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Mixed-Halide Complex *trans*-Tetrahalobis(triphenylphosphine oxide)rhenium(IV)

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Abstract

The molecule of the red title compound, *trans*-tetra-(chloro/bromo)bis(triphenylphosphine oxide-*O*)rhenium(IV), [ReBr$_{2.5}$Cl$_{1.5}${OP(C$_6$H$_5$)$_3$}$_2$], lies on a crystallographic centre of symmetry. Coordination of rhenium by the four halides is square planar, capped by two mutually-*trans* triphenylphosphine oxide groups.

Comment

In the course of our work investigating the binding of rhenium by hydroxyimino-2,2′-dipropionic acid, we isolated the title compound, (I), which lies on a crystallographic centre of symmetry. The rhenium is coordinated by four halides, which are square planar, and two mutually-*trans* OPPh$_3$ molecules. Trial site-occupancy and displacement-parameter refinements with various constraints suggested that the halogen Br:Cl stoichiometry is 5:3, *i.e.* an overall composition of [ReBr$_{2.5}$Cl$_{1.5}$(OP{C$_6$H$_5$}$_3$)$_2$]. This result is consistent with the elemental analysis.

$$\begin{array}{c} X\ X \\ \backslash / \\ Ph_3PO\!\!-\!\!Re\!\!-\!\!OPPh_3 \\ / \backslash \\ X\ X \end{array}$$

(I)
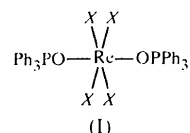
X = Cl/Br (stoichiometry 1.5:2.5)

The Re—O1 bond distance, 2.030 (7) Å, compares with those of 2.063 (9) and 2.053 (7) Å in [ReOCl$_3$-(PEt$_2$Ph)(OPEt$_2$Ph)] and [ReOBr$_3$(PEt$_2$Ph)(OPEt$_2$Ph)], respectively (Sergienko *et al.*, 1982). A search of the Cambridge Structural Database (Allen & Kennard, 1993) reveals very few structurally-characterized rhenium complexes with four halide ligands and a phosphine oxide group, making the structure of [ReBr$_{2.5}$-Cl$_{1.5}$(OPPh$_3$)$_2$] unusual. The Re^{IV} complex [ReCl$_4$-(dppom-*P,O*)] [dppom = Ph$_2$PCH$_2$P(=O)Ph$_2$] has been reported (Rossi *et al.*, 1993) from the reaction of [ReOCl$_3$(PPh$_3$)$_2$] and dppm (dppm = Ph$_2$PCH$_2$PPh$_2$) under aerobic conditions. The crystal structure showed that the complex forms with a Cl atom *trans* to the O atom. The Re—O [2.087 (7) Å] and P—O [1.523 (8) Å] distances were slightly longer, and the Re—O—P angle far smaller [130.1 (1)°] than are observed for [ReBr$_{2.5}$Cl$_{1.5}$(OPPh$_3$)$_2$]. Rossi *et al.* (1993) also reported the synthesis of the Re^V compound [AsPh$_4$]-[ReCl$_4${N(OPPh$_2$)(PPh$_2$)-*O,P*}], also with a Cl atom *trans* to the O atom; the Re—O [2.054 (3) Å] and P—O [1.543 (3) Å] distances are slightly longer, and the Re—O—P angle far smaller [128.2 (3)°] than were observed for [ReBr$_{2.5}$Cl$_{1.5}$(OPPh$_3$)$_2$]. However, the small Re—O—P angles observed for these two complexes are probably due to the bidentate nature of the dppom and N(OPPh$_2$)PPh$_2$ ligands. Comparison with monodentate OPPh$_3$-containing rhenium complexes [ReCl$_3$(NO)(NPPh$_3$)(OPPh$_3$)] [Re—O 2.092 (6), P—O 1.502 (7) Å and Re—O—P 148.7 (4)°; Mronga *et al.*, 1983] and [ReOI$_2$(PPh$_3$)(OPPh$_3$)(OReO$_3$)] [Re—O 2.075 (9), P—O 1.49 (1) Å and Re—O—P 151.5 (6)°; Ciana *et al.*, 1986] shows that the Re—O—P angle [158.1 (5)°] for [ReBr$_{2.5}$Cl$_{1.5}$(OPPh$_3$)$_2$] is not unusual. Comparisons of the Re—*X* bond lengths for these compounds with (I) show that, as expected, due to the mixed nature of the halogen atoms in (I), the bond lengths

