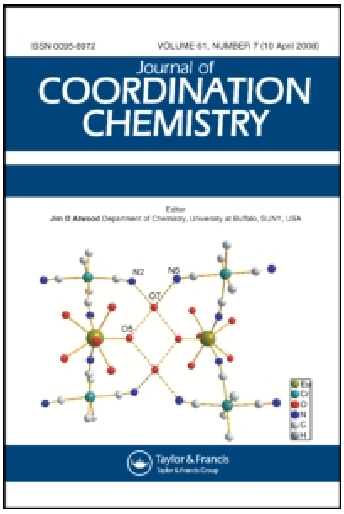

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THE MOLECULAR AND ELECTRONIC STRUCTURE OF [$ReOX_3(AsPh_3)(OAsPh_3)$] COMPLEXES ($X = Cl$, Br)

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New rhenium oxo-complexes [$ReOX_3(OAsPh_3)(AsPh_3)$] ($X = Cl$ and Br) have been synthesised and characterised by X-ray diffraction, IR, electronic and magnetochemical measurements. They were obtained in high yield in reactions between [$ReOX_3(AsPh_3)_2$] and acetonitrile in air.

Keywords: Rhenium; Oxo-complex; X-ray structure; Electronic structure

INTRODUCTION

Transition metal–oxo complexes show a fascinating variety of structures and reactivities and, therefore, have become the focus of a very active field of chemical research. Oxo-complexes are catalysts for organic reactions, models for active sites in heterogeneous processes and very useful starting reagents in coordination chemistry [1–14]. They also appear to be involved in the catalytic cycles of a variety of metalloenzymes, for instance those of cytochrome P-450, nitrogenase and xanthine oxidase [15–17]. Despite the large number of transition metal–oxo complexes discovered thus far, the chemistry of these compounds is still restricted and much remains to be done. There is an increasing demand for fundamental knowledge concerning structural and spectroscopic properties, redox, reactivities and mechanisms of ligand substitution reactions in order to develop new and improved catalysts for organic reactions and starting materials. Here we present synthetic methods for [$ReOBr_3(OAsPh_3)(AsPh_3)$]

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(**1**) and [ReOCl$_3$(OAsPh$_3$)(AsPh$_3$)] (**2**), their spectroscopic characterisation and determination of electronic, crystal and molecular structures.

EXPERIMENTAL

[ReOX$_3$(AsPh$_3$)$_2$] (X = Cl or Br) complexes were synthesized according to literature methods [18]. Other reagents and solvents were obtained from commercial sources and used without further purification. Solvents were dried prior to use.

[ReOBr$_3$(OAsPh$_3$)(AsPh$_3$)] (1)

[ReOBr$_3$(AsPh$_3$)$_2$] (1.0 g) and acetonitrile (50 cm^3) were heated in an open flask for 20 min, during which the initial yellow–green suspension turned to a dark green solution. The resulting solution was concentrated to 20 cm^3 on a rotary evaporator and allowed to stand in air for a few hours. Green crystals of [ReOBr$_3$(OAsPh$_3$)(AsPh$_3$)] were filtered off, washed with diethylether and dried. Yield: 85%.

[ReOCl$_3$(OAsPh$_3$)(AsPh$_3$)] (2)

This complex was prepared in the same manner as for **1**. The yield of green crystals of **2** was about 80%.

Physical Measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the range 2000–400 cm^{-1} with the samples in the form of potassium bromide pellets. Electronic spectra were measured on a Beckman 5240 spectrophotometer in the range 800–220 nm in deoxygenated dichloromethane solutions. Magnetic susceptibilities were measured at 296 K by the Faraday method.

Crystal Structure Determination and Refinement

Crystals of [ReOX$_3$(OAsPh$_3$)(AsPh$_3$)] suitable for X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of oxorhenium(V) complexes. X-ray intensity data were collected on a Kuma KM-4 diffractometer with graphite-monochromated Mo*Kα* radiation ($\lambda = 0.71073$ Å) at room temperature. Details concerning crystal data and refinement for **1** and **2** are given in Table I. Lorentz, polarisation and empirical absorption corrections were applied for **1** and **2**. The structures of the complexes were solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares techniques. Hydrogen atom positions of the phenyl rings were found from subsequent difference Fourier syntheses and were treated as riding on adjacent carbon atoms [d(C–H) = 0.96 Å] and refined with individual isotropic temperature factors equal to 1.2 times the value of the equivalent temperature factor of the parent carbon atom. SHELXL 97 [19] and SHELXTL [20] programs were used for all calculations. Atomic scattering factors were those incorporated in the computer programs.

