2-Pyridonate (Opy) Rhodium(I) Carbonyl Complexes. Crystal Structure of the Unusual Tetranuclear Complex $[Rh_4(\mu\text{-}Opy)_4(\mu\text{-}CO)_2(CO)_4]$†

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Reaction of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with 2-hydroxypyridine (HOpy) and potassium hydroxide in methanol yields the tetranuclear complex $[Rh_4(\mu\text{-}Opy)_4(\mu\text{-}CO)_2(CO)_4]$ (**1**), but the binuclear compound $[Rh_2(\mu\text{-}Opy)_2(CO)_4]$ (**2**) is obtained when the reaction is performed under one atmosphere of carbon monoxide. Both complexes interconvert: by addition of trimethylamine oxide [(**2**) ⟶ (**1**)], or bubbling of carbon monoxide [(**1**) ⟶ (**2**)]. The related complex $[Rh_2(\mu\text{-}Opy)(\mu\text{-}dppm)_2(CO)_2][ClO_4]$ (**3**) [dppm = bis(diphenylphosphino)methane] can be prepared by reaction of (**2**) with dppm and perchloric acid. Crystals of (**1**) are monoclinic, space group $P2_1/n$, with $a = 19.429\,3(9)$, $b = 8.782\,7(2)$, $c = 8.439\,9(2)$ Å, $\beta = 98.912(3)°$, and $Z = 2$. The structure was solved by Patterson and Fourier methods and refined by least-squares calculations to $R = 0.058$. The structure of the tetranuclear complex consists of two binuclear units, centrosymmetrically related, and joined together through 2-pyridonate groups. In each binuclear moiety a 2-pyridonate group and a carbonyl ligand bridge the two rhodium atoms, which are directly bonded [Rh–Rh 2.619 7(8) Å].

Several rhodium carbonyl compounds in the presence of promoters such as 2-hydroxypyridine (HOpy)[1] or 1-methylpyrrolidin-2-one[2] are active catalyst precursors in the conversion of carbon monoxide and hydrogen into ethylene glycol.[3] High pressure and temperature are required in this proposed homogeneously catalyzed pathway. Under these conditions anionic rhodium carbonyl clusters[1] or the anion[2] $[Rh(CO)_4]^-$ are formed and detected in the solutions. We have now studied the reactions of 2-hydroxypyridine [tautomer with pyridin-2(1*H*)-one[4]] towards the complexes $[\{RhX(CO)_2\}_n]$ [X = Cl, *n* = 2; X = acetylacetonate (acac), *n* = 1]; here we report these reactions and describe the structure of an unusual tetranuclear complex of formula $[Rh_4(\mu\text{-}Opy)_4(\mu\text{-}CO)_2(CO)_4]$ and other related binuclear complexes.

Results and Discussion

Reaction of the complex $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with a mixture of HOpy and potassium hydroxide in methanol at room temperature leads to the crystallization of a dark red solid (**1**), which shows bridging and terminal carbonyl groups [ν(CO) (CH_2Cl_2): 2 060s, 2 020m, and 1 855m cm^{-1}]. This solid is slightly soluble in organic solvents and its complete characterization as $[Rh_4(\mu\text{-}Opy)_4(\mu\text{-}CO)_2(CO)_4]$ (**1**) was achieved by single-crystal *X*-ray diffraction studies. Compound (**1**) is an unsaturated, 60-valence-electron four-vertex complex containing a planar ring of four metal atoms. The structure of this complex closely resembles that of the recently described 64-valence-electron complex $[Rh_4(\mu\text{-}Cl)_2(\mu\text{-}L)_2(\mu\text{-}CO)_2(CO)_2(nbd)_2]$ (HL = 1*H*-pyrrolo[2,3-*b*]pyridine, nbd = norborna-2,5-diene) which contains a strictly planar Rh_4Cl_2 ring.[5] Both complexes have in common two binuclear halves $Rh_2(\mu\text{-}L)(\mu\text{-}CO)(CO)(L')$ (L = Opy, L′ = CO; L = 1*H*-pyrrolo[2,3-*b*]pyridine anion, L′ = nbd) bridged by 2-pyridonate or chloro groups.

