Half-sandwich Ruthenium Complexes of a P–O Bifunctional Ligand. *X*-Ray Crystal Structure of $[Ru(\eta-C_5Me_5)(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}]$†

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The reaction of the phosphine $PPh_2(C_6H_4OH)$ with a reduced solution of $[\{Ru(\eta-C_5Me_5)Cl_2\}_n]$ (**1**) by zinc in methanol produces $[Ru(\eta-C_5Me_5)(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}]$ (**4**). This complex crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 11.070(1)$, $b = 18.582(2)$, $c = 19.393(2)$ Å, and $\beta = 106.05(1)^\circ$ and was refined to $R = 0.028$ with 4 383 reflections having $(F_o^2) > 3\sigma(F_o^2)$. The *X*-ray structure shows the compound to exhibit strong hydrogen bonding between the hydroxyl proton of the phosphine and the oxygen group of the chelating phenoxy diphenylphosphine ligand [O $\cdots$ O 2.534(3), O–H 0.97(3), and H $\cdots$ O 1.57(3) Å]. Compound (**4**) is unreactive towards H_2, $NaBH_4$, $LiBHEt_3$, CF_3CO_2H, and MeI probably because of electronic and co-ordinative saturation. Reaction of the hydroxyphosphine with $[\{Ru(\eta-C_5Me_5)Cl\}_4]$ followed by addition of NEt_3 leads to an insoluble solid (**5**) of the same composition as (**4**) but proposed to be oligomeric. Compound (**5**) is again unreactive except with $HBF_4 \cdot Et_2O$ in the presence of which it decomposes. Reaction of $PPh_2(C_6H_4OSiMe_3)$ with a reduced solution of (**1**) in methanol affords $[Ru(\eta-C_5Me_5)(OC_6H_4PPh_2)\{PPh_2(C_6H_4OSiMe_3)\}]$ (**6**) whereas addition of $PPh_2(C_6H_4OH)$ to (**1**) followed by reduction with $NaBH_4$ in ethanol affords the trihydride $[Ru(\eta-C_5Me_5)H_3\{PPh_2(C_6H_4OH)\}]$ (**8**).

The chemistry of pentamethylcyclopentadienyl ruthenium derivatives remained very little explored except for carbonyl derivatives[1] until the discovery of simple preparations of $[\{Ru(\eta-C_5Me_5)Cl_2\}_n]$ in 1984.[2] However, since then it has developed very rapidly. In particular, as part of our interest in polyhydride ruthenium derivatives, we have synthesized the compounds $[Ru(\eta-C_5Me_5)H_3(PR_3)]$[3] also prepared by other groups[4] and studied their reactivity. These compounds show anomalous n.m.r. properties[5] recently rationalized as due to quantum-mechanical effects.[6] They are also quite reactive and for example the protonation of $[Ru(\eta-C_5Me_5)H_3\{P(C_6H_{11})_3\}]$ by $HBF_4 \cdot Et_2O$ leads to the evolution of 3 mol of H_2 and formation of a cyclohexenyldicyclohexylphosphine ligand exhibiting a strong agostic interaction.[7]

Bifunctional ligands, for example ligands containing both a soft and a hard donor group, are increasingly important in organometallic chemistry. Examples of their use involve the activation of CO_2 and homogeneously catalysed reactions.[8,9] For example the Shell higher olefins process (SHOP) results from the use of a β-ketophosphine or rather of its enolate in a nickel complex.[9] Our interest in this type of ligand results from the possible bifunctional activation of dihydrogen which has recently been demonstrated in iridium amido[10] or ruthenium phosphido derivatives.[11] Another interest lies in the possible preparation of dihydrogen complexes.[12] We have recently prepared new dihydrogen derivatives containing oxygen donor ligands.[13] It was anticipated that the use of a functional phosphine containing an anionic oxygen donor moiety could lead to such complexes. Furthermore it has been shown that protonation of $[Ru(\eta-C_5H_5)H(dppe)]$ complexes could lead to the dihydrogen derivatives $[Ru(\eta-C_5H_5)(\eta^2-H_2)(dppe)]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$).[14]

The first ligand chosen was the hydroxyphosphine $PPh_2(C_6H_4OH)$ shown several years ago to be a good chelating and reactive ligand for Group 10 metals.[15] A derivative of this molecule, $PPh_2(C_6H_4OSiMe_3)$ was also employed.[16] We describe here our results concerning the complexation of these ligands with $Ru(\eta-C_5Me_5)$ moieties.

