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Synthesis, structure and reactivity of bromo- and aquatricarbonylrhenium(I) phosphinite and phosphonite derivatives

Rosa Carballo [a], Alfonso Castiñeiras [b], Soledad García-Fontán [a], Pilar Losada-González [a], Ulrich Abram [c], Ezequiel M. Vázquez-López [a,*]

[a] *Departamento de Química Inorgánica, Facultade de Ciencias-Química, Universidade de Vigo, E-36200 Vigo, Galicia, Spain*
[b] *Departamento de Química Inorgánica, Facultade de Farmacia, Universidade de Santiago de Compostela, E-15706 Santiago de Compostela, Galicia, Spain*
[c] *Institut für Chemie-Radiochemie, Freie Universität Berlin, D-14195 Berlin, Germany*

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Abstract

[ReBr(CO)$_5$] reacted with phosphinite or phosphonite ligands in benzene or toluene to yield *fac*-(**1**) or *mer,trans*-(**2**) complexes, ([ReBr(CO)$_3$(L)$_2$] L = PPh$_2$(OMe), **a**; PPh$_2$(OEt), **b**; PPh(OMe)$_2$, **c**; PPh(OEt)$_2$, **d**) characterized by elemental analysis, mass spectrometry, IR and NMR (^{1}H, ^{13}C and ^{31}P) spectroscopies, and for complexes **1b**, **2c** and **2d**, X-ray diffractometry was used. Complexes **2a**–**2d** reacted with Ag[BF$_4$] in wet acetone to form moderate yield of *mer,trans*-[Re(H$_2$O)(CO)$_3$(L)$_2$][BF$_4$] (**3**). Comparison of the spectra of compounds **3** with those of precursors **2** together with the diffractometric results for compounds **3a**–**3c**, show that all the complexes have the same configuration around the rhenium atom. Crystals of compounds **3** consist of centrosymmetric dimers formed by hydrogen bonds between the water molecules and the BF_4^- anions. The lability of compounds **3** was explored by ^{19}F and ^{31}P NMR, and in the case of **3c** the complex [Re(η^1-BF$_4$)(CO)$_3${PPh(OMe)$_2$}$_2$] (**4c**) was isolated from the mother liquor. Spectroscopic and diffractometric studies of **4c** show monodentate coordination of the tetrafluorborato ligand to the rhenium atom. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Rhenium(I) complexes; Lewis acid; Group 7 metals; NMR

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1. Introduction

The reactions of 18-electron, coordinatively saturated complexes generally occur at significantly slower rates than those of the 16-electron complexes. The 16-electron carbonyl complexes of the Group 7 metals are often generated by the abstraction of CH$_3$ from a methyl precursor [1] or by the protonation of a hydride to a thermally unstable dihydrogen complex:

$$[\mathrm{MH(L)}_n] + \mathrm{H}^+ \rightarrow [\mathrm{M(H_2)(L)}_n]^+ \rightarrow [\mathrm{M(L)}_n]^+ + \mathrm{H_2}$$

$$[\mathrm{MCH_3(L)}_n] + \mathrm{H}^+ \rightarrow [\mathrm{M(L)}_n]^+ + \mathrm{CH_4}$$

$$[\mathrm{MCH_3(L)}_n] + \mathrm{Ph_3C}^+ \rightarrow [\mathrm{M(L)}_n]^+ + \mathrm{Ph_3CCH_3}$$

Anions neutralizing the resulting products can be weakly coordinated to metals retaining high Lewis acid reactivity (this is the case of [Re(η^1-BF$_4$)(CO)$_5$]) [2]. When the anion is not coordinated, the system may be stabilized by agostic interactions between the metal and ancillary ligands [3] or by the coordination of weak donor solvents such as diethylether or CH$_2$Cl$_2$ [1b], as described recently for $[\mathrm{Re(CO)}_{4-n}\mathrm{L}_n]^+[\mathrm{BAr_F}]^-$ ($[\mathrm{BAr_F}]^- = [\mathrm{B(3,5\text{-}(CF_3)_2(C_6H_3))_4}]^-$). (The coordination of chlorinated solvents can lead to the evolution of chloro complexes [1c].)

On the other hand, weak basic 'hard' donor such as H$_2$O, MeOH or THF do not bind strongly to most low-valent transition metals. Owing to this, complexes including these donors can have interesting reactivities and catalytic properties [4]. Particularly, the coordination chemistry of water is attracting increasing attention [5], aqua or D$_2$O complexes having been used for the photolytic splitting of water [6], for C–H bond

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* Corresponding author. Tel.: + 34-986-812-319; fax: + 34-986-812-382.

E-mail address: ezequiel@uvigo.es (E.M. Vázquez-López).

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deuteration [7], in the water–gas shift reaction [8], and in organometallic synthesis [5,9]. For instance, the Re′ aqua complex *fac*-$[Re(H_2O)(bipy)(CO)_3]^+$, proved to be an ideal intermediate for the preparation of hydride, formate and hydrogen carbonate derivatives [9b]:

$$fac\text{-}[Re(H_2O)(bipy)(CO)_3]^+ + E^- \rightarrow [Re(E)(bipy)(CO)_3] + H_2O$$

$$E^- = H^-(BH_4^-),\ HCO_2^-,\ HCO_3^-$$

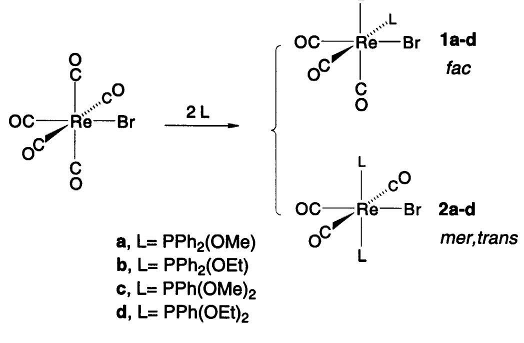
Some aqua complexes also have properties with potential applications in inorganic medicine, most of them likewise arising from the labile nature of the aqua ligand. For example, cationic aqua-carbonyl complexes $[M(H_2O)_3(CO)_3]^+$ (M = Re, ^{99}Tc, ^{99m}Tc) [10a] have been proposed as efficient labels for biological molecules owing to the ready displacement of water and formation of stable complexes with derivatized biomolecules. The inclusion of ancillary non-carbonyl ligands can add to the interest of the resulting complex; this is the case of the cations *fac*-$[Re(H_2O)(CO)_3(L\text{–}L)]^+$ (L–L = 2,2′-bipyridine or 1,10-phenanthroline), which have been proposed as agents for luminescent labeling of nucleotides [l0b] and proteins [l0c].

To further understand the aqua ligand in organometallic systems, in the work described here we prepared and characterized four aqua complexes with phosphorus ligand, namely *mer,trans*-$[Re(H_2O)(CO)_3(L)_2][BF_4]$ (L = $PPh_2(OMe)$, $PPh_2(OEt)$, $PPh(OMe)_2$ and $PPh(OEt)_2$). The precursor bromo complexes $[ReBr(CO)_3(L)_2]$, prepared earlier by Reiman and Singleton [11] were also fully characterized.

2. Results and discussion

2.1. Synthesis of $[ReBr(CO)_3(L)_2]$ complexes

Reiman and Singleton [11] obtained complexes **1b**–**1d** and **2b**–**2d** by refluxing $[ReBr(CO)_5]$ and ligand L in an equimolar mixture of petroleum ether and benzene.



Scheme 1.

In our work we obtained both these compounds and the $PPh_2(OMe)$ derivatives **1a** and **2a** using benzene or toluene as the solvent. The *fac* isomers, **1b**–**1d**, were always obtained after short reaction times but normally in lower yields than the *mer,trans* isomers **2b**–**2d**, which required longer reaction times [12] (Scheme 1).

