Journal of Organometallic Chemistry, 393 (1990) 403–414
Elsevier Sequoia S.A., Lausanne
JOM 20906

Dimethylselenide substituted mixed metal clusters: synthesis and crystal structures of $[HRuCo_3(CO)_{11}(SeMe_2)]$, $[HRuCo_3(CO)_{10}(SeMe_2)_2]$ and $[HRuRh_3(CO)_9]_2[SeMe_2]_3$

Sirpa Rossi, Jouni Pursiainen, Markku Ahlgren and Tapani A. Pakkanen
Department of Chemistry, University of Joensuu, P.O. Box 111, Joensuu SF-80101 (Finland)

(Received February 8th, 1990)

Abstract

The syntheses and crystal structure of three dimethylselenide mixed metal cluster compounds are described. The clusters $[HRuCo_3(CO)_{11}(SeMe_2)]$ (**1**) $[HRuCo_3(CO)_{10}(SeMe_2)_2]$ (**2**) and $[HRuRh_3(CO)_9]_2[SeMe_2]_3$ (**3**) have been prepared by reactions of $SeMe_2$ with the neutral parent clusters.

The dimethyl selenide ligands coordinate terminally as two-electron donors on basal cobalt atoms in the case of **1** and **2**, and as a bridging four-electron donor in **3**, giving rise to an unusual dimerization of the cluster. The carbonyl arrangement of the parent clusters is not changed by the ligand substitution, and hydride ligands bridge the three basal metals in all the compounds.

Introduction

There is considerable interest in metal carbonyl clusters and their ligand substitution reactions because of their special nature and potential applications. In addition to the commonly used phosphorus, nitrogen, and hydrocarbon ligands, several sulfur-containing ligands have been also employed [1]. Reactions of metal clusters with sulfur-containing compounds are important in the study of catalytic processes, because sulphur is one of the main catalyst poisons [2]. In general selenium compounds behave like the analogous sulfur compounds but there have been very few systematic studies of selenium ligands in metal clusters. Selenium ligands can show various coordination modes; usually elemental selenium is incorporated into the metal core. In $[CpMe_5(CO)RhSe]_2$ $2e^-$-μ_2-bridges are present [3]. In $[Ni_6(PPh_3)_6(\mu_3\text{-}Se)_2(\mu_4\text{-}Se)_3]$ seleniums cap the faces of the trigonal prismatic metal core [4]. Selenium can also be bound terminally, as in $[W_2(CpMe_5)_2(CO)_2(\mu_2\text{-}Se)Se]$ [5]. Metal complexes containing alkyl or aryl selenide ligands are less known. The three-electron donor ligand SePh is known to bridge one of the metal–metal

0022-328X/90/$03.50

bonds in $[HOs_3(CO)_{10}(SePh)]$ [6]. Dialkylselenides have been reported only in mono- and di-nuclear complexes, for example *cis*-$[PtCl_2(SeEt_2)]$ [7].

We describe here the synthesis and structure of $[HRuCo_3(CO)_{11}(SeMe_2)]$ (**1**), $[HRuCo_3(CO)_{10}(SeMe_2)_2]$ (**2**) and $[HRuRh_3(CO)_9]_2[SeMe_2]_3$ (**3**). These are analogous to the previously known $[HRuCo_3(CO)_{11}(SMe_2)]$ (**4**), $[HRuCo_3(CO)_{10}(SMe_2)_2]$ (**5**) and $[HRuRh_3(CO)_9]_2[SMe_2]_3$ (**6**) [8]. The clusters were prepared by displacement by $SeMe_2$ of carbonyl ligands from the parent clusters $[HRuCo_3(CO)_{12}]$ [9] and $[HRuRh_3(CO)_{12}]$ [10], which are members of the family of $[H_xRu_x\text{-}Co_yRh_z(CO)_{12}]$, ($x, y, z = 0$–$4$; $x + y + z = 4$) clusters, one of the best characterized mixed-metal systems [11]. Earlier studies have revealed variations in the nature of the clusters depending on the metal(s) present [12].

Experimental

General

Reactions were carried out under nitrogen in deoxygenated solvents. $SeMe_2$ was obtained from Aldrich Chemie. $[HRuCo_3(CO)_{12}]$ [9] and $[HRuRh_3(CO)_{12}]$ [10] were prepared by published methods. Infrared spectra were recorded in dichloromethane on a Nicolet 20SXC spectrometer. ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer at 0 °C with $CDCl_3$ solutions containing Me_4Si as reference.

X-ray crystallography

Data were collected on a Nicolet R3m diffractometer using Mo-K_α-radiation (λ 0.71073 Å). The atomic coordinates of the isomorphous sulphur clusters were used for the structure refinement for **1** and **3**. The structure of **2** was determined by direct methods and subsequent Fourier synthesis using the SHELXTL program package [13]. Metal, sulphur, oxygen and carbon atoms were anisotropically refined. Methyl protons were placed in calculated positions (C–H 96 pm, U 0.08) and not refined. Table 10 presents further crystallographic information. Tables of thermal parameters, a complete list of bond lengths and angles for **3**, and lists of structure factors are available from the authors.

For compound **3** the validity of the choice of absolute structure was confirmed by carrying out refinement with inverted coordinates, which gave significally higher R (0.0635) and R_W (0.0610) values.

