Synthetic, Spectroscopic and Structural Studies of the Rhenium(I) Dicarbonyl Complexes of Phosphite, Phosphonite, and Phosphinite Ligands: *cis,mer*-$[ReBr(CO)_2\{PPh_{3-n}(OR)_n\}_3]$ (R = Me, Et; n = 1−3)

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Dedicated to Professor Alfonso Castiñeiras on the Ocassion of his 60th Birthday

Abstract. The reaction of $[ReBr(CO)_5]$ with phosphite and phosphonite ligands in toluene yielded *cis,mer*-$[ReBr(CO)_2L_3]$ (**2**: L = $P(OMe)_3$ **2a**: $P(OEt)_3$ **2b**: $PPh(OMe)_2$ **2c**: $PPh(OEt)_2$ **2d**). Compounds **2c** and **2d** were also obtained, as were the phosphinite complexes **2e** [L = $PPh_2(OMe)$] and **2f** [L = $PPh_2(OEt)$], by reaction of the corresponding phosphorus ligand with *trans,mer*-$[ReBr(CO)_3L_2]$. Compounds **2** were all characterized by elemental analysis, mass spectrometry and NMR spectroscopy, and the structures of **2b**, **2c** and **2d** were determined by X-ray diffractometry. Compounds **2a-d** are stable in chloroform and dichloromethane, but **2e** and **2f** are transformed into the corresponding *trans,mer*-$[ReBr(CO)_3L_2]$ complexes by a reaction for which a partial mechanism is put forward.

Keywords: Phosphorus ligands; Dicarbonyl complexes; Rhenium(I) complexes; X-ray diffraction

Synthetische, spektroskopische und strukturelle Untersuchungen der Rhenium(I)-dicarbonyl-Komplexe mit Phosphit-, Phosphonit- und Phosphinit-Liganden: *cis,mer*-$[ReBr(CO)_2\{PPh_{3-n}(OR)_n\}_3]$ (R = Me, Et, n = 1−3)

Inhaltsübersicht. Die Reaktion von $[ReBr(CO)_5]$ mit Phosphit- und Phosphonit-Liganden in Toluol führt zu *cis,mer*-$[ReBr(CO)_2L_3]$ (**2**: L = $P(OMe)_3$ **2a**, $P(OEt)_3$ **2b**, $PPh(OMe)_2$ **2c**, $PPh(OEt)_2$ **2d**). Die Verbindungen **2c** und **2d** werden auch durch Umsetzung der Phosphinit-Komplexe **2e** [L = $PPh_2(OMe)$] und **2f** [L = $PPh_2(OEt)$] mit den entsprechenden Phosphorliganden und *trans,mer*-$[ReBr(CO)_3L_2]$ erhalten. Alle Verbindungen **2** werden durch Elementaranalysen, Massenspektrometrie und NMR-Spektroskopie charakterisiert; die Strukturen von **2b**, **2c** und **2d** werden durch Röntgenstrukturanalysen ermittelt. Die Verbindungen **2a−d** sind in Chloroform und Dichlormethan stabil, doch werden **2e** und **2f** in die entsprechenden **trans,mer**-$[ReBr(CO)_3L_2]$-Komplexe umgewandelt. Hierfür wird ein partieller Mechanismus vorgeschlagen.

1 Introduction

The design of 16-electron carbonyl complexes is often based on the inclusion of easily abstracted groups such as methyl or hydride in the coordination sphere of the metal the highly electrophilic, electronically and coordinationally unsaturated cation resulting from abstraction of these groups being very effective in the activation of small molecules [1]:

$$[MCH_3(L)_5] + Ph_3C^+ \rightarrow [M(L)_5]^+ + Ph_3CCH_3 \qquad (1)$$

where M is a Group 7 metal and L is a 2-electron donor ligand. However, interesting reactive fragments can also be obtained by encouraging dissociation by the use of bulky ligands such as $P(OR)_3$ (R = ortho-tolyl), the ligand in the complex employed in Du Pont hydrocyanation, $[Ni\{P(OR)_3\}_4]$ [2]:

$$[MX(L)_5] \rightarrow [MX(L)_4] + L \qquad (2)$$

where X is a 1-electron donor ligand. In eqs. (1) and (2), $[ML_5]^+$ and $[MXL_4]$ have the same formal electron deficiency, but their interactions with nucleophiles are likely to exhibit significant differences.