After the removal of the solvent in vacuo and addition of MeOH or EtOH, **1a**–**1d** and **2a**–**2d** were isolated as colorless solids that were moderately soluble in toluene and highly soluble in chloroform, dichloromethane and carbontetrachloride. Their stoichiometry was established by elemental analysis and mass spectrometry. All the mass spectra contain signals corresponding to the molecular ions; and fragmentation seems to be initiated by the loss of either two carbonyls or the bromo ligand, with intense peaks for $|M-2CO|$ or $|M-Br|$ appearing in most spectra.

The isomers **1** and **2** are differentiated by their vibrational and NMR spectra (Table 1). As reported by Reiman and Singleton [11] the IR spectra of the *fac* complexes show three equally strong ν(CO) bands ($2A' + B''$, for C_s local symmetry), while in those of the *mer,trans* isomers the band of highest wavenumber is weak ($2A_1 + B_1$, C_{2v}). The ^{31}P NMR spectra in $CDCl_3$ exhibit a single resonance suggesting the magnetic equivalence of the two phosphorus ligand, although as in the hydride complexes $[ReH(CO)_3(L)_2]$ [13a] the phosphorus nuclide is slightly more shielded in *fac*-isomers than in *mer,trans*-isomers. In the ^{13}C NMR spectra the two isomers are clearly differentiated by the multiplicities of the signals of the carbonyl groups coupled to the phosphorus nuclides: the *fac* and the *mer,trans* spectra show a triplet and a double doublet (sometimes collapsed to a multiplet) and two triplets, respectively.

2.2. Structure of *fac*-$[ReBr(CO)_3\{PPh_2(OEt)\}_2]$ (**1b**)

The structure of **1b** was determined by X-ray diffractometry. The **1b** crystals comprise discrete molecules with no intermolecular distances short enough to suggest bonding. Fig. 1 shows a ZORTEP plot [14] of the molecular structure, with the numbering scheme used. Selected bond distances and bond angles are given in Table 2.

The rhenium atom is located on a twofold axis perpendicular to the Br–Re–C(3)–O(3) axis. A 180° rotation generates two equivalent *cis*-phosphinite ligands and two carbonyl groups, and results in an orientational disorder [15] confounding the Br and C(3)–O(3) groups. Similar disorder has been found in **2a** and its carbon tetrachloride solvate [16] in this case owing to the rhenium atom lying in the center of symmetry.

Within the accuracy allowed by the disorder noted above, the Re–Br and Re–C distances are close to those

Table 1
Selected IR [a] and NMR [b] data for the complexes

Compound	IR		^{1}H NMR		^{13}C NMR		^{31}P NMR
	Assignment		Assignment		δ(CO)	$J(^{13}C–^{31}P)$	
1a	2031s	ν(CO)	3.29m	$\delta(CH_3)$	187.9t	8.4	99.4s
	1958s				189.1m		
	1892s						
1b	2031s	ν(CO)	1.03t ($J = 7.0$)	$\delta(CH_3)$	188.2t	8.6	96.4s
	1954s		3.49m	$\delta(CH_2)$	189.2dt		
	1899s						
1c	2039s	ν(CO)	3.51m	$\delta(CH_3)$	180.0t	9.45	131.7s
	1962s				187.5m		
	1906s						
1d	2033s	ν(CO)	1.21m	$\delta(CH_3)$	188.3t	10.5	125.5s
	1955s		3.75m	$\delta(CH_2)$	189.0m		
	1909s		3.97m				
			4.04m				
2a	2059w	ν(CO)	3.55t ($J = 6.5$)	$\delta(CH_3)$	187.3t	7.2	101.8s
	1964s				190.6t	9.8	
	1888s						
2b	2064m	ν(CO)	1.27t ($J = 6.9$)	$\delta(CH_3)$	188.2t	7.1	97.2s
	1955s		3.80m	$\delta(CH_2)$	191.6dd		
	1917s						
2c	2063w	ν(CO)	3.64t ($J = 6.0$)	$\delta(CH_3)$	185.4t	8.7	132.1s
	1957s				188.5	11.7	
	1901s						
2d	2069w	ν(CO)	1.36t ($J = 7.0$)	$\delta(CH_3)$	186.9t	9.1	126.4s
	1973s		3.94m	$\delta(CH_2)$	190.0t	11.1	
	1899s		4.17m				
3a	3418b,m	ν(OH)	4.50s,b	$\delta(H_2O)$	190.7t	6.5	112.8s
	2069w	ν(CO)	3.42t ($J = 6.0$)	$\delta(CH_3)$	191.2t	9.8	
	1974s						
	1927s						
	1635b,w	δ(HOH)					
3b	3418b,m	ν(OH)	4.30s,b	$\delta(H_2O)$	192.8t	6.5	109.1s
	2066w	ν(CO)	1.26t ($J = 7.0$)	$\delta(CH_3)$	194.2t	10.1	
	1977s		3.70m	$\delta(CH_2)$			
	1923s						
	1647b,w	δ(HOH)					
3c	3445b,m	ν(OH)	4.74s,b	$\delta(H_2O)$	188.8t	8.0	140.7s
	2083w	ν(CO)	3.90t ($J = 5.9$)	$\delta(CH_3)$	190.3t	11.2	
	1975s						
	1927s						
	1631b,w	δ(HOH)					
3d	3418b,m	ν(OH)	4.44s,b	$\delta(H_2O)$	189.2t	7.8	135.1s
	2072w	ν(CO)	1.42t ($J = 7.0$)	$\delta(CH_3)$	190.7t	11.1	
	1978s		4.02m	$\delta(CH_2)$			
	1924s		4.09m				
	1651b,w	δ(HOH)					
4c	2073w	ν(CO)	3.63t ($J = 5.8$)	$\delta(CH_3)$	189.2t	8.4	140.5s
	1973s				191.2t	10.9	
	1917s						

[a] ν in cm^{-1}, b = broad, m = medium, s = strong, w = weak.

[b] NMR spectra run in $CDCl_3$ except for **4c**, for which CD_2Cl_2 was used. δ in ppm, J in Hz; m = multiplet, s = singlet, t = triplet.

found in other bromocarbonylrhenium(I) compounds [17] The fact that the Re–P distance, 2.4557(13) Å, is slightly longer than the 2.415(2) Å [16] in **2a** is attributable to the P ligands being *trans* to the carbonyl groups in **1b**.

The $PPh_2(OEt)$ ligand does not seem to suffer any steric hindrance, the value of 88.81(6)° for the P–Re–P^{i} angle ($i = -x + 1, y, -z + 3/2$) being close to ideal (as in the bidentate phosphinite complex $[ReBr(CO)_3(L–L)]$ (L–L = 1,2-bis(diphenylphosphinite)ethane) where

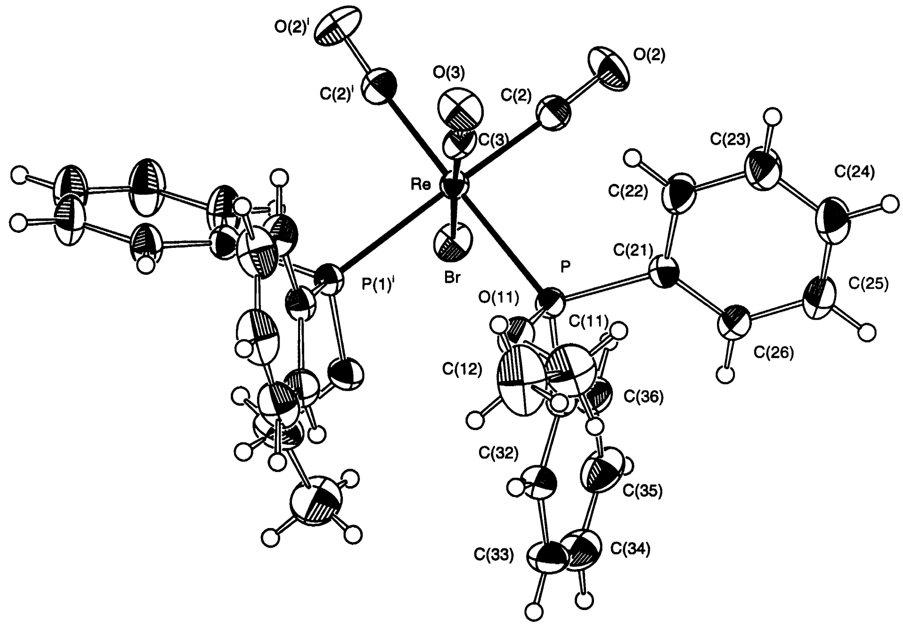


Fig. 1. Molecular structure of compound **1b** showing the numbering scheme (for clarity, just one position of the disordered groups is shown).

