ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 6, pp. 439–445. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 6, pp. 378–384.

Structural Features of Monomeric Octahedral d^2-Rhenium(V) Monooxo Complexes with Oxygen Atoms of Tridentate Chelating (O,P,O and O,P,N) Ligands

V. S. Sergienko[a, b, *]

[a]Kurnakov Instiute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia
[b]All-Russia Institute for Scientific and Technical Information, Russian Academy of Sciences, Moscow, 125190 Russia
*e-mail: sergienko@igic.ras.ru

Received July 16, 2018; revised September 12, 2018; accepted October 18, 2018

Abstract—The structural features of eleven mononuclear octahedral d^2-Re(V) monooxo complexes with tridentate chelating (O,P,O and O,P,N) ligands, $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})(\mathrm{L}^n_{\mathrm{bi}})]$, $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})\mathrm{Cl}_2]$, and $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})$-$\mathrm{Cl}(\mathrm{PPh}_3)]$, are considered. The Re–$\mathrm{O}(\mathrm{L}^m_{\mathrm{tri}})_{trans}$ bond lengths are commensurable (or somewhat shorter) with the Re–$\mathrm{O}(\mathrm{L}^m_{\mathrm{tri}})_{cis}$ or Re–O(ST) bond lengths, which is indicative of the presence of pseudo-dioxo ReO_2 groups with increased bond orders for both *trans*-arranged Re–O bonds. In the structures of two compounds, the Re–$\mathrm{O}(\mathrm{L}^2_{\mathrm{bi}})_{trans}$ bonds are, on average, 0.094 Å longer than Re–O(ST) and 0.189 Å longer than Re–$\mathrm{O}(\mathrm{H}\mathrm{L}^3_{\mathrm{bi}})_{cis}$, in accordance with the structural consequences of the *trans*-effect of a multiply bonded oxo ligand.

Keywords: crystal structure, X-ray diffraction analysis, six-coordinate d^2-Re monooxo compounds, tridentate chelating (O,P,O and O,P,N) ligands

