Inorganica Chimica Acta, 113 (1986) 61–65

Rhenium(V) Oxide Complexes. Crystal and Molecular Structures of $ReOI_2(PPh_3)_2(OReO_3)$ and of $ReOI_2(PPh_3)(OPPh_3)(OReO_3)\cdot0.5C_6H_6$ obtained from the Reaction of $ReO_2I(PPh_3)_2$ with Oxygen

G. CIANI*, A. SIRONI

Istituto di Chimica Strutturistica Inorganica, Via Venezian 21, 20133 Milan, Italy

T. BERINGHELLI, G. D'ALFONSO and M. FRENI

Dipartimento di Chimica Inorganica e Metallorganica, Via Venezian 21, 20133 Milan, Italy

Received July 8, 1985

Abstract

The oxygenation reaction of the five-coordinated violet species $ReO_2I(PPh_3)_2$ leads to isolation of two crystalline compounds, both characterized by X-ray diffraction analysis: the dark-red $ReOI_2(PPh_3)_2(OReO_3)$ (1), which is the main product, and the yellow $ReOI_2(PPh_3)(OPPh_3)(OReO_3)\cdot0.5C_6H_6$ (2). Compound 1 gives monoclinic crystals, space group $C2/c$, with $a = 25.033(8)$, $b = 16.944(5)$, $c = 19.495(8)$ Å, $\beta = 116.13(3)°$, $Z = 8$. Compound 2 is monoclinic, space group $P2_1/n$, with $a = 9.498(4)$, $b = 25.048(8)$, $c = 17.148(5)$ Å, $\beta = 92.47(3)°$, $Z = 4$. The structures of 1 and 2 were solved by Patterson and Fourier methods and refined by full-matrix least-squares, on the basis of 4229 (1) and 2672 (2) significant counter data ($I > 3\sigma(I)$), respectively. The final values of the conventional agreement indices R and R_w were 0.050 and 0.070 (1) and 0.033 and 0.039 (2), respectively. Both species contain a previously unexpected coordinated perrhenato ligand. The geometry of the two complexes is distorted octahedral: compound 1 contains two *trans* phosphine ligands (mean Re–P = 2.513 Å) and two *trans* iodides (mean Re–I 2.730 Å), the other two *trans* coordination sites being occupied by the oxide (Re–O = 1.670(7) Å) and the perrhenate. Compound 2 shows a similar coordination geometry, with one of the phosphine ligands replaced by a phosphine oxide. The main bond parameters in 2 are: Re–P 2.453(4) Å, Re–I (mean) 2.727 Å, Re–O($OPPh_3$) 2.075(9) Å, Re–O (oxide) 1.639(9) Å. The interactions Re(V)–perrhenate are similar in the two complexes, with Re(V)–O bonds of 2.031(6) Å (1) and 2.079(9) Å (2). The Re–O–Re angles show some difference: 164.3(4)° (1) and 153.5(5)° (2). Within the perrhenates, the Re–O bond involving the bridging oxygen atom is somewhat longer than the other Re–O bonds.

Introduction

We are currently investigating some Re(V) oxide complexes containing halogen and tertiary phosphine ligands and have recently reported the structural characterizations of the species *trans*-$ReOI_2(OR)(PPh_3)_2$ (R = Me, Et) and of their hydrolysis derivative $ReO_2I(PPh_3)_2$, a five-coordinate, 16-electron complex [1]. The latter species, due to its unsaturation, is expected to be quite reactive. In fact, its reaction with 2-butyne to give the very interesting derivative $ReOI(MeCCMe)_2$ [2] has been recently described. Some reactions of $ReO_2I(PPh_3)_2$ were described by one of us [3]. In particular, its reaction with O_2 in benzene led to a product which was tentatively formulated as an ionic species $[ReOI_2(PPh_3)_2][ReO_4]$, on the basis of conductivity measurements in nitrobenzene and the possibility of isolating the salt $[AsPh_4][ReO_4]$ by addition of $[AsPh_4]Cl$ to acetonic solutions of the compound. Rhenium complex cations with perrhenate as the counterion are known, such as the recently reported *trans*-$[ReO_2(PMe_3)_4][ReO_4]$ [4]. On the other hand, attempts to obtain salts of the hypothetical cation $[ReOI_2(PPh_3)_2]^+$ with anions different from ReO_4^- were unsuccessful [3].