Synthesis of $[HRuCo_3C(O)_{11}(SeMe_2)]$ (1) and $[HRuCo_3(CO)_{10}(SeMe_2)_2]$ (2)

The compound $SeMe_2$ (38 μl, 0.49 mmol) was added to a solution of $[HRuCo_3(CO)_{12}]$ (300 mg, 0.49 mmol) in CH_2Cl_2 (30 ml). The solution was refluxed for 43 h and the solvent then evaporated in vacuo, and the residue chromatographed on a silica column. Elution with hexane gave an orange band containing by-products. Further elution with hexane/dichloromethane (4/1)-mixture gave a reddish brown and a violet band. Product **1** was recovered from the reddish brown band, dried in vacuo, and recrystallized from hexane/dichloromethane at −40 °C. Air-stable black cubic crystals were formed, yield 203 mg, 60%. IR: ν(CO) 2085m, 2046s, 2012m, 1864m, 1846m cm^{-1}. The disubstituted product **2** was recovered from the violet band, dried, and recrystallized from hexane/dichloromethane mixture in the presence of free ligand at room temperature. The yield was 44 mg, 12%. The IR spectrum shows bands at 2067m, 2035s, 2003s, 1863m and 1844m cm^{-1}.

Synthesis of [$HRuRh_3(CO)_9$]$_2$[$SeMe_2$]$_3$ (3)

The compound $SeMe_2$ (88 μl, 1.13 mmol) was added to the solution of [$HRuRh_3(CO)_{12}$] (283 mg, 0.38 mmol) in CH_2Cl_2 (30 ml). The mixture was refluxed for 2 h, the solvent then evaporated in vacuo and the products then chromatographed on silica. Elution with hexane and hexane/dichloromethane (4/1) gave minor fractions containing by-products. Further elution with 2/1 solution gave a red band containing **3**, yield 109 mg, 35%. IR: ν(CO) 2054s, 2013m, 1976w, 1973w, 1842w cm^{-1}. Recrystallization from CH_2Cl_2 gave dark red air-stable crystals.

Results and discussion

Synthesis and structures of [$HRuCo_3(CO)_{11}(SeMe_2)$] (1) and [$HRuCo_3(CO)_{10}(SeMe_2)_2$] (2)

Compounds **1** and **2** were made by displacement of carbonyl ligand(s) from the parent cluster [$HRuCo_3(CO)_{12}$] by $SeMe_2$ in CH_2Cl_2 solution. The mixture was refluxed to give reasonable reaction rates; after 43 h the yield of **1** was 60% and that of **2** was 12%. With shorter reaction times the reaction may reach only the monosubstitution stage.

The crystal structures and numbering schemes for **1** and **2** are shown in Figs. 1 and 2. The atomic coordinates are listed in Tables 1 and 2, bond distances in Tables 4 and 5 and selected bond angles in Tables 7 and 8.

These compounds, like the parent cluster, have a closed tetrahedral metal core with three terminal carbonyls on the apical ruthenium and three carbonyls bridging the basal metal edges. The $SeMe_2$ ligands are axially coordinated to cobalt atoms.

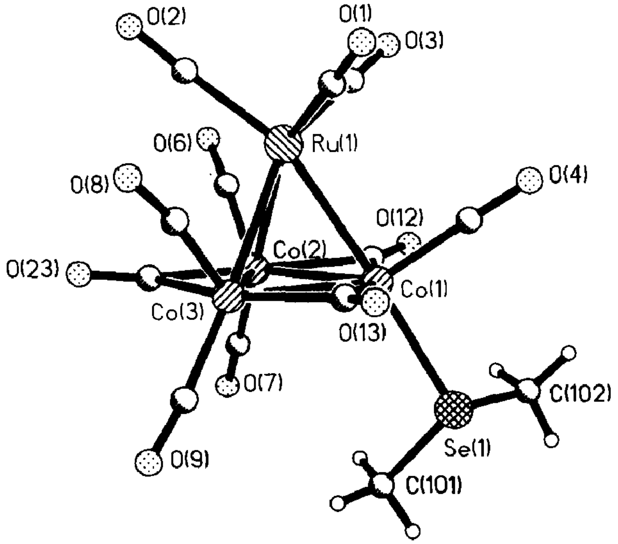


Fig. 1. Structure and numbering scheme for [$HRuCo_3(CO)_{11}(SeMe_2)$] (**1**).

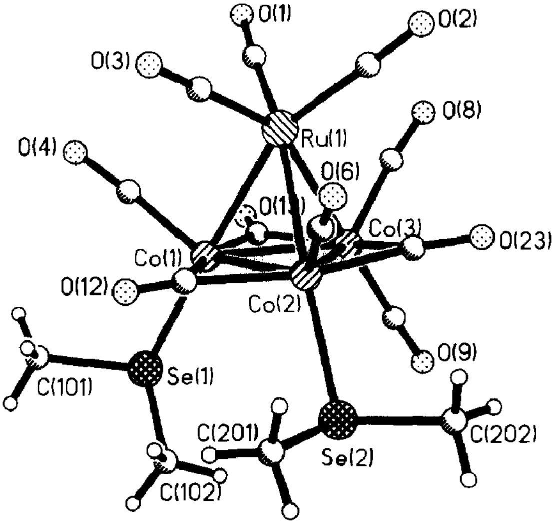


Fig. 2. Structure and numbering scheme for $[HRuCo_3(CO)_{10}(SeMe_2)_2]$ (**2**).