If the above mentioned preparative reaction is performed in methanol–dichloromethane (3:5) and under carbon monoxide (1 atm) the binuclear complex $[Rh_2(\mu\text{-}Opy)_2(CO)_4]$ (**2**) is obtained as dichroic dark blue or copper-like crystals. Its i.r. spectrum (hexane) shows four ν(CO) absorptions at 2 090s, 2 060m, 2 020vs, and 2 005 (sh) cm^{-1}, indicative of a *cis* disposition of the carbonyl groups on each rhodium centre. This pattern of ν(CO) bands is also displayed by the related complex $[Rh_2(\mu\text{-}L')_2(CO)_4]$ (HL′ = 1,8-naphthyridin-2-one), whose *X*-ray structure shows an approximately face-to-face disposition of the nearly square-planar environments of the rhodium atoms with a short intermetallic distance.[6] The 200-MHz ^1H n.m.r. spectrum of (**2**) is in accordance with a similar structure having a pseudo-C_2 symmetry axis since the chemically equivalent protons of both 2-pyridonate (Opy) ligands are not magnetically equivalent.

Complex (**2**) loses CO slowly in polar solvents. Thus, the scarcely soluble complex (**1**) crystallizes from a solution of (**2**) in methanol in 70% yield after 1 week. Furthermore, single crystals of (**1**) suitable for *X*-ray analysis were grown from dichloromethane–methanol by this procedure. Interestingly, the rate of formation of (**1**) from (**2**) in methanol is increased by addition of NMe_3O in such a way that 60% is formed after 1 h. This conversion can be reversed; therefore bubbling CO through a dichloromethane suspension of (**1**) yields (**2**).

A convenient route to prepare binuclear rhodium carbonyl complexes consists of the reaction of $[Rh(acac)(CO)_2]$ with a potentially binucleating ligand having an acidic hydrogen.[5,7] In this way, 2-hydroxypyridine reacts with $[Rh(acac)(CO)_2]$ in dichloromethane to give (**2**) as the only product detected by i.r. spectroscopy. Nevertheless, this is not an adequate preparative route for (**2**) since a mixture of this compound and the starting material precipitates upon addition of hexane.

Reaction of (**2**) with bis(diphenylphosphino)methane (dppm) in dichloromethane gives a purple solution showing several

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† 1,2;3,4-Di-μ-carbonyl-1,2,3,4-tetracarbonyl-1,2;2,3;3,4;1,4-tetra-μ-[pyridin-2(1*H*)-onato-*NO*]-tetrarhodium(I) (*Rh*^{1}–*Rh*^{2})(*Rh*^{3}–*Rh*^{4}).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses

Rh(1)–Rh(2)	2.619 7(8)	Rh(1)–C(7)	1.870(9)	Rh(2)–C(9)	1.815(9)	O(2)–C(12)	1.300(10)
Rh(1)–Rh(1^{i})	4.444 0(7)	Rh(1)–C(8)	1.967(8)	C(7)–O(7)	1.117(13)	N(1)–C(2)	1.335(11)
Rh(2)–Rh(2^{i})	3.516 6(8)	Rh(2)–N(11)	2.109(7)	C(8)–O(8)	1.161(10)	N(1)–C(6)	1.354(12)
Rh(1)–Rh(2^{i})	3.032 5(7)	Rh(2)–O(1)	2.038(6)	C(9)–O(9)	1.168(12)	N(11)–C(12)	1.344(10)
Rh(1)–N(1)	2.100(7)	Rh(2)–C(8)	1.998(9)	O(1)–C(2)	1.283(10)	N(11)–C(16)	1.351(11)
Rh(1)–O(2^{i})	2.069(6)						

