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Telluride-substituted mixed metal clusters. Crystal structures of [$HRuCo_3(CO)_{11}(TeMe_2)$], [$HRuCo_3(CO)_{10}(TeMe_2)_2$], and [$HRuCo_3(CO)_{11}(TePh_2)$]

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Abstract

The synthesis, structures and characterization of dimethyltelluride and diphenyltelluride derivatives of mixed metal clusters [$HRuCo_3(CO)_{12}$] and [$HRuRh_3(CO)_{12}$] are described. Telluride ligands displace carbonyl ligands in neutral parent clusters to give [$HRuCo_3(CO)_{11}(TeMe_2)$] (1), [$HRuCo_3(CO)_{10}(TeMe_2)_2$] (2), [$HRuCo_3(CO)_{11}(TePh_2)$] (3) and [$HRuRh_3(CO)_9]_2[TeMe_2]_3$ (4). The crystal structures of **1**, **2** and **3** have been determined.

The ligand substitutions are metalloselective. Dimethyltelluride displaces an apical carbonyl ligand at ruthenium in **1**; in **2** an additional axial ligand at cobalt is replaced by telluride. Diphenyltelluride coordinates axially at cobalt in **3**. Compound **4** has a dimeric structure in which the axial carbonyls at rhodium centers have been replaced by $TeMe_2$ ligands. In all four compounds the basic cluster arrangement is retained and the cluster hydride caps the basal metal face.

Introduction

Metal-sulfur and to some extent also metal-selenium and metal-tellurium compounds are much studied because of their significance in biology [1,2] and catalysis [3,4]. Mono- and bi-nuclear complexes have been studied extensively. In most of the larger clusters elemental sulfur, selenium, and tellurium have been incorporated into the metal core, but clusters containing chalcogen ligands are rarer [5].

In previous communications we described the dimethylsulfide and -selenide derivatives of valence isoelectronic tetrahedral mixed metal clusters [$HRuCo_3(CO)_{12}$] and [$HRuRh_3(CO)_{12}$] [6,7]. Studies of substitutions have revealed reactivity differences between the three transition metals. We describe here the synthesis and the characterization of [$HRuCo_3(CO)_{11}(TeMe_2)$] (1), [$HRuCo_3(CO)_{10}(TeMe_2)_2$] (2), [$HRuCo_3(CO)_{11}(TePh_2)$] (3) and [$HRuRh_3(CO)_9]_2[TeMe_2]_3$ (4).

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Results and discussion

The metalloselectivity of carbonyl substitution with telluride ligands is shown in Fig. 1.

Synthesis and structures of [HRuCo$_3$(CO)$_{11}$(TeMe$_2$)] (1), [HRuCo$_3$(CO)$_{10}$(TeMe$_2$)$_2$] (2) and [HRuCo$_3$(CO)$_{11}$(TePh$_2$)] (3)

Compounds **1** and **2** are obtained by treatment of [HRuCo$_3$(CO)$_{12}$] with dimethyltelluride TeMe$_2$ in CH$_2$Cl$_2$ solvent; the reaction time and the amount of the ligand can be varied in order to optimize the yield of the required product. The complex [HRuCo$_3$(CO)$_{11}$(TePh$_2$)] (**3**) is obtained in a similar way, but considerable longer reaction times are needed. Figures 2 and 3 present the structures, with numbering schemes, of **1** and **2**. The crystal of **2** contains two similar molecules in the asymmetric unit. In ligand substitutions the basic cluster core and the carbonyl arrangement with three bridging carbonyls at basal Co–Co bonds is retained. In **1** one apical carbonyl has been replaced by the telluride; in **2** an additional axial carbonyl on cobalt has been substituted. Tables 1 and 2 show the atomic coordinates of **1** and **2**, and the bond lengths and bond angles are listed in Tables 4 and 5. The metal core is symmetric, which is indicative of a basal Co$_3$(μ_3-Y) cluster hydride. Edge-bridging hydrides would lengthen the corresponding metal–metal bonds. Further evidence for μ_3-H bonding is provided by the bond angle data