We have therefore reinvestigated the oxygenation reaction of $ReO_2I(PPh_3)_2$ in benzene, performed as previously described [3]. From the brown reaction solution, on standing for many hours, dark-red bulk crystals separated as the main product (compound 1), together with minor amounts of needle-shaped yellow crystals (compound 2). We have investigated both crystal species by X-ray analysis, and we have found that the formulations of compounds 1 and 2 are $ReOI_2(PPh_3)_2(OReO_3)$ and $ReOI_2(PPh_3)(OPPh_3)(OReO_3)\cdot0.5C_6H_6$, respectively. Both the compounds are non-ionic and contain a hexa-coordinated Re(V) complex with a perrhenate group acting as a ligand through an oxygen bridge. The above mentioned behaviour in solution might

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

© Elsevier Sequoia/Printed in Switzerland

be explained in terms of a certain lability of the Re–OReO_3 bond. The complete results of the X-ray investigations on compounds **1** and **2** are here reported and discussed.

Experimental

Synthesis

The complexes were prepared according to the experimental procedure for the oxygenation reaction of the violet $ReO_2I(PPh_3)_2$ compound previously described [3]. The products were recrystallized from benzene/light petroleum. Both are diamagnetic. The IR spectra in the ν(Re–O) region show the following bands: 950sh, 945s, 920w, 845w and 795s(br) for compound **1**, and 945s, 940s, 855mw and 825s(br) for compound **2**.

X-ray Analyses

The principal crystallographic data are given in Table I. The intensities for both compounds were collected on an Enraf-Nonius CAD4 automatic diffractometer, using graphite monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The setting angles of 25 random intense reflections ($16 < 2\vartheta < 25°$) were used in each case to determine, by least-squares fit, accurate cell constants and orientation matrix. The data collections were performed by the ω-scan method, within the limits $3 < \vartheta < 25°$ (**1**) and $3 < \vartheta < 22°$ (**2**). A variable scan-speed (from 2 to 20°/min) and a variable scan-range of $(\alpha + 0.35 \tan \vartheta)°$, with $\alpha = 1.0°$ (**1**) and 0.8° (**2**), were used, with a 25% extension at each end of the scan-range for background determination. No significant decay of the crystal sample upon X-ray exposure was observed in either case. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to both data sets, based on ψ-scans (ψ 0–360° every 10°) of suitable reflections with χ values close to 90°; the relative transmission factors had values in the ranges 1.00–0.70 (**1**) and 1.00–0.94 (**2**), respectively.

The structure solutions were based on the deconvolution of three-dimensional Patterson maps, which gave the positions of the Re atoms. Successive-difference Fourier maps showed the locations of all the non-hydrogen atoms. In compound **1** a disorder of the perrhenate ligand was observed: the three oxygen atoms not involved in the Re–O–Re bridge were found to be doubled and were treated as six half atoms (labelled OA and OB in the two different images). In compound **2** a solvated molecule of benzene was found lying around an inversion centre.

The refinements were carried out by full-matrix least squares. Anisotropic thermal factors were assigned to all atoms except to the phenyl carbon atoms in compound **2**. In compound **1**, besides the phenyl carbons, the half-oxygen atoms of the perrhenate were also refined isotropically. The hydrogen atoms were neglected in both cases.

Weights were assigned according to the formula $w = 1/(\sigma(F_o))^2$, the σ of the reflections being corrected by a weighting factor of 0.05 (**1**) and 0.03 (**2**), respectively. The final values of the conventional R and R_w were 0.050 and 0.070 (**1**) and 0.033 and 0.039 (**2**), respectively.

