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

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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  $[Re_2I_2(CO)_6]$  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,  $\beta = 109.34(6)^\circ$ , 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),  $Sb \cdots Br$  3.640(3),  $Re \cdots Re$  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  $Br \cdots Br$  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  $Te;$   $M = Mn^{1g}$ ,  $X = Br, n = 2, E = As;$   $M = Mn^{1h}$ ,  $X = I, n = 2, E = P$ ) 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<sup>2</sup> 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  $\pm 1$   $cm^{-1}$ . 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,<sup>3</sup> arsenic,<sup>4</sup> antimony,<sup>5</sup> and bismuth<sup>6</sup> were prepared according

† Di- $\mu$ -bromo- $\mu$ -tetraphenyldistibane-bis[tricarboxylrhenium(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.

to literature methods. The rhenium complex  $[Re_2Br_2(CO)_6(thf)_2]$  was prepared as previously described.<sup>7</sup>  $[Re_2I_2(CO)_6]$  was prepared from  $[Re_2(CO)_{10}]$  and di-iodine in equimolar amounts at 20 °C under ultraviolet irradiation as previously reported,<sup>8</sup> except that solutions 10 times more concentrated were used.<sup>1f</sup> The tetraphenyldiphosphane complex  $[Re_2Br_2(CO)_6(P_2Ph_4)]$  was prepared according to an earlier paper.<sup>1b</sup>

**Preparation of  $[Re_2I_2(CO)_6(P_2Ph_4)]$ .**—The dimeric iodo-derivative  $[Re_2I_2(CO)_6]$  (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  $[Re_2I_2(CO)_6]$  (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<sup>6</sup> (0.100 g, 0.137 mmol) in toluene (10  $cm^3$ ) at room temperature for a few min. A black precipitate

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

Compound	Colour	Analysis <sup>a</sup> (%)			$\nu(\text{CO})^b/\text{cm}^{-1}$
		C	H	Halogen	
$[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{As}_2\text{Ph}_4)]$	Pale yellow	32.0 (31.1)	2.0 (1.7)	13.4 (13.8)	2 051m, 2 038s, 2 023w <sup>c</sup> , 1 960s, 1 955 (sh), 1 924s
$[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Sb}_2\text{Ph}_4)]$	Yellow	29.3 (28.8)	1.8 (1.6)	12.6 (12.8)	2 050s, 2 035s, 2 021w <sup>c</sup> , 1 959s, 1 952m, 1 924s
$[\text{Re}_2\text{I}_2(\text{CO})_6(\text{P}_2\text{Ph}_4)]$	Green-yellow	31.4 (30.9)	1.7 (1.7)	22.4 (21.8) <sup>d</sup>	2 049m, 2 036s, 2 019w <sup>c</sup> , 1 960s, 1 925s
$[\text{Re}_2\text{I}_2(\text{CO})_6(\text{As}_2\text{Ph}_4)]$	Yellow	29.0 (28.8)	1.5 (1.6)	20.4 (20.3)	2 049m, 2 036s, 2 022w <sup>c</sup> , 1 959s, 1 926s
$[\text{Re}_2\text{I}_2(\text{CO})_6(\text{Sb}_2\text{Ph}_4)]$	Yellow	27.2 (26.8)	1.5 (1.5)	19.4 (18.8)	2 046m, 2 033s, 2 019w <sup>c</sup> , 1 959s, 1 955 (sh), 1 926s

<sup>a</sup> Calculated values in parentheses. <sup>b</sup>  $\text{CCl}_4$  as solvent. <sup>c</sup> Assigned to a  $^{13}\text{CO}$  vibration. <sup>d</sup> P = 5.3 (5.3%).

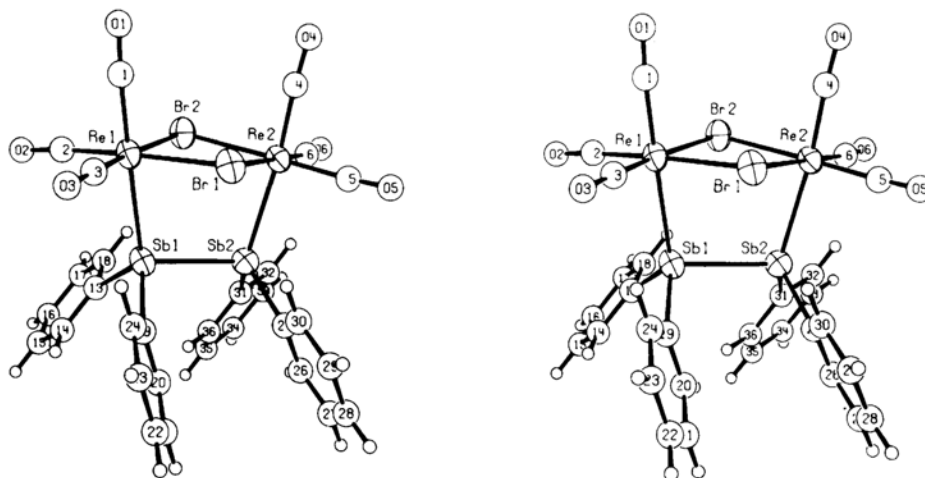
**Table 2.** Fractional atomic co-ordinates and their estimated standard deviations for  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Sb}_2\text{Ph}_4)]$ 

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)