P–Re–P = 88.92°) [18]. The coordination polyhedron around the rhenium atom can be accordingly described as a slightly distorted octahedron. The main distortions concern C(3)–Re–P (84.9(4)°), C(2)–Re–Br (86.75(16)°) and C(2)–Re–P^i (174.92(15)°).

2.3. *Structure of mer,trans-[ReBr(CO)$_3${PPh(OMe)$_2$}$_2$] (**2c**) and mer,trans-[ReBr(CO)$_3${PPh(OEt)$_2$}$_2$] (**2d**)*

Fig. 2 is a ZORTEP diagram of the molecular structure of **2c**, with the numbering scheme used. The chief bond distances and bond angles of **2c** and **2d** are listed in Table 2. Like that of **1b**, these structures are disordered. In agreement with the spectroscopic results (see above), both the compounds are *mer,trans* isomers. No significant intermolecular interactions have been observed.

The Re–C and Re–Br distances are normal (necessarily so for the former, which were constrained to take their usual values; see Section 3). The Re–P distances are shorter than in **1b** and **2a** (Table 2) probably because of both the *trans* influence of the CO group in the *fac* isomer and the narrower cone angle of the phosphonite ligand [19].

2.4. *Synthesis of mer,trans-[Re(H$_2$O)(CO)$_3$(L)$_2$][BF$_4$], (**3a–3d**) and the formation of mer,trans-[Re(η^1-BF$_4$)(CO)$_3$(PPh(OMe)$_2$}$_2$] (**4c**)*

Compounds **2** reacted with AgBF$_4$ in boiling wet acetone to form the cationic aqua complexes **3** (Scheme 2). Similar processes are experienced by hydride and methyl manganese(I) and rhenium(I) complexes [3,9c,13,20]. By contrast, the reaction of *fac* compounds **1** with AgBF$_4$ always yielded oily products from which we were unable to isolate pure solids (the ^{31}P NMR spectra of these reaction mixtures showed a complex group of signals that likely seem to reflect the co-existence of dinuclear compounds and the phosphine oxide derivatives O=PPh$_2$(OR) and O=PPh(OR)$_2$).

After the separation of AgBr, the ionic compounds *mer,trans*-[Re(H$_2$O)(CO)$_3$(L)$_2$][BF$_4$] were isolated as

Table 2
Main bond distances and bond angles in compounds **1b**, **2c** and **2d**

	1b	**2c**	**2d**
Bond distances			
Re–C(3)	1.932(15)		1.884(13)
Re–C(2)	1.954(5)	2.03(1) ^{a}	1.996(4)
Re–P	2.4557(13)	2.386(4), 2.389(4)	2.3912(11)
Re–Br	2.602(2)	2.625(4) ^{a}	2.5784(16)
Bond angles			
C(2)–Re–C(3)	91.8(5)		92.5(4)
C(2)^I–Re–C(3)	90.0(5)	90(1) ^{a}	87.5(4)
C(2)–Re–C(2)^i	88.0(3)	174.4(7) ^{a}	180.0
C(3)–Re–P	84.9(4)		86.5(4)
C(2)–Re–P	91.83(16)	90.0(3) ^{a}	90.13(12)
C(2)^I–Re–P	174.92(15)		89.87(12)
C(3)–Re–P^i	93.3(5)		93.5(4)
P–Re–P^i	88.81(6)	178.63(15)	180.0
C(3)–Re–Br	178.1(4)	152.9(3) ^{a}	175.9(4)
C(2)–Re–Br	86.75(16)		89.05(13)
C(2)^I–Re–Br	91.14(16)	90.0(3) ^{a}	90.95(13)
P–Re–Br	93.92(7)	90.42(9) ^{a}	88.68(3)
P^i–Re–Br	88.18(7)	89.58(9) ^{a}	91.32(3)

Symmetry codes: **1b**, $i = -x+1, y, -z+3/2$; **2c**, **2d**, $i = -x, -y+1, -z$.

[a] The listed Re–C and C–O distances and related values for **2c** are mean values. The standard deviations are estimated by $(\Sigma\sigma/n)/n^{1/2}$.

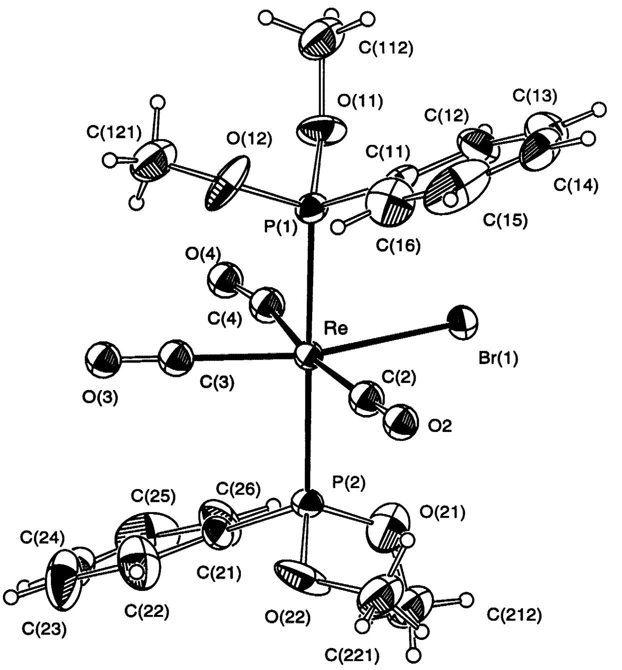
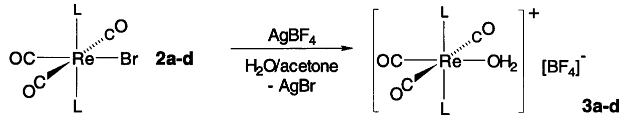


Fig. 2. Molecular structure of compound **2c** showing the numbering scheme (for clarity, just one position of the disordered groups is shown).



Scheme 2.

colorless solids that are stable in air and moisture and soluble in chloroform and alcohols but only very poorly soluble in diethylether. The resistance of derivatives **3** to moisture contrasts with the reported hygroscopic character of $[Re(H_2O)(CO)_5]^+Y^-$ ($Y^- = BF_4^-$, AsF_6^-) [21]

The mass spectra of the isolated aqua complexes show signals corresponding to the $[Re(H_2O)(CO)_3(L)_2]^+$ cation, but the base peak was always that of $[Re(CO)_3(L)_2]^+$. The IR spectra show the characteristic weak–strong–strong pattern of the ν(CO) bands of *mer,trans*-tricarbonylrhenium(I), although at higher wavenumbers than in compounds **2** (see Table 1). The 950–1150 cm^{-1} region is dominated by the (R)C–O bands of the phosphorus ligand, which prevent the identification of both the IR-active B–F absorptions of 'free' BF_4^- (expected to appear as a strong band in the 1000–1100 cm^{-1} range and a weak band around 525 cm^{-1}) [23] and the expected weak or medium bands at 1120, 1050 and 980 cm^{-1} owing to hydrogen bonding between the anion and the cation via the water molecule (vide infra) [22].

