1390 *Organometallics* **1991,** *10,* **1390–1394**

a senior fellowship. Mass spectra were obtained courtesy of Dr. Richard Smith of the McMaster Regional Centre for Mass Spectrometry.

Supplementary Material Available: Tables of cyrstallographic details, least-squares planes, hydrogen positional parameters, bond lengths and bond angles involving hydrogen atoms, and anisotropic thermal parameters (13 pages); a table of structure factors (31 pages). Ordering information is given on any current masthead page.

Tetranuclear Butterfly Cluster Derivatives of SMe_2. Preparation and Structures of $Ru_4(CO)_{13}(SMe_2)$, $H_2Ru_4(CO)_{12}(SMe_2)$, and $HRu_3Co(CO)_{12}(SMe_2)$

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Received June 18, 1990

The carbonyl clusters $Ru_4(CO)_{13}(SMe_3)$ (1), $H_2Ru_4(CO)_{12}(SMe_2)$ (2), and $HRu_3Co(CO)_{12}(SMe_2)$ (3) have been obtained in reactions between dimethyl sulfide and tri- or tetranuclear metal carbonyl clusters. These compounds have been characterized by X-ray diffraction studies. 1 crystallizes in space group $P2_1/n$ with $a = 9.406$ (3) Å, $b = 15.393$ (6) Å, $c = 15.812$ (6) Å, $\beta = 92.23$ (3)°, and $Z = 4$; 2, in space group $P2_1$ with $a = 8.18$ (1) Å, $b = 15.86$ (2) Å, $c = 9.55$ (1) Å, $\beta = 114.6$ (1)°, and $Z = 2$; 3, in space group $P2_1/n$ with $a = 9.349$ (4) Å, $b = 16.259$ (7) Å, $c = 14.469$ (6) Å, $\beta = 92.04$ (3)°, and $Z = 4$. The compounds are butterfly clusters, in which the four-electron SMe_2 ligand bridges the wing-tip positions. In 1 and 3 one of the carbonyls bridges the hinge of the butterfly; otherwise the compounds contain only terminal carbonyls. The hydrides occupy a wing and the hinge Ru–Ru bond in 2 and a wing Ru–Co bond in 3. In 3 the cobalt atom is in a hinge position. The chalcogenide derivatives of tetranuclear Ru–Co–Rh cluster compounds show a structural trend depending on the metal composition. Terminal coordination (Co_4, $RuCo_3$, and $RuCo_2Rh$), butterfly structures (Ru_4 and Ru_3Co), or dimerization of clusters ($RuRh_3$) is found.

Introduction

During the last 10 years much attention has been focused on the synthesis and characterization of butterfly clusters. The relationships between tetranuclear clusters and the butterfly clusters have become better understood. The M_4 butterfly skeleton appears to be structurally versatile, and the geometry is determined by the steric and electronic character of the ligands.[1] The reactivity of the metal core and the ligands attached to it has been explored, and the potential applications of butterfly clusters as chemisorption models or as direct catalysts have drawn attention.[2,3]

We have previously studied the substitution reactions of tetrahedral valence isoelectronic mixed-metal clusters $H_xRu_xCo_yRh_z(CO)_{12}$ ($x, y, z = 0$–4, $x + y + z = 4$) with phosphine or XR_2 (X = S, Se, Te, R = alkyl, aryl) ligands.[4-7] These studies revealed the versatility of XR_2 ligands. In $HRuCo_3(CO)_{12}$, $HRuCo_2Rh(CO)_{12}$,[8] or $Co_4(CO)_{12}$,[9] these ligands substitute carbonyls as terminal two-electron donors. With $HRuRh_3(CO)_{12}$, dialkyl chalcogen ligands act as four-electron donors, forming unusual dimeric structures $[HRuRh_3(CO)_9]_2[XMe_2]_3$.

In this work we have found that when the ruthenium content of the cluster is increased, butterfly formation becomes the most favorable reaction type. SMe_2 acts as a four-electron donor and causes a Ru–Ru bond breaking.

Results and Discussion

$Ru_4(CO)_{13}(SMe_2)$ (1) was prepared in the reaction between $Ru_3(CO)_{12}$ and SMe_2. Refluxing in tetrahydrofuran solvent produces 1 in 30% yield in a few hours—in dichloromethane the reaction does not occur in reasonable times.