Table 1

Atomic coordinates ($\times 10^4$) for $[HRuCo_3(CO)_{11}(SeMe_2)]$ (**1**)

Atom	*x*	*y*	*z*
Ru(1)	−927(1)	1641(1)	7135(1)
Se(1)	3264(1)	2630(1)	7105(1)
Co(1)	1274(1)	2124(1)	7069(1)
Co(2)	763(1)	826(1)	8287(1)
Co(3)	291(1)	2762(1)	8446(1)
O(1)	−2083(7)	3259(6)	5797(6)
O(2)	−3192(6)	997(8)	7898(6)
O(3)	−1090(6)	−36(6)	5610(5)
O(4)	848(7)	2392(6)	5068(4)
O(6)	−816(5)	−970(5)	8067(5)
O(7)	2612(5)	−212(5)	9518(4)
O(8)	−1991(6)	3725(7)	8468(5)
O(9)	1393(7)	4074(6)	9941(5)
O(12)	1797(5)	−104(4)	6653(4)
O(13)	634(6)	4403(4)	7028(4)
O(23)	−494(7)	1368(5)	9906(4)
C(1)	−1640(8)	2681(8)	6297(6)
C(2)	−2357(8)	1232(8)	7637(7)
C(3)	−1024(7)	578(7)	6165(6)
C(4)	1004(7)	2258(6)	5848(5)
C(6)	−240(6)	−233(6)	8121(5)
C(7)	1920(7)	207(6)	9046(5)
C(8)	−1116(8)	3287(7)	8385(6)
C(9)	1025(7)	3560(7)	9348(6)
C(12)	1494(6)	599(6)	7076(5)
C(13)	731(7)	3549(6)	7337(5)
C(23)	−40(7)	1529(6)	9247(5)
C(101)	4043(7)	2223(8)	8309(6)
C(102)	3989(8)	1601(7)	6341(7)

Table 2

Atomic coordinates ($\times 10^4$) for [$HRuCo_3(CO)_{10}(SeMe_2)_2$] (2)

Atom	x	y	z
Ru(1)	1346(1)	9599(1)	7832(1)
Se(1)	2491(2)	3748(2)	8538(1)
Se(2)	5438(2)	5773(2)	6155(1)
Co(1)	1957(2)	6537(2)	8229(1)
Co(2)	3605(2)	7626(2)	6992(1)
CO(3)	827(2)	8169(2)	6690(1)
O(1)	−1815(16)	10955(17)	8821(10)
O(2)	1312(13)	12787(12)	6669(8)
O(3)	3304(14)	9574(12)	9275(8)
O(4)	1037(17)	6881(14)	10104(8)
O(6)	5469(12)	9496(12)	6926(8)
O(8)	−1872(11)	11165(11)	6343(7)
O(9)	307(14)	6637(12)	5362(7)
O(12)	5163(11)	5781(11)	8756(7)
O(13)	−1347(13)	7160(14)	8080(8)
O(23)	2406(11)	9943(11)	5273(6)
C(1)	−620(20)	10422(18)	8466(10)
C(2)	1317(16)	11594(17)	7095(10)
C(3)	1400(19)	6797(17)	9350(11)
C(6)	4698(16)	8760(16)	6966(9)
C(8)	−806(15)	10024(17)	6526(9)
C(9)	514(14)	7219(14)	5881(9)
C(12)	4130(15)	6333(14)	8246(9)
C(13)	−123(16)	7171(16)	7814(10)
C(23)	2346(15)	9028(14)	5960(9)
C(101)	3234(25)	2952(19)	9767(11)
C(102)	4427(19)	2752(17)	7900(13)
C(201)	7438(17)	5086(21)	6715(14)
C(202)	5904(18)	7066(19)	5002(11)

Table 3

Atomic coordinates ($\times 10^4$) for [$HRuRh_3(CO)_9]_2[SeMe_2]_3$ (3)

Atom	x	y	z
Rh(1)	6159(3)	4205(2)	5472(3)
Rh(2)	7765(2)	5817(3)	7112(3)
Ru(1)	4515	4515	4515
Ru(2)	7656(2)	7656(2)	7656(2)
Se	7516(3)	4231(3)	6508(3)
O(11)	3937(21)	2384(23)	5588(21)
(O13)	4721(16)	3240(16)	7535(18)
O(12)	6817(24)	1899(20)	5366(22)
O(21)	8026(26)	6708(21)	9886(25)
O(22)	9699(18)	4848(20)	8069(19)
O(23)	6521(19)	5072(19)	9387(18)
C(11)	4146(33)	3222(25)	5185(27)
C(12)	6572(25)	2769(24)	5389(25)
C(13)	4890(22)	3928(22)	6831(21)
C(21)	7875(33)	7109(27)	9091(28)
C(22)	8974(24)	5213(24)	7676(23)
C(23)	6590(23)	5646(22)	8568(25)
C(31)	7281(24)	3143(21)	7791(23)
C(32)	8897(24)	3547(23)	5828(26)

Table 4

Bond lengths (pm) for $[HRuCo_3(CO)_{11}(SeMe_2)]$ (**1**)

