Hexacarbonyl Complexes of Dirhenium(I) containing E_2Ph_4 (E = P, As, or Sb) Ligands; *X*-Ray Crystal Structure of $[Re_2Br_2(CO)_6(Sb_2Ph_4)]$ †

Ivan Bernal * and James D. Korp
Chemistry Department, University of Houston, Houston, Texas 77004, U.S.A.
Fausto Calderazzo,* Rinaldo Poli, and Dario Vitali
Istituto Chimica Generale, University of Pisa, Via Risorgimento 35, 56100 Pisa, Italy

The E_2Ph_4 complexes of rhenium(I), $[Re_2X_2(CO)_6(E_2Ph_4)]$ (X = Br, E = As or Sb; X = I, E = P, As, or Sb), have been prepared by the reactions of $[Re_2Br_2(CO)_6(thf)_2]$ (thf = tetrahydrofuran) or $[Re_2I_2(CO)_8]$ with the appropriate E_2Ph_4. The crystal and molecular structure of one of the compounds, namely $[Re_2Br_2(CO)_6(Sb_2Ph_4)]$, has been solved by *X*-ray diffraction methods. The crystals are monoclinic, space group $P2_1/n$, with $a = 16.585(8)$, $b = 22.036(13)$, $c = 19.764(19)$ Å, $\beta = 109.34(6)°$, and $Z = 8$. Data collection yielded 2 197 observed reflections, $R = 0.040$. The molecule consists of two pseudo-octahedral rhenium(I) centres joined by bromide and Sb_2Ph_4 bridges. Average distances include Re–Br 2.663(4), Sb ··· Br 3.640(3), Re ··· Re 3.970(2), and Sb–Sb 2.826(4) Å. The rhenium–P_2Ph_4 complex undergoes nucleophilic attack by PPh_2^- to form an anionic rhenium(I) carbonyl species. The small angle of folding along the Br ··· Br vector produces the appearance of the number of i.r. carbonyl stretches expected for the local C_{2v} symmetry of the $Re_2(CO)_6$ core, presumably due to a better coupling of the two $Re(CO)_3$ moieties. Chemical evidence and mass spectral data indicate that the stability of the rhenium(I) complexes decreases with increasing atomic weight of the Group 5 donor atom.

Hexacarbonyl derivatives of general formula $[M_2X_2(CO)_6(E_2Ph_{2n})]$ (M = Mn[1a] or Re,[1b] X = Br, $n = 2$, E = P; M = Re,[1c–e] X = Br or I, $n = 1$, E = S, Se, or Te; M = Mn,[1f] X = Br, $n = 1$, E = Se or Te; M = Mn,[1g] X = Br, $n = 2$, E = As; M = Mn,[1g] X = I, $n = 2$, E = P) have been prepared and studied by *X*-ray diffraction methods. The compounds were all shown to consist of six-co-ordinated manganese(I) or rhenium(I) atoms surrounded by a set of ligands consisting of three terminal carbonyl groups, two bridging halides and one heteroatom E. The products are thus the result of the co-ordinative addition of E_2Ph_{2n} to the low-valent metal.

In view of the paucity of data concerning metal complexes of As_2Ph_4 and Sb_2Ph_4, and of the expected lower strength of the E–E bond on descending Group 5A [2] and to the subsequent possible tendency to the oxidative addition pathway, we decided to investigate the behaviour of $[Re_2X_2(CO)_6(thf)_2]$ (thf = tetrahydrofuran; X = Br or I) towards As_2Ph_4 and Sb_2Ph_4. In addition, we studied the reactivity of co-ordinated P_2Ph_4 towards nucleophiles.

Experimental

Unless otherwise stated, all operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were dried and purified prior to use by conventional methods. The i.r. spectra were measured with a Perkin-Elmer model 283 instrument equipped with grating and each spectrum was calibrated with both CO and water vapour, the values being probably accurate to ± 1 cm^{-1}. Mass spectra were measured with a VG-MM 16F instrument [50 eV ($\approx 8.0 \times 10^{-18}$ J), 150 °C]. The tetraphenyl derivatives (E_2Ph_4) of phosphorus,[3] arsenic,[4] antimony,[5] and bismuth [6] were prepared according to literature methods. The rhenium complex $[Re_2Br_2(CO)_6(thf)_2]$ was prepared as previously described.[7] $[Re_2I_2(CO)_8]$ was prepared from $[Re_2(CO)_{10}]$ and di-iodine in equimolar amounts at 20 °C under ultraviolet irradiation as previously reported,[8] except that solutions 10 times more concentrated were used.[1f] The tetraphenyldiphosphane complex $[Re_2Br_2(CO)_6(P_2Ph_4)]$ was prepared according to an earlier paper.[1b]

Preparation of $[Re_2I_2(CO)_6(P_2Ph_4)]$.—The dimeric iodo-derivative $[Re_2I_2(CO)_8]$ (1.269 g, 1.492 mmol) was treated with P_2Ph_4 (0.681 g, 1.839 mmol) in toluene (100 cm^3) at the reflux temperature of the solvent for *ca.* 20 h, monitoring the reaction by i.r. in the carbonyl stretching region. The reaction flask was maintained under a slightly reduced pressure with the temperature of the external bath at 110—120 °C. The reaction mixture was then filtered and slowly cooled down to 5 °C. The crystalline *product* was collected by filtration and dried *in vacuo* (yield 57%).