Table I. Atomic Coordinates (×10^4) for $Ru_4(CO)_{13}(SMe_2)$ (1)

atom	*x*	*y*	*z*
Ru(1)	1732 (1)	1887 (1)	6780 (1)
Ru(2)	−210 (1)	1297 (1)	7968 (1)
Ru(3)	551 (1)	3058 (1)	7978 (1)
Ru(4)	−1967 (1)	2549 (1)	7075 (1)
S(1)	−351 (1)	2276 (1)	5987 (1)
O(1)	2250 (6)	209 (3)	5821 (3)
O(2)	4040 (5)	1496 (3)	8134 (3)
O(3)	3785 (5)	2946 (3)	5733 (3)
O(4)	−1355 (6)	−61 (3)	6726 (3)
O(5)	1863 (6)	−61 (3)	8704 (4)
O(6)	−2487 (5)	890 (3)	9240 (3)
O(7)	−490 (7)	4145 (4)	9450 (4)
O(8)	3618 (5)	3702 (3)	7978 (3)
O(9)	−371 (6)	4605 (3)	6892 (3)
O(10)	−4146 (5)	1203 (3)	6511 (3)
O(11)	−3236 (5)	2897 (3)	8773 (3)
O(12)	−3615 (5)	4053 (3)	6227 (3)
O(13)	1468 (5)	2024 (3)	9570 (3)
C(1)	2040 (6)	828 (4)	6183 (4)
C(2)	3146 (6)	1637 (4)	7634 (3)
C(3)	2986 (6)	2581 (4)	6126 (4)
C(4)	−943 (6)	485 (4)	7164 (3)
C(5)	1131 (6)	451 (4)	8415 (4)
C(6)	−1649 (6)	1075 (4)	8774 (3)
C(7)	−154 (7)	3740 (4)	8907 (4)
C(8)	2481 (7)	3436 (4)	7971 (3)
C(9)	−145 (8)	3948 (4)	7214 (4)
C(10)	−3328 (6)	1700 (4)	6717 (4)
C(11)	−2720 (6)	2760 (4)	8145 (3)
C(12)	−2988 (6)	3493 (4)	6520 (4)
C(13)	966 (6)	2151 (3)	8906 (3)
C(21)	−950 (6)	1485 (4)	5202 (3)
C(22)	−121 (6)	3180 (4)	5280 (3)

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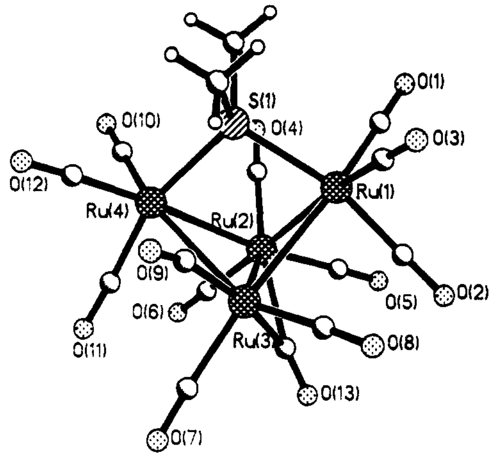

Figure 1. Structure and numbering scheme of $Ru_4(CO)_{13}(SMe_2)$ (**1**).

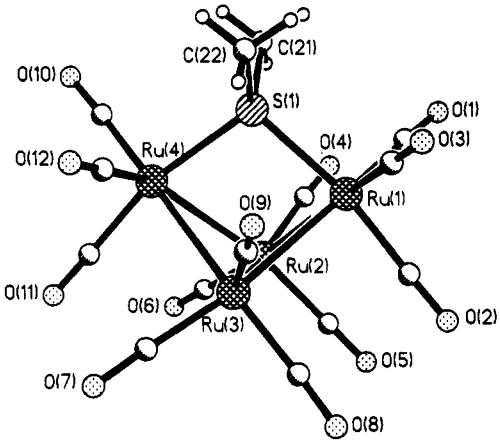

Figure 2. Structure and numbering scheme of $H_2Ru_4(CO)_{12}(SMe_2)$ (**2**).

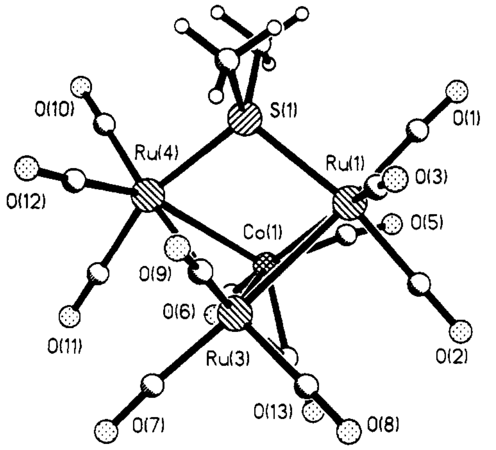

Figure 3. Structure and numbering scheme of $HRu_3Co(CO)_{12}(SMe_2)$ (**3**).