Ru(1)-Co(1)	263.4(1)	Ru(1)-Co(2)	264.7(1)
Ru(1)-Co(3)	265.2(1)	Ru(1)-C(1)	191.5(9)
Ru(1)-C(2)	194.3(9)	Ru(1)-C(3)	193.2(9)
Se(1)-Co(1)	239.0(1)	Se(1)-C(101)	194.4(8)
Se(1)-C(102)	195(1)	Co(1)-Co(2)	251.2(2)
Co(1)-Co(3)	251.5(2)	Co(1)-C(4)	176.3(8)
Co(1)-C(12)	194.0(8)	Co(1)-C(13)	195.5(7)
Co(2)-Co(3)	251.7(2)	Co(2)-C(6)	177.2(8)
Co(2)-C(7)	182.2(7)	Co(2)-C(12)	203.4(8)
Co(2)-C(23)	195.4(8)	Co(3)-C(8)	175.5(9)
Co(3)-C(9)	179.1(8)	Co(3)-C(13)	198.9(8)
Co(3)-C(23)	199.6(8)	O(1)-C(1)	111(1)
O(2)-C(2)	111(1)	O(3)-C(3)	111(1)
O(4)-C(4)	113(1)	O(6)-C(6)	114(1)
O(7)-C(7)	113.0(9)	O(8)-C(8)	117(1)
O(9)-C(9)	112(1)	O(12)-C(12)	114.9(9)
O(13)-C(13)	116.7(9)	O(23)-C(23)	115(1)

Table 5

Bond lengths (pm) for $[HRuCo_3(CO)_{10}(SeMe_2)_2]$ (**2**)

Ru(1)-Co(1)	261.9(2)	Ru(1)-Co(2)	261.7(2)
Ru(1)-Co(3)	263.7(3)	Ru(1)-C(1)	191(2)
Ru(1)-C(2)	190(1)	Ru(1)-C(3)	190(2)
Se(1)-Co(1)	239.2(2)	Se(1)-C(101)	191(2)
Se(1)-C(102)	192(2)	Se(2)-Co(2)	239.2(2)
Se(2)-C(201)	195(2)	Se(2)-C(202)	194(2)
Co(1)-Co(2)	251.4(3)	Co(1)-Co(3)	251.8(2)
Co(1)-C(4)	175(2)	Co(1)-C(12)	196(2)
Co(1)-C(13)	193(2)	Co(2)-Co(3)	251.2(3)
Co(2)-C(6)	173(2)	Co(2)-C(12)	196(1)
Co(2)-C(23)	193(1)	Co(3)-C(8)	178(1)
Co(3)-C(9)	180(1)	Co(3)-C(13)	198(1)
Co(3)-C(23)	197(1)	O(1)-C(1)	114(2)
O(2)-C(2)	114(2)	O(3)-C(3)	111(2)
O(4)-C(4)	115(2)	O(6)-C(6)	117(2)
O(8)-C(8)	113(2)	O(9)-C(9)	114(2)
O(12)-C(12)	117(2)	O(13)-C(13)	116(2)
O(23)-C(23)	117(2)		

Table 6

Bond lengths (pm) for $[HRuRh_3(CO)_9]_2[SeMe_2]_3$ (**3**)

Rh(1)-Ru(1)	269.6(4)	Rh(1)-Se	255.1(6)
Rh(1)-C(12)	187(3)	Rh(1)-C(13)	215(3)
Rh(1)-Rh(1A)	277.3(5)	Rh(1)-C(13A)	208(3)
Rh(2)-Ru(2)	268.5(6)	Rh(2)-Se	256.7(6)
Rh(2)-C(22)	185(3)	Rh(2)-C(23)	215(3)
Rh(2)-Rh(2A)	277.4(5)	Rh(2)-C(23A)	210(3)
Ru(1)-C(11)	184(3)	Ru(2)-C(21)	192(4)
Se-C(31)	194(3)	Se-C(32)	192(3)
O(11)-C(11)	117(4)	O(13)-C(13)	115(3)
O(12)-C(12)	112(4)	O(21)-C(21)	110(5)
O(22)-C(22)	115(4)	O(23)-C(23)	115(4)

Table 7

Selected bond angles (°) for [$HRuCo_3(CO)_{11}(SeMe_2)$] (**1**)