TABLE I Crystal data and structure refinement details for **1** and **2**

	1	**2**
Empirical formula	$C_{36}H_{30}Br_3O_2As_2Re$	$C_{36}H_{30}Cl_3O_2As_2Re$
Formula weight	1070.37	936.99
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	$a = 17.916(4)$ Å $b = 9.726(2)$ Å; $\beta = 94.70(3)^\circ$ $c = 20.051(6)$ Å	$a = 20.072(4)$ Å $b = 18.541(4)$ Å; $\beta = 118.17(3)^\circ$ $c = 20.918(4)$ Å
Volume	3482(2) $Å^3$	6863(2) $Å^3$
Z	4	8
Density(calculated)	2.042 Mg/m^3	1.814 Mg/m^3
Absorption coefficient	8.849 mm^{-1}	5.720 mm^{-1}
$F(000)$	2032	3632
Crystal size	0.105 × 0.237 × 0.237 mm	0.105 × 0.105 × 0.474 mm
θ range for data collection	1.14–25.07°	1.15–24.69°
Index ranges	$-21 \leq h \leq 21$; $-11 \leq k \leq 0$; $-23 \leq l \leq 2$	$-20 \leq h \leq 21$; $-21 \leq k \leq 2$; $-21 \leq l \leq 16$
Reflections collected	7148	13832
Independent reflections	6174($R_{int} = 0.0385$)	9593($R_{int} = 0.0478$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6145/0/398	9541/0/794
Goodness-of-fit on F^2	1.136	1.112
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0543$, $wR2 = 0.0954$	$R1 = 0.0616$, $wR2 = 0.0942$
R indices (all data)	$R1 = 0.1008$, $wR2 = 0.1157$	$R1 = 0.1188$, $wR2 = 0.1141$
Largest diff. peak and hole	0.841 and -0.936 e $Å^{-3}$	1.997 and -1.200 e $Å^{-3}$

RESULTS AND DISCUSSION

Complexes **1** and **2** have been synthesised in a similar way to $[ReOCl_3(OPh_3)(PPh_3)]$ [21] in a reaction of $[ReOX_3(AsPh_3)_2]$ ($X = Cl$ or Br) with acetonitrile in air. $[ReOX_3(AsPh_3)_2]$ complexes react much faster than $[ReOCl_3(PPh_3)_2]$ and the yields of **1** and **2**, in comparison to the phosphine analogues, are considerably higher.

Both complexes crystallise in space group $P2_1/c$, but the asymmetric unit of **1** comprises one molecule and complex **2** has two crystallographically independent molecules of $[ReOCl_3(OAsPh_3)(AsPh_3)]$ in the asymmetric unit. The numbering scheme of **1** is shown in Fig. 1. The relative orientation of molecules of **2** is depicted in Fig. 2. Final coordinates for the non-hydrogen atoms are given in Tables II and III.

Both complexes possess distorted octahedral geometry with a *meridional* arrangement of the three halogen ligands and the $AsPh_3$ molecule *cis* to the oxo group. The major distortion, an increase in O2–Re–X angles appears to be due to electronic factors and steric interactions with the oxo group as is commonly observed in octahedral complexes containing a multiply bonding ligand [22–24]. The *cis*-location of π-acid ligands to the oxo group seems to be the dominant electronic influence of the multiple bonded ligand, which forces the non-bonding metal d electrons to lie in the plane perpendicular to the M–O bond axis. This general rule appears

