# PHOSPHINE CONTAINING RHENIUM(III) CARBONYL COMPLEXES. THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIBROMODICARBONYLBIS(DIMETHYL-PHENYLPHOSPHINE)RHENIUM(III)

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Abstract—Bromine oxidation of  $[ReBr(CO)_3(PR_3)_2]$   $[PR_3 = PMe_2Ph, PEt_2Ph, PMePh_2, PPh_3, PPh_2C_6H_4Me-4 or P(C_6H_4OMe-4)_3]$  yields stable seven-coordinate rhenium(III) complexes  $[ReBr_3(CO)_2(PR_3)_2]$  only for the less sterically demanding phosphines PMe\_2Ph, PEt\_2Ph and PMePh\_2. Crystals of  $[ReBr_3(CO)_2(PMe_2Ph)_2]$  (1) are triclinic, space group PI, Z = 2, in a unit cell with lattice parameters a = 9.575(8), b = 14.705(11), c = 9.629(12) Å,  $\alpha = 77.71(7)$ ,  $\beta = 109.06(8)$  and  $\gamma = 115.02(8)^{\circ}$ . 2991 independent reflections above background were collected on a diffractometer and refined to R0.07. The metal atom has a capped octahedral environment with a carbonyl in the unique capping position [1.87(3) Å], two phosphines [2.456(13), 2.496(11) Å] and one carbonyl 1.85(5) Å in the capped face, and three bromine atoms in the uncapped face [2.589(5), 2.623(6), 2.622(5) Å]. Attempts to convert (1) to the six-coordinate  $d^4$  cation  $[ReBr_2(CO)_2(PMe_2Ph)_2]^+$  for structural comparison with the isoelectronic Group 6 analogues  $[MBr_2(CO)_2(PR_3)_2]$  (M = Mo or W) were unsuccessful.

Recent calculations by Kubáček and Hoffmann<sup>1</sup> have accounted for the deformations from octahedral geometry observed in several diamagnetic  $d^4$  complexes of molybdenum- and tungsten(II) of the type M(CO)<sub>2</sub>L<sub>2</sub>'L<sub>2</sub>". Such molecules containing *cis*-carbonyl ligands should be stabilised by either a substantial increase or decrease in the M(CO)<sub>2</sub> bond angle from the regular octahedral value of 90°, with the particular form of the distortion dependent upon the  $\sigma$ - and  $\pi$ - donor properties of the ligands L' and L".

Diamagnetic six-coordinate  $d^4$  complexes are comparatively rare, but one such group of compounds has been prepared by the following route, with the final decarbonylation reaction critically dependent upon the halogen and phosphine ligands.<sup>2,3</sup>

$$M(CO)_{6} \xrightarrow{X_{2}} M(CO)_{4}X_{2} \xrightarrow{PR_{3}} M(CO)_{3}(PR_{3})_{2}X_{2}$$
$$CO \ |\downarrow -CO$$
$$M(CO)_{2}(PR_{3})_{2}X_{2}$$

$$(X = Cl \text{ or } Br, M = Mo \text{ or } W).$$

Both  $[MoBr_2(CO)_2(PPh_3)_2]$  and  $[WBr_2(CO)_2(PPh_3)_2]$  have been prepared by this procedure, and their structures determined.<sup>4,5</sup> Their degree of distortion was found to exceed that predicted by extended Hückel calculations on model compounds,<sup>1</sup> and in an attempt further to define factors which affect the deformations in this class of

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molecule, we wished to synthesise  $d^4$  analogues containing other metals in combination with the same basic ligand set. One possible route to the isoelectronic rhenium, cation  $[\text{ReBr}_2(\text{CO})_2(\text{PR}_3)_2]^+$ is outlined below.

$$Re(CO)_{5}X \xrightarrow{2PR_{3}} Re(CO)_{3}(PR_{3})_{2}X$$
$$\xrightarrow{X_{2}} Re(CO)_{2} (PR_{3})_{2}X_{3}$$
$$\downarrow - X^{-}$$
$$[Re(CO)_{2}(PR_{3})_{2}X_{2}]^{+}.$$

