Crystal and Molecular Structure of Di-μ-bromo-μ-tetraphenyldiphosphane-bis[tricarbonylrhenium(I)]

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The title complex has been prepared by treating P_2Ph_4 either with $[ReBr(CO)_5]$ at the reflux temperature of benzene or with $[Re_2Br_2(CO)_6(thf)_2]$ (thf = tetrahydrofuran) at room temperature in toluene. Three-dimensional *X*-ray analysis has shown this to be the first example of a diphosphane bridging two co-ordination octahedra joined by a common edge. The substance crystallizes from toluene in the triclinic system, space group $P\bar{1}$, with cell constants a = 11.110(9), b = 11.538(9), c = 12.913(9) Å, α = 95.95(5), β = 102.54(5), γ = 95.92(5)°, and Z = 2. The molecule consists of two rhenium atoms linked by two bromine atoms and by a P–P bridge. The six carbonyl groups are distributed around the two rhenium atoms in two groups of three, each in a *fac* arrangement, thus completing the six-co-ordination. The normals to the planes defined by Re(1)–Br(1)–Br(2) and by the Re(2)–Br(1)-Br(2) intersect at an angle of 23.4°. Probably important P · · · Br interactions exist, as evidenced by the non-bonding distance of 3.49 Å observed, which is *ca.* 0.4 Å less than the van der Waals radii. The P–P bond is 2.308(6) Å. Evidence is presented that the products of formula $[Re_2X_2(CO)_6(P_2Ph_4)]$ (X = Cl or I) previously reported have structures probably similar to that of the present complex.

THE interaction of alkyl- or arylthio-groups, SR, or dialkyl- or diaryl-phosphido-groups, PR_2, with transition-metal complexes has been the subject of active investigation since the report in 1937 by Hieber and Spacu [1] of the preparation of complexes of the type $[\{Co(SR)(CO)_3\}_2]$. Early studies showed that the reaction of S_2R_2 or P_2R_4 most commonly resulted in

[1] W. Hieber and P. Spacu, *Z. anorg. Chem.*, 1937, **233**, 353.

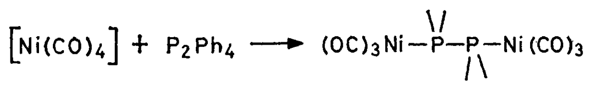
oxidative addition across the S–S or P–P bond [equations (1)—(3); M = Cr, Mo, or W, cp = η-C_5H_5].

$$[\{Fe(cp)(CO)_2\}_2] + S_2Me_2 \longrightarrow 2[Fe(cp)(CO)_2(SMe)] \quad \text{(ref. 2)} \quad (1)$$

$$2[V(cp)(CO)_4] + 2S_2Me_2 \longrightarrow [\{V(cp)(SMe)_2\}_2] + 8CO \quad \text{(ref. 3)} \quad (2)$$

$$2[M(CO)_6] + P_2Ph_4 \longrightarrow \{[M(CO)_4(PPh_2)\}_2] + 4CO \quad \text{(ref. 4)} \quad (3)$$

Indeed, the crystal structures of $[\{Fe(NO)_2(SEt)\}_2]$ [5] and $[\{Fe(CO)_3(SEt)\}_2]$ [6] confirmed that the S–S bond of the reacting disulphide had been cleaved. It has also been shown that in some cases the P–P bond might not be cleaved under the reaction conditions [7,8] [equation (4)].


(4)

Infrared evidence has been used to deduce the presence of S–S bridges in $[Co_2(CO)_6(C_6F_5SSC_6F_5)]$,[9] by analogy with $[Co_2(CO)_6(PhC_2Ph)]$,[10] and in trimeric $[Fe_3(CO)_6(S_2R_2)_3]$.[11]

We have recently given chemical, spectroscopic, and *X*-ray crystallographic proof of the intact disulphide bridge in $[Re_2Br_2(CO)_6(S_2R_2)]$ (R = Ph [12] or Me [13]). Herein is presented structural verification of the P–P bonded diphosphane ligand in $[Re_2Br_2(CO)_6(P_2Ph_4)]$. A preliminary account of this work has already appeared.[14] Evidence is also presented that the products $[Re_2X_2(CO)_6(P_2Ph_4)]$ (X = Cl or I) suggested [15] to be diphenylphosphide-bridged dimers of Re^{II} are probably tetraphenyldiphosphane- and halide-bridged dimers of Re^{I}, similar to the bromo-derivative of this paper.