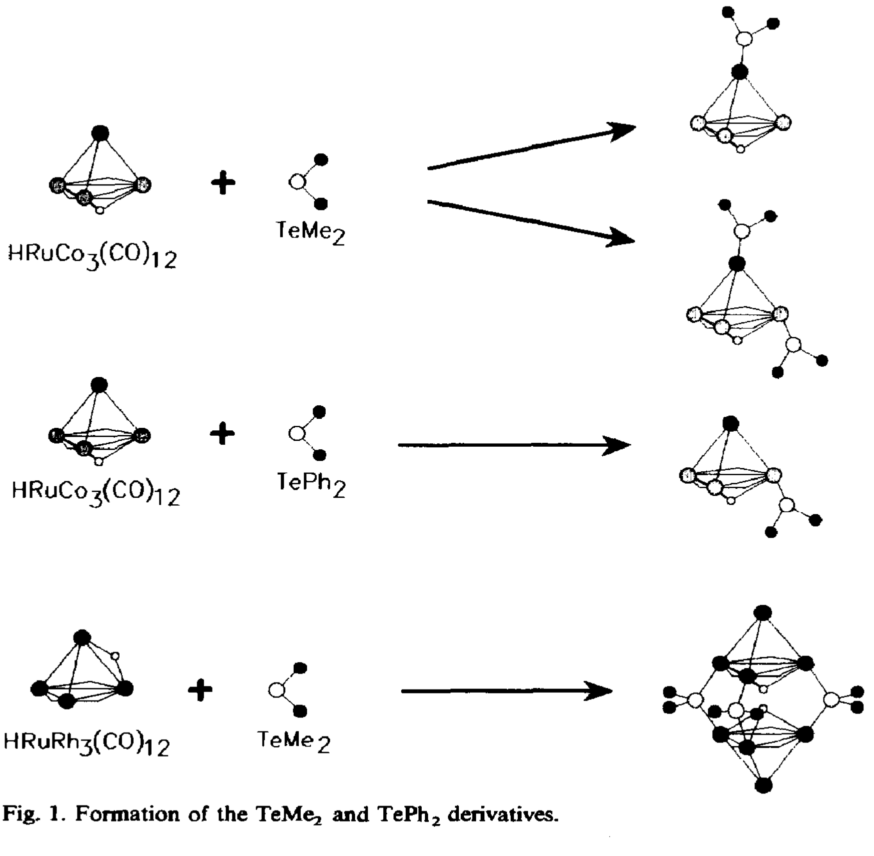


Fig. 1. Formation of the TeMe$_2$ and TePh$_2$ derivatives.

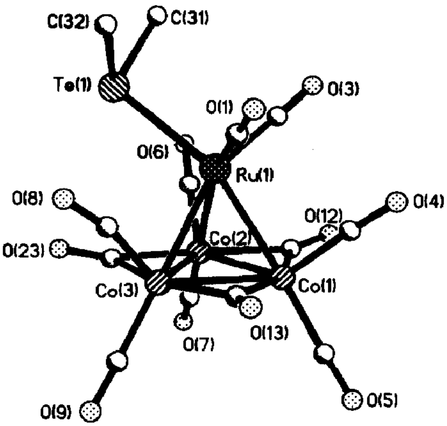


Fig. 2. Structure and numbering scheme for $[HRuCo_3(CO)_{11}(TeMe_2)]$.

(Table 5). The bond angles Ru–Co–C_{eq}, Co–Ru–C_{ap} and Co–Ru–Te are fairly small (av. 76.5, 102.3, and 105.4°, respectively) for the basal hydride in **1**. In **2** the corresponding values are 73, 102 and 109.3°. The edge-bridging hydride provides more space along the bridged bond, as for example in $[H_2Ru_2Rh_2(CO)_{12}]$, which has the M_{ap}–M_{bas}–CO bond angle values 110.7 and 115.5° for bridged metal–metal-bonds. The bond angles Co–Co–C_{ax} (av. 119.7° for **1** and 126° for **2**) and Co–Co–Te(1) (av. 118.1°) are also large enough for a basal hydride. In **2** carbonyl 8 seems to semibridge the Ru(1)–Co(3) bond (Ru(1)–C(8) 266 Ru(1B)–C(8B) 228 ppm, Ru(1B)–C(8B)–O(8B) 137°). Similar Ru(μ-CO)Co semibridge has been found also in $[HRuCoRh_2(CO)_{10}(PPh_3)_2]$.

The molecular structure and numbering scheme of **3** is presented in Fig. 4. $TePh_2$ is coordinated axially to a cobalt atom, but otherwise the cluster is unchanged. Table 3 lists the atomic coordinates for **3**, Table 4 the bond lengths, and Table 5 some selected bond angles. No metal–metal bond lengthening or carbonyl rearrangement effects due to a possible μ_2-H ligand are apparent from the data; Ru–Co–C_{eq} (av. 80.9°), Co–Ru–C_{ap} (av. 101°), Co–Co–Te (av. 111.7°) and Co–Co–C_{ax} (av. 121°) are of the appropriate size for a basal $Co_3(\mu$-H). In

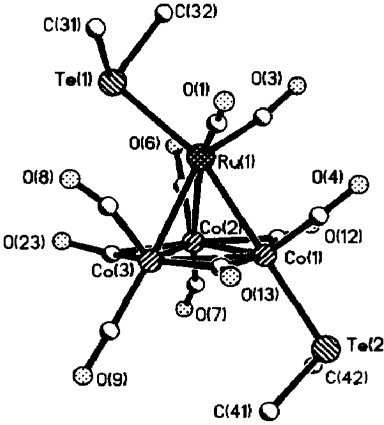


Fig. 3. Structure and numbering scheme for $[HRuCo_3(CO)_{10}(TeMe_2)_2]$.

