

Reactions of tridentate phosphine ligand $[\text{HC}(\text{PPh}_2)_3]$ with metal carbonyl clusters $\text{HRuCo}_3(\text{CO})_{12}$ and $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$: synthesis and crystal structures of $\text{HRuCo}_3(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ and $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3] \cdot 1/2\text{C}_6\text{H}_{14}$

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Abstract

Two tetranuclear phosphine-substituted mixed metal clusters of ruthenium and cobalt were made by reactions between tridentate phosphine ligand $\text{HC}(\text{PPh}_2)_3$ and the clusters $\text{HRuCo}_3(\text{CO})_{12}$ and $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$. The tridentate phosphine ligand is coordinated to a Co_3 face in $\text{HRuCo}_3(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ and to an Ru_2Co face in $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$. Both compounds contain an unusual bridging hydride ligand on the $\text{Ru}(\mu\text{-H})\text{Co}$ edge.

Keywords: Ruthenium; Cobalt; Cluster; Carbonyl; Tridentate ligand; Crystal structure

1. Introduction

The tetranuclear mixed metal clusters of the type $\text{H}_x\text{M}_x\text{M}'_{4-x}(\text{CO})_{12}$ ($x = 0$ to 4, $\text{M} \equiv \text{Ru}$; $\text{M}' \equiv \text{Co}$ or Rh) and their phosphine derivatives have been extensively studied [1]. Most of the known phosphine derivatives contain monodentate phosphine ligands; derivatives containing bi- or tri-dentate phosphine ligands are much less well known. Some have, however, been obtained from tridentate $\text{HC}(\text{PPh}_2)_3$ ligand and $\text{H}_x\text{M}_x\text{M}'_{4-x}(\text{CO})_{12}$ ($x = 0$ to 4, $\text{M} \equiv \text{Ru}$; $\text{M}' \equiv \text{Co}$ or Rh) clusters $\text{Co}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$. Owing to steric effects the tridentate phosphine ligand prefers to coordinate to a triangular M_3 face in $\text{Co}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$, $\text{Rh}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ and $\text{H}_4\text{Ru}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ [2–4]. Clusters coordinated to both $\text{HC}(\text{PPh}_2)_3$ and mono- or bi-dentate phosphine ligands are also known [5–8]. No mixed metal $\text{HC}(\text{PPh}_2)_3$ derivatives of the clusters $\text{H}_x\text{M}_x\text{M}'_{4-x}(\text{CO})_{12}$ ($x = 0$ to 4, $\text{M} \equiv \text{Ru}$; $\text{M}' \equiv \text{Co}$ or Rh) have yet been reported.

Coordination of a tridentate phosphine ligand to three different metal centres could provide a way of stabilizing transition metal clusters, which tend to decompose under catalytic reaction conditions. One example of such coordination is provided by the compound $\text{Ru}_3(\text{CO})_9(\text{MeSi}(\text{PBu}_2)_3)$, in which the phosphine ligand is coordinated to the triangular face. This compound has been found to remain stable under 100 bar H_2 – CO pressure at 300°C, unlike $\text{Ru}_3(\text{CO})_{12}$ which decomposes under these conditions [9].

The structures of the mixed metal clusters $\text{H}_x\text{M}_x\text{M}'_{4-x}(\text{CO})_{12}$ ($x = 0$ to 4, $\text{M} \equiv \text{Ru}$; $\text{M}' \equiv \text{Co}$ or Rh) are found to depend on the composition of the metal core and the number of hydride ligands. In compounds containing three or four hydride ligands, the hydrides prefer to bridge the Ru – Ru edges and the carbonyl ligands are usually terminal. If the compound contains less than three ruthenium atoms, rhodium and cobalt atoms tend to be located in the basal sites with the ruthenium atom preferring the apical position. Three carbonyl ligands usually bridge the basal metal–metal edges of the tetrahedron, with the other carbonyls terminal. Hydride ligands tend to bridge either Ru – Ru or Ru – Rh edges or the basal face of the metals. Reports of compounds with a hydride ligand bridging an Ru – Co edge are rare. The

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only crystallographically characterized derivative of $\text{HRuCo}_3(\text{CO})_{12}$ in which the hydride ligand bridges the Ru–Co edge is $\text{HRuCo}_3(\text{CO})_9(\text{trithiane})$, which has the cyclic thioether 1,3,5-trithiane coordinated to the Co_3 face [10].

The only previously characterized phosphine derivative of the parent cluster $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$ is $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{10}(\text{dppe})$, in which the bidentate phosphine ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2(\text{dppe})$ is chelated to the Ru atom. One hydride ligand is coordinated to an Ru–Co edge and the remaining hydrides to the Ru–Ru edges. Two carbonyl ligands semibridge Ru–Co edges [11].

Here we describe the synthesis and structural characterization of two new phosphine-substituted mixed metal clusters, $\text{HRuCo}_3(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ and $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3] \cdot 1/2\text{C}_6\text{H}_{14}$.

2. Results and discussion

Reaction of the mixed metal clusters $\text{HRuCo}_3(\text{CO})_{12}$ and $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$ with $\text{HC}(\text{PPh}_2)_3$ gave the clusters $\text{HRuCo}_3(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ (1) and $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ (2), in which the substitution has taken place at the triangular M_3 face. Compound 1 appears to be indefinitely stable in the solid state and in solution; however, even in the solid state compound 2 decomposes within 1 week when exposed to the atmosphere.

Compound 1 crystallizes in the monoclinic space group $P2_1/c$ and compound 2 in the triclinic space group $P-1$ with two $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ molecules and one C_6H_{14} molecule in an asymmetric unit. The crystal structures of compounds 1 and 2 are shown in Figs. 1 and 2, and the atomic coordinates, selected bond lengths and angles and crystallographic data are listed in Tables 1–5.

In compound 1 (Fig. 1) the Ru atom is in the apical position. Three carbonyl ligands bridge the basal Co_3 triangle and the other carbonyls remain terminal. The tridentate phosphine ligand is coordinated to the Co_3 face.

