Synthesis of Ruthenium–Rhodium Heterobimetallic Complexes *via* Ring-opening Reactions of Bidentate Phosphine Ligands; Crystal Structures of $[Ru(C_5H_5)Cl\{Ph_2PC(=CH_2)PPh_2\}]$ and $[(C_5H_5)Ru(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PC(=CH_2)PPh_2\}RhCl_2]$†

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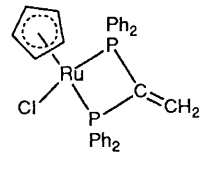
Treatment of $[Ru(C_5H_5)Cl(dppen)]$ **1** [dppen = 1,1-bis(diphenylphosphino)ethene] and $[Ru(C_5H_5)Cl(dppm)]$ **2** [dppm = bis(diphenylphosphino)methane] with $[\{RhCl(CO)_2\}_2]$ leads to the immediate formation of the heterobimetallic complexes $[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}L_2)RhCl_2]$ (L_2 = dppen **3** or dppm **4**) in high yield. The structures of complexes **1** and **3** have been determined by X-ray diffraction.

Ring-opening (or metal-insertion) reactions of chelated bidentate phosphine ligands provide a useful route to ligand-bridged heterobimetallic complexes.[1–3] In these reactions the reactant is usually a mononuclear complex containing a chelating phosphine ligand as part of a four-membered ring. On reaction with an appropriate metal complex, this four-membered ring opens to produce a ligand-bridged bimetallic complex in which the bidentate ligand becomes part of a less-strained five-membered ring. We recently reported an example of this type of reaction in which the ligand dppen [dppen = $Ph_2PC(=CH_2)PPh_2$] when chelated to an iron atom in the complex $[Fe(CO)_3(dppen)]$ undergoes a ring-opening (or metal-insertion) reaction on treatment with $[\{RhCl(CO)_2\}_2]$ to form the heterobimetallic complex $[(OC)_4Fe(\mu\text{-dppen})Rh(CO)Cl]$.[3,4]

We now report an extension of this work to ruthenium complexes. This paper describes the preparation and X-ray structures of $[Ru(C_5H_5)Cl(dppen)]$ **1** and $[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-dppen})RhCl_2]$ **3**, and the preparation and spectroscopic characterisation of the analogous bis(diphenylphosphino) methane (dppm) complexes.



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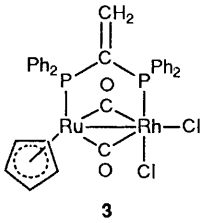

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Results and Discussion

The complex $[Ru(C_5H_5)Cl(dppm)]$ **2** is prepared by a ligand exchange reaction between $[Ru(C_5H_5)Cl(PPh_3)_2]$ and dppm.[5] A similar reaction using dppen in place of dppm gives rise to the complex $[Ru(C_5H_5)Cl(dppen)]$ **1** in high yield. This complex has been characterised spectroscopically (see Table 1) and by an X-ray crystal structure determination. The molecular structure of **1** is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The molecule has the expected piano-stool structure. The interesting feature of this molecule is the compression of the P(1)–C(25)–P(2) angle to 95.3(2)° compared to an angle of 119° in the free ligand,[6] brought about by the chelation of the dppen ligand to the Ru atom. An angle of about