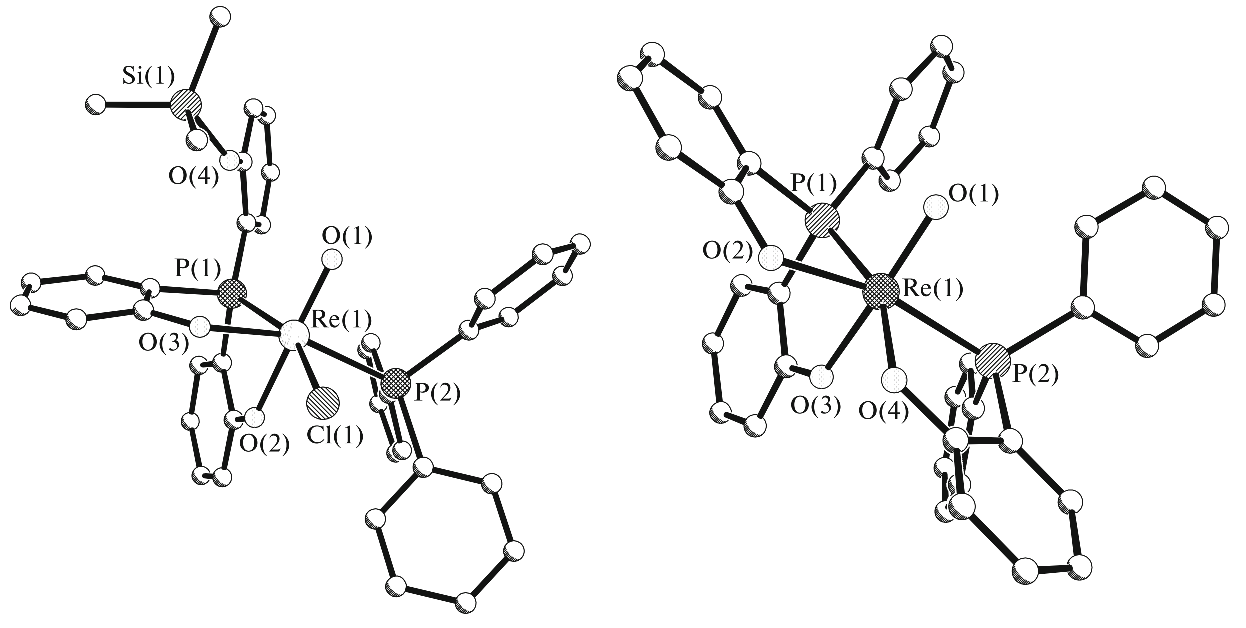
DOI: 10.1134/S1070328419060071

INTRODUCTION

The structures of monomeric octahedral complexes (MOCs) of Group 5–7 d^0- and d^2-metals (Nb, V, Mo, W, Re, Tc) with multiply bonded O(oxo) ligands are described in detail in the literature [1–7]. More than five hundred d^2-Re(V) compounds were studied by X-ray diffraction (see Cambridge Crystallographic Data Centre (CCDC), version 5.38, November 2017 [8]). Most of these complexes, $\mathrm{ReO_{oxo}O(Lig)}_{trans}$, contain oxygen atoms of mono- and polydentate ligands in the *trans*-position to the oxo ligands. Previously, we published a number of integrating papers dealing with d^2-Re(V) MOCs with ligands being represented by halogen, nitrogen, sulfur, and hydrogen atoms; oxygen atoms of monodentate anionic ligands [hydroxy, alkoxy (methoxy, ethoxy, propoxy), OR^{n-} (n = 1, 2; R = Ph, Cy, $\mathrm{C_6H_4OH}$, $\mathrm{C_6H_4OMe}$, $\mathrm{P(O)(OMe)_2}$, $\mathrm{C(O)(CF_3)}$, $\mathrm{OCMe(CF_3)_2}$, $\mathrm{BF_3}$), OER^{n-} (n = 1, 2; E = Si, B, S; R = $\mathrm{Me_3}$, $\mathrm{F_3}$, $\mathrm{O_2CF_3}$)], bidentate chelating (O,O), (O,S), (O,C), (O,P), and (O,N) singly charged ligands; singly and doubly charged tridentate chelating (O,N,O) [9], (O,O,O) [10], and (O,S,O and S,O,S) [11] ligands; and neutral oxygen-containing ligands (water molecules, phosphine oxides and arsine oxides $\mathrm{OER_3}$ (E = P, As; $\mathrm{R_3}$ = $\mathrm{Ph_3}$, $\mathrm{PhEt_2}$), OR' molecules [DMF, R''OH (R'' = Me, Et, Pr), L ($\mathrm{ON_4C_6} \cdot \mathrm{C_6H_{10}}$, $\mathrm{O^-(C_6H_3MeCH_2NH^+Et_2)}$, $\mathrm{O^-(NH^+C_5H_4)}$) in *trans*-positions to the multiply bonded O(oxo) ligands. Previously, we published reviews dealing with the structural details of d^0-Re(VII) [12] and d^0-, d^2-technecium(V, VII) MOCs [13].

The structural consequence of the *trans*-effect of the multiply bonded O(oxo) ligand, namely, elongation of the opposing Re–L_{trans} bond, is characterized by the parameter Δ (the difference between lengths of the like bonds {[Re–L_{trans}] – [Re–L_{cis}]}). If the structure contains no ligands of the same sort in both *trans* and *cis* positions to O(oxo), we used the parameter {[Re–L_{trans}] – [Re–L(ST)]}, where ST is the statistical mean standard length of the Re(V) bond with the ligand of the same sort as L_{trans}. As the parameter Re–O(ST), we took (as previously [4]) the value of 2.04 Å.

This communication discusses the structure of the monomeric octahedral monooxo complexes $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})(\mathrm{L}^n_{\mathrm{bi}})]$ and $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})\mathrm{Cl}_2]$ containing a triden-



(I) **(II)**

Fig. 1. Structure of the complexes: $[\mathrm{ReO}(\mathrm{L}^1_{\mathrm{tri}})\mathrm{Cl}(\mathrm{PPh}_3)]$ (**I**); $[\mathrm{ReO}(\mathrm{L}^2_{\mathrm{tri}})(\mathrm{L}^1_{\mathrm{bi}})]$ (**II**).

tate chelating (O,P,O or O,P,N), bidentate chelating, or two monodentate ligands.

Selected bond lengths for the eight structurally studied complexes of the above-indicated types are summarized in Table 1.

STRUCTURE OF COMPLEXES WITH THE TRIDENTATE CHELATING (O,P,O) LIGAND

In each of the two complexes considered in this chapter, all three atoms of the doubly charged tridentate chelating (O,P,O) ligands $\mathrm{L}^m_{\mathrm{tri}}$ (m = 1, 2) are located in the same face of the Re octahedron (*fac*-isomer). The *trans*-position relative to the multiply bonded oxo ligand is occupied, in both structures, by either of the two alkoxy oxygen atoms of the $\mathrm{L}^m_{\mathrm{tri}}$ ligand. The coordination of the $\mathrm{L}^m_{\mathrm{tri}}$ ligands to rhenium is accompanied by closure of two similar five-membered $\mathrm{ReOC_2P}$ rings fused at the Re–P bond.