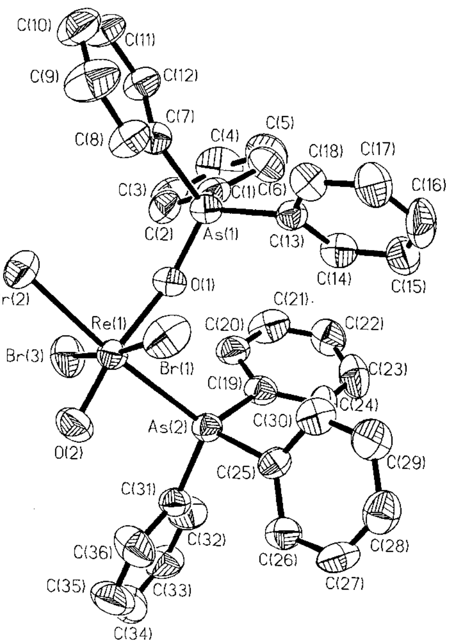

FIGURE 1 The molecular structure of **1**.

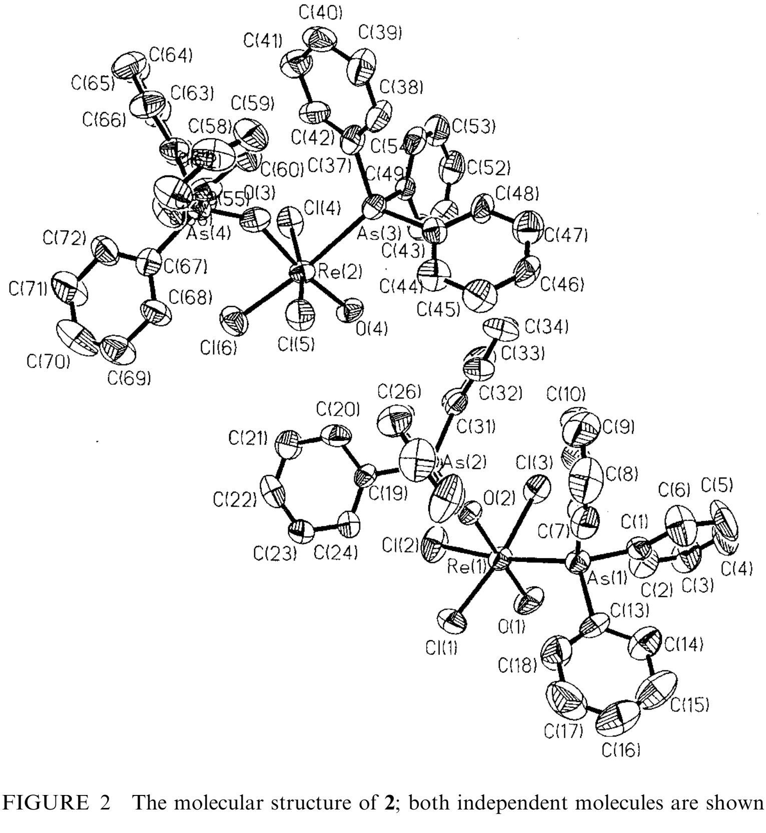

FIGURE 2 The molecular structure of **2**; both independent molecules are shown.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Re(1)	2591(1)	1910(1)	726(1)	42(1)
Br(1)	3992(1)	1436(2)	938(1)	67(1)
Br(2)	2846(1)	3233(1)	−309(1)	69(1)
Br(3)	1207(1)	2191(1)	384(1)	68(1)
O(1)	2555(4)	161(7)	190(3)	43(2)
O(2)	2624(5)	3178(8)	1282(4)	62(2)
As(1)	2834(1)	−994(1)	−357(1)	41(1)
As(2)	2254(1)	294(1)	1683(1)	39(1)
C(1)	1934(6)	−1883(13)	−700(5)	48(3)
C(2)	1311(6)	−1058(13)	−829(5)	53(3)
C(3)	636(7)	−1675(16)	−1093(6)	68(4)
C(4)	641(7)	−3081(18)	−1228(7)	82(4)
C(5)	1253(8)	−3877(16)	−1081(7)	80(4)
C(6)	1917(7)	−3303(12)	−820(6)	60(3)
C(7)	3285(5)	−171(11)	−1088(5)	42(2)
C(8)	3891(7)	708(14)	−996(6)	63(3)
C(9)	4212(8)	1222(17)	−1545(7)	83(5)
C(10)	3904(8)	922(15)	−2172(6)	72(4)
C(11)	3304(7)	74(14)	−2259(5)	58(3)
C(12)	2989(7)	−491(13)	−1730(5)	55(3)
C(13)	3502(6)	−2294(10)	94(5)	41(2)
C(14)	3217(6)	−3244(12)	522(5)	51(3)
C(15)	3706(7)	−4182(13)	851(6)	58(3)
C(16)	4444(8)	−4188(14)	722(7)	71(4)
C(17)	4718(7)	−3269(13)	285(7)	63(3)
C(18)	4255(6)	−2331(12)	−20(6)	49(3)
C(19)	1762(6)	−1444(11)	1438(5)	46(3)
