Journal of Organometallic Chemistry 552 (1998) 9–16

The control of the ligand substitution of $HRuRh_3(CO)_{12}$ with sulphur ligands

Tiina M. Räsänen *, Sirpa Jääskeläinen, Tapani A. Pakkanen

Department of Chemistry, University of Joensuu, P.O. Box 111, Joensuu FIN-80101, Finland

Received 12 May 1997; received in revised form 7 July 1997

Abstract

The syntheses and crystal structures of three trisubstituted derivatives of $HRuRh_3(CO)_{12}$ are described. The clusters $[HRuRh_3(CO)_9(SPh_2)_3]$ **1**, $[HRuRh_3(CO)_9(SPhMe)_3]$ **2** and $[HRuRh_3(CO)_9]_2[SEt_2]_3$ **3** were prepared by reactions of the parent cluster with thioethers SPh_2, SMePh and SEt_2. The thioethers replace carbonyl groups at rhodium atoms. Compounds **1** and **2** are formed when three axial CO groups are replaced at adjacent rhodiums, while compound **3** is a dimeric structure with three bridging thioether groups. The crystal structures of the compounds were solved: **1** triclinic, space group P-1, $a = 1265.2(8)$ pm, $b = 1338.1(6)$ pm, $c = 1561.2(7)$ pm, $\alpha = 77.25(3)°$, $\beta = 83.81(5)°$, $\gamma = 62.70(4)°$, $Z = 2$. **2** triclinic, space group P-1, $a = 1058.9(3)$ pm, $b = 1303.6(4)$ pm, $c = 1415.2(5)$ pm, $\alpha = 71.59(3)°$, $\beta = 78.72(2)°$, $\gamma = 82.62(2)°$, $Z = 2$. **3** monoclinic, space group $P2_1/n$, $a = 1872.2(4)$ pm, $b = 1275.4(3)$ pm, $c = 2148.7(4)$ pm, $\beta = 104.27(3)°$, $Z = 4$. © 1998 Elsevier Science S.A.

---

1. Introduction

The keen interest in compounds of sulphur-containing ligands and mixed-metal clusters is apparent in the extensive number of publications which have appeared in the recent literature [1–3]. Mixed-metal clusters and their ligand substitution offer great potential for a variety of applications [4].

We have earlier prepared several carbonyl substitution derivatives of the mixed metal cluster $[H_xRu_xCo_yRh_z(CO)_{12}]$ $(x,y,z = 0–4,\quad x+y+z = 4)$ [5–8]. The steric and donor properties of the ligand greatly affect the course of the reaction. The differences in reactions due to the presence of two different metals can be investigated by the use of mixed valence isoelectronic metal compounds. For example, the use of series of tetrahedral mixed-metal clusters can reveal how sulphur compounds react with different metals. In the various metal combinations we studied, the sulphur ligand displayed a preference to bind to the different metals in a specific order and to form specific types of complexes. For example, thioethers (SR_2) willingly formed with $HRuRh_3(CO)_{12}$ the dimeric cluster $[HRuRh_3(CO)_9]_2[SR_2]_3$ ($SR_2 = SMe_2$, tetrahydrothiophene) [5,7] which was not detected for other metal combinations. This shows the high reactivity of Rh compared with Ru [5–7]. With $HRuCO_3(CO)_{12}$ the thioethers prefer to form mono- and disubstituted compounds where both sulphur ligands are in axial positions at cobalt [5–7]. Trisubstituted compounds with all unconnected ligands in axial positions are generally rare. Tridentate ligands such as 1,3,5-trithiahexane may bind in axial position in the cluster [9,10].

In this work, we varied the steric properties of the thioether to find out how extensive the changes in the ligand must be to alter the structures of the final $HRuRh_3(CO)_{12}$ thioether products. The steric properties were varied by replacing one or two methyl groups of the simplest thioether with larger ethyl or phenyl groups. The phenyl group also slightly weakens the donor properties.

2. Results and discussion

SEt_2, SMePh and SPh_2 with varying sulphur environment, were chosen as test compounds. The steric

---

[*] Corresponding author.

Table 1
Atomic coordinates ($\times 10^4$) for $HRuRh_3(CO)_9(SPh_2)_3$ (**1**)