Table 1

Atomic coordinates for $[HRuCo_3(CO)_{12}(TeMe_2)]$ (1)

Atom	*x*	*y*	*z*
Te(1)	0.4193(1)	1.4747(1)	0.6753(1)
Ru(1)	0.2260(1)	1.3382(1)	0.7664(1)
Co(1)	0.0982(1)	1.1401(1)	0.8010(1)
Co(2)	0.3963(1)	1.0872(1)	0.7465(1)
Co(3)	0.1925(1)	1.1891(1)	0.6017(1)
O(1)	−0.0680(8)	1.5732(7)	0.7640(6)
O(3)	0.2741(11)	1.3876(8)	1.0067(6)
O(4)	−0.1054(9)	1.3072(7)	0.9716(6)
O(5)	−0.0342(10)	0.9157(7)	0.8363(7)
O(6)	0.6280(9)	1.1951(7)	0.8393(6)
O(7)	0.6082(10)	0.8183(7)	0.7390(8)
O(8)	0.1793(9)	1.4340(7)	0.4791(6)
O(9)	0.1301(11)	1.0510(8)	0.4123(7)
O(12)	0.3134(8)	1.0420(9)	0.9892(6)
O(13)	−0.1591(8)	1.2837(7)	0.6503(6)
O(23)	0.5351(7)	1.1465(6)	0.5218(5)
C(1)	0.0434(11)	1.4843(8)	0.7624(7)
C(3)	0.2559(11)	1.3681(9)	0.9159(7)
C(4)	−0.0233(11)	1.2462(9)	0.9029(8)
C(5)	0.0161(11)	1.0005(9)	0.8204(7)
C(6)	0.5275(11)	1.1623(8)	0.8004(7)
C(7)	0.5221(11)	0.9203(9)	0.7402(8)
C(8)	0.1827(10)	1.3450(9)	0.5384(7)
C(9)	0.1569(12)	1.0995(10)	0.4869(8)
C(12)	0.2862(10)	1.0686(9)	0.8952(8)
C(13)	−0.0283(10)	1.2305(8)	0.6698(7)
C(23)	0.4338(10)	1.1389(8)	0.5883(7)
C(31)	0.5215(15)	1.5292(11)	0.8140(10)
C(32)	0.2615(13)	1.6642(9)	0.6452(10)

$[HRuCo_3(CO)_{11}(SMe_2)]$ (axial SMe_2) the cluster proton was located crystallographically in $Co_3(\mu\text{-}H)$ position, and the corresponding bond angles were 79.4, 101.7, 115.5 (Co–Co–S) and 121.3°. The difference in Co–Co–Te and Co–Co–S angles is probably due to different steric requirements. One of the phenyl groups is bent over the hydride ligand.

The apical coordination of $TeMe_2$ causes a slight lengtening of the Ru–Co-bonds in **1** (av. 2.670 Å) and **2** (av. 2.68 Å) compared with those in $[HRuCo_3(CO)_{11}(SMe_2)]$ (av. 2.641 Å), $[HRuCo_3(CO)_{11}(SeMe_2)]$ (av. 2.644 Å) and **3** (ca. 2.633 Å).

The ^1H NMR signals of the $Co_3(\mu\text{-}H)$ hydride have clearly different chemical shifts dependency upon whether apical substituents are present or not. For **1** and **2** the resonances appear at −17.9 and −17.6 ppm, values in good agreement with those for the nitrogen-donor derivatives of $[HRuCo_3(CO)_{12}]$ in which the substituents are apically coordinated [8]. The $TePh_2$ derivative **3** has the hydride resonance at −19.6 ppm, which agrees well with that for the parent cluster and those for the phosphine-substituted derivatives that do not have apical phosphines [9].

The disubstituted derivatives $[HRuCo_3(CO)_{10}(XMe_2)]$ (X = S, Se or Te) show a structural change on going from X = S to Se to Te. The SMe_2 derivative contains

Table 2

Atomic coordinates of $[HRuCo_3(CO)_{10}(TeMe_2)_2]$ (**2**)

Atom	*x*	*y*	*z*
Ru(1)	0.5127(5)	0.3616(2)	0.3482(5)
Te(1)	0.6185(4)	0.2897(1)	0.3557(5)
Te(2)	0.2436(4)	0.4798(1)	0.4336(4)
Co(1)	0.3760(7)	0.4225(2)	0.3949(7)
Co(2)	0.4365(8)	0.3785(2)	0.5534(7)
Co(3)	0.3062(7)	0.3508(2)	0.4073(7)
O(1)	0.497(4)	0.3601(13)	0.103(5)
O(3)	0.721(4)	0.4123(12)	0.342(4)
O(4)	0.488(5)	0.462(2)	0.233(5)
O(6)	0.654(4)	0.3468(13)	0.590(4)
O(7)	0.384(4)	0.3925(13)	0.775(5)
O(8)	0.352(5)	0.285(2)	0.267(5)
O(9)	0.069(4)	0.3316(12)	0.445(4)
O(12)	0.538(5)	0.457(2)	0.536(5)
O(13)	0.236(5)	0.3968(14)	0.219(5)
O(23)	0.369(4)	0.2901(13)	0.576(4)
C(1)	0.509(5)	0.362(2)	0.201(6)
C(3)	0.636(5)	0.395(2)	0.349(5)
C(4)	0.431(7)	0.445(2)	0.285(7)
C(6)	0.559(6)	0.361(2)	0.571(5)
C(7)	0.412(10)	0.394(3)	0.695(11)
C(8)	0.343(6)	0.313(2)	0.310(6)
C(9)	0.162(6)	0.339(2)	0.435(5)
C(12)	0.473(8)	0.434(4)	0.504(7)
C(13)	0.284(5)	0.393(2)	0.298(5)
C(23)	0.366(6)	0.326(2)	0.560(5)
C(31)	0.618(7)	0.270(2)	0.189(6)
C(32)	0.783(8)	0.309(3)	0.327(8)
C(41)	0.091(7)	0.452(2)	0.420(7)
C(42)	0.278(10)	0.487(3)	0.613(8)
Ru(1B)	1.0187(4)	0.3566(1)	0.9553(4)
Te(1B)	1.1224(4)	0.2853(1)	0.9350(5)
Te(2B)	0.7481(4)	0.4763(1)	0.8934(4)
Co(1B)	0.8822(7)	0.4188(2)	0.9204(7)
Co(2B)	0.8071(7)	0.3474(2)	0.8963(7)
Co(3B)	0.9364(7)	0.3783(2)	0.7552(7)
O(1B)	1.218(4)	0.4085(12)	0.957(4)
O(3B)	0.998(4)	0.3558(12)	1.224(4)
O(4B)	1.009(4)	0.4632(13)	1.96(4)
O(6B)	0.853(5)	0.276(2)	1.025(5)
O(7B)	0.586(6)	0.328(2)	0.857(5)
O(8B)	1.150(5)	0.349(2)	0.711(5)
O(9B)	0.881(4)	0.4002(12)	0.523(4)
O(12B)	0.744(4)	0.3886(12)	1.108(4)
O(13B)	1.046(4)	0.4581(12)	0.770(4)
O(23B)	0.863(3)	0.2937(10)	0.708(3)
C(1B)	1.153(5)	0.384(2)	0.964(5)
C(3B)	1.021(8)	0.348(3)	1.139(9)
C(4B)	0.966(4)	0.4424(14)	1.032(4)
C(6B)	0.842(5)	0.307(2)	0.973(5)
C(7B)	0.679(7)	0.331(2)	0.881(6)
C(8B)	1.064(8)	0.357(3)	0.771(7)