Preparation of $[Re_2Br_2(CO)_6(As_2Ph_4)]$.—The thf adduct $[Re_2Br_2(CO)_6(thf)_2]$ (0.575 g, 0.681 mmol) and As_2Ph_4 (0.314 g, 0.685 mmol) were mixed at room temperature in toluene (50 cm^3) as solvent. Part of the solvent was evaporated under reduced pressure to remove the thf formed in the reaction; after 3 h, the reaction mixture was heated up to complete dissolution of the solid and the resulting solution was filtered rapidly and then slowly cooled down to 5 °C. The product was collected by filtration and dried *in vacuo* (yield 69%).

Other compounds reported in this paper, namely $[Re_2Br_2(CO)_6(Sb_2Ph_4)]$, $[Re_2I_2(CO)_6(As_2Ph_4)]$, and $[Re_2I_2(CO)_6(Sb_2Ph_4)]$, were prepared from the thf adduct $[Re_2Br_2(CO)_6(thf)_2]$ (for the bromo-derivatives) and $[Re_2I_2(CO)_8]$ (for the iodo-derivatives) by experimental procedures identical to those described above, giving yields of 78, 63, and 71% respectively.

Attempted Reaction of $[Re_2Br_2(CO)_6(thf)_2]$ *with* Bi_2Ph_4.—The thf complex (0.112 g, 0.133 mmol) was treated with tetraphenyldibismuthane [6] (0.100 g, 0.137 mmol) in toluene (10 cm^3) at room temperature for a few min. A black precipitate

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† Di-μ-bromo-μ-tetraphenyldistibane-bis[tricarbonylrhenium(I)].

Supplementary data available (No. SUP 23980, 18 pp.): thermal parameters, H-atom co-ordinates, selected least-squares planes and dihedral angles, torsional angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Analytical and i.r. spectrosopic data of rhenium(I) carbonyl complexes

Compound	Colour	Analysis [a] (%) C	H	Halogen	ν(CO) [b]/cm^{-1}
$[Re_2Br_2(CO)_6(As_2Ph_4)]$	Pale yellow	32.0 (31.1)	2.0 (1.7)	13.4 (13.8)	2 051m, 2 038s, 2 023w [c], 1 960s, 1 955 (sh), 1 924s
$[Re_2Br_2(CO)_6(Sb_2Ph_4)]$	Yellow	29.3 (28.8)	1.8 (1.6)	12.6 (12.8)	2 050s, 2 035s, 2 021w [c], 1 959s, 1 952m, 1 924s
$[Re_2I_2(CO)_6(P_2Ph_4)]$	Green-yellow	31.4 (30.9)	1.7 (1.7)	22.4 (21.8) [d]	2 049m, 2 036s, 2 019w [c], 1 960s, 1 925s
$[Re_2I_2(CO)_6(As_2Ph_4)]$	Yellow	29.0 (28.8)	1.5 (1.6)	20.4 (20.3)	2 049m, 2 036s, 2 022w [c], 1 959s, 1 926s
$[Re_2I_2(CO)_6(Sb_2Ph_4)]$	Yellow	27.2 (26.8)	1.5 (1.5)	19.4 (18.8)	2 046m, 2 033s, 2 019w [c], 1 959s, 1 955 (sh), 1 926s

[a] Calculated values in parentheses. [b] CCl_4 as solvent. [c] Assigned to a ^{13}CO vibration. [d] P = 5.3 (5.3%).

