Rhenium(V) Oxide Complexes. Crystal and Molecular Structures of the Compounds *trans*-$ReI_2O(OR)(PPh_3)_2$ (R = Et, Me) and of their Hydrolysis Derivative $ReIO_2(PPh_3)_2$

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The structure of the complex $ReI_2O(OEt)(PPh_3)_2 \cdot 3/2C_6H_6$ (I) has been investigated: the dark-yellow crystals are monoclinic, space group $P2_1/n$, with a = *17.410(8),* b = *17.322(6),* c = *15.039(5) Å, β = 103.49(3)°,* Z = *4. Least-squares refinements based on 3636 significant counter data led to a final* R *value of 0.059. The compound exhibits a slightly distorted octahedral coordination, with the two PPh_3 groups* trans *between themselves (mean Re–P 2.523 Å), as well as the two iodide ligands (mean Re–I 2.789 Å). The ethoxo group (Re–O 1.880(9) Å) and the oxide ligand (Re–O 1.715(9) Å) occupy the other two coordination sites. Compound I in methanol transforms into $ReI_2O(OMe)(PPh_3)_2$ (II), which has been characterized by X-ray analysis in crystals containing $CHCl_3$ molecules of solvation. The crystals are triclinic, space group* $P\bar{1}$, a = *12.835(3),* b = *13.067(4),* c = *13.485(4) Å, α = 89.71(2)°, β = 71.61(2)°, γ = 70.19(2)°,* Z = *2. The refinements gave a final* R *value of 0.036, on the basis of 4524 significant counter intensities. The stereochemistry and the bond parameters are similar to those found in compound I. In particular the Re–O (methoxo) and Re–O (oxide) bond lengths are 1.859(5) and 1.698(5) Å respectively.*

Hydrolysis reactions of both compounds I and II give the violet derivative $ReIO_2(PPh_3)_2$ (III). The crystal data are: orthorhombic, space group Aba2, a = *19.834(5),* b = *16.144(3),* c *=10.560(2) Å,* Z = *4. 1435 significant counter reflections were used in the refinements, the final* R *value being 0.039. The compound is an unusual example of a five coordinate Re(V) complex. It possesses a rigorous C_2 crystallographic symmetry and exhibits a distorted trigonal bipyramidal stereochemistry, with the two PPh_3 groups in an axial direction (Re–P 2.488(3) Å) and the two oxide and the iodide ligands in equatorial positions. The Re–I and Re–O interactions have values of 2.664(2) and 1.742(11) Å respectively.*

Introduction

The syntheses of a variety of Re(V) oxide complexes are known [1] but few structural characterizations of these species have, as yet, been reported. As a part of a study on rhenium complexes with oxygen donor ligands and on the nature of the Re–O interactions we decided to carry out an X-ray investigation of the well known complex $ReI_2O(OEt)(PPh_3)_2$ (I) [2, 3], whose structure has never been reported. It was so far suggested [3, 4] that in this type of Re(V) complexes the Re–O (oxide) interaction has a triple-bond character, on the basis of dipole moments and of a rough value of 1.60 Å for the Re–O bond length in $ReCl_3O(PEt_2Ph)_2$ [5]. Few other structural analyses on Re(V) oxide species were successively reported, showing more reliable values for the Re–O interactions, but affected in some cases by rather high uncertainties [6, 7]. We have, therefore, performed this study in order to achieve better bonding parameters and to clarify the nature of the rhenium–oxide bond in these species.

Compound I treated with methanol in acetone solution gives a species whose analytical and spectroscopic data suggest that the ethoxo ligand can be replaced by a methoxo group to form $ReI_2O(OMe)(PPh_3)_2$ (II). This formulation has been confirmed by a structural analysis of the compound. The hydrolysis reaction of $ReI_2O(OEt)(PPh_3)_2$, which was previously studied [8], has been re-investigated. The violet derivative has been fully characterized as the diamagnetic five coordinate Re(V) species $ReIO_2(PPh_3)_2$ (III). The complete results of the X-ray analyses and spectroscopic data of compounds I, II and III are here reported and discussed.

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TABLE I. Crystallographic Parameters.

Compound	$ReI_2O(OEt)(PPh_3)_2 \cdot 3/2C_6H_6$ (I)	$ReI_2O(OMe)(PPh_3)_2 \cdot CHCl_3$ (II)	$ReIO_2(PPh_3)_2$ (III)
Form. wt.	1142.8	1131.0	869.7
System	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$ (No 14)	$P\bar{1}$ (No 2)	$Aba2$ (No 41)
a, Å	17.410(8)	12.835(3)	19.834(5)
b, Å	17.322(6)	13.067(4)	16.144(3)
c, Å	15.039(5)	13.485(4)	10.560(2)
α, deg.	90.0	89.71(2)	90.0
β, deg.	103.49(3)	71.61(2)	90.0
γ, deg.	90.0	70.19(2)	90.0
U, Å^3	4410.3	2005.9	3381.3
D_c, g cm^{-3}	1.72	1.87	1.71
Z	4	2	4
$F(000)$	2212	1080	1680
μ(Mo-Kα), cm^{-1}	42.80	49.04	46.72
Crystal size, mm	0.06 × 0.11 × 0.36	0.15 × 0.18 × 0.30	0.24 × 0.30 × 0.34
θ range, deg.	3.5–25	3–23	3.5–28
No. collected data	8406	6247	2349
No. significant reflections	3636 ($I > 2.5\sigma(I)$)	4524 ($I > 3\sigma(I)$)	1435 ($I > 2.5\sigma(I)$)
R	0.059	0.036	0.039
Rw	0.061	0.046	0.054