Structure of the $[\mathrm{ReO}(\mathrm{L}^1_{\mathrm{tri}})\mathrm{Cl}(\mathrm{PPh}_3)] \cdot \mathrm{CH_3Cl_2}$ (I) complex. In the crystal structure of **I** [14] (Fig. 1), the $\mathrm{Me_3SiOC_6H_4}$ group in the tridentate bis(chelate) ((2-trimethylsilyloxy)phenyl)bis(2-phenolato)phosphine ligand $\mathrm{P(C_6H_4O)_2(C_6H_4OSiMe_3}(\mathrm{L}^1_{\mathrm{tri}})$ is terminal. The Re–O2($\mathrm{L}^1_{\mathrm{tri}}$) bond in the *trans*-position relative to O1(oxo) (2.047 Å) is 0.028 Å longer than the Re–O3$(\mathrm{L}^1_{\mathrm{tri}})_{cis}$ bond (2.019 Å). Of the two Re–P bonds, the bond with the P(1) atom of the ligand $\mathrm{L}^1_{\mathrm{tri}}$ (2.4833 Å) is markedly longer than the Re–P2($\mathrm{PPh_3}$) bond (2.4240 Å).

Structure of the $[\mathrm{ReO}(\mathrm{L}^2_{\mathrm{tri}})(\mathrm{L}^1_{\mathrm{bi}})]$ complex (II) with the bidentate chelating (O,P) ligand $\mathrm{L}^1_{\mathrm{bi}}$. In the crystal structure of **II** [15] (Fig. 1), the tridentate chelating bis(o-hydroxyphenyl)phenylphosphine ligand $\mathrm{(OC_6H_4)_2PPh}$ $(\mathrm{L}^2_{\mathrm{tri}})^{2-}$ closes two five-membered $\mathrm{ReOC_2P}$ rings, while the singly charged bidentate chelating (O,P) o-(hydroxyphenyl)diphenylphosphine ligand $\mathrm{OC_6H_4PPh_2}$ $(\mathrm{L}^1_{\mathrm{bi}})$ closes one such chelate ring. Note that in complex **II**, as distinct from **I**, the Re–O3$(\mathrm{L}^2_{\mathrm{tri}})_{trans}$ bond (2.026 Å) is somewhat shorter (by 0.024 Å) rather than longer than the Re–O2$(\mathrm{L}^2_{\mathrm{tri}})_{cis}$ bond (2.050 Å), and also the Re–P1$(\mathrm{L}^2_{\mathrm{tri}})$ bond (2.391 Å) is considerably shorter (by 0.092 Å) than the corresponding bond in **I** and 0.037 Å shorter than the P2$(\mathrm{L}^2_{\mathrm{bi}})$ bond in compound **II** (2.428 Å). In complex **II**, the rhenium atom is, as usual, displaced from the equatorial plane of the $\mathrm{O_2P_2}$ atoms towards the oxo ligand: the Δ_{Re} parameter is 0.273 Å.

STRUCTURE OF COMPLEXES WITH THE TRIDENTATE CHELATING (O,P,N) LIGAND

The crystal structures are known for six mononuclear octahedral complexes containing a tridentate bis(chelating) (O,P,N) ligand.

Table 1. Selected geometric parameters (Å) of monomeric octahedral complexes with tridentate chelating (O,P,O and O,P,N) ligands*

