1B	Ru3B	Ru4B	55.44 (7)	Ru5B	S1B	Ru4B	72.73 (8)
C11B	Ru1B	Ru3B	111.0 (3)	S1B	Ru3B	Ru2B	55.31 (7)	Ru5B	S1B	Ru3B	109.2 (1)
C43B	Ru1B	Ru5B	46.6 (3)	S1B	Ru3B	Ru1B	80.72 (7)	Ru5B	S1B	Ru2B	69.58 (8)
C43B	Ru1B	Ru4B	51.5 (3)	Ru4B	Ru3B	Ru2B	91.21 (4)	Ru4B	S1B	Ru3B	69.02 (8)
C43B	Ru1B	Ru2B	104.5 (3)	Ru4B	Ru3B	Ru1B	60.24 (4)	Ru4B	S1B	Ru2B	108.8 (1)
C43B	Ru1B	Ru3B	107.2 (3)	Ru2B	Ru3B	Ru1B	60.50 (4)	Ru3B	S1B	Ru2B	69.86 (8)
Ru5B	Ru1B	Ru4B	61.08 (4)	C41B	Ru4B	Ru3B	126.7 (3)	O11B	C11B	Ru1B	178 (1)
Ru5B	Ru1B	Ru2B	58.43 (4)	C41B	Ru4B	Ru1B	97.7 (3)	O12B	C12B	Ru1B	173 (1)
Ru5B	Ru1B	Ru3B	87.59 (4)	C41B	Ru4B	Ru5B	124.0 (3)	O13B	C13B	Ru1B	176 (1)
Ru4B	Ru1B	Ru2B	88.09 (4)	C42B	Ru4B	Ru3B	124.4 (4)	O21B	C21B	Ru2B	178 (1)
Ru4B	Ru1B	Ru3B	57.46 (4)	C42B	Ru4B	Ru1B	164.4 (4)	O22B	C22B	Ru2B	178 (1)
Ru2B	Ru1B	Ru3B	58.04 (3)	C42B	Ru4B	Ru5B	105.5 (4)	O23B	C23B	Ru3B	139.9 (9)
C22B	Ru2B	Ru5B	119.6 (3)	C33B	Ru4B	Ru3B	50.8 (3)	O23B	C23B	Ru2B	137.5 (8)
C22B	Ru2B	Ru3B	120.8 (3)	C33B	Ru4B	Ru1B	97.0 (3)	Ru3B	C23B	Ru2B	82.5 (4)
C22B	Ru2B	Ru1B	89.5 (3)	C33B	Ru4B	Ru5B	139.9 (3)	O31B	C31B	Ru3B	176 (1)
C21B	Ru2B	Ru5B	118.7 (3)	C43B	Ru4B	Ru3B	114.1 (3)	O32B	C32B	Ru3B	177 (1)
C21B	Ru2B	Ru3B	115.5 (3)	C43B	Ru4B	Ru1B	53.8 (3)	O33B	C33B	Ru4B	143.2 (9)
C21B	Ru2B	Ru1B	176.2 (3)	C43B	Ru4B	Ru5B	46.1 (3)	O33B	C33B	Ru3B	133.6 (8)
C53B	Ru2B	Ru5B	50.0 (3)	S1B	Ru4B	Ru3B	55.55 (7)	Ru4B	C33B	Ru3B	83.1 (4)
C53B	Ru2B	Ru3B	140.4 (3)	S1B	Ru4B	Ru1B	81.95 (7)	O41B	C41B	Ru4B	178 (1)
C53B	Ru2B	Ru1B	93.6 (3)	S1B	Ru4B	Ru5B	53.47 (7)	O42B	C42B	Ru4B	177 (1)
C23B	Ru2B	Ru5B	138.4 (3)	Ru3B	Ru4B	Ru1B	62.30 (4)	O43B	C43B	Ru5B	138 (1)
C23B	Ru2B	Ru3B	48.1 (3)	Ru3B	Ru4B	Ru5B	89.24 (4)	O43B	C43B	Ru4B	131 (1)
C23B	Ru2B	Ru1B	91.4 (3)	Ru1B	Ru4B	Ru5B	59.20 (4)	O43B	C43B	Ru1B	131 (1)
S1B	Ru2B	Ru5B	54.74 (7)	C52B	Ru5B	Ru2B	125.0 (4)	Ru5B	C43B	Ru4B	81.6 (4)
S1B	Ru2B	Ru3B	54.83 (7)	C52B	Ru5B	Ru1B	160.6 (3)	Ru5B	C43B	Ru1B	78.1 (4)
S1B	Ru2B	Ru1B	81.04 (7)	C52B	Ru5B	Ru4B	101.0 (3)	Ru4B	C43B	Ru1B	74.7 (4)
Ru5B	Ru2B	Ru3B	90.47 (4)	C51B	Ru5B	Ru2B	122.2 (3)	O51B	C51B	Ru5B	179 (1)
Ru5B	Ru2B	Ru1B	59.98 (4)	C51B	Ru5B	Ru1B	101.6 (3)	O52B	C52B	Ru5B	178 (1)
Ru3B	Ru2B	Ru1B	61.46 (4)	C51B	Ru5B	Ru4B	132.1 (3)	O53B	C53B	Ru2B	142 (1)
C31B	Ru3B	Ru4B	120.0 (4)	C43B	Ru5B	Ru2B	116.2 (4)	O53B	C53B	Ru5B	135 (1)
C31B	Ru3B	Ru2B	126.8 (4)	C43B	Ru5B	Ru1B	55.4 (4)	Ru2B	C53B	Ru5B	82.3 (4)

Results

When heated in the presence of $Ru(CO)_5$, compound 1 was readily enlarged by the capture of ruthenium carbonyl fragments. Three new compounds with the formulas $Ru_5(CO)_{15}(\mu_4\text{-}S)$ (2) $Ru_6(CO)_{18}(\mu_4\text{-}S)$ (3), and $Ru_7(CO)_{21}(\mu_4\text{-}S)$ (4) were obtained in yields which varied depending on the amount of $Ru(CO)_5$ that was initially present, the temperature, and the duration of the reaction period. When heated to 68 °C for 10 min in the presence of a 3/1 $Ru(CO)_5$/1 molar ratio, the yields of 2, 3, and 4 were 62%, 9%, and 0%, respectively, but when heated to 98 °C for 15 min. in a 10/1 $Ru(CO)_5$/1 molar ratio, the yields were 8%, 55%, and 23%, respectively.

It was believed that the larger clusters 3 and 4 were formed by the enlargement of the smaller ones 2 and 3. Independent experiments were found to support this idea. When 2 was heated to 98 °C in the presence of a 10-fold excess of $Ru(CO)_5$, 3 was obtained in 76% yield and 4 was obtained in 12% yield. When 3 was heated to 98 °C in the presence of a 20-fold excess of $Ru(CO)_5$, 4 was obtained in 88% yield.

When heated to 98 °C under an atmosphere of CO, the larger clusters were degraded to the smaller ones. Treatment of 4 with CO for 2 h yielded 3, 60%, and 2, 11%. Treatment of 3 with CO for 2 h yielded 2, 50%, and 1, 8%, but some 4, 18%, was also obtained. Treatment of 2 with CO for 1 h yielded 1, 63%, but some 3, 28%, and 4, 5%, were also obtained. $Ru_3(CO)_{12}$ was obtained in all of the degradation experiments. This will be in equilibrium with $Ru(CO)_5$ under the experimental conditions,[6]

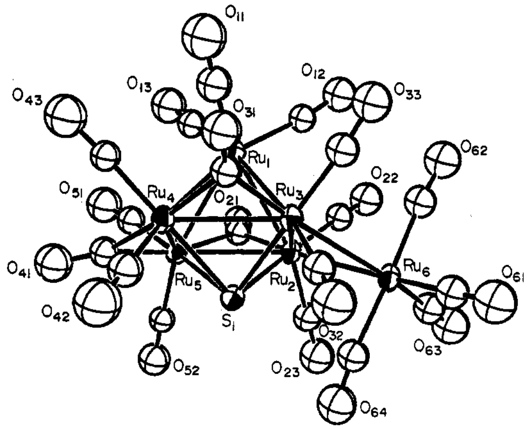

Figure 3. An ORTEP diagram of $Ru_6(CO)_{15}(\mu\text{-}CO)_3(\mu_4\text{-}S)$ (3) showing 50% probability thermal ellipsoids.