Experimental

Preparation of the Complexes

Diiodooxoethoxobis(triphenylphosphine)rhenium(V)(I)

The preparation was performed along the lines of previous reports [2, 3]. A mixture of perrhenic acid (1 g), 56% hydriodic acid (5 ml), triphenylphosphine (5 g) and ethanol (30 ml) was boiled for about 15 min. The green crystals were filtered off, washed successively with ethanol, and dried *in vacuo* over anhydrous $CaCl_2$. *Anal.*: Found C 44.7%, H 3.9%, I 25.1%, (OC_2H_5) 4.26%; calculated for $C_{38}H_{35}I_2O_2P_2Re$ C 44.5%, H 3.4%, I 24.7%, (OC_2H_5) 4.4%.

Crystals suitable for X-ray analysis were obtained by recrystallization of the product in benzene–ethanol, and contain benzene molecules of solvation.

Diiodooxomethoxobis(triphenylphosphine)rhenium(V)(II)

A suspension of compound I (1 g) in acetone (20 ml) and methanol (1 ml) was stirred at room temperature for 4 h. The yellow-grey plates were filtered off, washed successively with acetone, and dried *in vacuo* over anhydrous $CaCl_2$. *Anal.* data: Found C 43.2%, H 3.28%, I 25.68%; calculated for $C_{37}H_{33}I_2O_2P_2Re$ C 43.9%, H 3.3%, I 25.12%.

Crystals suitable for X-ray analysis were obtained by recrystallization of the product in chloroform– hexane and contain $CHCl_3$ molecules of solvation.

Iododioxobis(triphenylphosphine)rhenium(V) (III)

Compound I or II (1 g), in acetone (50 ml) and water (2 ml) suspension, was stirred at room temperature for 1 h. The resultant suspension deposited a violet microcrystalline compound which, recrystallized from benzene-hexane, gave violet crystals of compound III. (Yield 88%). *Anal.* data: Found C 49.7%, H 3.46%, I 14.4%, O 3.50%; calculated for $C_{36}H_{30}IO_2P_2Re$ C 49.7%, H 3.48%, I 14.6%, O 3.69%.

The complex is diamagnetic in the solid state at room temperature.

X-Ray Analyses

The principal crystallographic data are reported in Table I.

The intensities for compounds I and III were collected on the BASIC diffractometer [9], while those for compound II were measured on an ENRAF-NONIUS CAD-4 diffractometer. The collections were performed by the ω-scan method, using graphite monochromated Mo-K$_\alpha$ radiation. The treatment of the intensities was carried out, in the case of compound II, with the NONIUS structure determination

TABLE II.[a] Positional and Thermal Parameters within Compound $ReI_2O(OEt)(PPh_3)_2 \cdot 3/2C_6H_6$ (I).

Atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Re	0.11158(4)	0.12633(4)	0.22338(5)	0.00251(2)	0.00194(2)	0.00290(2)	−0.00018(5)	0.00094(3)	−0.00009(6)
I1	0.19739(8)	0.10040(7)	0.40333(8)	0.00406(5)	0.00441(5)	0.00365(6)	−0.00011(9)	0.00018(9)	0.00009(9)
I2	0.02337(7)	0.12376(8)	0.04432(7)	0.00341(4)	0.00398(4)	0.00353(5)	0.00013(9)	0.00037(8)	0.0008(1)
P1	−0.0135(2)	0.1329(2)	0.2809(2)	0.0027(1)	0.0028(1)	0.0033(1)	−0.0002(3)	0.0009(2)	−0.0002(3)
P2	0.2340(2)	0.1241(2)	0.1613(2)	0.0029(1)	0.0021(1)	0.0036(1)	−0.0001(3)	0.0018(2)	−0.0002(3)
O1	0.1214(7)	0.2247(5)	0.2320(9)	0.0050(4)	0.0011(3)	0.0078(6)	−0.0018(7)	0.0061(8)	−0.0005(9)
O2	0.1062(7)	0.0180(5)	0.2170(9)	0.0036(4)	0.0012(3)	0.0076(6)	−0.0022(7)	0.0056(7)	−0.0008(9)
C1	0.1074(13)	−0.0634(8)	0.2114(15)	0.0084(9)	0.0009(4)	0.0094(11)	−0.0024(13)	0.0103(15)	−0.0008(14)
C2	0.1326(16)	−0.0964(11)	0.3102(13)	0.0124(15)	0.0021(6)	0.0052(10)	0.0029(16)	0.0058(19)	0.0050(13)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C111	−0.0067(8)	0.1864(7)	0.3882(7)	3.5(3)	C211	0.3263(5)	0.1640(7)	0.2334(7)	3.6(3)
C112	0.0519(6)	0.2422(7)	0.4120(8)	4.6(4)	C212	0.3997(7)	0.1441(5)	0.2183(6)	5.0(4)
C113	0.0546(7)	0.2893(6)	0.4877(9)	5.4(4)	C213	0.4682(5)	0.1763(7)	0.2720(8)	4.5(4)
C114	−0.0012(8)	0.2805(7)	0.5397(7)	5.8(5)	C214	0.4633(5)	0.2284(7)	0.3409(7)	4.5(4)
C115	−0.0600(6)	0.2247(7)	0.5159(8)	5.4(4)	C215	0.3900(7)	0.2483(5)	0.3561(6)	4.4(4)
C116	−0.0627(7)	0.1776(6)	0.4401(9)	4.6(4)	C216	0.3215(5)	0.2161(7)	0.3024(8)	3.2(3)
C121	−0.0516(10)	0.0354(6)	0.2917(6)	3.5(3)	C221	0.2559(8)	0.0261(4)	0.1317(6)	3.0(3)
C122	−0.0539(8)	0.0004(6)	0.3744(6)	4.8(4)	C222	0.2118(6)	−0.0066(5)	0.0515(6)	3.5(3)
C123	−0.0811(8)	−0.0749(6)	0.3755(6)	6.1(5)	C223	0.2213(7)	−0.0843(5)	0.0331(5)	3.7(3)
C124	−0.1061(10)	−0.1154(6)	0.2939(6)	6.7(5)	C224	0.2751(8)	−0.1292(4)	0.0949(6)	4.2(3)
C125	−0.1038(8)	−0.0805(6)	0.2112(6)	5.4(4)	C225	0.3192(6)	−0.0964(5)	0.1751(6)	5.1(4)
C126	−0.0766(8)	−0.0050(6)	0.2101(6)	4.4(4)	C226	0.3096(7)	−0.0187(5)	0.1935(5)	4.5(4)
C131	−0.0990(6)	0.1839(7)	0.2104(8)	4.0(3)	C231	0.2284(9)	0.1830(6)	0.0572(7)	3.5(3)
C132	−0.1753(8)	0.1606(6)	0.2113(8)	4.9(4)	C232	0.1915(7)	0.2547(7)	0.0519(7)	4.5(4)
C133	−0.2398(6)	0.2033(8)	0.1641(9)	5.4(4)	C233	0.1882(8)	0.3018(5)	−0.0238(8)	5.7(5)
C134	−0.2279(6)	0.2691(7)	0.1159(8)	5.2(4)	C234	0.2218(9)	0.2771(6)	−0.0943(7)	5.6(4)
C135	−0.1515(8)	0.2923(6)	0.1150(8)	6.0(5)	C235	0.2586(7)	0.2054(7)	−0.0890(7)	5.2(4)
C136	−0.0871(6)	0.2497(8)	0.1622(9)	4.7(4)	C236	0.2619(8)	0.1583(5)	−0.0132(8)	4.1(3)

Solvent Molecules

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
CB11	−0.3052(20)	−0.0021(20)	0.2716(24)	10.4(9)	CB16	−0.3238(21)	−0.0055(20)	0.1757(24)	10.4(9)
CB12	−0.3652(24)	−0.0007(24)	0.3177(27)	12.4(12)	CB21	0.4374(16)	0.0493(15)	0.4630(19)	7.8(6)
CB13	−0.4439(22)	−0.0185(21)	0.2577(26)	11.3(10)	CB22	0.5074(19)	0.0818(18)	0.5134(22)	9.1(7)
CB14	−0.4635(27)	−0.0234(25)	0.1640(31)	13.8(13)	CB23	0.5707(17)	0.0264(16)	0.5521(20)	8.1(7)
CB15	−0.3997(29)	−0.0115(28)	0.1167(32)	14.9(14)					

[a] The form of the anisotropic thermal parameter is: $\exp(-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl))$.

TABLE III.[a] Positional and Thermal Parameters within Compound $ReI_2O(OMe)(PPh_3)_2 \cdot CHCl_3$ (II).

Atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Re	0.08006(3)	0.29479(3)	0.21384(3)	0.00445(2)	0.00371(2)	0.00399(2)	−0.00335(3)	−0.00265(3)	0.00156(3)
I1	0.00284(5)	0.50716(5)	0.16529(5)	0.00772(4)	0.00429(4)	0.00699(4)	−0.00418(6)	−0.00525(6)	0.00354(6)
I2	0.15939(5)	0.06744(5)	0.21678(5)	0.00817(4)	0.00422(4)	0.00875(4)	−0.00418(6)	−0.00644(7)	0.00317(7)
Cl1	0.2308(3)	0.1861(4)	0.6818(3)	0.0121(2)	0.0182(4)	0.0143(3)	−0.0067(5)	−0.0154(4)	0.0020(6)
Cl2	0.0758(3)	0.2624(3)	0.5627(2)	0.0123(2)	0.0171(3)	0.0087(2)	−0.0128(4)	−0.0089(3)	0.0051(4)
Cl3	0.0360(3)	0.1100(3)	0.7120(3)	0.0232(4)	0.0136(3)	0.0153(3)	−0.0198(5)	−0.0177(5)	0.0067(5)
P1	0.2884(2)	0.2915(2)	0.1609(2)	0.0050(1)	0.0047(1)	0.0045(1)	−0.0041(2)	−0.0021(2)	0.0016(2)
P2	−0.1293(2)	0.3034(2)	0.2745(2)	0.0049(1)	0.0049(1)	0.0045(1)	−0.0040(2)	−0.0035(2)	0.0025(2)
O1	0.0653(4)	0.3262(4)	0.3407(4)	0.0056(4)	0.0058(4)	0.0042(3)	−0.0052(6)	−0.0033(6)	0.0030(6)
O2	0.0983(5)	0.2579(5)	0.0749(4)	0.0061(4)	0.0057(4)	0.0052(4)	−0.0043(6)	−0.0035(6)	0.0010(7)
C1	0.1203(10)	0.2050(13)	−0.0316(8)	0.0144(9)	0.0306(16)	0.0044(6)	−0.028(2)	−0.009(1)	0.011(2)
CCl	0.0875(9)	0.2212(9)	0.6823(8)	0.0103(8)	0.0086(9)	0.0083(7)	−0.005(1)	−0.008(1)	0.002(1)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C111	0.3608(7)	0.2552(7)	0.0183(7)	3.3(2)	C211	−0.1679(7)	0.2730(7)	0.1631(6)	3.0(2)
C112	0.4420(8)	0.1524(9)	−0.0260(8)	4.6(2)	C212	−0.2025(8)	0.3571(8)	0.1020(8)	4.2(2)
C113	0.4905(9)	0.1293(9)	−0.1372(9)	5.3(3)	C213	−0.2247(9)	0.3357(9)	0.0100(8)	5.0(2)
C114	0.4543(9)	0.2079(9)	−0.1986(8)	4.9(2)	C214	−0.2111(10)	0.2302(10)	−0.0193(9)	6.2(3)
C115	0.3699(9)	0.3110(9)	−0.1554(8)	4.9(2)	C215	−0.1750(10)	0.1460(10)	0.0371(9)	6.0(3)
C116	0.3222(8)	0.3355(8)	−0.0436(8)	4.4(2)	C216	−0.1551(8)	0.1666(8)	0.1321(8)	4.6(2)
C121	0.3078(7)	0.4188(7)	0.1895(7)	3.2(2)	C221	−0.1685(7)	0.2137(7)	0.3740(6)	2.9(2)
C122	0.4096(8)	0.4387(8)	0.1285(8)	4.6(2)	C222	−0.2726(7)	0.1924(7)	0.3917(7)	3.6(2)
C123	0.4298(9)	0.5319(9)	0.1578(9)	5.4(3)	C223	−0.3105(8)	0.1366(8)	0.4765(8)	4.3(2)
C124	0.3485(9)	0.6044(9)	0.2438(9)	5.5(3)	C224	−0.2450(8)	0.1046(8)	0.5436(8)	4.2(2)
C125	0.2467(9)	0.5871(9)	0.3042(8)	5.0(2)	C225	−0.1430(8)	0.1269(8)	0.5258(7)	4.0(2)
C126	0.2283(8)	0.4904(8)	0.2769(8)	4.2(2)	C226	−0.1052(7)	0.1802(7)	0.4403(7)	3.7(2)
C131	0.3819(7)	0.1993(7)	0.2250(7)	3.3(2)	C231	−0.2389(7)	0.4342(7)	0.3454(7)	3.1(2)
C132	0.3294(7)	0.1703(7)	0.3235(7)	3.7(2)	C232	−0.3537(8)	0.4699(8)	0.3410(8)	4.2(2)
C133	0.3989(8)	0.1045(8)	0.3779(8)	4.6(2)	C233	−0.4385(9)	0.5668(9)	0.4070(8)	5.2(2)
C134	0.5201(9)	0.0697(9)	0.3348(9)	5.3(3)	C234	−0.4095(9)	0.6233(9)	0.4717(9)	5.3(3)
C135	0.5719(9)	0.0988(10)	0.2407(9)	5.6(3)	C235	−0.2948(9)	0.5865(9)	0.4772(8)	4.9(2)
C136	0.5047(8)	0.1659(9)	0.1846(8)	4.7(2)	C236	−0.2079(8)	0.4910(8)	0.4114(8)	4.2(2)

[a] The form of the anisotropic thermal parameter is: $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

TABLE IV.[a] Positional and Thermal Parameters within Compound $ReIO_2(PPh_3)_2$ (III).

Atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Re	0	0	0	0.0021(1)	0.0031(1)	0.0063(1)	0.0002(1)	0	0
I	0	0	0.2523(1)	0.0037(1)	0.0086(1)	0.0066(1)	–0.0031(1)	0	0
P	0.1068(1)	0.0789(2)	–0.0263(3)	0.0021(1)	0.0033(1)	0.0070(2)	0.0006(1)	0.0011(2)	0.0015(2)
O	–0.0392(4)	0.0886(6)	–0.0580(11)	0.0024(2)	0.0049(4)	0.0166(13)	0.0011(6)	0.0005(10)	0.0055(14)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C11	0.1224(5)	0.1627(5)	0.0868(9)	3.9(2)	C24	0.3003(5)	–0.0797(7)	–0.0203(10)	7.7(4)
C12	0.1835(4)	0.1731(5)	0.1494(10)	4.4(2)	C25	0.2462(6)	–0.0992(6)	0.0581(11)	8.7(5)
C13	0.1905(3)	0.2351(6)	0.2401(9)	5.2(3)	C26	0.1878(5)	–0.0513(7)	0.0547(11)	6.3(4)
C14	0.1363(5)	0.2867(5)	0.2681(9)	5.4(3)	C31	0.1058(8)	0.1290(10)	–0.1801(13)	4.9(3)
C15	0.0751(4)	0.2763(5)	0.2055(10)	5.3(3)	C32	0.0961(9)	0.0833(7)	–0.2905(17)	11.0(8)
C16	0.0682(3)	0.2143(6)	0.1148(9)	5.8(3)	C33	0.0935(6)	0.1234(10)	–0.4071(13)	11.4(9)
C21	0.1836(5)	0.0160(7)	–0.0271(10)	4.0(2)	C34	0.1004(8)	0.2091(10)	–0.4133(13)	11.0(8)
C22	0.2377(6)	0.0354(6)	–0.1055(11)	7.5(5)	C35	0.1101(9)	0.2547(7)	–0.3029(17)	10.5(8)
C23	0.2961(5)	–0.0124(7)	–0.1021(11)	7.3(5)	C36	0.1128(6)	0.2146(10)	–0.1836(13)	7.7(5)

