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Reactions of HRuCo₃(CO)₉[HC(PPh₂)₃] and H₃Ru₃Co(CO)₉[HC(PPh₂)₃] with PMe₂Ph. Crystal structures of clusters HRuCo₃(CO)₈[HC(PPh₂)₃](PMe₂Ph) and H₃Ru₃Co(CO)₉[HC(PPh₂)₃](PMe₂Ph)·CH₂Cl₂

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Abstract

The reaction of the clusters HRuCo₃(CO)₉[HC(PPh₂)₃] and H₃Ru₃Co(CO)₉[HC(PPh₂)₃] with the phosphine ligand PMe₂Ph produces two tetranuclear phosphine-substituted Ru–Co mixed metal clusters. In HRuCo₃(CO)₈[HC(PPh₂)₃](PMe₂Ph) the HC(PPh₂)₃ ligand caps the Co₃ face and the monodentate PMe₂Ph ligand is coordinated with the Ru atom by replacing one apical carbonyl ligand. In the compound H₃Ru₃Co(CO)₉[HC(PPh₂)₃](PMe₂Ph) the tridentate HC(PPh₂)₃ is disconnected from the Ru₂Co face and chelates to the Ru atom through two phosphorus atoms while the third phosphorus of the HC(PPh₂)₃ ligand remains uncoordinated. This leaves one coordination site vacant and the PMe₂Ph ligand is coordinated without changes in the amount of carbonyl ligands.

Keywords: Ruthenium; Cobalt; Carbonyl; Phosphine; Cluster; Crystal structure

1. Introduction

Phosphine derivatives have been prepared for most of the tetranuclear H$_x$M$_x$M′$_{4-x}$(CO)₁₂ (x = 0 to 4, M = Ru; M′ = Co or Rh) clusters and the structures of the derivatives have been studied [1]. In many cases the replacement site of the carbonyl ligands depends on the composition of the metal framework and the nature of the phosphine ligand.

In clusters containing the basal Co₃ face, like Co₄(CO)₁₂ and HRuCo₃(CO)₁₂, the replacement of the carbonyl ligands occurs mainly at the axial sites of the basal Co₃ face, although the preference of coordination between cobalt and ruthenium in HRuCo₃(CO)₁₂ is not clear. For example, the coordination of the PMe₂Ph ligand has been found to involve both the Co and Ru atoms in HRuCo₃(CO)₁₂ [2]. In some clusters containing Rh also equatorial coordination of the phosphine ligand is found.

It is possible to shield the basal face with a large fragment, and thus permit the phosphine ligand to coordinate with the Ru atom. One example of this is the cluster Ph₃PAuRuCo₃(CO)₁₁(PMe₂Ph), which is produced in a reaction between HRuCo₃(CO)₁₁(PMe₂Ph) and AuPPh₃Cl. In this derivative the gold phosphine unit occupies the basal face and the PMe₂Ph ligand moves from its original axial coordination site on the basal Co₃ face to the apical Ru atom [3]. However, in Ph₃PAuFeCo₃(CO)₁₁(PMe₂Ph), where the AuPPh₃ fragment covers the basal Co₃ face, the PMe₂Ph ligand is also coordinated on the basal face in an axial position [4].

In phosphine derivatives of HRuCo₃(CO)₁₂ the hydride ligand usually bridges the basal Co₃ face. Derivatives in which the hydride ligand bridges an Ru–Co edge are not so common; HRuCo₃(CO)₉(trithiane) and HRuCo₃(CO)₉[HC(PPh₂)₃] are examples which have been found earlier [5,6].

The tridentate HC(PPh₂)₃ ligand coordinates with the H$_x$M$_x$M′$_{4-x}$(CO)₁₂ (x = 0 to 4, M = Ru; M′ = Co or Rh) clusters forming derivatives such as Co₄(CO)₉[HC(PPh₂)₃], Rh₄(CO)₉[HC(PPh₂)₃], H₄Ru₄(CO)₉[HC-

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$(PPh_2)_3]$, $HRuCo_3(CO)_9[HC(PPh_2)_3]$ and H_3Ru_3Co $(CO)_9[HC(PPh_2)_3] \cdot 0.5$ C_6H_{14}, where the tridentate phosphine ligand is coordinated on a triangular M_3 face [6–10]. The tridentate ligand, when it coordinates with the three different metal centers, binds the metal centers together. This is one possible way of stabilizing the metal framework towards decomposition under catalytic reaction conditions.

In phosphine-substituted molecules the phosphine ligand adds electron density to the metal atoms and some of this electron density is passed on to the carbonyl groups. Thus further substitution requires stronger reaction conditions, which increases the possibility of the decomposition of the cluster molecule. Further replacement of the carbonyl ligands from the $HC(PPh_2)_3$ derivatives has been studied for the $Co_4(CO)_9[HC-(PPh_2)_3]$ cluster. In the reaction products the attached phosphine ligand prefers the apical coordination site if only one monodentate phosphine ligand is added. With two phosphine units coordination is also found in both the apical and an equatorial position. Bridging coordination between the apical and equatorial positions is also possible when the added phosphine ligand is bidentate. Examples of these are the clusters $Co_4(CO)_8$-$[HC(PPh_2)_3](PMe_3)$, $Co_4(CO)_7[HC(PPh_2)_3][(PMe_3)_2]$ and $Co_4(CO)_7[HC(PPh_2)_3]$ (dppm) (dppm = Ph_2PCH_2 PPh_2) [11,12].

2. Results and discussion

When the mixed metal cluster derivatives $HRuCo_3(CO)_9[HC(PPh_2)_3]$ and $H_3Ru_3Co(CO)_9[HC-(PPh_2)_3]$ are reacted with PMe_2Ph, two novel cluster derivatives are produced.

The crystal structures of compounds **1** and **2** are shown in Figs. 1 and 2. The atomic coordinates, se-
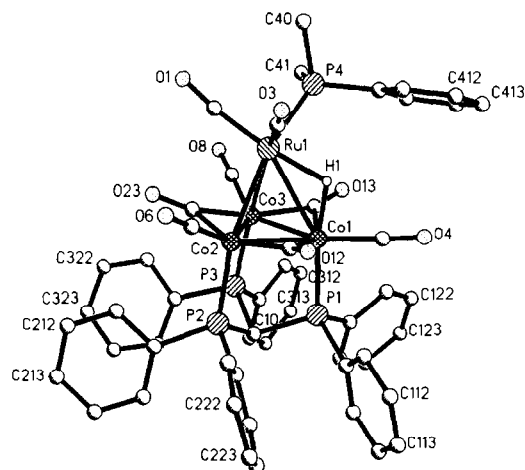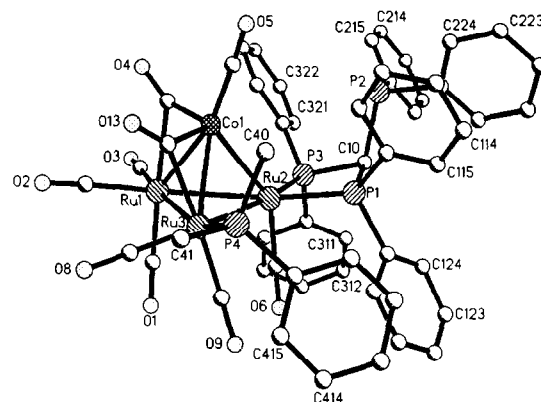

Fig. 2. Structure of $H_3Ru_3Co(CO)_9[HC(PPh_2)_3](PMe_2Ph)$ (**2**).

lected bond lengths and angles and crystallographic data are listed in Tables 1–5.