Table VII. Positional Parameters and *B*(eq) for $Ru_6(CO)_{15}(\mu\text{-}CO)_3(\mu_4\text{-}S)$ (3)

atom	*x*	*y*	*z*	*B*(eq), Å^2	atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru1A	0.271 805 (49)	0.295 863 (40)	0.674 464 (84)	2.2	O61B	0.071 87 (53)	0.172 26 (45)	0.296 48 (91)	5.2
Ru1B	0.278 275 (48)	0.807 809 (40)	0.560 523 (82)	2.0	O62A	0.280 44 (52)	0.526 70 (44)	0.559 61 (96)	5.3
Ru2A	0.326 106 (47)	0.372 310 (39)	0.914 319 (84)	2.0	O62B	0.284 22 (54)	1.036 73 (46)	0.686 40 (97)	5.5
Ru2B	0.156 015 (46)	0.932 905 (38)	0.386 963 (82)	1.9	O63A	0.374 68 (60)	0.567 61 (50)	1.018 5 (10)	6.2
Ru3A	0.154 957 (47)	0.425 916 (39)	0.747 817 (84)	2.1	O63B	0.172 15 (48)	1.021 64 (40)	−0.007 16 (86)	4.5
Ru3B	0.326 257 (46)	0.883 023 (39)	0.363 717 (85)	2.1	O64A	0.181 59 (54)	0.520 42 (46)	1.166 61 (98)	5.5
Ru4A	0.144 777 (47)	0.298 001 (40)	0.826 139 (85)	2.1	O64B	0.360 46 (56)	1.085 47 (47)	0.302 05 (96)	5.7
Ru4B	0.317 604 (47)	0.752 232 (39)	0.281 805 (85)	2.1	C11A	0.201 63 (77)	0.284 05 (64)	0.499 0 (14)	4.5
Ru5A	0.310 701 (47)	0.246 290 (39)	0.989 280 (83)	2.1	C11B	0.258 62 (78)	0.735 34 (68)	0.643 5 (14)	4.9
Ru5B	0.151 486 (47)	0.800 909 (40)	0.303 630 (85)	2.0	C12A	0.314 22 (62)	0.345 10 (53)	0.558 4 (11)	3.1
Ru6A	0.232 016 (52)	0.520 945 (40)	0.862 893 (90)	2.6	C12B	0.392 54 (75)	0.761 11 (61)	0.647 3 (13)	4.2
Ru6B	0.226 344 (51)	1.030 367 (40)	0.339 561 (86)	2.2	C13A	0.349 44 (65)	0.202 55 (56)	0.660 4 (11)	3.3
S1A	0.207 39 (15)	0.368 44 (12)	1.001 35 (26)	2.2	C13B	0.270 79 (73)	0.864 40 (63)	0.729 1 (13)	4.2
S1B	0.208 98 (14)	0.870 97 (12)	0.178 58 (25)	2.1	C21A	0.414 07 (63)	0.268 69 (52)	0.947 3 (11)	3.0
O11A	0.161 64 (64)	0.277 45 (54)	0.384 4 (11)	7.1	C21B	0.101 16 (65)	0.872 80 (54)	0.467 2 (11)	3.3
O11B	0.252 94 (68)	0.685 88 (60)	0.700 3 (12)	8.1	C22A	0.402 68 (66)	0.391 03 (54)	0.823 8 (11)	3.3
O12A	0.336 84 (50)	0.371 58 (42)	0.477 89 (89)	4.8	C22B	0.129 97 (62)	0.987 47 (54)	0.550 7 (11)	3.1
O12B	0.465 08 (63)	0.733 51 (53)	0.705 9 (11)	6.7	C23A	0.376 95 (67)	0.396 73 (56)	1.104 0 (12)	3.5
O13A	0.398 10 (55)	0.145 60 (47)	0.644 37 (96)	5.7	C23B	0.054 39 (61)	0.994 81 (51)	0.253 8 (11)	2.8
O13B	0.271 74 (64)	0.894 11 (55)	0.838 8 (12)	7.3	C31A	0.072 92 (63)	0.379 14 (53)	0.645 2 (11)	3.0
O21A	0.486 21 (46)	0.235 20 (39)	0.950 89 (80)	4.0	C31B	0.420 89 (61)	0.783 70 (50)	0.357 7 (10)	2.7
O21B	0.056 75 (47)	0.876 35 (4)	0.549 35 (83)	4.3	C32A	0.060 03 (67)	0.501 23 (56)	0.792 3 (11)	3.4
O22A	0.453 64 (52)	0.400 55 (44)	0.777 04 (91)	5.2	C32B	0.399 91 (73)	0.898 42 (61)	0.532 8 (13)	4.1
O22B	0.107 87 (50)	1.021 15 (42)	0.649 56 (88)	4.7	C33A	0.140 98 (68)	0.462 12 (58)	0.553 5 (12)	3.7
O23A	0.407 85 (55)	0.411 65 (47)	1.222 06	5.7	C33B	0.373 07 (69)	0.912 75 (58)	0.220 0 (12)	3.7
O23B	−0.008 08 (50)	1.030 08 (42)	0.164 90 (86)	4.6	C41A	0.213 27 (64)	0.212 08 (55)	0.981 1 (11)	3.3
O31A	0.016 38 (49)	0.388 55 (42)	0.539 43 (87)	4.6	C41B	0.225 10 (66)	0.711 30 (57)	0.213 2 (12)	3.4
O31B	0.495 03 (46)	0.757 22 (39)	0.380 84 (80)	4.0	C42A	0.048 71 (71)	0.320 59 (58)	0.904 5 (12)	3.8
O32A	0.000 65 (56)	0.544 37 (47)	0.821 64 (95)	5.7	C42B	0.351 49 (62)	0.728 93 (53)	0.095 9 (11)	3.1
O32B	0.447 69 (60)	0.905 61 (50)	0.635 9 (11)	6.4	C43A	0.118 61 (62)	0.232 60 (53)	0.703 0 (11)	3.0
O33A	0.131 16 (52)	0.480 86 (44)	0.426 29 (94)	5.2	C43B	0.386 70 (71)	0.662 48 (61)	0.381 5 (12)	3.9
O33B	0.404 45 (55)	0.926 83 (47)	0.133 85 (98)	5.7	C51A	0.378 49 (66)	0.149 79 (57)	0.975 9 (11)	3.4
O41A	0.203 51 (53)	0.164 75 (46)	1.036 86 (94)	5.4	C51B	0.052 61 (70)	0.826 19 (59)	0.146 0 (12)	3.8
O41B	0.217 58 (56)	0.661 53 (48)	0.152 70 (98)	5.8	C52A	0.351 27 (61)	0.235 22 (51)	1.203 0 (11)	2.9
O42A	−0.012 81 (61)	0.333 89 (51)	0.950 4 (11)	6.6	C52B	0.117 68 (66)	0.738 51 (57)	0.391 5 (12)	3.5
O42B	0.370 26 (48)	0.716 11 (41)	−0.017 64 (86)	4.5	C61A	0.143 44 (69)	0.613 25 (59)	0.809 6 (12)	3.6
O43A	0.102 99 (56)	0.188 79 (48)	0.630 35 (99)	5.9	C61B	0.130 57 (67)	1.120 32 (57)	0.317 2 (12)	3.4
O43B	0.428 27 (60)	0.606 51 (53)	0.444 4 (11)	6.6	C62A	0.263 76 (70)	0.521 08 (59)	0.671 3 (13)	3.9
O51A	0.420 21 (57)	0.090 11 (49)	0.976 22 (99)	6.0	C62B	0.262 40 (66)	1.031 89 (56)	0.558 0 (12)	3.5
O51B	−0.008 62 (59)	0.842 76 (50)	0.045 9 (10)	6.3	C63A	0.318 89 (72)	0.551 17 (60)	0.958 3 (12)	3.9
O52A	0.374 21 (49)	0.229 67 (41)	1.332 96 (88)	4.6	C63B	0.192 84 (62)	1.021 04 (52)	0.120 6 (11)	2.9
O52B	0.096 48 (54)	0.697 41 (47)	0.439 58 (96)	5.6	C64A	0.200 65 (67)	0.516 53 (56)	1.055 0 (12)	3.6
O61A	0.090 04 (56)	0.669 28 (48)	0.777 60 (97)	5.8	C64B	0.307 4 (69)	1.066 33 (57)	0.314 6 (12)	3.7