[a] The form of the anisotropic thermal parameter is: $\exp(-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl))$.

package on a PDP 11/34 computer; computations for compounds I and III were performed on a UNIVAC 1100/80 computer using local programs. The data were corrected for Lorentz and polarization effects. To data of compound II an empirical absorption correction, based on ψ-scan of suitable reflections, with χ close to 90°, was applied, the maximum, minimum and average relative transmission factors being 1.00, 0.89 and 0.96 respectively. No decay of the samples of II and III was observed during the collection, while compound I showed a total decay, at the end of the collection, of *ca.* 16%; a correction for this effect was applied.

The structure solutions were based on Patterson and Fourier methods. The complexes in I and II are in general positions, while in III it was found to lie in special position, with the Re and I atoms on a two-fold crystallographic axis. Benzene molecules of solvation were found in I, one in a general position and a second one about an inversion centre, coincident with the centre of the molecule. Chloroform molecules of solvation were found in II. The refinements were carried out assigning anisotropic thermal factors to all atoms of the complexes, except for the phenyl carbon atoms. Block-matrix least-squares were used in the case of compounds I and III, with the phenyl rings treated as rigid bodies (D_{6h} symmetry, C–C 1.392 Å). For the non-centrosymmetric compound III both the structure enantiomorphs were refined, keeping in account the anomalous scattering effects, the final solution giving slightly lower agreement indices. Compound II was refined by full-matrix least-squares, without constraints. The hydrogen atoms were not considered.

Weights were assigned for compounds I and III according to the formula $w = 1/(A + BF_o + CF_o^2)$, where, in the final cycles A, B and C, had values 176.7, –2.31, 0.0088 (for I) and 10.2, –0.20, 0.0047 (for III), respectively, and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. In the case of II the weighting formula was $w = 1/[\sigma(F_o)]^2$ where the σ of the reflections were corrected by a factor of 0.03 F_o^2.

The scattering factors for structures I and III were taken from ref. 10, corrected for the real and imaginary part of the anomalous dispersion [11]. The results of the refinements are reported in Tables II–IV. Lists of observed and computed structure factors moduli can be obtained on application to the authors.

Results and Discussion

The complex $ReI_2O(OEt)(PPh_3)_2$ (I), when suspended in acetone, reacts with methanol giving metathesis of the alkoxo group, according to reaction 1

TABLE V. Infrared[a] and Nuclear Magnetic Resonance[b] Data.

No.	Compound	ν_{Re-O} (cm^{-1})	Other bands	^{1}H δ ppm	Assignment	^{31}P δ ppm	Assignment
I	$ReI_2O(OC_2H_5)[P(C_6H_5)_3]_2$	945(ms)	910(vs) δ (OCH$_2$)	7.98*m*, 7.38*m*	$-C_6H_5$	−11.1*s*	$P(C_6H_5)_3$
				1.51q	$-CH_2$		
				−0.26*t*	$-CH_3$		
II	$ReI_2O(OCH_3)[P(C_6H_5)_3]_2$	930(s)		8.00*m*, 7.42*m*	$-C_6H_5$	−9.39*s*	$P(C_6H_5)_3$
				0.89*s*	$-CH_3$		
III	$ReIO_2[P(C_6H_5)_3]_2$	923(s), 843(s)		7.62*m*, 7.42*m*	$-C_6H_5$	4.57*s*	$P(C_6H_5)_3$

[a] Infrared spectra were performed on nujol mulls and recorded on a Perkin-Elmer model 781 spectrophotometer. [b] N.M.R. spectra were recorded on a Bruker-80 spectrometer in deuterochloroform solution at 35 °C, Me_4Si as internal standard. ^{31}P to 85% H_3PO_4 external.