C(20)	1244(7)	−1471(12)	869(6)	54(3)
C(21)	900(7)	−2714(14)	694(6)	66(4)
C(22)	1060(7)	−3892(13)	1038(7)	63(3)
C(23)	1547(7)	−3814(13)	1593(8)	70(4)
C(24)	1907(6)	−2622(11)	1805(6)	52(3)
C(25)	3069(6)	−371(11)	2311(5)	42(2)
C(26)	3105(7)	−31(12)	2993(5)	53(3)
C(27)	3690(7)	−598(15)	3409(6)	64(3)
C(28)	4188(7)	−1459(13)	3165(6)	61(3)
C(29)	4148(7)	−1794(14)	2492(6)	62(3)
C(30)	3595(6)	−1220(13)	2061(6)	55(3)
C(31)	1568(6)	1164(11)	2238(5)	44(2)
C(32)	882(6)	618(15)	2340(6)	61(3)
C(33)	400(7)	1277(16)	2728(6)	71(4)
C(34)	597(9)	2476(16)	3041(7)	80(4)
C(35)	1273(10)	3062(16)	2952(7)	88(5)
C(36)	1757(8)	2426(13)	2548(7)	75(4)

to hold for isonitrile, carbonyl, olefin, acetylene, thioether and often phosphine ligands [22–27].

The most important bond lengths and angles for **1** and **2** are reported in Tables IV and V, respectively. $Re–O_{oxo}$ bonds in **1** and **2** are typical of reported terminal multiple $Re–O_{oxo}$ distances in mononuclear $[ReO]^{3+}$ compounds; 1.691 Å in $[ReOCl_3(OPPh_2CH_2PPh_2)]$ [28], 1.663 Å in *trans*-$[ReOCl_3(PPh_3)_2]$ [29] and 1.673 Å in $[ReOMe_2Cl(PMe_3)_2]$ [30]. $Re–OAsPh_3$ single bonds in **1** and **2** are in good agreement with values found for $[ReOCl_3(PPh_3)(OPPh_3)]$ [31], 2.082 Å, and