Complex	Re=O	Re–L$_{cis}$	Re–O$_{trans}$	Δ, (Δ)	Reference
[ReO$(\mathrm{L}^1_{\mathrm{tri}})$Cl(PPh$_3$)] · CH$_3Cl_2$ (**I**)	1.670(3)	2.019(3) O$(\mathrm{L}^1_{\mathrm{tri}})$ 2.4833(12) P$(\mathrm{L}^1_{\mathrm{tri}})$ 2.4240(12) P(PPh$_3$) 2.3759(12) Cl	2.047(3) O$(\mathrm{L}^1_{\mathrm{tri}})$	0.028	[14]
[ReO$(\mathrm{L}^2_{\mathrm{tri}})(\mathrm{L}^1_{\mathrm{bi}})$] (**II**)	1.692(3)	2.050(3) O$(\mathrm{L}^2_{\mathrm{tri}})$ 1.994(2) O$(\mathrm{L}^1_{\mathrm{bi}})$ 2.391(1) P$(\mathrm{L}^2_{\mathrm{bi}})$ 2.428(1) P$(\mathrm{L}^1_{\mathrm{bi}})$	2.026(3) O$(\mathrm{L}^2_{\mathrm{tri}})$	–0.024	[15]
[ReO$(\mathrm{HL}^3_{\mathrm{tri}})Cl_2$] (**III**)	1.680(7)	2.224(8) N$(\mathrm{L}^3_{\mathrm{tri}})$ 2.414(2) P$(\mathrm{HL}^3_{\mathrm{tri}})$ 2.453(3) Cl(*trans* to P) 2.353(3) Cl(*trans* to N)	1.943(7) O$(\mathrm{HL}^3_{\mathrm{tri}})$	(–0.097)	[16]
[ReO$(\mathrm{L}^3_{\mathrm{tri}})Cl_2$] (**IV**)	1.695(9)	2.111(11) N$(\mathrm{L}^3_{\mathrm{tri}})$ 2.433(4) P$(\mathrm{L}^3_{\mathrm{tri}})$ 2.438(4) Cl(*trans* to P) 2.376(4) Cl(*trans* to N)	1.953(9) O$(\mathrm{L}^3_{\mathrm{tri}})$	(–0.087)	[16]
[ReO$(\mathrm{L}^3_{\mathrm{tri}})Cl_2$] · 0.25CH$_2Cl_2$ (**V**)	1.702(12) ± 0.009	2.123(15) ± 0.014 N$(\mathrm{L}^3_{\mathrm{tri}})$ 2.447(6) ± 0.005 P$(\mathrm{L}^3_{\mathrm{tri}})$ 2.438(6) ± 0.007 Cl(*trans* to P) 2.396(6) ± 0.007 Cl(*trans* to N)	1.966(12) ± 0.005 O$(\mathrm{L}^3_{\mathrm{tri}})$	(–0.080)	[17]
[ReO$(\mathrm{HL}^4_{\mathrm{tri}})Cl_2$] · MeOH (**VI**)	1.679(4)	2.195(4) N$(\mathrm{HL}^4_{\mathrm{tri}})$ 2.414(1) P$(\mathrm{HL}^4_{\mathrm{tri}})$ 2.429(1) Cl(*trans* to P) 2.344(1) Cl(*trans* to N)	1.976(3) O$(\mathrm{HL}^4_{\mathrm{tri}})$	(–0.064)	[18]
[ReO$(\mathrm{L}^5_{\mathrm{tri}})(\mathrm{L}^2_{\mathrm{bi}})$] · MeOH (**VII**)	1.6680(4)	1.951(4) O$(\mathrm{L}^5_{\mathrm{tri}})$ 2.025(5) N$(\mathrm{L}^5_{\mathrm{tri}})$ 2.471(2) P$(\mathrm{L}^5_{\mathrm{tri}})$ 2.459 P$(\mathrm{L}^2_{\mathrm{bi}})$	2.100(4) O$(\mathrm{L}^2_{\mathrm{bi}})$	(0.060) 0.149	[19]
[ReO$(\mathrm{L}^5_{\mathrm{tri}})(\mathrm{HL}^3_{\mathrm{bi}})$]Cl (**VIII**)	1.667 ± 0.004	1.939 ± 0.003 O$(\mathrm{L}^5_{\mathrm{tri}})$ 2.012 ± 0.017 N$(\mathrm{L}^5_{\mathrm{tri}})$ 2.465 ± 0.017 P$(\mathrm{L}^5_{\mathrm{tri}})$ 2.455 ± 0.004 P$(\mathrm{L}^3_{\mathrm{bi}})$	2.168(3) ± 0.003 O$(\mathrm{L}^2_{\mathrm{bi}})$	(0.128) 0.229	[19]

* $(\mathrm{L}^1_{\mathrm{tri}})^{2-}$ = P(C$_6$H$_4$O)$_2$C$_6$H$_5$OSiMe$_3$; $(\mathrm{L}^2_{\mathrm{tri}})^{2-}$ = (OC$_6$H$_4$)$_2$PPh; $(\mathrm{L}^3_{\mathrm{tri}})^{-}$ = OC$_6$H$_4$CH=NH(CH$_2$)$_3$PPh$_3$; $(\mathrm{HL}^4_{\mathrm{tri}})^{-}$ = Ph$_2$PC$_6$H$_4$CH$_2$NHC$_6$H$_4$O; $(\mathrm{L}^5_{\mathrm{tri}})^{2-}$ = OCH$_2$NC(=O)C$_6$H$_4$PPh$_2$; $(\mathrm{L}^1_{\mathrm{bi}})^{-}$ = OC$_6$H$_4$PPh$_2$; $(\mathrm{L}^2_{\mathrm{bi}})^{-}$ = OC(=O)C$_6$H$_4$PPh$_2$; and $\mathrm{HL}^3_{\mathrm{bi}}$ = OC{NH(CH$_2$)$_2$OH}C$_6$H$_4$PPh$_2$.