$H_2Ru_4(CO)_{12}(SMe_2)$ (**2**) was prepared by the treatment of $H_2Ru_4(CO)_{13}$ with SMe_2 in refluxing CH_2Cl_2, and **3** was synthesized by the corresponding procedure with $HRu_3Co(CO)_{13}$ and SMe_2. The yields are 16 and 18%, respec-

Table II. Atomic Coordinates ($\times 10^4$) for $H_2Ru_4(CO)_{12}(SMe_2)$ (2)

atom	x	y	z
Ru(1)	2537 (1)	5215	6896 (1)
Ru(2)	-123 (1)	3911 (1)	5703 (1)
Ru(3)	3608 (1)	3530 (1)	6653 (1)
Ru(4)	2215 (1)	3257 (1)	8879 (1)
S(1)	2744 (4)	4722 (2)	9290 (3)
O(1)	109 (18)	6715 (8)	6637 (16)
O(2)	2429 (16)	5533 (7)	3742 (10)
O(3)	6101 (14)	6179 (8)	8254 (13)
O(4)	-2751 (14)	5226 (7)	5836 (13)
O(5)	-817 (15)	4414 (9)	2453 (11)
O(6)	-2849 (15)	2474 (7)	4735 (16)
O(7)	4863 (24)	1701 (9)	6829 (22)
O(8)	4072 (16)	3841 (9)	3692 (12)
O(9)	7291 (13)	4181 (8)	8796 (14)
O(10)	436 (21)	2902 (11)	11099 (17)
O(11)	1313 (18)	1477 (7)	7567 (20)
O(12)	6025 (15)	2746 (11)	10970 (17)
C(1)	966 (18)	6164 (8)	6755 (15)
C(2)	2436 (17)	5404 (8)	4904 (15)
C(3)	4799 (19)	5810 (9)	7757 (15)
C(4)	-1714 (16)	4733 (8)	5836 (14)
C(5)	-532 (16)	4234 (9)	3656 (14)
C(6)	-1808 (16)	2990 (8)	5101 (14)
C(7)	4301 (21)	2382 (9)	6753 (19)
C(8)	3847 (16)	3741 (9)	4802 (13)
C(9)	5859 (18)	3951 (11)	7976 (17)
C(10)	1061 (22)	3056 (10)	10235 (18)
C(11)	1700 (18)	2135 (9)	8055 (18)
C(12)	4604 (21)	2942 (10)	10194 (18)
C(21)	1235 (20)	5213 (11)	9967 (16)
C(22)	4855 (20)	4987 (11)	10891 (14)

Table III. Atomic Coordinates ($\times 10^4$) for $HRu_3Co(CO)_{12}(SMe_2)$ (3)

atom	x	y	z
Ru(4)	1529 (1)	6160 (1)	6913 (1)
Ru(3)	-83 (1)	7244 (1)	8087 (1)
Ru(1)	-2245 (1)	6083 (1)	7595 (1)
Co(1)	-907 (2)	7041 (1)	6329 (1)
S(1)	-245 (3)	5224 (1)	7357 (2)
O(12)	3727 (9)	5690 (6)	8458 (6)
O(11)	3034 (10)	7704 (5)	6289 (5)
O(10)	2890 (9)	5099 (5)	5441 (5)
O(9)	1118 (11)	6259 (6)	9736 (6)
O(7)	2247 (11)	8549 (6)	8186 (6)
O(8)	-1993 (9)	8166 (5)	9387 (5)
O(13)	-1842 (10)	8610 (5)	6972 (6)
O(6)	-43 (14)	7974 (7)	4735 (7)
O(5)	-3651 (11)	6642 (6)	5463 (6)
O(3)	-2530 (12)	5546 (7)	9598 (7)
O(2)	-4427 (8)	7454 (5)	7777 (6)
O(1)	-4456 (9)	4911 (6)	6712 (7)
C(12)	2912 (13)	5878 (7)	7896 (8)
C(11)	2471 (12)	7139 (6)	6542 (7)
C(10)	2393 (11)	5472 (6)	5999 (7)
C(9)	659 (11)	6610 (7)	9078 (7)
C(7)	1416 (12)	8042 (7)	8137 (7)
C(8)	-1311 (12)	7827 (7)	8881 (7)
C(13)	-1282 (11)	7980 (6)	6988 (7)
C(6)	-331 (14)	7586 (8)	5363 (8)
C(5)	-2607 (13)	6717 (7)	5878 (8)
C(3)	-2410 (13)	5729 (7)	8860 (9)
C(2)	-3603 (12)	6946 (6)	7723 (7)
C(1)	-3628 (12)	5329 (6)	7021 (8)
C(22)	219 (12)	4542 (7)	8310 (8)
C(21)	-610 (12)	4463 (7)	6466 (8)

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Table IV. Selected Bond Lengths for $Ru_4(CO)_{13}(SMe_2)$ (1), $H_2Ru_4(CO)_{12}(SMe_2)$ (2), and $HRu_3Co(CO)_{12}(SMe_2)$ (3)[a]