TABLE III Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for **2**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
Re(2)	3793(1)	2033(1)	328(1)	40(1)
Re(1)	−963(1)	1907(1)	−4022(1)	43(1)
As(1)	−659(1)	2405(1)	−5023(1)	44(1)
As(2)	938(1)	1782(1)	2602(1)	39(1)
As(3)	4331(1)	3234(1)	112(1)	41(1)
As(4)	5516(1)	1214(1)	1522(1)	41(1)
Cl(1)	−894(2)	648(2)	−4259(2)	71(1)
Cl(2)	−1102(2)	1566(2)	−3006(2)	76(1)
Cl(3)	−807(2)	3115(2)	−3614(2)	59(1)
Cl(4)	3753(2)	2665(2)	1287(2)	56(1)
Cl(5)	4091(2)	1299(2)	−442(2)	62(1)
Cl(6)	3392(2)	990(2)	677(2)	62(1)
O(1)	−1885(4)	1960(6)	−4640(5)	65(3)
O(2)	170(4)	1797(4)	−3430(4)	40(2)
O(3)	4877(5)	1826(5)	1058(5)	54(2)
O(4)	2939(4)	2312(4)	−364(4)	48(2)
C(1)	−1174(9)	3320(7)	−5430(7)	52(4)
C(2)	−1872(9)	3474(9)	−5501(8)	65(4)
C(3)	−2229(9)	4093(9)	−5837(9)	78(5)
C(4)	−1924(12)	4593(11)	−6089(11)	99(7)
C(5)	−1240(13)	4442(9)	−6042(12)	109(7)
C(6)	−840(9)	3820(10)	−5709(10)	88(6)
C(7)	386(8)	2647(7)	−4688(8)	51(4)
C(8)	731(8)	3152(8)	−4143(8)	67(5)
C(9)	1463(10)	3322(10)	−3930(10)	81(6)
C(10)	1877(10)	3020(13)	−4196(11)	95(7)
C(11)	1561(10)	2541(11)	−4744(11)	87(6)
C(12)	795(10)	2344(9)	−5008(8)	69(5)
C(13)	−931(7)	1828(8)	−5881(7)	53(4)
C(14)	−1245(9)	2132(10)	−6561(9)	76(5)
C(15)	−1401(11)	1703(14)	−7160(10)	99(7)
C(16)	−1276(12)	995(15)	−7087(11)	98(7)
C(17)	−947(14)	673(10)	−6423(14)	115(8)
C(18)	−774(10)	1103(9)	−5815(9)	83(5)
C(19)	848(6)	1108(7)	−1953(7)	40(3)
C(20)	1276(7)	1215(8)	−1219(8)	59(4)
C(21)	1258(10)	681(9)	−758(8)	73(5)
C(22)	831(9)	88(8)	−1032(9)	68(5)
C(23)	408(8)	−13(8)	−1763(9)	67(5)
C(24)	404(8)	501(7)	−2239(8)	59(4)
C(25)	1729(6)	1439(6)	−2799(7)	36(3)
C(26)	2472(7)	1405(8)	−2258(8)	65(5)
C(27)	2998(8)	1166(8)	−2438(9)	67(5)
C(28)	2811(9)	938(9)	−3104(10)	73(5)
C(29)	2104(4)	983(10)	−3621(9)	87(6)
C(30)	1538(9)	1234(8)	−3492(9)	69(5)
C(31)	1175(7)	2727(7)	−2189(6)	43(3)
C(32)	1731(7)	3133(7)	−2203(7)	54(4)
C(33)	1831(9)	3829(8)	−1965(8)	66(5)
C(34)	1341(10)	4134(8)	−1741(8)	73(5)
C(35)	797(9)	3736(9)	−1709(8)	68(5)
C(36)	687(8)	3007(8)	−1929(7)	58(4)
C(37)	5385(7)	3416(7)	749(8)	48(4)
C(38)	5873(8)	3640(8)	475(8)	59(4)
C(39)	6616(9)	3749(9)	936(9)	73(5)
C(40)	6908(8)	3680(8)	1688(10)	75(6)
C(41)	6402(9)	3483(8)	1965(8)	67(5)
C(42)	5659(8)	3369(7)	1475(8)	57(4)

TABLE III Continued

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
C(43)	4136(7)	3457(7)	−863(7)	43(3)
C(44)	3954(8)	2933(9)	−1384(8)	60(4)
C(45)	3752(9)	3100(9)	−2091(9)	68(4)
C(46)	3728(8)	3798(10)	−2292(8)	63(4)
C(47)	3896(9)	4340(10)	−1794(9)	74(5)
C(48)	4100(8)	4166(7)	−1091(7)	57(4)
C(49)	3844(7)	4043(6)	293(7)	39(3)
C(50)	3046(7)	4045(7)	−55(8)	55(4)
C(51)	2689(8)	4641(8)	29(7)	54(4)
C(52)	3074(10)	5215(8)	460(8)	66(5)
C(53)	3836(10)	5203(8)	808(8)	70(5)
C(54)	4206(8)	4624(7)	697(7)	53(4)
C(55)	6254(7)	1138(8)	1190(7)	48(4)
C(56)	6521(9)	462(8)	1132(9)	63(4)
C(57)	7073(9)	440(8)	942(9)	67(4)
C(58)	7378(8)	1036(9)	807(9)	66(5)
C(59)	7108(9)	1707(9)	860(9)	68(5)
C(60)	6540(9)	1749(8)	1041(8)	60(4)
C(61)	5963(7)	1590(7)	2458(7)	44(3)
C(62)	5490(8)	1841(7)	2731(8)	57(4)
C(63)	5787(8)	2071(7)	3454(7)	52(4)
C(64)	6550(9)	2071(8)	3893(8)	62(4)
C(65)	7022(9)	1817(9)	3626(8)	72(5)
C(66)	6739(8)	1566(8)	2932(8)	64(4)
C(67)	5130(7)	287(7)	1556(7)	41(3)
C(68)	4772(8)	−135(7)	929(8)	58(4)
C(69)	4525(10)	−814(9)	989(10)	76(5)
C(70)	4614(12)	−1040(10)	1625(14)	100(7)
C(71)	4984(12)	−648(9)	2247(10)	93(7)
C(72)	5246(9)	25(7)	2214(9)	67(5)