and the $Ru(CO)_5$ could add to the starting material in some cases. This could explain the significant amounts of larger clusters that were obtained in the degradation experiments and could also explain the relatively small amounts of 1 obtained in the treatment of 3 with CO. The structures of 2, 3, and 4 were established by single-crystal x-ray diffraction analyses and are described below.

Description of the Structure of 2. Compound 2 crystallized in the monoclinic crystal system, space group $P2_1/c$, and contained two independent molecules in the asymmetric crystal unit. Surprisingly, the molecules were structurally different. For the sake of their descriptions, they have been labeled as molecules A and B. Final positional parameters are listed in Table II. An ORTEP diagram of A is shown in Figure 1, and an ORTEP diagram of B is shown in Figure 2. The bond distances and angles for A have been tabulated separately in Tables III and IV, respectively, and have been tabulated in Tables V and VI, respectively. Both molecules have the same molecular formulas and are composed of square-pyramidal clusters of five ruthenium atoms that have a quadruply bridging sulfido ligand spanning the square base of the pyramid. The principal difference between A and B lies in the arrangement of the bridging carbonyl ligands. Molecule A has four carbonyl ligands that bridge the four edges of the squares base of the pyramid. They lie approximately in the Ru_4 plane. Molecule B on the other hand has three edge-bridging carbonyl ligands and one asymmetric triply bridging carbonyl ligand, C(43). One could imagine that B was formed from A by shifting the edge bridging carbonyl C(43)–O(43) onto the Ru(1), Ru(4), Ru(5) face of the square pyramid and establishing a bond between Ru(1) and the carbon atom. The distance that C(43) would have to move is quite large. The nonbonding Ru(1)···C(43) distance in A is 3.74 (1) Å. The bonding Ru(1)–C(43) distance in B is 2.37 (1) Å. The different bonding modes of the ligands C(43)–O(43) appear to have a significant effect on the metal–metal bonding. The greatest effect was found for the Ru(4)–Ru(5) bond. In A, the Ru(4)–Ru(5) distance is 2.750 (1) Å. This is very similar to the Ru–Ru bond distance spanned by the three other bridging CO ligands. However, in B the Ru(4)–Ru(5) distance is over 0.10 Å longer than that in A, 2.866 (2) Å. The metal–metal bonds in B that contain only *edge-bridging* CO ligands are similar in length to those in A. The presence of the triply bridging CO ligand also affects the metal–metal bonding to the apical metal atom Ru(1). The Ru(1)–Ru(4) and Ru(1)–Ru(5) bonds in B are slightly *shorter* than those in A, Ru(1B)–Ru(4B) = 2.828 (2) Å vs Ru(1A)–Ru(4A) = 2.852 (2) Å and Ru(1B)–Ru(5B) = 2.813 (2) Å vs Ru(1A)–Ru(5A) = 2.824 (2) Å. The bonds to Ru(1) that are not bridged by the CO ligand are *longer* in B than in A,

Table VIII. Intramolecular Distances (Å) for $Ru_6(CO)_{15}(\mu\text{-}CO)_3(\mu_4\text{-}S)$ (3)

atom	atom	dist	atom	atom	dist
Ru1A	C11A	1.84 (1)	Ru1B	C12B	1.83 (1)
Ru1A	C13A	1.88 (1)	Ru1B	C11B	1.85 (1)
Ru1A	C12A	1.91 (1)	Ru1B	C13B	1.88 (1)
Ru1A	Ru3A	2.821 (1)	Ru1B	Ru2B	2.813 (1)
Ru1A	Ru2A	2.834 (1)	Ru1B	Ru3B	2.835 (1)
Ru1A	Ru4A	2.859 (1)	Ru1B	Ru5B	2.857 (1)
Ru1A	Ru5A	2.880 (1)	Ru1B	Ru4B	2.859 (1)
Ru2A	C22A	1.88 (1)	Ru2B	C22B	1.86 (1)
Ru2A	C23A	1.89 (1)	Ru2B	C23B	1.88 (1)
Ru2A	C21A	2.05 (1)	Ru2B	C21B	2.05 (1)
Ru2A	S1A	2.416 (2)	Ru2B	S1B	2.406 (2)
Ru2A	Ru5A	2.790 (1)	Ru2B	Ru6B	2.792 (1)
Ru2A	Ru3A	2.807 (1)	Ru2B	Ru5B	2.792 (1)
Ru2A	Ru6A	2.810 (1)	Ru2B	Ru3B	2.810 (1)
Ru3A	C33A	1.85 (1)	Ru3B	C32B	1.86 (1)
Ru3A	C32A	1.89 (1)	Ru3B	C33B	1.91 (1)
Ru3A	C31A	2.05 (1)	Ru3B	C31B	2.06 (1)
Ru3A	S1A	2.405 (2)	Ru3B	S1B	2.418 (2)
Ru3A	Ru4A	2.791 (1)	Ru3B	Ru4B	2.790 (1)
Ru3A	Ru6A	2.809 (1)	Ru3B	Ru6B	2.803 (1)
Ru4A	C43A	1.84 (1)	Ru4B	C43B	1.86 (1)
Ru4A	C42A	1.87 (1)	Ru4B	C42B	1.90 (1)
Ru4A	C41A	2.04 (1)	Ru4B	C41B	2.06 (1)
Ru4A	C31A	2.13 (1)	Ru4B	C31B	2.11 (1)
Ru4A	S1A	2.460 (2)	Ru4B	S1B	2.456 (2)
Ru4A	Ru5A	2.726 (1)	Ru4B	Ru5B	2.739 (1)
Ru5A	C51A	1.87 (1)	Ru5B	C52B	1.85 (1)
Ru5A	C52A	1.88 (1)	Ru5B	C51B	1.87 (1)
Ru5A	C41A	2.06 (1)	Ru5B	C41B	2.06 (1)
Ru5A	C21A	2.14 (1)	Ru5B	C21B	2.15 (1)
Ru5A	S1A	2.457 (2)	Ru5B	S1B	2.457 (2)
Ru6A	C63A	1.88 (1)	Ru6B	C64B	1.89 (1)
Ru6A	C61A	1.90 (1)	Ru6B	C61B	1.92 (1)
Ru6A	C62A	1.94 (1)	Ru6B	C62B	1.93 (1)
Ru6A	C64A	1.96 (1)	Ru6B	C63B	1.96 (1)
OA	CA_{av}	1.16 (1)	OB	CB_{av}	1.16 (1)

Ru(1B)–Ru(2B) = 2.857 (1) Å vs Ru(1A)–Ru(2A) = 2.782 (1) Å and Ru(1B)–Ru(3B) = 2.884 (2) Å vs Ru(1A)–Ru(3A) = 2.832 (2) Å. The conversion of the *edge-bridging* CO ligand into a triply bridging CO ligand does not appear to have a significant effect on the metal–sulfur bonding.