Atom	*x*	*y*	*z*
Rh(1)	−3391(1)	7625(1)	88654(1)
Rh(2)	5149(1)	7628(1)	7626(1)
Rh(3)	2936(1)	9549(1)	7539(1)
Ru(1)	4472(1)	8965(1)	8836(1)
S(1)	2075(2)	6853(1)	8510(1)
S(2)	5371(2)	6282(2)	3370(1)
S(3)	1533(2)	9643(1)	6462(1)
O(1)	2888(6)	10483(5)	10116(4)
O(2)	5500(6)	10625(5)	8049(4)
O(3)	6420(6)	7468(5)	10196(5)
O(4)	3342(6)	6986(5)	10835(4)
O(6)	7645(5)	7314(6)	7774(4)
O(8)	2072(6)	12076(5)	7411(5)
O(12)	5873(5)	5596(4)	9206(4)
O(13)	1132(5)	9833(4)	9084(3)
O(23)	4908(5)	9762(4)	6280(3)
C(1)	3466(7)	9911(7)	9636(5)
C(2)	5126(7)	9989(7)	8344(5)
C(3)	5693(8)	8014(7)	9690(6)
C(4)	3338(7)	7253(6)	10089(5)
C(6)	6718(7)	7412(6)	7698(5)
C(8)	2407(6)	11121(6)	7457(5)
C(12)	5182(6)	6412(6)	8788(4)
C(13)	1958(6)	9306(5)	8694(4)
C(23)	4536(6)	9234(6)	6805(5)
C(111)	2704(7)	5574(6)	8060(5)
C(112)	3890(8)	4804(7)	8151(6)
C(113)	4336(9)	3871(7)	7730(7)
C(114)	3603(11)	3689(8)	7265(6)
C(115)	2432(11)	4452(8)	7191(6)
C(116)	1959(9)	5408(7)	7575(6)
C(121)	1319(6)	6505(6)	9486(4)
C(122)	1538(7)	5403(7)	9858(5)
C(123)	878(9)	5216(9)	10602(6)
C(124)	38(9)	6126(10)	10958(6)
C(125)	−170(9)	7216(9)	10579(7)
C(126)	474(8)	7416(7)	9849(6)
C(211)	4577(6)	6939(6)	5659(5)
C(212)	4558(7)	7916(7)	5137(5)
C(213)	3881(8)	8430(7)	4390(5)
C(214)	3211(9)	7966(9)	4158(6)
C(215)	3221(9)	6995(9)	4674(7)
C(216)	3911(8)	6463(7)	5430(6)
C(221)	6900(7)	5541(6)	6350(5)
C(222)	7270(7)	5511(7)	5482(5)
C(223)	8465(8)	4874(8)	5292(6)
C(224)	9277(8)	4233(8)	5955(7)
C(225)	8895(8)	4278(7)	6814(6)
C(226)	7712(8)	4917(6)	7005(5)
C(311)	139(6)	10152(6)	7053(4)
C(312)	−356(7)	9409(6)	7349(5)
C(313)	−1371(8)	9747(8)	7874(6)
C(314)	−1904(7)	10821(8)	8073(5)
C(315)	−1408(7)	11548(7)	7777(5)
C(316)	−391(6)	11226(6)	7267(5)
C(321)	1221(6)	10822(6)	5539(4)
C(322)	141(7)	11332(7)	5111(5)
C(323)	−70(8)	12214(7)	4388(5)
C(324)	809(8)	12544(7)	4096(5)
C(325)	1890(8)	12019(8)	4511(5)
C(326)	2109(7)	11172(7)	5241(5)
H(11A)	4404	4913	8491
H(11B)	5168	3345	7769
H(11C)	3910	3031	6993
H(11D)	1920	4325	6863
H(11E)	1134	5947	7506
H(12A)	2128	4771	9612
H(12B)	1021	4447	10869
H(12C)	−407	5989	11469
H(12D)	−765	7849	10821
H(12E)	324	8186	9594
H(21A)	5021	8248	5296
H(21B)	3878	9111	4028
H(21C)	2740	8321	3635
H(21D)	2743	6678	4514
H(21E)	3924	5773	5786
H(22A)	6702	5930	5017
H(22B)	8723	4887	4690
H(22C)	10092	3759	5882
H(22D)	9462	3861	7280
H(22E)	7462	4923	7608
H(31A)	−5	8666	7195
H(31B)	−1702	9222	8100
H(31C)	−2621	11056	8419
H(31D)	−1771	12294	7925
H(31E)	−52	11748	7060
H(32A)	−457	11079	5312
H(32B)	−821	12591	4094
H(32C)	666	13154	3596
H(32D)	2500	12247	4284
H(32E)	2854	10825	5542
H(1)	3348(42)	7660(31)	22(13)

properties of the compounds differ and the phenyl group also modifies the donor properties of the sulphur.

2.1. Synthesis and structure of [$HRuRh_3(CO)_9(SPh_2)_3$] **1** and [$HRuRh_3(CO)_9(SPhMe)_3$] **2**

Thioethers SMePh and SPh_2 both displaced carbonyl ligands in the parent cluster $HRuRh_3(CO)_{12}$. Instead of the dimeric cluster familiar in earlier characterized thioether derivatives, novel types of substitution derivatives [$HRuRh_3(CO)_9(SPh_2)_3$] **1** and

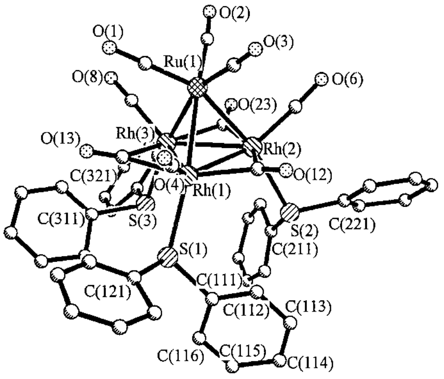

Fig. 1. Structure and numbering scheme for [$HRuRh_3(CO)_9(SPh_2)_3$] (**1**).

Table 2
Atomic coordinates ($\times 10^4$) for $HRuRh_3(CO)_9(SMePh)_3$ (**2**)