	1	2	3
Ru(1)–Ru(2)	282.0 (1)	287.7 (2)	
Ru(1)–Co(1)			273.9 (2)
Ru(2)–Ru(3)	280.4 (1)	*287.5* (2)	
Co(1)–Ru(3)			265.1 (2)
Ru(3)–Ru(4)	282.8 (1)	285.2 (3)	290.6 (2)
Ru(1)–Ru(3)	286.9 (1)	285.1 (2)	283.7 (2)
Ru(2)–Ru(4)	287.3 (1)	*302.0* (3)	
Co(1)–Ru(4)			*279.5* (2)
Ru(4)–S(1)	237.8 (2)	236.4 (4)	235.7 (3)
Ru(1)–S(1)	236.2 (2)	236.8 (4)	236.9 (3)
S(1)–C(21)	181.1 (6)	180 (2)	181 (1)
S(1)–C(22)	180.4 (6)	182 (1)	181 (1)
Ru(1)–C(1)	191.2 (6)	195 (1)	195 (1)
Ru(1)–C(2)	189.7 (5)	190 (2)	191 (1)
Ru(1)–C(3)	192.3 (6)	194 (1)	193 (1)
Ru(2)–C(4)	189.3 (6)	189 (2)	
Ru(2)–C(5)	192.8 (6)	192 (1)	
Co(1)–C(5)			178 (1)
Ru(2)–C(6)	192.6 (6)	193 (1)	
Co(1)–C(6)			176 (1)
Ru(3)–C(7)	194.4 (7)	190 (2)	191 (1)
Ru(3)–C(8)	190.6 (6)	190 (1)	191 (1)
Ru(3)–C(9)	192.4 (7)	188 (1)	188 (1)
Ru(4)–C(10)	190.0 (6)	193 (2)	193 (1)
Ru(4)–C(11)	188.8 (6)	192 (2)	191 (1)
Ru(4)–C(12)	193.4 (6)	190 (2)	194 (1)
Ru(3)–C(13)	205.2 (5)		226 (1)
Ru(2)–C(13)	224.1 (5)		
Co(1)–C(13)			184 (1)
C(1)–O(1)	113.3 (8)	110 (2)	111 (1)
C(2)–O(2)	115.2 (7)	113 (2)	114 (1)
C(3)–O(3)	114.1 (8)	114 (2)	112 (2)
C(4)–O(4)	114.7 (7)	116 (2)	
C(5)–O(5)	113.0 (8)	112 (2)	114 (2)
C(6)–O(6)	113.6 (8)	113 (2)	115 (2)
C(7)–O(7)	111.5 (9)	116 (2)	113 (2)
C(8)–O(8)	114.5 (8)	116 (2)	113 (1)
C(9)–O(9)	114.8 (8)	117 (2)	118 (1)
C(10)–O(10)	112.4 (7)	117 (3)	112 (1)
C(11)–O(11)	114.1 (7)	113 (2)	113 (1)
C(12)–O(12)	113.3 (7)	114 (2)	114 (2)
C(13)–O(13)	115.1 (7)		115 (1)

[a] The metal–metal bonds with hydride ligand are italic.

tively. With $H_4Ru_4(CO)_{12}$[10,11] and $H_3Ru_3Co(CO)_{12}$[12] as starting materials, the reactions were very slow and only traces of the butterfly derivatives were observed. The structures and numbering schemes are presented in Figures 1–3 for 1–3, respectively. Atomic coordinates are listed in Tables I–III, selected bond lengths, in Table IV, and selected bond angles, in Table V.

All three compounds are wing-tip-bridged 62-electron butterfly clusters with dihedral angles of approximately the same magnitude: 95.6, 94.8, and 96.1° for 1–3, respectively. These values are typical for wing-tip-bridged 62-electron butterfly clusters.[3]

In 2 the carbonyls are terminal; in 1 the additional carbonyl ligand is bridging the hinge Ru–Ru bond. The structure 3 is related to 1 with a $Co(CO)_2$ fragment replacing the hinge $Ru(CO)_3$.

Table V. Selected Bond Angles for $Ru_4(CO)_{13}(SMe_2)$ (1), $H_2Ru_4(CO)_{12}(SMe_2)$ (2), and $HRu_3Co(CO)_{12}(SMe_2)$ (3)