Co(1)-Ru(1)-C(1)	100.3(3)	Co(2)-Ru(1)-C(1)	155.2(3)
Co(3)-Ru(1)-C(1)	104.5(3)	Co(1)-Ru(1)-C(2)	160.1(3)
Co(2)-Ru(1)-C(2)	105.7(3)	Co(3)-Ru(1)-C(2)	106.9(3)
Co(1)-Ru(1)-C(3)	97.0(2)	Co(2)-Ru(1)-C(3)	99.9(2)
Co(3)-Ru(1)-C(3)	151.0(2)	Co(1)-Se(1)-C(101)	108.2(3)
Co(1)-Se(1)-C(102)	106.3(3)	C(101)-Se(1)-C(102)	98.0(4)
Ru(1)-Co(1)-Se(1)	176.1(1)	Se(1)-Co(1)-Co(2)	116.9(1)
Se(1)-Co(1)-Co(3)	114.2(1)	Ru(1)-Co(1)-C(4)	88.9(3)
Co(2)-Co(1)-C(4)	136.7(3)	Co(3)-Co(1)-C(4)	134.9(3)
Ru(1)-Co(1)-C(12)	84.2(2)	Co(2)-Co(1)-C(12)	52.5(2)
Co(3)-Co(1)-C(12)	112.5(2)	Ru(1)-Co(1)-C(13)	82.7(2)
Co(2)-Co(1)-C(13)	111.0(2)	Co(3)-Co(1)-C(13)	51.0(2)
Ru(1)-Co(2)-C(6)	76.8(2)	Co(1)-Co(2)-C(6)	126.4(3)
Co(3)-Co(2)-C(6)	126.7(3)	Ru(1)-Co(2)-C(7)	177.2(2)
Co(1)-Co(2)-C(7)	119.2(3)	Co(3)-Co(2)-C(7)	121.0(2)
Ru(1)-Co(2)-C(12)	82.1(2)	Co(1)-Co(2)-C(12)	49.2(2)
Co(3)-Co(2)-C(12)	109.1(2)	Ru(1)-Co(2)-C(23)	83.9(2)
Co(1)-Co(2)-C(23)	111.1(2)	Co(3)-Co(2)-C(23)	51.2(2)
Ru(1)-Co(3)-C(8)	74.9(3)	Co(1)-Co(3)-C(8)	125.0(3)
Co(2)-Co(3)-C(8)	124.8(3)	Ru(1)-Co(3)-C(9)	176.2(3)
Co(1)-Co(3)-C(9)	122.1(3)	Co(2)-Co(3)-C(9)	121.3(3)
Ru(1)-Co(3)-C(13)	81.7(2)	Co(1)-Co(3)-C(13)	49.8(2)
Co(2)-Co(3)-C(13)	109.6(2)	Ru(1)-Co(3)-C(23)	83.0(2)
Co(1)-Co(3)-C(23)	109.6(2)	Co(2)-Co(3)-C(23)	49.7(2)
Co(1)-C(12)-Co(2)	78.4(3)	Co(1)-C(12)-O(12)	144.0(6)
Co(2)-C(12)-O(12)	137.6(6)	Co(1)-C(13)-Co(3)	79.3(3)
Co(1)-C(13)-O(13)	142.5(7)	Co(3)-C(13)-O(13)	138.2(7)
Co(2)-C(23)-Co(3)	79.1(3)	Co(2)-C(23)-O(23)	142.6(7)
Co(3)-C(23)-O(23)	138.2(7)		

The presence of the $Co_3(\mu_3\text{-H})$ unit is obvious from the M-M-ligand bond angles and from M-M bond lengths. The Ru-Co-C_{eq} bond angles are < 90°, whereas the corresponding bond angles in [$H_2Ru_2Rh_2(CO)_{12}$] for $Ru_{ap}(\mu_2\text{-H})M_{bas}$ edges are 110.7 and 115.8° [14]. The basal μ_3-hydride opens the Co-Co-C_{ax}- and Co-Co-Se-angles to give average values of 115.5 and 120.9° in **1**, and of 119.0 and 115.4° in **2**. The bond length and bond angle data are also consistent with those for the structurally analogous clusters [$HRuCo_3(CO)_{11}(PMe_3)$] and [$HRuCo_3(CO)_{11}(PMe_2Ph)$] [15].

The bonds of the bridging carbonyls with Co(1) in **1** are slightly stronger. In **2** the bridges C(13) and C(23) are bent towards Co(1) and Co(2), which bear the $SeMe_2$ ligands.

In compound **1** one of the methyl groups of the selenide ligand is oriented above the hydride ligand, probably to minimize steric repulsion. In **2** there is less crowding when methyl groups of both ligands are bent outwards from the cluster.

The broad hydride resonance of both compounds at −19.6 ppm correspond well with the $Co_3(\mu_3\text{-H})$ resonances for [$HRuCo_3(CO)_{12}$] and its derivatives [12].

Structure isomerism was observed for the disubstituted species. In the reaction between the parent cluster and $SeMe_2$ a mixture of disubstituted products is formed. The ^1H NMR spectrum recorded immediately after the reaction showed

Table 8

Selected bond angles (°) for [HRuCo$_3$(CO)$_{10}$(SeMe$_2$)$_2$] (**2**)