Results and Discussion

Zinc reduction of $[\{Ru(\eta-C_5Me_5)Cl_2\}_n]$ (**1**) in various solvents has been shown previously to lead to $[\{Ru(\eta-C_5Me_5)Cl\}_4]$ (**2**) able to react with KPF_6 in acetone to give a $[Ru(\eta-C_5Me_5)S_3]^+$ cation.[17] The same reaction is possible in methanol, however prolonged reduction (6—48 h) leads to an intense cherry-red colour due to the presence of a mixture of the known $[\{Ru(\eta-C_5Me_5)(\mu-OMe)\}_2]$ (**3**)[18] and $[\{Ru(\eta-C_5Me_5)Cl\}_4]$ (**2**).[19] Compound (**3**) has been obtained by Koelle and Kossakowski[18] by reduction of (**1**) with K_2CO_3 in methanol.

Treatment of this deep red solution with 1 or 2 equivalents of $PPh_2(C_6H_4OH)$ leads to a colour change to orange and, after recrystallization, to yellow crystals analysing for $[Ru(\eta-C_5Me_5)(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}]$ (**4**). An AB spin system is observed in the ^{31}P n.m.r. spectrum ($\delta_A = 57.89$, $\delta_B = 48.53$ p.p.m. $J_{AB} = 33.2$ Hz) whereas the ^1H n.m.r. spectrum shows a triplet for the C_5Me_5 protons at δ 1.42 [J(HP) 1.5 Hz], a complex multiplet between δ 6.5 and 7.8 assigned to the phenyl protons, and a sharp singlet at δ 13.34 with the right integration ratio for the hydroxy proton.

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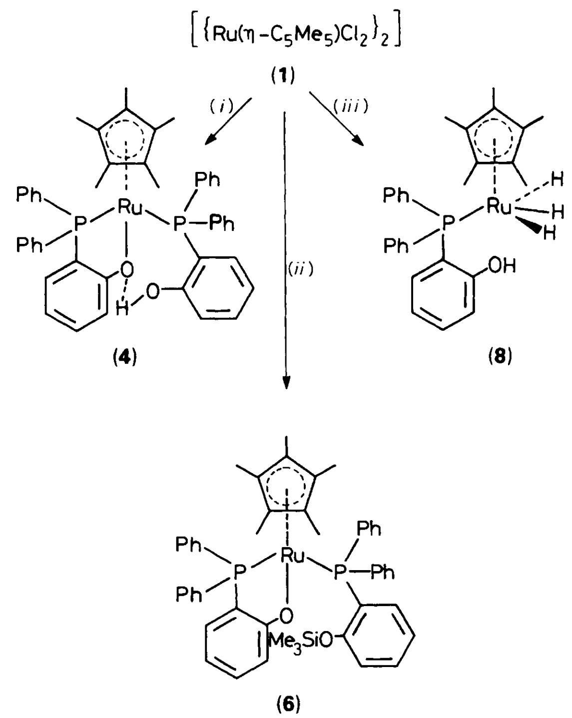
† [(2-Diphenylphosphino)phenoxo-OP][(2-hydroxyphenyl)diphenylphosphine](η-pentamethylcyclopentadienyl)ruthenium(II).

