Structural Trends in Phosphine-substituted $[RuCo_xRh_{3-x}H(CO)_{12}]$ (x = 0—3) Clusters. Crystal Structures of $[RuCo_3H(CO)_{11}(PR_3)]$ (PR_3 = PMe_3 or PMe_2Ph), $[RuCo_2RhH(CO)_{11}(PMe_2Ph)]$, $[RuCo_xRh_{3-x}H(CO)_{10}(PPh_3)_2]$ (x = 1—2), and $[RuRh_3H(CO)_{11}(PR_3)]$ (PR_3 = PMe_3 or PMe_2Ph)†

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The crystal structures of $[RuCo_3H(CO)_{11}(PMe_3)]$, $[RuCo_3H(CO)_{11}(PMe_2Ph)]$, $[RuCo_2RhH(CO)_{11}(PMe_2Ph)]$, $[RuCo_{1.75}Rh_{1.25}H(CO)_{10}(PPh_3)_2]$, $[RuCoRh_2H(CO)_{10}(PPh_3)_2]$, $[RuRh_3H(CO)_{11}(PMe_3)]$, and $[RuRh_3H(CO)_{11}(PMe_2Ph)]$ show $[Rh_4(CO)_{12}]$-like ligand arrangements with phosphines on basal rhodium or cobalt atoms. The phosphines are axially co-ordinated except in the last two compounds, where equatorial co-ordination is found. Hydrides bridge Ru–Rh edges in $[RuRh_3H(CO)_{11}(PR_3)]$ (PR_3 = PMe_3 or PMe_2Ph) and basal M_3 faces in the other compounds. Geometric parameters are discussed with respect to the metal combination or ligand site.

Systematic synthesis and characterization of mixed-metal clusters is important for the development of a theoretical understanding of the influence of the metal composition on the properties of such compounds. Trends in structural and physical properties and chemical reactivity for a large group of clusters are valuable for the understanding of the role of a particular element in a mixed-metal cluster.

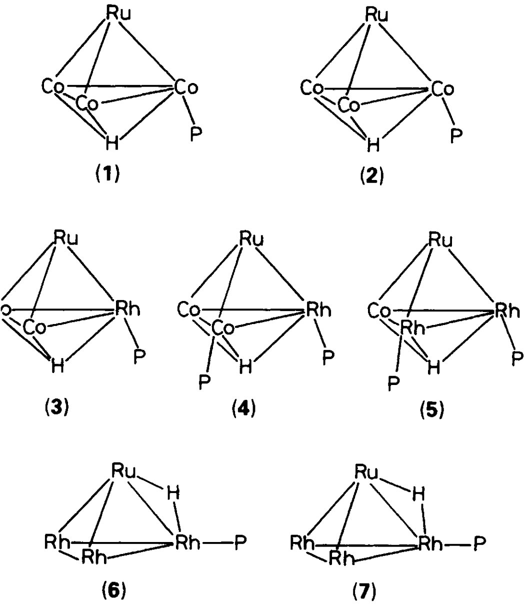
Tetranuclear dodecacarbonyl mixed-metal clusters of cobalt, rhodium, and ruthenium, $[M_4H_x(CO)_{12}]$ (x = 0—4), form an exceptionally large and well defined group of isoelectronic compounds. The parent carbonyl clusters of this group have been synthesized and characterized[1—6] except for $[CoRh_3(CO)_{12}]$, which is unstable.[7] These compounds can be expected to be important in studies of the influence of different metal combinations on the cluster properties, especially because most of the compounds have similar $[Rh_4(CO)_{12}]$-like carbonyl arrangements.

Phosphine-substituted derivatives of $[Co_xRh_{4-x}(CO)_{12}]$ (x = 0 or 2—4) have been widely studied.[8] We have previously studied trends in the hydride positions, reactivity with phosphines, and ^1H chemical shifts of $[RuCo_xRh_{3-x}H(CO)_{12}]$ (x = 0—3) and $[Ru_2Co_xRh_{2-x}H_2(CO)_{12}]$ (x = 0—2) clusters and their phosphine derivatives.[9,10]

In this work representative crystal structures of phosphine-substituted derivatives of $[RuCo_xRh_{3-x}H(CO)_{12}]$ (x = 0—3) have been determined and the structural differences observed with different metal compositions are discussed. The compounds are $[RuCo_3H(CO)_{11}(PMe_3)]$ (1), $[RuCo_3H(CO)_{11}(PMe_2Ph)]$ (2), $[RuCo_2RhH(CO)_{11}(PMe_2Ph)]$ (3), $[RuCo_{1.75}Rh_{1.25}H(CO)_{10}(PPh_3)_2]$ (4), $[RuCoRh_2H(CO)_{10}(PPh_3)_2]$ (5), $[RuRh_3H(CO)_{11}(PMe_3)]$ (6), and $[RuRh_3H(CO)_{11}(PMe_2Ph)]$ (7).

Results and Discussion

We have previously observed in solution systematic trends in hydride positions, reactivity with phosphines, and ^1H n.m.r. chemical shifts of $[RuCo_xRh_{3-x}H(CO)_{12}]$ (x = 0—3) and $[Ru_2Co_xRh_{2-x}H_2(CO)_{12}]$ (x = 0—2) clusters and their phosphine derivatives.[10] The crystal structures in this study were determined to establish in the solid state the main structural features deduced from the ^1H n.m.r. data and to obtain data on possible geometric trends with respect to the metal combinations or ligand sites. Schematic diagrams of the compounds are presented in Figure 1 and the crystal structures and numbering schemes of (2), (5), and (7) in Figures 2, 3, and 4, respectively. Metal–metal distances are presented in Table 1, metal–carbon, metal–phosphorus, and carbon–oxygen bond lengths in Table 2, and structurally important bond angles in Table 3.



(1) (2) (3) (4) (5) (6) (7)

Figure 1. Schematic structures of the seven compounds (1)—(7) showing the sites of metal atoms, hydride (H) and phosphine (P) ligands

All the compounds studied have closed tetrahedral metal cores surrounded by nine terminal carbonyl/phosphine ligands, three carbonyls bridging the basal metals, and one hydride ligand. In (5), however, carbonyl 8 semibridges the Ru(1)–Co(1) bond [Ru(1)–C(8) 253.1(6) and Co(1)–C(8) 176.2(9) pm].

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp xix—xxii.