Co(1)-Ru(1)-C(1)	102.8(5)	Co(2)-Ru(1)-C(1)	157.6(6)
Co(3)-Ru(1)-C(1)	104.7(6)	Co(1)-Ru(1)-C(2)	156.7(5)
Co(2)-Ru(1)-C(2)	101.0(4)	Co(3)-Ru(1)-C(2)	105.3(5)
Co(1)-Ru(1)-C(3)	97.4(4)	Co(2)-Ru(1)-C(3)	97.2(4)
Co(3)-Ru(1)-C(3)	150.2(3)	Co(1)-Se(1)-C(101)	104.0(6)
Co(1)-Se(1)-C(102)	108.2(5)	C(101)-Se(1)-C(102)	98.1(8)
Co(2)-se(2)-C(201)	105.1(6)	Co(2)-Se(2)-C(202)	105.4(5)
C(201)-Se(2)-C(202)	97.3(8)	Ru(1)-Co(1)-Se(1)	178.0(1)
Se(1)-Co(1)-Co(2)	117.9(1)	Se(1)-Co(1)-Co(3)	116.3(1)
Ru(1)-Co(1)-C(4)	83.8(5)	Se(1)-Co(1)-C(4)	97.9(5)
Co(2)-Co(1)-C(4)	131.7(6)	Co(3)-Co(1)-C(4)	132.2(4)
Ru(1)-Co(1)-C(12)	84.1(4)	Se(1)-Co(1)-C(12)	96.6(4)
Co(2)-Co(1)-C(12)	50.2(4)	Co(3)-Co(1)-C(12)	110.1(4)
Ru(1)-Co(1)-C(13)	84.5(5)	Se(1)-Co(1)-C(13)	94.3(5)
Co(2)-Co(2)-C(13)	110.8(4)	Co(3)-Co(1)-C(13)	50.9(4)
Ru(1)-Co(2)-Se(2)	173.4(1)	Se(2)-Co(2)-Co(1)	115.7(1)
Se(2)-Co(2)-Co(3)	111.5(1)	Ru(1)-Co(2)-C(6)	87.8(4)
Se(2)-Co(2)-C(6)	98.0(4)	Co(1)-Co(2)-C(6)	133.3(5)
Co(3)-Co(2)-C(6)	136.2(4)	Ru(1)-Co(2)-C(12)	84.1(3)
Se(2)-Co(2)-C(12)	98.4(4)	Co(1)-Co(2)-C(12)	50.1(4)
Co(3)-Co(2)-C(12)	110.2(4)	Ru(1)-Co(2)-C(23)	79.6(4)
Se(2)-Co(2)-C(23)	96.5(4)	Co(1)-Co(2)-C(23)	110.2(4)
Co(3)-Co(2)-C(23)	50.5(4)	Ru(1)-Co(3)-C(8)	77.3(6)
Co(1)-Co(3)-C(8)	124.6(5)	Co(2)-Co(3)-C(8)	128.2(6)
Ru(1)-Co(3)-C(9)	178.1(4)	Co(1)-Co(3)-C(9)	120.1(4)
Co(2)-Co(3)-C(9)	117.8(4)	Ru(1)-Co(3)-C(13)	83.0(5)
Co(1)-Co(3)-C(13)	49.0(4)	Co(2)-Co(3)-C(13)	108.9(4)
Ru(1)-Co(3)-C(23)	78.5(5)	Co(1)-Co(3)-C(23)	108.7(4)
Co(2)-Co(3)-C(23)	49.2(4)	Ru(1)-C(1)-O(1)	178(1)
Ru(1)-C(2)-O(2)	179(2)	Ru(1)-C(3)-O(3)	179(1)
Co(1)-C(4)-O(4)	176(1)	Co(2)-C(6)-O(6)	178(1)
Co(3)-C(8)-O(8)	173(2)	Co(3)-C(9)-O(9)	179(1)
Co(1)-C(12)-Co(2)	79.7(5)	Co(1)-C(12)-O(12)	140(1)
Co(2)-C(12)-O(12)	141(1)	Co(1)-C(13)-Co(3)	80.2(6)
Co(1)-C(13)-O(13)	141(1)	Co(3)-C(13)-O(13)	138(1)
Co(2)-C(23)-Co(3)	80.3(5)	Co(2)-C(23)-O(23)	141(1)
Co(3)-C(23)-O(23)	139(1)		

two cluster hydride resonances, at −17.8 and −19.6 ppm. The latter is the signal from **2**. In the solution **2b** isomerizes slowly to **2** (Fig. 3). The two signals did not coalesce when the solution was warmed to 47°C. The resonance at −17.8 is consistent with a hydride cluster in which the second ligand substitution has taken place at the ruthenium center (**2b**).

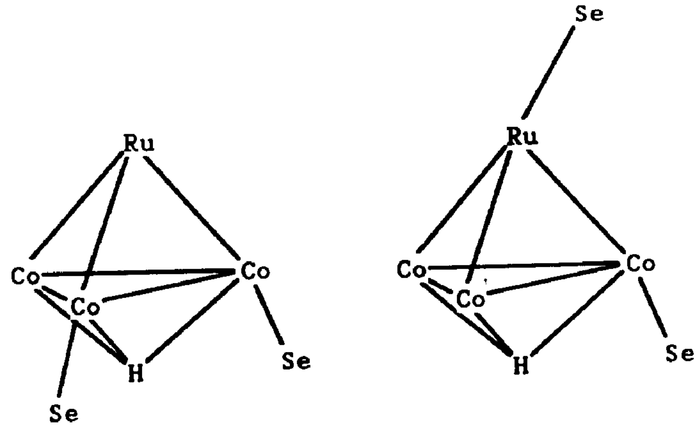
Examples of related compounds are HRuCo$_3$(CO)$_{12-x}$L$_x$ (L = amines) [16] and for HRuCo$_3$(CO)$_{10}$(TeMe$_2$)$_2$ [17], where substitution at ruthenium was demonstrated. The second isomer **2b** can be also characterized by IR spectrum (20656w, 2050w, 2012s, 2058w, 1853m, 1844m in CH$_2$Cl$_2$). The two isomers of HRuCo$_3$(CO)$_{10}$(SeMe$_2$)$_2$ can be thus characterized in solution, whereas in the solid state we have found only the isomer in which the substitution is at the cobalt centers (**2**).