Steric effects also play important or dominant roles in the substitution of $[ReBr(CO)_5]$ by $PPh_{3-n}(OR)_n$ ligands [3] and in the carbonylation of the resulting trisubstituted complexes $[ReBr(CO)_2\{PPh_{3-n}(OR)_n\}_3]$. Envisaging that these trisubstituted complexes may therefore prove useful as 16-electron intermediate sources, we have synthesized and spectroscopically characterized the six compounds *cis,mer*-$[ReBr(CO)_2\{PPh_{3-n}(OR)_n\}_3]$ [R = Me (**2a**, **2c**, **2e**) or Et (**2b**, **2d**, **2f**); n = 1 (**2e**, **2f**), 2 (**2c**, **2d**) or 3 (**2a**, **2b**)]; this is the first synthesis of **2e**, and the first time that **2a** and **2b** have

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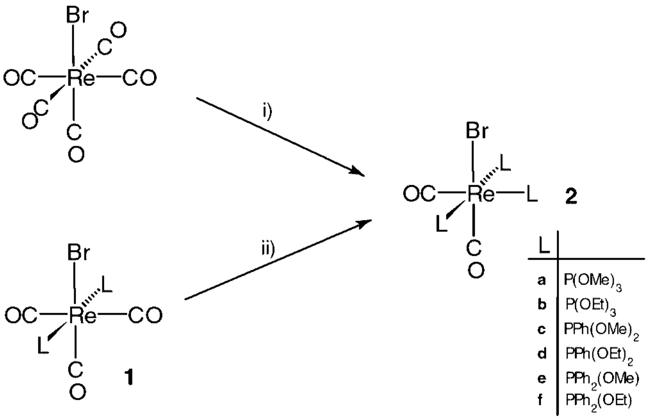
been obtained as solids. We also studied compounds **2b-d** by X-ray diffractometry, and propose a partial mechanism for the observed transformation of **2e** and **2f** into the corresponding *mer,trans*-[ReBr(CO)$_3$L$_2$] complexes in chloroform or dichloromethane (in both of which **2a-d** are stable).

2 Results and Discussion

2.1 Synthesis and spectral data

Attempts were made to synthesize all the compounds *cis,mer*-[ReBr(CO)$_2$L$_3$] (**2a-f**: L= PPh$_{3-n}$(OR)$_n$; R = Me, Et; n = 1-3) by two different routes (Scheme 1): i) by reaction of [ReBr(CO)$_5$] with an excess of the appropriate phosphorus ligand, and ii) by reaction of the ligand with previously prepared *mer,trans*-[ReBr(CO)$_3$L$_2$] (**1a-f**).



Scheme 1

The phosphite complexes (**2a** and **2b**) were only isolated as pure solids using path i, and the phosphinite complexes (**2e** and **2f**) by path ii, but the phosphonite complexes (**2c** and **2d**) were obtained by both routes. Note that **2a** and **2b**, which were obtained by *Reimann* and *Singleton* [3] only as oils, were in our study transformed into air-stable solids when the oils were subjected to long periods under vacuum. All of compounds **2** except **2e** and **2f** (*vide infra*) were apparently stable for weeks in chloroform and in dichloromethane.

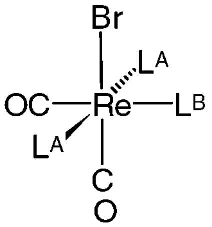
The mass spectra of compounds **2** all show a peak corresponding to the molecular ion, albeit with differing intensities, but the base peak for all except **2c** is the species resulting from loss of one L and one CO. In keeping with the tendency of **2e** and **2f** to lose a ligand in solution (*vide infra*), the spectra of these two complexes each show a moderately intense peak for |M−L| that is missing or weak in those of the other compounds.