The hydride ligand in molecule 1 was located from the difference electron density map and found to bridge the Ru–Co(1) edge. In $\text{HRuCo}_3(\text{CO})_{12}$ and its mono- and bi-dentate phosphine derivatives, the hydride ligand is located on the basal Co_3 face [1], but in compound 1 the large phosphine ligand shields the basal face, causing the hydride ligand to coordinate to an Ru–Co edge.

The site of the hydride ligand can also be inferred from the geostructural data. The hydride ligand causes repulsion of the carbonyl ligand CO(4), so that the bond angle Ru–Co(1)–C(4) is $118.3(3)^\circ$, while the angles Ru–Co(2)–C(6) and Ru–Co(3)–C(8) of the non-bridged edges are only $96.9(3)^\circ$ and $100.5(3)^\circ$. The hydride-bridged Ru–Co(1) bond is also ca. 0.1 \AA longer than the two other Ru–Co bonds: the length of the Ru–Co(1)

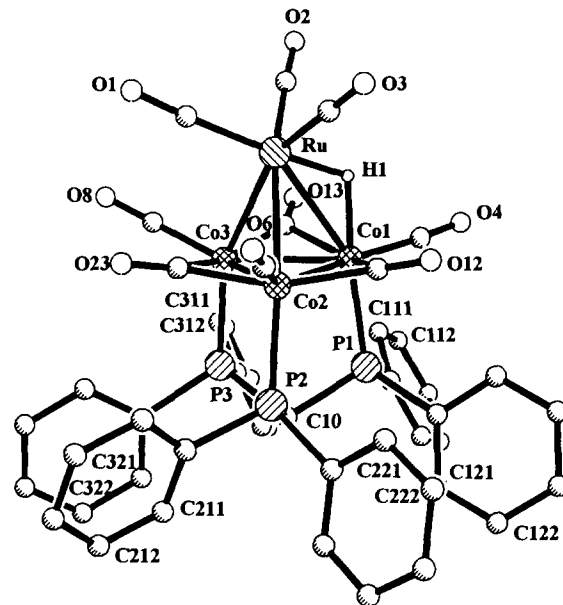


Fig. 1. Crystal structure of $\text{HRuCo}_3(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ (1).

bond is $2.740(1) \text{ \AA}$, while those of the Ru–Co(2) and Ru–Co(3) bonds are $2.646(2) \text{ \AA}$ and $2.654(2) \text{ \AA}$. In $\text{HRuCo}_3(\text{CO})_9$ (trithiane), which structurally resembles 1, the hydride-bridged Ru–Co bond is $2.697(3) \text{ \AA}$ and the non-bridged Ru–Co bonds average 2.620 \AA . The $\text{Ru}_{\text{ap}}\text{--Co}_{\text{bas}}\text{--C}_{\text{eq}}$ bond angle in the hydride-bridged edge of $\text{HRuCo}_3(\text{CO})_9$ (trithiane) is larger (113.0°) than the two other corresponding bond angles in non-bridged edges (average 100.7°).

In compound 2 (Fig. 2) the phosphine ligand is coordinated to an Ru_2Co face of the Ru_3Co tetrahedron.

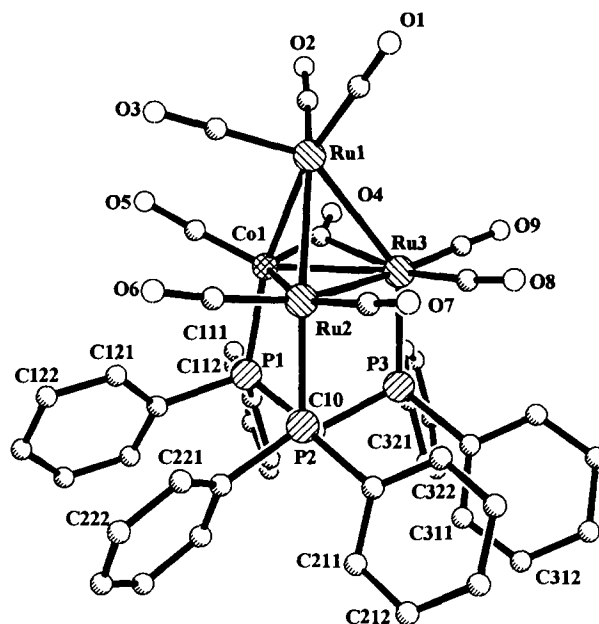


Fig. 2. Crystal structure of $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3] \cdot 1/2\text{C}_6\text{H}_{14}$ (2).

Of the nine remaining carbonyl ligands, eight are terminal and one semibridges the Co(1)–Ru(3) edge. The bond lengths Co(1)–C(4) and Ru(3)–C(4) are 1.760(18) Å and 2.401(18) Å in molecule A and 1.766(18) Å and 2.328(17) Å in molecule B. The hydride ligands could not be directly located from the difference electron density map for **2**. The hydride positions can, however, be inferred from the structural parameters. The bond lengths in the metal–metal edges Ru(1)–Ru(2), Ru(1)–Ru(3) and Co(1)–Ru(2) are 2.932(2) Å, 2.933(2) Å and 2.783(3) Å in molecule A, and 2.929(2) Å, 2.925(2) Å