Table 1. Metal–metal bond lengths (pm) in $[RuCo_3H(CO)_{11}(PMe_3)]$ (**1**), $[RuCo_3H(CO)_{11}(PMe_2Ph)]$ (**2**), $[RuCo_2RhH(CO)_{11}(PMe_2Ph)]$ (**3**), $[RuCo_{1.75}Rh_{1.25}H(CO)_{10}(PPh_3)_2]$ (**4**), $[RuCoRh_2H(CO)_{10}(PPh_3)_2]$ (**5**), $[RuRh_3H(CO)_{11}(PMe_3)]$ (**6**), and $[RuRh_3H(CO)_{11}(PMe_2Ph)]$ (**7**)

	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)	(**7**)
Ru(1)–M(1)	265.9(4)	256.4(1)	**270.7(1)**	269.9(2)	**274.9(1)**	**286.8(2)**	**287.0(1)**
Ru(1)–M(2)	266.9(4)	256.6(1)	264.2(1)	266.7(3)	**275.2(1)**	**272.4(3)**	**274.4(1)**
Ru(1)–M(3)	266.7(4)	256.5(1)	265.3(1)	266.3(3)	266.4(2)	**272.8(2)**	**272.5(1)**
M(1)–M(2)	252.5(5)	250.4(2)	*261.5(1)*	264.8(3)	**277.0(1)**	**272.2(2)**	**273.8(1)**
M(1)–M(3)	252.8(4)	249.1(1)	*261.9(1)*	259.5(3)	*266.1(1)*	**273.8(2)**	**272.9(1)**
M(2)–M(3)	251.5(5)	248.6(1)	256.5(1)	257.5(3)	*267.9(1)*	**279.2(2)**	**281.9(1)**

The Ru–Rh and Rh–Rh bonds are in bold and the Co–Rh bonds in italic type.

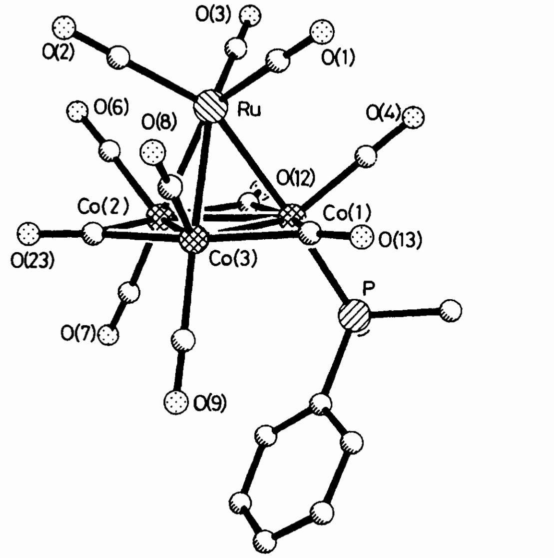

Figure 2. Crystal structure and numbering scheme of $[RuCo_3H(CO)_{11}(PMe_2Ph)]$, (**2**)

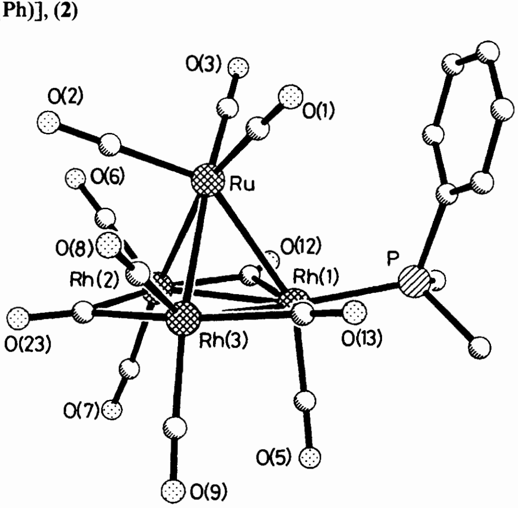

Figure 3. Crystal structure and numbering scheme of $[RuRh_3H(CO)_{11}(PMe_2Ph)]$, (**7**)

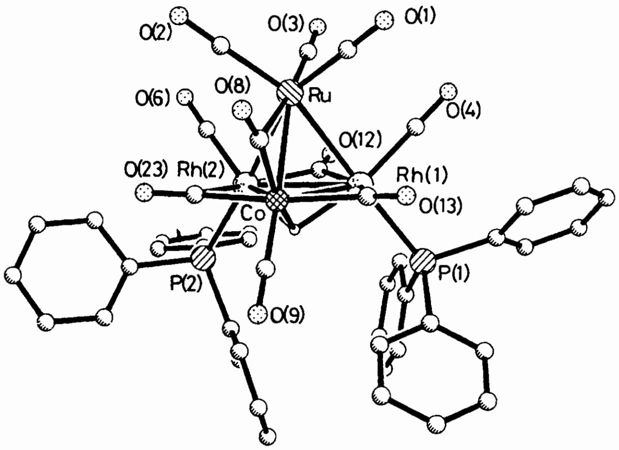

Figure 4. Crystal structure and numbering scheme of $[RuCoRh_2H(CO)_{10}(PPh_3)_2]$, (**5**)

The apical metal is ruthenium in all the compounds and phosphines are co-ordinated to basal cobalt or rhodium atoms. Due to the higher reactivity of rhodium with respect to cobalt, cobalt sites are occupied by phosphines only in compounds where no free rhodium sites are available.[9] Phosphines are axially co-ordinated in (**1**)—(**5**) and equatorially co-ordinated in (**6**) and (**7**). Equatorial phosphines are not common in mono- or di-substituted derivatives of $[M_4H_x(\mu\text{-}CO)_3(CO)_9]$ clusters (M_4 is a combination of Fe, Ru, Co, or Rh),[9] although examples like $[Rh_4(CO)_{10}(PPh_3)_2]$[11] are known. In the corresponding tri- and tetra-substituted clusters some of the phosphines are equatorially co-ordinated due to steric restrictions.