The presence of two mutually *cis* carbonyl ligands is indicated by the IR spectra of all of compounds **2** showing two strong bands centred near 1970 and 1870 cm^{-1}, close to where they are observed in other [ReBr(CO)$_2$L$_3$] complexes [4,5] (Table 1). The appearance of these bands at lower energies in the spectra of the phosphinite complexes than in those of the corresponding phosphite and phosphonite complexes is expected because of the greater donor capacity of phosphinite ligands.

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

	ν(CO)	^{1}H NMR	Assignment	^{31}P NMR	J(^{31}P-^{31}P)
2a	1975s	3.6m(27H)	CH$_3$(L^A,L^B)	118.5m	
	1873s				
2b	1976s	4.06m(18H)	CH$_2$(L^A,L^B)	114.3m	
	1882s	1.24m(27H)	CH$_3$(L^A,L^B)		
2c	1996s	3.4d(16H)	CH$_3$(L^A)	134.2d(L^A)	
	1886s	3.6q(6H)	CH$_3$(L^B)	135.3t(L^B)	33
2d	1980s	1.3m(12H)	CH$_3$	127.6d(L^A)	
	1870s	3.7m(24H)	CH$_2$	130.0t(L^B)	35
		3.8m			
		4.0m			
		4.2m			
2e	1948s	2.9d(3H)	CH$_3$(L^B)	101.0d(L^A)	
	1863s	3.2t(6H)	CH$_3$(L^A)	105.3t(L^B)	35
2f	1949s	0.99t(3H)	CH$_3$(L^B)	97.0d(L^A)	
	1866s	1.17t(6H)	CH$_3$(L^A)	103.6t(L^B)	32
		3.12m(2H)	CH$_2$(L^B)		
		3,37m,3.47m(4H)	CH$_2$(L^A)		

[a)] ν in cm^{-1}, s = strong. [b)] NMR spectra run in CDCl$_3$, δ in ppm, J in Hz, d = doublet, m = multiplet, q = quartet, t = triplet.



The *mer* configuration of the three phosphorus ligands is indicated in the ^{31}P NMR spectra of **2c-f** by the presence of two sets of signals (Table 1): a doublet (L^B) and, at slightly lower field, a triplet (L^A). The ^{31}P-^{31}P coupling constants of these compounds are similar to those of the hydride complexes [ReH(CO)$_2${PPh$_{3-n}$(OEt)$_n$}$_3$] (n = 1-3) [6], even though the ^{31}P signals of the bromide complexes all lie about 15 ppm upfield from those of the hydrides.

2.2 Structures of 2b, 2c and 2d

Figures 1−3 show PLATON [7] plots of asymmetric units of **2b**, **2c** and **2d**, together with the numbering schemes used. Selected bond lengths and angles are listed in Table 2. The crystals of all three compounds consist of isolated [ReBr(CO)$_2$L$_3$] molecules with slightly distorted *cis,mer* octahedral configurations and no unusually short interatomic distances. Compounds **2c** and **2d** are more distorted than **2b**, but in all three the main distortions concern the angle C2-Re-P3 and the P-Re-P angles.

In all three molecules, Re-C1 is shorter than Re-C2. This suggests that there is considerable back-donation from the metal atom to the C1 carbonyl group owing to the σ-donor

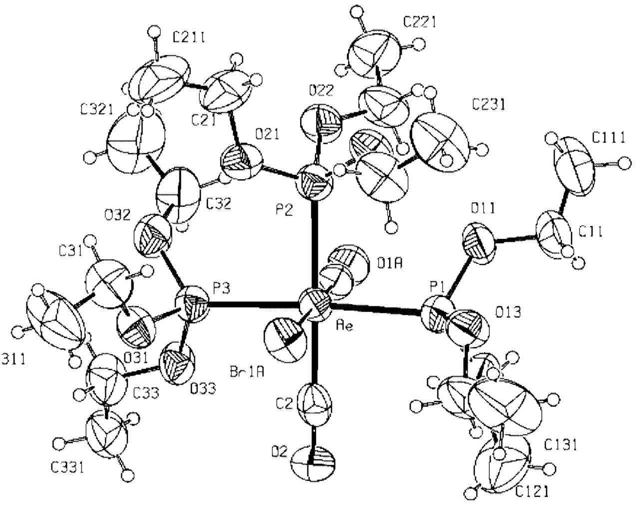


Fig. 1 Molecular structure of compound **2b**, showing the numbering scheme (for clarity, just one position of the disordered groups is shown).