	1	2	3
Ru(2)/Co(1)–Ru(1)–S(1)	83.7 (1)	83.2 (1)	81.7 (1)
Ru(3)–Ru(1)–S(1)	81.8 (1)	82.6 (1)	82.5 (1)
Ru(2)/Co(1)–Ru(4)–S(1)	82.3 (1)	80.0 (1)	80.7 (1)
Ru(3)–Ru(4)–S(1)	82.4 (1)	82.6 (1)	81.3 (1)
Ru(3)–Ru(1)–C(1)	158.7 (2)	159.2 (4)	169.3 (3)
Ru(2)/Co(1)–Ru(1)–C(1)	99.7 (2)	98.9 (4)	112.6 (3)
S(1)–Ru(1)–C(1)	95.2 (2)	95.6 (5)	94.7 (3)
Ru(2)/Co(1)–Ru(1)–C(2)	85.1 (2)	90.4 (4)	88.2 (3)
Ru(3)–Ru(1)–C(2)	86.4 (2)	87.2 (4)	87.6 (3)
S(1)–Ru(1)–C(2)	166.8 (2)	169.6 (4)	168.6 (3)
Ru(2)/Co(1)–Ru(1)–C(3)	164.6 (2)	162.8 (4)	149.0 (4)
Ru(3)–Ru(1)–C(3)	105.5 (2)	102.5 (4)	92.4 (4)
S(1)–Ru(1)–C(3)	95.0 (2)	94.7 (5)	93.0 (4)
Ru(1)–Ru(2)–C(4)	89.7	84.9 (4)	
Ru(3)–Ru(2)–C(4)	136.8 (2)	143.2 (4)	
Ru(4)–Ru(2)–C(4)	85.8 (2)	109.5 (4)	
Ru(1)–Ru(2)/Co(1)–C(5)	91.7 (2)	89.6 (4)	69.8 (4)
Ru(3)–Ru(2)/Co(1)–C(5)	119.2 (2)	95.0 (4)	128.0 (4)
Ru(4)–Ru(2)/Co(1)–C(5)	171.4 (2)	152.7 (4)	132.0 (4)
Ru(1)–Ru(2)/Co(1)–C(6)	171.1 (2)	174.4 (4)	168.3 (4)
Ru(3)–Ru(2)/Co(1)–C(6)	110.7 (2)	118.3 (4)	127.8 (4)
Ru(4)–Ru(2)/Co(1)–C(6)	92.2 (2)	96.7 (4)	103.3 (4)
Ru(1)–Ru(2)/Co(1)–C(13)	86.3 (1)		91.5 (3)
Ru(3)–Ru(2)/Co(1)–C(13)	46.4 (1)		56.9 (3)
Ru(4)–Ru(2)/Co(1)–C(13)	101.0 (1)		115.9 (3)
Ru(1)–Ru(3)–C(7)	172.2 (2)	172.1 (6)	167.7 (3)
Ru(2)/Co(1)–Ru(3)–C(7)	115.6 (2)	118.3 (5)	108.0 (3)
Ru(4)–Ru(3)–C(7)	103.2 (2)	91.2 (6)	92.2 (3)
Ru(1)–Ru(3)–C(8)	78.1 (2)	94.0 (4)	92.5 (3)
Ru(2)/Co(1)–Ru(3)–C(8)	122.5 (2)	100.7 (4)	118.7 (3)
Ru(4)–Ru(3)–C(8)	149.4 (2)	164.2 (3)	172.0 (3)
Ru(1)–Ru(3)–C(9)	99.4 (2)	82.1 (5)	93.8 (3)
Ru(2)/Co(1)–Ru(3)–C(9)	127.2 (2)	139.5 (5)	138.6 (3)
Ru(4)–Ru(3)–C(9)	67.8 (2)	98.0 (6)	85.9 (3)
Ru(1)–Ru(3)–C(13)	88.7 (2)		81.1 (3)
Ru(2)/Co(1)–Ru(3)–C(13)	52.2 (2)		43.1 (3)
Ru(4)–Ru(3)–C(13)	107.7 (2)		99.5 (3)
Ru(2)/Co(1)–Ru(4)–C(10)	93.0 (2)	116.9 (4)	116.5 (3)
Ru(3)–Ru(4)–C(10)	151.9 (2)	174.8 (4)	171.8 (3)
S(1)–Ru(4)–C(10)	96.0 (2)	99.1 (5)	97.4 (3)
Ru(2)/Co(1)–Ru(4)–C(11)	84.5 (2)	88.0 (4)	82.3 (3)
Ru(3)–Ru(4)–C(11)	80.6 (2)	85.5 (6)	85.0 (3)
S(1)–Ru(4)–C(11)	162.2 (2)	166.3 (5)	162.3 (3)
Ru(2)/Co(1)–Ru(4)–C(12)	173.2 (2)	143.3 (6)	148.9 (4)
Ru(3)–Ru(4)–C(12)	114.3 (2)	84.9 (6)	93.5 (4)
S(1)–Ru(4)–C(12)	97.2 (2)	94.6 (5)	96.0 (4)
Ru(1)–S(1)–Ru(4)	101.6 (1)	103.3 (1)	103.0 (1)
Ru(1)–S(1)–C(21)	115.0 (2)	115.4 (5)	112.1 (4)
Ru(4)–S(1)–C(21)	115.1 (2)	112.6 (6)	111.4 (4)
Ru(1)–S(1)–C(22)	114.0 (2)	113.5 (6)	114.8 (4)
Ru(4)–S(1)–C(22)	114.1 (2)	114.3 (5)	116.8 (4)
C(21)–S(1)–C(22)	97.8 (3)	98.8 (7)	99.0 (5)
Ru(1)–C(1)–O(1)	178.4 (5)	177 (2)	178 (1)
Ru(1)–C(2)–O(2)	177.6 (5)	178 (1)	178.2 (8)
Ru(1)–C(3)–O(3)	175.5 (5)	178 (1)	178 (1)
Ru(2)/Co(1)–C(4)–O(4)	174.2 (5)	176.2 (9)	
Ru(2)/Co(1)–C(5)–O(5)	176.4 (6)	178 (1)	166 (1)
Ru(2)/Co(1)–C(6)–O(6)	175.8 (5)	177 91)	175 (1)
Ru(3)–C(7)–O(7)	176.5 (6)	174 (2)	176 (1)
Ru(3)–C(8)–O(8)	176.7 (5)	177 (1)	176.7 (9)
Ru(3)–C(9)–O(9)	163.3 (6)	177 (2)	175.5 (9)
Ru(4)–C(10)–O(10)	179.1 (6)	176 (1)	177.0 (9)
Ru(4)–C(11)–O(11)	176.7 (5)	177 (2)	177.2 (9)
Ru(4)–C(12)–O(12)	177.0 (5)	179 (1)	178 (1)
Ru(2)/Co(1)–C(13)–O(13)	132.8 (5)		145.5 (9)
Ru(3)–C(13)–O(13)	145.8 (5)		134.5 (8)
Ru(2)/Co(1)–C(13)–Ru(3)	81.4 (2)		79.9 (4)