The final positional parameters are given in Tables II (compound **1**) and III (compound **2**). Atomic thermal parameters and lists of observed and calcu-

TABLE I. Crystallographic Parameters

Compound	$C_{36}H_{30}O_5I_2P_2Re_2$ (compound 1)	$C_{39}H_{33}O_6I_2P_2Re_2$ (compound 2)
Formula weight	1230.8	1285.8
System	monoclinic	monoclinic
Space group	$C2/c$ (No. 15)	$P2_1/n$ (non-standard set of No. 14)
a (Å)	25.033(8)	9.498(4)
b (Å)	16.944(5)	25.048(8)
c (Å)	19.495(8)	17.148(5)
β (deg)	116.13(3)	92.47(3)
U (Å^3)	7423.9	4075.8
D_c (g cm^{-3})	2.202	2.095
Z	8	4
F(000)	4576	2404
μ(Mo Kα) (cm^{-1})	83.76	76.35
Crystal size (mm)	0.16 x 0.27 x 0.34	0.05 x 0.06 x 0.30
θ range (deg)	3–25	3–22
Number collected data	6717	4923
Number significant reflections ($I > 3\sigma(I)$)	4229	2672
Weighting parameter	0.05	0.03
R	0.050	0.033
R_w	0.070	0.039

TABLE II. Final Positional Parameters within $ReOI_2(PPh_3)_2(OReO_3)$ (**1**)

Atom	x	y	z
Re1	0.23605(2)	0.18611(3)	0.21921(3)
Re2	0.19584(4)	−0.00860(4)	0.11257(5)
I1	0.17729(4)	0.21922(6)	0.06683(5)
I2	0.28422(4)	0.10228(6)	0.35242(5)
P1	0.3340(1)	0.1875(2)	0.2124(2)
P2	0.1382(1)	0.1917(2)	0.2261(2)
O	0.2499(4)	0.2773(6)	0.2553(5)
O1	0.2194(4)	0.0751(5)	0.1755(5)
O2A	0.233(1)	−0.025(2)	0.062(1)
O2B	0.2227(9)	0.004(1)	0.039(1)
O3A	0.1177(9)	0.016(1)	0.041(1)
O3B	0.126(1)	−0.020(2)	0.060(1)
O4A	0.190(1)	−0.083(2)	0.157(2)
O4B	0.249(1)	−0.085(2)	0.163(2)
C111	0.3993(6)	0.1880(8)	0.3057(7)
C112	0.4491(7)	0.144(1)	0.3230(9)
C113	0.5005(9)	0.154(1)	0.395(1)
C114	0.4964(8)	0.209(1)	0.447(1)
C115	0.4465(8)	0.255(1)	0.429(1)
C116	0.3969(6)	0.2453(9)	0.3574(8)
C121	0.3443(5)	0.1064(8)	0.1585(7)
C122	0.3597(6)	0.0331(9)	0.1920(8)
C123	0.3705(8)	−0.030(1)	0.151(1)
C124	0.3626(8)	−0.018(1)	0.078(1)
C125	0.3437(7)	0.0580(9)	0.0439(8)
C126	0.3353(7)	0.1183(9)	0.0834(8)
C131	0.3497(6)	0.2766(8)	0.1714(7)
C132	0.3103(6)	0.3416(9)	0.1468(7)
C133	0.3270(7)	0.4086(9)	0.1175(8)
C134	0.3804(8)	0.410(1)	0.1133(9)
C135	0.4197(8)	0.350(1)	0.141(1)
C136	0.4042(7)	0.280(1)	0.1700(9)
C211	0.1447(6)	0.2007(8)	0.3246(7)
C212	0.1790(6)	0.2644(9)	0.3675(8)
C213	0.1826(7)	0.278(1)	0.4398(9)
C214	0.1550(7)	0.229(1)	0.4692(9)
C215	0.1220(7)	0.167(1)	0.4277(9)
C216	0.1148(7)	0.153(1)	0.3520(9)
C221	0.0914(5)	0.1069(8)	0.1833(7)
C222	0.0413(7)	0.1165(9)	0.1121(8)
C223	0.0066(8)	0.048(1)	0.078(1)
C224	0.0216(8)	−0.023(1)	0.112(1)
C225	0.0742(8)	−0.033(1)	0.187(1)
C226	0.1083(7)	0.033(1)	0.2191(9)
C231	0.0931(6)	0.2787(8)	0.1844(7)
C232	0.1158(6)	0.3458(9)	0.1622(8)
C233	0.0797(7)	0.412(1)	0.1337(9)
C234	0.0225(8)	0.413(1)	0.126(1)
C235	0.0004(8)	0.349(1)	0.148(1)
C236	0.0363(7)	0.281(1)	0.1780(9)