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



Scheme. Reactions of $[\{Ru(\eta\text{-}C_5Me_5)Cl_2\}_n]$ with $PPh_2(C_6H_4OH)$. (*i*) (*a*) zinc in methanol, (*b*) 2 equivalent of $PPh_2C_6H_4OH$ for 2 h at 20 °C; (*ii*) (*a*) zinc in methanol, (*b*) 2 equivalents of $PPh_2(C_6H_4OSiMe_3)$ for 2 h at 20 °C, (*iii*) (*a*) addition of 1 equivalent of $PPh_2(C_6H_4OH)$ in methanol for 15 min at 20 °C, (*b*) excess of $NaBH_4$ for 3 h at 20 °C

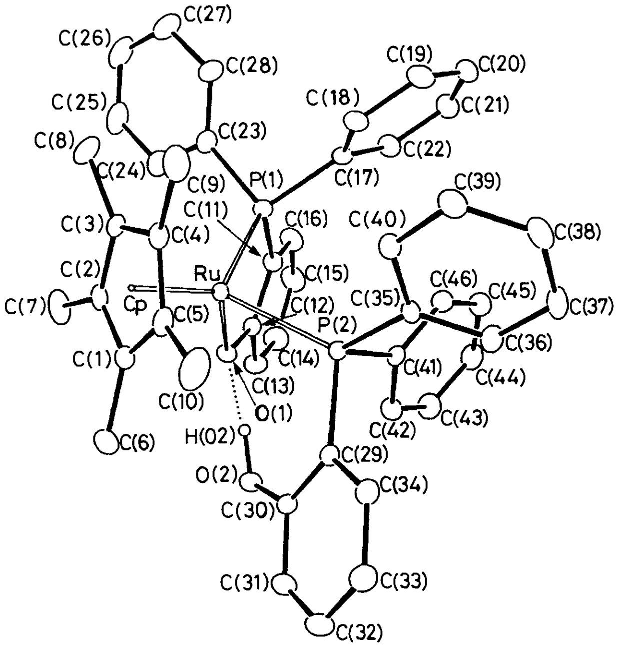


Figure. ORTEP view of $[Ru(\eta\text{-}C_5Me_5)(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}]$ (**4**). All protons except the phenoxo one have been omitted for clarity.

Interestingly, the chemical shift of the latter proton is very sensitive to its environment; thus it resonates at δ 6.00 for complexes $[MCl_2L_2]$ (M = Pd or Pt) but at δ 11.00 for $[PtH(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}]$.[15b] Hydrogen bonding with the hydride was then proposed to account for this chemical shift. In our case a strong hydrogen bond with the oxygen of the chelating diphenylphosphinophenoxy group would account for this observation.

An *X*-ray diffraction study was carried out in order to ascertain the structure of the complex. The results are shown in the Figure. Selected bond lengths and angles are given in Table 1. The complex adopts a characteristic piano-stool configuration with the two phosphorus atoms almost symmetrical with respect to the $(C_5Me_5)RuO(1)$ plane. The Ru–O(1) and Ru–P distances are in the range known for such compounds. The most interesting feature of this structure is the presence of a hydrogen bond between the phenoxy proton of the monodentate ligand and the oxygen of the bidentate one. The proton lies perfectly in the limit of the error on the O(1) ··· O(2) bond [O(2)–H(O2) ··· O(1) 173.0(4)°]. The O(2)–H(O2) bond [0.97(3) Å] is elongated whereas the hydrogen bond O(1) ··· H(O2) [1.57(3) Å] is short but in the range of known values.

The reactivity of complex (**4**) was studied towards H_2 (in the presence or not of NEt_3), CF_3CO_2H, $NaBH_4$, $LiBHEt_3$, and MeI. No reaction was detected. This surprising behaviour results probably from the steric crowding around the metal and from the saturation of the complex. Also probably from the steric bulk around the phenoxy group and from the strong hydrogen bonding of the phenoxy proton with the bidentate ligand. It is noteworthy that Shaw and co-workers [15b] observed that the reaction of the dichelated complex $[Pt(OC_6H_4PPh_2)_2]$ with $NaBH_4$ produced the hydride $[PtH(OC_6H_4PPh_2)(PPh_2C_6H_4OH)]$. When $PPh_2(C_6H_4OH)$ reacts with $[\{Ru(\eta\text{-}C_5Me_5)Cl\}_4]$ a very labile complex forms which we could not isolate. However addition of NEt_3 leads to the immediate precipitation of a white solid insoluble in all common organic solvents. A ^1H n.m.r. spectrum in $(CD_3)_2SO$ shows nevertheless the C_5Me_5 group at δ 1.35 and the aromatic protons between δ 6.5 and 8.0. Microanalytical and ^1H n.m.r. data suggest the same formulation as for (**4**), $[\{Ru(\eta\text{-}C_5Me_5)(OC_6H_4PPh_2)(PPh_2C_6H_4OH)\}_n]$ (**5**). However this compound must be at least dimeric or polymeric to account for its lack of solubility. Again the complex is unreactive with H_2 or CF_3CO_2H. With $HBF_4{\cdot}Et_2O$ an immediate reaction occurred but led to decomposition of the complex.