Table 2. Fractional atomic co-ordinates and their estimated standard deviations for $[Re_2Br_2(CO)_6(Sb_2Ph_4)]$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Re(1)	0.846 74(14)	0.110 40(8)	0.164 60(11)	C(19)	0.587(2)	0.148(1)	0.135(2)
Re(2)	0.782 47(13)	0.110 65(9)	−0.047 92(10)	C(20)	0.511(2)	0.181(1)	0.103(2)
Re(3)	0.866 28(14)	0.124 54(8)	0.656 93(11)	C(21)	0.434(2)	0.158(1)	0.105(2)
Re(4)	0.760 61(13)	0.107 21(9)	0.446 39(10)	C(22)	0.431(2)	0.103(1)	0.138(2)
Sb(1)	0.700 9(2)	0.177 7(1)	0.123 4(2)	C(23)	0.506(2)	0.070(1)	0.170(2)
Sb(2)	0.657 1(2)	0.180 6(1)	−0.027 1(2)	C(24)	0.584(2)	0.093(1)	0.168(2)
Sb(3)	0.721 0(2)	0.191 0(1)	0.632 0(2)	C(25)	0.532(2)	0.146(1)	−0.063(1)
Sb(4)	0.645 8(2)	0.179 0(1)	0.481 4(2)	C(26)	0.462(2)	0.182(1)	−0.102(1)
Br(1)	0.761 2(3)	0.040 4(2)	0.055 0(3)	C(27)	0.381(2)	0.157(1)	−0.129(1)
Br(2)	0.887 7(3)	0.171 0(2)	0.063 5(3)	C(28)	0.368(2)	0.096(1)	−0.117(1)
Br(3)	0.766 2(3)	0.046 5(2)	0.564 4(3)	C(29)	0.438(2)	0.060(1)	−0.078(1)
Br(4)	0.878 1(3)	0.175 8(2)	0.538 3(3)	C(30)	0.519(2)	0.085(1)	−0.051(1)
O(1)	1.012(2)	0.035(1)	0.202(2)	C(31)	0.634(2)	0.273(1)	−0.062(2)
O(2)	0.935(2)	0.202(1)	0.284(2)	C(32)	0.660(2)	0.294(1)	−0.118(2)
O(3)	0.790(2)	0.039(1)	0.268(2)	C(33)	0.646(2)	0.355(1)	−0.139(2)
O(4)	0.924(2)	0.023(1)	−0.055(2)	C(34)	0.606(2)	0.394(1)	−0.105(2)
O(5)	0.664(2)	0.033(1)	−0.164(2)	C(35)	0.579(2)	0.372(1)	−0.049(2)
O(6)	0.815(2)	0.193(1)	−0.160(1)	C(36)	0.593(2)	0.312(1)	−0.028(2)
O(7)	1.015(2)	0.039(1)	0.672(2)	C(37)	0.717(2)	0.282(1)	0.658(2)
O(8)	0.982(2)	0.221(1)	0.748(2)	C(38)	0.648(2)	0.319(1)	0.620(2)
O(9)	0.837(2)	0.060(1)	0.783(2)	C(39)	0.647(2)	0.380(1)	0.639(2)
O(10)	0.905(2)	0.024(1)	0.434(2)	C(40)	0.715(2)	0.404(1)	0.694(2)
O(11)	0.632(2)	0.022(1)	0.347(2)	C(41)	0.784(2)	0.368(1)	0.732(2)
O(12)	0.754(2)	0.183(1)	0.314(2)	C(42)	0.785(2)	0.307(1)	0.713(2)
C(1)	0.950(3)	0.063(2)	0.191(2)	C(43)	0.627(2)	0.154(1)	0.671(1)
C(2)	0.903(3)	0.164(2)	0.239(2)	C(44)	0.586(2)	0.192(1)	0.706(1)
C(3)	0.813(3)	0.067(2)	0.226(2)	C(45)	0.520(2)	0.170(1)	0.728(1)
C(4)	0.871(3)	0.059(2)	−0.051(2)	C(46)	0.495(2)	0.110(1)	0.716(1)
C(5)	0.706(3)	0.064(2)	−0.123(2)	C(47)	0.536(2)	0.071(1)	0.682(1)
C(6)	0.798(3)	0.159(2)	−0.117(2)	C(48)	0.602(2)	0.093(1)	0.659(1)
C(7)	0.959(3)	0.073(2)	0.667(2)	C(49)	0.523(1)	0.146(1)	0.476(1)
C(8)	0.942(3)	0.179(2)	0.720(2)	C(50)	0.468(1)	0.181(1)	0.500(1)
C(9)	0.851(3)	0.084(2)	0.736(3)	C(51)	0.388(1)	0.159(1)	0.497(1)
C(10)	0.847(3)	0.057(2)	0.437(2)	C(52)	0.363(1)	0.101(1)	0.469(1)
C(11)	0.674(3)	0.057(2)	0.385(2)	C(53)	0.418(1)	0.066(1)	0.445(1)
C(12)	0.755(3)	0.150(2)	0.365(3)	C(54)	0.498(1)	0.088(1)	0.448(1)
C(13)	0.707(2)	0.269(1)	0.159(2)	C(55)	0.624(2)	0.272(1)	0.447(1)
C(14)	0.662(2)	0.294(1)	0.201(2)	C(56)	0.695(2)	0.309(1)	0.466(1)
C(15)	0.669(2)	0.356(1)	0.218(2)	C(57)	0.686(2)	0.371(1)	0.451(1)
C(16)	0.722(2)	0.393(1)	0.193(2)	C(58)	0.605(2)	0.395(1)	0.416(1)
C(17)	0.768(2)	0.368(1)	0.152(2)	C(59)	0.533(2)	0.357(1)	0.397(1)
C(18)	0.761(2)	0.306(1)	0.135(2)	C(60)	0.543(2)	0.296(1)	0.413(1)

was noted in the reaction mixture and unreacted $[Re_2Br_2(CO)_6(thf)_2]$ remained at the end of the treatment (from i.r. carbonyl stretching region). Table 1 reports the analytical data and i.r. spectra of the complexes in the carbonyl stretching region.