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $\text{HRuCo}_3(\text{CO})_9[\text{HC}(\text{PPh}_3)_2]$ (**1**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ru	1783(1)	3488(1)	1189(1)	50(1)
Co(1)	3315(1)	2700(1)	1923(1)	37(1)
Co(2)	1618(1)	2014(1)	1832(1)	41(1)
Co(3)	2609(1)	1894(1)	992(1)	40(1)
P(1)	4040(2)	1498(2)	2370(1)	34(1)
P(2)	2006(2)	623(2)	2188(1)	38(1)
P(3)	3347(2)	556(2)	1233(1)	37(1)
O(1)	31(6)	3341(6)	209(4)	110(4)
O(2)	2814(8)	4963(7)	556(4)	123(5)
O(3)	663(6)	4735(6)	1941(4)	93(4)
O(4)	5026(5)	3834(5)	2348(3)	67(3)
O(6)	–441(5)	2358(6)	2026(4)	96(4)
O(8)	2231(6)	1853(6)	–286(3)	84(3)
O(12)	2131(4)	3209(5)	2855(3)	58(3)
O(13)	4341(5)	3042(4)	871(3)	53(3)
O(23)	489(5)	1342(5)	735(3)	68(3)
C(1)	675(8)	3370(7)	591(5)	73(5)
C(2)	2431(9)	4402(9)	777(5)	75(5)
C(3)	1070(8)	4263(8)	1661(5)	62(5)
C(4)	4331(7)	3387(6)	2209(4)	43(4)
C(6)	370(7)	2212(7)	1967(4)	60(4)
C(8)	2407(7)	1867(7)	221(5)	52(4)
C(10)	3366(6)	433(6)	2055(3)	36(3)
C(12)	2241(6)	2791(7)	2439(4)	45(4)
C(13)	3710(7)	2661(6)	1080(4)	43(3)
C(23)	1208(7)	1598(6)	1023(4)	44(4)
C(111)	5855(4)	1894(4)	1940(2)	41(3)
C(112)	6891	1873	1948	54(4)
C(113)	7487	1364	2373	71(5)
C(114)	7046	876	2789	69(5)
C(115)	6010	897	2780	51(4)
C(110)	5415	1406	2356	38(3)
C(121)	4130(4)	604(3)	3468(3)	43(4)
C(122)	4252	590	4077	56(4)
C(123)	4298	1407	4389	67(5)
C(124)	4222	2238	4092	58(4)
C(125)	4099	2252	3483	43(3)
C(120)	4053	1435	3170	33(3)
C(211)	1619(4)	–1233(5)	1837(3)	54(4)
C(212)	979	–1934	1612	70(5)
C(213)	–20	–1744	1404	87(6)
C(214)	–380	–854	1421	81(5)
C(215)	260	–152	1645	57(4)
C(210)	1259	–342	1853	43(4)
C(221)	1612(4)	1039(4)	3316(3)	53(4)
C(222)	1457	844	3888	65(5)

Table 1 (continued)

C(223)	1598	–42	4105	66(5)
C(224)	1894	–733	3750	67(5)
C(225)	2049	–538	3178	55(4)
C(220)	1908	348	2961	41(3)
C(311)	4908(4)	907(4)	596(2)	48(4)
C(312)	5863	812	436	67(5)
C(313)	6567	252	763	64(5)
C(314)	6315	–213	1249	57(4)
C(315)	5360	–118	1409	42(3)
C(310)	4657	442	1082	40(3)
C(321)	3368(4)	–1356(5)	1036(2)	55(4)
C(322)	3008	–2161	760	65(5)
C(323)	2148	–2143	349	77(5)
C(324)	1646	–1322	215	73(5)
C(325)	2005	–517	491	49(4)
C(320)	2866	–535	901	43(4)

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

and 2.784(3) Å in molecule B. They are longer than the bonds Ru(2)–Ru(3), Co(1)–Ru(1) and Co(1)–Ru(3), which are 2.886(2) Å, 2.672(3) Å and 2.638(3) Å in molecule A, and 2.876(2) Å, 2.685(3) Å and 2.654(3) Å in molecule B. The hydrides are thus bridging the first set of edges.

The hydride ligands also cause repulsion of the carbonyl ligands: the bond angles Ru(1)–Ru(2)–C(6), Ru(1)–Ru(2)–C(7), Ru(1)–Ru(3)–C(8) and Ru(1)–Ru(3)–C(9) next to the two hydride-bridged Ru–Ru edges are 103.7(6)°, 107.4(6)°, 99.9(6)° and 115.5(6)° in molecule A and 103.3(5)°, 106.9(6)°, 99.0(5)° and 115.3(5)° in molecule B, whereas the angle Ru(1)–Co(1)–C(5) next to the non-bridged edge is 95.3(9)° in molecule A and 97.9(7)° in molecule B. The third hydride ligand lies on the basal Co(1)–Ru(2) edge, the bond angles Co(1)–Ru(2)–C(6) and Ru(2)–Co(1)–C(5) being 107.5(6)° and 125.7(8)° in molecule A and 106.4(6)° and 127.1(7)° in molecule B. The values of the angles Ru(2)–Ru(3)–C(8) and Ru(3)–Ru(2)–C(7), which are 79.5(6)° and 100.6(5)° in molecule A and 79.9(5)° and 101.5(6)° in molecule B, are so small as to exclude the possibility of an edge-bridging hydride ligand in the basal Ru(2)–Ru(3) edge. Spacefilling diagram of **2** support these conclusion based on the structural data.

The structure of **2** is similar to that of the C_{1v} -isomer of the parent cluster $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$ (characterized by IR and ^1H NMR spectroscopy) in which one carbonyl ligand semibridges the Ru–Co edge, two hydride ligands bridge the Ru–Ru edges, and one hydride ligand bridges the Ru–Co edge. In the crystallographically characterized C_{3v} -isomer of the parent cluster $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$, all the hydride ligands bridge equivalent Ru–Ru edges, in which the bond lengths average 2.898 Å. The length of non-bridged Ru–Co in $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$ (C_{3v} -isomer) average 2.675 Å [12].