EXPERIMENTAL

Solvents were dried before use according to conventional methods. Infrared spectra were obtained with Perkin-Elmer model 337 and 225 instruments. Each solution spectrum was recorded on an expanded abscissa scale and calibrated with CO(g). The preparations and the manipulations of the complexes were normally carried out under an atmosphere of prepurified nitrogen, in view of the sensitivity to oxygen of the starting rhenium(I) complexes. The tetrahydrofuran adduct $[Re_2Br_2(CO)_6(thf)_2]$ was prepared as previously described.[16]

Preparation of Di-μ-bromo-μ-tetraphenyldiphosphane-bis-[tricarbonylrhenium(I)].—*Method A*. The tetrahydrofuran adduct $[Re_2Br_2(CO)_6(thf)_2]$ (1.447 g, 1.71 mmol) was placed in a flask (250 cm³) together with toluene (50 cm³) and tetraphenyldiphosphane (0.64 g, 1.73 mmol) at room temperature. Dissolution of the sparingly soluble thf adduct was observed, followed by precipitation of the new complex after a few minutes. The reaction mixture was stirred for *ca.* 14 h; the precipitate was then filtered off, washed with toluene (5 cm³), and dried *in vacuo* (0.87 g, 48% yield). The complex was recrystallized from toluene (Found: C, 34.05; H, 1.85; Br, 15.3; P, 5.70. Calc. for $C_{30}H_{20}Br_2O_6P_2Re_2$: C, 33.6; H, 1.90; Br, 14.95; P, 5.80%). The low solubility of the complex prevented the determination of its molecular weight by cryoscopy in benzene. The complex is diamagnetic ($\chi_M^{corr} = -150 \times 10^{-6}$ c.g.s. units, diamagnetic correction = -310×10^{-6} c.g.s. units). The i.r. spectrum in solution (CCl_4) had bands in the carbonyl-stretching region at 2 054s, 2 041s, 1 960s, 1 956(sh), and 1 923s cm⁻¹. The combined Nujol and $(C_2ClF_3)_n$ mull spectra showed bands (carbonyl-stretching region omitted) at 3 060w, 1 580w, 1 570w, 1 480w, 1 440m, 1 435m, 1 430w, 1 375w, 1 308w, 1 185w, 745s—m, 738s, 700m, 690s, 638s—m, 620m, 615m, 602m, 530m, 515s, 505s, 480s, 455w, 440m, 430m, 390s, 320s, 275w, 255w, and 245w cm⁻¹. The complex is stable in air in the solid state, as monitored by the invariance of the i.r. spectrum after exposure to air. The complex was recovered unchanged after thermal treatment with thf at reflux.

Method B. Bromopentacarbonylrhenium(I) (0.865 g, 2.13 mmol) and benzene (30 cm³) were placed in a flask (100 cm³). To the resulting suspension was added P_2Ph_4 (0.40 g, 1.08 mmol). The reaction mixture was heated under reflux for *ca.* 10 h. After cooling, the pale yellow complex was collected by filtration, dried *in vacuo* (0.85 g, 75% yield), and recrystallized from toluene (Found: C, 33.8; H, 1.90; Br, 15.15; P, 4.95%). Infrared spectra and *X*-ray powder patterns were substantially identical to those of the complex obtained according to method A.

Crystal Data.—$C_{30}H_{20}Br_2O_6P_2Re_2$, M = 1 070.7, Triclinic, a = 11.110(9), b = 11.538(9), c = 12.913(9) Å, α = 95.95(5), β = 102.54(5), γ = 95.92(5)°, U = 1 593.6 Å³, D_m = 2.23 g cm⁻³, Z = 2, D_c = 2.23 g cm⁻³, μ(Mo-K_α) = 108.2 cm⁻¹, $F(000)$ = 996, λ(Mo-K_α) = 0.710 69 Å, space group $P\bar{1}$. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 30°$) accurately centred on an Enraf–Nonius CAD-4 diffractometer.

X-*Ray Data Collection*.—A crystal of dimensions 0.20 × 0.42 × 0.45 mm was sealed in a thin-walled capillary under a nitrogen atmosphere. Data were taken on the diffractometer using graphite-monochromated molybdenum radiation. The diffracted intensities were collected by the ω—2θ scan technique in a manner similar to that described previously.[17] All the reflections in one independent hemisphere out to $2\theta \leqslant 60°$ were measured; 3 758 were considered observed [$I > 3\sigma(I)$]. The intensities were corrected for Lorentz, polarization, and absorption effects.

Full-matrix least-squares refinement was carried out

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using the Busing and Levy ORFLS program.* The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Re, P, O, and C were taken from Cromer and Waber,[18] and the scattering for Re was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[19] Scattering factors for hydrogen were from ref. 20.