Atom	x	y	z
Rh1	2550.6(3)	8165.6(2)	4394.6(2)
Rh2	3258.9(3)	9448.3(2)	2426.7(2)
Rh3	4456.6(3)	7394.0(2)	3095.0(2)
Ru1	1984.5(3)	7666.0(3)	2837.5(2)
S1	3547.7(10)	8677.9(9)	5592.1(7)
S2	4683.3(11)	10807.7(8)	2412.5(8)
S3	6638.6(10)	7582.1(8)	3341.1(8)
C1	1485(5)	6227(4)	3558(4)
C2	2194(5)	7472(5)	1537(4)
C3	313(5)	8381(4)	2803(4)
C4	985(5)	7675(4)	5175(4)
C6	2414(5)	10219(4)	1343(4)
C8	4740(5)	6156(4)	2672(4)
C12	1800(4)	9693(3)	3607(3)
C13	3639(4)	6651(3)	4588(3)
C23	4580(4)	8540(3)	1643(3)
C111	2765(4)	7985(3)	6828(3)
H111	3144(4)	8381(3)	6187(3)
C112	1606(5)	8350(5)	7249(4)
H112	1182(5)	8985(5)	6899(4)
C113	1064(6)	7763(6)	8207(5)
H113	272(6)	8016(6)	8502(5)
C114	1652(6)	6834(5)	8725(4)
H114	1270(6)	6445(5)	9368(4)
C115	2828(7)	6472(5)	8286(4)
H115	3248(7)	5836(5)	8638(4)
C116	3392(5)	7038(4)	7331(4)
H116	4182(5)	6785(4)	7033(4)
C121	3054(7)	10087(4)	5487(4)
H12A	3430(7)	10536(4)	4838(4)
H12B	3340(7)	10280(4)	6008(4)
H12C	2130(7)	10192(4)	5560(4)
C211	3966(4)	12137(3)	1897(3)
H211	4337(4)	11436(3)	2127(3)
C212	4343(7)	12751(4)	902(4)
H212	4969(7)	12476(4)	467(4)
C213	3753(10)	13792(5)	577(6)
H213	3969(10)	14214(5)	−0089(6)
C214	2853(8)	14199(5)	1236(8)
H214	2471(8)	14898(5)	1019(8)
C215	2532(8)	13588(6)	2184(8)
H215	1927(8)	13874(6)	2623(8)
C216	3066(7)	12538(5)	2543(5)
H216	2817(7)	2121(5)	3207(5)
C221	6118(5)	10714(4)	1510(4)
H22A	6567(5)	10015(4)	1732(4)
H22B	6670(5)	11268(4)	1452(4)
H22C	5883(5)	10809(4)	864(4)
C311	7734(4)	6818(3)	2636(3)
H311	7171(4)	7172(3)	3045(3)
C312	8307(5)	5820(4)	3058(4)
H312	8170(5)	5503(4)	3754(4)
C313	9093(6)	5293(5)	2431(5)
H313	9472(6)	4607(5)	2712(5)
C314	9326(6)	5752(5)	1414(5)
H314	9857(6)	5388(5)	999(5)
C315	8757(7)	6769(6)	1012(4)
H315	8907(7)	7094(6)	317(4)
C316	7983(5)	7302(5)	1613(4)
H316	7621(5)	7995(5)	1333(4)
C321	6831(5)	6892(5)	4623(4)
H32A	6273(5)	7249(5)	5062(4)
H32B	7712(5)	6900(5)	4697(4)
H32C	6613(5)	6155(5)	4798(4)
O1	1201(5)	5382(3)	3997(4)
O2	2325(5)	7347(5)	767(3)
O3	−679(4)	8837(4)	2790(5)
O4	37(4)	7374(4)	5631(3)
O6	1929(5)	10678(4)	682(3)
O8	4922(5)	5401(4)	2427(4)
O12	949(3)	10321(3)	3742(3)
O13	3691(4)	5815(3)	5213(3)
O23	5083(4)	8604(3)	826(2)

$[HRuRh_3(CO)_9(SPhMe)_3]$ **2** were formed as the main products. The ligands act as two electron donors and they are coordinated terminally at the three rhodium atoms; otherwise, the parent cluster structure is maintained.

According to IR spectra, mono- and disubstituted species were formed as reaction intermediates. In some reactions traces of dimeric clusters of type **3** were detected in addition. In both reactions, higher reaction temperature and longer reaction time gave higher yield of the dimeric cluster products. However, none of the derivatives was stable enough to be crystallized. Shorter reaction times and lesser amounts of ligand (for example 1:1 molar ratio with the cluster) give larger amounts of mono- and disubstituted products. The reaction conditions and the amount of ligand influenced directly the substitution mode of the cluster.

$HRuRh_3(CO)_{12}$ has also been used in ligand substitution reactions with phosphine compounds, but in these reactions only mono- and disubstituted products are formed. Thus, sulphur appears to have more versatile interactions with rhodium clusters than does phosphorus [11].

The crystal structures and numbering schemes for **1** and **2** are shown in Figs. 1 and 2. Atomic coordinates are shown in Tables 1 and 2, bond distances in Table 3 and selected bond angles in Table 4.

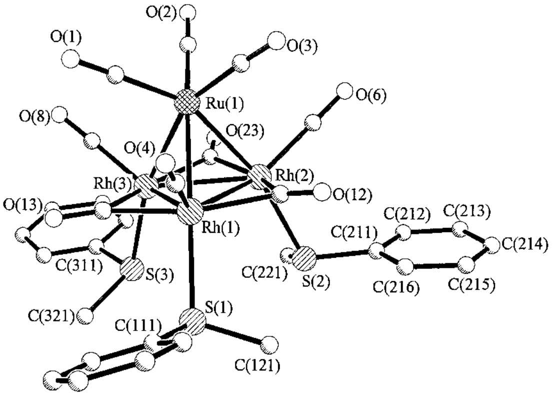

Fig. 2. Structure and numbering scheme for $[HRuRh_3(CO)_9(SMePh)_3]$ (**2**).

The basic tetrahedral unit remains unchanged in both compounds and all substituted carbonyls are coordinated axially to rhodium atoms. The bulky phenyl groups which have more electron density withdrawing character than methyl when bonded to sulphur made the dimeric cluster structure more unfavourable.

The presence of the $Rh_3(\mu3\text{-}H)$ hydride was evident from the ^{1}H-NMR spectrum, with a quartet at −15.05 ppm for **1** and at −15.3 ppm for **2**. This is close to the chemical shift for the parent cluster μ3-H at −15.5 ppm [12]. The position of the hydride could be concluded from the approximately equal Ru–Rh and Rh–Rh bond lengths: 2.676–2.684 pm and 2.768–2.771 pm. An edge-bridging hydride would not only lengthen the metal–metal bond but also cause distortion of the carbonyl geometry. No repulsion effect of an edge-bridging hydride can be seen in either **1** or **2**; the Ru–Rh–Ceq angles lie in a narrow range between 89.4 and 94.5°. The cluster hydride in structure **1** was found crystallographically.