In each of these compounds, all three atoms of the singly charged tridentate chelating (O,P,N) ligands L^m_{tri} (m = 3–5) are located in the common face of the Re octahedron (*fac*-isomer). The *trans*-position relative to the multiply bonded oxo ligand in all six structures is occupied by the phenolic oxygen atom of L^m_{tri}. The coordination of the L^m_{tri} ligands to rhenium is accompanied by closure of two chelate rings fused at the Re–N bond, one of the rings being always six-membered ($RePC_3N$), while the other ring may differ in the denticity (for details, see below).

Structure of the $[ReO(L^m_{tri})Cl_2)]$ complexes (m = 3, 4). The structures were determined for four title compounds containing singly charged tridentate bis(chelating) (O,P,N) ligands. In all complexes, chlorines are located in *cis*-positions relative to each other. The complex molecules of three compounds, $[ReOCl_2(HL^3_{tri})]$ (**III**) [16], $[ReOCl_2(L^3_{tri})]$ (**IV**) [16] (Fig. 2), and $[ReOCl_2(L^3_{tri})] \cdot 0.25CH_2Cl_2$ (**V**) [17], have similar structures. In complex **III**, the nitrogen atom of the (2-diphenylphosphinopropylaminomethyl)phenolato ligand, OC_6H_4-2-CH_2NH–$(CH_2)_3$-$PPh_2(HL^3_{tri})^-$, is protonated and sp^3-hybridized, unlike the sp^2-hybridized N atom of the (2-diphenylphosphinopropyliminomethyl)phenolato ligand, OC_6H_4-2-$CH{=}N$–$(CH_2)_3PPh_2$ (L^3_{tri}), in **IV** or **V** with the N=C(1) double bond. The bond lengths in the ReO_2NPCl_2 octahedra of the three structures are similar, with only one exception: the Re–N(L^3_{tri}) bonds in **IV** and **V** (2.111 and 2.123 ± 0.014 Å; structure **V** contains two independent molecules) are markedly shorter than that in **III** (2.224 Å). It is natural that the N=C(1) double bonds in **IV** and **V** (1.35(2) and 1.305(20) ± 0.005 Å) are shorter than the single bond in **III** (1.504(14) Å) and the ReNC1 angles in **IV** and **V** (127.5(11)° and 126.9(13)° ± 2.1°) are greater than the angle in **III** (111.8(6)°). Upon coordination to Re, (L^3_{tri}), and HL^3_{tri} form two six-membered metallacycles: $RePC_3N$ and $ReOC_3N$. Note that in all three structures, two independent Re–Cl bonds differ in length, the Re–Cl(1) bond in the *trans* position to P is longer than the Re–Cl(2) bond in the *trans* position to N (2.438–2.454 and 2.353–2.396 Å, respectively), evidently, due to the stronger *trans*-effect of phosphorus. Previously [17], the difference between the two Re–Cl bond lengths was erroneously attributed to the *trans*-effect of the stronger Re–N bond.