Reaction of $[Re_2Br_2(CO)_6(P_2Ph_4)]$ *with* PPh_2^-.—A thf solution of $Na(PPh_2)$ was prepared by a slight modification of the reported method[9] by reducing PPh_2Cl (0.597 g, 2.71 mmol) with the equivalent amount of sodium sand (0.115 g, 5.00 mmol) in thf (50 cm^3). To the resulting orange solution, $[Re_2Br_2(CO)_6(P_2Ph_4)]$ (0.432 g, 0.404 mmol) was added. The colour of the solution immediately turned to yellow and the i.r. spectrum showed bands at 2 011s, 1 994m, 1 944m, 1 908s, and 1 879m cm^{-1}, due to the $[Re(PPh_2)_3(CO)_3]^{2-}$ anion. The yellow solution was filtered and CH_3I (0.228 g, 1.616 mmol; $CH_3I : P = 0.65 : 1$) was added. This caused the precipitation of the colourless complex $[Re(PPh_2Me)_3(CO)_3]I$, which was collected by filtration and dried *in vacuo* to give a 43.4% yield (Found: C, 50.9; H, 4.2; I, 13.1; P, 9.8. Calc. for $C_{42}H_{39}IO_3P_3Re$: C, 50.6; H, 3.9; I, 12.7; P, 9.3%). The same compound was obtained when $[Re_2Br_2(CO)_6(thf)_2]$ (0.564 g, 0.668 mmol)

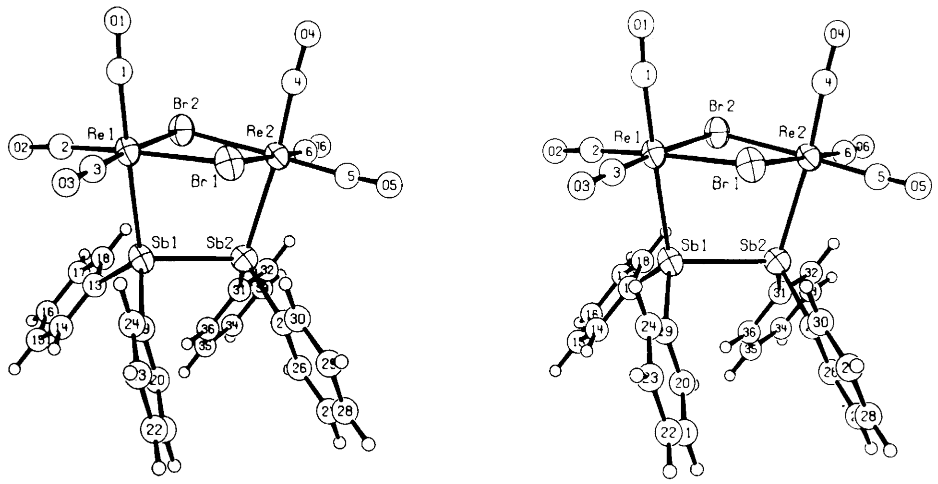

Figure 1. Stereoscopic view of one of the two $[Re_2Br_2(CO)_6(Sb_2Ph_4)]$ molecules comprising the asymmetric unit. To obtain the atomic labelling for the other molecule add 1 to the numbers of the six heavy atoms, 6 to the carbonyl atoms, and 24 to the phenyl atoms

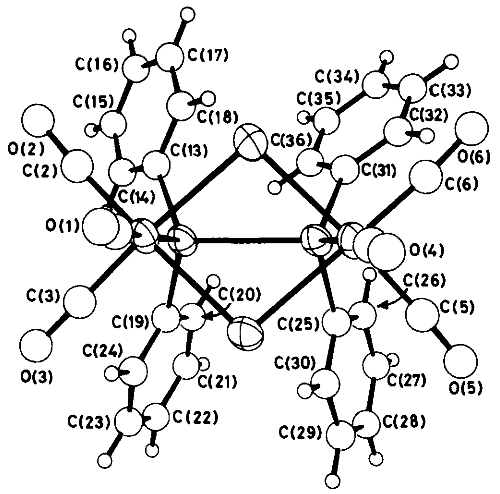

Figure 2. View from above the Re_2Br_2 section of $[Re_2Br_2(CO)_6(Sb_2Ph_4)]$ showing the orientation of the phenyl rings in one molecule