The triply bridging CO ligand in B is asymmetrically bonded to the three metal atoms, Ru(1B)–C(43B) = 2.37 (1) Å, Ru(4B)–C(43B) = 2.29 (1) Å, and Ru(5B)–C(43B) = 2.09 (1) Å. The Ru–C distances to the edge-bridging carbonyl ligands are very similar both in A and in B: bridging Ru–C_{av} = 2.11 Å in A vs 2.09 Å in B. Likewise the Ru–C distances to the terminal carbonyl ligands in A and B are similar: terminal Ru–C_{av} = 1.92 Å in A vs 1.90 Å in B. There are significant differences in the Ru–Ru–C bonds angles to the terminal ligands on Ru(4) and Ru(5). The angles closest to the triply bridging CO ligand are greater in B than in A: Ru(5B)–Ru(4B)–C(41B) = 124.0 (3)° vs Ru(5A)–Ru(4A)–C(41A) = 121.3 (3)° and Ru(4B)–Ru(5B)–C(51B) = 132.1 (3)° vs Ru(4A)–Ru(5A)–C(52A) = 118.2 (3)°. The angles to the terminal CO ligands most remote to the triply bridging CO ligand are smaller in B than in A: Ru(5B)–Ru(4B)–C(42B) = 105.5 (4)° vs Ru(5A)–Ru(4A)–C(42A) = 120.7 (3)° and Ru(4B)–Ru(5B)–C(52B) = 101.0 (3)° vs Ru(4A)–Ru(5A)–C(51A) = 120.0 (3)°.

The compounds $Ru_5(CO)_{15}(\mu_4\text{-}PR)$(R = Ph (5),[8] Et (6),[8] and $Os_5(CO)_{15}(\mu_4\text{-}S)$ (7)[9]) are structurally similar to 2, but none of these have bridging carbonyl ligands. The position of the C–O stretching frequency of the triply bridging CO ligand was easily ascertained from crystals that were ground and pressed into KBr, 1779 (w) cm^{-1}. A very weak and broad absorption centered at 1782 cm^{-1} was observed for solutions of 2 in CH_2Cl_2, and indicated that a portion of molecules of 2 retained the B structure in solution. Unfortunately, the low solubility of 2 prevented the recording of ^{13}C NMR spectra that might have revealed the relative amounts of A and B in solution and also the possibility of dynamical interconversions.

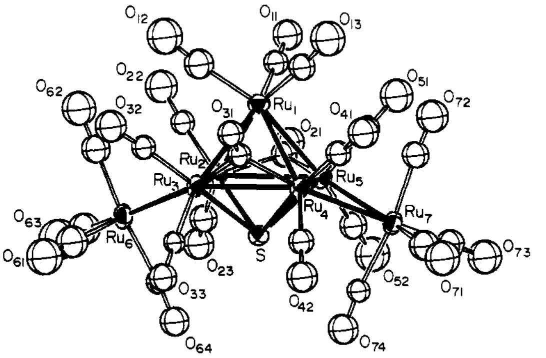

Figure 4. An ORTEP diagram of $Ru_7(CO)_{19}(\mu\text{-}CO)_2(\mu_4\text{-}S)$ (4) showing 50% probability thermal ellipsoids.

Description of the Structure of 3. Compound 3 crystallized in the triclinic crystal system, space group $P\bar{1}$, and contained two independent molecules in the asymmetric crystal unit. In this case, however, both molecules were structurally similar. An ORTEP diagram of 3 is shown in Figure 3. Final positional parameters are listed in Table VII. Intramolecular bond distances are listed in Table VIII. Bond angles for molecule A are listed in Table IX. Bond angles for molecule B have been submitted with the supplementary material. Compound 3 consists of a square-pyramidal cluster of five ruthenium atoms with a quadruply bridging sulfido ligand on the square base. The sixth ruthenium atom bridges a basal edge of the cluster in the form of a $Ru(CO)_4$ group. The remaining basal edges each contain one *edge-bridging* carbonyl ligand. The Ru(4)–Ru(5) edge of the cluster, which is located opposite the $Ru(CO)_4$-bridged edge (Ru(2)–Ru(3)), is significantly shorter than all the others, 2.726 (1) Å [2.739 (1) Å]. The quantity in brackets corresponds to the molecule 3B. The remaining basal edges including those bonds to the bridge Ru(6) all lie very close to 2.80 Å, range 2.790 (1)–2.810 (1) Å. The bonds to the apical atom Ru(1) show significant variation, but all are longer than those in the square base. The bonds to the Ru(6)-bridged edge of the base, Ru(1)–Ru(2) and Ru(1)–Bu(3), are systematically shorter, 2.813 (1)–2.835 (1) Å, than those to the opposite edge, Ru(1)–Ru(4) and Ru(1)–Ru(5), 2.857 (1)–2.880 (1) Å. The Ru–S bonding in 3 is similar to that found in 2.

Description of the Structure of 4. Compound 4 crystallized in the monoclinic crystal system, space group $P2_1/n$, and contained one complete formula equivalent of $Ru_7(CO)_{19}(\mu\text{-}CO)_2(\mu_4\text{-}S)$ in the asymmetric crystal unit. Final atomic positional parameters are listed in Table X. Selected intramolecular bond distances and angles are listed in Tables XI and XII, respectively. An ORTEP dia-

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[9] Adams, R. D.; Horvath, I. T.; Segmuller, B. E.; Yang, L. W. *Organometallics* 1983, *2*, 1301.

Table IX. Intramolecular Bond Angles (deg) for $Ru_6(CO)_{15}(\mu\text{-}CO)_3(\mu_4\text{-}S)$ (3)