In $HRuCo_3(CO)_8[HC(PPh_2)_3](PMe_2Ph)$ (**1**) (Fig. 1) the Ru atom is located on the apical position and the basal face is formed by the Co_3 triangle, where the axial sites are occupied by the $HC(PPh_2)_3$ ligand. Three carbonyl ligands bridge the basal edges and the rest of the carbonyls remain terminal. The PMe_2Ph ligand is coordinated with the apical Ru atom. The hydride ligand was located on the difference electron density map and bridges an Ru–Co edge, as in the original cluster. A more common coordination site for the hydride ligand in the phosphine derivatives of $HRuCo_3(CO)_{12}$ is the basal Co_3 face. As in the original cluster, in **1** the large phosphine ligand shields the basal face and the hydride ligand therefore coordinates with an Ru–Co edge and the phosphine ligand with an apical site. The site of the hydride ligand can also be deduced on the basis of the bond lengths and angles. The hydride-bridged Ru–Co (1) bond is longer than the two other Ru–Co bonds, the Ru(1)–Co(1), Ru(1)–Co(2) and Ru(1)–Co(3) bond lengths are 2.760(1), 2.658(1) and 2.656(1) Å in molecule **A** and 2.750(1), 2.631(1) and 2.691(1) Å in molecule **B** respectively. The hydride ligand also repulses the carbonyl ligand CO(4); the Ru(1)–Co(1)–C(4) bond angle is 116.1(3)° in molecule **A** and 112.4(3)° in molecule **B**, and the Ru(1)–Co(2)–C(6) and Ru(1)–Co(3)–C(8) angles on the non-bridged edges are 96.8(4) and 98.2(3)° in molecule **A** and 95.6(3) and 103.5(3)° in molecule **B** respectively. In the original cluster $HRuCo_3(CO)_9[HC(PPh_2)_3]$ the corresponding bond lengths were 2.740(1), 2.646(2) and 2.654(2) Å and the corresponding angles were 118.3(3)° in the hydride-bridged edge and 96.9(3) and 100.5(3)° in the non-bridged edges.

The ^1H NMR spectrum of **1** shows the doublet of doublets signal at −19.9 ppm. A similar signal at −19.9 ppm was observed in the compound produced in the reaction between $HRuCo_3(CO)_9[HC(PPh_2)_3]$ and PMe_3. According to the ^1H NMR and IR spectra,

Fig. 1. Structure of $HRuCo_3(CO)_8[HC(PPh_2)_3](PMe_2Ph)$ (**1**).

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for $HRuCo_3(CO)_8[HC(PPh_2)_3]$ (PMe_2Ph) (**1**)

Atom	x	y	z	U_{eq}
Ru(1)	2934(1)	1463(1)	1105(1)	32(1)
Co(1)	1559(1)	1351(1)	1095(1)	30(1)
Co(2)	2448(1)	1957(1)	1878(1)	32(1)
Co(3)	1972(1)	2333(1)	842(1)	29(1)
P(1)	613(1)	1769(1)	1195(1)	29(1)
P(2)	1678(1)	2418(1)	2204(1)	32(1)
P(3)	1175(1)	2944(1)	986(1)	29(1)
P(4)	2992(1)	1069(1)	237(1)	43(1)
O(1)	4231(3)	2167(3)	1136(3)	73(3)
O(3)	3837(4)	498(3)	1888(3)	92(4)
O(4)	920(4)	179(3)	756(3)	80(4)
O(6)	3751(4)	1825(4)	2887(3)	89(4)
O(8)	2475(4)	2985(4)	46(3)	71(3)
O(12)	2273(3)	737(3)	2213(3)	60(3)
O(13)	1190(3)	1600(3)	−165(2)	44(2)
O(23)	3229(3)	2962(3)	1631(2)	44(2)
C(1)	3719(5)	1914(4)	1144(3)	44(4)
C(3)	3490(5)	849(4)	1583(4)	53(4)
C(4)	1149(4)	641(4)	882(4)	44(4)
C(6)	3232(5)	1895(4)	2483(4)	49(4)
C(8)	2264(4)	2724(4)	350(3)	40(3)
C(10)	854(4)	2544(3)	1527(3)	26(3)
C(12)	2172(4)	1163(4)	1932(3)	40(3)
C(13)	1443(4)	1757(3)	323(3)	34(3)
C(23)	2782(4)	2586(4)	1522(3)	40(3)
C(40)	3874(5)	775(5)	325(4)	72(5)
C(41)	2835(6)	1571(4)	−373(4)	70(5)
C(111)	520(2)	844(2)	1939(2)	48(4)
C(112)	199	514	2261	64(5)
C(113)	−455	697	2285	65(5)
C(114)	−787	1210	1988	55(4)
C(115)	−465	1540	1666	47(4)
C(110)	188	1357	1642	34(3)
C(121)	−253(2)	1479(2)	48(2)	36(3)
C(122)	−859	1514	−463	52(4)
C(123)	−1389	1934	−505	57(4)
C(124)	−1312	2319	−38	50(4)
C(125)	−705	2284	473	40(3)
C(120)	−176	1864	516	33(3)
C(211)	2585(3)	3389(3)	2656(2)	49(4)
C(212)	2810	3916	2971	54(4)
C(213)	2382	4190	3239	60(4)
C(214)	1729	3936	3192	61(5)
C(215)	1504	3409	2877	53(4)
C(210)	1932	3135	2609	36(3)
C(221)	1923(2)	1694(3)	3168(2)	46(4)
C(222)	1796	1449	3647	64(4)
C(223)	1141	1540	3712	63(4)
C(224)	611	1876	3297	52(4)
C(225)	737	2121	2818	42(3)
C(220)	1393	2029	2753	37(3)
C(311)	336(2)	2981(2)	−202(2)	38(3)
C(312)	−221	3177	−702	49(4)
C(313)	−726	3576	−648	59(4)
C(314)	−676	3780	−95	56(4)
C(315)	−120	3584	405	43(3)
C(310)	386	3185	352	32(3)
C(321)	2055(3)	3935(2)	1174(2)	41(3)
C(322)	2280	4515	1353	52(4)
C(323)	1935	4849	1654	63(5)
C(324)	1366	4604	1777	51(4)
C(325)	1141	4024	1599	43(3)

Table 1 (continued)

Atom	x	y	z	U_{eq}
C(320)	1485	3690	1297	33(3)
C(411)	2550(3)	−78(3)	289(2)	74(5)
C(412)	2107	−575	101	103(7)
C(413)	1538	−561	−437	101(7)
C(414)	1410	−51	−786	102(7)
C(415)	1852	445	−598	77(5)
C(410)	2422	432	−61	46(4)
H(1)	2248	896	1088	80
Ru(1')	8313(1)	3877(1)	2089(1)	35(1)
Co(1')	7133(1)	3544(1)	1142(1)	33(1)
Co(2')	7569(1)	2899(1)	2037(1)	34(1)
Co(3')	6961(1)	3869(1)	2065(1)	33(1)
P(1')	6119(1)	3033(1)	779(1)	31(1)
P(2')	6611(1)	2333(1)	1898(1)	32(1)
P(3')	5860(1)	3507(1)	1834(1)	32(1)
P(4')	8629(1)	4860(1)	1990(1)	45(1)
O(1')	9157(5)	3967(4)	3398(3)	124(5)
O(3')	9571(4)	3377(3)	1845(4)	95(4)
O(4')	7236(5)	3959(3)	52(3)	97(4)
O(6')	8773(4)	2225(4)	2796(3)	93(4)
O(8')	6955(4)	4806(4)	2868(3)	102(4)
O(12')	8095(3)	2556(3)	1106(2)	55(3)
O(13')	6628(3)	4778(3)	1147(3)	48(3)
O(23')	7728(3)	3320(3)	3212(2)	50(3)
C(1')	8830(5)	3924(5)	2907(4)	65(4)
C(3')	9103(5)	3580(5)	1932(4)	56(4)
C(4')	7182(5)	3773(4)	482(4)	61(5)
C(6')	8292(5)	2475(4)	2489(4)	49(4)
C(8')	6953(5)	4437(5)	2544(4)	55(4)
C(10')	5843(4)	2794(3)	1411(3)	31(3)
C(12')	7767(4)	2816(4)	1346(3)	40(3)
C(13')	6791(4)	4314(4)	1369(3)	39(3)
C(23')	7527(4)	3351(4)	2696(4)	39(3)
C(40')	9505(5)	5048(5)	2512(4)	72(5)
C(41')	8069(5)	5445(4)	2124(4)	61(4)
C(131)	6589(3)	2380(2)	22(3)	50(4)
C(132)	6549	1932	−385	74(5)
C(133)	6064	1465	−465	83(6)
C(134)	5620	1445	−138	67(5)
C(135)	5659	1893	269	45(3)
C(130)	6144	2360	349	37(3)
C(141)	5344(3)	3991(2)	80(2)	50(4)
C(142)	4756	4248	−354	65(5)
C(143)	4151	3906	−645	75(5)
C(144)	4134	3306	−502	84(5)
C(145)	4722	3048	−69	67(4)
C(140)	5327	3390	222	42(3)
C(231)	6981(2)	2062(2)	3077(2)	42(3)
C(232)	6874	1862	3581	57(4)
C(233)	6188	1717	3556	58(4)
C(234)	5609	1772	3029	49(4)
C(235)	5715	1972	2526	43(3)
C(230)	6402	2118	2550	36(3)
C(241)	7124(2)	1392(3)	1419(2)	51(4)
C(242)	7118	822	1189	65(5)
C(243)	6530	450	1095	69(5)
C(244)	5949	647	1231	59(4)
C(245)	5955	1217	1462	47(4)
C(240)	6542	1589	1556	37(3)
C(331)	5173(3)	4578(2)	1478(2)	48(4)
C(332)	4593	4955	1212	59(5)
C(333)	3943	4720	841	68(5)
C(334)	3873	4108	737	61(4)
C(335)	4452	3731	1004	46(4)