Table 3. Interatomic distances (Å) and bond angles (°) for $[Re_2Br_2(CO)_6(Sb_2Ph_4)]$ *

Re–Br	2.663(4)	C–O	1.19(4)
Re–Sb	2.726(3)	Re · · · Re	3.970(2)
Re–C	1.87(4)	Br · · · Br	3.531(3)
Sb–Sb	2.826(4)	Br · · · Sb	3.640(3)
Sb–C	2.12(2)		

Br–Re–Br	83.1(1)	Re–Br–Re	96.4(1)
Br–Re–Sb	84.9(1)	Re–Sb–Sb	102.1(1)
Br–Re–C	177(1)	Re–Sb–C	120.9(8)
Br–Re–C	91(1)	Sb–Sb–C	104.2(7)
Sb–Re–C	174(1)	C–Sb–C	102(1)
Sb–Re–C	94(1)	Re–C–O	175(3)

* Averages of the values in the two independent molecules.

was treated with a thf (50 cm^3) solution containing 4.06 mmol of PPh_2^-, followed by filtration and addition of CH_3I (3.87 g, 27.3 mmol), yield 52.8%.

X-Ray Data Collection and Reduction.—The arsenic derivative $[Re_2Br_2(CO)_6(As_2Ph_4)]$ was recrystallized from toluene and attempts were made to determine its structure. However, both the poor quality of the crystals and disorder in the molecule did not allow the study to be carried out to completion.

Single crystals of the antimony derivative $[Re_2Br_2(CO)_6(Sb_2Ph_4)]$ were obtained by recrystallization from toluene. A single crystal having approximate dimensions 0.52 × 0.32 × 0.28 mm was chosen for *X*-ray diffraction study. An Enraf-Nonius CAD-4 automatic diffractometer was used with Mo-K_α radiation monochromatized by a dense graphite crystal assumed for all purposes to be ideally imperfect.

Crystal data. $C_{30}H_{20}Br_2O_6Re_2Sb_2$, M = 1 252.2, monoclinic, space group $P2_1/n$, a = 16.585(8), b = 22.036(13), c = 19.764(19) Å, β = 109.34(6)°, U = 6 815 Å^3, Z = 8, $F(000)$ = 4 560, D_c = 2.44 g cm^{-3}, λ = 0.710 73 Å, μ = 116 cm^{-1}.

The Läue symmetry was determined to be $2/m$ and from the systematic absences the space group was unambiguously shown to be $P2_1/n$, an alternative setting of the conventional $P2_1/c$. Intensities in the range $4 \leqslant 2\theta \leqslant 32°$ were measured using the θ—2θ scan technique with a scan width of $\Delta\theta = (0.90 + 0.35 \sin\theta)$ and maximum scan time 240 s. The scan rate (range 0.4—5.0° min^{-1}) depended on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored periodically during the course of the data collection, and they were found to undergo no significant change of intensity. A total of 3 640 data were collected, 2 197 of which were considered observed [$I > 3\sigma(I)$] and used in the refinement. In reducing the data, Lorentz and polarization factors were applied, as well as an analytical absorption correction based on crystal geometry.

The structure was solved by use of MULTAN,[10] which revealed the positions of all 12 of the heavy atoms of the two unique molecules in the asymmetric unit. The remaining atoms were easily located in difference-Fourier syntheses. Since there were so many atoms involved for the amount of observed data, it was decided to treat the phenyl rings, hydrogens included, as rigid bodies. Of the remaining atoms, the 12 heavy ones were refined anisotropically and the carbonyl groups isotropically. After all the shift to e.s.d. ratios were less than 0.1, the refinement converged to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.040$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.040$ using the weighting scheme $w = \sigma(F)^{-2}$. The atomic scattering factors used were computed from numerical Hartree-Fock wavefunctions;[11] for hydrogen, those of Stewart *et al.*[12] were used. The anomalous dispersion coefficients of Cromer and Liber-