Structure Determination and Refinement.—Inspection of

TABLE 1

Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Re(1)	0.256 99(8)	0.335 53(8)	0.102 70(6)
Re(2)	0.270 39(9)	0.042 61(7)	0.226 75(7)
Br(1)	0.419 5(3)	0.241 4(2)	0.244 6(2)
Br(2)	0.156 4(3)	0.114 9(2)	0.047 9(2)
P(1)	0.129 2(6)	0.338 0(6)	0.237 9(5)
P(2)	0.148 6(6)	0.173 1(6)	0.324 2(5)
O(1)	0.074 8(17)	0.424 9(14)	−0.074 6(12)
O(2)	0.368 3(19)	0.590 2(16)	0.182 5(14)
O(3)	0.422 9(20)	0.318 3(25)	−0.059 2(15)
O(4)	0.076 0(20)	−0.174 7(16)	0.186 4(16)
O(5)	0.397 9(19)	−0.064 6(16)	0.421 7(17)
O(6)	0.437 9(22)	−0.075 5(21)	0.105 1(21)
C(1)	0.140 0(28)	0.390 0(22)	−0.007 2(19)
C(2)	0.325 8(20)	0.491 1(19)	0.152 5(15)
C(3)	0.360 2(23)	0.328 9(29)	0.005 1(19)
C(4)	0.156 1(32)	−0.098 4(22)	0.201 1(21)
C(5)	0.345 5(31)	−0.017 0(23)	0.354 2(19)
C(6)	0.355 4(31)	−0.023 4(33)	0.163 7(29)
C(7)	0.179 4(17)	0.470 2(14)	0.337 4(12)
C(8)	0.297 2(18)	0.479 9(15)	0.406 4(14)
C(9)	0.343 8(20)	0.584 3(19)	0.475 1(16)
C(10)	0.275 8(24)	0.672 9(18)	0.475 9(17)
C(11)	0.160 7(24)	0.668 3(17)	0.401 8(19)
C(12)	0.114 1(19)	0.563 8(15)	0.333 9(15)
C(13)	−0.039 1(16)	0.335 5(14)	0.198 0(12)
C(14)	−0.111 3(20)	0.353 7(17)	0.270 0(15)
C(15)	−0.238 3(24)	0.349 1(22)	0.234 4(18)
C(16)	−0.293 4(20)	0.315 2(22)	0.128 7(20)
C(17)	−0.226 8(25)	0.296 7(20)	0.053 2(18)
C(18)	−0.098 3(20)	0.302 3(18)	0.087 4(15)
C(19)	−0.011 6(17)	0.109 7(16)	0.320 7(15)
C(20)	−0.052 6(20)	0.094 4(17)	0.409 9(15)
C(21)	−0.174 4(24)	0.040 7(21)	0.401 7(19)
C(22)	−0.252 9(22)	0.004 0(21)	0.303 8(20)
C(23)	−0.207 3(22)	0.016 8(20)	0.213 3(18)
C(24)	−0.087 8(18)	0.067 9(16)	0.220 9(15)
C(25)	0.216 0(20)	0.233 7(14)	0.463 6(12)
C(26)	0.339 5(20)	0.216 7(16)	0.508 1(13)
C(27)	0.392 6(20)	0.270 8(20)	0.614 0(15)
C(28)	0.327 0(25)	0.331 8(21)	0.672 5(17)
C(29)	0.206 9(24)	0.349 5(20)	0.628 7(17)
C(30)	0.153 8(20)	0.298 6(18)	0.521 7(16)

a Patterson map revealed the positions of the two independent rhenium atoms in the asymmetric unit, and the calculation of a Fourier map phased on the metal atoms led to the co-ordinates of the remaining 40 non-hydrogen atoms. Several cycles of least-squares refinement with isotropic temperature factors, followed by more cycles with anisotropic thermal parameters for non-hydrogen atoms (hydrogen atoms in calculated positions), led to final values of $R = (|F_o| - |F_c|)/|F_o| = 0.068$ and $R' = [w(|F_o| - |F_c|)^2/w(F_o)^2]^{\frac{1}{2}} = 0.068$. Unit weights were used through-

* Other crystallographic programs used on a UNIVAC 1110 include ORFFE (distance and angle with estimated standard deviations by W. R. Busing, K. O. Martin, and H. A. Levy), ORABS (absorption correction, by D. J. Wehe, W. R. Busing, and H. A. Levy), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), BPL (least-squares planes, by W. E. Hunter), and FOURIER (D. J. Hodgson's version of Dellaca and Robinson's program).

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TABLE 2

Interatomic bond lengths (Å) and angles (°)

