Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

[1,3-Bis(diphenylphosphino)propane]-trichlorooxorhenium(V)

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Received 10 December 1999
Accepted 10 May 2000

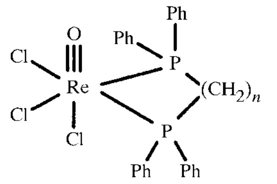
Trichlorooxo[1,3-propanediylbis(diphenylphosphine)-*P*,*P*′]-rhenium(V), $[ReCl_3O(C_{27}H_{26}P_2)]$, crystallizes with four formula units per unit cell. The crystal structure consists of neutral complexes of $[ReOCl_3(dppp)]$ [dppp is 1,3-bis(diphenylphosphino)propane] packed by H$\cdots\pi$-ring interactions. The Re atom is octahedrally coordinated to the oxo anion, three Cl atoms and two P atoms from the dppp ligand. The six-membered ring formed by the bidentate dppp ligand and the rhenium metal centre is in a chair conformation. The title compound is an intermediate in the synthesis of bis(dppp) complexes of rhenium.

Comment

Tertiary phosphine ligands have a strong stabilizing effect on rhenium complexes in most oxidation states. $[Re^{I}(dppm)_3]I$ (Rivero *et al.*, 2000) and $[Re^{V}O_2(dppe)_2]I$ (Kremer *et al.*, 1999) can be cited as good examples. The stability of such complexes has been exploited in two ways. Firstly, rhenium complexes are widely used as non-radioactive models for technetium equivalents used in nuclear medicine. Secondly, rhenium itself ($^{186/188}$Re) also has potential in radiotherapy. In the course of our investigation on Re^{V} complexes with diphosphines, we have prepared and characterized by single-crystal X-ray diffraction the mixed-ligand neutral complex $[Re^{V}OCl_3(dppp)]$, (I), analogous to $[Re^{V}OCl_3(dppe)]$ (Sergienko, 1994), (II), and $[Re^{V}OCl_3(dppm)]$ (Rossi *et al.*, 1993), (III), starting from $ReCl_5$.

Compounds (I), (II) and (III) share the $ReOCl_3P_2$ coordination polyhedra with the ring conformation changing as the Re—P—C_n—P ring grows from $n = 1$ in (III) to $n = 3$ in (I). The conformation of the ring causes severe distortions in (III) due to the rigidity of the four-membered ring formed, whereas there is no cause of distortion in (I) due to the flexibility of the six-membered ring formed. The compounds pack in the centrosymmetric space group $P2_1/c$, but are reported in different settings, *i.e.* $P2_1/a$ for (I), $P2_1/n$ for (II) and $P2_1/c$ for (III).