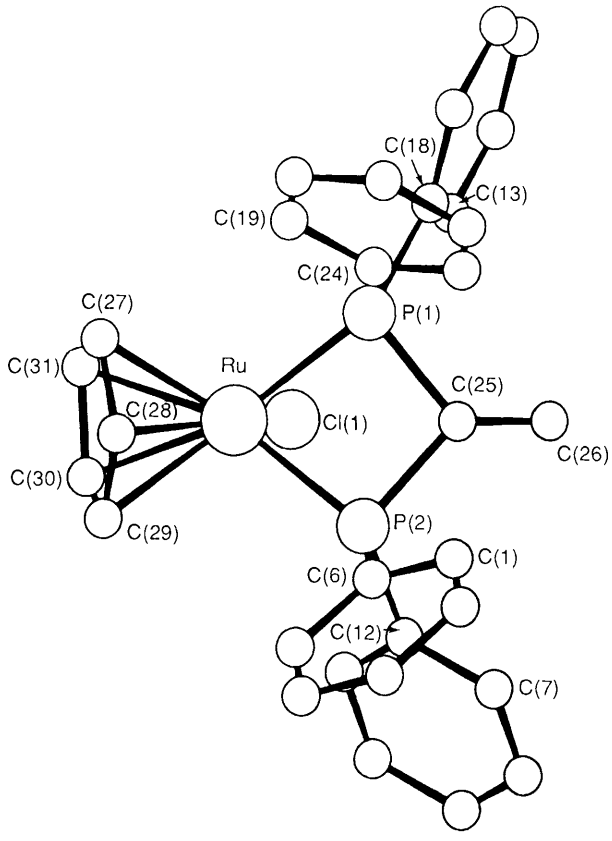

Fig. 1 The molecular structure of $[Ru(C_5H_5)Cl(dppen)]$ **1**

† [1,1-Bis(diphenylphosphino-κ*P*)ethene]chloro(η⁵-cyclopentadienyl)-ruthenium(II) and μ-[1,1-bis(diphenylphosphino)ethene-1κ*P*;2κ*P*′]-di-μ-carbonyl-dichloro-2κ²*Cl*-[1(η⁵)-cyclopentadienyl]rhodium-ruthenium(*Rh–Ru*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Spectroscopic data

Complex	$^{31}P-\{^1H\}$ NMR[a]	ν(CO)/cm^{-1}[b]
1 $[Ru(C_5H_5)Cl(dppen)]$	31.8 (s)	
2 $[Ru(C_5H_5)Cl(dppm)]$	12.4 (s)	
3 $[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppen)RhCl_2]$	56.8 (dd, J_{PP} 120, J_{PRh} 9.8) 43.6 (dd, J_{PP} 120, J_{PRh} 118)	1859w, 1820s
4 $[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppm)RhCl_2]$	55.9 (d, J_{PP} 69) 45.5 (dd, J_{PP} 69, J_{PRh} 124)	1855w, 1818s

[a] Recorded in $CDCl_3$ solution, chemical shift δ (ppm) relative to H_3PO_4. Coupling constants in Hz. [b] In CH_2Cl_2.

Table 2 Selected bond lengths (Å) and angles (°) for $[Ru(C_5H_5)Cl(dppen)]$ **1**

Ru(1)–Cl(1)	2.439(1)	Ru(1)–C(28)	2.183(5)
Ru(1)–P(1)	2.328(1)	Ru(1)–C(29)	2.207(5)
Ru(1)–P(2)	2.284(1)	Ru(1)–C(30)	2.187(5)
Ru(1)–C(27)	2.218(5)	Ru(1)–C(31)	2.235(5)
P(1)–Ru(1)–P(2)	71.7(1)	P(2)–Ru(1)–Cl(1)	91.7(1)
P(1)–Ru(1)–Cl(1)	91.1(1)	P(1)–C(25)–P(2)	95.3(2)

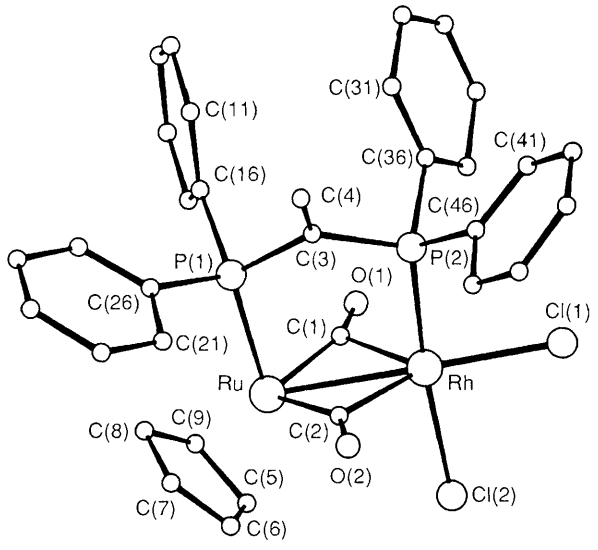

Fig. 2 The molecular structure of $[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppen)RhCl_2]$ **3**