observed are at the upper limit of those for Re—Cl (2.365–2.464 Å) and low for those of Re—Br (2.516–2.547 Å). Surprisingly, displacement ellipsoids for the halogen atoms are not elongated along the bonds. A further search of the Cambridge Structural Database reveals only four structurally characterized compounds of the type [MX_4(OPPh$_3$)$_2$]. Of these, two, [WCl$_4$-(OPPh$_3$)$_2$] (Szymańska-Buzar & Glowiak, 1995) and [SnBr$_4$(OPPh$_3$)$_2$] (Tudela et al., 1993), are arranged with the two OPPh$_3$ groups cis with respect to each other. The other two complexes, [UBr$_4$(OPPh$_3$)$_2$] (Bombieri et al., 1983) and [SnBr$_4$(OPPh$_3$)$_2$] (Tursina et al., 1986), are trans and show similar angles around the metal to those observed in (I).
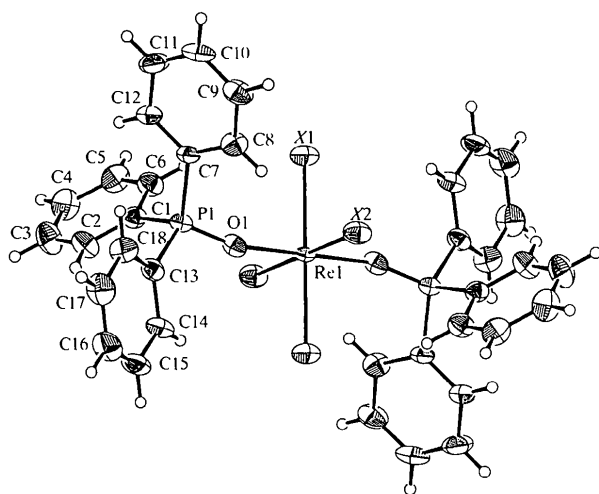

Fig. 1. The molecular structure of (I) with 30% probability ellipsoids.

Experimental

The title compound was obtained from the reaction of crude hydroxyimino-2,2′-dipropionic acid (hidpaH$_3$) (0.15 g, yellow syrup), prepared according to Felcman et al. (1984), with a suspension of [ReOCl$_3$(PPh$_3$)$_2$] (0.333 g, 0.4 mmol), prepared according to Chatt & Rowe (1962), in acetone (15 ml) and warmed for 4 h. A red–brown solid precipitated, which was collected by filtration and washed with Et$_2$O (3 × 15 ml). Crystals were obtained by dissolving the solid in a minimum of dry CH$_2$Cl$_2$ (ca 10 ml) and carefully layering with toluene (40 ml). After several days standing at room temperature, red tabular crystals of the title compound formed. Microanalysis calculated for C$_{36}$H$_{30}$Br$_{2.5}$Cl$_{1.5}$O$_2$P$_2$Re: C 43.4, H 3.0, P 6.2, Br 20.6, Cl 5.3%; found: C 45.3, H 3.1, P 6.4, Br 21.2, Cl 5.7%. The impure ligand mixture is the source of bromine in the final product (Harben et al., 1997) and the reduction of Re^V to Re^{IV} may be compared with the reaction of Roncari et al. (1981) who have reported the reduction of [Re^{V}OCl$_3$(PPh$_3$)$_2$] to [Re^{IV}Cl$_4$(PPh$_3$)$_2$] when reacted with N-methylsalicylideneimine using either ethanol or acetone as solvent. The IR spectrum of solid (I) shows three bands in the Re—Br region at 284, 262 and 251 cm^{-1}, three bands in the Re—Cl region at 457, 445 and 428 cm^{-1}, a band at

313 cm^{-1} due to an Re—O stretching mode, and bands due to OPPh$_3$ in the region 990–1120 cm^{-1}. Comparisons with the IR data for [AsPh$_4$][ReCl$_4${N(OPPh$_2$)(PPh$_2$)-P,O}] (Rossi et al., 1994) suggest that the band at 1118 cm^{-1} is due to the coordinated P=O and vibrations at 998, 1029 and 1085 cm^{-1} are attributed to the phenyl rings.