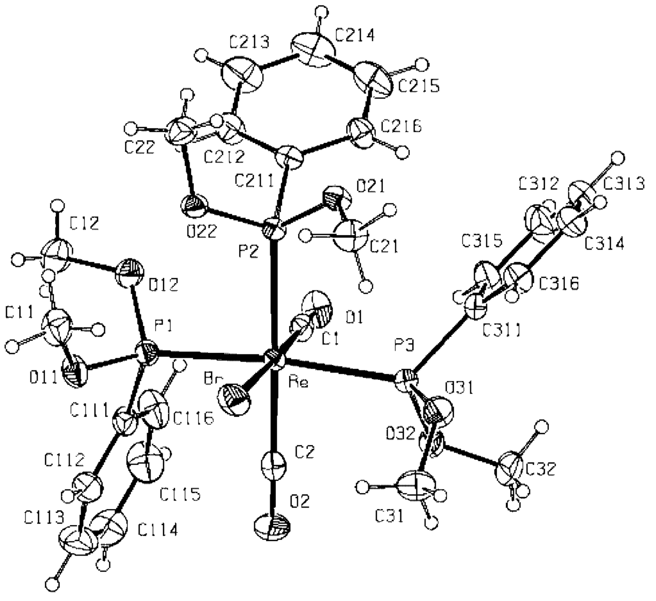


Fig. 2 Molecular structure of compound **2c**, showing the numbering scheme.

character of the *trans* bromine ligand, although there is surprisingly no concomitant lengthening of C1-O1.

Another feature common to the three molecules is that the distance Re-P2 is 0.03-0.06 Å longer than Re-P1 and Re-P3. These latter are both close to the Re-P distances in the *mer,trans* complexes **1c** and **1d** [8], while Re-P2 is similar to the corresponding distances in **1e** [2.415(2) Å] [9], in *cis,mer*-[ReBr(CO)$_2$(L-L)L'] (L-L = 1,2-bis(diphenylphosphonite)ethane, L' = P(OMe)$_3$, P(OEt)$_3$ or PPh(OEt)$_2$; 2.4390(9)-2.4631(11)Å) [4], in *fac*-[ReBr(CO)$_3$-{PPh$_2$(OEt)}$_2$] (2.4557(13) Å) [8] and in phosphine derivatives such as *cis,mer*-[Re(η^1-pentadienyl)(CO)$_2$(PMe$_3$)$_3$] (2.470(4) Å) [10] and [ReCl(CO)$_2$(L-L-L)] (L-L-L = η^3-Ph$_2$P(CH$_2$)$_2$P(Ph)(CH$_2$)$_2$PPh$_2$; 2.412(1)-2.420(3) Å) [5]. The lengthening of Re-P2 relative to Re-P1 and Re-P3 is usually attributed to the influence of the *trans* carbonyl group, but steric hindrance of the P2 position by the P1 and P3 ligands probably also contributes [5].

All three Re-P distances in **2b** are shorter than their counterparts in **2c** and **2d**, and Re-P2 is shorter in **2c** than in **2d**. Both these differences are again likely to be due to the greater steric demands of the more distant ligand.

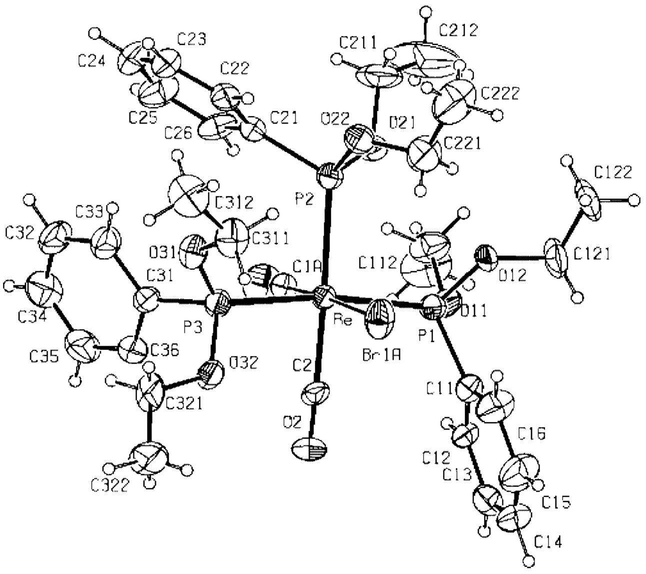


Fig. 3 Molecular structure of compound **2d**, showing the numbering scheme (for clarity, just one position of the disordered groups is shown).