$[ReOBr_3(OPPhEt_2)(PPhEt_2)]$ [32], 2.053 Å. In comparison with other arsine rhenium complexes the Re–As lengths in **1** and **2** are a little longer: 2.557 and 2.541 Å in $[ReO_2(dadpe)_2]^+$ and 2.532, 2.552, 2.541 and 2.546 Å in $[ReN(dpae)_2Cl]^+$ [33].

Re–Cl and Re–Br bond distances in **1** and **2** are in accordance with values found in the literature.

Both complexes are diamagnetic. IR spectra of **1** and **2** compounds exhibit characteristic Re=O stretching vibrations at 994 and 998 cm^{-1}, respectively. $[ReOCl_3(AsPh_3)_2]$ has $\nu_{Re=O}$ at 967 cm^{-1}, $[ReOBr_3(AsPh_3)_2]$ and $[ReOBr_3(PPh_3)_2]$ at 980 cm^{-1} and $[ReOCl_3(PPh_3)_2)]$ at 969 cm^{-1} [18]. A strong band corresponding to the As=O group appears in **1** and **2** at 848 and 842 cm^{-1}, respectively. The characteristic As=O stretch is recorded at 850 cm^{-1} for $[ReCl_3(OAsPh_3)]_n$ [18] and at 841 cm^{-1} for $[NiCl_2(OAsPh_3)_2]$ [34]. Table VI gives assignments for characteristic IR bands for **1** and **2**.

The positions, assignments and molar absorption coefficients of electronic absorption bands for **1** and **2** are shown in Table VII. From this data, values of ligand field parameters Dq, Ds and Dt have been defined and energies of molecular orbitals for **1** and **2** have been estimated. The values of ligand field parameters for 1 and 2 are given in Table VIII. The electronic configuration of Re(V), $(d_{xy})^2$, in compounds **1** and **2** is in full accordance with X-ray and magnetochemical data. Values in