The hydride sites can be inferred from the data in Tables 1 and 3. The Ru(1)–Rh(1) bonds in compounds (**6**) and (**7**) are significantly longer than the other Ru–Rh distances as a result of the hydride bridge. The carbonyls also bend away from these bridged Ru–Rh edges as a result of the steric demands of the hydrides. The angles Ru(1)–Rh(1)–P(1) (117.4 and 115.3°), Rh(1)–Ru(1)–C(1) (107.7 and 106.8°), and Rh(1)–Ru(1)–C(3) (105.5 and 108.2°) are significantly larger than other corresponding angles. The large Rh(3)–Ru(1)–C(1) and Rh(3)–Ru(1)–C(2) angles in compound (**5**) are caused by the repulsion of the semibridging carbonyl CO(8). The average $M\text{-}M\text{-}C_{ax}/P_{ax}$ (M = Co or Rh) values are 119.6, 116.8, 118.7, 118.9, 123.3, 105.2, and 107.3° for compounds (**1**), (**2**), (**3**), (**4**), (**5**), (**6**), and (**7**), showing the angle opening due to $M_3(\mu\text{-}H)$ hydride in (**1**)—(**5**).

In solution, equatorial phosphines are connected with edge-bridging Ru(μ-H)Rh hydrides and axial phosphines are connected with face-bridging $M_3(\mu\text{-}H)$ (M = Co or Rh) hydrides, so that for the rhodium-containing compounds both isomers are present in different relative abundances. The relative abundance of the equatorial co-ordination of phosphines, together with the Ru(μ-H)Rh hydrides, increases with the metal combination (independent of the type of phosphine ligand) in the order $RuCo_2Rh < RuCoRh_2 < RuRh_3$, whereas for $[RuCo_3H(CO)_{12}]$ derivatives only axial phosphines are found.[9,12] Additionally the relative abundancies of the Ru(μ-H)Rh forms increase with different ligands in the order $PPh_3 < PMePh_2 < PMe_2Ph < PMe_3$.[10] The forms that are dominant in solution were those found in the crystal state [Ru(μ-H)Rh for (**6**) and (**7**) and $M_3(\mu\text{-}H)$ for the other

Table 2. Metal–carbon, metal–phosphorus, and carbon–oxygen bond lengths (pm) in compounds (**1**)—(**7**)

	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)	(**7**)
Ru(1)–C(1)	189(3)	187.9(11)	190.3(1)	181(2)	190.5(9)	193(2)	191.8(9)
Ru(1)–C(2)	188(3)	189.6(11)	192.6(5)	188(3)	191.1(8)	194(2)	190.0(12)
Ru(1)–C(3)	191(4)	187.9(9)	191.0(5)	183(2)	189.2(6)	194(2)	193.4(10)
M(1)–P(1)	222.3(8)	222.8(2)	*233.4(1)*	*232.1(5)*	*237.9(2)*	*232.3(5)*	*232.4(2)*
M(2)–P(2)				229.1(6)	*237.1(2)*		
M(1)–C(4)	176(3)	176.4(9)	*188.3(5)*	*176(2)*	*188.0(7)*		
M(1)–C(5)						*190(2)*	*187.3(11)*
M(2)–C(6)	175(3)	176.6(9)	176.6(5)	178(2)	*186.6(7)*	*193(2)*	*189.6(12)*
M(2)–C(7)	182(3)	180.1(8)	179.4(4)			*194(2)*	*197.1(10)*
M(3)–C(8)	174(3)	177.7(8)	178.0(4)	171(2)	*175.8(8)*	*190(2)*	*190.4(10)*
M(3)–C(9)	178(3)	183.8(8)	182.1(4)	172(2)	*176.6(7)*	*195(2)*	*195.2(11)*
M(1)–C(12)	191(3)	189.2(9)	*208.2(4)*	*201(2)*	*212.2(6)*	*215(2)*	*214.1(10)*
M(1)–C(13)	186(3)	190.6(8)	*209.6(4)*	*197(2)*	*210.0(6)*	*212(2)*	*215.6(8)*
M(2)–C(12)	202(3)	198.9(9)	201.9(5)	196(2)	*211.6(5)*	*207(2)*	*208.1(10)*
M(2)–C(23)	196(3)	196.0(9)	198.9(5)	199(2)	*210.8(5)*	*213(2)*	*211.9(8)*
M(3)–C(13)	196(3)	200.5(10)	199.0(5)	196(2)	199.6(7)	*214(2)*	*208.4(9)*
M(3)–C(23)	202(3)	195.8(11)	196.8(6)	194(2)	200.6(7)	*211(2)*	*210.8(9)*
C(1)–O(1)	113(3)	113.3(13)	113.4(6)	118(3)	113.6(12)	114(2)	113.5(11)
C(2)–O(2)	121(4)	109.0(14)	112.1(7)	115(2)	113.8(1)	111(3)	114.8(15)
C(3)–O(3)	118(5)	110.3(11)	113.2(6)	118(2)	114.5(8)	113(3)	112.8(12)
C(4)–O(4)	113(3)	112.5(12)	112.5(7)	118(2)	112.4(8)		
C(5)–O(5)						111(2)	113.7(14)
C(6)–O(6)	118(4)	113.5(12)	114.6(6)	115(2)	113.7(9)	109(2)	114.4(15)
C(7)–O(7)	116(4)	111.1(10)	112.8(5)			115(2)	111.0(12)
C(8)–O(8)	117(4)	112.4(10)	113.0(5)	118(3)	116.2(9)	110(3)	113.7(13)
C(9)–O(9)	117(4)	110.3(11)	111.8(5)	118(2)	115.1(9)	115(3)	112.3(14)
C(12)–O(12)	119(4)	120.7(10)	115.0(5)	120(2)	115.8(6)	115(2)	115.6(13)
C(13)–O(13)	121(3)	117.8(13)	115.3(6)	120(2)	116.3(9)	114(2)	115.6(11)
C(23)–O(23)	111(4)	115.4(15)	115.6(8)	119(2)	115.5(8)	117(2)	116.6(11)

The Rh–C and Rh–P bonds are in italic type.