95° is commonly observed in chelating phosphine ligands involved in four-membered rings.[7]

We reasoned that the strain induced by chelation, as evidenced by the reduced PCP bond angle, should make complex **1** susceptible to ring opening reactions. Indeed, treatment of a toluene solution of **1** with an equimolar (with respect to Rh) quantity of $[\{RhCl(CO)_2\}_2]$ at room temperature leads to the immediate formation of the yellow heterobimetallic complex, $[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppen)RhCl_2]$ **3** in high yield. Complex **3** has been characterised both spectroscopically and by a single crystal X-ray structure determination. The $^{31}P-\{^1H\}$ NMR spectrum of complex **3** (see Table 1) shows a doublet of doublets centred at δ 56.8 ($^2J_{PP}$ 120, $^2J_{PRh}$ 9.8 Hz) and doublet of doublets centred at δ 43.6 ($^2J_{PP}$ 120, $^1J_{PRh}$ 118 Hz) due to the phosphorus atom co-ordinated to Ru and the phosphorus atom co-ordinated to Rh, respectively. The IR spectrum of **3** indicated the presence of bridging carbonyl ligands (ν_{CO} 1859 and 1820 cm^{-1}). In order fully to determine the structure of **3** an X-ray crystal structure determination was carried out. The molecular structure of **3** is shown in Fig. 2 and selected bond lengths and angles are given in Table 4. The molecule consists of a $(C_5H_5)Ru$ unit and an $RhCl_2$ unit joined together by a bridging dppen ligand, two semi-bridging CO ligands, and a metal–metal bond. The Ru–Rh distance, 2.697(1) Å, is somewhat shorter than those found, for example, in $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(C_5H_5)]$[8] (av. 2.719 Å), but similar to those in $[RuRh_3(\mu_3\text{-}CO)_2(CO)_3(C_5Me_5)_3]$ (av. 2.682 Å).[9] The carbonyl ligands do not bridge symmetrically the Ru–Rh bond, the Ru–C(1) and Ru–C(2) distances being significantly shorter than the Rh–C(1) and Rh–C(2) distances, and the Ru–C(1)–O(1) and Ru–C(2)–O(2) angles being significantly greater than the Rh–C(1)–O(1) and Rh–C(2)–O(2) angles. The P(1)–C(3)–P(2) angle of 115° is very close to that found in the free ligand (119°),[6] and reflects the lack of strain at that carbon atom when it is involved in a five-membered ring. The carbon–carbon double bond in the dppen ligand [C(3)–C(4) 1.31 Å] also has not changed significantly from that found in the free ligand. It is noteworthy that the two Cl ligands on the Rh atom show significantly different Rh–Cl bond lengths. The Rh–Cl bond *trans* to phosphine is longer [2.377(3) Å] than the Rh–Cl bond *trans* to Ru [2.329(3) Å].

In the ruthenium-dppm complex, $[Ru(C_5H_5)Cl(dppm)]$ **2**, there is somewhat less strain involved at the central carbon atom of the chelating dppm ligand since this carbon atom is sp^3 hybridised, and the PCP angle is thus only reduced from 109 to 95° on chelation in contrast to the dppen ligand, where the central carbon atom is sp^2 hybridised and the PCP angle is reduced from 119 to 95° on chelation. Nevertheless, we find that treatment of complex **2** with $[\{RhCl(CO)_2\}_2]$ at room temperature leads to the immediate formation of the heterobimetallic complex, $[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppm)RhCl_2]$ **4**. Complex **4** has been characterised spectroscopically (see Table 1). ^{31}P NMR and IR spectroscopic data show that **4** has an analogous structure to the dppen derivative **3**. The reactivity of **2** is in marked contrast to that of $[RuCl_2(dppm)_2]$ which does not react with $[\{RhCl(CO)_2\}_2]$.[10]

We are investigating the extension of these ring-opening reactions to the wide range of known derivatives of the type $[Ru(C_5H_5)X(dppm)]$.