Table 2 Main bond lengths/Å and angles/° in compounds **2b**, **2c** and **2d**.

	2b	**2c**	**2d**
Re−C(1)	1.851(9)/1.866(16)	1.917(6)	1.899(2)/1.899(2)
Re−C(2)	1.945(9)	1.969(6)	1.958(11)
Re−P(1)	2.3742(19)	2.3861(13)	2.384(3)
Re−P(2)	2.4188(19)	2.4266(13)	2.438(3)
Re−P(3)	2.3897(19)	2.3985(13)	2.382(3)
Re−Br	2.703(6)/2.734(8)	2.6712(6)	2.663(3)/2.669(4)
C(1)−O(1)	1.16(2)/1.19(4)	1.098(6)	1.100(2)/1.100(2)
C(2)−O(2)	1.150(8)	1.135(7)	1.137(10)
C(1)−Re−C(2)	91.0(4)/88.3(8)	91.9(3)	88.1(8)/90.1(10)
C(1)−Re−P(1)	88.5(3)/93.4(9)	86.55(15)	92.6(6)/87.0(8)
C(1)−Re−P(2)	92.5(3)/88.2(8)	89.42(16)	88.2(7)/93.6(9)
C(1)−Re−P(3)	89.7(3)/88.3(9)	87.08(15)	91.3(6)/88.8(8)
C(2)−Re−P(1)	88.5(2)	87.39(17)	87.0(3)
C(2)−Re−P(2)	176.5(2)	178.53(19)	176.3(4)
C(2)−Re−P(3)	87.1(2)	84.28(17)	85.6(3)
C(1)−Re−Br	178.8(3)/176.9(9)	178.25(16)	177.0(7)/179.3(9)
C(2)−Re−Br	88.0(2)/91.5(3)	89.38(19)	88.8(4)/89.4(4)
Br−Re−P(1)	91.93(7)/89.7(2)	92.36(4)	87.36(11)/92.47(13)
Br−Re−P(2)	88.53(7)/88.6(2)	89.25(3)	94.84(17)/86.94(13)
Br−Re−P(3)	89.74(7)/92.0(2)	94.20(4)	88.36(11)/91.58(13)
P(1)−Re−P(2)	91.84(7)	92.13(5)	93.88(9)
P(2)−Re−P(3)	92.69(7)	96.35(4)	93.79(10)
P(1)−Re−P(3)	175.21(7)	169.33(5)	171.50(10)

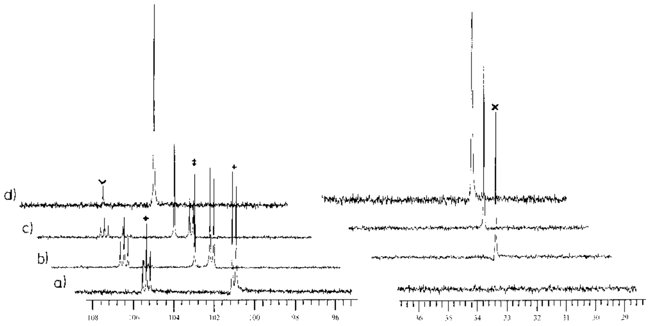


Fig. 4 ^{31}P NMR spectra of a solution of **2e** in $CDCl_3$ when freshly prepared (a) and after 24 h (b), 48 h (c) and 144 h (d). Origin of signals: +, **2e**; ‡, **1e**; X, O=PPh_2(OMe); ∨, unknown.