TABLE III. Final Positional Parameters within $ReOI_2(PPh_3)(OPPh_3)(OReO_3)\cdot 0.5C_6H_6$ (**2**)

Atom	x	y	z
Re1	0.00536(6)	0.10895(2)	0.27292(3)
Re2	0.40018(6)	0.11107(3)	0.29091(4)
I1	0.0203(1)	0.07708(5)	0.12089(6)
I2	0.0624(1)	0.13665(5)	0.42429(6)
P1	−0.0213(4)	0.2027(2)	0.2336(2)
P2	0.0523(4)	−0.0262(2)	0.3074(2)
O	−0.165(1)	0.1034(4)	0.2804(6)
O1	0.220(1)	0.1219(4)	0.2637(6)
O2	0.462(1)	0.1592(5)	0.3515(8)
O3	0.422(1)	0.0525(5)	0.3371(8)
O4	0.496(1)	0.1099(7)	0.2092(8)
OP	0.070(1)	0.0329(4)	0.3076(6)
C111	0.152(2)	0.2300(6)	0.2166(9)
C112	0.204(2)	0.2233(7)	0.142(1)
C113	0.345(2)	0.2399(7)	0.129(1)
C114	0.427(2)	0.2635(7)	0.189(1)
C115	0.379(2)	0.2676(8)	0.261(1)
C116	0.233(2)	0.2524(7)	0.276(1)
C121	−0.102(2)	0.2465(6)	0.3028(9)
C122	−0.065(2)	0.3015(7)	0.309(1)
C123	−0.136(2)	0.3340(8)	0.364(1)
C124	−0.238(2)	0.3138(8)	0.407(1)
C125	−0.281(2)	0.2595(7)	0.401(1)
C126	−0.207(2)	0.2268(7)	0.349(1)
C131	−0.135(2)	0.2125(6)	0.1454(9)
C132	−0.250(1)	0.1792(6)	0.1320(8)
C133	−0.343(2)	0.1890(6)	0.0657(9)
C134	−0.314(2)	0.2291(7)	0.014(1)
C135	−0.196(2)	0.2644(8)	0.027(1)
C136	−0.103(2)	0.2547(7)	0.096(1)
C211	0.111(1)	−0.0554(6)	0.2194(8)
C212	0.251(2)	−0.0438(6)	0.1993(9)
C213	0.307(2)	−0.0664(7)	0.132(1)
C214	0.223(2)	−0.1006(8)	0.087(1)
C215	0.083(2)	−0.1119(8)	0.104(1)
C216	0.026(2)	−0.0889(7)	0.1732(9)
C221	0.160(2)	−0.0540(6)	0.3870(8)
C222	0.199(2)	−0.1084(6)	0.3832(9)
C223	0.283(2)	−0.1292(7)	0.446(1)
C224	0.333(2)	−0.0967(7)	0.505(1)
C225	0.298(2)	−0.0428(8)	0.509(1)
C226	0.208(2)	−0.0198(7)	0.447(1)
C231	−0.129(1)	−0.0428(6)	0.3167(8)
C232	−0.228(2)	−0.0230(7)	0.2613(9)
C233	−0.370(2)	−0.0342(7)	0.269(1)
C234	−0.414(2)	−0.0679(7)	0.329(1)
C235	−0.318(2)	−0.0887(8)	0.383(1)
C236	−0.170(2)	−0.0774(8)	0.376(1)
CS1	0.134(2)	0.5135(8)	0.527(1)
CS2	0.071(2)	0.4707(8)	0.559(1)
CS3	−0.071(2)	0.4540(9)	0.533(1)

lated moduli of structural factors are available from the authors upon request. All computations were performed on a PDP 11/34 computer, using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein.

Results and Discusion

The structures of the two complexes are illustrated in Fig. 1 (compound **1**) and Fig. 2 (compound **2**).