The coordination around the Re metal centre is a distorted octahedron as in (II) and (III). Compound (I) shows an approximate C_s symmetry with the Re1, O1, Cl1 and C2 atoms located at the pseudo-mirror plane. This feature is also observed in the other odd *n* member of this series, (III). The equatorial plane of the octahedron is formed by both P atoms from dppp and two Cl atoms (Cl2 and Cl3). The apical positions are occupied by the oxygen (O1) and the third Cl atom (Cl1). The short Re1—O1 distance [1.671 (2) Å] indicates the presence of a triple bond, as in (II) and (III), with distances of 1.679 (5) and 1.671 (6) Å, respectively. The high electron density located in the Re1$\equiv$O1 region forces the negatively charged Cl atoms, located *cis* to the O1 atom, to be pushed away from the O1 atom. This effect is not observed for the neutral P atoms. The O1—Re1—P angles have values of 90.80 (9) (P1) and 89.33 (9)° (P2), while the O1—Re1—Cl angles are 100.54 (9) (Cl2) and 101.04 (10)° (Cl3). The same effect is observed in (II) and (III); the O—Re—P angles are 84.3 (2) and 91.4 (2)° in (II), and 88.7 (3) and 91.3 (3)° in (III), while the O—Re—Cl angles are 103.9 (2) and 101.4 (2)° in (II), and 105.1 (2) and 102.7 (2)° in (III). The Re atom of (I) is displaced 0.2246 (5) Å from the equatorial mean plane towards the O1 atom. The three Cl—Re—Cl angles are expected to be approximately constant within the different complexes and near to the ideal value of 90°. This is observed in (I) where the Cl—Re—Cl angles are 89.37 (3), 87.55 (4) and 86.03 (4)° for Cl1—Re1—Cl2, Cl1—Re1—Cl3 and Cl2—Re1—Cl3, respectively. The corresponding Cl—Re—Cl angles are 87.73 (8), 91.50 (8) and 86.32 (10)° in (II), and 89.1 (1), 87.7 (1) and 86.3 (1)° in (III). The P1—Re1—P2 angle is mainly affected by the size of the Re—P—C_n—P ring. This angle increases from 69.2 (1)° in (III) to 91.27 (3)° in (I), while in (II), the angle takes the intermediate value 83.29 (8)°. The O1—Re—Cl1 angle deviates significantly from linearity due to the influence of the Re1$\equiv$O1 bond and the consequent shift of the equatorial Cl atoms from the ideal location. This angle is 167.23 (9)° in (I), 163.0 (2)° in (II) and 162.8 (1)° in (III). The Re1—Cl1 bond distance is 2.4611 (9) Å, while the Re1—Cl2 and Re1—Cl3 bond distances are 2.3639 (10) and 2.3772 (10) Å, respectively. This difference in distances is ascribed to the *trans* influence suffered by the Cl1 atom. This is also observed in (II) and (III) where the equivalent bond distances are 2.4291 (15), 2.380 (3) and 2.377 (3) Å for (II), and 2.452 (3), 2.365 (4) and 2.373 (3) Å for (III). Finally, the Re—P bond distances show no systematic trend related to the



(I) $n = 3$ = dppp
(II) $n = 2$ = dppe
(III) $n = 1$ = dppm

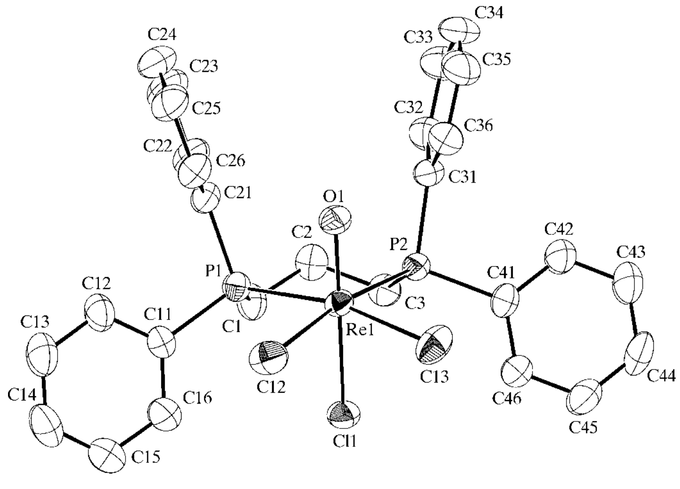


Figure 1
ZORTEP (Zsolnai & Pritzkow, 1995) drawing of (I) with displacement ellipsoids at the 50% probability level.

P—Re—C_n—P ring size. The values are 2.4578 (10) and 2.4777 (9) Å in (I), 2.463 (2) and 2.445 (2) Å in (II), and 2.439 (3) and 2.449 (2) Å in (III), for Re1—P1 and Re1—P2, respectively.