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C11A	Ru1A	Ru3A	97.7 (4)	C32A	Ru3A	Ru6A	80.2 (3)	S1A	Ru5A	Ru4A	56.38 (6)
C11A	Ru1A	Ru2A	156.0 (4)	C32A	Ru3A	Ru1A	166.7 (3)	S1A	Ru5A	Ru2A	54.39 (6)
C11A	Ru1A	Ru4A	86.6 (4)	C31A	Ru3A	Ru4A	49.4 (3)	S1A	Ru5A	Ru1A	81.50 (6)
C11A	Ru1A	Ru5A	133.6 (4)	C31A	Ru3A	Ru2A	133.9 (3)	Ru4A	Ru5A	Ru2A	90.91 (4)
C13A	Ru1A	Ru3A	169.4 (3)	C31A	Ru3A	Ru6A	166.0 (3)	Ru4A	Ru5A	Ru1A	61.26 (3)
C13A	Ru1A	Ru2A	116.3 (3)	C31A	Ru3A	Ru1A	79.6 (3)	Ru2A	Ru5A	Ru1A	59.96 (3)
C13A	Ru1A	Ru4A	112.6 (3)	S1A	Ru3A	Ru4A	55.92 (6)	C63A	Ru6A	Ru3A	158.3 (3)
C13A	Ru1A	Ru5A	82.7 (3)	S1A	Ru3A	Ru2A	54.58 (6)	C63A	Ru6A	Ru2A	98.4 (3)
C12A	Ru1A	Ru3A	91.8 (3)	S1A	Ru3A	Ru6A	86.39 (6)	C61A	Ru6A	Ru3A	104.6 (3)
C12A	Ru1A	Ru2A	83.2 (3)	S1A	Ru3A	Ru1A	83.64 (6)	C61A	Ru6A	Ru2A	164.3 (3)
C12A	Ru1A	Ru4A	149.7 (3)	Ru4A	Ru3A	Ru2A	89.24 (4)	C62A	Ru6A	Ru3A	88.5 (3)
C12A	Ru1A	Ru5A	135.8 (3)	Ru4A	Ru3A	Ru6A	141.70 (4)	C62A	Ru6A	Ru2A	90.8 (3)
Ru3A	Ru1A	Ru2A	59.51 (3)	Ru4A	Ru3A	Ru1A	61.26 (3)	C64A	Ru6A	Ru3A	89.4 (3)
Ru3A	Ru1A	Ru4A	58.85 (3)	Ru2A	Ru3A	Ru6A	60.06 (3)	C64A	Ru6A	Ru2A	87.0 (3)
Ru3A	Ru1A	Ru5A	87.06 (4)	Ru2A	Ru3A	Ru1A	60.49 (3)	Ru3A	Ru6A	Ru2A	59.94 (3)
Ru2A	Ru1A	Ru4A	87.34 (3)	Ru6A	Ru3A	Ru1A	112.76 (4)	Ru3A	S1A	Ru2A	71.20 (7)
Ru2A	Ru1A	Ru5A	58.45 (3)	C43A	Ru4A	Ru5A	113.0 (3)	Ru3A	S1A	Ru5A	107.7 (1)
Ru4A	Ru1A	Ru5A	56.71 (3)	C43A	Ru4A	Ru3A	129.7 (3)	Ru3A	S1A	Ru4A	69.99 (7)
C22A	Ru2A	Ru5A	133.0 (3)	C43A	Ru4A	Ru1A	92.0 (3)	Ru2A	S1A	Ru5A	69.86 (7)
C22A	Ru2A	Ru3A	116.0 (3)	C42A	Ru4A	Ru5A	126.4 (3)	Ru2A	S1A	Ru4A	107.5 (1)
C22A	Ru2A	Ru6A	84.1 (3)	C42A	Ru4A	Ru3A	108.1 (3)	Ru5A	S1A	Ru4A	67.34 (7)
C22A	Ru2A	Ru1A	95.9 (3)	C42A	Ru4A	Ru1A	166.9 (3)	O11A	C11A	Ru1A	175 (1)
C23A	Ru2A	Ru5A	103.3 (3)	C41A	Ru4A	Ru5A	48.7 (3)	O12A	C12A	Ru1A	174 (1)
C23A	Ru2A	Ru3A	130.3 (3)	C41A	Ru4A	Ru3A	137.6 (3)	O13A	C13A	Ru1A	176 (1)
C23A	Ru2A	Ru6A	83.6 (3)	C41A	Ru4A	Ru1A	100.9 (3)	O21A	C21A	Ru2A	140.7 (8)
C23A	Ru2A	Ru1A	163.4 (3)	C31A	Ru4A	Ru5A	133.4 (3)	O21A	C21A	Ru5A	135.8 (8)
C21A	Ru2A	Ru5A	49.7 (3)	C31A	Ru4A	Ru3A	47.0 (3)	Ru2A	C21A	Ru5A	83.5 (4)
C21A	Ru2A	Ru3A	128.8 (3)	C31A	Ru4A	Ru1A	77.5 (3)	O22A	C22A	Ru2A	175 (1)
C21A	Ru2A	Ru6A	168.9 (3)	S1A	Ru4A	Ru5A	56.28 (6)	O23A	C23A	Ru2A	179 (1)
C21A	Ru2A	Ru1A	72.5 (3)	S1A	Ru4A	Ru3A	54.09 (6)	O31A	C31A	Ru3A	140.1 (8)
S1A	Ru2A	Ru5A	55.75 (6)	S1A	Ru4A	Ru1A	81.88 (6)	O31A	C31A	Ru4A	136.2 (8)
S1A	Ru2A	Ru3A	54.22 (6)	Ru5A	Ru4A	Ru3A	90.75 (4)	Ru3A	C31A	Ru4A	83.6 (4)
S1A	Ru2A	Ru6A	86.15 (6)	Ru5A	Ru4A	Ru1A	62.03 (3)	O32A	C32A	Ru3A	176 (1)
S1A	Ru2A	Ru1A	83.16 (6)	Ru3A	Ru4A	Ru1A	59.88 (3)	O33A	C33A	Ru3A	175 (1)
Ru5A	Ru2A	Ru3A	89.10 (4)	C51A	Ru5A	Ru4A	117.7 (3)	O41A	C41A	Ru4A	138.9 (8)
Ru5A	Ru2A	Ru6A	141.36 (4)	C51A	Ru5A	Ru2A	131.5 (3)	O41A	C41A	Ru5A	137.8 (8)
Ru5A	Ru2A	Ru1A	61.59 (3)	C51A	Ru5A	Ru1A	98.8 (3)	Ru4A	C41A	Ru5A	83.3 (4)
Ru3A	Ru2A	Ru6A	60.00 (3)	C52A	Ru5A	Ru4A	127.3 (3)	O42A	C42A	Ru4A	178 (1)
Ru3A	Ru2A	Ru1A	60.00 (3)	C52A	Ru5A	Ru2A	102.6 (3)	O43A	C43A	Ru4A	176.9 (9)
Ru6A	Ru2A	Ru1A	112.29 (4)	C52A	Ru5A	Ru1A	162.1 (3)	O51A	C51A	Ru5A	176 (1)
C33A	Ru3A	Ru4A	126.6 (3)	C41A	Ru5A	Ru4A	48.0 (3)	O52A	C52A	Ru5A	178.5 (9)
C33A	Ru3A	Ru2A	112.5 (3)	C41A	Ru5A	Ru2A	137.2 (3)	O61A	C61A	Ru6A	180 (1)
C33A	Ru3A	Ru6A	88.5 (3)	C41A	Ru5A	Ru1A	99.7 (3)	O62A	C62A	Ru6A	175 (1)
C33A	Ru3A	Ru1A	87.2 (3)	C21A	Ru5A	Ru4A	128.0 (3)	O63A	C63A	Ru6A	178 (1)
C32A	Ru3A	Ru4A	106.9 (3)	C21A	Ru5A	Ru2A	46.8 (3)	O64A	C64A	Ru6A	174 (1)
C32A	Ru3A	Ru2A	128.5 (3)	C21A	Ru5A	Ru1A	70.3 (3)				