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3] \cdot 1/2\text{C}_6\text{H}_4$ (2)

Atom	x	y	z	U(eq)
Ru(1)	3088(1)	4465(1)	3834(1)	59(1)
Ru(2)	4163(1)	2746(1)	4064(1)	41(1)
Ru(3)	4806(1)	3929(1)	3121(1)	45(1)
Co(1)	2924(2)	3387(1)	3143(1)	40(1)
P(1)	3283(3)	2236(3)	2756(2)	36(2)
P(2)	4884(3)	1581(3)	3674(2)	36(2)
P(3)	5472(3)	2843(3)	2657(2)	36(2)
O(1)	3787(18)	5506(14)	4644(9)	167(13)
O(2)	1867(17)	5918(11)	3084(8)	140(11)
O(3)	1113(14)	3955(13)	4473(8)	137(10)
O(4)	2955(11)	4781(9)	2226(5)	80(6)
O(5)	704(14)	3592(12)	3146(9)	131(10)
O(6)	2717(12)	1860(10)	4934(6)	84(7)
O(7)	5888(11)	2774(8)	4889(5)	68(6)
O(8)	6670(13)	3944(10)	3861(6)	86(7)
O(9)	5561(13)	5324(8)	2245(6)	90(7)
C(1)	3524(23)	5119(17)	4338(10)	116(14)
C(2)	2361(22)	5361(16)	3366(11)	103(13)
C(3)	1876(19)	4163(13)	4219(8)	74(10)
C(4)	3187(14)	4240(13)	2620(7)	58(8)
C(5)	1646(23)	3491(13)	3135(10)	90(12)
C(6)	3309(17)	2165(12)	4602(7)	59(8)
C(7)	5271(15)	2754(11)	4556(6)	47(7)
C(8)	5980(19)	3882(11)	3600(8)	61(9)
C(9)	5252(15)	4791(13)	2560(8)	60(8)
C(10)	4733(12)	1867(9)	2900(6)	33(6)
C(111)	2368(9)	2842(7)	1752(5)	60(8)
C(112)	2183	2885	1192	79(10)
C(113)	2796	2354	894	69(9)
C(114)	3596	1780	1156	72(9)
C(115)	3781	1737	1716	50(8)
C(110)	3168	2267	2014	40(6)
C(121)	1925(9)	1348(7)	3521(4)	45(7)
C(122)	1250	730	3714	77(10)
C(123)	1063	135	3391	76(10)
C(124)	1552	158	2876	68(9)
C(125)	2227	776	2684	63(8)
C(120)	2414	1371	3006	42(6)
C(211)	6598(9)	323(7)	3897(4)	52(8)
C(212)	7616	7	4067	69(9)
C(213)	8316	554	4191	69(9)
C(214)	7998	1417	4145	54(8)
C(215)	6980	1733	3975	45(7)
C(210)	6280	1186	3851	37(6)
C(221)	4057(9)	259(7)	4400(4)	51(7)
C(222)	3721	-546	4561	67(9)
C(223)	3636	-1061	4170	76(10)
C(224)	3888	-771	3618	59(8)
C(225)	4224	34	3457	57(8)
C(220)	4309	549	3849	35(6)
C(311)	7310(9)	1652(6)	2712(4)	45(7)
C(312)	8397	1450	2700	52(7)
C(313)	9070	2082	2692	73(9)
C(314)	8654	2915	2695	73(10)
C(315)	7567	3116	2707	53(8)
C(310)	6895	2485	2715	41(7)
C(321)	6067(9)	2510(6)	1596(5)	61(8)
C(322)	6096	2691	1021	76(10)
C(323)	5504	3406	739	73(10)
C(324)	4883	3939	1032	85(10)
C(325)	4854	3758	1607	58(8)

Table 2 (continued)

Atom	x	y	z	U(eq)
C(320)	5446	3043	1889	39(6)
Ru(1')	709(1)	290(1)	-1267(1)	49(1)
Ru(2')	516(1)	2064(1)	-1820(1)	44(1)
Ru(3')	2357(1)	971(1)	-2015(1)	40(1)
Co(1')	2012(2)	1371(1)	-1022(1)	43(1)
P(1')	2887(3)	2503(3)	-1120(2)	37(2)
P(2')	1436(3)	3273(3)	-2096(2)	40(2)
P(3')	3413(3)	2101(3)	-2250(2)	37(2)
O(1')	-802(18)	-873(14)	-1631(8)	168(12)
O(2')	1901(14)	-1295(11)	-609(7)	108(8)
O(3')	-731(13)	796(11)	-351(6)	110(8)
O(4')	3652(10)	-19(8)	-922(5)	64(5)
O(5')	1716(15)	1040(10)	162(6)	117(9)
O(6')	-1353(11)	2818(9)	-1219(6)	97(7)
O(7')	-771(12)	2146(10)	-2853(6)	88(7)
O(8')	1275(11)	1051(8)	-3108(5)	69(6)
O(9')	4143(11)	-293(8)	-2264(6)	76(6)
C(1')	-239(18)	-447(13)	-1523(9)	76(10)
C(2')	1447(18)	-681(14)	-841(9)	75(10)
C(3')	-174(19)	571(13)	-691(8)	79(10)
C(4')	2982(14)	547(12)	-1119(7)	54(8)
C(5')	1836(15)	1191(11)	-343(10)	71(10)
C(6')	-618(15)	2555(12)	-1450(8)	62(8)
C(7')	-248(16)	2125(12)	-2474(8)	58(8)
C(8')	1656(14)	1069(10)	-2695(8)	46(7)
C(9')	3456(14)	179(11)	-2155(7)	50(7)
C(10')	2868(13)	2993(10)	-1890(6)	47(7)
C(131)	5035(11)	2927(6)	-1153(4)	49(7)
C(132)	6055	2819	-947	79(11)
C(133)	6337	2168	-505	94(13)
C(134)	5599	1626	-270	76(9)
C(135)	4579	1734	-476	50(7)
C(130)	4297	2384	-917	46(7)
C(141)	1357(10)	3331(8)	-513(5)	59(8)
C(142)	960	3916	-188	77(10)
C(143)	1603	4497	-53	77(10)
C(144)	2641	4492	-244	90(11)
C(145)	3037	3907	-570	59(8)
C(140)	2395	3326	-704	49(7)
C(231)	1216(9)	3261(5)	-3225(5)	52(7)
C(232)	1086	3619	-3781	71(9)
C(233)	1094	4492	-3951	72(9)
C(234)	1231	5006	-3566	73(9)
C(235)	1361	4647	-3010	50(7)
C(230)	1353	3775	-2839	42(7)
C(241)	1764(8)	4766(8)	-1682(5)	51(7)
C(242)	1403	5517	-1502	68(9)
C(243)	326	5741	-1455	96(12)
C(244)	-392	5215	-1588	79(10)
C(245)	-32	4465	-1768	64(8)
C(240)	1046	4240	-1815	47(7)
C(331)	5252(9)	1158(6)	-1767(4)	54(8)
C(332)	6336	973	-1697	65(8)
C(333)	7024	1529	-1972	84(11)
C(334)	6628	2270	-2319	69(10)
C(335)	5545	2456	-2389	56(7)
C(330)	4857	1900	-2114	41(7)
C(341)	3624(9)	1999(5)	-3360(5)	52(8)
C(342)	3814	2291	-3919	58(8)
C(343)	3924	3147	-4107	76(9)
C(344)	3846	3710	-3737	57(8)
C(345)	3656	3418	-3178	41(7)
C(340)	3545	2562	-2990	42(6)
C(40) ^a	125	1834	5252	100