Table 2 (continued)

Atom	*x*	*y*	*z*
C(9B)	0.910(7)	0.392(2)	0.636(7)
C(12B)	0.806(5)	0.385(2)	1.028(5)
C(13B)	0.987(5)	0.435(2)	0.809(5)
C(23B)	0.867(5)	0.327(2)	0.752(5)
C(31B)	1.112(5)	0.258(2)	1.109(5)
C(32B)	1.293(8)	0.305(3)	0.919(9)
C(41B)	0.714(7)	0.491(2)	1.085(6)

Table 3

Atomic coordinates for [HRuCo$_3$(CO)$_{11}$(TePh$_2$)] (3)

Atom	*x*	*y*	*z*
Te(1)	0.2591(2)	0.2620(1)	0.6024(1)
Ru(1)	0.0336(3)	−0.0834(2)	0.5538(1)
Co(1)	0.1284(4)	0.0975(3)	0.5788(2)
Co(2)	0.3033(4)	−0.0213(3)	0.5305(2)
Co(3)	0.2302(4)	−0.0480(3)	0.6357(1)
O(1)	−0.262(3)	−0.086(2)	0.6195(9)
O(2)	0.079(3)	−0.309(2)	0.5415(11)
O(3)	−0.111(2)	−0.056(2)	0.4340(8)
O(4)	−0.171(2)	0.165(2)	0.5522(10)
O(6)	0.256(3)	−0.146(2)	0.4285(9)
O(7)	0.600(3)	0.043(2)	0.4988(11)
O(8)	0.060(3)	−0.205(2)	0.6914(11)
O(9)	0.447(3)	−0.0325(14)	0.7296(9)
O(12)	0.172(2)	0.130(2)	0.4526(7)
O(13)	0.006(2)	0.075(2)	0.6958(8)
O(23)	0.418(2)	−0.204(2)	0.5865(8)
C(1)	−0.146(4)	−0.082(3)	0.5925(14)
C(2)	0.060(4)	−0.226(2)	0.5449(13)
C(3)	−0.058(3)	−0.065(2)	0.480(2)
C(4)	−0.050(3)	0.135(1)	0.5634(11)
C(6)	0.266(4)	−0.096(2)	0.4696(13)
C(7)	0.475(5)	0.017(3)	0.5141(14)
C(8)	0.127(3)	−0.143(3)	0.6670(11)
C(9)	0.364(3)	−0.033(2)	0.6922(11)
C(12)	0.186(3)	0.097(2)	0.4981(9)
C(13)	0.078(3)	0.060(2)	0.6577(12)
C(23)	0.349(3)	−0.125(2)	0.5864(11)
C(102)	0.154(2)	0.455(2)	0.6511(8)
C(103)	0.0550	0.5265	0.6714
C(104)	−0.0928	0.5014	0.6810
C(105)	−0.1417	0.4045	0.6702
C(106)	−0.0428	0.3327	0.6499
C(101)	0.1050	0.3577	0.6404
C(202)	0.319(2)	0.238(2)	0.7341(7)
C(203)	0.4049	0.2174	0.7829
C(204)	0.5533	0.1910	0.7764
C(205)	0.6155	0.1853	0.7210
C(206)	0.5293	0.2059	0.6722
C(201)	0.3809	0.2323	0.6787

Table 4

Bond lengths (pm) for [$HRuCo_3(CO)_{11}(TeMe_2)$] (**1**), [$HRuCo_3(CO)_{10}(TeMe_2)_2$] (**2**) and [$HRuCo_3(CO)_{11}(TePh_2)$] (**3**)