Table 3. Selected bond angles (°) for compounds (**1**)—(**7**)

	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)	(**7**)
M(1)–Ru(1)–C(1)	96.8(8)	97.5(3)	94.6(1)	99.7(2)	96.7(3)	107.7(6)	106.8(4)
M(3)–Ru(1)–C(1)	100.5(8)	97.8(2)	97.5(1)	100.9(1)	104.9(2)	97.8(6)	97.8(3)
M(2)–Ru(1)–C(2)	107.3(10)	100.5(3)	106.8(1)	100.3(1)	102.9(3)	94.3(5)	93.0(2)
M(3)–Ru(1)–C(2)	103.7(9)	100.8(3)	105.0(1)	101.7(1)	108.0(2)	95.2(6)	92.5(3)
M(1)–Ru(1)–C(3)	99.7(11)	97.5(3)	95.2(1)	98.4(2)	94.4(2)	105.5(5)	108.2(3)
M(2)–Ru(1)–C(3)	102.0(12)	99.8(3)	101.3(1)	101.5(2)	94.3(3)	97.7(5)	102.1(2)
Ru(1)–M(1)–C(4)	83.5(9)	88.5(3)	90.8(2)	88.7(2)	83.2(2)		
Ru(1)–M(1)–P(1)						117.4(1)	115.3(1)
Ru(1)–M(2)–C(6)	74.7(11)	83.6(3)	72.8(2)	78.0(2)	84.9(2)	91.9(6)	87.2(3)
Ru(1)–M(3)–C(8)	76.1(10)	84.9(2)	78.4(1)	76.0(1)	66.2(2)	87.4(6)	90.5(3)
Ru(1)–M(1)–P(1)	179.3(3)	175.8(1)	172.2(1)	172.6(1)	175.4(1)		
Ru(1)–M(1)–C(5)						148.8(5)	151.8(3)
M(2)–M(1)–P(1)	117.5(3)	117.1(1)	116.5(1)	113.0(1)	123.8(1)		
M(2)–M(1)–C(5)						93.7(5)	98.9(3)
M(3)–M(1)–P(1)	117.7(3)	114.9(1)	112.6(1)	114.5(1)	119.6(1)		
M(3)–M(1)–C(5)						97.9(4)	97.6(3)
Ru(1)–M(2)–P(2)				177.0(1)	174.9(1)		
Ru(1)–M(2)–C(7)	176.3(9)	177.6(3)	174.5(2)			167.3(6)	171.0(3)
M(1)–M(2)–P(2)				119.7(2)	124.3(1)		
M(1)–M(2)–C(7)	118.5(9)	117.3(3)	123.4(2)			105.5(5)	110.2(4)
M(3)–M(2)–P(2)				122.1(1)	119.7(1)		
M(3)–M(2)–C(7)	121.7(9)	117.0(3)	121.5(1)			110.3(5)	113.1(3)
Ru(1)–M(3)–C(9)	176.5(11)	177.6(3)	179.4(2)	175.7(2)	169.5(3)	171.8(7)	171.4(3)
M(1)–M(3)–C(9)	121.5(10)	116.8(3)	118.8(2)	120.7(2)	125.5(2)	110.3(6)	108.1(3)
M(2)–M(3)–C(9)	120.8(10)	117.5(3)	119.1(2)	123.1(2)	126.8(3)	113.6(7)	115.6(3)
M(1)–C(12)–O(12)	146.0(24)	143.8(9)	140.8(4)	138.2(15)	138.4(5)	137.6(15)	137.2(8)
M(1)–C(13)–O(13)	142.5(21)	142.9(8)	138.3(4)	141.5(14)	138.2(5)	141.4(15)	136.0(7)
M(2)–C(12)–O(12)	134.2(22)	135.8(8)	140.0(4)	137.5(15)	139.3(5)	141.8(15)	141.9(9)
M(2)–C(23)–O(23)	144.4(24)	139.9(8)	138.9(4)	140.3(14)	139.8(5)	136.8(15)	136.9(7)
M(3)–C(13)–O(13)	134.5(20)	138.0(7)	141.9(4)	135.2(12)	140.6(4)	139.1(15)	143.7(7)
M(3)–C(23)–O(23)	137.3(24)	141.1(8)	140.2(4)	137.8(13)	138.7(5)	140.5(15)	139.4(7)

Table 4. Crystallographic data for compounds (**1**)—(**7**)

	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)	(**7**)
M	663.07	725.14	769.11	1 138.55	1 171.51	794.98	857.06
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$Pna2_1$	$P1$	$P1$	$P2_1/c$	$P1$	$Pna2_1$	$P1$
a/Å	17.145(8)	8.846(3)	8.945(3)	17.365(7)	13.079(6)	11.089(4)	9.164(5)
b/Å	10.708(5)	11.260(3)	11.455(5)	21.109(13)	13.844(6)	11.887(6)	11.147(5)
c/Å	11.971(5)	13.716(5)	13.738(5)	13.303(6)	14.118(5)	17.873(9)	14.356(9)
α/°	90	110.12(2)	110.35(3)	90	99.35(4)	90	71.75(4)
β/°	90	95.21(2)	95.97(3)	107.74(3)	103.61(3)	90	82.58(5)
γ/°	90	74.16(2)	73.45(3)	90	102.05(4)	90	71.58(4)
U/Å^3	2 198(2)	1 234.0(7)	1 265.1(9)	4 645(4)	2 369(2)	2 356(2)	1 321(1)
Z	4	2	2	4	2	4	2
D_c/g cm^{-3}	2.00	1.95	2.02	1.63	1.64	2.23	2.15
F(000)	1 288	708	744	1 744	1 120	1 504	816
Centring 2θ	8—18	8—26	13—29	9—26	15—25	14—22	15—22
No. centring reflections	11	12	13	11	21	15	11
2θ limits	5—55	5—50	3—50	4—45	4—50	4—55	4—55
No. of unique reflections	2 640	4 356	7 385	6 259	8 366	2 844	6 059
Obs. data [$I \geqslant 3\sigma(I)$]	1 040	3 568	5 025	2 118	5 373	1 733	3 571
μ/mm^{-1}	3.01	2.69	2.61	1.48	1.45	2.76	2.47
No. of parameters	145	316	364	279	563	270	316
R	0.054	0.058	0.033	0.052	0.032	0.038	0.039
R'	0.052	0.067	0.034	0.062	0.032	0.037	0.039
G (weight)	0.001	0.000 99	0.000 66	0.0005	0.0005	0.0005	0.0006
Goodness of fit	1.131	2.592	1.047	2.015	1.031	1.100	1.095

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

Table 5. Atomic co-ordinates (× 10^4) for [$RuCo_3H(CO)_{11}(PMe_3)$], (**1**)