Table 1 (continued)

Atom	x	y	z	U_{eq}
C(330)	5102	3966	1374	36(3)
C(341)	6013(2)	3407(3)	3017(2)	56(4)
C(342)	5772	3336	3483	69(5)
C(343)	5051	3221	3371	58(4)
C(344)	4571	3176	2793	56(4)
C(345)	4812	3247	2327	44(3)
C(340)	5533	3363	2439	33(3)
C(421)	9382(3)	5029(3)	1233(3)	73(5)
C(422)	9456	5188	705	71(5)
C(423)	8861	5377	231	67(5)
C(424)	8193	5406	285	76(5)
C(425)	8119	5247	813	69(5)
C(420)	8713	5058	1287	47(4)
H(1')	7793	4037	1270	80

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$HRuCo_3(CO)_8[HC(PPh_2)_3](PMe_3)$ corresponds to compound 1.

In $H_3Ru_3Co(CO)_9[HC(PPh_2)_3](PMe_2Ph)$ (2) (Fig. 2) the tridentate $HC(PPh_2)_3$ ligand is disconnected from an Ru_2Co face of the tetrahedral Ru_3Co framework and coordinates with a ruthenium atom through two phosphorus atoms in a bidentate way. One phosphorus atom of the $HC(PPh_2)_3$ ligand remains uncoordinated. The PMe_2Ph ligand is coordinated with an Ru atom without replacing the carbonyl ligand and the number of carbonyl ligands remains unchanged when compared with the original cluster. However, the arrangement of the ligands changes. Of the nine carbonyl ligands, seven are terminal and two carbonyl ligands semibridge the Co(1)–Ru(1) and Co(1)–Ru(3) edges. Bond lengths Co(1)–C(4), Ru(1)–C(4), Co(1)–C(13) and Ru(3)–C(13) are 1.71(3), 2.34(3), 1.80(2) and 2.14(2) Å in molecule A and 1.77(2), 2.33(3), 1.82(2) and 2.17(3) Å in molecule B respectively. Co(1) remains electron deficient, which explains the semibridging carbonyl ligands CO(4) and CO(13). Corresponding semibridges are also found in $H_3Ru_3Co(CO)_{10}(dppe)$, where the structure resembles the structure of 2 [13]. In $H_3Ru_3Co(CO)_{10}$-(dppe) a bidentate $Ph_2PCH_2CH_2PPh_2$ (dppe) ligand is found in a location similar to that of the $HC(PPh_2)_3$ ligand in 2. In 2 one more carbonyl ligand is replaced by the PMe_2Ph ligand. The structure of the cluster $H_3Ru_3Co(CO)_9(HC(PPh_2)_3)$, which was used as a starting material in the synthesis of 2, corresponds to the structure of the C_1 isomer of the parent cluster $H_3Ru_3Co(CO)_{12}$. In both structures one carbonyl ligand semibridges an Ru–Co edge and one hydride ligand is located on an Ru–Co edge when the remaining two hydride ligands bridge the Ru–Ru edges [6,14].

Though the direct location of the hydride ligands on a difference electron density map was not successful, the hydride positions can be inferred from the structural parameters. The Ru(1)–Ru(3)–C(8), Ru(1)–Ru(3)–

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $H_3Ru_3Co(CO)_9[HC(PPh_2)_3]$ $(PMe_2Ph)\cdot CH_2Cl_2$ (2)

Atom	x	y	z	U_{eq}
Ru(1)	3226(1)	5733(1)	917(1)	60(1)
Ru(2)	2146(1)	6291(1)	1529(1)	42(1)
Ru(3)	2720(1)	6819(1)	567(1)	53(1)
Co(1)	3443(2)	6713(1)	1424(1)	51(1)
P(1)	1452(3)	6850(2)	2019(2)	44(2)
P(2)	2018(3)	6634(3)	3125(2)	55(2)
P(3)	1868(3)	5772(2)	2234(2)	44(2)
P(4)	2596(3)	7806(3)	469(2)	63(2)
O(1)	2184(11)	5307(10)	158(9)	134(10)
O(2)	4375(11)	5709(10)	127(8)	125(8)
O(3)	3645(14)	4581(10)	1383(10)	165(11)
O(4)	4517(9)	5942(8)	1641(7)	90(6)
O(5)	4090(10)	7563(9)	2046(7)	106(7)
O(6)	935(9)	5782(8)	978(6)	79(5)
O(8)	3373(11)	6672(10)	−477(7)	130(8)
O(9)	1323(10)	6545(9)	101(6)	115(8)
O(13)	4216(9)	7208(8)	638(6)	89(6)
C(1)	2596(17)	5490(13)	433(11)	95(10)
C(2)	3976(16)	5741(11)	422(10)	83(9)
C(3)	3518(17)	5024(13)	1220(10)	100(11)
C(4)	3984(14)	6148(11)	1492(10)	78(8)
C(5)	3818(16)	7213(14)	1807(10)	89(9)
C(6)	1405(11)	5991(10)	1180(8)	52(6)
C(8)	3117(15)	6733(12)	−80(10)	90(9)
C(9)	1865(14)	6648(11)	294(8)	75(8)
C(10)	1468(10)	6370(7)	2578(6)	38(5)
C(13)	3716(12)	7021(11)	832(8)	60(7)
C(40)	2987(13)	8241(10)	968(9)	86(9)
C(41)	3023(15)	8055(13)	−97(10)	123(12)
C(111)	2345(8)	7721(7)	2239(6)	76(8)
C(112)	2540(8)	8268(8)	2387(6)	96(10)
C(113)	2053(12)	8673(5)	2511(6)	93(11)
C(114)	1371(11)	8530(7)	2487(6)	95(11)
C(115)	1177(7)	7983(8)	2338(6)	69(7)
C(110)	1664(9)	7579(5)	2214(5)	51(6)
C(121)	501(8)	7133(7)	1307(6)	79(8)
C(122)	−145(10)	7190(7)	1103(5)	102(10)
C(123)	−703(7)	7023(8)	1385(8)	88(9)
C(124)	−615(7)	6799(7)	1870(7)	83(8)
C(125)	32(10)	6742(6)	2073(5)	70(7)
C(120)	590(7)	6909(6)	1792(6)	48(6)
C(211)	1222(8)	5883(8)	3718(6)	91(10)
C(212)	1136(9)	5501(8)	4117(7)	121(13)
C(213)	1689(12)	5332(7)	4409(5)	125(14)
C(214)	2328(10)	5546(8)	4303(6)	86(10)
C(215)	2414(7)	5928(7)	3904(6)	80(8)
C(210)	1861(9)	6097(6)	3612(5)	55(6)
C(221)	868(9)	7266(6)	3448(5)	77(8)
C(222)	577(7)	7739(8)	3680(6)	85(9)
C(223)	984(10)	8180(6)	3861(5)	83(9)
C(224)	1681(10)	8149(6)	3809(5)	63(7)
C(225)	1972(7)	7676(8)	3576(6)	64(7)
C(220)	1565(10)	7234(6)	3396(5)	52(6)
C(311)	631(10)	5174(7)	2359(6)	87(9)
C(312)	202(7)	4716(9)	2259(7)	133(13)
C(313)	406(10)	4280(7)	1935(8)	105(11)
C(315)	1039(11)	4302(6)	1712(6)	82(9)
C(314)	1469(7)	4760(7)	1812(6)	61(7)
C(310)	1264(8)	5196(5)	2135(6)	49(6)
C(321)	2303(8)	4980(6)	2941(6)	68(8)
C(322)	2770(11)	4711(6)	3258(5)	95(10)