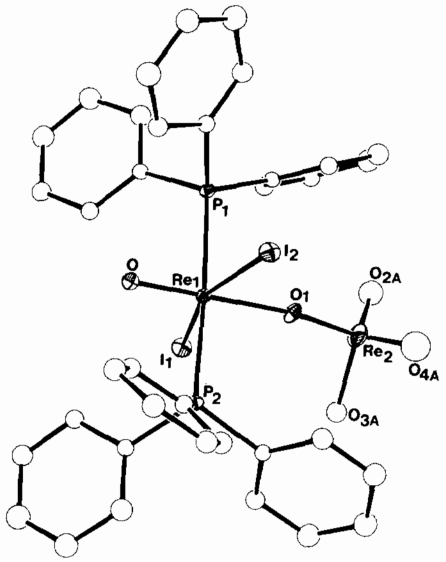

Fig. 1. A view of the complex $ReOI_2(PPh_3)_2(OReO_3)$ (1). Only one of the two images of the disordered perrhenate is shown for clarity.

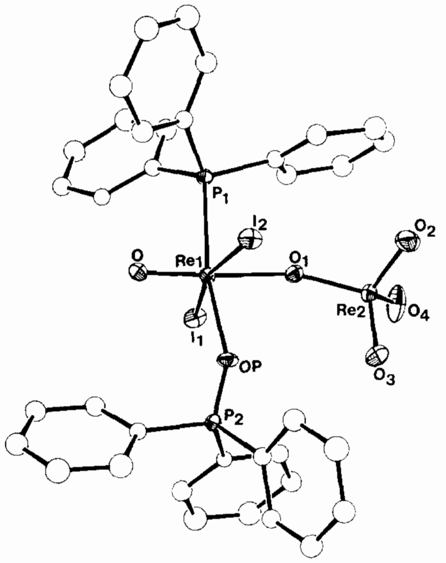

Fig. 2. A view of the complex $ReOI_2(PPh_3)(OPPh_3)(OReO_3)$ (2).

Interatomic distances and angles are listed in Tables IV and V, respectively. Both complexes show a distorted octahedral geometry, and the ligand stereochemistry can be related to that of the Re(V) complexes *trans*-$ReOI_2(OR)(PPh_3)_2$ [1]. In compound 1 a ReO_4^- ligand substitutes for the alkoxo ligand in *trans* position with respect to the oxide ligand. Compound 2 shows the same substitution and, moreover, a phosphine oxide group occupies the position of one of the two phosphines.

The $ReOI_2(PPh_3)_2$ moieties in this family, $ReOI_2(PPh_3)_2L$ (L = OMe, OEt, $OReO_3$), are similar: the P–Re–P interactions are linear, with values 177.31(7)°, 177.6(1)° and 177.31(8)°, respectively; the I–Re–I interactions are bent away from the oxide ligand, with values 166.89(2)°, 169.8(1)° and

TABLE IV. Selected Bond Distances and Angles within $ReOI_2(PPh_3)_2(OReO_3)$ (1)

Distances (Å)			
Re1–I1	2.730(1)	Re2–O3B	1.61(2)
Re1–I2	2.731(1)	Re2–O4A	1.57(2)
Re1–P1	2.514(3)	Re2–O4B	1.80(3)
Re1–P2	2.513(3)	Re2–O2,3,4	1.73(mean)
Re1–O	1.670(7)	P1–C111	1.83(1)
Re1–O1	2.031(6)	P1–C121	1.81(1)
Re2–O1	1.797(6)	P1–C131	1.83(1)
Re2–O2A[a]	1.66(2)	P2–C211	1.86(1)
Re2–O2B	1.85(2)	P2–C221	1.81(1)
R2–O3A	1.88(2)	P2–C231	1.82(1)
Angles (deg)			
I1–Re1–I2	160.43(3)	P1–Re1–P2	177.31(8)
I1–Re1–P1	90.63(6)	P1–Re1–O	89.3(3)
I1–Re1–P2	88.83(6)	P1–Re1–O1	90.6(2)
I1–Re1–O	100.4(3)	P2–Re1–O	88.2(3)
I1–Re1–O1	79.7(2)	P2–Re1–O1	91.8(2)
I2–Re1–P1	91.30(6)	O–Re1–O1	179.9(5)
I2–Re1–P2	90.09(6)	Re1–O1–Re2	164.3(4)
I2–Re1–O	99.1(3)	O1–Re2–O	104.5(6)– 117.8(8)
I2–Re1–O1	80.8(2)		

[a] The three oxygen atoms of the perrhenate not involved in the Re–O–Re bridge are doubled by disorder.