To date only one seven-coordinate rhenium(III)dicarbonyl complex containing monodentate phosphine ligands has been reported, namely [ReCl<sub>3</sub>(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] prepared by chlorine oxidation of chloro(tricarbonyl)bis(dimethylphenylphosphine)rhenium(I).<sup>6</sup> We have therefore sought to extend this reaction in order to prepare several [ReBr<sub>3</sub>(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] derivatives which we hoped would be of use in synthesising sixcoordinate  $d^4$  cationic rhenium complexes for direct structural comparison with their isoelectronic molybdenum and tungsten analogues.<sup>4,5</sup>

#### **RESULTS AND DISCUSSION**

Treatment of fac-[ReBr(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>] (PR<sub>3</sub> = PMe<sub>2</sub>Ph, PEt<sub>2</sub>Ph or PMePh<sub>2</sub>) with bromine in carbon tetrachloride solution at room temperature affords diamagnetic seven-coordinate rhenium(III) complexes [ReBr<sub>3</sub>(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] in high yields. These complexes provide further examples of the wellknown halogen oxidation reaction in which sixcoordinate  $d^6$  carbonyls are oxidised to sevencoordinate  $d^4$  derivatives.<sup>7</sup> Although this type of reaction is a very common one for phosphine or arsine substituted Group 6 carbonyl derivatives, few reports of Group 7 examples have been published. Thus [Re(CO)<sub>2</sub>(diars)<sub>2</sub>X] [diars = o-phenylenebis(dimethylarsine); X = Br or I] can be oxidised to the ionic derivative [Re(CO)- $(diars)_2 X_2 X_3,^8$ whilst  $[ReX_3(CO)(PMe_2Ph)_3]^6$ [ReCl<sub>3</sub>(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]<sup>6</sup> and [Re(CO)<sub>2</sub>(dppm)X<sub>3</sub>]<sup>9</sup> [dppm = bis(diphenylphosphino)methane; X = Clor Br] have also been prepared by oxidation of rhenium(I) precursors.

None of the three new rhenium(III) complexes formed appreciably conducting solutions at  $10^{-3}$ molar in acetone, and consequently simple monomeric structures were expected. Variable temperature <sup>1</sup>H NMR measurements revealed that the complexes were stereochemically non-rigid in solution at ambient temperatures, and on cooling to  $-40^{\circ}$ C, the broad aliphatic proton signals split into two components of unequal intensities indicating the formation of more than one isomeric form for each of the three complexes. In order to determine the solid-state stereochemistry of a representative example of this type of complex, a single crystal X-ray diffraction study was carried out on [ReBr<sub>3</sub>(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>].

## Discussion of the structure

The molecule [ReBr<sub>3</sub>(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] is shown in Fig. 1 together with the atomic numbering scheme. The rhenium environment is a capped octahedron with a carbonyl group in the unique capping position [1.87(3) Å]; two phosphines 2.496(11) Å] and one [2.456(13), carbonvl [1.85(5) Å] in the capped face, and three bromine atoms in the uncapped face [2.589(5), 2.623(6), 2.622(5) Å]. This is the expected geometry for such a stoichiometry. It has been shown previously<sup>10</sup> that seven-coordinate molecules with three halide ligands prefer to fall into two categories. They are either pentagonal pyramidal as in  $[NbCl_3(bidentate)_2]^{11}$  in which three halogens fit into the T formation with two in axial positions and one in the equatorial plane, or alternatively capped octahedral with three halogens in the unface as in  $[WBr_3(CO)_4]^{-12}$ capped and  $[Mo(PMe_2Ph)_3X_4]$  (X = halide).<sup>13</sup> The one exception is [ReBr<sub>3</sub>(bipy)(CO)<sub>2</sub>]<sup>14</sup> where the bidentate ligand prevents either geometric form. This structure is still a capped octahedron but with one bromine in the capped face and two in the uncapped face; the bidentate ligand as is usual for this



polyhedron occupying an edge between two faces. So the geometry of (1) is as predicted and is very close to an ideal capped octahedron, with an r.m.s. deviation<sup>10</sup> of 0.042 Å (0.115 Å for a capped trigonal prism) with  $\delta$  angles (after normalisation) of 18.1, 15.1, 10.5°. A search of the Cambridge data files<sup>15</sup> shows that there are very few rhenium(III) structures that have been determined and no other halocarbonyl apart from [ReBr<sub>3</sub>(bipy)(CO)<sub>2</sub>].<sup>14</sup>