Table 2 (continued)

Atom	x	y	z	U(eq)
C(41) ^a	-1525	3032	5521	100
C(42) ^a	-1657	2718	5864	100
C(43) ^a	-1268	3182	4985	100
C(44) ^a	-135	1385	5290	100
C(47) ^a	-1122	3570	5258	100
C(48) ^a	-47	1848	5570	100
C(49) ^a	-1693	2937	5256	100
C(50) ^a	-789	1832	5594	100
C(51) ^a	-1014	2650	5417	100
C(52) ^a	-248	2587	4937	100
C(53) ^a	-799	2309	5837	100
C(54) ^a	-1180	1540	5273	100

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

^a Site occupation factors 0.50, 0.50, 0.50, 0.50, 0.50, 0.50, 0.50, 0.50, 0.50, 0.50, 0.33, 0.33, 0.33 for C(40), C(41), C(42), C(43), C(44), C(47), C(48), C(49), C(50), C(51), C(52), C(53) and C(54) respectively.

The carbonyl and hydride ligands are arranged differently in $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{10}(\text{dppe})$ and $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$ (C_1 -isomer) and **2**. In $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{10}(\text{dppe})$ all the Ru–Co edges are bridged [11], one edge with a hydride ligand and the other two with semibringing carbonyl ligands. The lengths of the two hydride-bridged Ru–Ru bonds and one hydride-bridged Ru–Co bond are 3.015(1) Å, 2.993(1) Å and 2.748(1) Å. The length of the non-bridged Ru–Ru bond is 2.830(1) Å and the carbonyl-bridged Ru–Co bonds have lengths of 2.669(1) Å and 2.670(1) Å. The average value of the bond angles in the non-bridged Ru–Ru–C edge is 92.3°.

In $\text{H}_4\text{Ru}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$, in which the basal Ru_3 plane is capped by the $\text{HC}(\text{PPh}_2)_3$ ligand, two hydride ligands are found in the $\text{Ru}_{\text{ap}}\text{--Ru}_{\text{bas}}$ edges and the remaining two in the basal M–M edges [4]. The $\text{Ru}_{\text{ap}}\text{--Ru}_{\text{bas}}\text{--C}_{\text{eq}}$ angles in $\text{H}_4\text{Ru}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ average 105.2° when the bond is H bridged and 99.8° when it is not. In **2** the corresponding angles average 106.6° in molecule A and 106.1° in molecule B when the bond is hydride bridged, and 95.3(9)° in molecule A and 97.9(7)° in molecule B when it is non-bridged. In $\text{H}_4\text{Ru}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$, the $\text{Ru}_{\text{bas}}\text{--Ru}_{\text{bas}}\text{--C}_{\text{eq}}$ angles in the $[\text{HC}(\text{PPh}_2)_3]$ -capped Ru_3 face average 107.9° when the Ru–Ru bond is hydride bridged and 91.1° when it is non-bridged. The corresponding angles in **2** in the bridged Ru(2)–Co(1) edge average 116.6° in molecule A and 116.8° in molecule B. Because the Ru(2)–Ru(3) bond of **2** is not hydride bridged, the corresponding average $\text{Ru}_{\text{bas}}\text{--Ru}_{\text{bas}}\text{--C}_{\text{eq}}$ bond angle is smaller, 90.1° in molecule A and 90.7° in molecule B.

Examination of the basal face of the molecules **1**, **2** and $\text{H}_4\text{Ru}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ shows that molecule **2** is structurally intermediate between **1** and $\text{H}_4\text{Ru}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$. In **1** all the edges of the Co_3 face are

carbonyl bridged, whereas in **2** only one carbonyl ligand semibrings a basal Ru–Co edge of the Ru_2Co face and one hydride ligand bridges another Ru–Co edge. Two hydride ligands of **2** bridge apical basal Ru–Ru edges. In **2** carbonyl ligands CO(6) and CO(8) are terminally located, whereas in molecule **1** the corresponding carbonyls bridge the basal Co–Co edges. In $\text{H}_4\text{Ru}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ all the carbonyl ligands are terminally located and two basal edges of the Ru_3 face are hydride bridged and the other two hydrides bridge apical-basal metal–metal edges, as in **2**.

In the ¹H NMR spectrum the hydride of **1** appears as a moderately sharp doublet at -20.6 ppm, with coupling constant ²J(P–H) 27.5 Hz. In the case of $\text{HRuCo}_3(\text{CO})_9(\text{trithiane})$ also, the coupling to the quadrupolar ⁵⁹Co nucleus caused only moderate line broadening of the ¹H NMR signal of the hydride (at -23.7 ppm) [10]. The ¹H NMR spectrum of compound **2** recorded at 273 K shows only one sharp singlet at -15.8 ppm, indicating a fluxional process involving the hydride ligands. In the ¹H NMR spectrum of the C_1 -isomer of the parent cluster $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$, the signal of non-equivalent hydride ligands was likewise observed as a singlet (-17.2 ppm, 0°C) owing to rapid exchange of the hydride ligands between the metal–metal edges [12]. Similarly, in the ¹H NMR spectra of $\text{H}_4\text{Ru}_4(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$, the hydride signal was observed as a singlet at -15.76 ppm, at temperatures from -80 to +30°C, because of exchange of the hydride ligands [4].