Scheme I

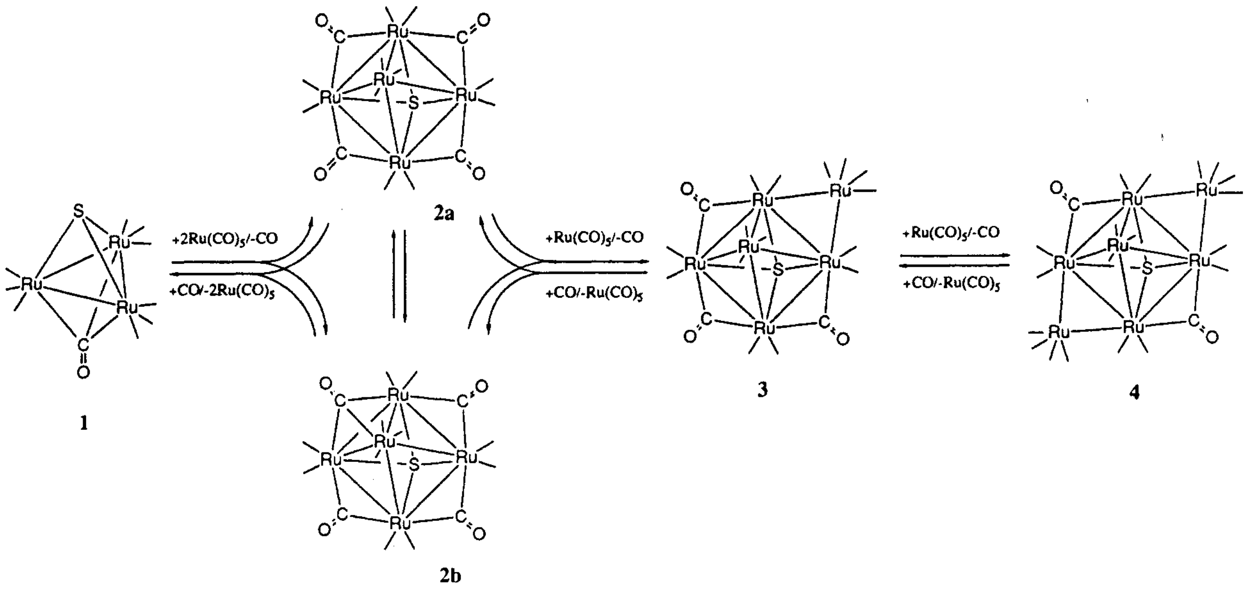

Table X. Positional Parameters and *B*(eq) for $Ru_7(CO)_{19}(\mu\text{-}CO)_2(\mu_4\text{-}S)$ (4)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru1	1.07819 (12)	0.199301 (88)	0.827933 (86)	2.33 (6)
Ru2	0.87113 (12)	0.209685 (82)	0.707971 (89)	2.10 (6)
Ru3	1.00014 (12)	0.074516 (81)	0.710167 (88)	2.13 (6)
Ru4	1.17344 (12)	0.167217 (80)	0.689024 (89)	2.02 (6)
Ru5	1.04507 (12)	0.303514 (81)	0.684739 (86)	2.05 (6)
Ru6	0.77130 (13)	0.061161 (88)	0.664100 (99)	2.70 (7)
Ru7	1.22049 (12)	0.301741 (89)	0.605312 (92)	2.51 (6)
S	0.98385 (35)	0.18136 (24)	0.60827 (26)	2.0 (2)
O11	1.0157 (11)	0.34041 (82)	0.92078 (83)	4.4 (3)
O12	1.0151 (14)	0.0928 (10)	0.9598 (10)	6.5 (4)
O13	1.3111 (13)	0.22273 (95)	0.92940 (98)	6.1 (4)
O21	0.8543 (11)	0.38721 (80)	0.73570 (83)	4.2 (3)
O22	0.7749 (12)	0.21444 (88)	0.85862 (93)	5.3 (3)
O23	0.6643 (12)	0.26748 (84)	0.58458 (89)	4.9 (3)
O31	1.2299 (10)	0.02377 (74)	0.80454 (76)	3.5 (3)
O32	0.9919 (12)	−0.05498 (88)	0.83421 (91)	5.1 (3)
O33	1.0058 (10)	−0.05082 (77)	0.57574 (80)	3.9 (3)
O41	1.4131 (12)	0.16908 (82)	0.77910 (85)	4.7 (3)
O42	1.2428 (12)	0.07186 (85)	0.55239 (89)	4.9 (3)
O51	1.1431 (12)	0.43857 (92)	0.80043 (94)	5.5 (4)
O52	0.9588 (13)	0.41560 (98)	0.5373 (10)	6.2 (4)
O61	0.7631 (14)	−0.1159 (11)	0.6257 (10)	6.8 (4)
O62	0.7766 (13)	0.03478 (92)	0.8521 (10)	5.9 (4)
O63	0.5241 (17)	0.0823 (12)	0.6254 (12)	8.4 (5)
O64	0.7700 (11)	0.10145 (79)	0.47877 (87)	4.3 (3)
O71	1.4238 (14)	0.24555 (95)	0.55217 (98)	6.2 (4)
O72	1.3575 (12)	0.35554 (87)	0.77637 (95)	5.2 (3)
O73	1.2257 (13)	0.46309 (95)	0.52048 (99)	5.8 (4)
O74	1.0692 (12)	0.23753 (82)	0.43829 (88)	4.6 (3)
C11	1.0368 (15)	0.2859 (11)	0.8833 (11)	3.0 (4)
C12	1.0365 (17)	0.1303 (13)	0.9070 (14)	4.4 (5)
C13	1.2212 (16)	0.2131 (12)	0.8849 (12)	3.5 (4)
C21	0.9075 (15)	0.3321 (11)	0.7226 (12)	3.3 (4)
C22	0.8111 (14)	0.2118 (10)	0.7986 (11)	2.8 (4)
C23	0.7421 (17)	0.2409 (12)	0.6304 (13)	3.9 (4)
C31	1.1682 (15)	0.0687 (11)	0.7609 (11)	2.8 (4)
C32	0.9937 (15)	−0.0031 (11)	0.7894 (11)	3.0 (4)
C33	1.0009 (14)	−0.0040 (10)	0.6273 (10)	2.3 (3)
C41	1.3154 (16)	0.1716 (11)	0.7449 (12)	3.2 (4)
C42	1.2163 (16)	0.1089 (11)	0.6067 (12)	3.3 (4)
C51	1.1039 (15)	0.3861 (11)	0.7554 (11)	3.0 (4)
C52	0.9928 (17)	0.3718 (12)	0.5932 (13)	3.8 (4)
C61	0.7599 (19)	−0.0496 (14)	0.6398 (14)	5.2 (5)
C62	0.7730 (17)	0.0463 (12)	0.7819 (13)	4.2 (5)
C63	0.6208 (20)	0.0753 (14)	0.6429 (14)	5.1 (5)
C64	0.7776 (15)	0.0882 (11)	0.5484 (12)	3.0 (4)
C71	1.3451 (18)	0.2687 (13)	0.5712 (13)	4.5 (5)
C72	1.3021 (6)	0.3349 (12)	0.7151 (13)	3.7 (4)
C73	1.2232 (17)	0.4028 (13)	0.5528 (13)	4.1 (5)
C74	1.1189 (15)	0.2593 (10)	0.4993 (11)	2.7 (4)

Table XI. Selected Intramolecular Distances (Å) for $Ru_7(CO)_{19}(\mu\text{-}CO)_2(\mu_4\text{-}S)$ (4)

atom	atom	dist	atom	atom	dist
Ru1	C13	1.81 (2)	Ru4	C41	1.79 (2)
Ru1	C11	1.85 (2)	Ru4	C42	1.84 (2)
Ru1	C12	1.89 (2)	Ru4	C31	2.04 (2)
Ru1	Ru2	2.838 (2)	Ru4	S	2.422 (5)
Ru1	Ru4	2.842 (2)	Ru4	Ru7	2.774 (2)
Ru1	Ru3	2.845 (2)	Ru4	Ru5	2.788 (2)
Ru1	Ru5	2.857 (2)	Ru5	C51	1.84 (2)
Ru2	C22	1.80 (2)	Ru5	C52	1.87 (2)
Ru2	C23	1.86 (2)	Ru5	C21	2.02 (2)
Ru2	C21	2.11 (2)	Ru5	S	2.425 (4)
Ru2	S	2.434 (4)	Ru5	Ru7	2.797 (2)
Ru2	Ru3	2.782 (2)	Ru6	C63	1.84 (2)
Ru2	Ru5	2.783 (2)	Ru6	C61	1.90 (2)
Ru2	Ru6	2.805 (2)	Ru6	C62	1.92 (2)
Ru3	C32	1.85 (2)	Ru6	C64	1.95 (2)
Ru3	C33	1.89 (2)	Ru7	C71	1.86 (2)
Ru3	C31	2.06 (2)	Ru7	C73	1.90 (2)
Ru3	S	2.416 (4)	Ru7	C72	1.91 (2)
Ru3	Ru4	2.755 (2)	Ru7	C74	2.00 (2)
Ru3	Ru6	2.781 (2)	O	C_{av}	1.16 (2)

gram of **4** is shown in Figure 4. Like **2** and **3**, **4** also consists of a square pyramidal cluster of five ruthenium atoms with a quadruply bridging sulfido ligand spanning the square base. $Ru(CO)_4$ groups bridge oppositely positioned basal edges, Ru(2)–Ru(3) and Ru(4)–Ru(5), of the square pyramid. The two remaining basal edges are bridged by carbonyl ligands. The metal–metal bonds within the square base and those that extend to the bridging $Ru(CO)_4$ groups are all very similar in length and lie within the range 2.755 (2)–2.805 (2) Å. The metal–metal bonds between the apical atom Ru(1) and those of the square base are all significantly longer than the others and, unlike those in **2** and **3**, all lie in the relatively narrow range of 2.838 (2)–2.857 (2) Å. The metal–metal bond distances in **5**, **6**, and **7** showed considerable variation, but there were no significant differences between the apical–basal and the basal–basal bonding distances.[8,9] It is believed that the relative shortness of the basal Ru–Ru bonds in **4** can be attributed to the presence of the bridging CO and $Ru(CO)_4$ groups since **5**, **6**, and **7** did not possess either of these bridging groups. The Ru–S bonding in **4** is similar to that in **2** and **3**. Overall, the molecule has approximate mirror symmetry (not crystallographic) with the atoms Ru(1), S, and the carbonyl ligands C(11)–O(11), C(21)–O(21), and C(31)–O(31) lying in this approximate plane.