TABLE V. Selected Bond Distances and Angles within the Complex $ReOI_2(PPh_3)(OPPh_3)(OReO_3)\cdot0.5C_6H_6$

Distances (Å)			
Re1–I1	2.736(1)	Re2–O4	1.71(1)
Re1–I2	2.719(1)	OP–P2	1.49(1)
Re1–P1	2.453(4)	P1–C111	1.82(2)
Re1–O	1.639(9)	P1–C121	1.81(2)
Re1–OP	2.075(9)	P1–C131	1.84(1)
Re1–O1	2.079(9)	P2–C211	1.79(1)
Re2–O1	1.78(1)	P2–C221	1.81(1)
Re2–O2	1.68(1)	P2–C231	1.78(1)
Re2–O3	1.68(1)		
Angles (deg)			
I1–Re1–I2	165.43(4)	O–Re1–OP	100.3(4)
I1–Re1–P1	91.5(1)	O–Re1–O1	175.9(4)
I1–Re1–O	98.2(3)	OP–Re1–O1	83.5(4)
I1–Re1–OP	88.8(3)	Re1–OP–P2	151.5(6)
I1–Re1–O1	83.2(3)	Re1–O1–Re2	153.5(5)
I2–Re1–P1	91.8(1)	O1–Re2–O2	111.1(5)
I2–Re1–O	96.0(3)	O1–Re2–O3	110.9(5)
I2–Re1–OP	85.2(3)	O1–Re2–O4	109.4(5)
I2–Re1–O1	83.0(3)	O2–Re2–O3	107.6(6)
P1–Re1–O	90.7(3)	O2–Re2–O4	109.5(7)
P1–Re1–OP	168.8(3)	O3–Re2–O4	108.2(7)
P1–Re1–O1	85.4(3)		

160.43(3)°, respectively. The larger bending in the perrhenate complex can be related to the weaker Re–$OReO_3$ bond *vs.* the Re–OR ones. This is also reflected in the values of the O(oxide)–Re–I mean angles: 96.5° (in the methoxo species), 95.1° (in the ethoxo species) and 99.7° (in the perrhenato complex). The distortion of the octahedral geometry is present also in compound **2**, where the I–Re–I angle is 165.43(4)° and the mean O(oxide)–Re–I angle is 97.1°. In slight contrast with the linear P–Re–P interactions in the other species, the P–Re–O($OPPh_3$) angle in this complex is 168.8(3)°.

The Re–P bond lengths in compound **1** (mean 2.513 Å) are strictly comparable to the corresponding bonds in $ReOI_2(OR)(PPh_3)_2$ [mean 2.518 Å (R = Me) and 2.523 Å (R = Et)]. In compound **2** the Re–P bond [2.453(4) Å] is slightly shorter, very probably because of a higher Re to P π-back-donation, due to the presence of the electron donor oxygen atom of the $OPPh_3$ ligand in *trans* position. The Re–I bonds (mean values 2.730 Å and 2.727 Å in **1** and **2**, respectively) are intermediate between the corresponding mean values in $ReOI_2(OR)(PPh_3)_2$ [2.782 Å (R = Me), 2.789 Å (R = Et)] and in $ReO_2I(PPh_3)_2$ [2.664(2) Å].