Experimental

All reactions were carried out under nitrogen using dry, distilled solvents. Infrared spectra were recorded on a Perkin-Elmer 681 spectrophotometer using CH_2Cl_2 solutions in 0.5 mm NaCl cells. NMR spectra were obtained using a Bruker WM250 instrument and measured in $CDCl_3$; ^{31}P NMR spectra were referenced to 85% H_3PO_4 (δ = 0). The compounds $[Ru(C_5H_5)Cl(PPh_3)_2]$,[11] $[Ru(C_5H_5)Cl(dppm)]$[5] and dppen[12] were prepared by published procedures.

Preparation of $[Ru(C_5H_5)Cl(dppen)]$ **1**.—The complex $[Ru(C_5H_5)Cl(PPh_3)_2]$ (0.362 g, 0.48 mmol) and dppen (0.203 g, 0.52 mmol) were refluxed in benzene (100 cm^3) for 5 h. The volume was reduced to 15 cm^3 *in vacuo*, and hexane (50 cm^3) was added. On standing for 24 h at −20 °C the solution gave dark red crystals of **1** (0.24 g, 85%) [Found: C, 61.9; H, 4.4%; M^+ at *m/z* 598. Calc. for $C_{31}H_{27}ClP_2Ru$: C, 62.2; H, 4.5%; M^+(^{101}Ru,^{35}Cl) at *m/z* 598].

Preparation of $[(C_5H_5)Ru(\mu\text{-}CO)_2(\mu\text{-}dppen)RhCl_2]$ **3**.—To a

Table 3 Fractional atomic coordinates for [Ru(C_5H_5)Cl(dppen)] **1**

Atom	*x*	*y*	*z*
Ru	0.182 27(3)	0.103 80(2)	0.210 79(2)
P(1)	0.130 1(1)	0.116 6(1)	0.348 5(1)
P(2)	0.022 8(1)	0.013 9(1)	0.215 7(1)
Cl(1)	0.323 1(1)	−0.013 7(1)	0.262 2(1)
C(1)	−0.217 4(3)	0.051 5(3)	0.228 8(2)
C(2)	−0.335 1(3)	0.073 3(3)	0.193 5(2)
C(3)	−0.366 5(3)	0.092 8(3)	0.104 7(2)
C(4)	−0.280 1(3)	0.090 6(3)	0.051 2(2)
C(5)	−0.162 4(3)	0.068 8(3)	0.086 6(2)
C(6)	−0.131 0(3)	0.049 2(3)	0.175 4(2)
C(7)	−0.072 0(3)	−0.157 3(2)	0.197 3(3)
C(8)	−0.073 5(3)	−0.244 0(2)	0.167 6(3)
C(9)	0.012 3(3)	−0.272 4(2)	0.119 9(3)
C(10)	0.099 5(3)	−0.214 3(2)	0.101 8(3)
C(11)	0.101 1(3)	−0.127 7(2)	0.131 4(3)
C(12)	0.015 3(3)	−0.099 2(2)	0.179 2(3)
C(13)	0.306 5(4)	0.039 6(2)	0.474 2(2)
C(14)	0.380 0(4)	0.032 3(2)	0.555 8(2)
C(15)	0.370 7(4)	0.093 3(2)	0.621 3(2)
C(16)	0.287 9(4)	0.161 6(2)	0.605 2(2)
C(17)	0.214 3(4)	0.168 9(2)	0.523 6(2)
C(18)	0.223 6(4)	0.107 9(2)	0.458 1(2)
C(19)	0.050 9(3)	0.290 4(2)	0.341 2(2)
C(20)	−0.020 8(3)	0.359 6(2)	0.360 3(2)
C(21)	−0.115 6(3)	0.343 1(2)	0.404 0(2)
C(22)	−0.138 6(3)	0.257 5(2)	0.428 6(2)
C(23)	−0.067 0(3)	0.188 4(2)	0.409 5(2)
C(24)	0.027 8(3)	0.204 8(2)	0.365 8(2)
C(25)	0.042 0(4)	0.015 3(3)	0.334 7(3)
C(26)	0.035 5(7)	−0.048 4(4)	0.391 7(4)
C(27)	0.231 1(7)	0.238 9(4)	0.176 6(4)
C(28)	0.119 6(6)	0.212 8(5)	0.123 2(5)
C(29)	0.147 8(7)	0.141 0(5)	0.071 4(4)
C(30)	0.320 5(6)	0.182 1(5)	0.158 8(4)
C(31)	0.267 0(6)	0.121 5(4)	0.096 2(1)