Discussion

In previous studies, it was shown that certain cluster compounds having sulfido ligands that contained a lone pair of electrons were able to add unsaturated metal carbonyl fragments by the formation of a S→M donor–acceptor bond.[10,11] $Ru(CO)_5$ is known to lose CO upon mild heating.[12] When solutions of **1** and $Ru(CO)_5$ were heated, the metal nuclearity of **1** was increased. The smallest of the three higher clusters that were formed was $Ru_5(CO)_{15}(\mu_4\text{-}S)$ (**2**). We have found no evidence for a tetraruthenium species under these conditions even though two tetraosmium species, $Os_4(CO)_{13}(\mu_3\text{-}S)$[9] and $Os_4(CO)_{12}(\mu_3\text{-}S)$,[13] are known and stable.[9,13] The latter was made from $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ and $Os(CO)_5$ by exposure to UV irradiation. It is possible that **2** was formed by the addition of $Ru(CO)_4$ fragments to **1** via the intermediacy of a S→Ru interaction prior to the incorporation of the metal into the cluster although there was no evidence for a stable species of this type. The addition of the two Ru fragments to **1** to form **2** results in an enlargement of the basic cluster unit (i.e., size of the polyhedron) to that of a square pyramid. It is both interesting and unusual to observe the existence of two structural isomers of a compound in the same crystal lattice, but this was the case in the crystal of **2**. Isomer A contained four *edge-bridging* carbonyl ligands on the four basal Ru–Ru bonds of the cluster. Isomer B had three *edge-bridging* carbonyl ligands in positions similar to A and one *triply bridging* carbonyl ligand.

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Table XII. Intramolecular Bond Angles (deg) for $Ru_7(CO)_{19}(\mu\text{-}CO)_2(\mu_4\text{-}S)$ (4)

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C13	Ru1	Ru2	163.9 (6)	S	Ru3	Ru4	55.4 (1)	Ru4	Ru5	Ru1	60.42 (5)
C13	Ru1	Ru4	83.0 (6)	S	Ru3	Ru6	88.1 (1)	Ru7	Ru5	Ru1	113.10 (7)
C13	Ru1	Ru3	124.8 (6)	S	Ru3	Ru2	55.3 (1)	C63	Ru6	Ru3	167.1 (7)
C13	Ru1	Ru5	105.4 (6)	S	Ru3	Ru1	82.4 (1)	C63	Ru6	Ru2	107.6 (7)
C11	Ru1	Ru2	88.2 (6)	Ru4	Ru3	Ru6	143.03 (7)	C61	Ru6	Ru3	98.9 (7)
C11	Ru1	Ru4	138.9 (5)	Ru4	Ru3	Ru2	90.32 (6)	C61	Ru6	Ru2	158.6 (7)
C11	Ru1	Ru3	144.7 (6)	Ru4	Ru3	Ru1	60.96 (5)	C62	Ru6	Ru3	88.9 (6)
C11	Ru1	Ru5	84.7 (5)	Ru6	Ru3	Ru2	60.57 (5)	C62	Ru6	Ru2	88.1 (6)
C12	Ru1	Ru2	98.5 (6)	Ru6	Ru3	Ru1	113.69 (7)	C64	Ru6	Ru3	87.7 (5)
C12	Ru1	Ru4	131.0 (6)	Ru2	Ru3	Ru1	60.56 (6)	C64	Ru6	Ru2	85.2 (5)
C12	Ru1	Ru3	84.0 (6)	C41	Ru4	Ru3	132.3 (6)	Ru3	Ru6	Ru2	59.72 (5)
C12	Ru1	Ru5	156.4 (6)	C41	Ru4	Ru7	85.0 (6)	C71	Ru7	Ru4	101.2 (7)
Ru2	Ru1	Ru4	87.46 (6)	C41	Ru4	Ru5	118.2 (6)	C71	Ru7	Ru5	161.1 (7)
Ru2	Ru1	Ru3	58.61 (5)	C41	Ru4	Ru1	98.3 (6)	C73	Ru7	Ru4	167.3 (6)
Ru2	Ru1	Ru5	58.51 (5)	C42	Ru4	Ru3	99.4 (6)	C73	Ru7	Ru5	107.3 (6)
Ru4	Ru1	Ru3	57.95 (5)	C42	Ru4	Ru7	86.9 (6)	C72	Ru7	Ru4	84.9 (6)
Ru4	Ru1	Ru5	58.59 (5)	C42	Ru4	Ru5	133.5 (6)	C72	Ru7	Ru5	82.4 (6)
Ru3	Ru1	Ru5	87.09 (6)	C42	Ru4	Ru1	158.2 (6)	C74	Ru7	Ru4	87.9 (5)
C22	Ru2	Ru3	111.1 (6)	C31	Ru4	Ru3	48.2 (5)	C74	Ru7	Ru5	89.7 (5)
C22	Ru2	Ru5	126.2 (6)	C31	Ru4	Ru7	169.7 (5)	Ru4	Ru7	Ru5	60.07 (5)
C22	Ru2	Ru6	88.7 (6)	C31	Ru4	Ru5	125.8 (5)	Ru3	S	Ru4	69.4 (1)
C22	Ru2	Ru1	86.1 (6)	C31	Ru4	Ru1	67.9 (5)	Ru3	S	Ru5	108.5 (2)
C23	Ru2	Ru3	130.0 (6)	S	Ru4	Ru3	55.2 (1)	Ru3	S	Ru2	70.0 (1)
C23	Ru2	Ru5	108.9 (6)	S	Ru4	Ru7	87.2 (1)	Ru4	S	Ru5	70.2 (1)
C23	Ru2	Ru6	79.7 (6)	S	Ru4	Ru5	54.9 (1)	Ru4	S	Ru2	107.9 (2)
C23	Ru2	Ru1	167.1 (6)	S	Ru4	Ru1	82.4 (1)	Ru5	S	Ru2	69.9 (1)
C21	Ru2	Ru3	133.5 (5)	Ru3	Ru4	Ru7	142.06 (7)	O11	C11	Ru1	177 (2)
C21	Ru2	Ru5	46.2 (5)	Ru3	Ru4	Ru5	90.26 (6)	O12	C12	Ru1	174 (2)
C21	Ru2	Ru6	165.5 (5)	Ru3	Ru4	Ru1	61.09 (5)	O13	C13	Ru1	173 (2)
C21	Ru2	Ru1	81.2 (5)	Ru7	Ru4	Ru5	60.38 (5)	O21	C21	Ru5	143 (2)
S	Ru2	Ru3	54.7 (1)	Ru7	Ru4	Ru1	114.31 (7)	O21	C21	Ru2	132 (1)
S	Ru2	Ru5	54.9 (1)	Ru5	Ru4	Ru1	60.99 (5)	Ru5	C21	Ru2	84.8 (7)
S	Ru2	Ru6	87.2 (1)	C51	Ru5	Ru2	123.5 (6)	O22	C22	Ru2	178 (2)
S	Ru2	Ru1	82.3 (1)	C51	Ru5	Ru4	117.8 (6)	O23	C23	Ru2	174 (2)
Ru3	Ru2	Ru5	89.82 (6)	C51	Ru5	Ru7	93.2 (6)	O31	C31	Ru4	139 (1)
Ru3	Ru2	Ru6	59.70 (6)	C51	Ru5	Ru1	90.0 (6)	O31	C31	Ru3	136 (1)
Ru3	Ru2	Ru1	60.83 (5)	C52	Ru5	Ru2	108.9 (6)	Ru4	C31	Ru3	84.5 (7)
Ru5	Ru2	Ru6	141.62 (7)	C52	Ru5	Ru4	127.9 (6)	O32	C32	Ru3	84.5 (7)
Ru5	Ru2	Ru1	61.10 (5)	C52	Ru5	Ru7	78.6 (6)	O32	C32	Ru3	175 (2)
Ru6	Ru2	Ru1	113.18 (7)	C52	Ru5	Ru1	168.0 (6)	O33	C33	Ru3	177 (1)
C32	Ru3	Ru4	130.9 (6)	C21	Ru5	Ru2	49.0 (5)	O41	C41	Ru4	175 (2)
C32	Ru3	Ru6	85.1 (6)	C21	Ru5	Ru4	135.6 (5)	O42	C42	Ru4	179 (2)
C32	Ru3	Ru2	117.6 (6)	C21	Ru5	Ru7	164.2 (5)	O51	C51	Ru5	179 (2)
C32	Ru3	Ru1	96.9 (6)	C21	Ru5	Ru1	82.2 (5)	O52	C52	Ru5	178 (2)
C33	Ru3	Ru4	99.7 (5)	S	Ru5	Ru2	55.2 (1)	O61	C61	Ru6	174 (2)
C33	Ru3	Ru6	86.3 (5)	S	Ru5	Ru4	54.8 (1)	O62	C62	Ru6	177 (2)
C33	Ru3	Ru2	131.8 (5)	S	Ru5	Ru7	86.6 (1)	O63	C63	Ru6	176 (2)
C33	Ru3	Ru1	159.2 (5)	S	Ru5	Ru1	82.0 (1)	O64	C64	Ru6	173 (2)
C31	Ru3	Ru4	47.4 (5)	Ru2	Ru5	Ru4	89.60 (6)	O71	C71	Ru7	177 (2)
C31	Ru3	Ru6	169.4 (5)	Ru2	Ru5	Ru7	141.27 (7)	O72	C72	Ru7	174 (2)
C31	Ru3	Ru2	125.0 (5)	Ru2	Ru5	Ru1	60.39 (6)	O73	C73	Ru7	179 (2)
C31	Ru3	Ru1	67.5 (5)	Ru4	Ru5	Ru7	59.55 (5)	O74	C74	Ru7	175 (2)