3. Experimental details

3.1. General

$\text{HRuCo}_3(\text{CO})_{12}$ and $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$ were prepared according to published methods [12,13]. The $\text{HC}(\text{PPh}_2)_3$ and all solvents were of commercial origin. All manipulations except chromatographic separations were carried out under N_2 with deoxygenated solvents. The FT-IR spectra were recorded on a Galaxy 6020 spectrometer, and the ¹H NMR spectra on a Bruker AM-250 spectrometer at 273 K in CDCl_3 with Me_4Si as reference. Crystals were grown by evaporation of the solvent from a saturated solution in hexane– CH_2Cl_2 . The air stable crystal of **1** was mounted exposed to the atmosphere and the air sensitive crystal of **2** was in a sealed glass capillary.

3.2. Synthesis

3.2.1. $\text{HRuCo}_3(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$

A heptane solution (30 ml) of $\text{HRuCo}_3(\text{CO})_{12}$ (126 mg, 0.20 mmol) and $\text{HC}(\text{PPh}_2)_3$ (132 mg, 0.23 mmol) was stirred under reflux for 2 h. The solvent was then

evaporated off and the residual mixture of cluster compounds was separated by column chromatography on silica. Elution with *n*-hexane–CH₂Cl₂ (1:2) mixture gave compound **1** as the fifth, red, fraction (51.5 mg, 0.047 mmol, 23.5%). The reaction also took place in refluxing *n*-hexane, but the reaction time was 18 h. The yield of **1** was the same.

3.2.2. H₃Ru₃Co(CO)₉[HC(PPh₂)₃] · 1/2C₆H₁₄

An *n*-hexane solution (30 ml) of H₃Ru₃Co(CO)₁₂ (267.8 mg, 0.38 mmol) and HC(PPh₂)₃ (217 mg, 0.38 mmol) was stirred under reflux for 4 h. The *n*-hexane was then evaporated off and the residual mixture of cluster compounds was separated by column chro-

matography on silica. Elution with *n*-hexane–CH₂Cl₂ (1:2) mixture gave compound **2** as the fourth, red, fraction (78.8 mg, 0.066 mmol, 17.4%).

3.3. Spectroscopic data for **1**

¹H NMR (in ppm): –20.6 d (²J(P–H) = 27.5 Hz).
IR (in cm⁻¹): 2062vs, 1993vs, 1804m, 1767m, CH₂Cl₂.

3.4. Spectroscopic data for **2**

¹H NMR (in ppm): –15.8 s.
IR (in cm⁻¹): 2075s, 2061m, 2010vs, 1984s, 1958m, 1799m, CH₂Cl₂.

Table 3
Selected bond lengths and angles for HRuCo₃(CO)₉[HC(PPh₃)₂] (**1**) (Å, deg)

Ru–Co(1)	2.740(1)	Ru–Co(2)	2.646(2)
Ru–Co(3)	2.654(2)	Ru–C(1)	1.899(11)
Ru–C(2)	1.923(13)	Ru–C(3)	1.921(12)
Co(1)–Co(2)	2.482(2)	Co(1)–Co(3)	2.523(2)
Co(1)–C(4)	1.755(9)	Co(1)–C(12)	2.003(10)
Co(1)–C(13)	2.090(9)	Co(2)–Co(3)	2.509(2)
Co(2)–C(6)	1.778(10)	Co(2)–C(12)	1.909(9)
Co(2)–C(23)	1.971(9)	Co(3)–C(8)	1.765(10)
Co(3)–C(13)	1.852(9)	Co(3)–C(23)	1.949(9)
Co(1)–Ru–Co(2)	54.8(1)	Co(1)–Ru–Co(3)	55.7(1)
Co(2)–Ru–Co(3)	56.5(1)	Co(1)–Ru–C(1)	149.6(3)
Co(2)–Ru–C(1)	102.5(3)	Co(3)–Ru–C(1)	95.8(3)
Co(1)–Ru–C(2)	104.1(3)	Co(2)–Ru–C(2)	157.7(4)
Co(3)–Ru–C(2)	107.3(4)	C(1)–Ru–C(2)	93.9(5)
Co(1)–Ru–C(3)	107.0(3)	Co(2)–Ru–C(3)	94.4(3)
Co(3)–Ru–C(3)	150.8(3)	C(1)–Ru–C(3)	93.6(5)
C(2)–Ru–C(3)	99.5(5)	Ru–Co(1)–Co(2)	60.7(1)
Ru–Co(1)–Co(3)	60.4(1)	Co(2)–Co(1)–Co(3)	60.2(1)
Ru–Co(1)–C(4)	118.3(3)	Co(2)–Co(1)–C(4)	158.1(3)
Co(3)–Co(1)–C(4)	140.6(3)	Ru–Co(1)–C(12)	78.1(3)
Co(2)–Co(1)–C(12)	49.0(3)	Co(3)–Co(1)–C(12)	108.6(3)
C(4)–Co(1)–C(12)	109.2(4)	Ru–Co(1)–C(13)	72.7(2)
Co(2)–Co(1)–C(13)	105.1(3)	Co(3)–Co(1)–C(13)	46.2(3)
C(4)–Co(1)–C(13)	94.6(4)	C(12)–Co(1)–C(13)	148.7(4)
Ru–Co(2)–Co(1)	64.5(1)	Ru–Co(2)–Co(3)	61.9(1)
Co(1)–Co(2)–Co(3)	60.7(1)	Ru–Co(2)–C(6)	96.9(3)
Co(1)–Co(2)–C(6)	143.5(3)	Co(3)–Co(2)–C(6)	139.9(3)
Ru–Co(2)–C(12)	82.1(3)	Co(1)–Co(2)–C(12)	52.3(3)
Co(3)–Co(2)–C(12)	112.5(3)	C(6)–Co(2)–C(12)	96.1(4)
Ru–Co(2)–C(23)	75.8(3)	Co(1)–Co(2)–C(23)	109.9(3)
Co(3)–Co(2)–C(23)	49.8(3)	C(6)–Co(2)–C(23)	93.9(4)
C(12)–Co(2)–C(23)	156.7(4)	Ru–Co(3)–Co(1)	63.9(1)
Ru–Co(3)–Co(2)	61.6(1)	Co(1)–Co(3)–Co(2)	59.1(1)
Ru–Co(3)–C(8)	100.5(3)	Co(1)–Co(3)–C(8)	149.1(3)
Co(2)–Co(3)–C(8)	139.2(3)	Ru–Co(3)–C(13)	78.2(3)
Co(1)–Co(3)–C(13)	54.5(3)	Co(2)–Co(3)–C(13)	112.1(3)
C(8)–Co(3)–C(13)	97.7(4)	Ru–Co(3)–C(23)	76.0(3)
Co(1)–Co(3)–C(23)	109.1(3)	Co(2)–Co(3)–C(23)	50.6(3)
C(8)–Co(3)–C(23)	90.9(4)	C(13)–Co(3)–C(23)	153.9(4)
Co(1)–C(12)–Co(2)	78.7(4)	Co(1)–C(13)–Co(3)	79.4(4)
Co(2)–C(23)–Co(3)	79.6(3)		