Atom	x	y	z
Ru	743(1)	1 444(2)	2 500
Co(1)	1 293(2)	3 719(3)	2 916(3)
Co(2)	935(2)	2 354(3)	4 558(3)
Co(3)	−123(2)	3 278(3)	3 358(3)
P	1 744(5)	5 622(7)	3 281(7)
O(1)	453(12)	1 762(20)	33(19)
O(2)	−235(13)	−972(20)	2 611(21)
O(3)	2 305(14)	92(22)	2 080(20)
O(4)	2 191(11)	3 415(20)	896(17)
O(6)	1 342(13)	−264(23)	4 906(21)
O(7)	1 252(13)	3 225(21)	6 872(19)
O(8)	−1 240(13)	1 973(19)	1 946(18)
O(9)	−1 195(14)	5 235(23)	4 157(21)
O(12)	2 640(11)	2 579(19)	4 109(16)
O(13)	168(11)	4 805(18)	1 364(16)
O(23)	−658(14)	1 619(22)	5 155(21)
C(1)	557(14)	1 684(25)	963(22)
C(2)	97(17)	26(29)	2 619(27)
C(3)	1 701(23)	577(35)	2 264(33)
C(4)	1 839(15)	3 456(25)	1 697(23)
C(6)	1 167(16)	766(31)	4 657(28)
C(7)	1 129(17)	2 929(26)	5 957(27)
C(8)	−766(18)	2 473(26)	2 497(29)
C(9)	−750(18)	4 460(30)	3 887(26)
C(12)	1 979(17)	2 841(28)	3 898(24)
C(13)	394(14)	4 205(26)	2 161(22)
C(23)	−193(15)	2 096(24)	4 675(25)
C(41)	2 683(20)	5 790(35)	3 774(37)
C(51)	1 210(32)	6 540(49)	4 311(49)
C(61)	1 713(29)	6 564(39)	2 125(36)

compounds] and the relationship between the hydride and phosphine positions was observed in each of the crystal structures.

The average metal–metal bond distances are [Table 1, excluding bonds of (**4**) because of mixed occupancy): Ru–Co 262.8 (range 256.4—266.7), Ru–Rh 273.7 (272.5—274.9), Ru(μ-H)Rh 286.9, Co–Co 251.6 (248.6—256.5), Co–Rh 264.4 (261.5—267.9), and Rh–Rh 275.8 pm (272.2—281.9). Equatorial phosphines in compounds (**6**) and (**7**) make the Rh(1)–Rh(2) and Rh(1)–Rh(3) bonds (which are *trans* to the phosphine) shorter with respect to the Rh(2)–Rh(3) bond, whereas the axial phosphines in (**1**) and (**2**) seem to have no effect on the Ru–Co and Co–Co distances.

The phosphine ligands cause asymmetry of the carbonyls, which bridge a metal with a M–P bond and a metal without a M–P bond. In the $RuCo_3$ compounds (**1**) and (**2**) the carbonyls CO(12) and CO(13) have stronger bonds to M(1) as evidenced by shorter M–C bonds and larger M(1)–C(12)–O(12) and M(1)–C(13)–O(13) angles. The corresponding carbonyls in $RuRh_3$ compounds (**6**) and (**7**), however, have stronger bonds to metals M(2) and M(3) on grounds of the M–C bond distances. In the latter compounds there is no significant difference in the M–C–O bond angles. This reflects the different influence of axial and equatorial phosphines. In both [$RuCo_3H(CO)_{11}(PPh_3)_2$] and [$RuRh_3H(CO)_{11}(PPh_3)_2$],[6] which have axial phosphines, the bridging carbonyls have stronger bonds to metals with phosphines but the carbonyls CO(13) and CO(23) in (**5**) are relatively symmetrical according to the M–C–O angles (Co–C and Rh–C bond lengths are naturally different). Bridging carbonyls are asymmetric also in [$Rh_4(CO)_{10}(PPh_3)_2$],[11] [$Co_4(CO)_{11}(PPh_3)$],[13] and [$Co_4(CO)_{10}\{P(OCH_3)_3\}_2$].[13] This reflects electronic differences between the carbonyl and phosphine ligands.

The phenyl groups in the PMe_2Ph derivatives (**2**), (**3**), and (**7**) are oriented so as to cap the hydride ligand. This implies that the steric demands of the hydride ligand cause the carbonyl coverage to open so as to make room for the phenyl group.[14] In compound (**7**) the Ru(1)–Rh(1)–P(1)–C(41) (phenyl carbon) torsion angle is 13.1°. In (**6**) the corresponding Ru–Rh(1)–P–C(41) (methyl carbon) torsion angle is only −2.1°, showing the more symmetrical structure of (**6**). The axial phenyl groups are also orientated asymmetrically. The M(2)–M(1)–P–C and M(3)–M(1)–P–C torsion angles {C is the carbon which is nearest the M_3(μ-H) hydride [phenyl carbon for (**2**) and (**3**)

Table 6. Atomic co-ordinates (× 10^4) for [$RuCo_3H(CO)_{11}(PMe_2Ph)$], (**2**)

Atom	*x*	*y*	*z*
Ru	3 523(1)	2 067(1)	1 315(1)
Co(1)	3 432(1)	4 498(1)	2 183(1)
Co(2)	2 674(1)	3 298(1)	3 216(1)
Co(3)	919(1)	3 832(1)	1 820(1)
P	3 166(2)	6 639(2)	2 955(2)
O(1)	3 662(9)	1 970(8)	−898(5)
O(2)	2 432(10)	−348(7)	901(6)
O(3)	6 943(8)	995(8)	1 606(7)
O(4)	6 090(8)	4 088(7)	918(6)
O(6)	4 284(9)	847(7)	3 536(6)
O(7)	1 665(8)	4 740(7)	5 358(5)
O(8)	−307(9)	2 224(7)	−52(5)
O(9)	−2 014(9)	5 909(8)	2 441(7)
O(12)	5 769(7)	3 923(7)	3 748(5)
O(13)	1 651(8)	5 170(7)	451(5)
O(23)	−146(9)	2 307(8)	2 860(6)
C(1)	3 612(11)	1 994(8)	−69(8)
C(2)	2 840(11)	531(9)	1 061(7)
C(3)	5 677(11)	1 389(8)	1 500(7)
C(4)	5 061(10)	4 245(8)	1 415(6)
C(6)	3 656(10)	1 789(8)	3 383(6)
C(7)	2 041(9)	4 221(8)	4 535(6)
C(8)	188(10)	2 847(8)	664(6)
C(9)	−901(11)	5 143(9)	2 218(7)
C(12)	4 556(9)	3 962(8)	3 265(6)
C(13)	1 918(9)	4 748(7)	1 142(6)
C(23)	667(10)	2 882(9)	2 727(7)
C(41)	1 197(9)	7 603(7)	3 463(6)
C(42)	757(11)	7 700(9)	4 429(7)
C(43)	−681(13)	8 431(11)	4 816(9)
C(44)	−1 746(14)	9 010(11)	4 220(10)
C(45)	−1 335(15)	8 953(12)	3 285(10)
C(46)	149(12)	8 268(11)	2 899(8)
C(51)	4 454(11)	7 088(9)	4 056(7)
C(61)	3 681(13)	7 373(10)	2 094(8)