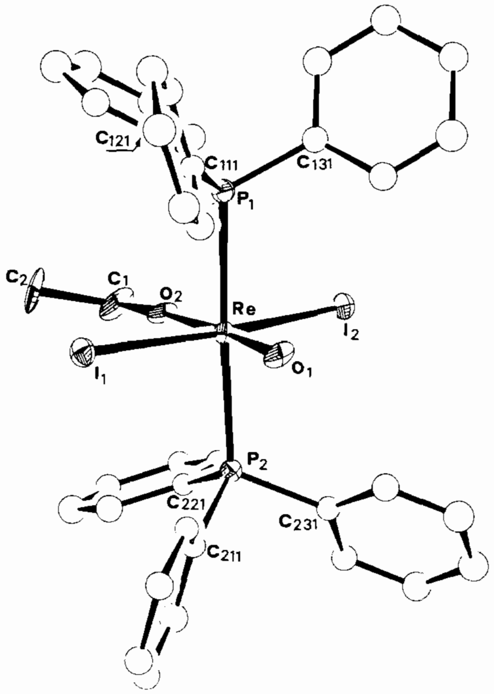

Fig. 1. A view of the complex $ReI_2O(OEt)(PPh_3)_2$.

$$ReI_2O(OEt)(PPh_3)_2\ (I) + MeOH \xrightarrow{acetone} ReI_2O(OMe)(PPh_3)_2\ (II) + EtOH \qquad (1)$$

The process can be reversed by suspending (II) in ethanol. It seems very probable that these substitutions take place because of the presence of a large excess of the alcohol which furnishes the entering OR group. Compound II was previously obtained in a different way [2, 3].

I.R. and ^{1}H and ^{31}P N.M.R. spectra are reported in Table V. The Re–O(oxide) stretching frequencies of I and II fall in the usual range 1000–900 cm^{-1}. An interesting feature concerns their ^{1}H NMR spectra, which were not previously reported: the signals of the ethyl and methyl hydrogens of the alkoxo groups are found at anomalously high field.

The reaction of $ReI_2O(OR)(PPh_3)_2$ with water in acetone occurs as previously described [8], according to reaction 2:

$$ReI_2O(OR)(PPh_3)_2 + H_2O \xrightarrow{acetone} ReIO_2(PPh_3)_2\ (III) + ROH + HI \qquad (2)$$

Since the violet product III appeared rather surprising, (because five-coordinate species are unusual in the chemistry of Re(V)), we have reinvestigated the reaction. The formulation of III, based essentially

TABLE VI. Selected Bond Distances and Angles within the Compound $ReI_2O(OEt)(PPh_3)_2 \cdot 3/2C_6H_6$ (I).

Distances (Å)		Angles (deg.)	
$Re–I_1$	2.806(1)	$I_1–Re–I_2$	169.8(1)
$Re–I_2$	2.772(1)	$I_1–Re–P_1$	89.1(1)
$Re–P_1$	2.528(5)	$I_1–Re–P_2$	92.8(1)
$Re–P_2$	2.519(5)	$I_1–Re–O_1$	93.7(4)
$Re–O_1$	1.715(9)	$I_1–Re–O_2$	84.1(4)
$Re–O_2$	1.880(9)	$I_2–Re–P_1$	90.4(1)
$P_1–C_{111}$	1.841(12)	$I_2–Re–P_2$	88.0(1)
$P_1–C_{121}$	1.835(13)	$I_2–Re–O_1$	96.5(4)
$P_1–C_{131}$	1.839(12)	$I_2–Re–O_2$	85.7(4)
$P_2–C_{211}$	1.850(11)	$P_1–Re–P_2$	177.6(1)
$P_2–C_{221}$	1.817(10)	$P_1–Re–O_1$	90.4(5)
$P_2–C_{231}$	1.852(12)	$P_1–Re–O_2$	91.5(4)
$O_2–C_1$	1.41(2)	$P_2–Re–O_1$	88.0(5)
$C_1–C_2$	1.56(3)	$P_2–Re–O_2$	90.1(4)
		$O_1–Re–O_2$	177.1(5)
		$Re–O_2–C_1$	176.2(14)
		$O_2–C_1–C_2$	108.4(16)

TABLE VII. Selected Bond Distances and Angles within the Compound $ReI_2O(OMe)(PPh_3)_2 \cdot CHCl_3$ (II).

Distances (Å)		Angles (deg.)	
$Re–I_1$	2.764(1)	$I_1–Re–I_2$	166.89(2)
$Re–I_2$	2.800(1)	$I_1–Re–P_1$	90.91(5)
$Re–P_1$	2.525(2)	$I_1–Re–P_2$	88.47(5)
$Re–P_2$	2.512(2)	$I_1–Re–O_1$	97.2(2)
$Re–O_1$	1.698(5)	$I_1–Re–O_2$	83.8(2)
$Re–O_2$	1.859(5)	$I_2–Re–P_1$	90.57(5)
$P_1–C_{111}$	1.835(8)	$I_2–Re–P_2$	90.63(5)
$P_1–C_{121}$	1.824(8)	$I_2–Re–O_1$	95.9(2)
$P_1–C_{131}$	1.818(8)	$I_2–Re–O_2$	83.1(2)
$P_2–C_{211}$	1.808(7)	$P_1–Re–P_2$	177.31(7)
$P_2–C_{221}$	1.840(7)	$P_1–Re–O_1$	88.5(2)
$P_2–C_{231}$	1.832(8)	$P_1–Re–O_2$	91.0(2)
$O_1–C_1$	1.497(12)	$P_2–Re–O_1$	89.0(2)
C–C (phenyl)	1.35(1)–1.43(1) (mean 1.40)	$P_2–Re–O_2$	91.5(2)
		$O_1–Re–O_2$	178.9(2)
C–Cl (chloroform)	1.73(1)–1.78(1)	$Re–O_2–C_1$	168.4(7)