The ^{1}H NMR spectra run in chloroform show the expected signal around 4.5 ppm owing to coordinated water. This value contrasts with those reported for $[Mn(H_2O)(CO)_3(L–L)][BF_4]$ 2.78 ppm for L–L = depe, 2.03 ppm for L–L = dppe [9c]. The ^{13}C NMR CO signals appear around 190 ppm at slightly lower frequencies than for **2**, and confirm the persistence of *mer,trans* coordination in solution. The ^{31}P NMR spectra consist of single signals owing to the two magnetically equivalent ^{31}P nuclei and lying about 10 ppm downfield from the ^{31}P NMR signals of **2**. The ^{19}F NMR spectra of freshly prepared solutions in $CDCl_3$ exhibit two sharp singlets at -151.80 and -151.95 ppm with an intensity ratio of approximately 1:4. A similar pattern in the spectrum of $[PdH(H_2O)(PCy_3)_2][BF_4]$ [23] is understood to be a $B^{11}–B^{10}$ isotopic shift effect rather than an indication of the presence of different kinds of fluoride. The spectra of **3** therefore suggest the presence of 'free' BF_4^- in freshly prepared solutions of **3** in chloroform.

When the mother liquor of **3c** was slowly concentrated at room temperature it formed pale-pink single crystals that were stable in air and moisture, and the spectral data of which (Table 1) showed no signals for the coordinated water. An X-ray diffraction study identified the new compound as *mer,trans*-$[Re(\eta^1\text{-}BF_4)(CO)_3\{PPh(OMe)_2\}_2]$, **4c** (vide infra). The stability of this compound contrasts with the ready hydrolysis of $[Re(BF_4)(CO)_5]$ and the related compounds prepared by Beck and Sünkel [4].

The ^{31}P NMR spectrum of **4c** shows a singlet slightly shifted with respect to the aqua complex **3c**. At room temperature, in the ^{19}F NMR spectrum of the freshly prepared solutions of **4c**, there is a weak, complex multiplet centered at -149.4 ppm. Although two different signals are expected for the coordinated BF_4^-, they are observed as separate signals at low temperature [24].

The formation of **4c** from the mother liquor of **3c** is in keeping with the known lability of organometallic aqua complexes. Likewise, solutions of isolated **3c** in $CDCl_3$ or CD_2Cl_2 also formed **4c**; Fig. 3 shows the ^{19}F NMR spectrum of a one week-old solution of **3c** in $CDCl_3$ where the formation of **4c** is reflected by the appearance of the characteristic pattern of coordinated BF_4^- (although the free ligand is a more abundant species). The intensity ratio between the signals of **3c** and **4c** remained constant for several weeks and was not affected by temperature (20–70 °C). ^{31}P and ^{19}F NMR studies of chloroform solutions of **3a**, **3b** and **3d** showed similar 4:3 ratios, which implies that the affinity of $[Re(CO)_3(L)_2]^+$ for water is not very sensitive to the identity of the phosphorus ligand.

Horn and Snow [21] have reported that in CH_2Cl_2 solutions of *fac*-$[Re(H_2O)(CO)_3(tmen)][BF_4]$ (tmen = tetramethylethylidenediammine) the main species is the tetrafluorborato complex. Surprisingly, the ratio seems to be inverted for the corresponding phosphonite and

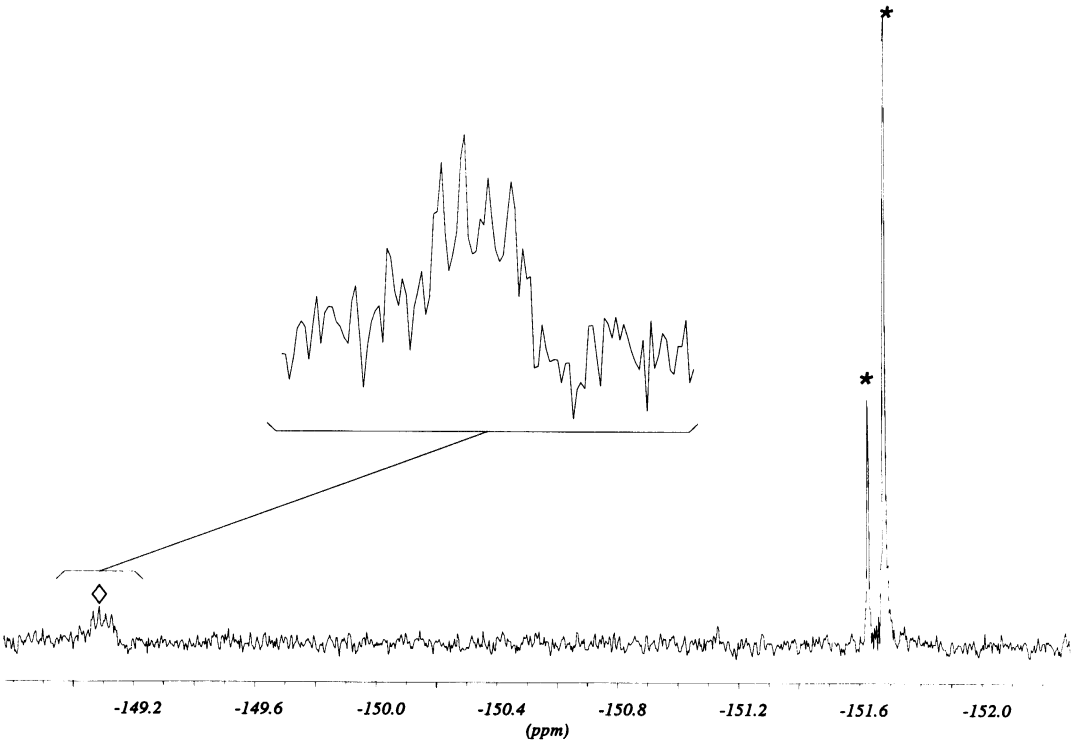


Fig. 3. ^{19}F NMR spectrum of a $CDCl_3$ solution of **3c** after 1 week showing the signals corresponding to free BF_4^- (*) and coordinated BF_4^- (◇).

phosphinite compounds. The difference may be because of the electronic differences between tmen and $PPh_{2-n}(OR)_n$ and the differences in the steric demands imposed at the 'vacant' positions by the different configurations around the rhenium atom. Specifically, coordination of BF_4^- to the metal should be easier when the ancillary ligand has a *fac*,*cis* arrangement, as in tmen derivatives, than the *mer*,*trans* configuration. We plan our further investigation towards the effect of the identity of the counter-ion on the behavior and reactivity of aqua complexes with other ligands.

2.5. *Structure of mer,trans-*$[Re(H_2O)(CO)_3(L)_2][BF_4]$ *(L = $PPh_2(OMe)$ [**3a**], $PPh_2(OEt)$ [**3b**] or $PPh(OMe)_2$ [**3c**])*

Figs. 4 and 5 are ZORTEP plots of the *mer*,*trans*-$[Re(H_2O)(CO)_3\{PPh_2(OMe)\}_2]^+$ and *mer*,*trans*-$[Re(H_2O)(CO)_3\{PPh(OMe)_2\}_2]^+$ cations, showing the atom-numbering scheme employed. Table 3 lists a selection of bond distances and bond angles for the three aqua complexes.

The rhenium atom lies in an octahedral coordination environment formed by the two mutually *trans* phosphinite or phosphonite ligands, three *mer* carbonyl groups and an oxygen atom of the coordinated water. The main distortion of ideal geometry in the phosphinite derivatives concerns the P(2)–Re–P(1) angle (174.76(3)° in **3a**, 174.33(11)° in **3b**). In keeping with the smaller bulk of the phosphonite ligand [19] in **3c**, this angle is 179.2(5)° close to the ideal value. The Re–C and Re–P distances are close to those found in **2a** [16] and **2c**.