(*a*) Bonded			
Re(1)−Br(1)	2.679(2)	Re(2)−Br(1)	2.643(2)
Re(1)−Br(2)	2.632(2)	Re(2)−Br(2)	2.646(2)
Re(1)−P(1)	2.478(5)	Re(2)−P(2)	2.538(5)
Re(1)−C(1)	1.91(3)	Re(2)−C(4)	1.91(3)
Re(1)−C(2)	1.87(2)	Re(2)−C(5)	1.91(3)
Re(1)−C(3)	1.88(3)	Re(2)−C(6)	1.57(5)
C(1)−O(1)	1.14(3)	C(4)−O(4)	1.15(3)
C(2)−O(2)	1.18(2)	C(5)−O(5)	1.16(3)
C(3)−O(3)	1.20(3)	C(6)−O(6)	1.45(4)
P(1)−P(2)	2.308(6)	P(1)−C(7)	1.84(2)
P(2)−C(19)	1.84(2)	P(1)−C(13)	1.82(2)
P(2)−C(25)	1.83(1)	C(7)−C(8)	1.40(2)
C(19)−C(20)	1.35(2)	C(8)−C(9)	1.40(2)
C(20)−C(21)	1.41(3)	C(9)−C(10)	1.33(3)
C(21)−C(22)	1.37(3)	C(10)−C(11)	1.41(3)
C(22)−C(23)	1.39(3)	C(11)−C(12)	1.39(2)
C(23)−C(24)	1.38(3)	C(12)−C(7)	1.36(2)
C(24)−C(19)	1.39(2)	C(13)−C(14)	1.37(2)
C(25)−C(26)	1.41(3)	C(14)−C(15)	1.38(3)
C(26)−C(27)	1.42(2)	C(15)−C(16)	1.37(3)
C(27)−C(28)	1.35(3)	C(16)−C(17)	1.36(3)
C(28)−C(29)	1.38(3)	C(17)−C(18)	1.39(3)
C(29)−C(25)	1.42(3)	C(18)−C(13)	1.43(2)
C(30)−C(25)	1.35(3)		
(*b*) Non-bonded			
Re(1)−Re(2)	3.890(1)	Br(1)−P(1)	3.506(4)
Br(1)−P(2)	3.428(4)	Br(2)−P(1)	3.450(4)
Br(2)−P(2)	3.583(4)	Re(1)−P(2)	3.909(3)
Re(2)−P(1)	3.898(3)		
(*c*) Bond angles			
Br(1)−Re(1)−Br(2)	82.48(6)	Br(1)−Re(2)−Br(2)	82.90(6)
Br(1)−Re(1)−C(1)	174.8(7)	Br(1)−Re(2)−C(4)	174.8(7)
Br(1)−Re(1)−C(2)	95.3(7)	Br(1)−Re(2)−C(5)	100.3(7)
Br(1)−Re(1)−C(3)	91.2(7)	Br(1)−Re(2)−C(6)	90.0(9)
Br(1)−Re(1)−P(1)	85.6(1)	Br(1)−Re(2)−P(2)	82.7(1)
Br(2)−Re(1)−C(1)	93.2(2)	Br(2)−Re(2)−C(4)	92.0(7)
Br(2)−Re(1)−C(2)	175.4(6)	Br(2)−Re(2)−C(5)	176.8(7)
Br(2)−Re(1)−C(3)	94.3(9)	Br(2)−Re(2)−C(6)	90.1(9)
Br(2)−Re(1)−P(1)	84.9(1)	Br(2)−Re(2)−P(2)	87.5(1)
P(1)−Re(1)−C(1)	97.0(9)	P(2)−Re(2)−C(4)	97.9(9)
P(1)−Re(1)−C(2)	90.9(6)	P(2)−Re(2)−C(5)	92.8(9)
P(1)−Re(1)−C(3)	176.7(7)	P(2)−Re(2)−C(6)	172.6(10)
C(1)−Re(1)−C(2)	89.2(9)	C(4)−Re(2)−C(5)	84.8(9)
C(1)−Re(1)−C(3)	86.3(11)	C(4)−Re(2)−C(6)	89.2(13)
C(2)−Re(1)−C(3)	89.8(11)	C(5)−Re(2)−C(6)	90.1(13)
Re(1)−Br(1)−Re(2)	93.88(6)	Re(1)−Br(2)−Re(2)	95.06(6)
Re(1)−P(1)−C(7)	110.8(5)	Re(2)−P(2)−C(19)	115.3(6)
Re(1)−P(1)−C(13)	120.8(5)	Re(2)−P(2)−C(25)	118.9(7)
Re(1)−P(1)−P(2)	109.5(3)	Re(2)−P(2)−P(1)	107.0(2)
Re(1)−C(1)−O(1)	177(2)	Re(2)−C(4)−O(4)	172(4)
Re(1)−C(2)−O(2)	179(2)	Re(2)−C(5)−O(5)	170(3)
Re(1)−C(3)−O(3)	176(3)	Re(2)−C(6)−O(6)	176(2)
P(2)−P(1)−C(7)	109.1(5)	P(1)−P(2)−C(19)	105.5(6)
P(2)−P(1)−C(13)	102.5(5)	P(1)−P(2)−C(25)	103.4(5)
C(7)−P(1)−C(13)	103.5(8)	C(19)−P(2)−C(25)	105.4(8)
P(1)−C(7)−C(8)	118(1)	P(2)−C(19)−C(20)	122(1)
P(1)−C(7)−C(12)	120(1)	P(2)−C(19)−C(24)	117(2)
P(1)−C(13)−C(14)	123(2)	P(2)−C(25)−C(26)	118(1)
P(1)−C(13)−C(18)	118(1)	P(2)−C(25)−C(30)	122(1)
C(7)−C(8)−C(9)	119(1)	C(19)−C(20)−C(21)	120(2)
C(8)−C(9)−C(10)	120(2)	C(20)−C(21)−C(22)	121(2)
C(9)−C(10)−C(11)	121(2)	C(21)−C(22)−C(23)	118(2)
C(10)−C(11)−C(12)	118(2)	C(22)−C(23)−C(24)	121(2)
C(11)−C(12)−C(7)	121(2)	C(23)−C(24)−C(19)	120(2)
C(12)−C(7)−C(8)	120(1)	C(24)−C(19)−C(20)	120(2)
C(13)−C(14)−C(15)	120(2)	C(25)−C(26)−C(27)	117(2)
C(14)−C(15)−C(16)	120(2)	C(26)−C(27)−C(28)	122(2)
C(15)−C(16)−C(17)	122(2)	C(27)−C(28)−C(29)	121(2)
C(16)−C(17)−C(18)	118(2)	C(28)−C(29)−C(30)	118(2)
C(17)−C(18)−C(13)	120(2)	C(29)−C(30)−C(25)	122(2)
C(18)−C(13)−C(14)	119(2)	C(30)−C(25)−C(26)	120(2)