Table 4

Selected bond lengths and angles for $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3] \cdot 1/2\text{C}_6\text{H}_{14}$ (2) (Å, deg)

Ru(1)–Ru(2)	2.932(2)	Ru(1')–Ru(2')	2.929(2)
Ru(1)–Ru(3)	2.933(2)	Ru(1')–Ru(3')	2.925(2)
Ru(1)–Co(1)	2.672(3)	Ru(1')–Co(1')	2.685(3)
Ru(1)–C(1)	1.896(29)	Ru(1')–C(1')	1.971(25)
Ru(1)–C(2)	1.862(24)	Ru(1')–C(2')	1.899(21)
Ru(1)–C(3)	1.854(23)	Ru(1')–C(3')	1.880(22)
Ru(2)–Ru(3)	2.886(2)	Ru(2')–Ru(3')	2.876(2)
Ru(2)–Co(1)	2.783(3)	Ru(2')–Co(1')	2.784(3)
Ru(2)–C(6)	1.871(19)	Ru(2')–C(6')	1.875(19)
Ru(2)–C(7)	1.892(18)	Ru(2')–C(7')	1.891(20)
Ru(3)–Co(1)	2.638(3)	Ru(3')–Co(1')	2.654(3)
Ru(3)–C(4)	2.401(18)	Ru(3')–C(4')	2.328(17)
Ru(3)–C(8)	1.922(23)	Ru(3')–C(8')	1.898(19)
Ru(3)–C(9)	1.894(19)	Ru(3')–C(9')	1.868(18)
Co(1)–C(4)	1.760(18)	Co(1')–C(4')	1.766(18)
Co(1)–C(5)	1.624(30)	Co(1')–C(5')	1.659(25)
Ru(2)–Ru(1)–Ru(3)	59.0(1)	Ru(2')–Ru(1')–Ru(3')	58.9(1)
Ru(2)–Ru(1)–Co(1)	59.3(1)	Ru(2')–Ru(1')–Co(1')	59.3(1)
Ru(3)–Ru(1)–Co(1)	55.9(1)	Ru(3')–Ru(1')–Co(1')	56.3(1)
Ru(2)–Ru(1)–C(1)	110.3(8)	Ru(2')–Ru(1')–C(1')	116.2(6)
Ru(3)–Ru(1)–C(1)	112.9(9)	Ru(3')–Ru(1')–C(1')	118.9(6)
Co(1)–Ru(1)–C(1)	167.0(9)	Co(1')–Ru(1')–C(1')	174.4(6)
Ru(2)–Ru(1)–C(2)	151.7(9)	Ru(2')–Ru(1')–C(2')	152.8(7)
Ru(3)–Ru(1)–C(2)	102.2(8)	Ru(3')–Ru(1')–C(2')	102.0(7)
Co(1)–Ru(1)–C(2)	92.9(9)	Co(1')–Ru(1')–C(2')	94.5(8)
C(1)–Ru(1)–C(2)	96.3(12)	C(1')–Ru(1')–C(2')	89.5(10)
Ru(2)–Ru(1)–C(3)	94.0(6)	Ru(2')–Ru(1')–C(3')	90.4(6)
Ru(3)–Ru(1)–C(3)	145.4(7)	Ru(3')–Ru(1')–C(3')	140.6(7)
Co(1)–Ru(1)–C(3)	92.7(7)	Co(1')–Ru(1')–C(3')	87.8(7)
C(1)–Ru(1)–C(3)	95.9(11)	C(1')–Ru(1')–C(3')	95.8(10)
C(2)–Ru(1)–C(3)	92.7(10)	C(2')–Ru(1')–C(3')	95.9(9)
Ru(1)–Ru(2)–Ru(3)	60.5(1)	Ru(1')–Ru(2')–Ru(3')	60.5(1)
Ru(1)–Ru(2)–Co(1)	55.7(1)	Ru(1')–Ru(2')–Co(1')	56.0(1)
Ru(3)–Ru(2)–Co(1)	55.4(1)	Ru(3')–Ru(2')–Co(1')	55.9(1)
Ru(1)–Ru(2)–C(6)	103.7(6)	Ru(1')–Ru(2')–C(6')	103.3(5)
Ru(3)–Ru(2)–C(6)	160.8(6)	Ru(3')–Ru(2')–C(6')	160.2(5)
Co(1)–Ru(2)–C(6)	107.5(6)	Co(1')–Ru(2')–C(6')	106.4(6)
Ru(1)–Ru(2)–C(7)	107.4(6)	Ru(1')–Ru(2')–C(7')	106.9(6)
Ru(3)–Ru(2)–C(7)	100.6(5)	Ru(3')–Ru(2')–C(7')	101.5(6)
Co(1)–Ru(2)–C(7)	154.6(5)	Co(1')–Ru(2')–C(7')	155.6(6)
C(6)–Ru(2)–C(7)	94.5(8)	C(6')–Ru(2')–C(7')	94.0(9)
Ru(1)–Ru(3)–Ru(2)	60.5(1)	Ru(1')–Ru(3')–Ru(2')	60.6(1)
Ru(1)–Ru(3)–Co(1)	57.0(1)	Ru(1')–Ru(3')–Co(1')	57.3(1)
Ru(2)–Ru(3)–Co(1)	60.3(1)	Ru(2')–Ru(3')–Co(1')	60.3(1)
Ru(1)–Ru(3)–C(4)	69.6(4)	Ru(1')–Ru(3')–C(4')	69.0(4)
Ru(2)–Ru(3)–C(4)	100.3(4)	Ru(2')–Ru(3')–C(4')	100.4(4)
Co(1)–Ru(3)–C(4)	40.5(4)	Co(1')–Ru(3')–C(4')	40.9(5)
Ru(1)–Ru(3)–C(8)	99.9(6)	Ru(1')–Ru(3')–C(8')	99.0(5)
Ru(2)–Ru(3)–C(8)	79.5(6)	Ru(2')–Ru(3')–C(8')	79.9(5)
Co(1)–Ru(3)–C(8)	139.5(6)	Co(1')–Ru(3')–C(8')	139.6(5)
C(4)–Ru(3)–C(8)	167.4(8)	C(4')–Ru(3')–C(8')	165.3(7)
Ru(1)–Ru(3)–C(9)	115.5(6)	Ru(1')–Ru(3')–C(9')	115.3(5)
Ru(2)–Ru(3)–C(9)	173.3(7)	Ru(2')–Ru(3')–C(9')	173.9(6)
Co(1)–Ru(3)–C(9)	123.1(6)	Co(1')–Ru(3')–C(9')	122.2(5)
C(4)–Ru(3)–C(9)	82.6(7)	C(4')–Ru(3')–C(9')	81.5(7)
C(8)–Ru(3)–C(9)	96.3(8)	C(8')–Ru(3')–C(9')	96.8(8)
Ru(1)–Co(1)–Ru(2)	65.0(1)	Ru(1')–Co(1')–Ru(2')	64.7(1)
Ru(1)–Co(1)–Ru(3)	67.1(1)	Ru(1')–Co(1')–Ru(3')	66.4(1)
Ru(2)–Co(1)–Ru(3)	64.3(1)	Ru(2')–Co(1')–Ru(3')	63.8(1)
Ru(1)–Co(1)–C(4)	85.3(7)	Ru(1')–Co(1')–C(4')	82.6(6)
Ru(2)–Co(1)–C(4)	125.7(6)	Ru(2')–Co(1')–C(4')	122.2(6)
Ru(3)–Co(1)–C(4)	62.5(6)	Ru(3')–Co(1')–C(4')	59.6(6)