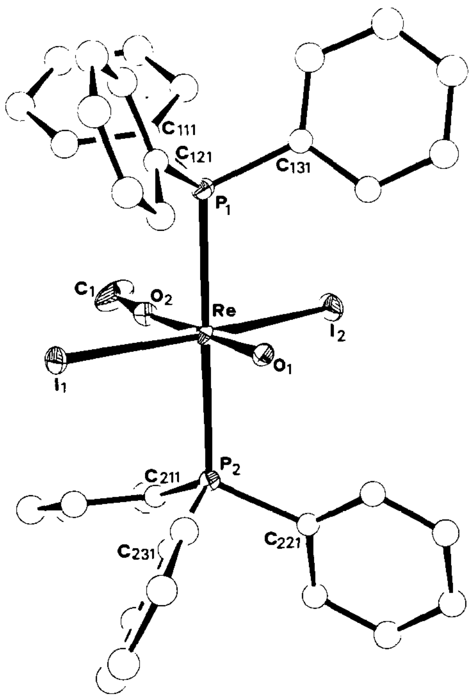

Fig. 2. A view of the complex $ReI_2O(OMe)(PPh_3)_2$.

on elemental analysis and I.R. spectra [8], has now been confirmed by X-ray investigation.

Description of the Structures

The structures of the hexa-coordinate species *trans*-$ReI_2O(OR)(PPh_3)_2$ are illustrated in Figs. 1 (I) and 2 (II). Bond distances and angles are listed in Tables VI and VII. The stereochemistries are very similar, with a *trans* disposition of the two phosphines, of the two iodide ligands and of the two oxygen donor ligands. While the two PPh_3 groups are almost exactly *trans* between themselves, with P–Re–P angles of 177.6(1)° (I) and 177.31(7)° (II), some distorsions of the octahedral coordination are present within the other four ligands. In particular, the two iodides exhibit a bent I–Re–I interaction of 169.8(1)° (I) and 166.89(2)° (II), with larger I–Re–O (oxide) angles (mean values 95.1° (I) and 96.5° (II)) than the I–Re–O(alkoxo) ones (mean values 84.9° (I) and 83.5° (II)). These distortions are related to the higher bond order associated to the Re–O(oxide) *vs.* the Re–O(alkoxo) bond.

The Re–P bond lengths (mean 2.523 Å (I) and 2.518 Å (II)), although slightly longer, are comparable with similar interactions *e.g.* 2.45–2.48 Å in $ReCl_3O(PEt_2Ph)_2$ [5], 2.41–2.43 Å in $Re(CO)_2(HCS_2)(PPh_3)_2$ [12], 2.45 Å in $ReCl_2N(PPh_3)_2$ [13] and 2.44–2.49 Å in $ReCl_2N(PEt_2Ph)_3$ [14].

The Re–I interactions (mean 2.789 Å (I) and 2.782 Å (II)) are similar to the corresponding Re–I-(terminal) bonds in $[Re_3H_3I(CO)_{11}]^-$ (2.839(4) Å) [15] and in $[Re_4H_4I(CO)_{15}]^-$ (2.813(2) Å) [16]. The values, however, are somewhat longer than

TABLE VIII. Interatomic Distances and Angles within the Complex $ReIO_2(PPh_3)_2$ (III).

Distances (Å)		Angles (deg.)	
Re–I	2.664(2)	I–Re–P	96.4(1)
Re–P	2.488(3)	I–Re–O	110.6(4)
Re–O	1.742(11)	P–Re–P′	167.2(1)
$P–C_{11}$	1.832(10)	P–Re–O	85.4(3)
$P–C_{21}$	1.832(12)	P–Re–O′	90.1(3)
$P–C_{31}$	1.814(15)	O–Re–O′	138.7(6)
P····O	2.921(10)	$Re–P–C_{11}$	116.7(3)
P····O′	3.038(11)	$Re–P–C_{21}$	115.1(4)
$O····C_{31}$	3.22(2)	$Re–P–C_{31}$	108.6(5)
		$C_{11}–P–C_{21}$	105.8(5)
		$C_{11}–P–C_{31}$	104.9(6)
		$C_{21}–P–C_{31}$	104.6(7)

expected, when compared with the Re–I (terminal) intramolecular bond contacts in Re_3I_9, 2.580(5)–2.744(3) Å [17] and with the Re(V)–Br bond lengths, *e.g.* 2.51(1) Å in $[ReBr_4O(H_2O)]^-$ [6], keeping into account the different covalent radii of Br and I, 1.11 *vs.* 1.28 Å.

The values of the rhenium–oxygen bonds are discussed below.

The coordination geometry of the alkoxo groups is almost linear (Re–O–C angles of 176.2(14)° (I) and 168.4(7)° (II)). These M–O–C interactions are dictated by intramolecular and, possibly, intermolecular non-bonding contacts, and exhibit a variety of values (see *e.g.* a bent interaction of 149° in $NbCl_2O(OEt)(bipy)$ [18]). Differently coordinated alcohols show considerably smaller M–O–C angles, as, for instance, in $[ReBr_4(NO)(EtOH)]^-$ (Re–O–C 132.1(13)°) [19].