	1	**2a**	**2b**	**3**
Ru(1)–Co(1)	266.5(2)	267(1)	266.7(9)	263.6(5)
Ru(1)–Co(2)	267.5(2)	269(1)	270(1)	263.0(5)
Ru(1)–Co(3)	267.9(2)	266(1)	269(1)	263.3(4)
Co(1)–Co(2)	252.8(2)	249(1)	253(1)	250.4(5)
Co(1)–Co(3)	251.4(2)	250(1)	247(1)	252.3(5)
Co(2)–Co(3)	252.8(2)	253(1)	254(1)	253.5(5)
Te(1)–Ru(1)	266.6(2)	269.0(7)	267.0(7)	
Te(2)–Co(1)	252.7(9)	252.6(9)	252.0(9)	
Te(1)–C(31)	211(1)	210(7)	228(6)	
Te(1)–C(101)				209(2)
Te(1)–C(32)	211.9(9)	215(9)	220(10)	
Te(1)–C(201)				212(2)
Te(2)–C(41)		209(8)	238(7)	
Te(2)–C(42)	220(10)	194(9)		
Ru(1)–C(1)	187.7(8)	176(7)	189(6)	185(3)
Ru(1)–C(2)				194(3)
Ru(1)–C(3)	186.6(9)	187(6)	221(10)	190(3)
Co(1)–C(4)	176.5(9)	165(8)	185(5)	173(3)
Co(1)–C(5)	183(1)			
Co(2)–C(6)	175(1)	163(7)	167(6)	176(3)
Co(2)–C(7)	180.4(8)	180(10)	167(8)	168(5)
Co(3)–C(8)	177.1(9)	178(8)	173(10)	174(3)
Ru(1)–C(8)		266	228(9)	
Co(3)–C(9)	180(1)	185(7)	153(9)	178(3)
Co(1)–C(12)	198.8(9)	179(9)	194(6)	193(2)
Co(2)–C(12)	196.5(9)	195(8)	201(6)	205(3)
Co(1)–C(13)	200.6(8)	188(6)	193(6)	194(3)
Co(3)–C(13)	196.0(9)	191(6)	207(5)	206(3)
Co(2)–C(23)	195.2(8)	192(6)	200(6)	194(3)
Co(3)–C(23)	200.5(9)	212(7)	188(60	187(3)
O(1)–C(1)	114(1)	119(9)	112(7)	122(4)
O(2)–C(2)				113(4)
O(3)–C(3)	114(1)	119(8)	109(11)	118(4)
O(4)–C(4)	115(1)	109(10)	115(7)	119(4)
O(5)–C(5)	112(1)			
O(6)–C(6)	117(1)	127(8)	119(8)	116(4)
O(7)–C(7)	113(1)	102(14)	118(11)	123(5)
O(8)–C(8)	115(1)	106(9)	131(11)	116(4)
O(9)–C(9)	112(1)	117(9)	141(10)	114(3)
O(12)–C(12)	116(1)	116(11)	123(8)	115(3)
O(13)–C(13)	115(1)	112(8)	115(7)	111(3)
O(23)–C(23)	115(1)	120(8)	121(6)	123(3)

two axial ligands; the disubstituted $SeMe_2$ compound is present immediately after the synthesis in two forms one with two axial and the other with one apical and one axial ligand (in time the former is favoured) whereas the $TeMe_2$ derivative is entirely in the form with one apical and one axial ligand (Fig. 5).

It has been previously observed that amines favour apical coordination sites in [$HRuCo_3(CO)_{12}$]. Among phosphines, PPh_3 coordinates axially (in mono- or di-sub-

Table 5

Selected bond angles (°) for [$HRuCo_3(CO)_{11}(TeMe_2)$] (**1**), [$HRuCo_3(CO)_{10}(TeMe_2)_2$] (**2**) and [$HRuCo_3(CO)_{11}(TePh_2)$] (**3**)