Reaction of compound (**3**) with 1 or 2 equivalents of diphenyl(2-trimethylsiloxyphenyl)phosphine led to a product analogous to (**4**) $[Ru(\eta\text{-}C_5Me_5)(OC_6H_4PPh_2)\{PPh_2(C_6H_4\text{-}OSiMe_3)\}]$ (**6**) which was characterized by n.m.r. spectroscopy and microanalysis. In particular in the ^1H n.m.r. spectrum a triplet is observed for the C_5Me_5 ligand at δ 1.25 [*J*(HP) 1.5 Hz], a singlet for the trimethylsilyl group at δ 0.08, and multiplets between δ 6.5 and 8 for the phenyl groups.

Any attempt to prepare monophenoxophosphine derivatives failed. In particular reaction of $Li(OC_6H_4PPh_2)$ [obtained by deprotonation of $PPh_2(C_6H_4OH)$ with LiBu] with compound (**2**) only yielded (**4**).

A similar reaction in the presence of 1 equivalent of PMe_3 afforded a mixture of (**4**) and a new complex for which we tentatively propose the structure $[Ru(\eta\text{-}C_5Me_5)(OC_6H_4PPh_2)(PMe_3)]$ (**7**) on the basis of its ^{31}P (AB pattern, δ_A 63.2, δ_B −1.9 p.p.m., J_{AB} = 40.5 Hz) and ^1H n.m.r. spectra [δ 1.60 (t), *J*(HP) = 1.5, C_5Me_5; 0.88 (d), *J*(HP) = 8.1 Hz, PMe_3; δ 6.5—8.1, aromatic protons]. However it was not possible to separate the components of the mixture.

Finally the preparation of hydride derivatives was attempted in a one-pot reaction. The trihydrides $[Ru(\eta\text{-}C_5Me_5)H_3(PR_3)]$ mentioned in the Introduction have been prepared by us by successive addition of PR_3 and 2 equivalents of $LiBHEt_3$ to compound (**1**) in tetrahydrofuran (thf),[3] whereas Suzuki *et al.*[4b] obtained these complexes by successive addition of PR_3 and excess of $NaBH_4$ to (**1**) in ethanol. Both methods were employed in the case of $PPh_2(C_6H_4OH)$ and both led to the desired

Table 1. Selected bond lengths (Å) and angles (°) of $[Ru(\eta-C_5Me_5)(OC_6H_4PPh_2)(PPh_2C_6H_4OH)]$ (**4**) with estimated standard deviations (e.s.d.s) in parentheses

Ru–P(1)	2.307(1)	Ru–O(1)	2.133(2)
Ru–P(2)	2.348 1(7)	Ru–Cp	1.865(4)
Ru–C(1)	2.215(5)	Ru–C(4)	2.232(4)
Ru–C(2)	2.187(4)	Ru–C(5)	2.240(4)
C(12)–O(1)	1.328(5)	C(30)–O(2)	1.342(4)
O(2)–H(O2)	0.97(3)	O(2) ••• O(1)	2.534(3)
		H(O2) ••• O(1)	1.57(3)
P(1)–Ru–P(2)	95.68(3)	P(2)–Ru–O(1)	82.25(6)
P(1)–Ru–O(1)	80.49(7)	P(2)–Ru–Cp	128.6(1)
P(1)–Ru–Cp	129.7(1)	O(1)–Ru–Cp	122.7(1)
O(1)–C(12)–C(11)	121.7(3)	O(2)–C(30)–C(29)	126.1(3)
O(1)–C(12)–C(13)	119.7(3)	O(2)–C(30)–C(31)	114.5(3)
C(30)–O(2)–H(O2)	117.0(2)	O(2)–H(O2) ••• O(1)	173.0(4)