Table 3
Bond lengths (pm) for $HRuRh_3(CO)_9(SPh_2)_3$ (**1**) and $HRuRh_3(CO)_9(SMePh)_3$ (**2**)

	(**1**)	(**2**)
Rh(1)–Ru(1)	269.9(2)	267.6(4)
Rh(2)–Ru(1)	269.0(2)	268.3(8)
h(3)–Ru(1)	269.1(2)	267.6(5)
Rh(1)–Rh(2)	278.6(2)	277.1(10)
Rh(1)–Rh(3)	279.1(2)	276.8(2)
Rh(2)–Rh(3)	279.2(2)	276.9(7)
Rh(1)–S(1)	248.5(3)	245.5(3)
Rh(2)–S(2)	248.6(3)	246.3(3)
Rh(3)–S(3)	251.7(3)	245.6(5)
Ru(1)–C(1)	191.3(8)	191.7(6)
Ru(1)–C(2)	189.4(1)	190.3(5)
Ru(1)–C(3)	191.8(8)	189.3(5)
Rh(1)–C(4)	186.7(8)	186.8(5)
Rh(1)–C(12)	210.7(6)	209.3(4)
Rh(1)–C(13)	212.5(6)	212.1(4)
Rh(2)–C(6)	188.3(10)	186.9(5)
Rh(2)–C(12)	214.7(7)	211.7(4)
Rh(2)–C(23)	208.2(7)	209.4(4)
Rh(3)–C(8)	187.0(8)	186.2(4)
Rh(3)–C(13)	212.5(7)	208.7(4)
Rh(3)–C(23)	212.6(7)	211.6(4)
S(1)–C(111)	179.3(8)	178.5(4)
S(1)–C(121)	179.8(7)	181.1(5)
S(2)–C(211)	178.7(7)	178.7(4)
S(2)–C(221)	179.7(7)	180.2(5)
S(3)–C(311)	180.3(7)	179.2(4)
S(3)–C(321)	180.8(7)	179.2(5)
O(1)–C(1)	114.2(10)	112.7(6)
O(2)–C(2)	114.5(13)	113.1(6)
O(3)–C(3)	113.6(11)	113.9(6)
O(4)–C(4)	114.0(9)	112.5(6)
O(6)–C(6)	113.5(12)	111.9(6)
O(8)–C(8)	113.4(10)	112.6(6)
O(12)–C(12)	114.7(7)	116.6(5)
O(13)–C(13)	115.5(8)	117.0(5)
O(23)–C(23)	116.5(10)	115.6(5)

Table 4
Selected bond angles for $HRuRh_3(CO)_9(SPh_2)_3$ (**1**) and $HRuRh_3(CO)_9(SMePh)_3$ (**2**)

	(**1**)	(**2**)
Ru(1)–Rh(1)–S(1)	162.7(1)	167.24(3)
Ru(1)–Rh(2)–S(2)	165.9(1)	165.65(3)
Ru(1)–Rh(3)–S(3)	166.8(1)	166.66(3)
Rh(1)–Rh(2)–S(2)	107.0(1)	109.26(4)
Rh(1)–Rh(3)–S(3)	108.1(1)	112.42(3)
Rh(2)–Rh(1)–S(1)	116.0(1)	111.91(3)
Rh(2)–Rh(3)–S(3)	113.9(1)	108.34(4)
Rh(3)–Rh(1)–S(1)	104.1(1)	109.41(3)
Rh(3)–Rh(2)–S(2)	114.8(1)	109.36(3)
Ru(1)–Rh(1)–C(4)	94.5(3)	90.4(2)
Ru(1)–Rh(1)–C(12)	80.1(2)	81.11(12)
Ru(1)–Rh(1)–C(13)	76.6(2)	81.52(12)
Rh(2)–Rh(1)–C(4)	134.8(3)	134.0(2)
Rh(2)–Rh(1)–C(12)	49.6(2)	49.21(12)
Rh(2)–Rh(1)–C(13)	108.3(2)	108.32(12)
Rh(3)–Rh(1)–C(4)	139.1(2)	134.6(2)
Rh(3)–Rh(1)–C(12)	109.4(2)	109.11(12)
Rh(3)–Rh(1)–C(13)	49.0(2)	48.35(12)
Ru(1)–Rh(2)–C(6)	89.4(3)	93.6(2)
Ru(1)–Rh(2)–C(12)	79.7(2)	80.51(12)
Ru(1)–Rh(2)–C(23)	80.1(2)	79.18(12)
Rh(1)–Rh(2)–C(6)	134.0(2)	136.5(2)
Rh(1)–Rh(2)–C(12)	48.5(2)	48.45(12)
Rh(1)–Rh(2)–C(23)	109.0(2)	108.86(12)
Rh(3)–Rh(2)–C(6)	133.1(3)	136.5(2)
Rh(3)–Rh(2)–C(12)	108.3(2)	108.30(12)
Rh(3)–Rh(2)–C(23)	49.1(2)	49.20(12)
Ru(1)–Rh(3)–C(8)	93.4(3)	92.1(2)
Ru(1)–Rh(3)–C(13)	76.8(2)	82.10(13)
Ru(1)–Rh(3)–C(23)	79.4(2)	79.00(12)
Rh(1)–Rh(3)–C(8)	137.4(2)	135.2(2)
Rh(1)–Rh(3)–C(13)	48.9(2)	49.39(12)
Rh(1)–Rh(3)–C(23)	107.5(2)	108.28(12)
Rh(2)–Rh(3)–C(8)	135.4(3)	135.9(2)
Rh(2)–Rh(3)–C(13)	108.1(2)	109.40(12)
Rh(2)–Rh(3)–C(23)	47.8(2)	48.53(11)

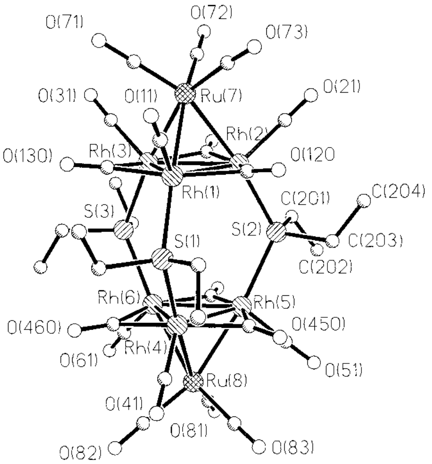

Fig. 3. Structure and numbering scheme for $[HRuRh_3(CO)_9][SEt_2]_3$ (**3**).