Table 9

Selected bond angles (°) for $[HRuRh_3(CO)_9]_2[SeMe_2]_3$ (3)

Ru(1)–Rh(1)–Se	169.1(2)	Ru(1)–Rh(1)–C(12)	92(1)
Se–Rh(1)–C(12)	98(1)	Ru(1)–Rh(1)–C(13)	78.9(9)
Se–Rh(1)–C(13)	96.6(9)	Se–Rh(1)–Rh(1A)	113.9(1)
C(12)–Rh(1)–Rh(1A)	139(1)	C(13)–Rh(1)–Rh(1A)	107.7(7)
Se–Rh(1)–Rh(1B)	110.6(1)	C(12)–Rh(1)–Rh(1B)	133(1)
C(13)–Rh(1)–Rh(1B)	48.0(7)	Ru(1)–Rh(1)–C(13A)	80.2(9)
Se–Rh(1)–C(13A)	101.7(9)	Rh(1A)–Rh(1)–C(13A)	50.2(7)
Rh(1B)–Rh(1)–C(13A)	109.9(7)	Ru(2)–Rh(2)–Se	169.0(2)
Ru(2)–Rh(2)–C(22)	90(1)	Se–Rh(2)–C(22)	101(1)
Ru(2)–Rh(2)–C(23)	81.0(9)	Se–Rh(2)–C(23)	95.5(9)
Se–Rh(2)–Rh(2A)	113.2(1)	C(22)–Rh(2)–Rh(2A)	133(1)
C(23)–Rh(2)–Rh(2A)	108.5(7)	Se–Rh(2)–Rh(2B)	111.1(1)
C(22)–Rh(2)–Rh(2B)	135(1)	C(23)–Rh(2)–Rh(2B)	48.6(7)
Ru(2)–Rh(2)–C(23A)	81.7(9)	Se–Rh(2)–C(23A)	99(1)
Rh(2A)–Rh(2)–C(23A)	50.0(8)	Rh(2B)–Rh(20)–C(23A)	109.8(8)
Rh(1)–Ru(1)–C(11)	96(1)	Rh(1)–Ru(1)–C(11A)	103(1)
Rh(1)–Ru(1)–C(11B)	156 2b(1)	Rh(2)–Ru(2)–C(21)	99(1)
Rh(2)–Ru(2)–C(21A)	102(1)	Rh(2)–Ru(2)–C(21B)	159(1)
Rh(1)–Se–Rh(2)	128.1(2)	Rh(1)–Se–C(31)	105(1)
Rh(2)–Se–C(31)	106(1)	Rh(1)–Se–C(32)	108(1)
Rh(2)–Se–C(32)	107(1)	C(31)–Se–C(32)	99(1)
Ru(1)–C(11)–O(11)	178(3)	Rh(1)–C(12)–O(12)	178(3)
Rh(1)–C(13)–O(13)	137(2)	O(13)–C(13)–Rh(1B)	142(2)
Ru(2)–C(21)–O(21)	174(4)	Rh(2)–C(22)–O(22)	177(3)
Rh(2)–C(23)–O(23)	137(2)	O(23)–C(23)–Rh(2B)	141(2)
C(12)–Rh(1)–C(13)	93(1)	C(12)–Rh(1)–C(13A)	100(1)
C(13)–Rh(1)–C(13A)	156(1)		

The facile isomerization is indicative of different preferences of the ligand for the metals in the ligand substitution process. In $HRuCo_3(CO)_{12}$ dimethyl sulfide prefers cobalt centers in mono- and di-substitution. The corresponding substitution with



(2) (2b)

Fig. 3. The forms (2) and (2b) of $[HRuCo_3(CO)_{10}(SeMe_2)_2]$.

Table 10

Crystallographic data for $[HRuCo_3(CO)_{11}(SeMe_2)]$ (**1**), $[HRuCo_3(CO)_{10}(SeMe_2)_2]$ (**2**) and $[HRuRh_3(CO)_9]_2[SeMe_2)]_3$ (**3**)

	1	**2**	**3**
Formula weight	696.02	777.04	1512.22
Crystal system	monoclinic	triclinic	trigonal
Space group	$P2_1/n$	$P1$	$R3c$
a (pm)	1159.6(4)	931.1(3)	1329.2(5)
b (pm)	1261.1(5)	940.3(3)	
c (pm)	1440.7(5)	1504.0(7)	
α (deg)	90.00	74.76(3)	74.86(3)
β (deg)	95.67(3)	82.03(3)	
γ (deg)	90.00	66.53(3)	
V (nm^3)	2.096(1)	1.1645(8)	2.140(2)
Z	4	2	2
No. centering refl.	20	25	23
Centering 2θ	9–24	15–30	8–29
D_{calc} (g cm^{-3})	2.21	2.22	2.35
Cryst. dim. (mm)	0.3×0.3×0.3	0.3×0.3×0.2	0.2×0.2×0.2
2θ-limits	0–55	4–50	4–55
h,k,l range	15,16,±18	12,±12,±18	±18,±18,18
No. of unique refl.	4807	4110	2585
Obsd. data $I = 3\sigma(I)$	3049	2605	1296
μ (cm^{-1})	47.9	55.8	52.5
No. param.	262	271	160
R [a]	0.0400	0.0561	0.0552
R_w [b]	0.0373	0.0548	0.0528

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

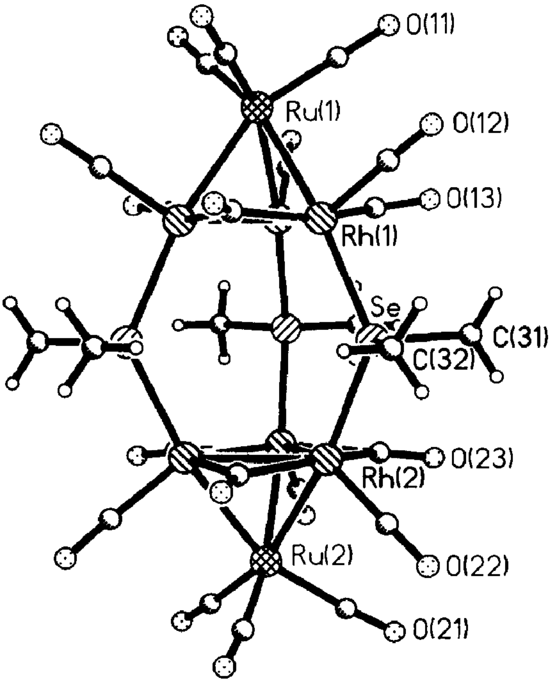


Fig. 4. Structure and numbering scheme for $[HRuRh_3(CO)_9]_2[SeMe_2]_3$ (**3**).

dimethyl telluride takes place first at the ruthenium center. With dimethyl selenide, cobalt is a slightly prefered substitution center, but in disubstitution displacement of carbonyls from ruthenium is also available.