One obvious asymmetry that is introduced is in the angles in the capped face of (1). Thus the P-Re-P angle (116.1°) is greater than the P-Re-C angles (110.8, 107.3°). The positions of the carbon. atoms on the phosphorus atoms are such as to be staggered with respect to adjacent atoms. Thus P(1) has three adjacent neighbours Br(1), Br(3) and C(51) but there is no torsion angle of the type L-Re-P-C less than  $37.3^{\circ}$ . For P(2) the smallest torsion angle is  $43.2^{\circ}$ . The Re-Br distances in (1) [2.589(5), 2.623(6), 2.622(5) Å] are slightly longer uncapped face than those in the of [ReBr<sub>3</sub>(bipy)(CO)<sub>2</sub>], namely 2.576(4), 2.551(5) Å. The shorter bond Re-Br(1) [2.589(5) Å] is unique in that Br(1) is trans to carbonyl while the others are trans to phosphine. It seems unlikely that this could be an electronic effect; steric constraints with the phosphines could cause such distortions. The three Br-Re-Br angles are irregular ranging from 84.5(2) to 90.7(2)°, and the two Re-P distances are also unequal at 2.453(13) and 2.496(11) A, but there seems to be no obvious reason for the difference.

Repeated attempts to prepare other sevencoordinate complexes by bromine oxidation of fac-[ReBr(CO)<sub>3</sub>L<sub>2</sub>] [L = PPh<sub>3</sub>, P(C<sub>6</sub>H<sub>4</sub>OMe)<sub>3</sub> or  $PPh_2C_6H_4Me$ ] in CCl<sub>4</sub> were unsuccessful. The reactions were monitored by infrared spectroscopy which showed that despite varying the amount of bromine used and the temperature of the bromination reaction, no significant concentration of dicarbonyl-products was evident in the course of the reaction. Under forcing conditions, oily solids containing non-carbonyl products were formed. The room temperature bromination of fac-[ReBr(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] in CHCl<sub>3</sub> did not cause oxidation, but rather resulted in the formation of the known<sup>16</sup> mer-trans-isomer  $[v_{max}(CO) 2060w,$ 1958s, 1908s]. Such isomerisation reactions have been reported previously for several phosphine substituted rhenium carbonyl bromides.<sup>17, 18</sup> Thermal rearrangements are slow,<sup>18</sup> but in the presence of a strong oxidant, isomerisation is fast due to the intermediacy of kinetically labile 17-electron rhenium(II) species which are light sensitive and rapidly reform rhenium(I) derivatives in the presence of dichloromethane.<sup>18</sup> Bromine in chloroform appears to cause  $fac \rightarrow mer$  isomerism in an analogous manner as the reaction did not proceed cleanly in the dark. Under these conditions several carbonyl containing species as well as unchanged starting material were revealed by infrared spectroscopy, indicating decompositon of the reactive intermediate(s) in the absence of a photochemically induced reaction with the solvent.

Steric constraints caused by the phosphine ligands are apparent in (1) and molecular models of [ReBr<sub>3</sub>(CO)<sub>2</sub>L<sub>2</sub>] (L = tertiary phosphine containing one or more phenyl groups) reveal considerable steric interactions for both capped octahedral and pentagonal bipyramidal geometries. The degree of steric hindrance is clearly related to the effective size of the phosphine and increases in the order L = PMe<sub>2</sub>Ph < PMePh<sub>2</sub>  $\approx$  PEt<sub>2</sub>Ph < PPh<sub>3</sub>  $\approx$ PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me  $\approx$  P(C<sub>6</sub>H<sub>4</sub>OMe)<sub>3</sub>. It is noticeable that the only seven-coordinate tribromodicarbonyl complexes we have been able to prepare contain good  $\sigma$ -donor phosphorus ligands with relatively small cone angles (PMe<sub>2</sub>P, 122°; PMePh<sub>2</sub>, 132°; PEt<sub>2</sub>Ph, 136°).<sup>19</sup>