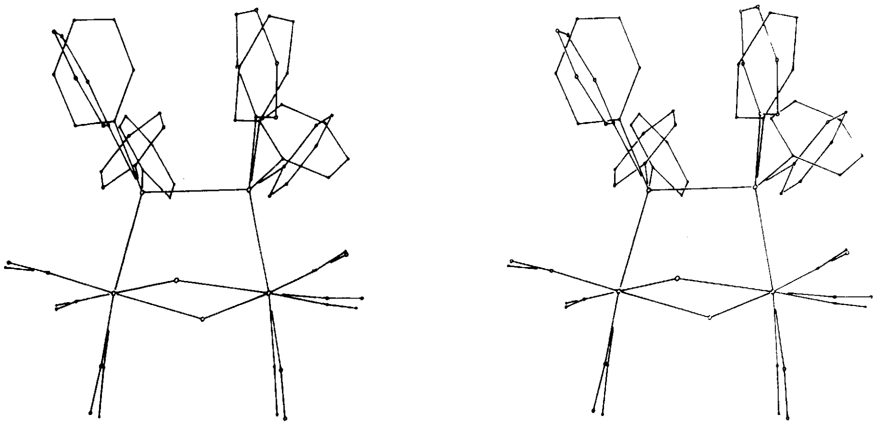

Figure 3. Stereoscopic comparison of the two independent molecular geometries of $[Re_2Br_2(CO)_6(Sb_2Ph_4)]$. The $Re_2Br_2Sb_2$ fragments have been superimposed; the open circles are for molecule 1 (compare with Figure 1) and the filled circles for molecule 2. The opposite cant of the phenyls from one molecule to the other is clear

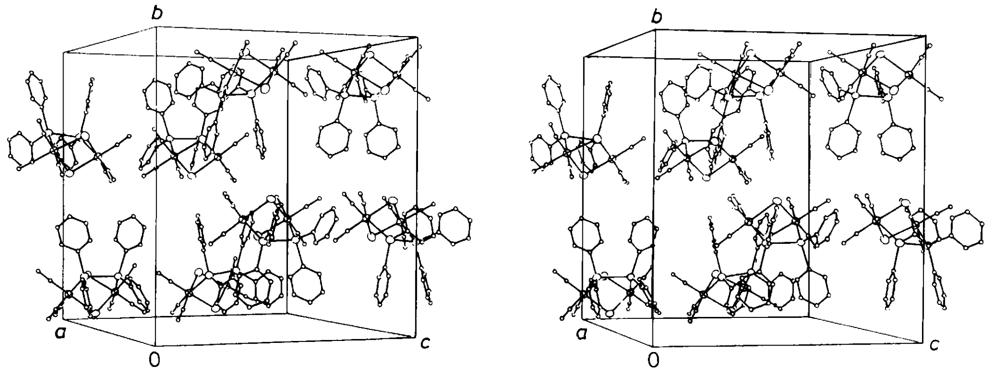

Figure 4. Stereoscopic view of the molecular packing in the unit cell. Note how pairs of molecules along *c* show oppositely twisted phenyls

man[13] were used for Re, Br, and Sb. Bond lengths and angles are given in Table 3, based on the positional parameters of Table 2. Figure 1 shows one of the two molecules of the asymmetric unit, together with the numbering scheme used. Other views of the compound and of the crystal packing are in Figures 2—4.

Results and Discussion

The compounds reported in this paper have been obtained by reactions (1) and (2) using toluene as solvent.

$$[Re_2Br_2(CO)_6(thf)_2] + E_2Ph_4 \longrightarrow [Re_2Br_2(CO)_6(E_2Ph_4)] + 2\,thf \quad (1)$$
$$(E = As\ or\ Sb)$$

$$[Re_2I_2(CO)_8] + E_2Ph_4 \longrightarrow [Re_2I_2(CO)_6(E_2Ph_4)] + 2\,CO \quad (2)$$
$$(E = P,\ As,\ or\ Sb)$$

The complex $[Re_2Br_2(CO)_6(P_2Ph_4)]$ reported in an earlier publication[1b] has also been obtained according to equation (1). The products, which may be regarded as arising from the co-ordinative addition of E_2Ph_4 to rhenium(I), appear to be characterized by a decreasing stability from phosphorus to antimony through arsenic. This is qualitatively substantiated by the observations concerning the displacement reaction (3).

$$[Re_2X_2(CO)_6(E_2Ph_4)] + 4\,thf \rightleftarrows 2\,[ReX(CO)_3(thf)_2] + E_2Ph_4 \quad (3)$$

Complete reaction to the thf adduct was found in the case of X = Br, E = Sb, while both the thf and the E_2Ph_4 derivatives were detected spectroscopically in solution in the case of X = Br, E = As and X = I, E = Sb. On the other hand, no displacement of E_2Ph_4 was observed with X = Br, E = P and with X = I, E = P or As. That the failure of the P_2Ph_4 derivative to react was not due to some kinetic barrier was shown by the fact that the phosphorus adduct could be obtained according to reaction (1) in thf as solvent. Moreover, the data confirm that the stability of the complexes probably increases from bromide to iodide. Increased stabilities in the sequence P > As > Sb > Bi have usually been found for transition metal complexes,[14] thus our results seem to conform to this Group trend. In agreement with this, no stable complex could be obtained from $[Re_2Br_2(CO)_6(thf)_2]$ and the newly prepared[6] Bi_2Ph_4. The decomposition of the latter, presumably to $BiPh_3$ and elemental bismuth, was found to be accelerated by the presence of the rhenium(I) complex. A possible explanation of this fact may arise from the transitory formation of an unstable $[Re_2Br_2(CO)_6(Bi_2Ph_4)]$ containing an ever looser Bi–Bi bond as a result of electron donation to the metal. Disproportionation to BiR_3 and elemental bismuth is the usually observed decomposition path for Bi_2R_4 (R = Me or Et) complexes.[15] Although a few complexes of Sb_2Ph_4 have been reported in the literature,[16] structural information