N(1)–Rh(1)–O(2^{i})	85.0(3)	N(11)–Rh(2)–C(9)	92.5(3)	Rh(2)–C(8)–O(8)	136.3(7)	C(12)–N(11)–Rh(2)	122.8(5)
N(1)–Rh(1)–C(7)	177.1(3)	N(11)–Rh(2)–C(8)	133.0(3)	Rh(1)–C(8)–O(8)	140.9(7)	C(16)–N(11)–Rh(2)	117.9(6)
N(1)–Rh(1)–C(8)	89.1(3)	N(11)–Rh(2)–Rh(1)	168.7(2)	Rh(2)–C(9)–O(9)	176.9(8)	N(1)–C(2)–C(3)	119.2(7)
N(1)–Rh(1)–Rh(2)	85.4(2)	Rh(1)–Rh(2)–C(9)	98.9(3)	Rh(1)–C(7)–O(7)	174.7(9)	N(1)–C(2)–O(1)	121.9(7)
Rh(2)–Rh(1)–C(7)	95.8(3)	Rh(1)–Rh(2)–C(8)	98.2(2)	Rh(2)–O(1)–C(2)	125.8(5)	O(1)–C(2)–C(3)	119.0(7)
Rh(2)–Rh(1)–C(8)	49.2(2)	C(9)–Rh(2)–C(8)	89.2(4)	Rh(1)–O(2^{i})–C(12^{i})	124.4(5)	N(11)–C(12)–C(13)	119.5(8)
C(7)–Rh(1)–C(8)	89.7(4)	C(8)–Rh(2)–O(1)	92.1(3)	C(2)–N(1)–Rh(1)	121.3(5)	N(11)–C(12)–O(2)	120.7(7)
C(8)–Rh(1)–O(2^{i})	160.4(3)	C(9)–Rh(2)–O(1)	175.5(3)	C(6)–N(1)–Rh(1)	117.7(5)	O(2)–C(12)–C(13)	119.8(8)
C(7)–Rh(1)–O(2^{i})	95.3(3)	Rh(2)–C(8)–Rh(1)	82.7(3)	C(12)–N(11)–Cl(6)	119.1(7)	C(2)–N(1)–C(6)	121.0(7)
N(11)–Rh(2)–O(1)	83.5(3)						

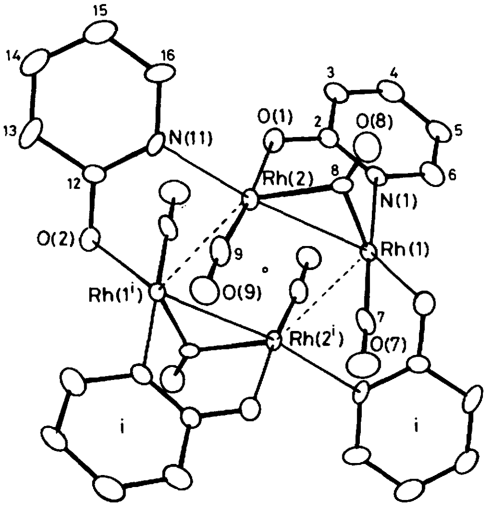

Figure. View of the structure of $[Rh_4(\mu\text{-Opy})_4(\mu\text{-CO})_2(CO)_4]$ (**1**) with the atom numbering scheme. The symbols of the carbon atoms are omitted for clarity

ν(CO) bands suggesting the presence of the species $[Rh_2(\mu\text{-Opy})(\mu\text{-dppm})_2(CO)_2]^+$ (1 995s, 1 980s cm^{-1}) and free pyridin-2(1*H*)-one (1 670m, 1 650s cm^{-1}). The cationic complex can be isolated as $[Rh_2(\mu\text{-Opy})(\mu\text{-dppm})_2(CO)_2][ClO_4]$ (**3**) by addition of perchloric acid.

Complex (**3**) can be alternatively obtained by reaction of the 2-pyridonate anion to the solvated species $[Rh_2(\mu\text{-dppm})_2(CO)_2(Me_2CO)_2]^{2+}$.[8] This cationic complex containing the Opy group as capping ligand is related to some A-frame complexes $[Rh_2(\mu\text{-L})(\mu\text{-dppm})_2(CO)_2][ClO_4]$ (L = pyrazolate derivative[9] or *NN'*-diphenylbenzamidinate[8]) recently prepared in our laboratory containing nitrogen-donor groups as capping ligands.