Of particular interest are the values of the Re–O bonds. A variety of such interactions are present in compounds **1** and **2**. This type of bond was found to have a rather wide range of values, *ca.* 1.60–2.32 Å. In previous reports of correlations between bond order and bond length, theoretical values of 2.04, 1.86 and 1.75 Å were assigned to single, double and triple Re–O bonds, respectively [5, 6]. This trend suggests that the Re–O(oxide) bonds in this family of compounds are essentially triple bonds. This fact implies, through a relevant overlap with the $2p_x$ and $2p_y$ oxygen orbitals, the destabilization of the metal d_{xz} and d_{yz} orbitals (the z axis being the Re–O(oxide) direction), thus accounting for the diamagnetism of these complexes (the two d electrons of the metal occupying the non-bonding d_{xy} orbital)*. The Re–O(oxide) bonds in compounds **1** and **2**, 1.670(7) Å and 1.639(9) Å, are even shorter than those found in the $ReOI_2(OR)(PPh_3)_2$ species [1.698(5) Å (R = Me), 1.715(9) Å (R = Et)]. This is due to the already mentioned weaker Re–O interactions with the ligands in *trans* position, perrhenates *vs.* alkoxydes. The Re–O($OPPh_3$) bond in compound **2**, 2.075(9) Å, can be considered as a normal single metal–oxygen bond.

The bonding parameters within the ReO_4^- ligands deserved some comment. These ligands are quite unusual in transition metal complexes. A square-pyramidal Cu(II) species contains a ReO_4^- group in apical position, namely Cu(PnAO-H)($OReO_3$) [PnAO-H = 2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone oximato)] [8]. In compound $Re_2O(\mu\text{-}O)_2(C_5Me_5)(OReO_3)_2$ two perrhenato ligands are bound to the same Re atom [9]. Moreover, a bridging perrhenate was found in $Re_2(\mu\text{-}O)(NBu^t)_4(OSiMe_3)_2(\mu\text{-}OSiMe_3)(\mu\text{-}OReO_3)$ [10]. The Re–$OReO_3$ bonds in compounds **1** and **2**, 2.031(6) Å and 2.079(9) Å, are very close to the values for normal single metal–oxygen bonds, and are comparable to the corresponding interactions in $Re_2O(\mu\text{-}O)_2(C_5Me_5)(OReO_3)_2$, 2.096(9) Å. Within the perrhenates, the Re–O bond involving the bridging oxygen atom is slightly longer than the other three Re–O bonds, 1.797(6) Å *vs.* a mean value of 1.73 Å in compound **1**, and 1.78(1) Å *vs.* 1.69 Å (mean) in compound **2**. This feature is also observed in the other complexes mentioned above, but in the Cu(II) compound the difference is less pronounced (1.72(1) Å *vs.* 1.69 Å). Finally, the values of the Re–O–Re angles are rather scattered, probably being influenced by *intra* and intermolecular non-bonding repulsions; they range from 143.1(5)° in $Re_2O(\mu\text{-}O)_2(C_5Me_5)(OReO_3)_2$ to 153.5(5)° in compound **2**, to 164.3(4)° in compound **1**.

Acknowledgement

We thank the Italian Ministero della Pubblica Istruzione for financial support.

References

1 G. Ciani, G. D'Alfonso, P. Romiti, A. Sironi and M. Freni, *Inorg. Chim. Acta, 72*, 29 (1983).

2 J. M. Mayer and T. H. Tulip, *J. Am. Chem. Soc., 106*, 3878 (1984).

3 M. Freni, D. Giusto, P. Romiti and G. Minghetti, *Gazz. Chim. Ital., 99*, 286 (1969).

4 P. G. Edwards, A. C. Skapski, A. M. Z. Slawin and G. Wilkinson, *Polyhedron, 3*, 1083 (1984).

5 F. A. Cotton and S. J. Lippard, *Inorg. Chem., 5*, 416 (1966).

6 R. J. Doedens and J. A. Ibers, *Inorg. Chem., 6*, 204 (1967).

7 F. A. Cotton and S. J. Lippard, *Inorg. Chem., 5*, 9 (1966).

8 I. B. Liss and E. O. Schlemper, *Inorg. Chem., 14*, 3035 (1975).

9 W. A. Herrmann, R. Serrano, U. Kusthardt, M. L. Ziegler, E. Guggolz and T. Zahn, *Angew. Chem., Int. Ed. Engl., 23*, 515 (1984).

10 W. A. Nugent and R. L. Harlow, *J. Chem. Soc., Chem. Commun.*, 1105 (1979).

---

*Similar arguments were used to explain the dimagnetism of the square-pyramidal $[ReOBr_4]^-$ [7].