out the refinement. The largest parameter shifts in the final cycle were less than a tenth of their estimated standard deviation. A final difference Fourier showed no unaccounted electron density. The standard deviation of an observation of unit weight was 4.59. No systematic variation of $w(|F_o| - |F_c|)$ against $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameter are given in Table 1, bond lengths and angles in Table 2. The observed and calculated structure-factor amplitudes, hydrogen-atom co-ordinates, thermal parameters, and least-squares planes are given in Supplementary Publication No. SUP 22290 (33 pp.).*

culary with the observed diamagnetism. Under these circumstances, only a full X-ray investigation was appropriate to solve this problem.

The unique type (1) bridging arrangement of the P_2Ph_4 unit is shown clearly in Figure 1. The P–P bond is not cleaved and the bond length [2.308(6) Å] shows that it is a normal single bond. It may be compared with P–P distances of 2.20 Å from a sum of covalent radii,[21] 2.192 Å from an electron-diffraction study of P_2Me_4,[22a] and 2.277(4) Å found in $[Ni_2(CO)_6(P_2Ph_4)]$.[8]

The Re_2Br_2 fragment possesses significant differences

TABLE 3

Structural properties of the $Re_2Br_2E_2$ fragment

		Bond length/Å						Angle/°			
Complex	E	Re···Re	Br···Br	E···Br	E–E	Re–E	Re–Br	Br–Re–Br	Br–Re–Br	Δ [a]/°	Ref.
$[Re_2Br_2(CO)_6(S_2Ph_2)]$	S	3.782	3.411	3.534	2.140	2.487	2.607	81.7	93.0	33	12
$[Re_2Br_2(CO)_6(S_2Me_2)]$	S	3.790		3.452	2.110	2.486	2.599	82.6	93.6	28.0	13
$[Re_2Br_2(CO)_6(P_2Ph_4)]$	P	3.890	3.500	3.492	2.308	2.508	2.650	82.7	94.5	23.4	b

[a] Δ is defined as the ' angle of fold ' along the Br ··· Br vector. It is calculated as the angle between the normals to the planes defined by Re(1), Br(1), Br(2), and Re(2), Br(1), Br(2). [b] This study.

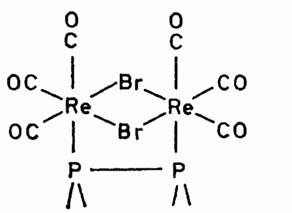
DISCUSSION

The tetraphenyldiphosphane derivative of Re^I was prepared either from the thf adduct at room temperature

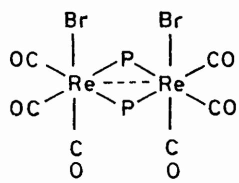
$$[Re_2Br_2(CO)_6(thf)_2] + P_2Ph_4 \longrightarrow 2\,thf + [Re_2Br_2(CO)_6(P_2Ph_4)] \quad (5)$$

$$2\,[ReBr(CO)_5] + P_2Ph_4 \longrightarrow 4\,CO + [Re_2Br_2(CO)_6(P_2Ph_4)] \quad (6)$$

or from $[ReBr(CO)_5]$ at the reflux temperature of benzene [equations (5) and (6)]. In view of the previous results obtained with the S_2Ph_2 [12] and S_2Me_2 derivatives [13] (where no cleavage of the S–S bond had occurred) and



(1)



(2)

considering, on the other hand, the ready cleavage of P–P bonds with complexes of low-valent transition elements,[4] two main structural possibilities existed for the product of reactions (5) and (6), namely a tetraphenyldiphosphane- and bromide-bridged structure of type (1) and a diphenylphosphide-bridged structure of Re^{II} with terminal bromide ligands, (2).

It will be noted that both structures (1) and (2) have the same symmetry C_{2v} for the $Re_2(CO)_6$ core for which five i.r. bands $(2A_1 + 2B_1 + B_2)$ are expected. Bending of these structures (see below) would not in fact invalidate the argument. Both structures would also be in agreement with the other experimental observations, parti-

from those found in the related molecules $[Re_2Br_2(CO)_6(S_2Ph_2)]$ [12] and $[Re_2Br_2(CO)_6(S_2Me_2)]$,[13] as is shown in Table 3. The Re ··· Re separation [3.890(1) Å] is