X-Ray Crystal Structure of $[Rh_4(\mu\text{-Opy})_4(\mu\text{-CO})_2(CO)_4]$.—The complex appears in the crystal as units composed of two moieties centrosymmetrically related and bridged through 2-pyridonate groups. Each unit is structured around four coplanar metallic centres with distances Rh(1)–Rh(2) 2.619 7(8) and Rh(1)–Rh(2^{i}) 3.032 5(7) Å (Figure; i indicates symmetry related atom through $-x$, $1 - y$, $1 - z$). The Rh(1)–Rh(2) distance is shorter than that observed for the tetranuclear 60-valence-electron cluster $[Rh_4(\mu\text{-PPh})_2(cod)_4]$ (cod-cyclo-octa-1,5-diene) (average 2.843 Å),[10] but similar to those found for complexes with a relatively short Rh–Rh single bond bridged by a carbonyl group and by a bidentate $N\overset{C}{\frown}X$ ligand {*e.g.* X = P, 2-(diphenylphosphino)pyridine, 2.612(1) Å,[11] or X = N, 1*H*-pyrrolo[2,3-*b*]pyridinate 2.686(2) Å[5]}. Rhodium–rhodium distances in the range 2.359(1)—2.410(1) Å have been found in binuclear dirhodium(II) complexes with ligands like Opy.[12–14] Furthermore, the Rh(1)–Rh(2^{i}) separation could be considered indicative of a weak metal–metal interaction.[5,15] This relatively wide range of intermetallic separations [2.359(1)—3.032 5(7) Å] found in rhodium complexes with Opy bridging groups shows the remarkable flexibility of this type of ligand. The features describing the complex around the central four-metal ring and showing the different geometry around each rhodium atom are given in Table 1. The Rh(1)–C(8) and Rh(2)–C(8) distances and the Rh(2)–C(8)– Rh(1) angle [82.7(3)°] are in the range reported for complexes in which a carbonyl ligand bridges a Rh–Rh bond.[5] The differences of values describing the CO bridge (see Table 1) are at the limit of significance with the precision achieved. It is noteworthy that the five-membered rings involving two rhodium atoms and an Opy group have the same conformation, but that with the longest metal–metal distance is much more puckered than the other: the intracyclic torsion angles are: at Rh(1)–Rh(2) 4.4(3), Rh(2)–O(1) −6.5(6), O(1)–C(2) 5.0(10), C(2)–N(1) 1.0(10), and N(1)–Rh(1) −4.5(5)°; Rh(2)–Rh(1^{i}) −27.6(3), Rh(1^{i})–O(2) 41.6(6), O(2)–C(12) −35.0(10), C(12)–N(11) −9.0(10), and N(11)–Rh(2) 28.4(6)°.

The complex conforms around the central four-metal ring, with a crystallographic centre of symmetry and in such a way that the dihedral angles of this ring with the planes through the Rh(2),Rh(1^{i}),O(2),C(12),N(11) and Rh(2),O(1),C(2),N(1),Rh(1) sets are 8.9(1) and 78.6(1)° respectively. The angles between these five-membered rings and their respective pyridinic rings are 21.6(3) and 3.5(2)° respectively.

The complex unit repeats along the *c* axis with intermetallic distances Rh(1)···Rh(1^{ii}) (ii indicates symmetry related atom at $-x$, $1 - y$, $2 - z$) of 4.661 8(8) Å, similar to Rh(1)···Rh(1^{i}) of 4.444 0(7) Å within each unit, the Rh(1^{i})···Rh(1)···Rh(1^{ii}) angle being 135.89(2)°. In this way the crystal is built of packed chains along (001).

Experimental

Reactions were carried out at room temperature (r.t.) under oxygen-free nitrogen (1 atm). Solvents were purified by standard methods prior to use. Measurements were carried out

Table 2. Final atomic co-ordinates with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh(1)	0.021 00(3)	0.414 24(6)	0.750 53(6)
Rh(2)	0.075 64(3)	0.606 04(6)	0.567 37(6)
O(1)	0.142 7(3)	0.433 4(7)	0.538 5(8)
N(1)	0.102 3(3)	0.267 9(8)	0.712 4(8)
C(2)	0.146 7(4)	0.305 6(9)	0.613 0(9)
C(3)	0.200 4(5)	0.201 8(11)	0.589 8(10)
C(4)	0.206 8(5)	0.067 2(11)	0.671 4(12)
C(5)	0.159 2(5)	0.028 8(10)	0.773 4(12)
C(6)	0.108 1(5)	0.133 5(11)	0.791 7(11)
O(2)	0.034 9(3)	0.783 8(7)	0.231 4(8)
N(11)	0.132 3(3)	0.723 8(7)	0.411 8(8)
C(12)	0.101 4(4)	0.798 1(9)	0.280 5(10)
C(13)	0.141 4(6)	0.894 5(12)	0.197 4(13)
C(14)	0.211 4(6)	0.902 6(12)	0.242 9(14)
C(15)	0.243 5(5)	0.818 6(13)	0.372 0(14)
C(16)	0.202 2(5)	0.732 3(11)	0.452 8(13)
C(7)	−0.049 4(5)	0.545 0(11)	0.795 4(10)
O(7)	−0.087 6(4)	0.629 7(10)	0.828 7(10)
C(8)	0.089 7(4)	0.577 9(9)	0.805 1(10)
O(8)	0.124 9(4)	0.631 4(10)	0.914 7(8)
C(9)	0.021 2(5)	0.770 2(10)	0.589 4(10)
O(9)	−0.015 0(4)	0.872 4(9)	0.609 3(10)

