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Structure of (*OC*-6-14)-Chlorodiiodooxobis(triphenylphosphine)rhenium(V)

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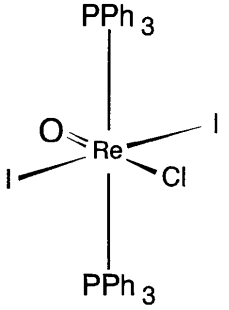
Abstract

The title compound is isostructural with the monoclinic polymorph of $[ReOCl_3\{P(C_6H_5)_3\}_2]$. It consists of octahedral $[ReOClI_2\{P(C_6H_5)_3\}_2]$ molecules of the *trans-trans* isomer, with the O═Re—Cl unit lying on a twofold axis. The bond lengths are Re═O 1.671 (8), Re—P 2.517 (2), Re—Cl 2.383 (4) and Re—I 2.734 (2) Å.

Comment

The triiodo complex $[ReOI_3\{P(C_2H_5)_3\}_2]$ was prepared by Fergusson & Heveldt (1976) by reacting KI with $[ReOCl_3\{P(C_2H_5)_3\}_2]$ in acetone. As a route to the corresponding $P(C_6H_5)_3$ complex, the same reaction was carried out on $[ReOCl_3\{P(C_6H_5)_3\}_2]$. Crystals of the mixed halide compound of the title were obtained when the product was recrystallized from CH_2Cl_2. Attempts are currently being made to determine whether this mixed chloro–iodo molecule was present in the reaction product or was generated by recrystallization.



The compound is isostructural with the monoclinic form of $[ReOCl_3\{P(C_6H_5)_3\}_2]$ (Lebuis & Beauchamp, 1993). The perfectly linear Cl—Re═O unit occupies a crystallographic twofold axis. The octahedron is remarkably regular, all *cis* angles being within 90.0 ± 2.3°. The largest distortion, found for the P—Re—P angle [175.46 (8)°], results from a small displacement of the Re—P bonds away from Re═O. The Re—P distance is the same as in $[ReOCl_3\{P(C_6H_5)_3\}_2]$ and on the short side of the range (2.519–2.553 Å) observed for the ethoxo–halide compounds $[ReO(OC_2H_5)X_2\{P(C_6H_5)_3\}_2]$ (Lebuis, Roux & Beauchamp, 1993). The Re—Cl and Re═O distances are also similar to those of the trichloro complex. On the other hand, the Re—I bonds [2.734 (2) Å] are shorter than in the iodo–alkoxo molecules $[ReO(OR)I_2\{P(C_6H_5)_3\}_2]$ ($R = CH_3$, C_2H_5) (2.764–2.806 Å) (Ciani, D'Alfonso, Romiti, Sironi & Freni, 1983). The Re═O distances in these alkoxo compounds (mean 1.707 Å) are also greater than in the present case [1.671 (8) Å]. The difference of ~0.04 Å, also found between $[ReOCl_3\{P(C_6H_5)_3\}_2]$ and $[ReO(OC_2H_5)Cl_2\{P(C_6H_5)_3\}_2]$ (Graziani, Casellato, Rossi & Marchi, 1985), most likely reflects the variation in *trans* influence between the ethoxo and chloro ligands.

The P—C bonds (mean 1.822 Å) are normal. The phenyl rings are planar, but the P atom is displaced by 0.150 (15) Å from the plane of ring 3. Unequal Re—P—C angles [116.0 (3), 121.4 (3) and 104.4 (3)°] show that coordination does not take place exactly along the lone-pair direction. The phosphines adopt the same conformation as in the monoclinic form of $[ReOCl_3\{P(C_6H_5)_3\}_2]$ (Lebuis & Beauchamp, 1993). The P—C31 bond is nearly eclipsed with the Re═O bond [O—Re—P—C31, −7.1 (3)°], whereas one of the phenyl rings is roughly parallel to the Re—P bond [Re—P—C_{para}—C_{ortho} angles of 68.8 (5), −6.6 (5) and 58.8 (5)° for rings 1, 2 and 3, respectively].

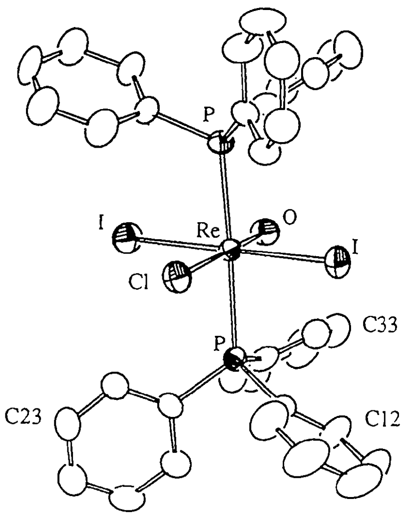


Fig. 1. Structure and numbering scheme of the $[ReOClI_2\{P(C_6H_5)_3\}_2]$ molecule. The atoms in the phenyl rings are assigned C_{ij} symbols, where i is the ring number and j corresponds to sequential numbering around the ring, starting with $j = 1$ for the C atoms bound to P. The Cl—Re═O unit lies on a crystallographic twofold axis. Ellipsoids correspond to 50% probability and H atoms are omitted for simplicity.