#### Cationic rhenium(III) species

Attempts to isolate pure six-coordinate rhenium(III) species by halide abstraction from  $[ReBr_3(CO)_2(PR_3)_2]$  were not successful. All three complexes reacted with an equimolar quantity of  $MBF_4$  (M = Ag or Tl) to produce MBr, but only (1) yielded small quantities of a new rhenium dicarbonyl species containing borofluoride. The product was very unstable even in the solid state, and could not be obtained analytically pure. Attempts to recrystallise the material were also unsuccessful and resulted in the reformation of [ReBr<sub>3</sub>(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] together with traces of [ReBr(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] and non-carbonyl products. However, in view of the relatively low carbonyl stretching modes observed for the original material it seems unlikely to contain the required cation  $[\text{ReBr}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]^+$ .

#### EXPERIMENTAL

All syntheses were carried out in an atmosphere of dry  $N_2$  gas using solvents and liquid reagents freed from moisture and oxygen by standard procedures. Infrared spectra in the region 200–4000 cm<sup>-1</sup> were recorded on a Perkin–Elmer 597 spectrophotometer. Hydrogen-1 and <sup>13</sup>C NMR spectra were recorded on JEOL PS 100 and FX 90Q instruments respectively with SiMe<sub>4</sub> as internal standard. Microanalyses are by Butterworth Laboratories Limited.

Liquid phosphines were stored in an inert atmosphere over molecular sieves. The solid phosphines were used as received. The complexes  $[ReBr(CO)_5]$ and *fac*- $[ReBr(CO)_3L_2]$  (L = PPh<sub>3</sub>, PMePh<sub>2</sub>, PMe<sub>2</sub>Ph or PEt<sub>2</sub>Ph) were prepared by literature procedures or simple extensions thereof.<sup>18, 20</sup>

Synthesis of fac-[ReBr(CO)<sub>3</sub>[P(C<sub>6</sub>H<sub>4</sub>OMe-4)<sub>3</sub>]<sub>2</sub>]. The compounds [ReBr(CO)<sub>5</sub>] (0.54 g, 1.3 mmol) and P(C<sub>6</sub>H<sub>4</sub>OMe-4)<sub>3</sub> (0.94 g, 2.7 mmol) were heated in refluxing benzene (20 cm<sup>3</sup>) for 3 hr. The solution was cooled, evaporated to 5 cm<sup>3</sup> under reduced pressure, and treated with ethanol (25 cm<sup>3</sup>) to precipitate the product. Recrystallisation was from chloroform/hexane (1:1). Yield 86%, m.p. 179–180°C. (Found: C, 49.9; H, 3.98%);  $\nu_{max}$ (CO) 2032s, 1950s, 1895s cm<sup>-1</sup> (chloroform); NMR: <sup>13</sup>C-[<sup>1</sup>H] (25°C, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  31.8 (OMe), 113.9, 125.2, 136.2 and 161.6 (aromatics), 191.6 and 206.2 ppm (CO).

Synthesis of fac-[ReBr(CO)<sub>3</sub>[PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4]<sub>2</sub>]-[ReBr(CO),] (0.35 g, 0.87 mmol) and  $PPh_2C_6H_4Me-4$  (0.48 g, 1.7 mmol) were heated in refluxing benzene (20 cm<sup>3</sup>) for 7 hr. The solution was evaporated to dryness and the residue recrystallised from dichloromethane/hexane (1:1), affording the product as white needles (78%), m.p. 180–181°C. (Found: C, 52.8; H, 3.84%  $C_{41}H_{34}O_{3}BrP_{2}Re$  requires C, 54.4; H, 3.77%);  $v_{\text{max}}$ (CO) 2038s, 1952s, 1897s cm<sup>-1</sup> (chloroform); NMR:  ${}^{13}C-{}^{[1}H]$  (25°C, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  21.3 (Me), 128.4, 129.2, 130.6, 133.7, 134.7 and 141.1 (aromatics), 192.1 and 205.8 ppm (CO).