Clearly, the energy difference between A and B must be very small. Markó has reported the existence of a facile *edge-bridge–triple*-bridge carbonyl ligand exchange for the compound $Fe_3(CO)_{10}S$.[14] It seems that isomers A and B of 2 might undergo a rapid interconversion via a similar process, but this could not be determined due to its low solubility.

The addition of a third Ru fragment leads to $Ru_6(CO)_{15}(\mu\text{-}CO)_3(\mu_4\text{-}S)$ (**3**). This was apparently formed by the addition of a mononuclear ruthenium unit to 2, as indicated by the independent synthesis from 2 plus $Ru(CO)_5$. Curiously, the formation of 3 did not result in an enlargement of the basic cluster unit but instead resulted in the addition of a $Ru(CO)_4$ bridging group across one of the basal edges of the square pyramid through the replacement of one of the bridging CO groups. Mingos has recently pointed out the bonding advantages of bridging $M(CO)_4$ groupings.[14] These apparently override the advantages of enlargement of the cluster polyhedron in this case. It is possible that the initial addition of the fragment to 2 also occurred at the sulfur atom. An S→M donor–acceptor interaction was observed for the osmium homologue of **2**.[11] It is interesting to compare the chemistry of Ru_6S carbonyl clusters with that of the Os_6S clusters. $Os_6(CO)_{18}(\mu_4\text{-}S)$ has not yet been reported although $Os_6(CO)_{19}(\mu_3\text{-}S)$ (**8**) and $Os_6(CO)_{17}(\mu_4\text{-}S)$ (**9**) are known.[15] Interestingly, compound **9** was prepared from **8** by de-

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carbonylation. Compound **9** contains a square pyramid of five osmium atoms with an $Os(CO)_3$ capping group. It seems reasonable to expect that the analogous $Ru_6(CO)_{17}(\mu_4\text{-}S)$ could be prepared by the decarbonylation of **3**; however, this has not yet been achieved.

The addition of yet another ruthenium carbonyl fragment results in the formation of $Ru_7(CO)_{19}(\mu\text{-}CO)_2(\mu_4\text{-}S)$ (**4**). This product was made independently by the addition of a mononuclear fragment to **3**. The structure of **4** shows that it contains two $Ru(CO)_4$ groups which bridge diametrically opposed basal edges of the square pyramid and was formed by the replacement of a second bridging CO ligand in **3** with a $Ru(CO)_4$ group. The osmium homologue of **4** has not yet been reported. The closest related osmium compound is $Os_7(CO)_{19}(\mu_4\text{-}S)$ which contains a sulfur-bridged square pyramid of five osmium atoms that is fused to a trigonal-bipyramidal cluster of five osmium atoms through a triangular face.[13]

Compounds **2**, **3**, and **4** can be degraded by treatment with CO at 98 °C. Curiously, small amounts of **4** were formed in the degradation of **3** and small amounts of **3** and **4** were obtained in the degradation of **2**. The degradation reactions will lead to the formation of mononuclear ruthenium fragments which could be added to unreacted clusters. It is believed that under suitable conditions cluster enlargement and degradation will be ongoing and competing reactions in solutions that contain the appropriate species. These transformations are summarized in Scheme I.

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Registry No. 1, 105121-22-0; **2A**, 111976-49-9; **2B**, 111976-50-2; 3, 111976-47-7; 4, 111976-48-8; $Ru(CO)_5$, 16406-48-7.

Supplementary Material Available: Labeling diagram and a table of bond angles for molecule B of **3** and tables anisotropic thermal parameters (*U* values) for **2–4** (9 pages); listings of structure factor amplitudes for **2–4** (89 pages). Ordering information is given on any current masthead page.

AM1 Calculations for Compounds Containing Boron

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AM1 has been parametrized for boron. Calculations are reported for an extensive set of boron-containing compounds. Most of the results are better than those given by MNDO. AM1 is especially successful in dealing with boron hydrides containing three-center bonds with bridging hydrogen atoms. Studies of some reactions of boron compounds have given satisfactory results.

Introduction

The chemistry of boron is particularly rich and interesting because it forms a large variety of unusual molecules containing three-center, two-electron bonds of the kind first proposed by Longuet-Higgins.[2] It also forms a number of cage compounds containing three-dimensional delocalized systems, as Longuet-Higgins[3] also first pointed out in the case of the dodecaboride dianion ($B_{12}H_{12}^{2-}$). Interest in boron chemistry is moreover not confined to theory. Hydroboration has become a major tool in chemical synthesis, and the boron halides are widely used as Lewis acid catalysts. The need for an effective theoretical treatment of boron compounds is therefore evident, and none is yet available.

Current quantum mechanical treatments have encountered major problems in attempts to interpret the structures of the boron hydrides and carboranes. Their properties are not interpreted satisfactorily at the Hartree–Fock (HF) level. Thus ab initio HF methods fail to reproduce the heat of dimerization of borane (**1**) to diborane (**2**), even if a large basis set is used, and the same is true[4] for the pyramidal geometry (**3**) of pentaborane (B_5H_9). It is necessary to use a large basis set together with adequate allowance for electron correlation. The same situation holds generally for reactions, the hydroboration of ethylene being a typical example.[5] Such procedures can be applied only to small molecules.

Similar problems arise generally in attempts to use ab initio calculations as a direct aid in chemical research. In

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