	1	**2a**	**2b**	**3**
Ru(1)–Te(1)–C(32)	104.0(3)	101(3)	102(3)	
Ru(1)–Te(1)–C(31)	105.3(3)	104(2)	104(2)	
Co(1)–Te(2)–C(41)		104(2)	99(2)	
Co(1)–Te(2)–C(42)		98(3)	96(2)	
C(41)–Te(2)–C(42)		107(4)	92(3)	
C(32)–Te(1)–C(31)	94.5(4)	86(3)	105(3)	
Co(1)–Te(1)–C(101)				108.1(5)
Co(1)–Te(1)–C(201)				104.8(5)
C(101)–Te(1)–C(201)				96.7(7)
Te(1)–Ru(1)–Co(1)	158.6(1)	162.1(3)	162.2(3)	
C(2)–Ru(1)–Co(1)				153(1)
Te(1)–Ru(1)–Co(2)	105.2(1)	108.7(3)	109.7(2)	
C(2)–Ru(1)–Co(2)				100(1)
Te(1)–Ru(1)–Co(3)	105.6(1)	109.7(3)	109.1(3)	
C(2)–Ru(1)–Co(3)				99.8(9)
Co(3)∃1Ru(1)–C(1)	104.6(3)	104(2)	104(2)	104(1)
Co(1)–Ru(1)–C(1)	102.7(3)	101(2)	101(2)	100(1)
Co(2)–Ru(1)–C(1)	156.7(3)	155(2)	155(1)	155(1)
Co(1)–Ru(1)–C(2)				153(1)
Co(2)–Ru(1)–C(2)				100(1)
Co(3)–Ru(1)–C(2)				99.8(9)
Co(1)–Ru(1)–C(3)	99.9(3)	94(2)	105(2)	102.3(9)
Co(2)–Ru(1)–C(3)	101.9(3)	100(2)	104(3)	100.4(9)
Co(3)–Ru(1)–C(3)	153.3(3)	148(2)	157(3)	155.1(9)
Ru(1)–Co(1)–C(4)	81.4(4)	84(3)	82(2)	85.3(9)
Co(2)–Co(1)–C(4)	130.7(3)	138(3)	132(2)	133.1(9)
Co(3)–Co(1)–C(4)	129.9(3)	127(3)	131(2)	132.1(9)
Ru(1)–Co(1)–C(5)	177.7(3)			
Ru(1)–Co(1)–Te(1/2)		178.3(4)	177.6(4)	171.5(2)
Co(2)–Co(1)–C(5)	116.2(3)			
Co(2)–Co(1)–Te(1/2)		118.6(4)	116.0(4)	110.6(2)
Co(3)–Co(1)–C(5)	116.2(3)			
Co(3)–Co(1)–Te(1/2)		117.6(4)	118.5(4)	112.8(2)
Ru(1)–Co(1)–C(12)	82.4(3)	84(3)	77(2)	82.8(7)
Co(2)–Co(1)–C(12)	49.9(3)	51(3)	52(2)	53.1(8)
Co(3)–Co(1)–C(12)	110.0(3)	112(3)	111(2)	113.5(8)
Co(2)–Co(1)–C(13)	109.9(3)	110(2)	115(2)	113.5(8)
Co(3)–Co(1)–C(13)	49.9(2)	49(2)	54(2)	52.9(8)
Ru(1)–Co(2)–C(6)	74.9(3)	74(2)	73(2)	79(1)
Co(1)–Co(2)–C(6)	125.0(3)	125(2)	126(2)	127(1)
Co(3)–Co(2)–C(6)	125.5(3)	123(2)	121(2)	129(1)
Ru(1)–Co(2)–C(7)	175.5(3)	169(4)	165(2)	179(2)
Co(1)–Co(2)–C(7)	121.2(3)	120(4)	131(2)	119(2)
Co(3)–Co(2)–C(7)	122.6(3)	130(4)	130(2)	120(1)
Ru(1)–Co(2)–C(12)	82.6(3)	80(3)	75(2)	80.9(7)
Co(1)–Co(2)–C(12)	50.7(3)	46(3)	49(2)	48.9(6)
Ru(1)–Co(2)–C(23)	88.3(2)	91(2)	84(2)	80.5(8)
Co(1)–Co(2)–C(23)	110.8(3)	114(2)	106(2)	107.2(8)
Co(3)–Co(2)–C(23)	51.2(3)	55(2)	47(2)	47.2(8)
Ru(1)–Co(3)–C(8)	73.2(3)	71(3)	57(3)	78.5(8)
Co(1)–Co(3)–C(8)	127.0(3)	122(2)	113.3(3)	126.0(9)

Table 5 (continued)

	1	2a	2b	3
Co(2)–Co(3)–C(8)	120.5(3)	123(3)	110(3)	129.7(9)
Ru(1)–Co(3)–C(9)	175.4(3)	174(2)	170(3)	176(1)
Co(1)–Co(3)–C(9)	119.4(3)	122(2)	123(3)	123(1)
Co(2)–Co(3)–C(9)	122.7(3)	124(2)	128(3)	120.3(9)
Ru(1)–Co(3)–C(13)	82.2(2)	82(2)	82(2)	81.5(8)
Co(1)–C(3)–C(13)	51.5(3)	48(2)	49(2)	48.8(8)
Co(2)–Co(3)–C(13)	111.5(2)	108(2)	110(2)	108.1(8)
Ru(1)–Co(3)–C(23)	83.4(2)	86(2)	87(2)	81.6(8)
Co(1)–Co(3)–C(23)	109.5(2)	107(2)	112(2)	108.8(8)
Co(2)–Co(3)–C(23)	49.4(2)	48(2)	51(2)	49.5(8)
Ru(1)–C(1)–O(1)	177.6(8)	173(4)	162(5)	176(3)
Ru(1)–C(2)–O(2)				177(3)
Ru(1)–C(3)–O(3)	179(1)	171(4)	154(7)	177(2)
Co(1)–C(4)–O(4)	175(1)	161(8)	168(4)	177(2)
Co(1)–C(5)–O(5)	177.5(8)			
Co(2)–C(6)–O(6)	170.7(7)	177(6)	171(6)	174(3)
Co(2)–C(7)–O(7)	176(1)	160(8)	165(6)	176(3)
Co(3)–C(8)–O(8)	167.3(8)	163(7)	139(7)	176(3)
Co(3)–C(9)–O(9)	175.6(8)	175(5)	174(4)	174(3)
Co(1)–C(12)–O(12)	139.5(7)	145(7)	141(4)	148(2)
Co(2)–C(12)–O(12)	140.7(8)	131(7)	132(5)	134(2)
Co(1)–C(13)–O(13)	139.4(7)	140(5)	154(5)	146(2)
Co(3)–C(13)–O(13)	141.8(7)	137(5)	130(4)	136(2)
Co(2)–C(23)–O(23)	142.0(7)	151(6)	132(4)	137(2)
Co(3)–C(23)–O(23)	138.4(6)	122(5)	146(5)	140(2)

stitution) [9], whereas the disubstituted PMe_2Ph derivative exists as two isomers corresponding to those for the $SeMe_2$ compound, but the form with one apical and one axial PMe_2Ph ligand is more stable [10]. The behaviour of the phosphines therefore resembles that of the $TeMe_2$ and $TePh_2$ ligands, in both cases the methyl groups in the ligand increasing the tendency towards apical coordination.