Synthesis of [ReBr<sub>3</sub>(CO)<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>]. A solution of Br<sub>2</sub> (0.22 g, 1.4 mmol) in anhydrous CCl<sub>4</sub> (25 cm<sup>3</sup>) was stirred at room temperature with fac-[ReBr(CO)<sub>3</sub>(PMePh<sub>2</sub>)<sub>2</sub>] (1.0 g, 1.3 mmol) for 2 hr. The yellow product tribromodicarbonylbis(methyldiphenylphosphine)rhenium(III) precipitated during the course of the reaction and was finally collected, washed with CCl4 and dried Recrystallisation from in vacuo. was dichloromethane/hexane (1:1). Yield 85%, m.p. 142-143°C. (Found: C, 37.7; H, 3.00; Br, 26.4% C<sub>28</sub>H<sub>26</sub>O<sub>2</sub>Br<sub>3</sub>P<sub>2</sub>Re requires C, 38.1, H, 2.94; Br, 27.2%);  $v_{max}(CO)$  2036s, 1940s cm<sup>-1</sup> (chloroform); NMR: <sup>1</sup>H (25°C, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  2.56 [6H, br d, J(PH) 11 Hz 2 Me], 7.38 ppm (20 H, br m, aromatics).

(a) In a similar way pale yellow crystals of tribromodicarbonylbis(dimethylphenylphosphine)rhenium(III), m.p. 148–149°C were isolated in a 92% yield. (Found: C, 28.0; H, 2.80; Br, 30.2%  $C_{18}H_{22}O_2Br_3P_2Re$  requires C, 28.5; H, 2.90; Br, 31.6%);  $v_{max}$ (CO) 2046s, 1935s cm<sup>-1</sup> (chloroform); NMR: <sup>1</sup>H (25°C, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  2.22 (12 H, vbr s, 4 Me), 7.42 (4 H, m, aromatics), 7.72 ppm (6H, m, aromatics).

(b) Reaction of bromine with [Re-

Br(CO)<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>2</sub>] as above afforded yellow *crys*tals of tribromodicarbonylbis(diethylphenylphosphine)rhenium(III), m.p. 138–140°C (dec), in 76% yield. (Found: C, 32.0; H, 3.91; Br, 29.3% C<sub>22</sub>H<sub>30</sub>O<sub>2</sub>Br<sub>3</sub>Re requires C, 32.4; H, 3.72; Br, 29.5%);  $v_{max}$ (CO) 2050s, 1938s cm<sup>-1</sup> (chloroform); NMR: <sup>1</sup>H (25°C, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  1.00 (12 H, vbr s, 4 Me), 2.90 (8 H, vbr s, 4 CH<sub>2</sub>), 7.36 (6 H, m, aromatics), 7.61 ppm (4 H, m, aromatics); <sup>13</sup>C-[<sup>1</sup>H] (25°C, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.9 (Me), 20.7 (m, CH<sub>2</sub>), 128.3, 128.5, 128.7, 129.2, 131.5, 132.6, 132.7 and 132.8 ppm (aromatics).

Halide abstraction from  $[\text{ReBr}_3(\text{CO})_2^-$ (PMe<sub>2</sub>Ph)<sub>2</sub>]. A solution of  $[\text{ReBr}_3(\text{CO})_2^-$ (PMe<sub>2</sub>Ph)<sub>2</sub>] (0.39 g, 0.51 mmol) in anhydrous acetone (15 cm<sup>3</sup>) was stirred at room temperature with MBF<sub>4</sub> (M = Ag or Tl, 0.51 mmol) dissolved in acetone (3 cm<sup>3</sup>). After 0.5 hr, the precipitated MBr was filtered from the solution and the filtrate was concentrated to low bulk (5 cm<sup>3</sup>) at 0°C, and treated dropwise with heptane to initiate crystallisation. On further cooling yellow microcrystals were deposited. Yield 0.067 g;  $\nu_{max}$  (CO) 2028s, 1928 cm<sup>-1</sup>;  $\nu_{max}$ (BF) 1080 cm<sup>-1</sup> (Nujol).

Crystal structure determination of  $[ReBr_3(CO)_2(PMe_2Ph)_2]$ . Crystals of (1) were obtained as yellow needles by recrystallisation from  $CH_2Cl_2$ .