Table 5
Atomic coordinates ($\times 10^4$) for $[HRuRh_3(CO)_9]_2[SEt_2]_3$ (**3**)

Atom	x	y	z
Rh1	7346(8)	7624(11)	1093(6)
Rh2	8483(8)	8438(11)	621(7)
Rh3	7091(8)	9341(11)	285(6)
Rh4	6757(8)	5522(11)	−525(6)
Rh5	7882(8)	6352(12)	−1005(7)
Rh6	6486(8)	7221(11)	−1349(6)
Ru7	7947(9)	9481(12)	1487(7)
Ru8	6754(9)	5312(12)	−1767(7)
S1	6821(3)	5981(3)	594(2)
S3	6378(3)	8906(4)	−812(2)
S2	8798(3)	7425(4)	−242(2)
C11	7293(11)	7434(15)	1930(9)
C21	9425(13)	9039(18)	1012(10)
C31	6709(14)	10684(16)	393(9)
C41	6327(12)	4216(15)	−588(9)
C51	8447(14)	5739(17)	−1507(13)
C61	5875(13)	7455(17)	−2141(9)
C71	7299(13)	9957(17)	1913(10)
C72	8367(14)	10800(18)	1450(12)
C73	8657(13)	9002(17)	2259(9)
C81	6919(12)	5591(17)	−2587(10)
C82	5769(13)	4809(17)	−2145(9)
C83	7190(15)	3947(20)	−1709(10)
C101	7282(13)	4962(16)	1144(10)
C102	7046(13)	3818(17)	1000(9)
C103	5865(10)	5864(14)	674(8)
C104	5760(14)	6037(19)	1333(9)
C120	8480(9)	7286(17)	1230(8)
C130	6421(10)	8571(12)	794(7)
C201	9213(13)	8408(19)	−659(10)
C202	9511(16)	7980(22)	−1214(12)
C203	9565(12)	6508(20)	76(10)
C204	10232(12)	6960(23)	529(13)
C230	8101(12)	9711(21)	121(10)
C301	6557(12)	9880(13)	−1377(9)
C302	6479(16)	11008(17)	−1190(10)
C303	5389(10)	9088(15)	−778(8)
C304	4846(12)	8915(20)	−1427(11)
C450	7843(10)	5099(17)	−438(8)
C460	5782(10)	6327(13)	−953(7)
C560	7489(11)	7536(16)	−1599(11)
O11	7247(9)	7329(12)	2454(7)
O21	9961(9)	9378(14)	1240(8)
O31	6510(10)	11462(12)	482(7)
O41	6061(10)	3409(13)	−624(8)
O51	8814(10)	5325(14)	−1779(8)
O61	5527(10)	7613(14)	−2664(7)
O71	6870(9)	10239(13)	2201(7)
O72	8627(11)	11614(14)	1416(8)
O73	9075(10)	8684(14)	2678(7)
O81	6983(10)	5795(14)	−3090(8)
O82	5213(10)	4508(15)	−2369(7)
O83	7451(13)	3161(13)	−1626(8)
O120	8898(8)	6673(12)	1592(7)
O130	5838(7)	8673(11)	882(6)
O230	8288(9)	10460(13)	−149(8)
O450	8224(8)	4366(12)	−181(7)
O460	5166(8)	6304(10)	−951(6)
O560	7670(9)	8180(13)	−1950(6)
S99	9236(5)	4163(7)	1241(4)
S98	9772(7)	3333(9)	2519(5)
C99	9487(19)	4369(27)	2027(16)

The Ru–Rh–S bond angles are slightly smaller (average 165.1° for **1** and 166.3° for **2**) than in the dimeric structures (average 170.1° for SMe_2 and 171.0° for tetrahydrothiophene) [5,7].

In **2**, the phenyl rings are approximately parallel with the Rh_3-plane (Rh–S–C(Ph) angles average 108.1°) and the methyl and phenyl groups are in alternate positions pointing out in turns. In **1**, the ligands cause more crowding and for steric reasons the phenyl groups are more twisted relative to the Rh_3-plane.

2.2. Synthesis and structure of $[HRuRh_3(CO)_9]_2[SEt_2]_3$ *3*

Reaction between $HRuRh_3(CO)_{12}$ and SEt_2 in refluxing CH_2Cl_2 gave compound **3**. Here, the sulphur ligand has less steric requirements and is able to form a dimeric cluster structure. According to IR, the mono-, di- and trisubstituted species are formed to lesser extent, but they are more unstable and decompose during crystallization back to the primary compounds, or else react further to the dimeric compound.