trihydride $[Ru(\eta-C_5Me_5)H_3\{PPh_2(C_6H_4OH)\}]$ (**8**) but in low yield (10—25%). The best results were obtained with the borohydride method.

Compound (**8**) shows spectroscopic properties similar to those of other known trihydrides of general formula $[Ru(\eta-C_5Me_5)H_3(PR_3)]$. In particular, a doublet is observed for the hydrides at δ −9.50 [J(HP) 19 Hz], whereas the methyl groups of C_5Me_5 and the hydroxy proton are observed at δ 1.98 and 13.33. Again the latter high value is probably indicative of hydrogen bonding. However the reactivity of this complex again proved disappointing. Protonation causes decomposition whereas no reaction is observed with NEt_3 and thermal activation up to 100 °C does not lead to clean hydrogen evolution.

In conclusion, we have described the preparation of some half-sandwich ruthenium compounds containing the bifunctional ligand (2-hydroxyphenyl)diphenylphosphine. The reactivity of the resulting complexes proved very low perhaps because of the high stabilizing effect of the chelated ligand, and also the absence of co-ordinative unsaturation.

We are presently looking at other bifunctional ligands in order to try to observe bifunctional activation.

Experimental

[*(2-Diphenylphosphino)phenoxo-*OP][*(2-hydroxyphenyl)diphenylphosphine*]*(η-pentamethylcyclopentadienyl)ruthenium*(II) (**4**).—A brown suspension of $[\{Ru(\eta-C_5Me_5)Cl_2\}_n]$ (**1**) (400 mg, 1.30 mmol) in methanol (20 cm^3) was treated with zinc powder (excess) and the mixture stirred at 20 °C for 6 h. The mixture was filtered and the deep red filtrate treated with (2-hydroxyphenyl)diphenylphosphine (725 mg, 2.60 mmol). After 2 h at 20 °C the red-brown solution was concentrated to *ca.* 20 cm^3. Yellow crystals separated and were filtered off and dried *in vacuo.* Yield 670 mg, 65% (Found: C, 69.55; H, 5.65. Calc. for $C_{46}H_{44}O_2Ru$: C, 69.75; H, 5.60%).

$[\{Ru(\eta-C_5Me_5)(OC_6H_4PPh_2)(PPh_2C_6H_4OH)\}_2]$ (**5**).—The red-brown filtrate from which compound (**4**) was separated was treated with trimethylamine (1 cm^3). A white precipitate formed immediately and was collected by filtration, washed with methanol (2 × 5 cm^3) and dried *in vacuo.* Yield 200 mg, 10% (Found: C, 68.50; H, 4.60. Calc. for $C_{46}H_{44}O_2Ru{\cdot}CH_3OH$: C, 68.45; H, 5.80%).

[*(2-Diphenylphosphino)phenoxo-*OP][*diphenyl(2-trimethylsiloxyphenyl)phosphine*]*(η-pentamethylcyclopentadienyl)ruthenium*(II), (**6**).—A brown suspension of compound (**1**) (350 g, 1.14 mmol) in methanol (20 cm^3) was treated with zinc powder (excess) and the mixture stirred at 20 °C for 2 h. The mixture was filtered and the intense cherry-red filtrate was treated with diphenyl(2-trimethylsiloxyphenyl)phosphine (800 mg, 2.29 mmol). The resulting solution was stirred at 20 °C for 12 h, then concentrated to *ca.* 20 cm^3 and cooled at −20 °C. The yellow microcrystals which formed were separated by filtration, washed with methanol (2 × 5 cm^3), and dried *in vacuo.* Yield 390 mg, 40% (Found: C, 67.50; H, 5.35. Calc. for $C_{49}H_{52}O_2RuSi$: C, 68.10; H, 6.05%).