Table 4. Mass spectra of the complexes [$Re_2Br_2(CO)_6(E_2Ph_4)$] (E = P, As, or Sb)

	E = P		E = As		E = Sb	
Ion	Mass	Intensity (%)	Mass	Intensity (%)	Mass	Intensity (%)
[$Re_2Br_2(CO)_6(E_2Ph_4)$]	1 066	26	1 154	81	1 246	37
$Re_2Br_2(CO)_5(E_2Ph_4)$	1 038	18	1 126	40	1 218	12
$Re_2Br_2(CO)_4(E_2Ph_4)$	1 010	62	1 098	62	1 190	6
$Re_2Br_2(CO)_3(E_2Ph_4)$	982	15	1 070	24	1 162	14
$Re_2Br_2(CO)_2(E_2Ph_4)$	954	100	1 042	24	1 134	9
$Re_2Br_2(CO)(E_2Ph_4)$	926	2	1 014	23	1 106	12
$Re_2Br_2(E_2Ph_4)$	898	64	986	51	1 078	19
$Re_2Br_2(E_2Ph_3)$	821	45	—		—	
$Re_2Br_2(CO)_6(EPh_2)$	—		925	24	971	100
$Re_2Br_2(CO)_5(EPh_2)$	—		897	21	943	25
$Re_2Br_2(CO)_4(EPh_2)$	—		869	16	915	<5
$Re_2Br_2(CO)_3(EPh_2)$	797	<1	841	13	887	8
$Re_2Br_2(CO)_2(EPh_2)$	769	2	813	5	859	<5
$Re_2Br_2(E_2Ph_2)$	744	2	—		—	
$Re_2Br(E_2Ph_3)$	742	3	—		—	
$Re_2Br_2(CO)(EPh_2)$	741	15	785	8	831	6
$Re_2(E_2Ph_4)$	740	7	—		—	
$Re_2Br_2(EPh_2)$	713	13	757	51	803	25
$Re_2Br_2(CO)_6(EPh)$	—		—		894	<1
$Re_2Br_2(CO)_5(EPh)$	—		—		866	<1
$Re_2Br_2(CO_4(EPh)$	—		—		838	<1
$Re_2Br_2(CO)_3(EPh)$	—		—		810	18
$Re_2Br_2(CO)_2(EPh)$	—		—		782	25
$Re_2Br_2(CO)(EPh)$	—		—		754	21
$Re_2Br_2(EPh)$	—		680	100	726	56
$Re_2(E_2Ph_3)$	663	13	—		—	
Re_2Br_2E	—		603	8	649	25
$Re_2(EPh_2)$	555	6	—		—	
$ReBr(CO)_3(EPh_2)$	533	21	—		—	
$ReBr(CO)_2(EPh_2)$	505	5	—		—	
$ReBr(CO)(EPh_2)$	477	5	—		—	
$ReBr(EPh_2)$	449	18	493	38	539	18
$ReBr(EPh)$	—		416	70	462	24
$ReBrE$	—		—		385	6

about them is still limited.[16b] It was then decided to study the complex [$Re_2Br_2(CO)_6(Sb_2Ph_4)$] by *X*-ray diffraction methods. As shown in Figure 1, the molecular structure has two rhenium atoms each in a distorted octahedral environment consisting of three carbonyl groups, two bridging bromides, and an antimony atom of the Sb–Sb bridge. The Re–Br distance of 2.663(4) Å (average) compares quite well with values found for other complexes of the same series with P_2Ph_4,[1b] S_2Ph_2,[1c] Se_2Ph_2,[1d] and Te_2Ph_2.[1e] The Sb–Sb distance of 2.826(4) Å (see Table 3) is somewhat shorter than in the uncomplexed molecule [17] [2.837(1) Å] and in the complex [{$Cr(CO)_5$}$_2$(Sb_2Ph_4)] [2.866(1) Å].[16b] This is somewhat unusual for complexes of E_2Ph_{2n} ligands, for which a lengthening of the E–E bond upon complexation was regularly observed both for P_2Ph_4 [1b] and for chalcogenides.[1c–e]