Table 7. Atomic co-ordinates (× 10^4) for [$RuCo_2RhH(CO)_{11}(PMe_2Ph)$], (**3**)

Atom	*x*	*y*	*z*
Ru	3 452(1)	2 059(1)	1 363(1)
Rh	3 514(1)	4 562(1)	2 210(1)
Co(2)	2 604(1)	3 425(1)	3 304(1)
Co(3)	847(1)	3 962(1)	1 834(1)
P	3 204(1)	6 782(1)	2 971(1)
O(1)	3 756(5)	1 911(4)	−861(3)
O(2)	2 424(5)	−416(4)	787(3)
O(3)	6 929(4)	957(4)	1 628(3)
O(4)	6 259(5)	4 028(5)	879(3)
O(6)	4 093(5)	881(3)	3 429(3)
O(7)	1 694(4)	4 622(4)	5 484(3)
O(8)	−217(4)	2 219(4)	−25(3)
O(9)	−2 091(4)	6 013(4)	2 328(3)
O(12)	5 771(4)	3 857(4)	3 876(3)
O(13)	1 636(4)	5 062(4)	340(3)
O(23)	−261(4)	2 523(4)	2 891(3)
C(1)	3 633(5)	1 980(4)	−28(3)
C(2)	2 793(5)	501(4)	1 010(3)
C(3)	5 634(6)	1 363(4)	1 528(4)
C(4)	5 246(5)	4 241(5)	1 393(4)
C(6)	3 553(6)	1 831(4)	3 268(3)
C(7)	2 030(5)	4 209(4)	4 639(3)
C(8)	274(5)	2 846(4)	693(3)
C(9)	−952(5)	5 256(5)	2 160(4)
C(12)	4 620(5)	3 926(4)	3 414(3)
C(13)	1 816(5)	4 738(4)	1 060(3)
C(23)	582(5)	3 052(4)	2 757(3)
C(41)	1 261(5)	7 700(4)	3 478(3)
C(42)	836(6)	7 714(5)	4 427(4)
C(43)	−648(7)	8 390(6)	4 817(5)
C(44)	−1 729(7)	8 999(6)	4 248(6)
C(45)	−1 341(8)	8 987(7)	3 336(6)
C(46)	145(7)	8 346(6)	2 918(4)
C(51)	4 495(6)	7 281(5)	4 058(4)
C(61)	3 592(7)	7 502(5)	2 072(4)
H(1)	1 867(62)	4 745(52)	2 957(41)

and methyl carbon for (**1**)]} are −46.4 and 21.9, −50.5 and 14.5, and −43.5 and 24.9° for compounds (**1**), (**2**), and (**3**), respectively.

Experimental

Preparations of the compounds have been described previously.[10] Pure samples of (**3**) and (**5**) were obtained by t.l.c. on silica gel 60 F_{254} plates (Merck) using hexane–CH_2Cl_2 mixtures as eluants, suitable crystals of (**1**)—(**7**) were grown from CH_2Cl_2–hexane mixtures by slow evaporation at room temperature.

Crystallography.—Details of crystal parameters, data collection parameters, and refined data for complexes (**1**)—(**7**) are summarized in Table 4. Intensity measurements were made on a Nicolet R3m diffractometer using graphite-monochromatized Mo-K_α radiation (ω scan mode with scan width 1° from $K_{\alpha_{12}}$ and scan speed 2.02—29.3° min^{-1}) for (**1**)—(**3**) and (**5**)—(**7**) and on a Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo-K_α radiation ($\omega - 2\theta$ scan mode, scan width $0.80 + 0.35 \tan\theta$, and scan speed 1 − 16.5° min^{-1}) for (**4**). All data sets were corrected for Lorentz and polarization factors. Empirical absorption corrections were made from ψ-scan data for (**1**)—(**3**) and (**5**)—(**7**) and for (**4**) as described by Walker and Stuart.[15] For (**1**) and (**6**) the values of R, R', and the goodness of fit for the two alternative absolute structures were effectively the same.