[*(2-Hydroxyphenyl)diphenylphosphine*]*trihydrido(η-pentamethylcyclopentadienyl)ruthenium*(IV) (**8**).—A suspension of $[\{Ru(\eta-C_5Me_5)Cl_2\}_n]$ (**1**) (200 mg, 0.65 mmol) in ethanol (40 cm^3) was treated with (2-hydroxyphenyl)diphenylphosphine (180 mg, 0.65 mmol) and the mixture stirred at 20 °C for 15 min. Then $NaBH_4$ (excess) was added and the mixture stirred at 20 °C for 3 h. The solvent was removed under reduced pressure at *ca.* 30 °C and the residue extracted into hexane (30 cm^3). The mixture was filtered and the pale red-beige filtrate concentrated to *ca.* 5 cm^3 and cooled at −20 °C. The pale red-beige microcrystals which formed were separated by filtration and dried *in vacuo.* Yield 80 mg, 23%.

X-Ray Crystal-structure Determination of $[Ru(\eta-C_5Me_5)(OC_6H_4PPh_2)]\{PPh_2(C_6H_4OH)\}]$.—*Crystal data.* $C_{46}H_{44}O_2P_2Ru$, M = 791.9, monoclinic, space group $P2_1/c$ (no. 14), a = 11.070(1), b = 18.582(2), c = 19.393(2) Å, β = 106.05(1)°, U = 383 4(1) $Å^3$, D_c = 1.37 g cm^{-3}, Z = 4, F(000) = 1 640, Mo-K_α radiation, λ = 0.710 73 Å, μ = 5.2 cm^{-1}, T = 293 K.

Data collection and processing. A yellow square-plate crystal of dimensions 0.35 × 0.35 × 0.075 mm was centred on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The unit-cell dimensions were determined from the setting angles of 25 reflections in the range $9 < \theta < 12°$. A data set of 6 343 reflections ($1.5 < \theta < 24°$, $h, k, \pm l$) was recorded as described previously[20] by the θ—2θ scan technique (scan width 0.70 + 0.35 tanθ, scan speed 1.1—5.5° min^{-1}). The intensities of three standard reflections monitored every 2 h showed no significant variation during data collection. Data reflections were corrected for Lorentz and polarization effects[21] but not for absorption. Equivalent reflections (0kl and 0$k\bar{l}$) were merged ($R_{av.}$ = 0.016). 4 383 Reflections with $F_o^2 > 3\sigma(F_o^2)$ were considered 'observed' and used for the structure solution and least-squares refinement.

Structure determination. The structure was solved by the heavy-atom method. After locating the Ru atom by a Patterson map, subsequent full-matrix least-squares refinement and interpretation of Fourier difference maps using SHELX[22] enabled all the non-hydrogen atoms in the structure to be located. They were refined anisotropically. All hydrogen atoms were located on a Fourier difference map. Atom H(O2) was refined isotropically [U = 0.07(1) $Å^2$]. All other hydrogens were introduced with constrained geometry (C–H 0.97 Å) with two isotropic thermal parameters allowed to vary, one for methyl H, one for the others. Neutral-atom scattering factors were used, those for non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[23] Unit weights gave satisfactory weight analysis. In the last full-matrix least-squares refinement cycle the greatest parameter shift was 0.04 times the estimated standard deviation (a H parameter) and the final R value 0.028 (R' = 0.029). A final Fourier difference map showed a residual electron density of 0.2 e $Å^{-3}$. All calculations were performed on a VAX-11/730 DEC computer. Atomic co-ordinates are listed in Table 2.