Crystal data

[ReBr$_{2.5}$Cl$_{1.5}$(C$_{18}$H$_{15}$OP)$_2$]	Cu Kα radiation
M_r = 995.69	λ = 1.54178 Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
a = 9.728 (2) Å	θ = 14.7–20.0°
b = 10.556 (2) Å	μ = 12.046 mm^{-1}
c = 9.499 (3) Å	T = 293 (2) K
α = 108.59 (2)°	Tabular
β = 93.55 (2)°	0.20 × 0.17 × 0.10 mm
γ = 102.414 (15)°	Red
V = 894.0 (3) Å^3	
Z = 1	
D_x = 1.849 Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-5R diffractometer	2538 reflections with $I > 2\sigma(I)$
ω–2θ scans	R_{int} = 0.054
Absorption correction:	θ_{max} = 60.07°
refined from ΔF	$h = -9 \rightarrow 10$
(DIFABS; Walker &	$k = -11 \rightarrow 11$
Stuart, 1983)	$l = -10 \rightarrow 10$
T_{min} = 0.130, T_{max} = 0.300	3 standard reflections
2822 measured reflections	every 150 reflections
2640 independent reflections	intensity decay: 1.35%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$\Delta\rho_{max}$ = 1.794 e Å^{-3}
$wR(F^2)$ = 0.148	$\Delta\rho_{min}$ = -1.414 e Å^{-3}
S = 1.095	Extinction correction: none
2637 reflections	Scattering factors from
205 parameters	International Tables for
H atoms not refined	Crystallography (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0756P)^2$	
$+ 7.75P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (Å, °)

Re1—O1†	2.030 (7)	Re1—X2^i	2.426 (2)
Re1—X1^i†	2.445 (2)	P1—O1	1.459 (8)
O1—Re1—X1^i	89.4 (2)	X1^i—Re1—X2^i	89.65 (6)
O1—Re1—X2^i	90.6 (2)	P1—O1—Re1	158.1 (5)

Symmetry code: (i) $-x, -y, -z$.

† X = Cl/Br.

Data were collected to a θ_{max} of 60°, since an evacuated beam tunnel has to be removed beyond this angle, causing the intensity to be reduced by about 40%, due to air scatter. The halide positions were mixed bromine and chlorine. From the analysis it was found that the Br/Cl ratio was about 2.5:1.5, so this ratio was used in the refinement. A refined absorption correction was applied, since there were no suitable

reflections accessible for ψ scans with the helium tunnel in place, and the crystal did not have sufficiently well defined faces for indexing for a numerical correction. The positions and anisotropic displacement parameters for the Br and Cl atoms at each site were constrained to be the same. H atoms were included in calculated positions using the riding model, with displacement parameters 1.2 times U_{eq} of the atoms to which they were bonded. The largest peaks on the final difference map were close to the Re atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1176). Services for accessing these data are described at the back of the journal.

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Hexacarbonyl-1κ³C,2κ³C-bis{1,2(η^5)-1-[2-(trimethylsiloxy)ethyl]cyclopentadienyl}dimolybdenum(Mo—Mo)

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Abstract

The title complex molecule, $[Mo_2(C_{10}H_{17}OSi)_2(CO)_6]$, lies on a crystallographic inversion center. Each Mo atom exhibits 'four-legged piano-stool' bond geometry, with the other Mo atom at a basal position [Mo—Mo 3.219(1) Å].

Comment

We have shown (Covert *et al.*, 1992) that the cage effect for the photogenerated radical pair [(MeCp)(CO)₃Mo, Mo(CO)₃(MeCp)] is smaller than for the heavier tungsten analogue (MeCp is methylcyclopentadienyl). In order to separate changes due to difference in radical mass from changes due to bond energies or spin–orbit coupling, we have synthesized and studied the title molecule, $(CpCH_2CH_2OSiMe_3)_2Mo_2(CO)_6$, (I). This molecule has a similar mass to $(MeCp)_2W_2(CO)_6$. The –CH₂CH₂– spacer insulates the Cp ring from substituent electronic effects. A comparison of the cage effects for the three molecules has allowed us to consider the influence of different M—M bond energies.

(I)
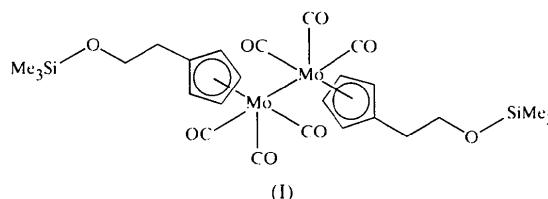
The molecule lies on a crystallographic inversion center. The side chain in each moiety is directed away from the Mo₂(CO)₆ region in such a way that one