Structure analysis and refinement. The crystal structures were determined by direct methods and subsequent Fourier synthesis using the SDP program package[16] for compound (**4**) and SHELXTL[17] for the others. Cobalt atoms were distinguished from the second-row transition metals crystallographically [for compound (**4**) mixed occupancies were observed]. Compounds (**3**)—(**7**) contain second-row metals both in the apical site and in at least one of the basal sites. The apical metal in each of the compounds was deduced to be ruthenium from ^1H n.m.r. spectra.[9,10] Metal, phosphorus, oxygen, and carbon atoms were refined anisotropically except in (**1**), where only isotropic refinement was possible for oxygen and carbon atoms due to the low-reflection-to-parameter ratio (small crystal). The phenyl rings were refined as rigid groups with individual isotropic thermal parameters except in (**3**) and (**4**) where also the phenyl carbon atoms were refined independently, anisotropically in (**3**) and isotropically in (**4**). Hydrogen atoms were placed at calculated positions with fixed isotropic thermal parameters except in (**3**), where they were refined isotropically. The hydride ligand could be located only in (**3**) and (**5**) from final difference maps and was found to bridge the basal metal atom face as indicated also by ^1H n.m.r. results.[10] In (**4**) the metal atom sites M(1) and M(2) are disordered, being occupied by Rh and Co with population parameters 0.75, 0.5 for Rh and 0.25, 0.5 for Co, respectively. The final atomic co-ordinates for compounds (**1**)—(**7**) are presented in Tables 5—11, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Table 8. Atomic co-ordinates for $[RuCo_{1.75}Rh_{1.25}H(CO)_{10}(PPh_3)_2]$, (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.712 6(1)	0.176 83(7)	0.298 1(1)	C(116)	0.853(1)	−0.095 0(8)	0.419(1)
M(1)	0.709 8(1)	0.049 04(7)	0.301 7(1)	C(121)	0.603(1)	−0.084 2(9)	0.324(1)
M(2)	0.801 4(1)	0.108 89(9)	0.205 3(1)	C(122)	0.566(1)	−0.053(1)	0.381(2)
Co	0.646 4(1)	0.108 5(1)	0.125 1(2)	C(123)	0.495(2)	−0.071(1)	0.405(2)
P(1)	0.696 1(3)	−0.060 2(2)	0.307 6(4)	C(124)	0.459(2)	−0.121(1)	0.360(2)
P(2)	0.880 2(3)	0.059 8(2)	0.118 5(3)	C(125)	0.489(2)	−0.151(1)	0.295(2)
O(1)	0.576 1(9)	0.205 0(7)	0.384(1)	C(126)	0.564(1)	−0.138(1)	0.279(2)
O(2)	0.737 3(9)	0.309 4(6)	0.226(1)	C(131)	0.696(1)	−0.104 4(9)	0.190(1)
O(3)	0.835 4(8)	0.191 2(6)	0.512(1)	C(132)	0.641(1)	−0.090 2(9)	0.095(1)
O(4)	0.710 1(8)	0.065 0(7)	0.521(1)	C(133)	0.632(1)	−0.123 4(9)	0.004(1)
O(6)	0.912 0(8)	0.214 8(6)	0.287(1)	C(134)	0.682(1)	−0.169(1)	0.008(2)
O(8)	0.545 7(9)	0.219 2(8)	0.089(1)	C(135)	0.744(2)	−0.186(1)	0.089(2)
O(9)	0.554 5(8)	0.045 1(6)	−0.067(1)	C(136)	0.748(2)	−0.155(1)	0.190(2)
O(12)	0.889 1(7)	0.053 5(6)	0.412 1(9)	C(211)	0.826 1(9)	0.038 5(7)	−0.020(1)
O(13)	0.529 7(7)	0.066 0(6)	0.230 8(9)	C(212)	0.757(1)	0.003 5(8)	−0.039(1)
O(23)	0.731 7(8)	0.182 2(6)	0.005(1)	C(213)	0.709(1)	−0.010 2(9)	−0.144(1)
C(1)	0.630(1)	0.194(1)	0.350(2)	C(214)	0.738(1)	0.010 5(8)	−0.225(1)
C(2)	0.727(1)	0.259 4(9)	0.254(1)	C(215)	0.806(1)	0.042 6(8)	−0.206(1)
C(3)	0.789(1)	0.185 7(8)	0.427(1)	C(216)	0.854(1)	0.059 7(8)	−0.201(1)
C(4)	0.706(1)	0.059 8(9)	0.431(1)	C(221)	0.962 9(9)	0.109 2(8)	0.108(1)
C(6)	0.867(1)	0.174 6(9)	0.253(1)	C(222)	0.946(1)	0.172 0(9)	0.070(1)
C(8)	0.593(1)	0.177(1)	0.115(2)	C(223)	1.006(1)	0.215 1(9)	0.065(1)
C(9)	0.592(1)	0.071 8(9)	0.010(1)	C(224)	1.085(1)	0.191 4(9)	0.095(1)
C(12)	0.830(1)	0.062 5(9)	0.339(1)	C(225)	1.103(1)	0.134 0(8)	0.126(1)
C(13)	0.597(1)	0.068 1(8)	0.223(1)	C(226)	1.042(1)	0.090 9(8)	0.131(1)
C(23)	0.729(1)	0.148 6(8)	0.076(1)	C(231)	0.930(1)	−0.013 3(7)	0.177(1)
C(111)	0.774(1)	−0.096 8(8)	0.414(1)	C(232)	0.988(1)	−0.010 9(8)	0.278(1)
C(112)	0.754(1)	−0.122 8(9)	0.498(1)	C(233)	1.029(1)	−0.064 6(9)	0.325(1)
C(113)	0.816(1)	−0.149(1)	0.585(2)	C(234)	1.014(1)	−0.120 3(9)	0.274(1)
C(114)	0.894(1)	−0.148(1)	0.586(2)	C(235)	0.958(1)	−0.124 2(9)	0.175(1)
C(115)	0.913(1)	−0.121 3(9)	0.502(1)	C(236)	0.917(1)	−0.070 0(8)	0.128(1)

Table 9. Atomic co-ordinates (× 10^4) for $[RuCoRh_2H(CO)_{10}(PPh_3)_2]$, (**5**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	1 770(1)	2 188(1)	8 949(1)	C(120)	4 408(4)	1 769(4)	9 146(4)
Rh(2)	1 603(1)	3 214(1)	7 414(1)	C(121)	4 883(5)	1 210(5)	8 558(5)
Ru	132(1)	3 148(1)	8 527(1)	C(122)	5 861(5)	1 640(6)	8 412(5)
Co	140(1)	1 488(1)	7 277(1)	C(123)	6 392(5)	2 633(6)	8 853(6)
P(1)	3 086(1)	1 253(1)	9 341(1)	C(124)	5 949(5)	3 194(5)	9 460(6)
P(2)	2 740(1)	3 258(1)	6 329(1)	C(125)	4 961(5)	2 780(5)	9 599(5)
O(1)	−1 061(5)	2 404(6)	9 982(5)	C(130)	2 686(4)	−71(4)	8 670(4)
O(2)	−1 547(5)	4 120(5)	7 444(5)	C(131)	2 149(6)	−315(4)	7 656(5)
O(3)	1 386(5)	5 124(4)	10 014(5)	C(132)	1 859(6)	−1 296(5)	7 108(5)
O(4)	1 762(4)	2 906(4)	11 072(3)	C(133)	2 087(6)	−2 054(5)	7 571(6)
O(6)	1 509(5)	5 374(4)	7 501(4)	C(134)	2 609(6)	−1 832(5)	8 563(6)
O(8)	−2 115(4)	1 410(4)	7 100(5)	C(135)	2 920(5)	−854(4)	9 125(5)
O(9)	−302(6)	−440(4)	5 866(4)	C(210)	2 010(5)	3 312(5)	5 074(4)
O(12)	3 380(3)	4 288(3)	9 386(3)	C(211)	2 003(6)	2 674(5)	4 218(5)
O(13)	25(4)	277(4)	8 836(4)	C(212)	1 415(8)	2 732(7)	3 274(5)
O(23)	−392(4)	2 466(4)	5 563(3)	C(213)	855(7)	3 436(8)	3 185(6)
C(1)	−627(6)	2 661(6)	9 422(6)	C(214)	852(7)	4 080(8)	4 004(7)
C(2)	−917(6)	3 753(6)	7 835(6)	C(215)	1 408(6)	4 016(7)	4 953(5)
C(3)	930(6)	4 374(6)	9 454(6)	C(220)	3 906(5)	4 363(5)	6 687(5)
C(4)	1 756(5)	2 631(5)	10 276(5)	C(221)	4 633(6)	4 579(6)	7 608(5)
C(6)	1 518(5)	4 548(5)	7 450(4)	C(222)	5 557(7)	5 394(7)	7 905(6)
C(8)	−1 171(6)	1 592(6)	7 301(6)	C(223)	5 739(7)	6 004(7)	7 270(7)
C(9)	−113(6)	323(6)	6 424(5)	C(224)	5 028(9)	5 818(8)	6 358(8)
C(12)	2 706(5)	3 603(4)	8 861(4)	C(225)	4 112(7)	4 995(6)	6 044(6)
C(13)	422(5)	921(5)	8 497(5)	C(230)	3 324(5)	2 183(5)	6 101(4)
C(23)	157(5)	2 396(5)	6 306(5)	C(231)	2 629(7)	1 220(5)	5 862(5)
C(110)	3 399(5)	1 159(4)	10 652(4)	C(232)	3 038(10)	382(7)	5 633(7)
C(111)	4 447(5)	1 422(5)	11 285(5)	C(233)	4 084(11)	496(9)	5 652(8)
C(112)	4 630(7)	1 347(6)	12 282(5)	C(234)	4 776(9)	1 432(10)	5 890(7)
C(113)	3 777(7)	1 012(6)	12 647(5)	C(235)	4 408(6)	2 301(7)	6 110(6)
C(114)	2 731(6)	737(5)	12 029(5)	H(1)	1 581(36)	1 905(34)	7 603(33)
C(115)	2 530(5)	808(5)	11 039(5)				