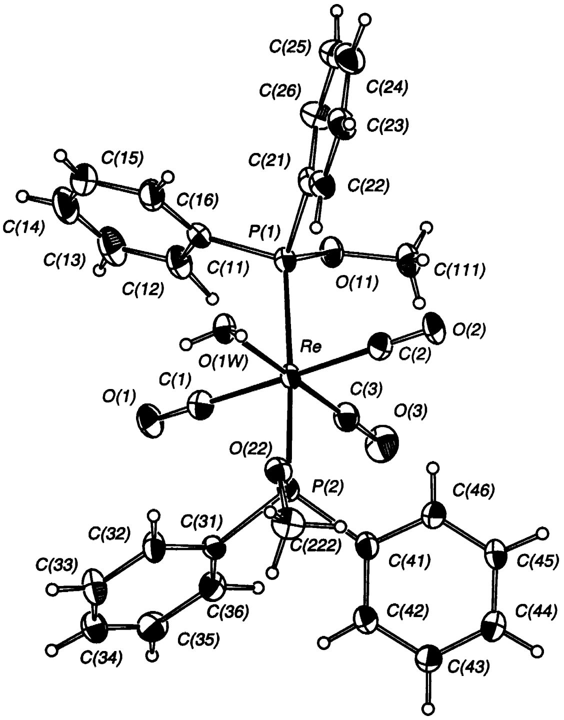


Fig. 4. Molecular structure of *mer*,*trans*-$[Re(H_2O)(CO)_3\{PPh_2(OMe)\}_2]^+$ cation, showing the numbering scheme.

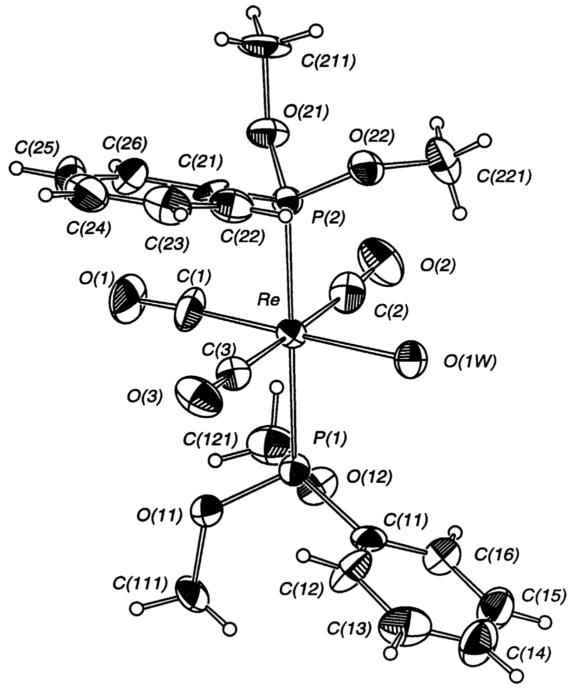


Fig. 5. Molecular structure of *mer*,*trans*-$[Re(H_2O)(CO)_3\{PPh(OMe)_2\}_2]^+$ cation, showing the numbering scheme.

Table 3
Main bond distances and bond angles in **3a**, **3b** and **3c**

	3a	**3b**	**3c**
Bond distances			
Re–C(1)	2.012(5)	2.017(8)	1.917(13)
Re–C(2)	1.978(5)	2.010(9)	1.869(16)
Re–C(3)	1.887(5)	1.873(8)	1.894(15)
Re–O(1W)	2.216(3)	2.214(6)	2.263(8)
Re–P(1)	2.4151(11)	2.4084(18)	2.391(3)
Re–P(2)	2.4132(12)	2.4295(19)	2.381(3)
Bond angles			
C(1)–Re–C(2)	177.70(18)	177.4(3)	179.2(5)
C(1)–Re–C(3)	90.64(19)	87.4(4)	90.0(6)
C(2)–Re–C(3)	88.05(19)	90.1(4)	89.8(6)
C(1)–Re–O(1W)	89.19(17)	94.5(3)	88.6(4)
C(2)–Re–O(1W)	92.12(17)	88.1(3)	91.5(5)
C(3)–Re–O(1W)	179.73(17)	178.1(3)	177.9(5)
C(1)–Re–P(1)	89.67(15)	88.8(2)	88.6(3)
C(2)–Re–P(1)	88.52(14)	91.9(2)	92.2(4)
C(3)–Re–P(1)	93.20(15)	90.8(2)	92.7(4)
C(1)–Re–P(2)	89.63(14)	86.1(2)	88.0(3)
C(2)–Re–P(2)	92.30(14)	99.3(2)	91.3(4)
C(3)–Re–P(2)	92.00(15)	92.0(3)	88.8(4)
O(1W)–Re–P(1)	86.60(10)	87.79(16)	88.9(2)
O(1W)–Re–P(2)	88.20(10)	87.57(16)	89.5(2)
P(1)–Re–P(2)	174.76(3)	174.14(6)	176.27(12)

To the best of our knowledge only four other aquacarbonylrhenium(I) complexes have been characterized diffractometrically: $[Re(H_2O)(CO)_5][AsF_6]$, *fac*-$[Re(H_2O)(CO)_3(tmen)][AsF_6]$ and its tetrafluorborate analog [21a] and the recently reported $[Re(H_2O)(CO)_3(phen)][CF_3SO_3]\cdot H_2O$ (phen = 1,10-phenanthroline) [21b]. The Re–O(1W) distances in the phosphinite compounds are similar to those for the phen derivatives (2.214(6) and 2.210(6) Å) and the intermediate between those found in the pentacarbonyl compound (2.206(8) Å) and its tmen-substituted derivative (2.239(4) Å). However, the metal–O(1W) distance in **3c** is the longest of all, and similar to those found in other complexes with d^6 electronic configuration [9c,25,26] in $[W(H_2O)(CO)_3(P^iPr_3)_2]\cdot THF$ [5], e.g. the longest M–O(W) distance is 2.320(5) Å.

The hydrogen atoms of the water molecule were successfully located and refined in **3a**, and the Re–H distances (2.59(5) and 2.61(6) Å) and Re–O(1W)–H angles (111(4) and 112(4)°) suggest that the water is coordinated as usual by the σ donation of oxygen lone pairs [5]. Although we were unable to locate the H_2O hydrogen atoms of **3c**, or to refine their locations in **3b**, the Re–O(1W) distances and O(1W)–Re–C/P angles in this compounds are close to those found in **3a** and together with the spectroscopic similarities to **3a** (vide supra) suggest that in all the three water molecules have the same coordination mode. This conclusion is reinforced by the fact that molecular association is similar in all the three compounds (vide infra).

The arrangement of ions in the crystals of compounds of cationic aqua-organometallic complexes [25] is usually governed by hydrogen bonds. In all aqua,tmen-rhenium compounds, e.g. the cation and anion are linked by hydrogen bonds between the aqua ligand and fluorine atoms. In **3a** and **3b** both the aqua ligands of the two cations are linked by O–H···F hydrogen bonds to the same two anions, thus forming dimeric structures (Fig. 6). In **3a** the parameters of these bonds are O(1W)–H(1)···F(1) = 0.76(5), 1.96(5),

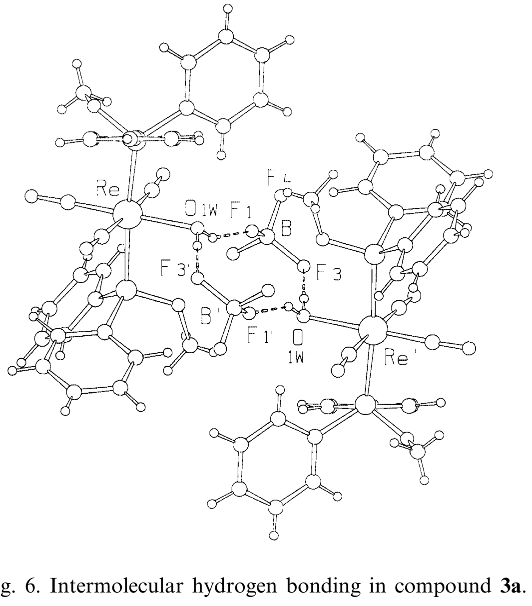


Fig. 6. Intermolecular hydrogen bonding in compound **3a**.