Table 4 Selected bond lengths (Å) and angles (°) for [(C_5H_5)-Ru(μ-CO)$_2${$Ph_2PC(=CH_2)PPh_2$}RhCl$_2$]·1.6CH_2Cl_2 **3**

Ru–Rh	2.697(1)	Rh–Cl(1)	2.329(3)
Ru–P(1)	2.301(3)	Rh–Cl(2)	2.377(3)
Ru–C(1)	1.931(9)	Rh–C(1)	2.07(1)
Ru–C(2)	1.961(9)	Rh–C(2)	2.03(1)
Ru–C(5)	2.26(2)	P(1)–C(3)	1.831(9)
Ru–C(6)	2.25(2)	P(2)–C(3)	1.823(9)
Ru–C(7)	2.20(2)	C(1)–O(1)	1.18(1)
Ru–C(8)	2.19(2)	C(2)–O(2)	1.16(1)
Ru–C(9)	2.24(2)	C(3)–C(4)	1.31(1)
Rh–P(2)	2.259(3)		
Rh–Ru–P(1)	94.4(1)	Cl(1)–Rh–Cl(2)	88.4(1)
P(1)–Ru–C(1)	90.7(3)	Ru–C(1)–O(1)	150.9(7)
P(1)–Ru–C(2)	88.3(3)	Rh–C(1)–O(1)	123.7(7)
Ru–Rh–P(2)	95.3(1)	Ru–C(2)–O(2)	147.7(8)
Ru–Rh–Cl(1)	174.4(1)	Rh–C(2)–O(2)	126.9(7)
Ru–Rh–Cl(2)	90.0(1)	P(1)–C(3)–P(2)	115.1(5)
P(2)–Rh–C(1)	91.4(3)	P(1)–C(3)–C(4)	122.4(7)
P(2)–Rh–C(2)	89.5(3)	P(2)–C(3)–C(4)	122.4(7)

solution of complex **1** (0.10 g, 0.17 mmol) in toluene (25 cm^3) was added a solution of [{$RhCl(CO)_2$}$_2$] (0.033 g, 0.085 mmol) in toluene (10 cm^3). A yellow precipitate of **3** was formed immediately. This precipitate was filtered off, washed with toluene, and dried *in vacuo* (0.11 g, 80%). An analytically pure sample was obtained by recrystallisation from acetone [Found: C, 49.7; H, 3.6%; $(M - Cl)^+$ at *m/z* 756. Calc. for $C_{33}H_{27}Cl_2O_2P_2RhRu$: C, 50.0; H, 3.4%; M^+(^{101}Ru,^{35}Cl) at *m/z* 791].

Preparation of [(C_5H_5)Ru(μ-CO)$_2$(μ-dppm)RhCl$_2$] **4**.—This was prepared in the same way as **3** above [Found: C, 49.4; H, 3.6%; $[M - Cl]^+$ at *m/z* 745. Calc. for $C_{32}H_{27}Cl_2O_2P_2RhRu$: C, 49.2; H, 3.5%; M^+(^{101}Ru,^{35}Cl) at *m/z* 780].

Crystal Structure Determination of [Ru(C_5H_5)Cl(dppen)] **1**.—Crystals of complex **1** were grown from a CH_2Cl_2–heptane solution and a suitable red-orange crystal of dimensions 0.8 × 0.25 × 0.2 mm was mounted in a Lindemann tube.

Crystal data. $C_{31}H_{27}ClP_2Ru$, M = 598, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), a = 11.379(3), b = 15.211(3), c = 15.544(3) Å, β = 100.18(12)°, U = 2648.1 Å^3 (by least-squares refinement of angles from 25 reflections), Mo-Kα radiation, λ = 0.710 69 Å, Z = 4, D_c = 1.50 g cm^{-3}, $F(000)$ = 1216, μ = 2.39 cm^{-1}.