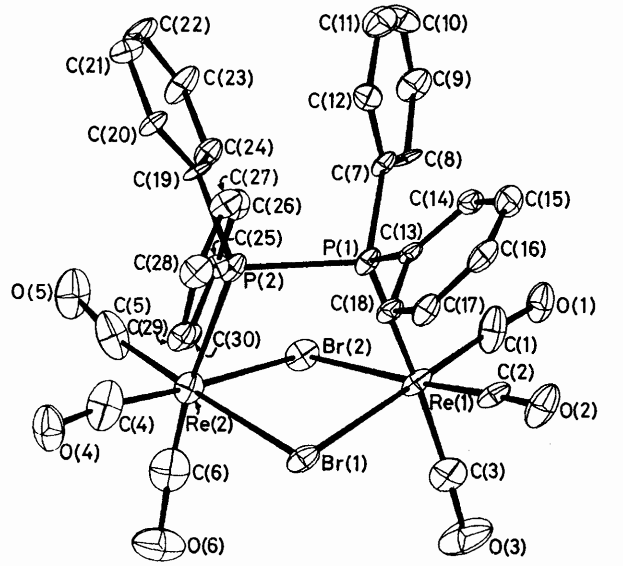


FIGURE 1 View of the molecule showing the numbering system employed in the crystallographic study. The atoms are represented by their 40% probability ellipsoids for thermal motion

0.1 Å greater than that found in the S_2R_2 derivatives, and the Re–Br bond length [2.650(18 Å] is 0.05 Å longer. However, the Br–Re–Br [82.7(3)°] and Re–Br–Re angles [94.5(8)°] are similar to those in the S_2R_2 structures. The major structural change is seen in the decrease in the ' angle of fold ' about the Br ··· Br vector from 33° in $[Re_2Br_2(CO)_6(S_2Ph_2)]$ to 23.4° in $[Re_2Br_2(CO)_6(P_2Ph_4)]$. There appear to be two ways

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[21] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 225.

[22] (*a*) A. McAdam, B. Beagley, and T. G. Hewitt, *Trans. Faraday Soc.*, 1970, **66**, 2732, (*b*) J. Korp, I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *J.C.S. Dalton*, submitted for publication.

to view the origin of this effect. First, it may be assumed that in the absence of a metal–metal bond the Re_2Br_2 unit would adopt a planar configuration. The presence of the E–E bridge then causes the deformation (non-zero angle of fold). Since the P–P bond [2.308(6) Å] is longer than the S–S bond [2.140(9) Å] the molecule which considered with respect to the S_2Me_2 complex [13] but is probably more important for the P_2Ph_4 case. The value given by Pauling for the van der Waals radius of Br is 1.95 Å, while those of S and P are 1.85 and 1.90 Å, respectively.[23] Thus, the sum for S · · · Br is 3.80 Å, while that for P · · · Br is 3.85 Å. From Table 3 the

TABLE 4

Comparison of Re–P bond lengths with standard deviations in parentheses [a]

Complex	Rhenium oxidation state	Re–P/Å Values	Re–P/Å Average	Ref.
$[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$	I	2.19(1)	2.19(1)	24
$[ReCl(N_2)(PMe_2Ph)_4]$	I	2.413(4)		25
		2.418(4)		
		2.421(3)	2.422(8)	
		2.435(3)		
$[ReCl(N_2)(PMe_2Ph)_4\{MoCl_4(OMe)\}]$	I	2.471(6)		26
		2.471(6)		
		2.486(6)	2.476(6)	
		2.477(6)		
$[Re_2Br_2(CO)_6(P_2Ph_4)]$	I	2.478(5)		*b*
		2.538(5)	2.508(42)	
$[Re_2Cl_4(PEt_3)_4]$	II	2.53(3)	2.53(3)	27
$[ReH_3(dppe)_2]$ [c]	III	2.34(2)	2.34(1)	28
		2.35(2)		
$[Re_2Cl_6(dppe)_2]\cdot 2MeCN$	III	2.370(3)		29
		2.371(5)	2.370(1)	
$[ReCl_3(PMe_2Ph)_3]$	III	2.401(6)		30
		2.458(6)	2.430(40)	
$[Re_2Cl_6(PEt_3)_2]$	III	2.449(6)	2.449(6)	31
$[ReCl_2(pd)(PPh_3)_2]$ [d]	III	2.469(4)		32
		2.485(4)	2.477(11)	
$[ReCl_2(NCMe)(PPh_3)_2]$	III	2.47		
		2.48	2.48(1)	33
$[ReCl_4(PMe_2Ph)_2]$	IV	2.505(3)	2.505(3)	31
$[ReNCl_2(PPh_3)_2]$	V	2.448(2)	2.448(2)	34
$[ReCl_3(NC_6H_4COMe)(PEt_2Ph)_2]$	V	2.457(4)		35
		2.461(4)	2.459(3)	
$[ReNCl_2(PEt_2Ph)_3]$	V	2.442(4)		36
		2.469(5)	2.467(20)	
		2.490(5)		
$[ReCl_3(NC_6H_4OMe)(PEt_2Ph)_2]$	V	2.470(1)	2.470(1)	35
$[ReCl_3(NMe)(PEtPh_2)_2]$	V	2.482(7)		37
		2.486(7)	2.484(3)	