2.3 *Behaviour in chloroform and dichloromethane*

At room temperature, **2a-d** can be stored for weeks in chloroform or dichloromethane without apparent decomposition, but **2e** and **2f** slowly decompose under these conditions. After 24 h in $CDCl_3$ the ^{31}P NMR signals of **2e** have weakened and signals at 101.8 and 32.9 ppm due respectively to **1e** [8] and phosphinic acid methyl ester [11] have appeared; and after 1 week the signals of **2e** have completely vanished (Fig. 4), leaving solutions that yield a solid with an IR spectrum confirming the presence of **1e** and P(O)Ph_2(OMe). Compound **2f** behaves similarly.

Similar reactions have been reported previously. *Carriedo* and *Riera* [12] observed the formation of [Mn(diphos)-$(CO)_4$][ClO_4] (diphos = dpm, dpe, dpp or dbp) when solutions containing *fac*-[MnBr$(CO)_3$(diphos)] and $AgClO_4$ were stirred; in this case the presence of Ag^+ seems necessary because pure *fac*-[MnBr$(CO)_3$(diphos)] does not decompose. Also, *Darensbourg* et al. [13, 14] have reported that certain pentacarbonyl amine complexes of Group 6 metals decompose to the corresponding hexacarbonyl compounds in both hexane and carbon disulphide; in this case the authors put forward a dissociative mechanism in which the rate-limiting step is the cleavage of the metal-nitrogen bond, which is followed by the released amine's displacing CO from a second molecule of the pentacarbonyl amine complex and by coordination of this CO to the de-aminated molecule. Weighing against this mechanistic hypothesis is the fact that the complex [M$(CO)_4$$(amine)_2$] was neither isolated nor characterized, but assuming that pK_a is correlated with the coordinating strength of the ligand it does explain why the rate constant of these reactions decreases as the basicity of the amine rises.

$$\textit{cis,mer}\text{-}[\mathrm{ReBr(CO)_2(L)_3}] \rightarrow [\mathrm{ReBr(CO)_2(L)_2}] + \mathrm{L} \qquad (3)$$

$$[\mathrm{ReBr(CO)_2(L)_2}] \xrightarrow{[\mathrm{CO}]} \textit{mer,trans}\text{-}[\mathrm{ReBr(CO)_3(L)_2}] \qquad (4)$$

$$\mathrm{L} \xrightarrow{[\mathrm{O_2}]} \mathrm{O{=}L} \qquad (5)$$

Scheme 2

We hypothesize that the spontaneous transformation of **2e** and **2f** into **1e** and **1f** starts in the same way as the mechanism postulated by *Darensbourg* et al., by release of a molecule of the non-carbonyl ligand (Scheme 2, eq. (3)); this is supported by the fact that, as in the reaction studied by *Darensbourg* et al., the transformation of the substrate is halted by addition of free ligand. The resulting 16-electron product, [ReBr$(CO)_2$$L_2$], is expected to be highly reactive and readily carbonylated to **1e** or **1f** (Scheme 2, eq. (4)), but the source of the carbonyl required for this step remains uncertain. It seems unlikely to be an unaltered substrate molecule, because this ought to lead to the formation of [ReBr(CO)L_4] in amounts similar to the yields of **1e** or **1f**, and this is not observed in the ^{31}P NMR spectra of the reaction mixture (instead, the ligand released in the first step, eq. (3), is oxidized to the corresponding phosphinic acid ester; Scheme 2, eq. (5)). Our research plans in this area accordingly include not only investigation of possible applications of this reaction, but also experiments to identify the CO source that it involves.

3 Experimental

3.1 *Materials and instrumentation*

All operations were carried out under an atmosphere of dry argon. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled in an Ar atmosphere [15].

[ReBr$(CO)_5$] was synthesized by the published method [16]. Phosphorus ligands were used as supplied by Aldrich without any further purification. Complexes **1** (*mer,trans*-[ReBr$(CO)_3$$L_2$]) were obtained as previously described [8]. 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 FAB conditions (nitrobenzyl alcohol matrix). Infrared spectra were recorded on a Bruker Vector 22FT spectrophotometer. NMR spectra were obtained on a Bruker AMX 400 spectrometer; ^{1}H chemical shifts are referred to internal tetramethylsilane (TMS) and ^{31}P{^{1}H} chemical shifts to H_3PO_4.