Table 6
Bond lengths (pm) for $[HRuRh_3(CO)_9]_2[SEt_2]_3$ (**3**)

Rh(1)–Rh(2)	277.4(2)
Rh(1)–Rh(3)	276.3(2)
Rh(1)–Ru(7)	266.9(2)
Rh(2)–Ru(7)	267.6(2)
Rh(3)–Rh(2)	277.6(2)
Rh(3)–Ru(7)	269.1(2)
Rh(4)–Ru(8)	268.0(2)
Rh(4)–Rh(6)	276.5(2)
Rh(4)–Rh(5)	277.4(2)
Rh(5)–Ru(8)	268.3(2)
Rh(6)–Ru(8)	268.5(2)
Rh(6)–Rh(5)	276.8(2)
Rh(1)–S(1)	244.8(4)
Rh(2)–S(2)	245.0(5)
Rh(3)–S(3)	246.8(5)
Rh(4)–S(1)	245.0(4)
Rh(5)–S(2)	247.1(5)
Rh(6)–S(3)	247.1(5)
Rh(1)–C(11)	184(2)
Rh(1)–C(120)	211(2)
Rh(1)–C(130)	208(2)
Rh(2)–C(21)	192(2)
Rh(2)–C(120)	197(2)
Rh(2)–C(230)	198(3)
Rh(3)–C(31)	189(2)
Rh(3)–C(130)	210(2)
Rh(3)–C(230)	206(2)
Rh(4)–C(41)	184(2)
Rh(4)–C(450)	207(2)
Rh(4)–C(460)	210(2)
Rh(5)–C(51)	186(3)
Rh(5)–C(450)	202(2)
Rh(5)–C(560)	200(3)
Rh(6)–C(61)	183(2)
Rh(6)–C(460)	208(2)
Rh(6)–C(560)	212(2)

Table 7
Selected bond angles for $[HRuRh_3(CO)_9]_2[SEt_2]_3$ (**3**)

S(1)–Rh(1)–Ru(7)	172.52(12)
S(1)–Rh(1)–Rh(2)	114.96(12)
S(1)–Rh(1)–Rh(3)	114.49(11)
S(1)–Rh(4)–Ru(8)	171.47(12)
S(1)–Rh(4)–Rh(5)	114.58(12)
S(1)–Rh(4)–Rh(6)	113.44(11)
S(2)–Rh(2)–Ru(7)	172.18(14)
S(2)–Rh(2)–Rh(1)	115.39(13)
S(2)–Rh(2)–Rh(3)	114.06(13)
S(2)–Rh(5)–Ru(8)	172.39(13)
S(2)–Rh(5)–Rh(4)	115.52(13)
S(2)–Rh(5)–Rh(6)	114.23(13)
S(3)–Rh(3)–Ru(7)	170.37(12)
S(3)–Rh(3)–Rh(1)	113.01(12)
S(3)–Rh(3)–Rh(2)	114.01(13)
S(3)–Rh(6)–Ru(8)	171.26(12)
S(3)–Rh(6)–Rh(4)	113.94(11)
S(3)–Rh(6)–Rh(5)	113.83(13)
C(11)–Rh(1)–Ru(7)	85.8(6)
C(11)–Rh(1)–Rh(2)	129.7(6)
C(11)–Rh(1)–Rh(3)	132.5(6)
C(21)–Rh(2)–Ru(7)	87.6(6)
C(21)–Rh(2)–Rh(1)	134.0(6)
C(21)–Rh(2)–Rh(3)	130.6(7)
C(31)–Rh(3)–Ru(7)	88.7(6)
C(31)–Rh(3)–Rh(1)	130.8(6)
C(31)–Rh(3)–Rh(2)	134.6(7)
C(41)–Rh(4)–Ru(8)	86.7(6)
C(41)–Rh(4)–Rh(5)	132.6(7)
C(41)–Rh(4)–Rh(6)	130.9(6)
C(51)–Rh(5)–Ru(8)	85.0(8)
C(51)–Rh(5)–Rh(4)	130.4(7)
C(51)–Rh(5)–Rh(6)	130.4(8)
C(61)–Rh(6)–Ru(8)	87.8(6)
C(61)–Rh(6)–Rh(4)	134.3(7)
C(61)–Rh(6)–Rh(5)	130.4(7)
C(71)–Ru(7)–Rh(1)	100.2(6)
C(71)–Ru(7)–Rh(3)	101.2(7)
C(72)–Ru(7)–Rh(2)	100.6(8)
C(72)–Ru(7)–Rh(3)	100.1(8)
C(73)–Ru(7)–Rh(1)	97.9(6)
C(73)–Ru(7)–Rh(2)	98.2(6)
C(81)–Ru(8)–Rh(4)	161.0(6)
C(81)–Ru(8)–Rh(5)	101.0(6)
C(81)–Ru(8)–Rh(6)	103.2(7)
C(82)–Ru(8)–Rh(4)	102.6(6)
C(82)–Ru(8)–Rh(5)	161.3(6)
C(82)–Ru(8)–Rh(6)	101.8(7)
C(83)–Ru(8)–Rh(6)	97.5(6)
C(83)–Ru(8)–Rh(4)	98.7(7)
C(83)–Ru(8)–Rh(5)	156.2(6)
C(120)–Rh(1)–Ru(7)	78.9(5)
C(120)–Rh(1)–Rh(2)	45.0(6)
C(120)–Rh(2)–Ru(7)	81.1(5)
C(120)–Rh(2)–Rh(1)	49.4(5)
C(130)–Rh(1)–Ru(7)	80.6(4)
C(130)–Rh(1)–Rh(3)	49.0(4)
C(130)–Rh(3)–Ru(7)	79.7(4)
C(130)–Rh(3)–Rh(1)	48.3(5)
C(230)–Rh(2)–Ru(7)	79.8(5)
C(230)–Rh(2)–Rh(3)	47.8(5)
C(230)–Rh(3)–Ru(7)	78.2(6)
C(230)–Rh(3)–Rh(2)	45.4(8)
C(450)–Rh(4)–Ru(8)	80.0(4)
C(450)–Rh(4)–Rh(5)	46.7(6)
C(450)–Rh(5)–Ru(8)	80.6(5)
C(450)–Rh(5)–Rh(4)	47.9(5)
C(460)–Rh(4)–Ru(8)	79.9(4)
C(460)–Rh(4)–Rh(6)	48.2(5)
C(460)–Rh(6)–Ru(8)	80.1(5)
C(460)–Rh(6)–Rh(4)	48.8(5)
C(560)–Rh(5)–Ru(8)	82.7(5)
C(560)–Rh(5)–Rh(6)	49.5(5)
C(560)–Rh(6)–Ru(8)	80.6(5)
C(560)–Rh(6)–Rh(5)	45.9(7)

The crystal structure and numbering scheme of the compound **3** is presented in Fig. 3. Atomic coordinates are shown in Table 5, bond distances in Table 6 and selected bond angles in Table 7.