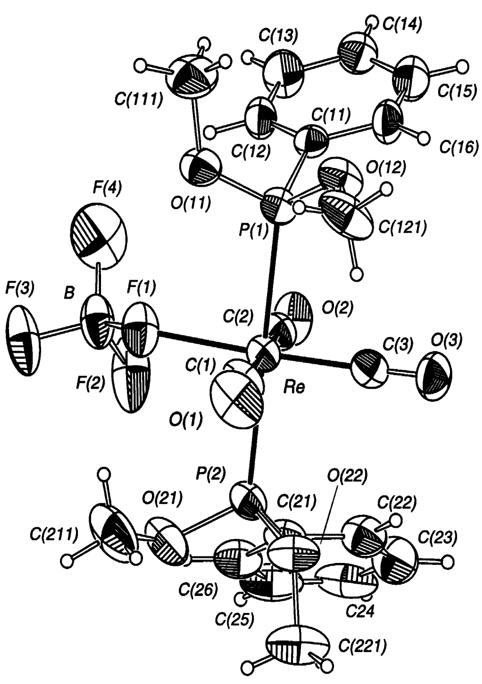


Fig. 7. Molecular structure of compound **4c**, showing the numbering scheme.

Table 4
Main bond distances and bond angles in compound **4c**

Bond distances			
Re–C(1)	1.895(15)	Re–C(3)	1.995(13)
Re–C(2)	1.968(14)	Re–F(1)	2.213(8)
Re–P(1)	2.388(3)	Re–P(2)	2.390(3)
Bond angles			
C(1)–Re–C(3)	89.0(5)	C(1)–Re–P(1)	89.8(4)
C(2)–Re–C(3)	92.9(6)	C(3)–Re–P(2)	90.7(4)
C(1)–Re–C(2)	176.5(5)	C(1)–Re–P(2)	89.2(4)
C(3)–Re–F(1)	177.4(4)	C(2)–Re–P(2)	87.9(4)
C(1)–Re–F(1)	89.5(4)	F(1)–Re–P(1)	88.6(2)
C(2)–Re–F(1)	88.7(5)	F(1)–Re–P(2)	91.4(2)
C(3)–Re–P(1)	89.3(4)	P(1)–Re–P(2)	179.02(12)
C(2)–Re–P(1)	93.1(4)		

2.652(2) Å, 152(5)° and O(1W)–H(2)···F(3)^i = 0.78(6), 1.88(6), 2.649(5) Å, 169(6)°; and in **3b**, O(1W)–H(1)···F(1)^i = 0.648(8), 2.011(10), 2.651(13) Å, 170.2(8)° and O(1W)–H(2)···F(4) = 0.763(10), 1.906(13), 2.657(16) Å, 167.6° ($i = 1/2 - x, 3/2 - y, -z$). Although the H_2O hydrogen atoms in **3c** cannot be located, short O(1W)···F distances suggest the same arrangement (O(1W)–F(2) = 2.597(13) Å, O(1W)–F(1)^i = 2.634(12) Å, $i = -x, y - 1/2, -z + 1/2$). This contrasts with the formation of polymeric chains by pentacarbonylrhenium(I) and its tmen derivatives or other d^6 systems such as $[IrH_2(H_2O)(THF)(PPh_3)_2][SbF_6]$ [25], $[RuH(H_2O)(CO)_2(PPh_3)_2][BF_4]\cdot EtOH$ [26], $[W(H_2O)(CO)_3(P^iPr_3)_2]\cdot THF$ [5] and *fac*-$[Mn(H_2O)(CO)_3(L\text{–}L)]$ [9c] (in the THF complexes case the chains are formed by O(THF)···H–O hydrogen bonds). However, dimeric structures like those of **3a** and **3b** have been observed before in $[Pd(H)(H_2O)(PCy_3)_2][BF]_4$ [23], $[RuCl(\eta^3{:}\eta^2{:}\eta^2\text{-}C_{12}H_{18})(H_2O)][BF_4]$ [27] and $[Mo(acac)(\eta^7\text{-}C_7H_7)(H_2O)][BF_4]$ [28]. It is noteworthy that the hydrogen bonds in **3a** and **3b** are slightly longer than in *fac*-$[Re(H_2O)(CO)_3(tmen)][BF_4]$ but shorter than in the AsF_6^- derivative, suggesting a significant influence of steric factors.

However, the water molecule does not establish intramolecular hydrogen bonding with the oxygen atoms of the corresponding phosphorus ligand. In this case, the existence of significant interaction can be rejected by the long distance and unsuitable angles for the closest contacts (O(1W)–H...(O22) = 0.76(5), 2.63(5), 3.040(5) Å, 116(4)° for **3a**; O(1W)–H...(O11) = 0.764(10), 2.754(7), 2.996(11) Å, 101.0(6)° for **3a**;O(1W)...O(22) = 3.290(10) Å for **3c**.

2.6. Structure of *mer,trans*-$[Re(\eta^1\text{-}BF_4)(CO)_3\{PPh(OMe)_2\}_2]$ (4c)

An X-ray study of the crystals isolated by the slow evaporation of the mother liquor of **3c** showed them to be $[Re(\eta^1\text{-}BF_4)(CO)_3\{PPh(OMe)_2\}_2]$ (**4c**), in keeping with the non-observation of signals for the coordinated water in the IR and NMR spectra. Fig. 7 shows the molecular structure and the numbering scheme used. The chief bond distances and bond angles are listed in Table 4. The rhenium atom is six-coordinated by three carbonyl atoms, two phenyldimethylphosphonite phosphorus atoms and the fluorine atom of the tetrafluoroborato ligand.

The coordination geometry around the rhenium atom is *mer,trans*, as in the precursor aqua complex, **3c**. The Re–P distances are close to those observed in the corresponding bromo complex (vide supra). The Re–F distance (2.213(8) Å) is longer than in $[ReF(CO)(NO)(PPh_3)_3]^+$ (1.97(1) Å) [29], $[Re_3H_2(CO)_9(BF_4)]^{2-}$ (2.138(7) and 2.146(7) Å) [30] and $[ReF(CCH_2C^tBu)(dppme)_2]^+$ (2.134(4) Å) [31], but similar to those of compounds with the bridging ligand, such as $[ReF(CO)_3]_4$ (2.200(5) Å, average) [32] the mixed valence complex $[Re(I)(Fre(V)F_5)(CO)_5]$ (2.20(2)–2.13(3) Å) [33] and other d^6 organometallic systems with monodentate BF_4^- ligands [34].

The replacement of water by the η^1-BF_4 ligand does not affect the geometry of the coordination polyhedron around rhenium significantly. The main deviations from the ideal octahedral angles are around 2°.

3. Experimental

3.1. Materials and instrumentation

All operations were carried out under dry dinitrogen or argon atmosphere using standard Schlenk techniques. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled in an Ar atmosphere [35].

$Re_2(CO)_{10}$ (ABCR), $AgBF_4$ (Fluka), and methyldiphenylphosphinite [$PPh_2(OMe)$] and ethyldiphenylphosphinite [$PPh_2(OEt)$] (Aldrich), were used as supplied, without any further purification. [$ReBr(CO)_5$] [36], dimethylphenylphosphonite [$PPh(OMe)_2$] and diethylphenylphosphonite [$PPh(OMe)_2$] were synthesized by methods reported in Ref. [37].

Elemental analyses were carried out on a Fisons EA-1108. Melting points (m.p.) were determined on a Gallenkamp MFB-595 and are uncorrected. Mass spectra were recorded on a Micromass spectrometer operating under EI (direct insertion probe, 70 eV, 250 °C) or FAB (nitrobenzyl alcohol matrix) conditions. IR spectra were recorded on a Bruker Vector 22FT spectrophotometer. NMR spectra were obtained on a Bruker AMX 400 spectrometer; ^1H and $^{13}C\{^1H\}$ chemical shifts are referred to internal tetramethylsilane (TMS), and $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4 or $CFCl_3$.