and starting materials were prepared as described previously.[5] Hydrogen-1 n.m.r. spectra were recorded with a Varian XL-200 spectrometer operating at 200.057 MHz.

Preparation of the Complexes.—$[Rh_4(\mu\text{-}Opy)_2(\mu\text{-}CO)_2(CO)_4]$ (**1**). The compound $[Rh(\mu\text{-}Cl)_2(CO)_4]$ (58 mg, 0.15 mmol) was added to a mixture of 2-hydroxypyridine (29 mg, 0.3 mmol) and potassium hydroxide (16.8 mg, 0.3 mmol) in methanol (10 cm^3) to give a dark red solution. The reaction was continued for 2 h at r.t. to afford a dark red suspension of (**1**). The solid was separated by filtration, washed with methanol and vacuum-dried (yield 36 mg, 50%) (Found: C, 32.4; H, 1.7; N, 5.8. $C_{26}H_{16}N_4O_{10}Rh_4$ requires C, 32.7; H, 1.7; N, 5.9%). $\nu_{max.}$(CO) (carbonyl) at 2 060s, 2 055s, 2 030s, 2 000w, 1 990w, 1 840 (sh), and 1 818m cm^{-1}; ν(C=O) (2-pyridonate) at 1 615s cm^{-1} (Nujol).

$[Rh_2(\mu\text{-}Opy)_2(CO)_4]$ (**2**). The compound $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (58 mg, 0.15 mmol) was added to a mixture of 2-hydroxypyridine (29 mg, 0.3 mmol) and potassium hydroxide (16.8 mg, 0.3 mmol) in methanol (3 cm^3). Dichloromethane (5 cm^3) was then added and carbon monoxide was bubbled through the solution for 2 h to give dichroic deep blue or copper-like crystals of (**2**) which were separated by filtration and washed with cold methanol (yield 35 mg, 45%) [Found: C, 33.3; H, 1.6; N, 5.7%; *M* (in $CHCl_3$), 504. $C_{14}H_8N_2O_6Rh_2$ requires C, 33.2; H, 1.6; N, 5.5%; *M*, 506]. $\nu_{max.}$(CO) (carbonyl) at 2 080s, 2 060s, 2 025s, and 1 990s cm^{-1}; ν(C=O) (2-pyridonate) at 1 610s cm^{-1} (Nujol); δ_H ($CDCl_3$, −30 °C) 7.80 (1 H, d, H^6), 7.70 (1 H, d, $H^{6'}$), 7.31 (1 H, td, H^4 or $H^{4'}$), 7.28 (1 H, td, H^4 or $H^{4'}$), 6.56 (1 H, d, H^3 or $H^{3'}$), 6.48 (1 H, d, H^3 or $H^{3'}$), 6.43 (2 H, m, H^5 or $H^{5'}$).

$[Rh_2(\mu\text{-}Opy)(\mu\text{-}dppm)_2(CO)_2][ClO_4]$ (**3**). *Method A.* Solid dppm (77 mg, 0.2 mmol) was added to a solution of $[Rh_2(\mu\text{-}Opy)_2(CO)_4]$ (50 mg, 0.1 mmol) in dichloromethane (10 cm^3) giving a purple solution and evolution of carbon monoxide. Further treatment with perchloric acid (6.5 × 10^{-3} cm^3, 9.2 mol dm^{-3} in water, 0.1 mmol), evaporation of the solution to 1 cm^3, and addition of diethyl ether (10 cm^3) gave (**3**) (90 mg, 75%).