The structure is closely similar to the earlier characterized dimeric thioether derivatives [5,7]. SMe_2 substitution gave at room temperature exclusively the dimeric cluster. Replacement of methyl groups with ethyl groups was not sufficient to change the structure of the final product. The weaker donor ability of SEt_2 was clearly seen, however. SEt_2 formed a separable fraction of less substituted species, but the stable product was clearly the dimeric cluster.

The presence of the $Rh_3(\mu_3\text{-H})$ hydride was evident from the ^{1}H-NMR spectrum. As in compounds **1** and **2**, the signal is still a quartet, but the chemical shift (-16.8 ppm) now differs from the value of the parent cluster and is very close to the value of dimeric structures (-17.2 ppm).

Solution of the crystallographic structure revealed slightly disordered Et groups of which the best structure was chosen. A disordered free molecule $1/2$ SEt_2 was also found in the crystal structure.

3. Conclusions

The structures of sulphur derivatives of tetrahedral Ru-Rh clusters can be controlled through changes in reaction conditions and the steric surroundings of sulphur in the thioether ligand. Adequate modification in the organic group blocks the dimerization of clusters. Aliphatic groups seem to be too flexible to stop the dimerization, and also severe reaction conditions favour the dimerization process. SMePh and SPh_2 form stable trisubstituted $HRuRh_3(CO)_{12}$ derivatives under mild conditions, and also a minor amount of dimeric cluster compound in longer reaction times. Attempts to crystallize the dimeric clusters did not succeed. The dimeric cluster compound with SEt_2 was the most stable form.

4. Experimental

4.1. General comments

If not otherwise stated, all manipulations were carried out under nitrogen atmosphere with deoxygenated solvents. SPh_2, SEt_2 and SMePh were of commercial origin (Aldrich Chemie). $HRuRh_3(CO)_{12}$ [12] was prepared by published methods.

Infrared spectra were recorded in dichloromethane on a Nicolet 750 spectrometer. ^1H NMR spectra were measured on a Bruker AM-250 spectrometer with $CDCl_3$ as solvent and TMS as reference.

4.1.1. Synthesis of [HRuRh$_3$(CO)$_9$(SPh$_2$)$_3$] **1**

The compound SPh_2 (1.3 ml, 7.80 mmol) was added to a solution of $HRuRh_3(CO)_{12}$ (200 mg, 0.267 mmol) in CH_2Cl_2 (40 ml). The mixture was refluxed for 1 h and the solvent was evaporated in vacuo. The residue was chromatographed on a silica column. Elution with hexane gave a yellow band containing impurities of starting material and some byproducts. Further elution with hexane–dichloromethane 3:1 mixture gave the reddish band of the product (98 mg, 43%). IR (CH_2Cl_2): 2072 s, 2057 vs, 2048 s, 2015 vs, 1980 m, 1862 w, 1837 m cm^{-1}. ^1H-NMR: -15.05 ppm (q, $^1J_{Rh-H} = 11$ Hz). Found: C 44.28%; H 2.60%. $RuRh_3S_3C_{45}O_9H_{31}$ Calc.: C 44.24%; H 2.56%. Recrystallization from CH_2Cl_2 in the presence of excess SPh_2 gave dark red crystals. The crystalline form is air stable.

4.1.2. Synthesis of [HRuRh$_3$(CO)$_9$(SMePh)$_3$] **2**

A mixture of $HRuRh_3(CO)_{12}$ (150 mg, 0.20 mmol) and SMePh (100 μl, 0.84 mmol) in 40 ml of CH_2Cl_2 was stirred for 24 h at room temperature. The mixture was dried in vacuo and the residue was chromatographed on a silica column in air. Elution with hexane gave a yellow fraction. Further elution with hexane–dichloromethane 1:1 gave a red fraction of the main product (106 mg, 64%). Dark red crystals were obtained from CH_2Cl_2. IR (CH_2Cl_2): 2074 s, 2053 vs, 2043 vs, 2012 vs, 1980 m, 1831 m cm^{-1}. ^1H NMR: -15.3 (q, $^1J_{Rh-H} = 11$ Hz), 2.5 ppm (CH_3), 7.4 ppm (m, Ph). Found: C 35.02%; H 2.49%. $RuRh_3S_3C_{30}O_9H_{25}$ Calc.: C 34.80%; H 2.43%.