3.2 *Synthesis of cis,mer-[ReBr(CO)$_2$L$_3$] [L = phosphite (P(OR)$_3$; **2a** and **2b**) or phosphonite (PPh(OR)$_2$; **2c** and **2d**)] from [ReBr(CO)$_5$].*

An excess of the appropriate phosphorus ligand (**2a** 0.17 mL, 1.44 mmol; **2b** 0.34 mL, 1.97 mmol; **2c** 0.47 mL, 2.95 mmol; **2d** 0.57 mL, 2.95 mmol) was added to a suspension of [ReBr$(CO)_5$] (**2a,b** 200 mg, 0.49 mmol; **2c,d** 300 mg, 0.74 mmol) in toluene (30 mL) and the mixture was refluxed for 4 h and gently stirred for another 18 h at room temperature. The solvent was then removed under vacuum and the resulting oil was stirred with MeOH or EtOH (4 mL). The white precipitate thereupon formed was filtered off, washed with MeOH or EtOH and vacuum dried. Yields: **2a**, 160 mg (47%); **2b**, 185 mg (46%); **2c**, 431 mg (70%); **2d**, 543 mg (80%).

Analytical and spectral data. Data for **2a**. M.p.: 198 °C. Anal. found: C, 19.6; H, 4.2%. $C_{11}H_{27}O_{11}P_3BrRe$ requires: C, 19.0; H, 3.9%.

Mass spectrum (FAB): |M| 693(15), |M−CO| 666(70), |M−(CO,OR)| 635(18), |M−Br| 615(21), |M−(CO,L)| 542(100), |M−(CO,OR,L)| 511(54).

Data for **2b**. M.p.: 57 °C. Anal. found: C, 29.7; H, 5.8%. $C_{20}H_{45}O_{11}P_3BrRe$ requires: C, 29.3; H, 5.5%.

Mass spectrum (FAB): |M| 820(62), |M−CO| 792(75), |M−(CO,OR)| 747(44), |M−Br| 741(52), |M−L| 654(7), |M−(CO,L)| 626(100), |M−(CO,OR,L)| 581(71).

Data for **2c**. M.p.: 125 °C (lit. 123 °C [3]). Anal. found: C, 38.1; H, 4.0%. $C_{26}H_{33}O_8P_3BrRe$ requires: C, 37.5; H, 4.0%.

Mass spectrum (FAB): |M| 832(46), |M−CO| 804(100), |M−(CO,OR)| 773(39), |M−Br| 753(52), |M−(CO,Br)| 725(15), |M−(CO,L)| 634(96), |M−(CO,OR,L)| 603(96).

Data for **2d**. M.p.: 133 °C (lit. 129 °C [3]). Anal. found: C, 42.3; H, 4.9%. $C_{32}H_{45}O_8P_3BrRe$ requires: C, 41.4; H, 5.0%.

Mass spectrum (FAB): |M| 916(46), |M−CO| 888(90), |M−(CO,OR)| 843(45), |M−Br| 837(39), |M−L| 718(7), |M−(CO,L)| 690(100), |M−(CO,OR,L)| 843(45).

3.3 Synthesis of the phosphonite complexes ***2c*** *and* ***2d*** *from mer,trans-[ReBr(CO)$_3$L$_2$]*

To a suspension of *mer,trans*-[ReBr(CO)$_3$L$_2$] (**2c** 100 mg, 0.14 mmol; **2d** 100 mg, 0.13 mmol) in toluene (20 mL) was added an excess of the phosphorus ligand (**2c** 0.1 mL, 0.63 mmol; **2d** 0.1 mL, 0.54 mmol) and the mixture was refluxed for 4 h. The solvent was then removed under vacuum and the resulting oil was stirred with MeOH or EtOH (4 mL). The white precipitate formed was filtered off, washed with MeOH or EtOH and vacuum dried. Yields: **2c**, 28 mg (24%); **2d**, 68 mg (57%).