Method B. A solution of the solvated species $[Rh_2(\mu\text{-}dppm)_2(CO)_2(Me_2CO)_2]^{2+}$ in acetone {prepared by reaction of $Ag[ClO_4]$ (20.7 mg, 0.1 mmol) with $[Rh_2Cl_2(\mu\text{-}dppm)_2(CO)_2]$ (55 mg, 0.05 mmol) in acetone (10 cm^3), with filtering off of the precipitated AgCl} was added to a mixture of 2-hydroxypyridine (4.7 mg, 0.05 mmol) and potassium hydroxide (0.05 mmol) in methanol (5 cm^3) to give a purple solution. Evaporation to dryness, extraction of the residue with dichloromethane (5 cm^3), and evaporation of the extract under an atmosphere of carbon monoxide gave purple crystals of (**3**) (yield 46 mg, 75%) (Found: C, 56.8; H, 4.3; N, 1.1. $C_{57}H_{44}ClNO_7P_4Rh_2$ requires C, 56.1; H, 3.6; N, 1.15%). Λ_{eq} = 115 S cm^2 mol^{-1} (in 1.3 × 10^{-4} mol dm^{-3} acetone solution); ν(CO) (carbonyl) at 1 977s and 1 960s cm^{-1}; ν(C=O) (2-pyridonate) at 1 610m cm^{-1} (Nujol).

Reaction of (**1**) *with Carbon Monoxide.*—Carbon monoxide was bubbled through a suspension of complex (**1**) (47 mg, 0.05 mmol) in dichloromethane (15 cm^3) for 3 h to give an orange solution of complex (**2**). Addition of hexane (10 cm^3) and evaporation of the mixture of solvents under CO (1 atm) to 5 cm^3 gave dark blue needles of (**2**) in 50% yield.

Reaction of (**2**) *with Trimethylamine* N-*Oxide.*—To a solution of (**2**) (50 mg, 0.1 mmol) in warm methanol (15 cm^3), a solution of NMe_3O (14.1 mg, 0.1 mmol) in the same solvent was added dropwise. The mixture was stirred for 30 min at r.t. to give a dark red suspension of (**1**) in 60% yield.

Crystal Structure Determination.—*Crystal data.* $C_{26}H_{16}N_4O_{10}Rh_4$, $M = 924.06$, monoclinic, $Z = 2$, $a = 19.429\,3(9)$, $b = 8.782\,7(2)$, $c = 8.439\,9(2)$ Å, $\beta = 98.912(3)°$, $U = 1\,422.81(8)$ Å^3, $F(000) = 888$, $D_c = 2.157$ g cm^{-3}, space group $P2_1/n$.

A sample of dimensions 0.30 × 0.27 × 0.30 × 0.07 mm with a prismatic hexagonal base was used for the analysis on a Philips PW 1100 diffractometer, with Cu-K_α radiation ($\lambda = 1.541\,8$ Å), graphite monochromator, ω—2θ scan, bisecting geometry, 1 × 1 detector apertures, 1.4° scan width and 1 min per reflection. The stability was checked every 90 min and variation was not observed during the data collection. The cell parameters were obtained from a least-squares fit of the angular position of 85 reflections with θ up to 45°.

The solution was given from the Patterson function,[16] completed through the DIRDIF System[17] and refined by least-squares methods on F_o. The linear absorption coefficient μ for the Cu-K_α radiation was 193.8 cm^{-1}. The first isotropic refinement and empirical correction for absorption[18] lowered the *R* factor from 0.16 to 0.09. The maximum and minimum transmission factors were 1.595 and 0.550. All the H atoms were obtained from a difference synthesis and included isotropically in the last cycles of the refinement, the other atoms being treated anisotropically. 2 413 Reflections were collected up to 65° in θ of which 2 300 were considered as observed $[I > 3\sigma(I)]$. Refinement converged at $R = 0.058$ and $R' = 0.071$. Weights were chosen as to give no trends in $\langle w^2F\rangle$ *vs.* F_o and $\langle \sin\theta/\lambda\rangle$ using functions of the type $K/|f(F_o)||g(\sin\theta/\lambda)|$, *K* being a scale factor to ensure that $\langle w\Delta^2F\rangle = 1$. The final average shift/error was 0.04 for 231 variables. A final difference synthesis gave residual electron density near the rhodium atoms of 2.1 and 1.8 e Å^{-3} for Rh(2) and Rh(1) respectively. The final maximum thermal parameter was U_{22} for O(7) [0.072(5) Å^2]. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2. As far as the analysis has been carried out it seems that the e.s.d.s for the Rh atoms could be underestimated by a factor of ten, as pointed out in a recent survey on the accuracy of error estimates.[19]

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