Table 4 (continued)

Ru(1)–Co(1)–C(5)	95.3(9)	Ru(1')–Co(1')–C(5')	97.9(7)
Ru(2)–Co(1)–C(5)	125.7(8)	Ru(2')–Co(1')–C(5')	127.1(7)
Ru(3)–Co(1)–C(5)	155.1(8)	Ru(3')–Co(1')–C(5')	156.4(7)
C(4)–Co(1)–C(5)	100.1(9)	C(4')–Co(1')–C(5')	102.4(8)
Ru(3)–C(4)–Co(1)	77.0(6)	Ru(3')–C(4')–Co(1')	79.5(6)

3.5. Structure determination

Diffraction data were recorded on a Nicolet R3m diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and with an ω scan mode. Intensities were corrected for Lorentz, polarization and background effects.

For both compounds, metal atoms were located by direct methods, and coordinates for non-metal atoms were determined from subsequent difference electron density calculations. All calculations were performed

using the SHELXTL Plus [14] program package. All non-hydrogen atoms were refined anisotropically, except for the phenyl carbons, which were refined isotropically with the phenyl rings as rigid groups. Hydrogen atoms were placed in calculated positions (0.96 \AA , $U = 0.06 \text{ \AA}^2$ in **1** and $U = 0.08 \text{ \AA}^2$ in **2**) and were not refined.

Complete lists of bond lengths and angles and tables of atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Table 5
Crystallographic data for compounds **1** and **2**

	1	2
Formula	C ₄₆ H ₃₂ O ₉ P ₃ Co ₃ Ru	C ₄₉ H ₄₁ O ₉ P ₃ CoRu ₃
FW	1099.5	1228.9
Colour habit	Brown rectangle	Brown rectangle
Crystal Size	0.2 × 0.3 × 0.5	0.3 × 0.3 × 0.25
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> – 1
<i>a</i> (Å)	13.487(4)	12.777(4)
<i>b</i> (Å)	14.654(4)	16.134(5)
<i>c</i> (Å)	23.104(7)	24.644(7)
α (deg)	—	79.56(2)
β (deg)	97.91(2)	88.38(2)
γ (deg)	—	84.15(2)
<i>V</i> (Å ³)	4541(2)	4970(6)
<i>Z</i>	4	4
Calculated density (g cm ⁻³)	1.608	1.642
μ (mm ⁻¹)	1.552	1.351
<i>F</i> (000)	2200	2404
Number of centring reflections	34	25
Centring 2θ	14–29	15–26
Scan range (2θ)	4–50	5–50
Scan speed (deg min ⁻¹)	2.49–29.30	3.00–29.30
<i>h</i> , <i>k</i> , <i>l</i> range	16, 17, ± 27	15, ± 19 , ± 29
Reflections collected	8941	17603
Number of unique reflections	8053	17603
Observed data [$F \geq 2\sigma(F)$]	3944	7007
Number of parameters varied	487	973
<i>R</i>	0.0548	0.0690
<i>R'</i>	0.0460	0.0638
<i>G</i> (weight)	0.0003	0.0005
Goodness of fit	1.21	1.21
Largest diff. peak (e Å ⁻³)	0.64	1.20
Largest diff. hole (e Å ⁻³)	–0.62	–0.79

$R = (\sum ||F_o| - |F_c||) / \sum |F_o|$, $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, and goodness of fit is $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ where N_o is the number of observed reflections and N_v is the number of variables. Weighting scheme used of form $w^{-1} = [\sigma^2(F) + gF^2]$.

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