The five-coordinate species $ReIO_2(PPh_3)_2$ (III) possesses a rigorous C_2 crystallographic symmetry, the two-fold axis passing through the Re and I atoms. In contrast with the suggested square-pyramidal geometry of the anion $[ReOBr_4]^-$ [20], this complex shows a stereochemistry intermediate between the trigonal-bipyramidal and the square-pyramidal one, as in the case of the nitrido species $ReCl_2N(PPh_3)_2$ [13]. The structure of $ReIO_2(PPh_3)_2$ is illustrated in Fig. 3 and the bond distances and angles are reported in Table VIII.

It resembles more a trigonal-bipyramid, the major deviations being the value of the P–Re–P′ angle of the two axial phosphines, 167.2(1)°, and the difference between the bond angles involving the equatorial I and O ligands, I–Re–O 110.6(4)° and O–Re–O′ 138.7(6)°. The two axial PPh_3 groups are bent toward the oxide ligands (I–Re–P 96.4(1)° *vs.* O–Re–P (mean) 87.7°). The Re–P bonds are only slightly shorter than in the six-coordinate species, while the Re–I interaction is quite shorter (of *ca.* 0.12 Å, on average). Analogous Re–ligand shortenings were previously observed in $ReCl_2N(PPh_3)_2$ *vs.* $ReCl_2N(PEt_2Ph)_3$ and were attributed to steric factors on passing from the six-coordinate to the five-coordinate species [13].

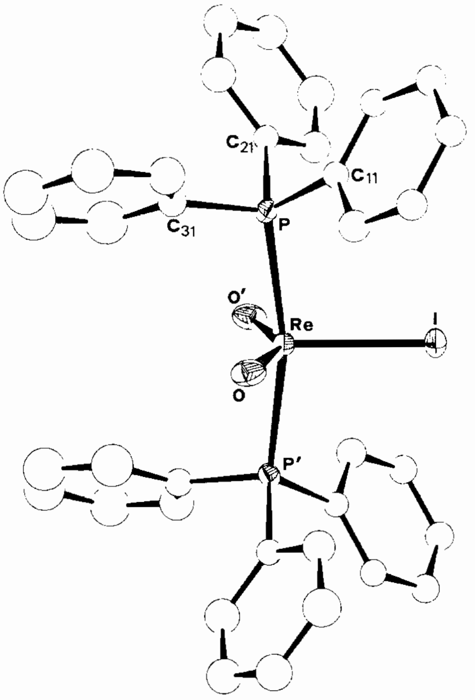

Fig. 3. A view of the complex $ReIO_2(PPh_3)_2$. A two-fold crystallographic axis passes through atoms Re and I.

The Rhenium–Oxygen Bond

The previous suggestions of a considerable triple-bond character in the rhenium–oxygen interactions for terminal oxides in Re(V) species [4, 20] have been confirmed by the Re–O (oxide) bond lengths found in the six-coordinate species $ReI_2O(OR)(PPh_3)_2$, 1.715(9) Å (I) and 1.698(5) Å (II), values more reliable than the much too short bond of 1.60 Å reported for the similar species $ReCl_3O(PEt_2Ph)_2$ [5]. The Re–O bond order exceeds two since both the p_x and p_y oxygen orbitals overlap with the rhenium d_{xz} and d_{yz} orbitals (z axis in the Re–O direction). This fact accounts also for the diamagnetism of the compounds, the two d electrons of the metal occupying the non-bonding d_{xy} orbital. Similar arguments were used to explain the diamagnetism of the square-pyramidal $[ReOBr_4]^-$ anion [20]. Rhenium–oxygen bond contacts were found in the range 1.60–2.32 Å. A rationalization of the bond orders was previously attempted [7, 13], assigning to Re–O single, double and triple bonds the theoretical values of 2.04, 1.86 and 1.75 Å, respectively. On that basis,

TABLE IX. Rhenium–Oxide (terminal) Bond Lengths in Mononuclear Re(V) Species.

Compound	Distance (Å)	Ref.
$ReCl_3O(PEt_2Ph)_2$	1.60	5
$[ReBr_4O(H_2O)]^-$	1.71(4)	6
$[ReBr_4O(MeCN)]^-$	1.73(6)	7
$ReI_2O(OMe)(PPh_3)_2$	1.698(5)	this work
$ReI_2O(OEt)(PPh_3)_2$	1.715(9)	this work
$[ReO_2(py)_4]^+$	1.76(3)	21
$[ReO_2(CN)_4]^{3-}$	1.773(8)	22
	1.781(3)	23
$ReIO_2(PPh_3)_2$	1.742(11)	this work

however, not only the Re–O(oxide) bonds reported here must be considered triple, but also the Re–O-(alkoxo) interactions, 1.880(9) Å (I) and 1.859(5) Å (II), must have a considerable double bond character. Rhenium–oxide bond lengths in Re(V) species are reported in Table IX. As can be seen, the Re–oxide bonds are longer in dioxide species, close to the values expected for double bonds, probably as a consequence of a certain competition in the Re–O π-bonding.

It is interesting to note that $ReIO_2(PPh_3)_2$ is unique, showing the two oxide ligands not in *trans* positions between themselves.

The relatively lower values of the Re–O interactions in III, with respect to the other dioxide species, can be explained by taking into account the five-coordination of the compound (see above).

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