Table 2 (continued)

Atom	x	y	z	U_{eq}
C(323)	3442(10)	4884(8)	3257(6)	102(11)
C(324)	3646(7)	5326(9)	2940(7)	100(10)
C(325)	3179(9)	5595(6)	2624(6)	77(8)
C(320)	2507(8)	5422(6)	2624(5)	56(7)
C(411)	1436(11)	8396(8)	804(5)	101(10)
C(412)	786(12)	8610(8)	739(9)	137(14)
C(413)	437(8)	8513(10)	287(11)	125(13)
C(414)	738(11)	8201(10)	−99(8)	117(12)
C(415)	1388(11)	7986(8)	−34(5)	102(11)
C(410)	1737(7)	8083(7)	417(7)	57(6)
Ru(1')	1699(1)	4464(1)	6136(1)	53(1)
Ru(2')	2830(1)	3834(1)	6645(1)	44(1)
Ru(3')	2208(1)	3461(1)	5638(1)	51(1)
Co(1')	1538(2)	3407(1)	6514(1)	49(1)
P(1')	3561(3)	3222(2)	7051(2)	45(2)
P(2')	3009(3)	3271(3)	8172(2)	56(2)
P(3')	3148(3)	4247(2)	7401(2)	49(2)
P(4')	2377(3)	2499(3)	5436(2)	57(2)
O(1')	2706(11)	5121(9)	5513(8)	114(7)
O(2')	535(10)	4568(9)	5340(7)	108(8)
O(3')	1172(12)	5437(8)	6783(8)	119(8)
O(4')	423(10)	4090(8)	6826(7)	92(6)
O(5')	902(9)	2471(9)	7028(7)	92(6)
O(6')	3978(8)	4428(7)	6097(6)	76(5)
O(8')	1464(11)	3712(9)	4670(6)	116(7)
O(9')	3453(11)	3882(9)	5104(6)	113(7)
O(13')	725(8)	3016(8)	5676(6)	84(6)
C(1')	2292(15)	4844(13)	5746(9)	85(9)
C(2')	977(14)	4518(10)	5632(10)	70(8)
C(3')	1369(15)	5072(13)	6555(11)	86(9)
C(4')	951(14)	3959(10)	6645(8)	60(7)
C(5')	1203(13)	2855(12)	6842(9)	68(8)
C(6')	3558(12)	4182(8)	6297(8)	50(6)
C(8')	1732(12)	3611(11)	5046(9)	71(8)
C(9')	2991(15)	3729(12)	5352(8)	87(9)
C(10')	3551(11)	3607(7)	7689(6)	43(6)
C(13')	1220(13)	3188(10)	5894(8)	63(7)
C(40')	1982(12)	1989(9)	5867(9)	77(8)
C(41')	2002(14)	2311(10)	4826(8)	85(9)
C(131)	3867(7)	2045(9)	7170(5)	71(8)
C(132)	3690(11)	1472(7)	7222(6)	99(10)
C(133)	3013(13)	1318(6)	7260(6)	85(9)
C(134)	2514(8)	1737(9)	7245(6)	79(8)
C(135)	2692(8)	2309(7)	7193(5)	66(7)
C(130)	3368(10)	2463(6)	7155(5)	51(6)
C(141)	5006(9)	3299(6)	7124(5)	70(7)
C(142)	5644(7)	3255(7)	6909(8)	79(8)
C(143)	5708(8)	3113(8)	6399(8)	119(12)
C(144)	5134(11)	3017(8)	6104(5)	111(11)
C(145)	4497(9)	3061(7)	6318(6)	66(7)
C(140)	4433(6)	3203(7)	6828(6)	54(6)
C(231)	2637(8)	3871(6)	9018(7)	75(8)
C(232)	2723(10)	4179(7)	9466(6)	77(8)
C(233)	3366(12)	4351(7)	9618(5)	108(11)
C(234)	3923(9)	4214(8)	9323(7)	110(11)
C(235)	3837(8)	3906(7)	8876(6)	84(8)
C(230)	3194(10)	3735(6)	8723(4)	55(6)
C(241)	4159(10)	2574(7)	8402(5)	69(7)
C(242)	4455(8)	2089(9)	8613(6)	93(9)
C(243)	4052(12)	1649(6)	8796(6)	83(9)
C(244)	3353(12)	1694(6)	8768(5)	92(10)
C(245)	3056(8)	2179(8)	8558(6)	75(8)
C(240)	3459(10)	2619(6)	8375(5)	54(6)
C(331)	4416(9)	4826(7)	7594(6)	94(10)

Table 2 (continued)

Atom	x	y	z	U_{eq}
C(332)	4845(7)	5290(9)	7528(7)	107(11)
C(333)	4648(10)	5743(7)	7218(8)	118(12)
C(334)	4022(11)	5731(6)	6975(6)	96(10)
C(335)	3594(8)	5266(8)	7041(6)	71(8)
C(330)	3791(8)	4813(6)	7351(6)	65(7)
C(341)	2727(8)	4967(7)	8194(6)	74(8)
C(342)	2254(12)	5202(6)	8521(5)	89(11)
C(343)	1581(10)	5034(8)	8490(6)	105(13)
C(344)	1381(7)	4630(9)	8131(8)	109(12)
C(345)	1854(10)	4395(7)	7803(6)	78(8)
C(340)	2527(9)	4564(6)	7835(5)	51(6)
C(421)	3507(11)	1868(8)	5744(6)	114(12)
C(422)	4167(12)	1671(7)	5696(8)	111(11)
C(423)	4557(7)	1845(10)	5287(10)	106(11)
C(424)	4287(10)	2215(10)	4926(7)	119(12)
C(425)	3627(11)	2411(7)	4973(6)	88(9)
C(420)	3237(7)	2237(8)	5382(7)	59(7)
[a]Cl(51)	4375(12)	9312(10)	3810(9)	179(6)
[a]Cl(52)	3710(13)	8480(10)	3283(9)	179(6)
[a]C(50)	4427(26)	8621(22)	3536(28)	179(6)
[a]Cl(61)	604(13)	4313(11)	3591(9)	186(7)
[a]Cl(62)	1409(13)	3429(11)	3249(9)	186(7)
[a]C(60)	600(24)	3642(23)	3300(29)	186(7)
[a]Cl(71)	4229(14)	5467(12)	4508(10)	202(7)
[a]Cl(72)	4567(14)	5943(12)	5373(10)	202(7)
[a]C(70)	4845(30)	5834(34)	4805(19)	202(7)
[a]Cl(81)	800(14)	672(12)	4597(10)	205(9)
[a]Cl(82)	416(31)	1463(25)	5237(20)	205(9)
[a]Cl(83)	397(30)	695(24)	5491(21)	205(9)
[a]C(80)	345(95)	742(34)	5138(48)	205(9)
[a]C(80')	387(105)	1143(45)	4996(34)	205(9)

[a] Site occupation factors 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.25, 0.25, 0.5, 0.25, 0.25 for C(50), Cl(51), Cl(52), C(60), Cl(61), Cl(62), C(70), Cl(71), Cl(72), C(80), C(80)', Cl(81), Cl(82), Cl(83) respectively.