Of considerable interest is the folding angle, *i.e.* the angle between the normals to the Re–Br–Br planes (10.7°, averaged over the two independent molecules). This finding confirms that the major factor in determining the folding angle is the E–E distance of the bridge. As a matter of fact, the folding angle in this antimony derivative is the same, within experimental error, as that of the Te_2Ph_2 derivative [1d] [folding angle is 10.7° with a Te–Te distance of 2.794(5) Å]. Although chemical evidence suggests, as mentioned above, a decreased stability on going from the phosphorus to the antimony derivative, this is not substantiated by a corresponding increase of the apparent covalent radius of the metal. Application of the r_M relationship [1g] ($r_M = r_{Re-E} - \frac{1}{2}r_{E-E}$) to the Re–P and Re–Sb cases gives apparent metal radii, 1.354 and 1.313 Å respectively, with a small and perhaps scarcely significant decrease from the lighter to heavier donor atom.

The Re–P complex [$Re_2Br_2(CO)_6(P_2Ph_4)$] has been found to undergo nucleophilic attack by PPh_2^-, according to the stoicheiometry of equation (4). The dianion has not been

$$[Re_2Br_2(CO)_6(P_2Ph_4)] + 6\ PPh_2^- \xrightarrow{thf} 2\ [Re(PPh_2)_3(CO)_3]^{2-} + P_2Ph_4 + 2\ Br^- \quad (4)$$

isolated and the i.r. spectrum in solution shows more bands than expected for the C_{3v} symmetry ($A_1 + E$) of the *fac* structure. The existence of intermediate solvated products of lower substitution, such as [$Re(PPh_2)_2(CO)_3(thf)$]$^-$, or of the *mer* isomer, may be responsible for the higher number of carbonyl stretching bands. An alternative explanation is the presence in solution of a species resulting from distortion by the cation, a frequent case in alkali carbonylmetalates,[18] in addition to the unperturbed one. Whatever the nature of the carbonyl species in solution is, it must contain terminal PPh_2 groups of sufficiently high nucleophilicity to react with methyl iodide [equation (5)]. The same product was obtained

$$[Re(PPh_2)_3(CO)_3]^{2-} + 3\ CH_3I \longrightarrow [Re(PPh_2Me)_3(CO)_3]I + 2\ I^- \quad (5)$$

by treatment of the thf adduct [$ReBr(CO)_3(thf)_2$] with PPh_2^- [equation (6)] followed by reaction (5) with methyl iodide.

$$[ReBr(CO)_3(thf)_2] + 3\ PPh_2^- \longrightarrow [Re(PPh_2)_3(CO)_3]^{2-} + 2\ thf + Br^- \quad (6)$$

The ionic nature of the iodide obtained by reaction (5) is indicated by its low solubility in organic solvents, and by the fact that the dichloromethane solution of the compound shows only two carbonyl bands at 2 042s and 1 961s cm^{-1} in agreement with the C_{3v} symmetry of the *fac* structure, thus making a seven-co-ordinate structure of lower symmetry less probable. It is worth noting that a limited number of metal complexes containing *terminal* PR_2 groups have been reported in the literature [19] and most of them contain electron-withdrawing R groups such as perfluoroalkyl. Thus, the compound obtained by reactions (4) and (6) is one of the few examples known.

The i.r. spectra of the [$Re_2Br_2(CO)_6(E_2Ph_4)$] complexes in the carbonyl stretching region confirm the earlier findings [1g] concerning the i.r. activity of the carbonyl stretching vibration as a function of the folding angle. As was the case with the Te_2Ph_2-bridged complexes of both manganese[1e] and rhenium,[1e] the fifth stretching vibration expected for compounds having C_{2v} symmetry ($2A_1 + 2B_1 + B_2$) is found for the Sb_2Ph_4 derivative as a well separated band at *ca.* 1 955 cm^{-1}. It is notable that the Sb_2Ph_4 compound shares with the Te_2Ph_2 derivatives mentioned above [1g,1e] a small folding angle of the Re_2Br_2 moiety along the line of the Br ··· Br vector. Relevant to this point is the observation that the compound [$Re_2Cl_2(CO)_6(Ph_2AsCH_2AsPh_2)$], whose Re_2Cl_2 fragment is only slightly distorted from planarity,[20] shows five well defined i.r.

carbonyl stretching vibrations[21] in n-heptane at 2 058m, 2 040m, 1 966m, 1 951m, and 1 928s cm^{-1}.

Finally, the mass spectral data of the rhenium complexes (see Table 4) may give some indication concerning the relative stability of these complexes. For instance, the peak of highest intensity in the phosphorus derivative is that resulting from the loss of four carbonyl groups, whereas the most intense fragments of the arsenic and antimony complexes are those arising from the loss of a EPh_2 group, in agreement with the alleged lower stability of the Re–E bond.

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