The wing Ru–Ru bonds are nearly equal in 1, but in 2 Ru(2)–Ru(4) (302.8 pm) is clearly longer than the remaining bonds, which implies a hydrogen-bridged bond. For the same reason the hinge Ru–Ru bond is longer in 2 (287.5 pm) than in 1 (280.4 pm). The metal core in 3 is not distorted to any considerable extent, giving no direct evidence of the cluster hydride position.

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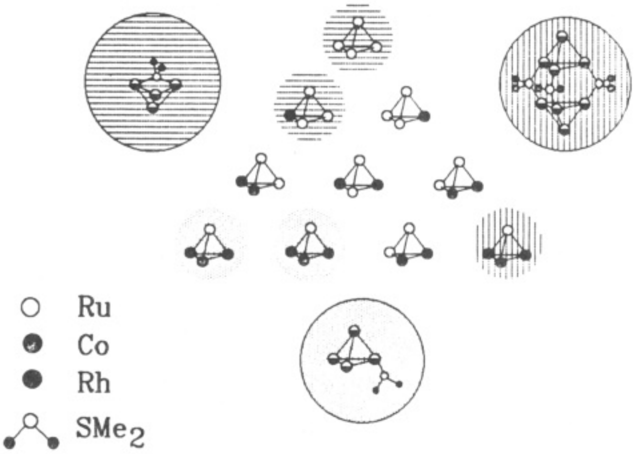

Figure 4. Different coordination modes of SMe_2 with tetranuclear $Ru_xCo_yRh_z$ ($x = 1$–4, $x + y + z = 4$) metal cores.

The cluster hydride positions in **2** and **3** can be derived indirectly. ^1H NMR spectrum of **2** shows two signals of equal intensity at −15.6 and −16.7 ppm, indicating different chemical environments for the hydrides. At −40 °C coupling between the hydride resonances with a coupling constant of 2.1 Hz was observed. The most probable positions of the hydrides can be identified on the basis of the carbonyl conformations. Space-filling models[13] show that steric pressure from the hydride ligands resulted in an opening up of Ru–Ru–CO angles along the Ru(2)–Ru(3) and Ru(2)–Ru(4) edges. The models suggest also that the Ru(2)(μ_2-H)Ru(4) hydride is bent toward the sulfide from the Ru(2)–Ru(3)–Ru(4) plane; the bond angles Ru(2)–Ru(4)–C(10) and Ru(4)–Ru(2)–C(4) are larger (average 113.5°) than the angles Ru(2)–Ru(4)–C(11) and Ru(4)–Ru(2)–C(6) (average 90.9°). The corresponding values along the other wing Ru–Ru bonds are smaller with an average of 90.8°. Correspondingly, in **3** the hydride occupies the wing Ru(1)–Co(1) bond on the sulfide facing side. The bond angles Co(1)–Ru(1)–C(2) and Ru(1)–Co(1)–C(5) are small (88.2 and 69.8°) compared to those of Co(1)–Ru(1)–C(1) and Ru(1)–Co(1)–C(6) (112.6 and 168.3°). This hydride gives rise to a broad ^1H NMR resonance at −13.4 ppm.

The Ru–S bond lengths lie within the narrow range 235.7–237.8 pm, average 236.5 pm, in all the compounds. Coordination of the SMe_2 ligand has little effect on the C–S–C bond angle, which is 97.8° in **1**, 98.8° in **2**, and 99.0° in **3**, very close to the corresponding free ligand angle of 98.8°. The S–C bond length has also been maintained (average 181 pm in **1** and **2** and 180 pm in free SMe_2).[14]

The structures are related to those of $H_3Ru_4(CO)_{12}(\mu_2\text{-NCO})$[15] and $[Ru_4(CO)_{13}(\mu_2\text{-Cl})]^-$[16], both of which are derived from $Ru_3(CO)_{12}$. There is an obvious structural trend in the XMe_2 derivatives within the tetrahedral clusters containing ruthenium, cobalt, and rhodium, as illustrated in Figure 4. In the cobalt corner of the $H_xRu_xCo_yRh_z(CO)_{12}$ ($x = 1$–4, $x + y + z = 4$) triangle, terminal coordination is favored. The rhodium corner shows bridging XMe_2 ligands, which cause dimerization of the parent clusters. In the ruthenium corner butterfly compounds with bridging XMe_2 ligands are found. This is not unexpected, since most of the known wing-tip-bonded butterfly clusters consist of Fe–Ru–Os group metals.