Data collection and processing. Nonius CAD-4 diffractometer (Queen Mary College, London), ω–2θ scan mode. 5118 Unique reflections recorded (θ_{max} = 25°, h 0→13, k 0→18, l −18 to +18) of which 4912 with $F_o > 4\sigma(F_o)$ were used in refinement. Empirical absorption correction based on azimuthal scans applied. Three standard reflections showed no significant intensity variation during data collection.

Structure analysis and refinement. The Ru, P and Cl atoms were located by heavy-atom methods using SHELX 86 [13] and other non-hydrogen atoms by Fourier techniques (SHELX 76 [14]). Full-matrix least-squares refinement (anisotropic Ru, P, Cl and non-phenyl C). Phenyl rings were constrained to be regular hexagons (C–C 1.395 Å, C–C–C 120°), with individual isotropic thermal parameters assigned to each phenyl carbon atom. All hydrogen atoms were placed in calculated positions (C–H 1.08 Å) and refined isotropically. The weighting scheme, $w = 0.1372/[\sigma^2(F) + 0.014\,65F_o^2]$, gave satisfactory agreement analyses. Final R and R' values were 0.065 and 0.079. Atom scattering factors were taken from ref. 15. A list of fractional atomic coordinates is given in Table 3.

Crystal Structure Determination of [(C_5H_5)Ru(μ-CO)$_2$(μ-dppen)RhCl$_2$] **3**.—Crystals of **3** were grown from a CH_2Cl_2–heptane solution, and a suitable yellow crystal was mounted in a Lindemann tube together with a small amount of mother-liquor, as the crystal was sensitive to loss of solvent.

Crystal data. $C_{33}H_{27}Cl_2O_2P_2RhRu·1.6CH_2Cl_2$, M = 792.39 + 135.89 (= 928.28), monoclinic, a = 12.885(2), b = 17.552(4), c = 16.524(1) Å, β = 93.63(1)°, U = 3729.5 Å^3, space group $P2_1/n$, Z = 4, D_c = 1.65 g cm^{-3}, $F(000)$ = 1845, μ(Mo-Kα) = 77.32 cm^{-1}.

Data collection and processing. Nonius CAD4 diffractometer, ω–2θ mode with ω scan width = 0.80 + 0.35 tan θ, graphite-monochromated Mo-Kα radiation, λ = 0.710 69 Å, 7490 reflections measured (1.5 ≤ θ ≤ 25°; h, 0–15; k, 0–20; l, −19 to 19), 6551 unique (merging R = 0.026 after absorption correction based on azimuthal scans), giving 3867 with $F > 4\sigma(F)$.

Structure analysis and refinement. The Rh, Ru and both P atoms were located by the Patterson method [13] and C, Cl and O atoms were located by Fourier and Fourier-difference syntheses.[14] Full-matrix least-squares refinement was carried out with Rh, Ru, P, Cl and the cyclopentadienyl C atoms given anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (C–H 1.08 Å) and, with the exception of those on the CH_2 group, were allowed to ride on their respective C atoms.

The dichloromethane molecules gave problems during refinement due to partial site occupancy and disorder. The first of these molecules [C(50), Cl(3), Cl(4)] was treated as follows: the C–Cl and Cl···Cl distances were constrained to 1.77(2) and 2.92(4) Å, respectively, during refinement, C(50) was given a fixed U_{iso} value of 0.10 Å^2 and the three atoms were given a common site occupancy factor which was initially allowed to refine but which was then fixed (at 0.868) during the later stages of refinement. The hydrogen atoms were ignored. Disorder at the second site appeared to be even more severe and inspection of the Fourier difference maps suggested an approximate model