Amines, which are strong σ-donors, favour apical coordination. The methyl-containing PR_3 and XR_2 (X = S, Se or Te) (R = Me or Ph) ligands can be assumed to be stronger σ-donors than the phenyl analogues because methyl groups are less

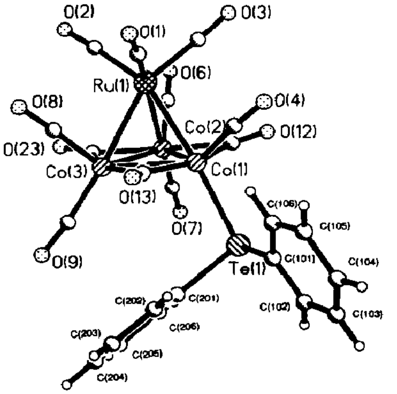
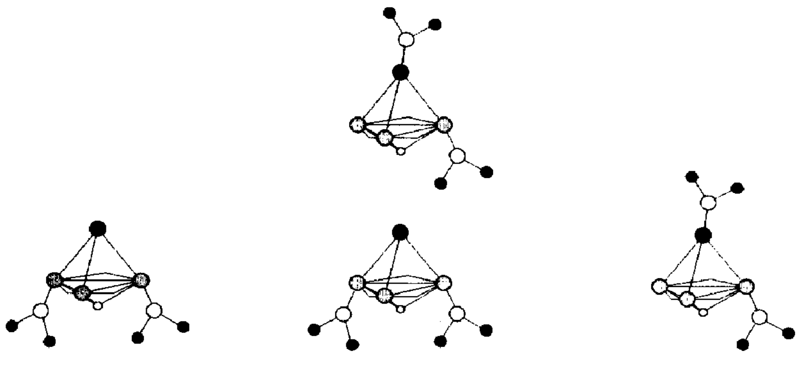


Fig. 4. Structure and numbering scheme of $[HRuCo_3(CO)_{11}(TePh_2)]$.



SMe$_2$ SeMe$_2$ TeMe$_2$

Fig. 5. Schematic structures of [HRuCo$_3$(CO)$_{10}$(XMe$_2$)$_2$] (X = S, Se or Te).

electron withdrawing, and can be suggested that the increasing σ-donor ability favours the tendency for apical coordination in this cluster. On the other hand, the strong σ-donors above are also poor π-acceptors, which also may be important for the site selectivity. In this connection it is noteworthy that in [HRuCo$_3$(CO)$_{12}$] the ruthenium atom is formally electron deficient.

When ligands can be ordered in terms of their σ-donor, π-acceptor and steric properties, they can be used as qualitative probes of the electronic and steric properties of the different metal sites in a cluster compound.

Apical coordination of phosphine substituents is not common in M$_4$(CO)$_{12}$-type clusters; it is mainly found in multisubstituted clusters [11].

Structure of [HRuRh$_3$(CO)$_9$]$_2$[TeMe$_2$]$_3$ (4)

The higher reactivity of the rhodium than of the ruthenium and cobalt centres was observed in the formation of [HRuRh$_3$(CO)$_9$]$_2$[TeMe$_2$]$_3$ (**4**), which is a dimeric compound with all axial rhodium sites occupied by the telluride (Fig. 1). Its structure was deduced by comparing its IR- and NMR-spectra with those of the corresponding SMe$_2$- and SeMe$_2$-derivatives. The IR-spectrum (see Experimental section) is almost identical with those of the corresponding sulfur and selenium derivatives.

In compounds **1**–**3** the dimethyltelluride acts as a two electron donor. In **4** bidentate four-electron TeMe$_2$ groups replace axial carbonyls on the rhodiums, leading to a dimeric structure. The rest of the structure is unchanged. In the parent cluster [HRuRh$_3$(CO)$_{12}$] the hydride ligand bridges either one Ru–Rh edge or the basal Rh$_3$ face. In the case of **4** the Rh$_3$(μ_3-H) cluster proton signal is a quartet with ^1J(Rh–H) = 10.8 Hz at δ −17.6, which is characteristic of a dimeric structure. Typical resonances for the parent cluster and its mono- and di-substituted phosphine derivatives appear at δ −15.5 ppm.

Experimental

Reactions were carried out under nitrogen. Deoxygenated solvents were used. Chromatographic separations were carried out in the air. TeMe$_2$ and TePh$_2$ were from commercial sources. [HRuCo$_3$(CO)$_{12}$] [12] and [HRuRh$_3$(CO)$_{12}$] [13] were prepared by published methods.