Table VI. Crystallographic Data for $Ru_4(CO)_{13}(SMe_2)$ (1), $H_2Ru_4(CO)_{12}(SMe_2)$ (2), and $HRu_3Co(CO)_{12}(SMe_2)$ (3)

	1	2	3
fw	830.54	808.54	762.40
cryst syst	monocl	monocl	monocl
space group	$P2_1/n$	$P2_1$	$P2_1/n$
a, Å	9.406 (3)	8.18 (1)	9.349 (4)
b, Å	15.393 (6)	15.86 (2)	16.259 (7)
c, Å	15.812 (6)	9.55 (1)	14.469 (6)
β, deg	92.23 (3)	114.78 (4)	92.04 (3)
V, Å^3	2287.55	1127 (3)	2197.88
Z	4	2	4
D_{calc}, g cm^{-3}	2.41	2.36	2.30
cryst dimens, mm	0.1 × 0.2 × 0.5	0.1 × 0.2 × 0.3	0.2 × 0.2 × 0.2
no. of centering reflns	30	25	25
centering 2θ	14–25	11–27	14–25
2θ limits, deg	4–50	4–50	5–50
hkl range	12, 19, ±19	11, 21, ±13	12, 20, ±18
no. of unique rflns	4017	2718	3872
no. of obsd data, $I > 3\sigma(I)$	3031	2439	2564
μ, cm^{-1}	2.69	2.83	2.87
no. of params	298	278	280
R^a	0.0253	0.0316	0.0425
$R_w{}^b$	0.0257	0.0317	0.0421

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] Weight $= 1/(\sigma^2(F) + 0.0005F^2)$.

Conclusion

The structures of dialkyl chalcogenide derivatives of tetranuclear Ru–Co–Rh cluster compounds are sensitive to the metal composition. Chalcogenide ligands are found in terminal positions or as bridging ligands in butterfly clusters or as bridging ligands connecting two clusters together. The ability to engage on different coordination modes makes chalcogenide ligands particularly attractive, when compared with, e.g., tertiary phosphines, which coordinate terminally.

Experimental Section

General Comments. Reactions were performed under a nitrogen atmosphere. Deoxygenated solvents were used, and THF was distilled from sodium–benzophenone. $H_2Ru_4(CO)_{13}$[17–19] and $HRu_3Co(CO)_{13}$[20] were prepared by published methods. $Ru_3(CO)_{12}$ and SMe_2 were of commercial origin. Infrared spectra were recorded in dichloromethane solvent on a Nicolet 20SXc spectrometer. ^1H NMR spectra were measured in $CDCl_3$ solvent at 273 K on a Bruker AM-250 spectrometer using Me_4Si as reference.

Synthesis of $[Ru_4(CO)_{13}(SMe_2)]$ (1). The compound SMe_2 (1 mL, 13.7 mmol) was added to a THF solution of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol). The solution was refluxed for 3 h and evaporated in vacuo to dryness. Chromatographic separation on a silica gel column with hexane removed the remaining starting material (40 mg, 0.06 mmol). Further elution with a 1:1 hexane–dichloromethane mixture gave the title compound; yield 58 mg, 30%. Black crystals were formed on crystallization from CH_2Cl_2. IR (CH_2Cl_2): ν(CO) 2081 (w), 2046 (vs), 2034 (s), 2026 (m), 1989 (w), 1872 cm^{-1} (w). ^1H NMR spectrum ($CDCl_3$): 3.3 ppm (s, CH_3). Anal. Calcd for $C_{15}Ru_4H_6SO_{13}$: C, 21.69; H, 0.73. Found: C, 21.87; H, 0.89.

Synthesis of $[H_2Ru_4(CO)_{12}(SMe_2)]$ (2). $H_2Ru_4(CO)_{13}$ (270 mg, 0.351 mmol) was dissolved in CH_2Cl_2 (40 mL). SMe_2 (60 μL, 0.819 mmol) was added, and the solution was refluxed for 1 h. After evaporation of the solvent in vacuo, the products were

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chromatographed on silica. Elution with hexane gave $Ru_3(CO)_{12}$ (32 mg, 11%) and unreacted starting material (26 mg, 10%). Cluster 2 was obtained by elution with 1:3 hexane–dichloromethane solution; yield 44 mg, 16%. IR (CH_2Cl_2): 2088 (w), 2061 (s), 2040 (s), 2022 (s), 2003 (m), 1974 cm^{-1} (w). ^1H NMR spectrum: −15.6, −16.7 ppm; 2.9 ppm (s, CH_3). Anal. Calcd for $C_{14}Ru_4H_8SO_{12}$: C, 20.90; H, 1.00. Found: C, 20.96; H, 0.99.