C(9), Ru(3)–Ru(1)–C(2) and Ru(3)–Ru(1)–C(1) bond angles, which are 92.8(9), 104.3(8), 92.4(8) and 79.7(9)° (av. 92.3°) in molecule **A** and 93.0(8), 102.1(9), 90.0(7) and 84.8(9)° (av. 92.5°) in molecule **B** respectively approach the values (av. 92.3°) found in the structure of $H_3Ru_3Co(CO)_{10}$(dppe), where this bond was not hydride-bridged. The small values of these Ru–Ru–C angles in **2** thus exclude the possibility of an edge-bridging hydride ligand on the Ru(1)–Ru(3) edge. This leaves three M–M edges free for the three existing hydride ligands: the edges Co(1)–Ru(2), Ru(1)–Ru(2) and Ru(2)–Ru(3). These bonds are also longer than the other bonds because the hydride ligand lengthens the metal–metal bond. The bond lengths of the Co(1)–Ru(2), Ru(1)–Ru(2) and Ru(2)–Ru(3) edges are 2.766(4), 2.987(3) and 3.044(2) Å in molecule **A** and 2.764(3), 2.989(2) and 3.043(2) Å in molecule **B** respectively. The bond lengths Ru(1)–Ru(3), Co(1)–Ru(3) and Co(1)–Ru(1) are shorter, 2.876(3), 2.674(3) and 2.684(4) Å in molecule **A** and 2.871(3), 2.672(3) and 2.683(4) Å in molecule **B** respectively.

Hydride ligands also require space and therefore the ligands adjacent to the hydride-bridged edges are re-

Table 3
Selected geometric parameters (Å, °) for HRuCo$_3$(CO)$_8$[HC(PPh$_2$)$_3$](PMe$_2$Ph) (1)

Ru(1)-Co(1)	2.760(1)	Ru(1')-Co(1')	2.750(1)
Ru(1)-Co(2)	2.658(1)	Ru(1')-Co(2')	2.631(1)
Ru(1)-Co(3)	2.656(1)	Ru(1')-Co(3')	2.691(1)
Ru(1)-P(4)	2.337(3)	Ru(1')-P(4')	2.331(3)
Ru(1)-C(1)	1.845(9)	Ru(1')-C(1')	1.893(9)
Ru(1)-C(3)	1.887(9)	Ru(1')-C(3')	1.883(11)
Co(1)-Co(2)	2.496(1)	Co(1')-Co(2')	2.501(2)
Co(1)-Co(3)	2.508(2)	Co(1')-Co(3')	2.506(2)
Co(1)-P(1)	2.209(2)	Co(1')-P(1')	2.221(2)
Co(1)-C(4)	1.782(9)	Co(1')-C(4')	1.729(12)
Co(1)-C(12)	2.013(7)	Co(1')-C(12')	2.020(8)
Co(1)-C(13)	2.028(9)	Co(1')-C(13')	2.009(9)
Co(2)-Co(3)	2.505(1)	Co(2')-Co(3')	2.509(2)
Co(2)-P(2)	2.229(3)	Co(2')-P(2')	2.226(2)
Co(2)-C(6)	1.733(7)	Co(2')-C(6')	1.754(8)
Co(2)-C(12)	1.883(9)	Co(2')-C(12')	1.875(10)
Co(2)-C(23)	1.903(9)	Co(2')-C(23')	1.928(9)
Co(3)-P(3)	2.229(2)	Co(3')-P(3')	2.227(2)
Co(3)-C(8)	1.749(9)	Co(3')-C(8')	1.733(10)
Co(3)-C(13)	1.853(7)	Co(3')-C(13')	1.892(9)
Co(3)-C(23)	1.941(7)	Co(3')-C(23')	1.938(8)
P(1)-C(10)	1.905(7)	P(1')-C(10')	1.894(9)
P(2)-C(10)	1.891(6)	P(2')-C(10')	1.881(7)
P(3)-C(10)	1.890(8)	P(3')-C(10')	1.898(8)
P(4)-C(40)	1.826(10)	P(4')-C(40')	1.810(8)
P(4)-C(41)	1.802(10)	P(4')-C(41')	1.833(10)
Co(1)-Ru(1)-Co(2)	54.8(1)	Co(1')-Ru(1')-Co(2')	55.3(1)
Co(1)-Ru(1)-Co(3)	55.1(1)	Co(1')-Ru(1')-Co(3')	54.8(1)
Co(2)-Ru(1)-Co(3)	56.3(1)	Co(2')-Ru(1')-Co(3')	56.2(1)
Co(1)-Ru(1)-P(4)	109.4(1)	Co(1')-Ru(1')-P(4')	110.8(1)
Co(2)-Ru(1)-P(4)	162.2(1)	Co(2')-Ru(1')-P(4')	162.8(1)
Co(3)-Ru(1)-P(4)	109.1(1)	Co(3')-Ru(1')-P(4')	108.3(1)
Co(1)-Ru(1)-C(1)	151.8(3)	Co(1')-Ru(1')-C(1')	151.7(4)
Co(2)-Ru(1)-C(1)	105.0(3)	Co(2')-Ru(1')-C(1')	100.5(3)
Co(3)-Ru(1)-C(1)	98.1(3)	Co(3')-Ru(1')-C(1')	100.9(4)
Co(1)-Ru(1)-C(3)	107.8(3)	Co(1')-Ru(1')-C(3')	105.4(3)
Co(2)-Ru(1)-C(3)	98.7(3)	Co(2')-Ru(1')-C(3')	101.4(3)
Co(3)-Ru(1)-C(3)	154.4(3)	Co(3')-Ru(1')-C(3')	155.4(3)
Ru(1)-Co(1)-Co(2)	60.5(1)	Ru(1')-Co(1')-Co(2')	59.9(1)
Ru(1)-Co(1)-Co(3)	60.3(1)	Ru(1')-Co(1')-Co(3')	61.4(1)
Co(2)-Co(1)-Co(3)	60.1(1)	Co(2')-Co(1')-Co(3')	60.1(1)
Ru(1)-Co(1)-P(1)	148.8(1)	Ru(1')-Co(1')-P(1')	149.6(1)
Co(2)-Co(1)-P(1)	95.1(1)	Co(2')-Co(1')-P(1')	91.8(1)
Co(3)-Co(1)-P(1)	91.5(1)	Co(3')-Co(1')-P(1')	96.1(1)
Ru(1)-Co(1)-C(4)	116.1(3)	Ru(1')-Co(1')-C(4')	112.4(3)
Co(2)-Co(1)-C(4)	146.9(3)	Co(2')-Co(1')-C(4')	150.1(4)
Co(3)-Co(1)-C(4)	150.8(3)	Co(3')-Co(1')-C(4')	145.5(3)
Ru(1)-Co(1)-C(12)	76.5(3)	Ru(1')-Co(1')-C(12')	74.8(2)
Co(2)-Co(1)-C(12)	47.9(3)	Co(2')-Co(1')-C(12')	47.5(3)
Co(3)-Co(1)-C(12)	107.3(3)	Co(3')-Co(1')-C(12')	107.0(3)
Ru(1)-Co(1)-C(13)	75.4(2)	Ru(1')-Co(1')-C(13')	79.0(2)
Co(2)-Co(1)-C(13)	106.1(2)	Co(2')-Co(1')-C(13')	107.7(2)
Co(3)-Co(1)-C(13)	46.8(2)	Co(3')-Co(1')-C(13')	48.0(2)
Ru(1)-Co(2)-Co(1)	64.7(1)	Ru(1')-Co(2')-Co(1')	64.7(1)
Ru(1)-Co(2)-Co(3)	61.8(1)	Ru(1')-Co(2')-Co(3')	63.1(1)
Co(1)-Co(2)-Co(3)	60.2(1)	Co(1')-Co(2')-Co(3')	60.0(1)
Ru(1)-Co(2)-P(2)	157.7(1)	Ru(1')-Co(2')-P(2')	158.0(1)
Co(1)-Co(2)-P(2)	97.5(1)	Co(1')-Co(2')-P(2')	100.7(1)
Co(3)-Co(2)-P(2)	98.2(1)	Co(3')-Co(2')-P(2')	95.6(1)
Ru(1)-Co(2)-C(6)	96.8(4)	Ru(1')-Co(2')-C(6')	95.6(3)
Co(1)-Co(2)-C(6)	142.1(3)	Co(1')-Co(2')-C(6')	144.5(4)
Co(3)-Co(2)-C(6)	141.8(4)	Co(3')-Co(2')-C(6')	139.0(3)
Ru(1)-Co(2)-C(12)	81.2(3)	Ru(1')-Co(2')-C(12')	80.0(3)
Co(1)-Co(2)-C(12)	52.5(2)	Co(1')-Co(2')-C(12')	52.7(2)

Table 3 (continued)