3.2. Synthesis of *fac*-[$ReBr(CO)_3(L)_2$] ($L = PPh_2(OMe)$ [**1a**]; $L = PPh_2(OEt)$ [**1b**]; $L = PPh(OMe)_2$ [**1c**]; $L = PPh(OEt)_2$) [**1d**]

For **1a**, 0.3 ml (1.40 mmol) of $PPh_2(OMe)$ was added to a solution of [$ReBr(CO)_5$] (300 mg, 0.74 mmol) in benzene (20 ml), and the mixture was heated at reflux for 3 h. The solvent was removed under vacuum and the resulting oil was stirred with MeOH (4 ml) in an acetone/$N_{2(l)}$ bath. The white precipitate formed was then filtered off, washed with MeOH and vacuum dried. Additional fractions of this compound were obtained by cooling the mother liquor to − 18 °C. Compounds **1b**–**1d** were obtained in a similar way, except that for **1b** and **1d** precipitation and washing were performed with EtOH.

Data for **1a**. Yield: 25%; m.p. (dec.), 134 °C. *Anal*. Found: C, 44.2; H, 3.2. Calc. for $C_{29}H_{26}BrO_5P_2Re$: C, 44.5; H, 3.4%. EI MS; *m*/*z* (%): 782(11) [*M*], 754(11) [*M* − CO], 726(16) [*M* − 2CO], 703(29) [*M* − Br], 675(8) [*M* − (Br,CO)].

Data for **1b**. Yield: 87%; m.p. (dec.), 151 °C (lit. value 189–192 °C [11]). *Anal*. Found: C, 46.0; H, 3.4. Calc. for $C_{31}H_{30}BrO_5P_2Re$: C, 45.9; H, 3.7%. EI MS; *m*/*z* (%): 810(2) [*M*], 782(10) [*M* − CO], 754(22) [*M* − 2(CO)], 731(3) [*M* − Br], 201(100) [Ph_2PO].

Data for **1c**. Yield: 47%; m.p. (dec.), 95 °C (lit. value 94 °C [11]). *Anal*. Found: C, 33.5; H, 3.1. Calc. for $C_{19}H_{22}BrO_7P_2Re$: C, 33.1; H, 3.2%. FAB MS; *m*/*z* (%): 690(29) [*M*], 662(27) [*M* − CO], 634(59) [*M* − 2CO], 611(69) [*M* − Br], 603(21) [*M* − {2CO,OR}], 583(20) [*M* − (Br,CO)].

Data for **1d**. Yield: 45%; m.p. (dec.), 95 °C (lit. value 96 °C [11]). *Anal*. Found: C, 37.2; H, 4.3. Calc. for $C_{23}H_{30}BrO_7P_2Re$: C, 37.0; 4.1%. FAB MS (FAB); *m*/*z* (%): 746(33) [*M*], 718(45) [*M* − CO], 690(93) [*M* − 2CO], 667(100) [*M* − Br], 639(39) [*M* − (Br,CO)].

3.3. Synthesis of *mer,trans*-[$ReBr(CO)_3(L)_2$] ($L = PPh_2(OMe)$ [**2a**]; $L = PPh_2(OEt)$ [**2b**]; $L = PPh(OMe)_2$ [**2c**]; $L = PPh(OEt)_2$ [**2d**])

The *mer,trans* isomers were obtained easily by following the procedure described for **1a** except that the solvent was toluene and the mixture of [$ReBr(CO)_5$] and phosphorus ligand was first heated at reflux for 4 h and then gently stirred for another 18 h room temperature (r.t.).

Data for **2a**. Yield: 84%; m.p. (dec.), 161–180 °C. *Anal*. Found: C, 44.8; H, 3.5. Calc for $C_{29}H_{26}BrO_5P_2Re$: C, 44.5; H, 3.4%. FAB MS; *m*/*z* (%): 782(19) [*M*], 754(41) [*M* − CO], 726(100) [*M* − 2CO], 703(29) [*M* − Br], 698(13) [*M* − 3CO].

Data for **2b**. Yield: 94%; m.p. (dec.), 185 °C (lit. value 177–182 °C [11]). *Anal*. Found: C, 45.7; H, 3.6. Calc. for $C_{31}H_{30}BrO_5P_2Re$: C, 45.9; H, 3.7%. EI MS; *m*/*z* (%): 810(21) [*M*], 782(46) [*M* − CO], 754(87) [*M* − 2CO], 731(100) [*M* − Br], 703(54) [*M* − (Br,CO)].

Data for **2c**. Yield: 60%; m.p. (dec.), 144 °C (lit. value 145–147 °C [11]). *Anal*. Found: C, 33.4; H, 3.5. Calc. for $C_{19}H_{22}BrO_7P_2Re$: C, 33.1; H, 3.2%. FAB MS; *m*/*z* (%): 690(16) [*M*], 662(32) [*M* − CO], 634(100) [*M* − 2CO], 606(14) [*M* − 3CO].

Data for **2d**. Yield: 82%; m.p. (dec.), 155 °C (lit. value 155–147 °C [11]). *Anal*. Found: C, 37.0; H, 4.6. Calc. for $C_{23}H_{30}BrO_7P_2Re$: C, 37.0; H, 4.1%. FAB MS; *m*/*z* (%): 746(14) [*M*], 718(27) [*M* − CO], 690(100) [*M* − 2CO], 662(5) [*M* − 3CO], 645(7) [*M* − {2CO, OR}].

3.4. Synthesis of the *mer,trans*-[$Re(H_2O)(CO)_3(L)_2$][BF_4] complexes (**3a**–**3d**)

For *mer,trans*-[$Re(H_2O)(CO)_3\{PPh_2(OMe)\}_2$][$BF_4$] (**3a**), an excess of $AgBF_4$ (150 mg, 0.77 mmol) was added to a solution of **2a** (300 mg, 0.38 mmol) in 22 ml of a 1:10 water–acetone mixture. The mixture was refluxed for 1 h, and on cooling to r.t. a black precipitate was formed. The decanted solution was concentrated to dryness and the residue was dissolved in 1:1 toluene–ether and cooled to − 90 °C. The resulting grey precipitate was redissolved in CH_2Cl_2 and this solution was filtered through Celite. The filtrate was concentrated to dryness, the resulting residue was dissolved in 3 ml of CH_2Cl_2/ether, and this solution was cooled to −90 °C, forming a precipitate that was then filtered out and vacuum dried. Compounds **3b**–**3d** were also prepared similarly, except that for **3b** the mixture of $AgBF_4$ and **2b** was refluxed for 3 h.

Slow evaporation of the last mother liquor of **3c** yielded pale-pink crystals that elemental analysis and spectroscopic and diffractometric studies showed to be $[Re(\eta^1\text{-}BF_4)(CO)_3\{PPh(OMe)_2\}_2]$ (**4c**).

Data for **3a**. Yield: 55%; m.p. (dec.), 165 °C. *Anal.* Found: C, 43.6; H, 3.4. Calc. for $C_{29}H_{28}BF_4O_6P_2Re$: C, 43.1; H, 3.5%. FAB MS; *m*/*z* (%): 721(12) $[M-(BF_4)]$, 703(100) $[M-(BF_4\ H_2O)]$, 675(28) $[M-(BF_4\ H_2O, CO)]$.

Data for **3b**. Yield: 47%; m.p. (dec.), 144 °C. *Anal.* Found: C, 44.6; H, 4.2. Calc. for $C_{31}H_{32}BF_4O_6P_2Re$: C, 44.6; H, 3.9%. FAB MS; *m*/*z* (%): 743(6) $[M-(BF_4)]$, 731(100) $[M-(BF_4\ H_2O)]$, 703(34) $[M-(BF_4\ H_2O, CO)]$.