Table 5 Fractional atomic coordinates for $[(C_5H_5)Ru(\mu\text{-}CO)_2\{Ph_2PC(=CH_2)PPh_2\}RhCl_2]\cdot 1.6CH_2Cl_2$ **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.1440(1)	0.1677(0)	0.4522(0)	C(23)	0.5553(13)	0.2466(9)	0.6009(9)
Rh	−0.0261(1)	0.2538(0)	0.4711(0)	C(24)	0.5239(15)	0.1811(11)	0.6369(11)
P(1)	0.2109(2)	0.1846(1)	0.5834(1)	C(25)	0.4187(10)	0.1618(8)	0.6338(8)
P(2)	0.0147(2)	0.2818(1)	0.6027(1)	C(26)	0.3473(8)	0.2055(6)	0.5904(6)
Cl(1)	−0.1823(2)	0.3172(2)	0.4870(2)	C(31)	−0.0083(11)	0.2157(8)	0.7511(8)
Cl(2)	−0.0804(3)	0.2347(2)	0.3324(2)	C(32)	−0.0612(14)	0.1696(9)	0.8083(11)
C(1)	0.0106(7)	0.1402(5)	0.4904(5)	C(33)	−0.1489(14)	0.1378(10)	0.7829(11)
O(1)	−0.0500(5)	0.0939(4)	0.5083(4)	C(34)	−0.1929(15)	0.1427(10)	0.7113(10)
C(2)	0.1226(7)	0.2782(5)	0.4454(5)	C(35)	−0.1423(10)	0.1896(7)	0.6501(8)
O(2)	0.1553(5)	0.3371(4)	0.4285(4)	C(36)	−0.0531(8)	0.2243(6)	0.6753(6)
C(3)	0.1520(7)	0.2666(5)	0.6314(5)	C(41)	−0.0683(9)	0.3979(7)	0.6928(7)
C(4)	0.2057(8)	0.3126(6)	0.6807(6)	C(42)	−0.0751(12)	0.4741(9)	0.7178(9)
C(5)	0.1293(11)	0.1087(11)	0.3307(8)	C(43)	−0.0219(10)	0.5302(8)	0.6791(7)
C(6)	0.1981(15)	0.1654(9)	0.3250(7)	C(44)	0.0339(9)	0.5112(7)	0.6162(7)
C(7)	0.2774(13)	0.1544(10)	0.3769(10)	C(45)	0.0437(8)	0.4362(6)	0.5924(6)
C(8)	0.2628(16)	0.0868(13)	0.4172(8)	C(46)	−0.0060(7)	0.3792(5)	0.6327(5)
C(9)	0.1643(16)	0.0571(8)	0.3872(11)	C(50)[a]	0.2313(11)	0.0143(9)	0.0652(8)
C(11)	0.2201(8)	0.1202(6)	0.7387(6)	Cl(3)[a]	0.1540(6)	−0.0255(4)	−0.0087(3)
C(12)	0.2048(8)	0.0641(6)	0.7941(7)	Cl(4)[a]	0.1497(7)	0.0528(3)	0.1390(3)
C(13)	0.1661(8)	−0.0062(7)	0.7686(7)	C(51)[b]	0.6181(0)	0.1087(0)	0.4942(0)
C(14)	0.1440(8)	−0.0200(7)	0.6864(7)	Cl(5)[b]	0.6705(13)	0.1606(10)	0.4153(9)
C(15)	0.1581(7)	0.0375(6)	0.6297(6)	Cl(6)[b]	0.5504(14)	0.0321(8)	0.4453(11)
C(16)	0.1964(7)	0.1084(5)	0.6559(5)	C(52)[c]	0.6953(0)	0.1407(0)	0.4158(0)
C(21)	0.3806(11)	0.2706(8)	0.5514(8)	Cl(7)[c]	0.6960(11)	0.0921(7)	0.5088(7)
C(22)	0.4867(11)	0.2908(8)	0.5558(8)	Cl(8)[c]	0.5793(9)	0.1066(11)	0.3649(7)

Site occupancy factors: [a] 0.868, [b] 0.325, [c] 0.394.

based on two alternative positions of partial site occupancy. Each of the two molecules [C(51), Cl(5), Cl(6) and C(52), Cl(7), Cl(8)] was treated exactly as above and the partial site occupancy factors refined to 0.325 and 0.394 respectively and they were then fixed at these values. That these models were only approximate was indicated by some anomalously high anisotropic thermal parameters for the Cl atoms.

A weighting scheme of the form $w = [\sigma^2(F) + 0.000\,575F^2]^{-1}$ gave satisfactory analysis of variance. Refinement converged at $R = 0.055$ ($R' = 0.060$) and the final electron density difference synthesis showed no peaks > 0.94 or < -0.62 e Å^{-3}. A list of fractional atomic coordinates is given in Table 5.

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

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