Co(3)-Co(2)-C(12)	112.0(2)	Co(3')-Co(2')-C(12')	111.9(3)
Ru(1)-Co(2)-C(23)	72.8(3)	Ru(1')-Co(2')-C(23')	73.4(3)
Co(1)-Co(2)-C(23)	109.0(2)	Co(1')-Co(2')-C(23')	108.5(2)
Co(3)-Co(2)-C(23)	50.0(2)	Co(3')-Co(2')-C(23')	49.7(2)
Ru(1)-Co(3)-Co(1)	64.5(1)	Ru(1')-Co(3')-Co(1')	63.8(1)
Ru(1)-Co(3)-Co(2)	61.9(1)	Ru(1')-Co(3')-Co(2')	60.7(1)
Co(1)-Co(3)-Co(2)	59.7(1)	Co(1')-Co(3')-Co(2')	59.8(1)
Ru(1)-Co(3)-P(3)	156.2(1)	Ru(1')-Co(3')-P(3')	155.2(1)
Co(1)-Co(3)-P(3)	100.6(1)	Co(1')-Co(3')-P(3')	96.4(1)
Co(2)-Co(3)-P(3)	94.8(1)	Co(2')-Co(3')-P(3')	97.1(1)
Ru(1)-Co(3)-C(8)	98.2(3)	Ru(1')-Co(3')-C(8')	103.5(3)
Co(1)-Co(3)-C(8)	146.2(3)	Co(1')-Co(3')-C(8')	149.1(4)
Co(2)-Co(3)-C(8)	139.7(2)	Co(2')-Co(3')-C(8')	141.2(3)
Ru(1)-Co(3)-C(13)	80.8(2)	Ru(1')-Co(3')-C(13')	82.5(3)
Co(1)-Co(3)-C(13)	52.9(3)	Co(1')-Co(3')-C(13')	52.1(3)
Co(2)-Co(3)-C(13)	111.8(3)	Co(2')-Co(3')-C(13')	111.5(3)
Ru(1)-Co(3)-C(23)	72.4(3)	Ru(1')-Co(3')-C(23')	71.9(3)
Co(1)-Co(3)-C(23)	107.3(3)	Co(1')-Co(3')-C(23')	107.9(3)
Co(2)-Co(3)-C(23)	48.7(3)	Co(2')-Co(3')-C(23')	49.4(3)
Co(1)-P(1)-C(10)	109.7(2)	Co(1')-P(1')-C(10')	108.4(2)
Co(2)-P(2)-C(10)	104.9(3)	Co(2')-P(2')-C(10')	104.3(3)
Co(3)-P(3)-C(10)	105.1(2)	Co(3')-P(3')-C(10')	105.5(3)
Ru(1)-P(4)-C(40)	113.1(3)	Ru(1')-P(4')-C(40')	112.3(3)
Ru(1)-P(4)-C(41)	117.4(3)	Ru(1')-P(4')-C(41')	116.9(3)
C(40)-P(4)-C(41)	101.4(5)	C(40')-P(4')-C(41')	102.0(4)
P(1)-C(10)-P(2)	104.1(3)	P(1')-C(10')-P(2')	104.9(4)
P(1)-C(10)-P(3)	103.7(4)	P(1')-C(10')-P(3')	104.6(4)
P(2)-C(10)-P(3)	105.8(4)	P(2')-C(10')-P(3')	105.7(3)
Co(1)-C(12)-Co(2)	79.6(3)	Co(1')-C(12')-Co(2')	79.8(4)
Co(1)-C(13)-Co(3)	80.4(3)	Co(1')-C(13')-Co(3')	79.9(3)
Co(2)-C(23)-Co(3)	81.3(3)	Co(2')-C(23')-Co(3')	80.9(3)

pulsed. The bond angles Ru(1)-Ru(2)-P(3), Ru(1)-Ru(2)-C(6), Ru(2)-Ru(1)-C(3) and Ru(2)-Ru(1)-C(1) on the hydride-bridged Ru(1)-Ru(2) edge are 112.6(2), 97.7(7), 111.4(9) and 91.4(9)° (av. 103.3°) in molecule A and 112.4(2), 98.1(6), 111.3(8) and 90.5(8)° (av. 103.1°) in molecule B respectively. On the Ru(2)-Ru(3) edge, which is also hydride-bridged, the bond angles Ru(3)-Ru(2)-P(1), Ru(3)-Ru(2)-C(6), Ru(2)-Ru(3)-P(4) and Ru(2)-Ru(3)-C(9) are 117.7(2), 92.3(6), 116.9(2) and 83.8(7)° (av. 102.7°) in molecule A and 118.5(2), 90.3(7), 114.6(2) and 85.6(7)° (av. 102.3°) in molecule B respectively. On the third hydride-bridged edge the angles Co(1)-Ru(2)-P(1), Co(1)-Ru(2)-P(3) and Ru(2)-Co(1)-C(5) are 114.3(2), 119.9(2) and 125.7(10)° (av. 120.0°) in molecule A and 114.4(2), 120.5(2) and 125.3(8)° (av. 120.1°) in molecule B respectively and therefore large enough for the edge-bridging hydride ligand.

In H$_3$Ru$_3$Co(CO)$_{10}$(dppe) all three hydride ligands were crystallographically located on the corresponding edges, as in molecule (2). In H$_3$Ru$_3$Co(CO)$_{10}$(dppe) the two hydride-bridged Ru-Ru bonds and one hydride-bridged Ru-Co bond are 3.015(1), 2.993(1) and 2.748(1) Å. The non-bridged Ru-Ru bond is 2.830(1) Å and the carbonyl-bridged Ru-Co bonds 2.669(1) and 2.670(1) Å. The Ru-Ru-C/P bond angles on the hydride-bridged edges average 103.7° on the first hydride-bridged Ru-Ru

Table 4
Selected geometric parameters (Å,°) for $H_3Ru_3Co(CO)_9[HC(PPh_2)_3](PMe_2Ph)\cdot CH_2Cl_2$ (2)