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

Table 2. Fractional atomic co-ordinates with (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	0.426 16(2)	0.365 91(1)	0.697 34(1)	C(21)	0.071 4(5)	0.248 5(3)	0.847 1(3)
P(1)	0.221 10(8)	0.350 90(5)	0.700 85(5)	C(22)	0.094 4(4)	0.300 1(2)	0.801 6(2)
P(2)	0.512 29(8)	0.373 30(5)	0.822 19(4)	C(23)	0.096 4(4)	0.330 3(3)	0.618 2(2)
O(1)	0.378 6(2)	0.475 4(1)	0.710 4(1)	C(24)	0.059 7(4)	0.383 9(3)	0.566 4(2)
O(2)	0.583 7(2)	0.533 1(1)	0.779 5(1)	C(25)	−0.031 0(5)	0.369 7(4)	0.501 7(3)
H(O2)	0.506(2)	0.508(2)	0.756(2)	C(26)	−0.083 6(5)	0.302 9(4)	0.488 9(3)
C(1)	0.569 9(4)	0.390 1(2)	0.640 7(2)	C(27)	−0.049 0(5)	0.250 5(4)	0.539 5(3)
C(2)	0.448 9(4)	0.384 6(2)	0.590 3(2)	C(28)	0.039 0(4)	0.263 7(3)	0.603 5(3)
C(3)	0.405 6(3)	0.313 7(2)	0.590 9(2)	C(29)	0.663 3(3)	0.423 1(2)	0.846 9(2)
C(4)	0.495 6(4)	0.274 4(2)	0.644 3(2)	C(30)	0.675 6(3)	0.493 7(2)	0.822 6(2)
C(5)	0.598 4(4)	0.321 4(2)	0.673 6(2)	C(31)	0.792 1(4)	0.528 2(2)	0.844 5(2)
C(6)	0.656 7(5)	0.453 6(3)	0.648 4(3)	C(32)	0.897 1(4)	0.494 0(3)	0.886 3(2)
C(7)	0.381 4(5)	0.443 1(3)	0.540 4(3)	C(33)	0.887 5(4)	0.424 2(3)	0.907 7(2)
C(8)	0.297 9(4)	0.279 4(3)	0.537 3(2)	C(34)	0.773 2(3)	0.390 2(2)	0.888 5(2)
C(9)	0.495 3(6)	0.193 6(2)	0.650 4(3)	C(35)	0.552 9(3)	0.290 0(2)	0.875 0(2)
C(10)	0.724 2(4)	0.299 7(3)	0.722 1(2)	C(36)	0.586 3(4)	0.290 3(2)	0.949 7(2)
C(11)	0.176 3(3)	0.441 3(2)	0.718 5(2)	C(37)	0.609 2(4)	0.226 7(2)	0.988 0(2)
C(12)	0.268 2(3)	0.492 8(2)	0.720 1(3)	C(38)	0.599 0(4)	0.162 2(2)	0.952 5(2)
C(13)	0.241 2(4)	0.565 2(2)	0.730 4(2)	C(39)	0.565 6(4)	0.160 5(2)	0.878 9(2)
C(14)	0.126 7(4)	0.584 4(2)	0.737 8(3)	C(40)	0.543 0(4)	0.224 7(2)	0.840 3(2)
C(15)	0.033 5(4)	0.533 4(3)	0.733 8(3)	C(41)	0.422 4(3)	0.419 0(2)	0.876 6(2)
C(16)	0.057 4(4)	0.462 7(2)	0.723 4(2)	C(42)	0.430 2(4)	0.492 3(2)	0.890 2(2)
C(17)	0.179 8(3)	0.287 4(2)	0.762 4(2)	C(43)	0.356 6(5)	0.524 0(2)	0.929 5(2)
C(18)	0.239 5(4)	0.221 2(2)	0.770 0(2)	C(44)	0.277 5(4)	0.484 6(3)	0.956 9(2)
C(19)	0.215 3(5)	0.169 5(2)	0.816 0(3)	C(45)	0.269 2(4)	0.411 8(3)	0.944 0(2)
C(20)	0.131 5(5)	0.183 7(3)	0.854 9(2)	C(46)	0.339 7(3)	0.379 6(2)	0.904 0(2)

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