The six-membered ring is in a chair conformation in (I), as can be clearly observed by the shifts of the Re1 and C2 atoms from the P1—C1—P2—C3 mean plane [0.840 (3) Å for Re1 and −0.736 (5) Å for C2]. Other conformations were observed in $[\mathrm{Re^{V}O_2(dppp)_2}]^+$ complexes like $[\mathrm{ReO_2(dppp)_2}]\mathrm{I}\cdot\mathrm{H_2O}\cdot\mathrm{CH_4O}$ (Suescun *et al.*, 1999), while the compound $[\mathrm{ReO(OCH_3)(dppp)Cl_2}]\cdot\mathrm{C_2H_6O}$ (Kremer *et al.*, 1999) contains a single dppp ligand in a chair conformation. The phenyl rings bonded to P1 form a dihedral angle of 77.07 (12)° and those bonded to P2 an angle of 82.05 (12)°. Similar values were observed for the equivalent angles between adjacent phenyl rings in dppp complexes (Kremer *et al.*, 1999; Suescun *et al.*, 1999). The packing of the structure is directed by H$\cdots\pi$-ring interactions forming a three-dimensional network. The main C—H$\cdots\pi$-ring interactions are: C2—H2*B*$\cdots$(C41–C46)$^{\mathrm{i}}$, with H$\cdots$ring = 2.961 Å, a C—H$\cdots$ring-centroid = 163.63° and C$\cdots$ring-centroid = 3.950 Å; C25—H25$\cdots$(C11–C6)$^{\mathrm{ii}}$ with the respective parameters 3.157 Å, 129.76° and 4.015 Å; C26—H26$\cdots$(C11–C16)$^{\mathrm{ii}}$ with parameters 2.960 Å, 130.02° and 4.013 Å and C35—H35$\cdots$(C11–C16)$^{\mathrm{iii}}$ 2.726 Å, 163.58° and 3.645 Å [symmetry codes: (i) $-\frac{1}{2}+x, \frac{3}{2}-y, -z$; (ii) $-x, 2-y, -z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, z$].

Experimental

Dppp (0.97 g, 2.35 mmol) was dissolved in dry methanol (20 ml). $\mathrm{ReCl_5}$ (0.51 g, 1.40 mmol) was added and the mixture was refluxed for 1 h. Dichloromethane (5 ml) was then added and the suspension was refluxed for 10 h. A green solid was obtained and filtered off from a brown solution (yield 25–30%). The solid was recrystallized from a mixture of $\mathrm{CH_2Cl_2}$ and methanol (10:3 *v*/*v*). The presence of the Re═O bond was confirmed by the IR stretching frequency of 998 $\mathrm{cm^{-1}}$, consistent with that observed in (III) (Rossi *et al.*, 1993) of ν (Re═O) 990 $\mathrm{cm^{-1}}$.

Crystal data

$[\mathrm{ReCl_3O(C_{27}H_{26}P_2)}]$
$M_r = 720.97$
Monoclinic, $P2_1/a$
$a = 16.5579\ (19)$ Å
$b = 10.9208\ (13)$ Å
$c = 16.5426\ (19)$ Å
$\beta = 114.748\ (8)°$
$V = 2716.6\ (5)$ Å^3
$Z = 4$

$D_x = 1.763$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 24 reflections
$\theta = 18.41$–$19.81°$
$\mu = 4.905$ mm^{-1}
$T = 293\ (2)$ K
Plate, green
0.35 × 0.20 × 0.05 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1993)
$T_{\min} = 0.279$, $T_{\max} = 0.792$
7599 measured reflections
6247 independent reflections
5069 reflections with $I > 2\sigma(I)$

$R_{\mathrm{int}} = 0.023$
$\theta_{\max} = 27.50°$
$h = -1 \rightarrow 21$
$k = -1 \rightarrow 14$
$l = -21 \rightarrow 19$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.072$
$S = 1.049$
6247 reflections
307 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 0.5301P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.36$ e Å^{-3}
$\Delta\rho_{\min} = -1.17$ e Å^{-3}

Data collection, cell refinement and data reduction: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *PLATON*98 (Spek, 1990) and *CSD* (Allen & Kennard, 1993).

The authors gratefully thank PEDECIBA-Química and CONICYT (Uruguayan Organizations) for financial aid and the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1104). Services for accessing these data are described at the back of the journal.

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