Data for **3c**. Yield: 18%; m.p. (dec.), 112–115 °C. *Anal.* Found: C, 32.1; H, 3.4. Calc. for $C_{15}H_{24}BF_4O_8P_2Re$: C, 31.9; H, 3.4%. FAB MS; *m*/*z* (%): 629(13) $[M-(BF_4)]$, 611(100) $[M-(BF_4\ H_2O)]$, 583(39) $[M-(BF_4\ H_2O, CO)]$.

Data for **3d**. Yield: 27%; m.p. (dec.), 123–125 °C. *Anal.* Found: C, 35.6; H, 4.4. Calc. for $C_{23}H_{32}BF_4O_8P_2Re$: C, 35.8; H, 4.2%. FAB MS; *m*/*z* (%): 685(7) $[M-(BF_4)]$, 607(100) $[M-(BF_4\ H_2O)]$, 639(49) $[M-(BF_4\ H_2O, CO)]$.

Data for **4c**. m.p. (dec.), 155–159 °C. *Anal.* Found: C, 32.5; H, 3.3. Calc. for $C_{19}H_{22}BF_4O_7P_2Re$: C, 32.7; H, 3.2%.

3.5. X-ray data collection, structure and refinement

Crystallographic data collection and refinement parameters are listed in Table 5. Colorless single crystals suitable for X-ray diffractometric studies were obtained by storing the mother liquors at 0 °C (**1b**, **2c** and **2d**) or at r.t. (**3a** and **3b**).

Three different diffractometers were used: Enraf–Nonius CAD4 for **3a** and **3b**; Enraf–Nonius MACH3 for **1b**, **2c** and **4c**; Bruker Smart CCD for **2d** and **3c**. The data were corrected for absorption effects using Ψ-scans [38a] except for **2d** and **3c** where an empirical correction was applied (SADABS [38b]).

Structure analyses were carried out by direct methods [39]. Least-squares full-matrix refinement on F^2 was performed using the program SHELXL-97 [39]. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from Ref. [40]. Graphics were obtained with ZORTEP [14] and SCHAKAL [41].

3.5.1. fac-[ReBr(CO)$_3$(PPh$_2$(OEt)}$_2$] (1b)

Inspection of the reflections revealed systematic absences for space groups *C*2/*c* or *Cc*. Solution in the centro-symmetric group placed the rhenium atom on the twofold axis (position e in Wyckoff notation), with a consequent orientational disorder in the bromide and C(3)–O(3) groups. This was modeled using alternative sites for each in the 50:50 occupancy ratio. The solution in the space group *Cc* showed the same kind of disorder and the refinement was unstable.

3.5.2. mer,trans-[ReBr(CO)$_3${PPh(OMe)$_2$}$_2$] (2c)

The crystals of **2c** were of poor quality and had disordered bromide, carbonyl and methyl groups. However, this was modeled successfully using four alternative sites with different occupancy factors for the bromide and carbonyl groups (two with 68% carbonyl and 32% bromide occupancy and two with 82% carbonyl and 18% bromide occupancy). The occupancy factor of the two methyl sites refined to values close to 50% that were kept fixed in the final run.

All non-H atoms were refined anisotropically except the carbonyl C and O atoms, for which fixed isotropic temperature factors were fixed. The Re–C and C–O distances were also restrained (DFIX [39]) to about their usual values (2.0 and 1.1 Å, respectively).

3.5.3. mer,trans-[ReBr(CO)$_3${PPh(OEt)$_2$}$_2$] (2d)

The structure of **2d** was orientationally disordered owing to the rhenium atom lying at a center of symmetry (position c in Wyckoff notation). All non-H atoms were refined anisotropically except those of the disordered carbonyl group, which were refined isotropically and had their Re–C(3) and C(3)–O(3) restrained to values close to 2.0 and 1.1 Å, respectively.

3.5.4. mer,trans-[Re(H$_2$O)(CO)$_3${PPh$_2$(OMe)}$_2$][BF$_4$] (3a)

Data collection at 213 K allowed the location of hydrogen atoms from Fourier maps. All non-H atoms were refined anisotropically, and hydrogen atoms isotropically.

3.5.5. mer,trans-[Re(H$_2$O)(CO)$_3${PPh$_2$(OEt)}$_2$][BF$_4$] (3b)

All non-H atoms except C(1) and C(2) were refined anisotropically. H atoms were calculated and refined as riders except those belonging to the water ligand, which were located and included in fixed positions with a common refined B_{iso}.

3.5.6. mer,trans-[Re(H$_2$O)(CO)$_3${PPh$_2$(OMe)}$_2$][BF$_4$] (3c)

All non-H atoms were refined anisotropically. H atoms were calculated and refined as riders except those belonging to the water ligand, which were not included.

Table 5
Crystal and structure refinement data

	1b	**2c**	**2d**	**3a**	**3b**	**3c**	**4c**
Empirical formula	$C_{31}H_{30}BrO_5P_2Re$	$C_{19}H_{22}BrO_7P_2Re$	$C_{23}H_{30}BrO_7P_2Re$	$C_{29}H_{28}BF_4O_6P_2Re$	$C_{31}H_{32}BF_4O_6P_2Re$	$C_{19}H_{24}BF_4O_8P_2Re$	$C_{19}H_{22}BF_4O_7P_2Re$
Formula weight	810.60	690.42	746.52	807.46	835.52	715.33	697.32
Temperature (K)	298	298	298	213	213	293	293
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	13.413(3)	7.483(1)	10.1110(4)	23.912(3)	10.5016(5)	9.6620(15)	9.5138(10)
b (Å)	15.229(3)	25.253(4)	12.4636(5)	11.6636(5)	12.3560(8)	12.0801(19)	14.5048(12)
c (Å)	15.687(3)	13.007(3)	11.0619(5)	22.744(3)	13.9908(7)	22.719(4)	19.4552(12)
α (°)	90	90	90	90	94.590(7)	90	90
β (°)	99.192(18)	102.71(1)	96.1912(1)	104.75(5)	90.629(6)	93.479(4)	94.406(2)
γ (°)	90	90	90	90	110.284(5)	90	90
V (Å^3)	3163.2(11)	2397.6(8)	1385.88(10)	6134.4(11)	1695.91(16)	2646.8(7)	2676.8(4)
Z	4	4	2	8	2	4	4
Absorption coefficient (mm^{-1})	5.243	6.904	5.979	9.317	8.447	4.780	4.721
Reflections collected	3357	6183	8947	11120	6462	14540	6634
Independent reflections	3217 [$R_{int} = 0.0184$]	5761 [$R_{int} = 0.0719$]	3390 [$R_{int} = 0.0431$]	5170 [$R_{int} = 0.0437$]	5732 [$R_{int} = 0.0465$]	5987 [$R_{int} = 0.1165$]	6449 [$R_{int} = 0.0487$]
R indices (all data)	$R_1 = 0.0496$, $wR_2 = 0.0729$	$R_1 = 0.2093$, $wR_2 = 0.1731$	$R_1 = 0.0404$, $wR_2 = 0.0702$	$R_1 = 0.0342$, $wR_2 = 0.0763$	$R_1 = 0.0553$, $wR_2 = 0.1350$	$R_1 = 0.1997$, $wR_2 = 0.1150$	$R_1 = 0.2000$, $wR_2 = 0.1964$
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0295$, $wR_2 = 0.0680$	$R_1 = 0.0548$, $wR_2 = 0.1216$	$R_1 = 0.0273$, $wR_2 = 0.0642$	$R_1 = 0.0290$, $wR_2 = 0.0723$	$R_1 = 0.0451$, $wR_2 = 0.1263$	$R_1 = 0.0642$, $wR_2 = 0.0898$	$R_1 = 0.0508$, $wR_2 = 0.14934$

3.5.7. *mer,trans-[Re(η^1-BF_4)$(CO)_3$$\{PPh(OMe)_2\}_2$]* (**4c**)

Pale-pink crystals of this compound were isolated after evaporation of solvents from a $CHCl_3$–Et_2O solution of compound **3c**. All non-H atoms were refined anisotropically. H atoms were calculated and refined as riders.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 152292–152298. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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