Synthesis of $[HRu_3Co(CO)_{12}(SMe_2)]$ (3). The compounds $[HRu_3Co(CO)_{13}]$ (88 mg, 0.12 mmol) and SMe_2 (28.5 μL, 0.39 mmol) were refluxed in CH_2Cl_2 for 45 min. Chromatographic separation with hexane gave first a yellow and then a red fraction (unreacted starting material 26 mg, 0.04 mmol). Elution with 1:1 hexane–dichloromethane gave first a minor orange fraction of 2 and then the title compound. Crystallization from hexane–dichloromethane mixture gave crystals; yield 17 mg, 18%. IR (CH_2Cl_2): ν(CO) 2088 (w), 2061 (vs), 2034 (s), 2020 (s), 1835 cm^{-1} (w, br). ^1H NMR spectrum: −13.1 ppm (s, br); 3.1 and 2.8 ppm (s, CH_3, equal intensity). Anal. Calcd for $C_{14}Ru_3CoH_7SO_{12}$: C, 22.08; H, 0.93. Found: C, 22.36; H, 1.00.

Crystallographic Studies. Intensity data were collected on a Nicolet R3m diffractometer. Mo Kα radiation with λ = 0.71073 Å was used. Intensities were corrected for Lorenz, polarization, and background effects. An empirical absorption correction was made, based on ψ-scans. Table VI presents further crystallographic data.

The structures were solved by direct methods using the SHELXTL program package. Anisotropic refinement was carried out for all non-hydrogen atoms. Methyl protons were placed in idealized positions with C–H distance of 96 pm and isotropic temperature factors of 0.08. The cluster hydrides were not found in the Fourier maps.

Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond distances and angles (12 pages); listings of structure factors (39 pages). Ordering information is given on any current masthead page.

Reduction of Acyl Ligand in Transition-Metal Complexes by Catalytic Hydrosilylation

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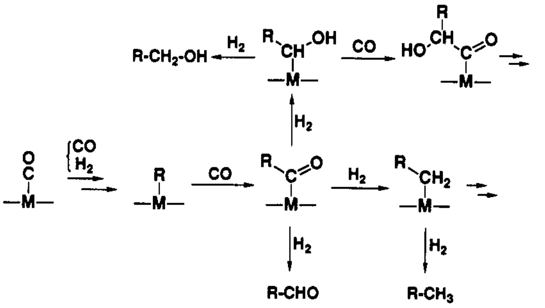
Received October 15, 1990

Hydrosilylation of acyl–transition-metal complexes M–C(O)R (1) with H_2SiPh_2 in the presence of a catalytic amount of $RhCl(PPh_3)_3$ leads to the formation of the corresponding α-siloxyalkyl complexes M–CH($OSiHPh_2$)R (2). In case 1 contains a ligand or a substituent which stabilizes a transient cationic alkylidene intermediate $M^+{=}CHR$ (5), overreduction takes place to afford M–CH_2R (3) via 5. The mechanism of the overreduction has been studied by using α-methoxyalkyl complexes M–CH(OMe)R in place of 2. In addition, the chain propagation step in the Pichler–Schulz mechanism is mimiced by combination of the overreduction and carbonylation. Thus, the acetyl ligand in $CpFe(CO)(PPh_3)[C(O)CH_3]$ (**1f**) is elongated to the pentanoyl ligand by repeating the homologation three times. Transformation of 1 to an α-alkoxyalkyl complex and an α-hydroxycarboxylic acid ester is also described.

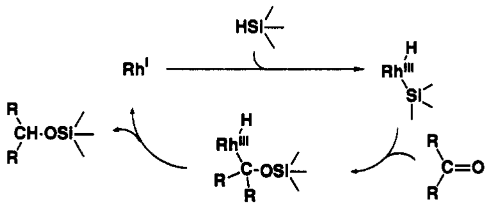
Introduction

In the Pichler–Schulz mechanism (one of the plausible mechanisms proposed for catalytic hydrogenation of carbon monoxide) an acyl species is included as a key intermediate in the chain propagation step (Scheme I).[1] The acyl species is formed by carbonylation of an alkyl–metal intermediate. The fate of the acyl species is decided by the subsequent reduction step. Successive reduction to the alkyl species and CO insertion results in homologation. Complete reduction produces a hydrocarbon. On the other hand, partial reduction of the acyl species or hydrogenolysis of the metal–acyl bond may finally lead to the formation of oxygenated products such as alcohols and aldehydes.

Scheme I



Scheme II



In model reactions using discrete isolable complexes the reduction of an acyl ligand has been acheived by electrophilic activation followed by hydridic reduction[2] (eq 1).

$$\left[M{-}C(=O)R \longleftrightarrow M^{+}{=}C(O^{-})R \right] \xrightarrow{+\,R'^{+}} M^{+}{=}C(OR')R \xrightarrow{+\,H^{-}} M{-}CH(OR')R \qquad (1)$$

Such activation is essential, because the electrophilicity of the acyl carbon atom is reduced by backdonation from the metal center compared to that of an organic carbonyl carbon atom. The action of strong reducing reagents such as $LiAlH_4$ results in reduction of a coexisting CO ligand.[3]

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