Experimental

Crystal data

$[ReOClI_2(C_{18}H_{15}P)_2]$
$M_r = 1016.1$
Monoclinic
*C*2/*c*
$a = 24.375$ (9) Å
$b = 9.791$ (6) Å
$c = 16.127$ (6) Å
$\beta = 115.66$ (3)°
$V = 3469.2$ (3) Å^3
$Z = 4$
$D_x = 1.945$ Mg m^{-3}
$D_m = 1.93$ (2) Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.0$–15.0°
$\mu = 5.51$ mm^{-1}
$T = 293$ K
Elongated prism
0.464 ($\bar{1}00/100$) × 0.137 ($0\bar{1}0/010$) × 0.099 ($\bar{1}01/10\bar{1}$) mm
Red

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian by integration from crystal shape (10 × 10 × 10)
$T_{min} = 0.34$, $T_{max} = 0.74$
3061 measured reflections
3061 independent reflections

2113 observed reflections $[I \geq 3\sigma(I)]$
$\theta_{max} = 25°$
$h = -29 \rightarrow 29$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 19$
7 standard reflections frequency: 60 min intensity variation: 2%

Refinement

Refinement on *F*
Final $R = 0.038$
$wR = 0.048$
$S = 1.20$
2113 reflections
196 parameters

H positions fixed (C—H = 0.95 Å, $U_{iso} = 0.06$ Å^2)
$w = 1/[\sigma^2(F) + 0.0009F^2]$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.9$ e Å^{-3} (near Re)
$\Delta\rho_{min} = -0.9$ e Å^{-3} (near I)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Re	0.0	0.17338 (5)	0.25000	0.027
I	0.05961 (2)	0.17184 (7)	0.43784 (3)	0.047
Cl	0.0	0.4168 (3)	0.25000	0.041
P	0.0989 (1)	0.1836 (2)	0.2361 (1)	0.031
O	0.0	0.0027 (8)	0.25000	0.039
C11	0.0941 (4)	0.2440 (9)	0.1267 (6)	0.034
C12	0.1040 (5)	0.1626 (10)	0.0648 (6)	0.052
C13	0.0989 (6)	0.2137 (12)	−0.0172 (7)	0.069
C14	0.0844 (5)	0.3491 (11)	−0.0390 (7)	0.072
C15	0.0746 (6)	0.4300 (10)	0.0211 (8)	0.072
C16	0.0798 (5)	0.3802 (10)	0.1038 (7)	0.063
C21	0.1627 (4)	0.2843 (9)	0.3154 (6)	0.035
C22	0.1584 (4)	0.3690 (9)	0.3798 (6)	0.040
C23	0.2081 (4)	0.4450 (10)	0.4361 (6)	0.051
C24	0.2623 (5)	0.4353 (11)	0.4315 (6)	0.057
C25	0.2664 (4)	0.3520 (13)	0.3665 (7)	0.073
C26	0.2171 (4)	0.2760 (12)	0.3076 (7)	0.059
C31	0.1245 (4)	0.0060 (9)	0.2483 (6)	0.039
C32	0.0865 (4)	−0.0909 (9)	0.1857 (6)	0.044
C33	0.1017 (5)	−0.2275 (10)	0.1964 (7)	0.058
C34	0.1543 (6)	−0.2660 (10)	0.2704 (8)	0.073
C35	0.1916 (5)	−0.1733 (12)	0.3322 (7)	0.067
C36	0.1772 (5)	−0.0361 (10)	0.3225 (6)	0.049

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Re—O	1.671 (8)	P—C11	1.817 (8)
Re—Cl	2.383 (4)	P—C21	1.818 (9)
Re—P	2.517 (2)	P—C31	1.830 (9)
Re—I	2.734 (2)		
I—Re—P	91.65 (6)	P—Re—O	92.27 (5)
I—Re—P^i	88.38 (6)	P—Re—P^i	175.46 (8)
I—Re—O	89.68 (2)	Cl—Re—O	180.0
I—Re—Cl	90.32 (2)	Re—P—C11	116.0 (3)
I—Re—I^i	179.37 (3)	Re—P—C21	121.4 (3)
Cl—Re—P	87.73 (5)	Re—P—C31	104.4 (3)
C11—P—C21	100.4 (4)	C11—P—C31	106.8 (4)
C21—P—C31	106.9 (4)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