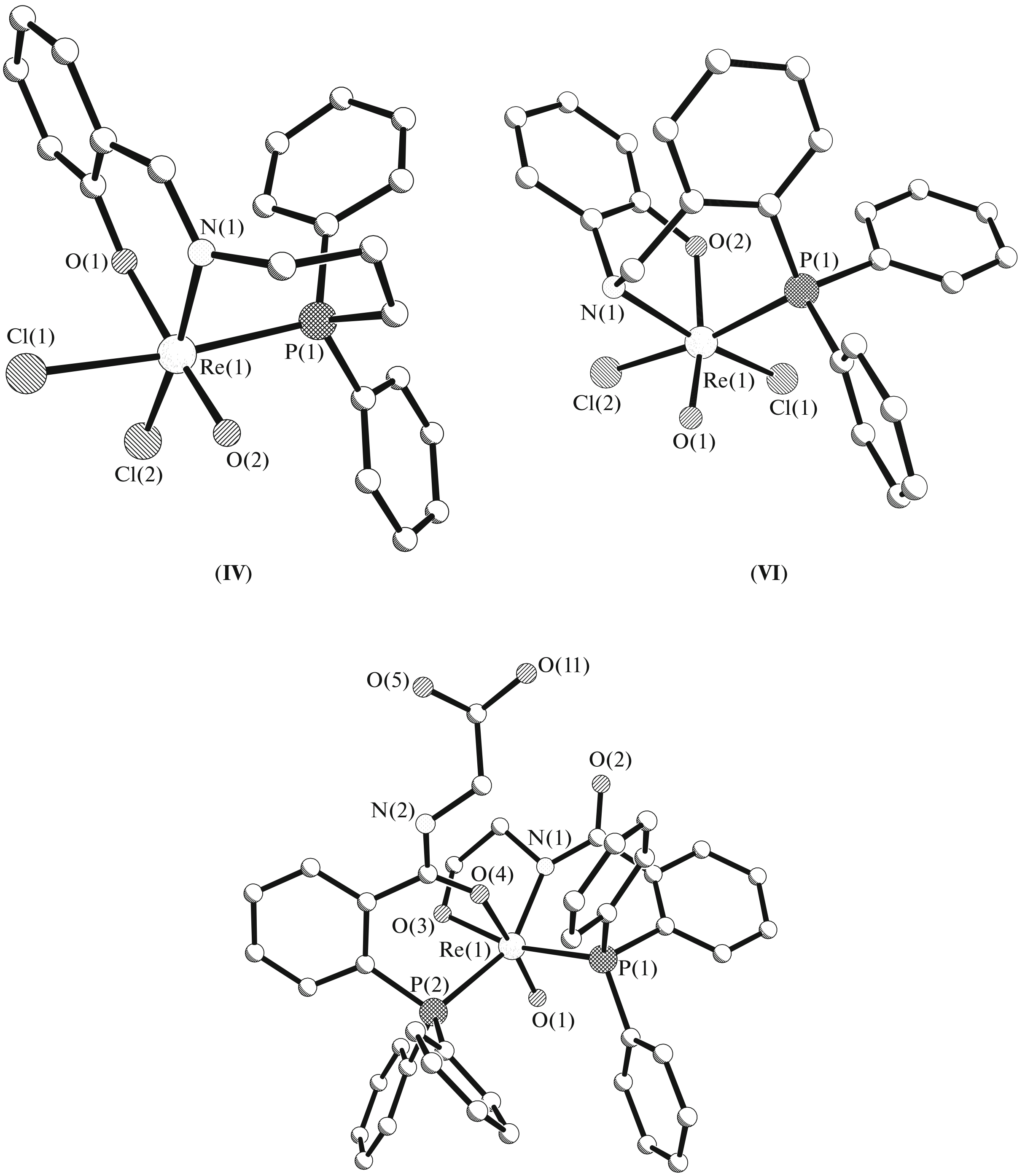
In the crystal structure of $[ReOCl_2(HL^4_{tri})]$ (**VI**) [18] (Fig. 2), the 2-(2-diphenylphosphinobenzylamino)phenolato ligand, $Ph_2PC_6H_4$-2-CH_2N-$HC_6H_4O^-$ (HL^4), being coordinated to rhenium, closes two metallacycles (a six-membered $RePC_3N$ and five-membered $ReOC_2N$ rings fused at the Re–N bond).

Structure of the $[ReO(L^5_{tri})(L^n_{bi})]$ complexes with bidentate chelating (O,P) ligands. The crystal structure was determined for two $[ReO(L^5_{tri})(L^n_{bi})]$ compounds [19] containing the doubly charged 2-(diphenylphosphinyl)-N-(2-oxoethyl)benzamide ligand $O(CH_2)_2$-$NC(=O)C_6H_4PPh_2(L^5_{tri})$. The compounds differ by the bidentate chelating (O,P) ligands, namely, singly charged 2-(diphenylphospanyl)benzoato ligand, $OC(=O)C_6H_4PPh_2(L^n_{bi})$, is present in the neutral methanol solvate complex $[ReO(L^5_{tri})(L^n_{bi})] \cdot MeOH$ (**VII**) and neutral 2-(2-(diphenylphospanyl)-N-(2-hydroxyethyl)benzamide, $OC\{NH(CH_2)_2CO_2\}C_6H_4$-$PPh_2(HL^3_{bi})$, is present in the cationic singly charged complex with the chloride counter-ion $[ReO(L^5_{tri})(HL^3_{bi})]Cl$ (**VIII**) (Fig. 2). The structures of the two complexes are similar. The L^5_{tri}, ligand has a meridional (*mer*) geometry in **VII** and **VIII** and closes six- and five-membered metallacycles, $RePC_3N$ (**A**) and $ReOC_2N$ (**B**), fused at the Re–N bond upon coordination to Re. The bidendate chelating L^n_{bi} ligands in **VII** and **VIII** form five-membered $ReOC_3P$ (**C**) chelate rings with metal atoms. Structure **VIII**, which contains two crystallographic molecules, was solved to a moderate accuracy, and its geometric parameters are not discussed in [19]. In structure **VII**, the six-membered metallacycle **A** is substantially nonplanar; the maximum deviation from the mean plane (Δ_{av}) is 0.223 Å. The five-membered chelate ring **B** has an N-envelope conformation with a 0.179 Å deviation of the nitrogen atom from the $ReOC_2$ mean plane (±0.022 Å). Like ring **A**, rings **C** in both complexes of **VIII** are essentially nonplanar (Δ_{av} of 0.341 Å). The *trans*-positions relative to the oxo ligands in **VII** and **VIII**, unlike that in complex **II**, are occupied by the oxygen atoms of the bidentate chelating L^n_{bi} ligands (rather than by tridentate chelating L^2_{tri}, as in **II**). The Re–O(L^n_{bi}) bonds in **VII** and **VIII** (2.100, 2.168 Å) are considerably longer than Re–O(L^m_{tri}) in **I**–**VI** (1.943–2.047 Å) (for more detail, see below).