[a] The standard deviation of the average was calculated as $\sigma(\text{av.}) = [\sum_{i=1}^{n}(X_i - \bar{X})/n]^{\frac{1}{2}}$; the standard deviation of the mean of two values was calculated as $\sigma(\text{av.}) = (\text{difference})/2^{\frac{1}{2}}$. [b] This study. [c] dppe = 1,2-Bis(diphenylphosphino)ethane. [d] pd = Pentane-2,4-dionate.

contains the former exhibits a smaller deformation of the Re_2Br_2 fragment (lower angle of fold). That this is not the only effect operating is indicated by the observation that in $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ where the E–E bridge is even longer [2.411(23) Å] [22b] the folding angle is larger (31°). Another possibility to explain the folding of this molecule is the E · · · Br contact. An attractive force may exist between the negatively charged bromine atom and the δ^+ charge on the four-co-ordinate phosphorus atom. This situation has been previously average S · · · Br approach is 3.49 Å, and that of P · · · Br is 3.49 Å. The P · · · Br contact is not only *ca.* 0.4 Å less than the sum of the van der Waals radii, it is also the same as that of S · · · Br. An attractive interaction between $Br^{\delta-}$ and $P^{\delta+}$ would decrease the angle of fold.

The Re–Br bond length [2.650(18) Å] is the same as that calculated on the basis of covalent radii. A tabulation of Re–Br distances has been recently published.[13]

A summary of Re–P bond lengths [24-37] is given in

[23] Ref. 21, p. 260.

[24] O. M. A. Salah, M. T. Bruce, and A. D. Redhouse, *J.C.S. Chem. Comm.*, 1974, 855.

[25] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 578.

[26] M. Mercer, *J.C.S. Dalton*, 1974, 1637.

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[28] V. G. Albano and P. L. Bellon, *J. Organometallic Chem.*, 1972, **37**, 151.

[29] J. A. Jaecker, W. R. Robinson, and R. A. Walton, *J.C.S. Chem. Comm.*, 1974, 306.

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[31] F. A. Cotton and B. M. Foxman, *Inorg. Chem.*, 1968, **7**, 2135.

[32] I. D. Brown, C. J. L. Lock, and C. Wan, *Canad. J. Chem.*, 1974, **52**, 1704.

[33] M. G. B. Drew, D. G. Tisley, and R. A. Walton, *Chem. Comm.*, 1970, 600.

[34] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 204.

[35] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1099.

[36] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[37] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 703.

Table 4. All fall within the range 2.34—2.54 Å, with the exception of the anomalously low 2.19(1) Å given for $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$.[24] It is commonly assumed that the bond length decreases as the positive oxidation number of the metal increases, but other factors clearly overshadow this one with respect to the Re–P bond lengths in the 16 structures listed in Table 4. The average of 10 independent rhenium(I) bond distances is 2.461 Å, and that for the nine rhenium(V) lengths is 2.467 Å. Those in $[Re_2Br_2(CO)_6(P_2Ph_4)]$ are the longest of any rhenium(I) derivative and the Re(2)–P(2) separation [2.538(5) Å] is the longest yet recorded for a Re–P bond. On the other hand, the Re–P bond in this molecule appears to be rather stable. Contrary to what happens with the S_2R_2 and Se_2Ph_2 derivatives, no displacement of the P_2Ph_4 ligand by tetrahydrofuran was observed even at reflux temperature [equation (7)].

$$[Re_2Br_2(CO)_6(P_2Ph_4)] + 4\ \mathrm{thf} \longrightarrow 2[ReBr(CO)_3(\mathrm{thf})_2] + P_2Ph_4 \quad (7)$$

This is suggestive of a rather stable system. Further support for this comes from the observation that the P_2Ph_4 derivative has no tendency to evolve thermally to some other molecular arrangement, as evidenced by the fact that the same complex was obtained at the reflux temperature of benzene from $[ReBr(CO)_5]$ [see method B of the Experimental section and reaction (6)]. Moreover, reaction (5) should not be regarded as a mere substitution of the thf ligands by P_2Ph_4: the molecular structure of the dimeric thf adduct is close to C_{2h},* in agreement with the i.r. data in the carbonyl-stretching region.[16]

The average of the Re–C distances for C(1)—C(5) is 1.90 Å, a value in close agreement with the 1.89 Å in $[Re_2Br_2(CO)_6(S_2Ph_2)]$ [12] and 1.87 Å in $[Re_2Br_2(CO)_6(S_2Me_2)]$.[13] However, the Re(2)–C(6) length [1.57(5) Å] is an artifact of the refinement which could not be remedied. O(6) is correctly located, as evidenced by the Re(2) · · · O(6) separation of 3.02 Å (the other five Re · · · O distances range from 3.05 to 3.08 Å), but C(6) refined near the Re atom regardless of its original placement or the damping factor applied. In its potential minimum, C(6) still exhibits abnormally high thermal motion, and its r.m.s. thermal displacement along the Re(2)–C(6) bond vector is much larger than for any of the other five carbon atoms. The parameters associated with C(6) are therefore to be taken as *crystallographically* correct, but devoid of chemical implications.