4.1.3. Synthesis of [HRuRh$_3$(CO)$_9$]$_2$[SEt$_2$]$_3$ **3**

$HRuRh_3(CO)_{12}$ (150 mg, 0.20 mmol) was dissolved in 40 ml of CH_2Cl_2. 0.65 ml (6.0 mmol) of SEt_2 was

Table 8
Crystal data and collection parameters for $HRuRh_3(CO)_9(SPh_2)_3$ **1**, $HRuRh_3(CO)_9(SPhMe)_3$ **2** and $[HRuRh_3(CO)_9]_2[SEt_2]_3$ **3**

	1	2	3
Formula	$RuRh_3S_3C_{45}O_9H_{31}$	$RuRh_3S_3C_{30}O_9H_{16}$	$Ru_2Rh_6S_3C_{40}O_{18}H_{32}$
Formula weight (g mol^{-1})	1221.678	1026.4274	1596.336
Colour, habit	dark red	dark red	dark red
Crystal size (mm)	0.2 × 0.2 × 0.3	0.8 × 0.4 × 0.2	0.5 × 0.5 × 0.5
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	$P2_1/n$
a (Å)	12.652(8)	10.589(3)	18.722(6)
b (Å)	13.381(6)	13.036(4)	12.754(6)
c (Å)	15.612(7)	14.152(5)	21.487(7)
α (°)	77.25(3)	71.59(3)	90
β (°)	83.81(5)	78.72(2)	104.27(3)
γ (°)	62.70(4)	82.62(2)	90
V (Å^3)	2290.50	1813(1)	4972(3)
Z	2	2	4
μ (mm^{-1})	1.55	1.97	2.72
Calculated density (g cm^{-3})	1.77	1.897	2.132
Number of centring reflections	14	25	28
Centring 2θ (°)	11–24	15–25	15–25
Scan range 2θ (°)	4–50	4–50	4–50
Scan speed (° min^{-1})	3–30	3–30	3–30
h,k,l range	16, ±16, ±19	13, ±16, ±17	23, 16, ±26
Number of unique reflections	8046	6284	8761
Number of observed data ($F > 4\sigma(F)$)	5021	5765	4171
Number of parameters	554	415	544
R	0.0333	0.0308	0.0800
R_w	0.0336[a]	0.1069[b]	0.2107[b]
GOOF	1.0009	0.988	0.941

[a] Weight = $1/(\sigma^2(F) + 0.0005F^2)$.
[b] $w = 1/[\sigma^2(F_0^2) + (0.0600 * p)^2 + 0.15 * p]$.
$p = [\max(F_0^{2.0}) + 2 * F_c^2]/3$.

added and the solution was refluxed for 1 h. Chromatographic separation on silica column in air gave with hexane a yellow fraction consisting of byproducts. Further elution with hexane–dichloromethane 4:1 mixture gave an orange fraction, yield 42 mg. Finally elution with CH_2Cl_2 gave a red fraction of the product, yield 93 mg, 58%. Crystallization from CH_2Cl_2 gave dark red crystals. IR (CH_2Cl_2): 2054 vs, 2010 s, 1972 w, 1879 w, 1840 s cm^{-1}. ^1H-NMR: -16.8 ppm (q,$^1J_{Rh-H} = 11.5$ Hz), 1.8 ppm (t, CH_3, $^1J_{H-H} = 7.2$ Hz), 3.3 ppm (q, CH_2). Found: C 23.66%; H 2.37%; Calc.: C 23.41%; H 2.27% for $Ru_2Rh_6S_3C_{40}O_{18}H_{32} + 1/2$ SEt_2. The second orange front fraction of the product contains according to the IR spectrum almost pure product, but an additional peak is observed at 2067 cm^{-1}. In addition to the dimeric cluster, this fraction clearly also contains less substituted species.

4.1.4. X-ray crystallography

Data were collected on a Nicolet R3m diffractometer using Mo–Kα radiation ($\lambda = 71.073$ pm). Intensities were corrected for background, polarization and Lorentz factors. Absorption correction was made for **1**. Table 8 presents further crystallographic data. The structures **1** and **2** were solved with use of the SHELXL93 program [13], and the structure of **3** was solved with use of the SHELXTL program [14]. Anisotropic refinement was carried out for all non-hydrogen atoms. Methyl and methylene protons were placed in idealized positions with C–H distances 96 pm and isotropic temperature factors of 0.08. The cluster hydride for **1** was found in the Fourier map.

Acknowledgements

The financial support of the Technology Development Centre is gratefully acknowledged.

References

[1] T.P. Fehlner, Inorganometallic Chemistry, Plenum, New York, 1992, pp. 147–163.

[2] P. Braunstein, J. Rose, D. Toussanint, S. Jääskeläinen, M. Ahlgren, T.A. Pakkanen, J. Pursiainen, L. Toupet, D. Grandjean, Organometallics 13 (1994) 2472.

[3] D.F. Shriver, H.D. Kaesz, R.D. Adams, The Chemistry of Metal Cluster Complexes, VCH Publishers, New York, 1990, pp. 252–259.

[4] M. Rakowski DuBois, Chem. Rev. 89 (1989) 1.

[5] S. Rossi, J. Pursiainen, M. Ahlgren, T.A. Pakkanen, Organometallics 9 (1990) 475.

[6] S. Rossi, J. Pursiainen, M. Ahlgren, T.A. Pakkanen, J. Organomet. Chem. 393 (1990) 403.

[7] T. Teppana, S. Jääskeläinen, M. Ahlgren, J. Pursiainen, T.A. Pakkanen, J. Organomet. Chem. 486 (1995) 217.

[8] T.A. Pakkanen, J. Pursiainen, T. Venäläinen, T.T. Pakkanen, J. Organomet. Chem. 372 (1989) 129.

[9] S. Rossi, J. Pursiainen, T.A. Pakkanen, J. Organomet. Chem. 397 (1990) 81.

[10] S. Rossi, K. Kallinen, T.T. Pakkanen, T.A. Pakkanen, J. Organomet. Chem. (1992).

[11] H.J. Kakkonen, M. Ahlgren, J. Pursiainen, T.A. Pakkanen, J. Organomet. Chem. 491 (1995) 195.

[12] J. Pursiainen, T.A. Pakkanen, J. Jääskeläinen, J. Organomet. Chem. 290 (1985) 85.

[13] G.M. Sheldrick, SHELXL93, Program for the refinement of crystal structures, Univ. of Göttingen, Germany, 1993.

[14] G.M. Sheldrick, SHELXTL Plus, Release 4.11, 1990, Siemens Analytical X-ray Instruments, Madison, WI, USA.