D_m was measured by flotation in ether/1,2-tetrabromoethane. Data were corrected for Lp. Space groups *C*2/*c* and *Cc* were consistent with the monoclinic Laue symmetry and systematic absences ($hkl\ h+k \neq 2n$ and $h0l\ l \neq 2n$). The structure was solved in the centrosymmetric space group *C*2/*c* by the heavy-atom method. The non-H atoms were refined anisotropically by full-matrix least-squares methods. *SHELX*76 (Sheldrick, 1976) and local programs (Authier-Martin & Beauchamp, 1977) were used for calculations.

Atomic scattering factors were taken from Cromer & Liberman (1970) for non-H atoms and from Stewart, Davidson & Simpson (1965) for H atoms. The anomalous-dispersion terms of Re, I, P and Cl were taken from Cromer (1965).

We wish to thank M. Simard for assistance in collecting the X-ray data.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles in the phosphine ligand and weighted least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71068 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1027]

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Functionalized Hydrocarbons with Condensed Ring Skeletons. XIII. A Substituted 1-Methyltricyclo[7.4.0.0^{2,6}]-tridec-7-ene

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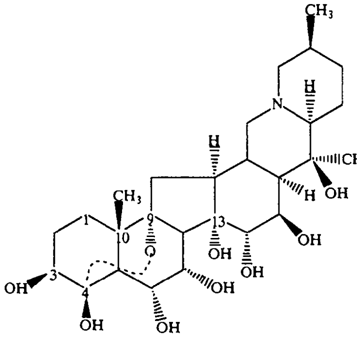
Abstract

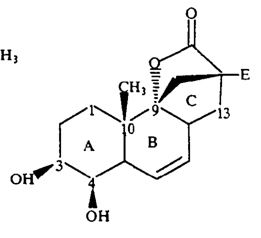
The structure of *rel*-(1*S*,2*R*,4*R*,6*S*,9*S*,10*R*,11*S*)-4-methoxycarbonyl-1-methyltricyclo[7.4.0.0^{2,6}]tridec-7-ene-10,11-diol-4,2-carbolactone monohydrate (methyl 7,8-dihydroxy-10a-methyl-2-oxo-3,10b-methano-3,4,4a,6a,7,8,9,10,10a,10b-decahydro-2*H*-benzo[*h*]chromene-3-carboxylate monohydrate) has been determined. The tricyclic compound has the same configuration at C3 (*S*), C9 (*R*) and C10 (*S*) (steriod numbering) as Veratrum alkaloids. The relative stereochemistry is *cis* for the *A*/*B* ring junction, *anti* between C10 methyl and C9 carbolactone and *cis* for the *B*/*C* ring junction.

Comment

The natural Veratrum alkaloids are well known for their important biological activity (Krayer & Acheson, 1946), in particular for their ability to lower blood pressure (Gerber & Nies, 1991; Krayer & Drill, 1958; Meilman & Krayer, 1950). The large number of asymmetric centers [17 in protoverine (1)] and the unusual presence of a tertiary hydroxyl group at position 9 (steroid numbering) present an ambitious goal for total synthesis. Intramolecular processes usually give excellent control on chemo-, regio- and stereoselectivity, such as transannular Diels–Alder cyclization of macrocyclic trienes to synthesize functionalized tricyclic *A*.*B*.*C*[6.6.5] compounds (Quimpère, Ruest & Deslongchamps, 1992*a*). These preliminary results were used to devise a synthetic strategy for the *A*.*B*.*C*[6.6.5] portion of the Veratrum skeleton by Quimpère, Ruest & Deslongchamps (1992*b*), where the introduction of the oxygen bridge between positions 9 and 4 was investigated. These authors supplied a sample of suitable crystalline material; this paper reports the crystallographic structure of (2) containing a 9-hydroxyl group lactonized with the adjacent methyl ester of the malonate moiety. The predicted stereochemistry (Quimpère, Ruest & Deslongchamps, 1992*a*) of all the asymmetric centers of the molecule is confirmed.



(1)



(2) $E = CO_2Me$

The crystal structure, anisotropic thermal ellipsoids and atomic numbering are shown in Fig. 1. As predicted, the C3 proton is α and axially oriented. Ring *A* has a chair conformation, ring *B* a half-chair [C5—C6—C7—C8 = −1.7 (5)°], and ring *C* is in a β-envelope conformation; C11 is 0.873 (4) Å from the plane defined by atoms C8, C9, C12 and C13. The *A*/*B* ring junction is *cis*; *B*/*C* is