STRUCTURAL FEATURES OF MONOMERIC OCTAHEDRAL RHENIUM(V) MONOOXO COMPLEXES WITH TRIDENTATE CHELATING LIGANDS (O,P,O AND O,P,N)

Table 2 summarizes the average values for the selected geometric parameters of **I**–**VIII**.

We will consider two stereochemical features of the octahedral Group 5–7 metal (including rhenium) monooxo complexes.



(IV) **(VI)**

(VIII)

Fig. 2. Structures of the complexes: $[\mathrm{ReO}(\mathrm{L}^3_{\mathrm{tri}})\mathrm{Cl}_2]$ (**IV**); $[\mathrm{ReO}(\mathrm{HL}^4_{\mathrm{tri}})\mathrm{Cl}_2]$ (**VI**); and $[\mathrm{ReO}(\mathrm{L}^5_{\mathrm{tri}})(\mathrm{HL}^3_{\mathrm{bi}})]^+$ (**VIII**).

(1) The choice of the *trans*-partner (in the presence of competing ligands) is determined by the self-consistency rule [2]: the *trans*-position relative to the multiply bonded O(oxo) ligand is mainly occupied by the least polarizable neutral σ-donor ligand (atom), the bond to which is weakened more easily, rather than by the negatively charged ligand (atom).

(2) the Re–L bonds in the *trans* position to O(oxo) are elongated because of the *trans*-effect of the multiply bonded oxo ligand.

The first rule does not hold for any of the eight complexes considered in the review: in compounds **I**–**VIII**, the *trans*-positions to O(oxo) are occupied by negatively charged oxygen atoms of the $\mathrm{L}_{\mathrm{tri}}$ and L_{bi}

Table 2. Selected geometric parameters (Å) of the monomeric octahedral d^2-Re(V) monooxo complexes with tridentate chelating (O,P,O and N,P,O) ligands

Parameter	Value (Å)*
Re–O(oxo)	1.667–1.702 {8} (1.682 ± 0.020)
Re–O$(\mathrm{L}^{n}_{\mathrm{bi}})_{trans}$	2.100, 2.168 {2} (2.134 ± 0.034)
Re–O$(\mathrm{L}^{m}_{\mathrm{tri}})_{trans}$	1.943–2.047 {6} (2.003 ± 0.060)
Re–O$(\mathrm{L}^{m}_{\mathrm{tri}})_{cis}$	1.939–2.050 {4} (1.990 ± 0.060)
Δ{Re–O$(\mathrm{L}^{m}_{\mathrm{tri}})$}	0.028, –0.024 {2} (0.002 ± 0.026)
(Δ){Re–O$(\mathrm{L}^{m}_{\mathrm{tri}})$}	–0.097...–0.064 {4} (–0.082 ± 0.018)
(Δ){Re–O$(\mathrm{L}^{n}_{\mathrm{bi}})$}	0.149, 0.229 {2} (0.189 ± 0.040)
Re–N$(\mathrm{L}^{m}_{\mathrm{tri}})_{cis}$	2.001–2.224 {6} (2.115 ± 0.109)
Re–Cl(*trans* relative to P)	2.424–2.454 {5} (2.437 ± 0.014)
Re–Cl(*trans* relative to N)	2.344–2.396 {4} (2.368 ± 0.028)
Δ{Re–Cl(*trans* to P–*trans* to N)}	0.042–0.101 {4} (0.072 ± 0.030)
Re–P$(\mathrm{L}^{m}_{\mathrm{tri}})$	2.391–2.483 {8} (2.440 ± 0.049)
Re–P$(\mathrm{L}^{n}_{\mathrm{bi}})$	2.428–2.459 {3} (2.442 ± 0.017)
Re–P($\mathrm{Ph_3}$)	2.424 {1}

* The presented data include the ranges of values, the number of examples (in braces), and the average values with the scatter (in parentheses).