Synthesis and structure of $[HRuRh_3(CO)_9]_2[SeMe_2]_3$ *(3)*

$[HRuRH_3(CO)_{12}]$ was found to be more reactive towards $SeMe_2$ than $[HRuCo_3(CO)_{12}]$ owing to the higher reactivity of rhodium sites. Treatment of dichloromethane solution of $[HRuRh_3(CO)_{12}]$ with $SeMe_2$ smoothly gave **3** in 35% yield. The compound has maintained the basic cluster geometry. The four electron-donating ability of $SeMe_2$ facilitates the unusual formation of intercluster bridges.

The crystal structure and the numbering scheme are presented in Fig. 4. Atomic coordinates are shown in Table 3, bond distances in Table 6. and selected bond angles in Table 9. The hydride position can also be inferred from the data in Tables 6 and 7, as for compounds **1** and **2**.

The presence of the $Rh_3(\mu_3\text{-}H)$ hydride bridge was evident from the ^1H NMR spectrum. Compound **3** gives a quartet at -17.2 ppm ($^1J(RhH)$ 12.0 Hz). The chemical shift differs from that for the $Rh_3(\mu_3\text{-}H)$ signal from $[HRuRh_3(CO)_{12}]$ and its phosphine derivatives (ca. -15.5 ppm), but is similar to that for the sulfur analogue **6** (δ_H 17.0 ppm). No $^2J(SeH)$ couplings were observed.

The Co–Se–C angles in **1** (av. 107.3°), **2** (av. 105.7°) are similar to the Rh–Se–C angles in **3** (av. 106.6°), and the C–Se–C angles in **1** (98.0°) and **2** (av. 97.7) are similar to that (99°) in **3**, indicating that the bridging $SeMe_2$ in **3** is not distorted with respect to the terminal $SeMe_2$ groups in **1** and **2**. The bite of the bidentate ligand is wide enough to accommodate the facing triply bridged hydrogens of the cluster monomers. The distance between the two hydrides can be estimated by assuming a Rh–H bond length of 185 pm, the value observed crystallographically for $[HRuRh_3(CO)_{10}(PPh_3)_2]$. On this basis the H–H-distances in **3** and **6** are ca. 270 and 250 pm, somewhat more than twice the Van der Waals radius of hydrogen (240 pm) [18].

Acknowledgements

Neste Ltd. and the Academy of Finland are thanked for financial support.

References

1 G. Wilkinson, F.G.A. Stone, E.W. Abel, Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982.

2 M. Rakowski Dubois, Chem. Rev., 89 (1989) 1.

3 H. Brunner, N. Janietz, W. Meier, J. Wachter, E. Herdtweck, W.A. Herrmann, G. Serhadli and M.L. Ziegler, J. Organomet. Chem., 347 (1988) 237.

4 D. Fenske and J. Ohmer, Angew. Chem. Int. Ed. Engl., 26 (1987) 148.

5 H. Brunner, J. Wachter and H. Wintergerst, J. Organomet. Chem., 235 (1982) 77.

6 R.D. Adams and I. Horvath, Inorg. Chem. 23 (1984) 4718.

7 Gmelins Handbuch der Anorganischen Chemie, Verlag Chemie, Weinheim, 1957, Vol 68D.

8 S. Rossi, J. Pursiainen, M. Ahlgren and T.A. Pakkanen, Organometallics, 9 (1990) 475.

9 M. Hidai, M. Orisaku, M. Ue, Y. Koyasu, T. Kodama and Y. Uchida, Organometallics, 2 (1983) 292.

10 J. Pursiainen, T.A. Pakkanen and J. Jääskeläinen, J. Organomet. Chem., 290 (1985) 85.

11 T.A. Pakkanen, J. Pursiainen, T. Venäläinen and T.T. Pakkanen, J. Organomet. Chem., 372 (1989) 129, and refs. therein.

12 J. Pursiainen and T.A. Pakkanen, Acta Chem. Scand., 43 (1989) 483.
13 SHELXTL PLUS, Release 3.4, Nicolet Co., Madison, Wisconsin, 1988.
14 J. Pursiainen, T.A. Pakkanen, B.T. Heaton, C. Seregni, R.J. Goodfellow, J. Chem. Soc. Dalton Trans., (1986) 681.
15 J. Pursiainen, M. Ahlgren, T.A. Pakkanen and J. Valkonen, J. Chem. Soc. Dalton Trans., in press.
16 H. Matsuzaka, T. Kodama, Y. Uchida, M. Hidai, Organometallics, 7 (1988) 1608.
17 S. Rossi, J. Pursiainen and T.A. Pakkanen, in preparation.
18 M.C.F. Ladd, Structure and Bonding in Solid State Chemistry, John Wiley & Sons, Chichester, 1979, p. 253.