Ru(1)–C(1)	1.86(3)	Ru(1′)–C(1′)	1.80(3)
Ru(1)–C(3)	1.93(3)	Ru(1′)–C(3′)	1.92(3)
Ru(1)–C(2)	1.98(3)	Ru(1′)–C(2′)	1.95(3)
Ru(1)–C(4)	2.34(3)	Ru(1′)–C(4′)	2.33(3)
Ru(1)–Co(1)	2.684(4)	Ru(1′)–Co(1′)	2.683(4)
Ru(1)–Ru(3)	2.876(3)	Ru(1′)–Ru(3′)	2.871(3)
Ru(1)–Ru(2)	2.987(3)	Ru(1′)–Ru(2′)	2.989(2)
Ru(2)–C(6)	1.86(2)	Ru(2′)–C(6′)	1.90(2)
Ru(2)–P(3)	2.288(5)	Ru(2′)–P(3′)	2.295(6)
Ru(2)–P(1)	2.298(6)	Ru(2′)–P(1′)	2.293(6)
Ru(2)–Co(1)	2.766(4)	Ru(2′)–Co(1′)	2.764(3)
Ru(2)–Ru(3)	3.044(2)	Ru(2′)–Ru(3′)	3.043(2)
Ru(3)–C(9)	1.88(3)	Ru(3′)–C(9′)	1.84(3)
Ru(3)–C(8)	1.89(3)	Ru(3′)–C(8′)	1.85(2)
Ru(3)–C(13)	2.14(2)	Ru(3′)–C(13′)	2.17(3)
Ru(3)–P(4)	2.334(7)	Ru(3′)–P(4′)	2.335(7)
Ru(3)–Co(1)	2.674(3)	Ru(3′)–Co(1′)	2.672(3)
Co(1)–C(4)	1.71(3)	Co(1′)–C(4′)	1.77(2)
Co(1)–C(5)	1.71(3)	Co(1′)–C(5′)	1.69(3)
Co(1)–C(13)	1.80(2)	Co(1′)–C(13′)	1.82(2)
P(1)–C(10)	1.85(2)	P(1′)–C(10′)	1.91(2)
P(2)–C(10)	1.90(2)	P(2′)–C(10′)	1.84(2)
P(3)–C(10)	1.85(2)	P(3′)–C(10′)	1.86(2)
P(4)–C(41)	1.82(2)	P(4′)–C(41′)	1.82(2)
P(4)–C(40)	1.83(2)	P(4′)–C(40′)	1.83(2)
C(1)–Ru(1)–Co(1)	134.7(9)	C(1′)–Ru(1′)–Co(1′)	138.2(9)
C(3)–Ru(1)–Co(1)	118.7(9)	C(3′)–Ru(1′)–Co(1′)	115.2(8)
C(2)–Ru(1)–Co(1)	101.7(8)	C(2′)–Ru(1′)–Co(1′)	102.9(7)
C(4)–Ru(1)–Co(1)	39.1(6)	C(4′)–Ru(1′)–Co(1′)	40.6(6)
C(1)–Ru(1)–Ru(3)	79.7(9)	C(1′)–Ru(1′)–Ru(3′)	84.8(9)
C(3)–Ru(1)–Ru(3)	173.7(8)	C(3′)–Ru(1′)–Ru(3′)	171.8(8)
C(2)–Ru(1)–Ru(3)	92.4(8)	C(2′)–Ru(1′)–Ru(3′)	90.0(7)
C(4)–Ru(1)–Ru(3)	93.6(7)	C(4′)–Ru(1′)–Ru(3′)	94.4(6)
Co(1)–Ru(1)–Ru(3)	57.37(8)	Co(1′)–Ru(1′)–Ru(3′)	57.39(8)
C(1)–Ru(1)–Ru(2)	91.4(9)	C(1′)–Ru(1′)–Ru(2′)	90.5(8)
C(3)–Ru(1)–Ru(2)	111.4(9)	C(3′)–Ru(1′)–Ru(2′)	111.3(8)
C(2)–Ru(1)–Ru(2)	153.3(8)	C(2′)–Ru(1′)–Ru(2′)	151.7(7)
C(4)–Ru(1)–Ru(2)	85.8(6)	C(4′)–Ru(1′)–Ru(2′)	88.2(6)
Co(1)–Ru(1)–Ru(2)	58.10(8)	Co(1′)–Ru(1′)–Ru(2′)	58.03(8)
Ru(3)–Ru(1)–Ru(2)	62.53(6)	Ru(3′)–Ru(1′)–Ru(2′)	62.52(6)
P(3)–Ru(2)–P(1)	72.4(2)	P(1′)–Ru(2′)–P(3′)	71.9(2)
C(6)–Ru(2)–Co(1)	144.4(6)	C(6′)–Ru(2′)–Co(1′)	143.1(7)
P(3)–Ru(2)–Co(1)	119.9(2)	P(3′)–Ru(2′)–Co(1′)	120.5(2)
P(1)–Ru(2)–Co(1)	114.3(2)	P(1′)–Ru(2′)–Co(1′)	114.4(2)
C(6)–Ru(2)–Ru(1)	97.7(7)	C(6′)–Ru(2′)–Ru(1′)	98.1(6)
P(3)–Ru(2)–Ru(1)	112.6(2)	P(3′)–Ru(2′)–Ru(1′)	112.4(2)
P(1)–Ru(2)–Ru(1)	169.8(2)	P(1′)–Ru(2′)–Ru(1′)	169.8(2)
Co(1)–Ru(2)–Ru(1)	55.45(8)	Co(1′)–Ru(2′)–Ru(1′)	55.44(8)
C(6)–Ru(2)–Ru(3)	92.3(6)	C(6′)–Ru(2′)–Ru(3′)	90.3(7)
P(3)–Ru(2)–Ru(3)	169.4(2)	P(3′)–Ru(2′)–Ru(3′)	169.3(2)
P(1)–Ru(2)–Ru(3)	117.7(2)	P(1′)–Ru(2′)–Ru(3′)	118.5(2)
Co(1)–Ru(2)–Ru(3)	54.54(7)	Co(1′)–Ru(2′)–Ru(3′)	54.54(7)
Ru(1)–Ru(2)–Ru(3)	56.94(6)	Ru(1′)–Ru(2′)–Ru(3′)	56.85(6)
C(9)–Ru(3)–Co(1)	141.2(7)	C(9′)–Ru(3′)–Co(1′)	142.7(7)
C(8)–Ru(3)–Co(1)	121.8(8)	C(8′)–Ru(3′)–Co(1′)	119.0(8)
C(13)–Ru(3)–Co(1)	42.2(6)	C(13′)–Ru(3′)–Co(1′)	42.6(6)
P(4)–Ru(3)–Co(1)	103.9(2)	P(4′)–Ru(3′)–Co(1′)	103.0(2)
C(9)–Ru(3)–Ru(1)	104.3(8)	C(9′)–Ru(3′)–Ru(1′)	102.1(9)
C(8)–Ru(3)–Ru(1)	92.8(9)	C(8′)–Ru(3′)–Ru(1′)	93.0(8)
C(13)–Ru(3)–Ru(1)	76.8(6)	C(13′)–Ru(3′)–Ru(1′)	77.2(6)
P(4)–Ru(3)–Ru(1)	160.6(2)	P(4′)–Ru(3′)–Ru(1′)	160.3(2)
Co(1)–Ru(3)–Ru(1)	57.70(8)	Co(1′)–Ru(3′)–Ru(1′)	57.77(8)
C(9)–Ru(3)–Ru(2)	83.8(7)	C(9′)–Ru(3′)–Ru(2′)	85.6(7)
C(8)–Ru(3)–Ru(2)	150.0(9)	C(8′)–Ru(3′)–Ru(2′)	151.8(8)

Table 4 (continued)

C(13)–Ru(3)–Ru(2)	99.6(6)	C(13′)–Ru(3′)–Ru(2′)	100.0(6)
P(4)–Ru(3)–Ru(2)	116.9(2)	P(4′)–Ru(3′)–Ru(2′)	114.6(2)
Co(1)–Ru(3)–Ru(2)	57.42(8)	Co(1′)–Ru(3′)–Ru(2′)	57.42(8)
Ru(1)–Ru(3)–Ru(2)	60.53(6)	Ru(1′)–Ru(3′)–Ru(2′)	60.63(6)
C(4)–Co(1)–Ru(3)	119.4(9)	C(4′)–Co(1′)–Ru(3′)	117.6(7)
C(5)–Co(1)–Ru(3)	131.5(10)	C(5′)–Co(1′)–Ru(3′)	132.5(8)
C(13)–Co(1)–Ru(3)	52.8(8)	C(13′)–Co(1′)–Ru(3′)	53.7(8)
C(4)–Co(1)–Ru(1)	59.4(9)	C(4′)–Co(1′)–Ru(1′)	58.8(8)
C(5)–Co(1)–Ru(1)	160.7(10)	C(5′)–Co(1′)–Ru(1′)	160.1(9)
C(13)–Co(1)–Ru(1)	87.5(8)	C(13′)–Co(1′)–Ru(1′)	88.1(8)
Ru(3)–Co(1)–Ru(1)	64.92(9)	Ru(3′)–Co(1′)–Ru(1′)	64.84(8)
C(4)–Co(1)–Ru(2)	107.2(9)	C(4′)–Co(1′)–Ru(2′)	108.7(9)
C(5)–Co(1)–Ru(2)	125.7(10)	C(5′)–Co(1′)–Ru(2′)	125.3(8)
C(13)–Co(1)–Ru(2)	120.8(8)	C(13′)–Co(1′)–Ru(2′)	121.8(8)
Ru(3)–Co(1)–Ru(2)	68.04(9)	Ru(3′)–Co(1′)–Ru(2′)	68.04(9)
Ru(1)–Co(1)–Ru(2)	66.46(9)	Ru(1′)–Co(1′)–Ru(2′)	66.53(9)
C(10)–P(1)–Ru(2)	95.5(6)	C(10′)–P(1′)–Ru(2′)	96.1(6)
C(10)–P(3)–Ru(2)	95.9(6)	C(10′)–P(3′)–Ru(2′)	97.5(6)
Co(1)–C(4)–Ru(1)	81.5(11)	Co(1′)–C(4′)–Ru(1′)	80.6(10)
P(3)–C(10)–P(1)	94.1(8)	P(3′)–C(10′)–P(1′)	91.5(8)
P(3)–C(10)–P(2)	111.8(10)	P(2′)–C(10′)–P(3′)	112.0(11)
P(1)–C(10)–P(2)	114.4(10)	P(2′)–C(10′)–P(1′)	114.7(10)
Co(1)–C(13)–Ru(3)	85.0(10)	Co(1′)–C(13′)–Ru(3′)	83.6(10)

edge and 101.0° on the second. The two Co–Ru–P bond angles and the Ru–Co–C bond angle are 104.7(1), 114.2(1) and 120.1(2)° (av. 113.0°) respectively.