TABLE IV Selected bond lengths (Å) and angles (°) for **1**

Bond lengths		*Angles*	
Re(1)–O(2)	1.660(7)	O(2)–Re(1)–O(1)	170.2(3)
Re(1)–O(1)	2.010(7)	O(2)–Re(1)–Br(2)	100.1(3)
Re(1)–Br(2)	2.5146(14)	O(1)–Re(1)–Br(2)	89.6(2)
Re(1)–Br(3)	2.533(2)	O(2)–Re(1)–Br(3)	94.7(3)
Re(1)–Br(1)	2.554(2)	O(1)–Re(1)–Br(3)	87.6(2)
Re(1)–As(2)	2.5898(12)	Br(2)–Re(1)–Br(3)	87.78(5)
O(1)–As(1)	1.675(7)	O(2)–Re(1)–Br(1)	92.4(3)
As(1)–C(1)	1.907(11)	O(1)–Re(1)–Br(1)	85.7(2)
As(1)–C(7)	1.906(10)	Br(2)–Re(1)–Br(1)	89.29(5)
As(1)–C(13)	1.917(10)	Br(3)–Re(1)–Br(1)	172.71(5)
As(2)–C(31)	1.922(10)	O(2)–Re(1)–As(2)	87.2(3)
As(2)–C(25)	1.958(10)	O(1)–Re(1)–As(2)	83.3(2)
As(2)–C(19)	1.950(11)	Br(2)–Re(1)–As(2)	172.28(4)
C(1)–C(6)	1.40(2)	Br(3)–Re(1)–As(2)	89.08(5)
C(1)–C(2)	1.38(2)	Br(1)–Re(1)–As(2)	92.99(5)
C(2)–C(3)	1.41(2)	As(1)–O(1)–Re(1)	156.9(4)
C(3)–C(4)	1.39(2)	O(1)–As(1)–C(1)	104.5(4)
C(4)–C(5)	1.36(2)	O(1)–As(1)–C(7)	113.0(4)
C(5)–C(6)	1.38(2)	C(1)–As(1)–C(7)	108.3(4)
		O(1)–As(1)–C(13)	109.9(4)
		C(1)–As(1)–C(13)	110.4(5)
		C(7)–As(1)–C(13)	110.6(4)
		C(31)–As(2)–C(25)	104.5(4)
		C(31)–As(2)–C(19)	103.3(4)
		C(25)–As(2)–C(19)	100.0(5)
		C(31)–As(2)–Re(1)	111.2(3)
		C(25)–As(2)–Re(1)	118.1(3)
		C(19)–As(2)–Re(1)	117.9(3)
		C(6)–C(1)–C(2)	122.3(11)
		C(6)–C(1)–As(1)	121.0(8)
		C(2)–C(1)–As(1)	116.8(9)
		C(3)–C(2)–C(1)	118.5(12)
		C(2)–C(3)–C(4)	118.1(12)
		C(5)–C(4)–C(3)	122.4(12)
		C(6)–C(5)–C(4)	120.7(14)
		C(5)–C(6)–C(1)	118.1(13)

Tables VII and VIII show a quantitative accordance with X-ray data, considering electron density distribution in compounds **1** and **2**. A higher donor ability of both Cl^- and Br^- ions results in a higher value of molar extinction coefficients of $Hal^- \rightarrow Re$ electron transitions, and a higher covalency for the Hal–Re bond in **2** ($\Delta = 17794\,cm^{-1}$). Lower electron density on the central ion in **1**, resulting from $Hal^- \rightarrow Re$ transitions, causes more effective electron transfer from O atoms in As–Ö and Re=Ö groups towards the central ion. This in turn leads to a shortening of Re–O and As–O bonds in **1**, compared to compound **2**. The lower electron density on Re(V) in **1** also causes a more effective electron density transfer from arsine, leading to shortening of Re–As in the bromide. The *trans* influence in the Hal–Re–As group is stronger in the chloride case, causing greater lowering of electron density on As in compound **2**. This leads to an increase for the probability of the electron transfer $\pi^b_{C_6H_5} \rightarrow 3d_{As}$ in the chloride.