The plane of the Re and P atoms makes an angle of 92° with that of the Re and Br atoms. The P–C bond lengths average 1.83 Å, and the parameters associated with the phenyl rings are normal. There are no abnormally short intermolecular distances: Figure 2 shows a stereoscopic view of the unit-cell packing.

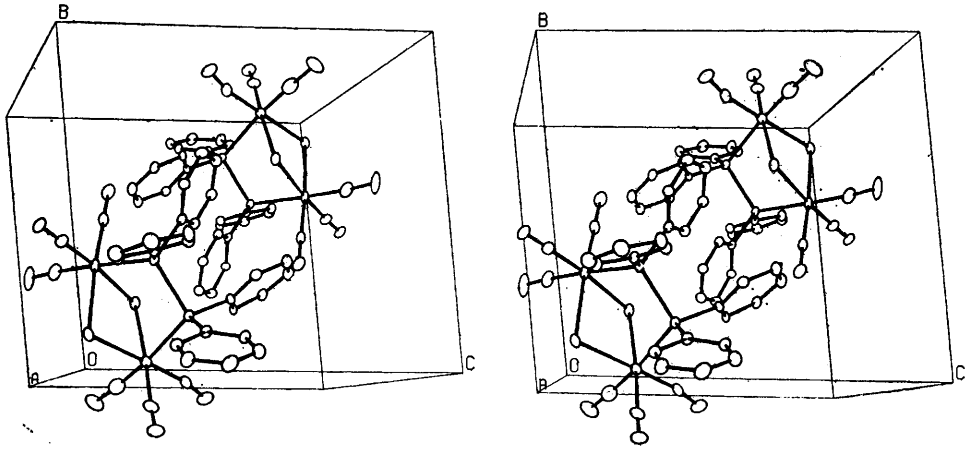
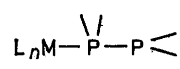
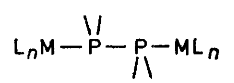


FIGURE 2 Stereographic plot of the packing of the molecules in the unit cell

The molecular arrangement of $[Re_2Br_2(CO)_6(P_2Ph_4)]$ may be described as consisting of two co-ordination octahedra joined by a common edge and containing a bridging P_2Ph_4 group, together with bridging bromides. This molecular arrangement is unique, since, to the best of our knowledge, there are no precedents of co-ordination complexes containing this kind of bridging arrangement for a diphosphane. Organic diphosphanes have been found to be terminally bonded [39] to transition elements as in (3), or to have the bridging arrangement (4).[8,40]



(3)



(4)

Complexes of formula $[Re_2X_2(CO)_6(P_2Ph_4)]$ (X = Cl or I) have been prepared [15] by the reaction of $[ReX(CO)_5]$ (X = Cl or I) with the diphosphane in refluxing benzene, *i.e.* under conditions similar to those used for our reaction (6). These complexes were reported [15] to have a diphenylphosphide-bridged structure of type (2). It would be highly surprising if changing the halide would

* Preliminary results of an *X*-ray investigation [38] show that $[Re_2Br_2(CO)_6(\mathrm{thf})_2]$ has the thf groups on opposite sides of the $(OC)_2ReBr_2Re(CO)_2$ plane.

[38] I. Bernal and J. Korp, unpublished work.

[39] M. Brockhaus, F. Staudacher, and H. Vahrenkamp, *Chem. Ber.*, 1972, **105**, 3716.

[40] L. R. Nassimbeni, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 187.

alter so drastically the structure of the product. We therefore suggest that the chloro- and iodo-derivatives also have structures similar to that reported here for the bromo-derivative. This is substantiated by the observation that the i.r. spectra [15] in the carbonyl-stretching region of the chloro- and iodo-derivatives are very similar to ours, as far as both the number of bands and their ν(CO) values are concerned. Structures of type (2), where the oxidation number of the metal has increased to II, should involve a considerable increase of the ν(CO) values, which is not observed. Under conditions of high resolution $[Re_2Br_2(CO)_6(P_2Ph_4)]$ has a shoulder at 1 956 cm^{-1} (CCl_4 solution), in addition to the four main bands in the carbonyl-stretching region. This is in agreement with the approximate C_{2v} symmetry of the $Re_2(CO)_6$ core of the molecule.

It may be concluded that the determining factors in stabilizing complexes of the type $[Re_2Br_2(CO)_6(E_2R_{2n})]$ ($n = 1$, E = S,[12,13] Se,[22b] or Te [41]; $n = 2$, E = P) are probably: (*a*) the length of the E–E bridge and (*b*) the dipolar interaction between the bromide ligand and the E atoms of the bridge. Relevant to this point is the observation that no reaction was observed when tetraphenylhydrazine was treated with $[Re_2Br_2(CO)_6(thf)_2]$ under conditions similar to those used for P_2Ph_4. Both the short N–N distance and the absence of low-lying *d* orbitals for nitrogen capable of accommodating the bromide lone pairs may well explain the failure to observe reaction with tetraphenylhydrazine.

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[7/2172 *Received, 12th December,* 1977]

41 F. Calderazzo and D. Vitali, unpublished work.