In solution the ^1H NMR spectrum of 2 at 273 K shows a broadened multiplet at −16.2 ppm (intensity 1), which arises from the Ru–Co edge-bridging hydride ligand and a doublet of doublets signal at −19.50 ppm (intensity 2) assigned to the remaining two hydride ligands.

In the original cluster the signal was observed as a singlet at −15.8 ppm and in the parent cluster $H_3Ru_3Co(CO)_{12}$ (C_1 isomer) at −17.2 ppm (0°C), indicating a fluxional process of the hydride ligands in these molecules. In the ^1H NMR spectrum of $H_3Ru_3Co(CO)_{10}$(dppe) the hydrides showed two resonances, a sharp singlet at −16.6 ppm (Ru–H–Ru) and a broad singlet at −14.2 ppm (Ru–H–Co).

3. Experimental details

3.1. General

$H_3Ru_3Co(CO)_9[HC(PPh_2)_3]$ and $HRuCo_3(CO)_9[HC(PPh_2)_3]$ were prepared by previously published methods [6]. PMe_2Ph, PMe_3 and all the solvents were of commercial origin. All manipulations except the chromatographic separations were done with deoxygenated solvents under N_2 atmosphere. The FT–IR spectra were recorded on a Galaxy 6020 spectrometer. The ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer at 273 K in $CDCl_3$. Chemical shifts are relative to Me_4Si. Crystals were grown by evaporation of the solvent from a saturated hexane–CH_2Cl_2 solution. The

Table 5
Crystallographic data for compounds 1 and 2

	1	2
Formula	$C_{53}H_{43}O_8P_4Co_3Ru$	$C_{54}H_{45}O_9P_4CoRu_3$ $+CH_2Cl_2$
FW	1209.7	1408.9
Colour; habit	Brown; rectangle	Brown; rectangle
Crystal size (mm³)	0.5×0.5×0.3	0.6×0.5×0.5
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/c$
a (Å)	20.053(3)	19.789(4)
b (Å)	22.448(4)	23.368(5)
c (Å)	24.399(4)	26.334(6)
β (°)	111.10(1)	90.42(2)
V (Å³)	10247(3)	12177(5)
Z	8	8
Calc. density (g cm⁻³)	1.568	1.534
μ (mm⁻¹)	1.411	1.240
$F(000)$	4880	5592
No. of centering reflections	28	28
Centering 2θ (°)	19–32	15–22
Scan range 2θ (°)	5–50	5–42
Scan speed (° min⁻¹)	2.49–29.3	3.00–29.3
h, k, l range	23,26,±29	23,28,±31
Reflections collected	19304	13530
No. of independent reflections	18244	12880
Obs. data [$I \geq 2\sigma(I)$]	10509	6314
No. of parameters	1075	1158
R [$I \geq 2\sigma(I)$]	5.48	9.08
R'	5.59	—
wR^2 [$I \geq 2\sigma(I)$]	—	18.18
g (weight)	0.0005	0.0839
Goodness of fit	1.29	1.02
Largest difference peak (e Å⁻³)	0.80	1.33
Largest difference hole (e Å⁻³)	−0.68	−0.82

$R = (\Sigma ||F_o| - |F_c||)/\Sigma |F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1/[\sigma^2(F) + gF^2]$. $wR^2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, weighting scheme used $w = 1/[\sigma^2(F_o^2) + (gP)^2 + 45.8P]$, where $P = (F_o^2 + 2F_c^2)/3$. Goodness of fit $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observed reflections and N_v the number of variables.

crystal of **1** was measured at room temperature exposed to normal atmosphere, and the crystal of **2** in a sealed glass capillary.

3.2. Synthesis

3.2.1. HRuCo₃(CO)₈[HC(PPh₂)₃] (PMe₂Ph)

A tetrahydrofuran solution (30 ml) of HRuCo₃(CO)₉-[HC(PPh₂)₃] (29 mg, 0.026 mmol) and an excess of PMe₂Ph (30 μl, 0.211 mmol) were reacted at refluxing temperature. After 3.5 h the reaction was complete. After evaporation of the solvent the residue was purified by column chromatography on silica. Elution with an

n-hexane/CH₂Cl₂ (1 : 2) mixture gave a fraction which was identified as compound **1** (red, 24.7 mg, 0.020 mmol, 76.9%). IR (cm⁻¹): 2011 vs, 1962 vs, 1783 m, 1753 m, CH₂Cl₂. ¹H NMR (ppm): −19.9 dd [²$J(P_{ax}$–H) = 36.6 Hz, ²$J(P_{ap}$–H) = 7.3 Hz and ³$J(P_{ax}$–H) = 3.3 Hz].

3.2.2. H₃Ru₃Co(CO)₉[HC(PPh₂)₃] (PMe₂Ph) · CH₂Cl₂

A tetrahydrofuran solution (30 ml) of H₃Ru₃Co-(CO)₉[HC(PPh₂)₃] (27.4 mg, 0.023 mmol) and an excess of PMe₂Ph (10 μl, 0.070 mmol) were reacted at room temperature for 3 h. The THF was evaporated and the resulting mixture of cluster compounds was separated by column chromatography on silica. Elution with an n-hexane/CH₂Cl₂ (1 : 2) mixture gave compound **2** as a third fraction (red, 13.0 mg, 0.010 mmol, 43.5%). IR (cm⁻¹): 2054 vs, 2005 vs, 1993 vs, 1976 m,br, 1827 w, 1778 w, CH₂Cl₂. ¹H NMR (ppm): −16.2 m, −19.50 dd [$J(P$–H) = 23.8 Hz, $J(P$–H) = 12.3 Hz].

3.2.3. HRuCo₃(CO)₈[HC(PPh₂)₃](PMe₃)

A tetrahydrofuran solution (30 ml) of HRuCo₃(CO)₉-[HC(PPh₂)₃] (44 mg, 0.040 mmol) and an excess of PMe₃ (25 μl, 0.241 mmol) were reacted at +45 °C for 14 h. After evaporation of the solvent the residue was purified by column chromatography on silica. Elution with an n-hexane/CH₂Cl₂ (1 : 2) mixture gave a fraction which was identified as HRuCo₃(CO)₈[HC(PPh₂)₃] (PMe₃) with IR and ¹H NMR spectroscopy (reddish-brown, 45.5 mg, 0.039 mmol, 97.5%). IR (cm⁻¹): 2012 vs, 1969 vs, 1753 m,br, CH₂Cl₂. ¹H NMR (ppm): −19.9 dd [²$J(P_{ax}$–H) = 36.0 Hz, ²$J(P_{ap}$–H) = 7.0 Hz and ³$J(P_{ax}$–H) = 3.0 Hz].

3.3. Structure determination

Diffraction data were recorded on a Nicolet R3m diffractometer with graphite-monochromated Mo -K α radiation ($\lambda = 0.71073$ Å) and ω scan mode. Intensities were corrected for Lorentz, polarization and background effects. An absorption correction was applied for **1**.

In both structures metal atom positions were located by applying direct methods, and the coordinates for non-metal atoms were determined from subsequent difference electron density calculations. All calculations were performed using the SHELXTL PLUS [15] program package, except for the final structure refinement of **2** where the SHELXTL93 [16] program was used. For **2**, 23033 reflections were collected with scan range 5° ≤ 2θ ≤ 50°, but within the range 42–50° the crystal showed no diffraction.

All non-hydrogen atoms were refined anisotropically, but the phenyl rings as rigid groups. The solvent molecules in **2** were refined isotropically. Hydrogen atoms were placed in calculated positions and not re-

fined. The hydride ligand in **1** was located on the difference electron density map but could not be refined.

4. Supplementary material available

For both structures a complete list of bond lengths and angles and tables of hydrogen coordinates, thermal parameters and structure factors have been deposited at the Cambridge Crystallographic Data Centre.

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