Crystal data.  $C_{18}H_{27}O_2Br_3P_2Re$ , M = 863.1, Triclinic, Spacegroup PI, Z = 2, a = 9.575(8), b = 14.705(11), c = 9.629(12) Å,  $\alpha = 77.71(7)$ ,  $\beta = 109.06(8)$ ,  $\gamma = 115.02(8)^\circ$ , U = 1 156.8 Å<sup>3</sup>,  $D_m = 2.48 \text{ g cm}^{-3}$ , F(000) = 722, Mo- $K_{\alpha}$  radiation,  $\lambda = 0.7107 \text{ Å}$ ,  $\mu = 141.4 \text{ cm}^{-1}$ .

Structure solution and refinement. The chosen crystal was mounted on a Stoe STADI-2 diffractometer and data was collected via variable width  $\omega$  scan. Background counts were 20s and the scan rate of 0.033°/s was applied to a width of  $(1.5 + \sin \mu/\tan \theta)$ . 2991 independent reflections with  $2\theta < 50^{\circ}$  were measured of which 1957 with  $I > 3\sigma(I)$  were used in subsequent refinement. An empirical absorption correction was applied. The structure was solved by the Patterson method. The positions of the remaining non-hydrogen atoms were obtained from Fourier syntheses. The phenyl hydrogen atoms were positioned in trigonal positions and those in the same ring were given a common thermal parameter. Those on methyl groups were located by rigid body refinement and each group was given a common thermal parameter which was refined.

The structure was then refined using full-matrix least-squares using SHELX76.<sup>21</sup> The weighting scheme used was chosen to give equivalent values of  $w\Delta^2$  over ranges of  $F_0$  and  $(\sin \theta/\lambda)$ . This was

			180		
DIMENSIONS IN THE COORDINATION SPHERE					
DISTANCES, A, ANGLES, DEGREES					
RE	-	BR	(1)	2.589(	5)
RE	-	BR	(2)	2.623(	6)
RE	-	BR	(3)	2.622(	5)
RE	-	Ρ(	1)	2.454(	13)
RE	-	Ρ(	2)	2.496(	11)
RE	-	C(	41)	1.85(	5)
RE	-	C(	51)	1.87(	3)
BR(1)	-	RE	-	BR(2)	90.68(18)
BR(1)	-	RE	-	BR(3)	87.37(18)
BR(2)	-	RE	-	BR(3)	84.52(18)
BR(1)	-	ŘE	-	P(1)	77.85(29)
BR(2)	-	RE	-	P(1)	160.8(3)
BR(3)	-	RE	-	P(1)	79.7(3)
BR(1)	-	RE	-	P(2)	80.1(3)
BR(2)	-	RE	-	P(2)	76.2(3)
BR(3)	-	RE	-	P(2)	156.8(3)
P(1)	-	RE	-	P(2)	116.1( 4)
BR(1)	-	RE	-	C(41)	163.0(11)
BR(2)	-	RE	-	C(41)	76.7(12)
BR(3)	-	RE	-	C(41)	80.2(14)
P(1)	-	RE	-	C(41)	110.8(14)
P(2)	-	RE	-	C(41)	107.3(15)
BR(1)	-	RE	-	C(51)	127.1(17)
BR(2)	-	RE	-	C(51)	126.5(19)
BR(3)	- 1	RE	-	C(51)	127.4(17)
P(1)	-	RE	-	C(51)	72.4(19)
P(2)	-	RE	-	C(51)	75.4(17)
C(41)	) _	RE	-	C(51)	69.9(21)

 $w^{1/2} = 1/(\sigma^2(F) + 0.003 \text{ F}^2)$  where  $\sigma(F)$  was taken from counting statistics. The Re, Br and P atoms were refined anisotropically. Scattering factors were taken from International Tables.<sup>22</sup> Calcu-

with the Editor and with the Cambridge Data Centre.

lations were made using SHELX76 on the CDC 7600 computer at the University of Manchester Computer Centre.

Details of interatomic distances and angles are listed in Table 1. Atomic coordinates, anisotropic thermal parameters, observed and calculated structure factors and hydrogen atom positions are given in the Supplementary Publication.<sup>†</sup>

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