Synthesis

Preparation of [$HRuCo_3(CO)_{11}(TeMe_2)$] (1) and [$HRuCo_3(CO)_{10}(TeMe_2)_2$] (2). To a solution of [$HRuCo_3(CO)_{12}$] (200 mg, 0.325 mmol) in CH_2Cl_2 (30 ml) was added $TeMe_2$ (60 μl). The solution was stirred for 2 ha at room temperature. Chromatographic separation on silica with hexane as eluent gave a yellow fraction congaining by products. Elution with 4 : 1 hexane-CH_2Cl_2-mixture gave a red band of **1**. Further elution with 1 : 1 mixture gave **2**. The yields were **1** 158 mg, 68%; **2** 22 mg, 8%. When larger amounts of ligand (108 μl) were used and the solution was refluxed for 4 h, **2** was formed exclusively in 70% yield. Both compounds were crystallized from hexane-dichloromethane at −40 ° C. IR: 2076m, 2042s, 2021s, 1972m, 1864ms for **1** and 2047w, 1009s, 1977w(sh), 1958w(sh), 1851w, 1834w for **2**.

Preparation of [$HRuCo_3(CO)_{11}(TePh_2)$] (3). The CH_2Cl_2 solution of $HRuCo_3(CO)_{12}$ (200 mg, 0.325 mmol) and $TePh_2$ (200 μl) was refluxed for 20 h. Chromatographic separation with 5 : 1 hexane-dichloromethane as eluent gave **4** (110 mg; 39%). IR: 2083m, 2046s, 2011m, 1862m, 1845m.

Preparation of [$HRuRh_3(CO)_9$]$_2$[$TeMe_2$]$_3$ (4). $TeMe_2$ (40 μl) was added to a solution of $HRuRh_3(CO)_{12}$ (300 mg, 0.402 mmol) in CH_2Cl_2 (30 ml). The solution was refluxed for 1 h and chromatographed on a silica column. The impurities were removed with hexane, and elution with a 1 : 1 mixture of hexanes-CH_2Cl_2 gave the title compound in 66% yield (237 mg). IR: 2051s, 2016m, 1976w, 1844w.

Table 6

Crystallographic data for [$HRuCo_3(CO)_{11}(TeMe_2)$] (1), [$HRuCo_3(CO)_{10}(TeMe_2)_2$] (2) and [$HRuCo_3(CO)_{11}(TePh_2)$] (3)

	1	2	3
Formula weight	617.05	874.30	741.18
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a(Å)	8.699(3)	12.280(7)	9.037(6)
b(Å)	10.701(5)	32.71(2)	13.410(8)
c(Å)	11.827(5)	11.959(6)	23.01(1)
α(deg)	86.78(4)	90	90
β(deg)	85.61(3)	90.48(4)	90
γ(deg)	73.02(3)	90	90
V(Å^3)	1049.2(7)	4803(4)	2789(3)
Z	2	8	4
No. centering reflections	25	25	25
Centering 2θ	13–25	10–21	15–23
D_{calc} (g cm^{-3})	1.95	2.42	1.77
Crystal dimensions (mm)	0.5×0.3×0.1	0.2×0.2×0.1	0.2×0.2×0.4
2θ-limits	4–50	5–50	4–50
h,k,l range	11, ±13, ±15	±9,9,16	11,16,18
No unique reflections	3706	8379	2802
Observed data $I > 3\sigma(I)$	2508	3560	1327
μ(cm^{-1})	4.44	3.88	3.36
No. param.	262	301	268
R^a	0.0360	0.1554	0.0503
$R_w{}^b$	0.0358	0.1454	0.0468

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

X-ray crystallography

Data were collected on a Nicolet R3m diffractometer. Mo-K_α radiation with $\lambda = 0.71073$ Å was used. 25 automatically centered reflections in the range $13 < 2\theta < 25°$ for **1**, $10 < 2\theta < 21°$ for **2** and $15 < 2\theta < 23°$ for **3** were used for determination of accurate cell parameters. Intensities were corrected for Lorentz, polarisation and background effects. An empirical absorption correction was applied, based on ψ-scans. Table 6 gives further details of the crystallographic procedure.

The structures were solved by use of the SHELXTL program. Anisotropic refinement was carried out for all non-hydrogen atoms in **1**, and for metal and tellurium atoms in **2**. Attempts to refine the carbon and oxygen atoms of **2** anisotropically were unssuccessful, and so the R values remained high and the standard deviations of the bond lengths and bond angles are large. The values of these parameters are, however, in good agreement with those for **1** and **2** (Tables 4 and 5). Methyl protons were placed in calculated positions (C–H = 0.96Å, $U = 0.08$ Å^2). In the case of **3** anisotropic refinement was carried out for the metal tellurium atoms and oxygen and the carbon atoms of carbonyl groups, while the phenyls were refined as rigid groups with calculated hydrogen positions, with C–C = 1.395 and C–H = 0.96 Å, $U(\mathrm{H}) = 0.08$ Å^2.

Complete lists of bond lengths for **5**, and lists of thermal parameters and structure factors for all three compounds are available form the authors.

Conclusion

Diaryl and dialkyl tellurides have been shown to coordinate to metal cluster compounds in different coordination modes. Different electronic properties lead to different reactions of SMe_2, $SeMe_2$ and $TeMe_2$ with $[HRuCo_3(CO)_{12}]$, the tendency to coordinate apically to ruthenium increasing on going to the heavier chalcogens.

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