3.4 Synthesis of the phosphinite complexes cis,mer-[ReBr(CO)$_2$L$_3$] [L = PPh$_2$(OR); ***2e*** *and* ***2f****].*

To a suspension of **1** (200 mg; **1e** 0.26 mmol, **1f** 0.25 mmol) in toluene (20 mL) was added an excess of the corresponding phosphinite ligand (**2e** 0.2 mL, 0.99 mmol; **2f** 0.4 mL, 1.85 mmol) and refluxing of the mixture was begun. Without halting refluxing, further amounts of ligand (**2e** 0.15 mL, 0.75 mmol; **2f** 0.3 mL, 1.35 mmol) were added 7 and 14 h later. Nine hours after the last addition (23 h fater the start of refluxing), the solvent was removed under vacuum and the resulting oil was stirred with MeOH (**2e**) or EtOH (**2f**). The white solid formed thereby was filtered off, washed with MeOH or EtOH, and vacuum dried.

Data for **2e**. M.p.: 155−8 °C (dec.). Yield: 189 mg (75%). Anal. found: C, 50.8; H, 4.7%. $C_{41}H_{39}O_5P_3BrRe$ requires: C, 50.7; H, 4.5%.

Mass spectrum (FAB): |M| 970(51), |M−CO| 942(15), |M−(CO,OR)| 911(19), |M−Br| 891(29), |M−L| 754(36), |M−(L,CO)| 726(100), |M−(L,CO,OR)| 695(25).

Data for **2f**. M.p.: 150 °C (dec., lit. 142−5 °C [3]). Yield: 190 mg (75%). Anal. found: C, 50.6; H, 5.0%. $C_{44}H_{45}O_5P_3BrRe$ requires: C, 52.2; H, 4.5%.

Mass spectrum (FAB): |M| 1012(25), |M−(CO,OR)| 939(14), |M−Br| 933(17), |M−L| 782(43), |M−(L,CO)| 754(100), |M−(L,CO,OR)| 709(22).

3.5 X-ray data collection, structure solution and refinement

Crystallographic measurements of compounds **2b**, **c** and **d** were performed on a Bruker CCD (**2b**, **c**) or Enraf-Nonius CAD4 (**2d**) diffractometers. Crystal data and experimental conditions are listed in Table 3. Data were corrected for polarization and Lorentz effects. Ψ-scan or multi-scan (SADABS) absorption corrections were also applied [17].

Table 3 Crystal and structure refinement data.

	2b	**2c**	**2d**
Chemical formula	$C_{20}H_{45}O_{11}P_3BrRe$	$C_{26}H_{33}O_8P_3BrRe$	$C_{32}H_{45}O_8P_3BrRe$
Formula weight	820.58	832.54	916.70
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$ (No. 14)	C2/c (No. 15)	Pbca (No. 61)
a/Å	11.6710(19)	35.500(7)	17.626(2)
b/Å	16.2028(13)	9.8693(12)	18.649(2)
c/Å	18.2417(14)	20.826(4)	23.253(2)
β/°	99.318(2)	120.110(14)	−
V/Å^3	3404.0(5)	6306(2)	7643.3(12)
Z	4	8	8
D_X/Mg m^{-3}	1601	1741	1593
Temperature/K	293	293	293
μ/mm^{-1}	4929	5316	4395
Reflections measured	17694	6494	6450
Independent reflections (R_{int})	7373(0.0743)	6387(0.0379)	6450(0)
R1/wR2 (I>2σ(I))	0.0377/0.0662	0.0364/0.0720	0.0470/0.0662

The structures of the compounds were analysed out by the heavy atom method [18] followed by Fourier techniques until all non-hydrogen atoms were located. The mutually *trans* bromide and carbonyl groups of **2b** and **2d** are orientationally disordered but this was modelled successfully using occupancy factors of 75 and 25% for **2b** and 54 and 46% for **2d** in the two alternative sites. The positions of H atoms were calculated geometrically and refined with the atoms as riders.

Scattering factors and anomalous dispersion terms were taken from Ref. [18]. Most calculations were performed with the programs SHELX97 [19] and PLATON [7].

Crystallographic data for the structures reported in this paper (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications CCDC-194218 (**2b**), CCDC-194219 (**2c**) and CCDC-194220 (**2d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. Code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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