TABLE V Selected bond lengths (Å) and angles (°) for **2**

Bond lengths		*Angles*	
Re(2)–O(4)	1.720(7)	O(4)–Re(2)–O(3)	169.6(4)
Re(2)–O(3)	2.019(8)	O(4)–Re(2)–Cl(6)	99.1(3)
Re(2)–Cl(6)	2.339(4)	O(3)–Re(2)–Cl(6)	90.8(3)
Re(2)–Cl(4)	2.359(4)	O(4)–Re(2)–Cl(4)	98.3(3)
Re(2)–Cl(5)	2.389(4)	O(3)–Re(2)–Cl(4)	84.7(3)
Re(2)–As(3)	2.607(2)	Cl(6)–Re(2)–Cl(4)	89.38(14)
Re(1)–O(1)	1.688(8)	O(4)–Re(2)–Cl(5)	94.1(3)
Re(1)–O(2)	2.021(7)	O(3)–Re(2)–Cl(5)	83.0(3)
Re(1)–Cl(2)	2.358(4)	Cl(6)–Re(2)–Cl(5)	88.43(14)
Re(1)–Cl(3)	2.365(4)	Cl(4)–Re(2)–Cl(5)	167.56(13)
Re(1)–Cl(1)	2.403(4)	O(4)–Re(2)–As(3)	85.8(3)
Re(1)–As(1)	2.611(2)	O(3)–Re(2)–As(3)	84.6(3)
As(1)–C(7)	1.925(14)	Cl(6)–Re(2)–As(3)	172.74(11)
As(1)–C(13)	1.934(13)	Cl(4)–Re(2)–As(3)	84.61(9)
As(1)–C(1)	1.959(14)	Cl(5)–Re(2)–As(3)	96.57(10)
As(2)–O(2)	1.689(7)	O(1)–Re(1)–O(2)	170.1(4)
As(2)–C(31)	1.911(12)	O(1)–Re(1)–Cl(2)	98.7(4)
As(2)–C(19)	1.916(13)	O(2)–Re(1)–Cl(2)	89.9(3)
As(2)–C(25)	1.927(12)	O(1)–Re(1)–Cl(3)	97.5(4)
As(3)–C(37)	1.924(13)	O(2)–Re(1)–Cl(3)	87.4(2)
As(3)–C(49)	1.922(12)	Cl(2)–Re(1)–Cl(3)	88.9(2)
As(3)–C(43)	1.931(13)	O(1)–Re(1)–Cl(1)	92.8(4)
As(4)–O(3)	1.643(9)	O(2)–Re(1)–Cl(1)	82.6(2)
As(4)–C(61)	1.862(12)	Cl(2)–Re(1)–Cl(1)	88.2(2)
As(4)–C(67)	1.901(13)	Cl(3)–Re(1)–Cl(1)	169.61(13)
As(4)–C(55)	1.914(13)	O(1)–Re(1)–As(1)	87.3(3)
		O(2)–Re(1)–As(1)	84.6(2)
		Cl(2)–Re(1)–As(1)	171.96(12)
		Cl(3)–Re(1)–As(1)	85.02(10)
		Cl(1)–Re(1)–As(1)	96.92(11)
		C(7)–As(1)–C(13)	104.4(6)
		C(7)–As(1)–C(1)	102.6(6)
		C(13)–As(1)–C(1)	102.4(6)
		C(7)–As(1)–Re(1)	114.7(4)
		C(13)–As(1)–Re(1)	118.6(5)

TABLE VI Characteristic infrared data for **1** and **2**

Band positions (cm^{-1})		*Assignments*
$[ReOBr_3(OAsPh_3)(AsPh_3)]$	$[ReOCl_3(OAsPh_3)(AsPh_3)]$	
1482	1483	δ(C–CH in plane)
1436	1437	ν(As–C_6H_5)
1085	1085	δ(C–H in plane)
994	998	ν(Re=O)
848	842	ν(As=O)
742	742	δ(C–C out of plane)
690	692	δ(C–C in plane)

Supplementary Material

Supplementary data for $C_{36}H_{30}Br_3O_2As_2Re$ (**1**) and $C_{36}H_{30}Cl_3O_2As_2Re$ (**2**) are available on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, quoting numbers CCDC 162043 and CCDC 162044.

TABLE VII Band positions in electronic spectra molar absorption coefficients and assignments for **1** and **2**

[ReOBr$_3$(OAsPh$_3$)(AsPh$_3$)]		*[ReOCl$_3$(OAsPh$_3$)(AsPh$_3$)]*		*Assignments*
Band positions (cm^{-1})	*Molar absorption coefficients* (M^{-1}/cm^{-1})	*Band positions* (cm^{-1})	*Molar absorption coefficients* (M^{-1}/cm^{-1})	
13826	19	17794	24	$d_{xy} \rightarrow d_{yz}$
23256	131	24938	152	$d_{xy} \rightarrow d_{xz}$
27933	487	30960	908	$d_{xy} \rightarrow d_{x^2-y^2}$
37454	10850	38024	14200	$\mathrm{Hal}^- \rightarrow d_{\mathrm{Re}}; \pi^{\mathrm{o}}_{\mathrm{O=As}} \rightarrow d_{\mathrm{Re}}$
42194	11602	42017	15106	$\pi^b_{\mathrm{C_6H_5}} \rightarrow 3d_{\mathrm{As}}$

TABLE VIII Values of ligand field parameters for **1** and **2**

Ligand field parameter	*Value* (cm^{-1})	
	[ReOBr$_3$(OAsPh$_3$)(AsPh$_3$)]	*[ReOCl$_3$(OAsPh$_3$)(AsPh$_3$)]*
Dq	2 793.3	3096
Ds	− 7608	− 8277
Dt	86.4	21.4

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