Table 10. Atomic co-ordinates (× 10^4) for [$RuRh_3H(CO)_{11}(PMe_3)$], (**6**)

Atom	*x*	*y*	*z*
Rh(1)	3 635(1)	1 313(1)	2 500
Rh(2)	4 820(1)	2 644(1)	1 773(2)
Rh(3)	3 673(1)	3 720(2)	3 011(1)
Ru	4 713(1)	2 293(2)	4 036(2)
P	3 175(3)	−603(4)	2 879(5)
O(1)	3 999(10)	2 235(14)	6 385(11)
O(2)	5 792(8)	4 321(14)	4 643(12)
O(3)	5 916(9)	340(14)	4 261(14)
O(5)	2 821(8)	1 513(14)	286(10)
O(6)	6 509(8)	2 619(17)	1 835(16)
O(7)	6 547(11)	2 913(16)	−777(12)
O(8)	3 719(9)	5 308(16)	5 056(14)
O(9)	2 534(12)	5 113(17)	1 550(20)
O(12)	5 002(9)	−82(14)	1 566(12)
O(13)	2 410(8)	2 254(12)	4 142(13)
O(23)	4 932(10)	5 395(12)	2 129(12)
C(1)	4 273(12)	2 276(17)	5 518(15)
C(2)	5 389(12)	3 606(17)	4 409(13)
C(3)	5 483(11)	1 075(16)	4 176(15)
C(5)	3 116(10)	1 433(13)	1 105(13)
C(6)	5 898(10)	2 654(18)	1 835(18)
C(7)	4 657(11)	2 883(16)	173(16)
C(8)	3 701(11)	4 714(15)	4 316(16)
C(9)	2 957(12)	4 599(19)	2 091(20)
C(12)	4 688(10)	795(17)	1 765(14)
C(13)	2 913(11)	2 351(16)	3 566(15)
C(23)	4 619(10)	4 473(18)	2 222(13)
C(41)	3 530(20)	−1 318(27)	4 061(33)
C(51)	2 201(15)	−690(25)	3 127(36)
C(61)	3 277(26)	−1 636(20)	1 785(38)

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Table 11. Atomic co-ordinates (× 10^4) for [$RuRh_3H(CO)_{11}$-(PMe_2Ph)], (**7**)

Atom	*x*	*y*	*z*
Ru	1 655(1)	8 491(1)	2 221(1)
Rh(1)	3 628(1)	9 597(1)	2 874(1)
Rh(2)	4 616(1)	7 063(1)	2 746(1)
Rh(3)	2 332(1)	7 791(1)	4 147(1)
P	3 281(3)	11 839(2)	2 135(2)
O(1)	−1 619(9)	10 267(9)	2 374(6)
O(2)	675(9)	6 024(8)	2 509(6)
O(3)	1 897(9)	9 215(8)	−22(5)
O(5)	6 033(8)	9 382(9)	4 209(6)
O(6)	4 683(10)	5 669(8)	1 222(6)
O(7)	7 839(9)	5 586(10)	3 582(7)
O(8)	−699(9)	7 152(9)	4 783(6)
O(9)	3 335(10)	7 280(9)	6 230(6)
O(12)	5 893(10)	9 091(8)	1 152(6)
O(13)	778(8)	10 708(6)	4 097(5)
O(23)	3 567(8)	4 830(6)	4 267(5)
C(1)	−408(11)	9 602(10)	2 307(7)
C(2)	1 050(10)	6 951(10)	2 397(6)
C(3)	1 832(10)	8 945(9)	804(7)
C(5)	5 118(10)	9 474(9)	3 705(7)
C(6)	4 657(11)	6 189(9)	1 798(7)
C(7)	6 672(11)	6 152(10)	3 299(7)
C(8)	433(11)	7 390(9)	4 534(6)
C(9)	3 060(10)	7 420(9)	5 456(7)
C(12)	5 179(11)	8 736(9)	1 851(7)
C(13)	1 686(10)	9 831(9)	3 893(6)
C(23)	3 517(9)	5 939(8)	3 927(6)
C(41)	1 530(11)	12 651(8)	1 455(7)
C(42)	165(12)	13 222(11)	1 881(9)
C(43)	−1 184(16)	13 717(16)	1 403(16)
C(44)	−1 189(26)	13 696(19)	486(18)
C(45)	118(29)	13 151(19)	−5(14)
C(46)	1 494(17)	12 613(13)	508(9)
C(51)	3 163(14)	12 777(10)	2 988(9)
C(61)	4 779(12)	12 278(10)	1 266(9)

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