ligands. The Re–O$(\mathrm{L}^{m}_{\mathrm{tri}})_{trans}$ bonds (1.943–2.047 Å) in six out of eight considered complexes (**I**–**VI**) are commensurable in length with the Re–O$(\mathrm{L}^{m}_{\mathrm{tri}})_{cis}$ bonds in **I**, **II**, **VII**, and **VIII**: 1.939–2.050 Å [but not longer as the Re–O$(\mathrm{L}^{n}_{\mathrm{bi}})_{trans}$ bonds in **VII** and **VIII** (by 0.149 and 0.229 Å) and in most octahedral d^2-Re(V) monooxo complexes due to the *trans*-effect]. It may seem that this fact is at variance with the "self-consistency rule" [2]. However, in reality, the Re–O($\mathrm{L_{tri}}$) distances in the *trans*-positions relative to the oxo ligands in compounds **I**–**VI** can be considered as having a higher order, as they are markedly shorter than the Re–O(ST) bond (2.04 Å) [4]. In this case, one deals with pseudo-dioxo complexes containing two multiply bonded ligands, O(oxo) and O$(\mathrm{L})_{trans}$. Recall that in the Group 5–7 d^2 metal dioxo complexes, two multiply bonded ligands are always located in *trans*-positions to each other.

It is noteworthy that in complexes **III**–**VI**, the two types of rhenium–chlorine bonds, located in *trans*-positions relative to phosphorus and to nitrogen of the $\mathrm{L}^{m}_{\mathrm{tri}}$ ligands, have substantially different lengths. The former type of bonds (Re–Cl(1) 2.424–2.454 Å, average, 2.437 Å) is markedly (on average, by 0.069 Å) longer than the latter type (Re–Cl(2) 2.344–2.396 Å, average, 2.368 Å).

ACKNOWLEDGMENTS

The author is grateful to A.V. Churakov for providing a CCDC database selection.

REFERENCES

1. Porai-Koshits, M.A. and Gilinskaya, E.A., *Kristallokhimiya* (Crytsal Chemistry), Moscow: VINITI, 1966.
2. Porai-Koshits, M.A. and Atovmyan, L.O., *Koord. Khim.*, 1975, vol. 1, p. 1271.
3. Griffith, F. and Wicing, C., *J. Chem. Soc. A*, 1968, p. 379.
4. Porai-Koshits, M.A., *Izv. Yugosl. kristallogr. tsentra*, 1974, vol. 9, p. 19.
5. Porai-Koshits, M.A. and Atovmyan, L.O. *Kristallokhimiya Koordinatsionnykh Soedinenii Molibdena* (Crystal Chemistry of Coordinaion Compounds of Molybdenum), Moscow: Nauka, 1974.
6. Shustorovich, E.M., Porai-Koshits, M.A., and Buslaev, Yu.A., *Coord. Chem. Rev.*, 1975, vol. 17, p. 1.
7. Porai-Koshits, M.A. and Sergienko, V.S., *Usp. Khim.*, 1990, vol. 59, p. 86.
8. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, p. 380.
9. Sergienko, V.S., *Russ. J. Inorg. Chem.*, 2018, vol. 63, no. 14, p. 1757.
10. Sergienko, V.S., *Russ. J. Inorg. Chem.*, 2019 (in press).
11. Sergienko, V.S., *Russ. J. Inorg. Chem.*, 2019, vol. 64, no. 3, p. 260.

12. Sergienko, V.S. and Churakov, A.V., *Crystallogr. Rep.*, 2014, vol. 59, no. 3, p. 300. https://doi.org/10134/ S106377451140301711
13. Sergienko, V.S. and Churakov, A.V., *Crystallogr. Rep.*, 2013, vol. 58, no. 1, p. 5. https://doi.org/101134/ S1063774513010112
14. Cavell, R.G., Hilts, R.W., Luo, H., and McDonald, R., *Inorg. Chem.*, 1999, vol. 38, p. 897.
15. Lao, H., Setyawati, I., Rettig, S.J., and Orvig, C., *Inorg. Chem.*, 1995, vol. 34, p. 2287.
16. Banbery, H.J., Hussain, W., Hamor, T.A., et al., *Polyhedron*, 1991, vol. 10, p. 243.
17. Banbery, H.J., Hussain, W., Hamor, T.A., et al., *Dalton Trans.*, 1990, p. 657.
18. Barandov, A. and Abram, U., *Polyhedron*, 2009, vol. 28, p. 1355.
19. Correia, J.D., Domingos, A., Paulo, A., and Santos, I., *Dalton Trans.*, 2000, p. 2477.

Translated by Z. Svitanko