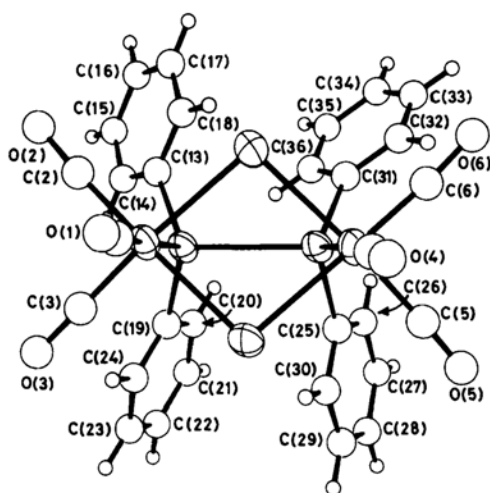
was noted in the reaction mixture and unreacted  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{thf})_2]$  remained at the end of the treatment (from i.r. carbonyl stretching region). Table 1 reports the analytical data and i.r. spectra of the complexes in the carbonyl stretching region.

**Reaction of  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{P}_2\text{Ph}_4)]$  with  $\text{PPh}_2^-$ .**—A thf solution of  $\text{Na}(\text{PPh}_2)$  was prepared by a slight modification of the reported method <sup>9</sup> by reducing  $\text{PPh}_2\text{Cl}$  (0.597 g, 2.71 mmol) with the equivalent amount of sodium sand (0.115 g, 5.00 mmol) in thf (50  $\text{cm}^3$ ). To the resulting orange solution,

$[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{P}_2\text{Ph}_4)]$  (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  $\text{cm}^{-1}$ , due to the  $[\text{Re}(\text{PPh}_2)_3(\text{CO})_3]^{2-}$  anion. The yellow solution was filtered and  $\text{CH}_3\text{I}$  (0.228 g, 1.616 mmol;  $\text{CH}_3\text{I} : \text{P} = 0.65 : 1$ ) was added. This caused the precipitation of the colourless complex  $[\text{Re}(\text{PPh}_2\text{Me})_3(\text{CO})_3]\text{I}$ , 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  $\text{C}_{42}\text{H}_{39}\text{IO}_3\text{P}_3\text{Re}$ : C, 50.6; H, 3.9; I, 12.7; P, 9.3%). The same compound was obtained when  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{thf})_2]$  (0.564 g, 0.668 mmol)



**Figure 1.** Stereoscopic view of one of the two  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Sb}_2\text{Ph}_4)]$  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  $\text{Re}_2\text{Br}_2$  section of  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Sb}_2\text{Ph}_4)]$  showing the orientation of the phenyl rings in one molecule

was treated with a thf (50 cm<sup>3</sup>) solution containing 4.06 mmol of  $\text{PPh}_2^-$ , followed by filtration and addition of  $\text{CH}_3\text{I}$  (3.87 g, 27.3 mmol), yield 52.8%.

**X-Ray Data Collection and Reduction.**—The arsenic derivative  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{As}_2\text{Ph}_4)]$  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  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Sb}_2\text{Ph}_4)]$  were obtained by recrystallization from toluene. A single crystal having approximate dimensions  $0.52 \times 0.32 \times 0.28$  mm was chosen for X-ray diffraction study. An Enraf-Nonius CAD-4 automatic diffractometer was used with  $\text{Mo-K}\alpha$  radiation monochromatized by a dense graphite crystal assumed for all purposes to be ideally imperfect.

**Crystal data.**  $\text{C}_{30}\text{H}_{20}\text{Br}_2\text{O}_6\text{Re}_2\text{Sb}_2$ ,  $M = 1252.2$ , monoclinic, space group  $P2_1/n$ ,  $a = 16.585(8)$ ,  $b = 22.036(13)$ ,  $c = 19.764(19)$  Å,  $\beta = 109.34(6)^\circ$ ,  $U = 6815$  Å<sup>3</sup>,  $Z = 8$ ,  $F(000) = 4560$ ,  $D_c = 2.44$  g cm<sup>-3</sup>,  $\lambda = 0.71073$  Å,  $\mu = 116$  cm<sup>-1</sup>.

The Laue symmetry was determined to be  $2/m$  and from the systematic absences the space group was unambiguously

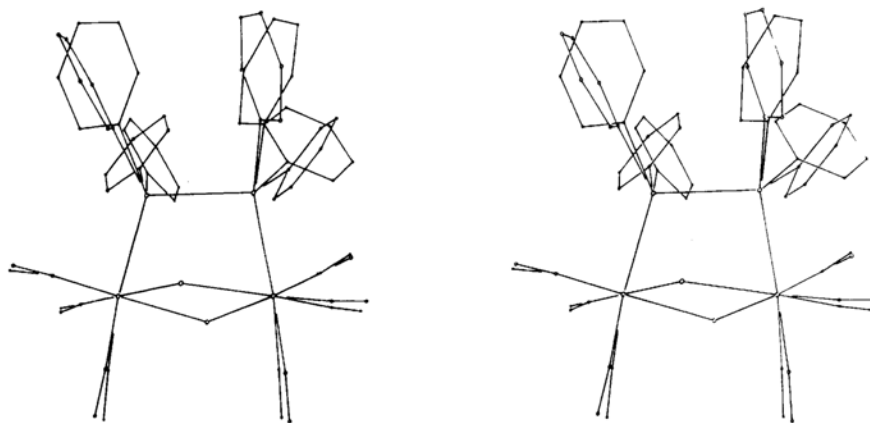
**Table 3.** Interatomic distances (Å) and bond angles ( $^\circ$ ) for  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Sb}_2\text{Ph}_4)]^*$

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)
Sb—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)

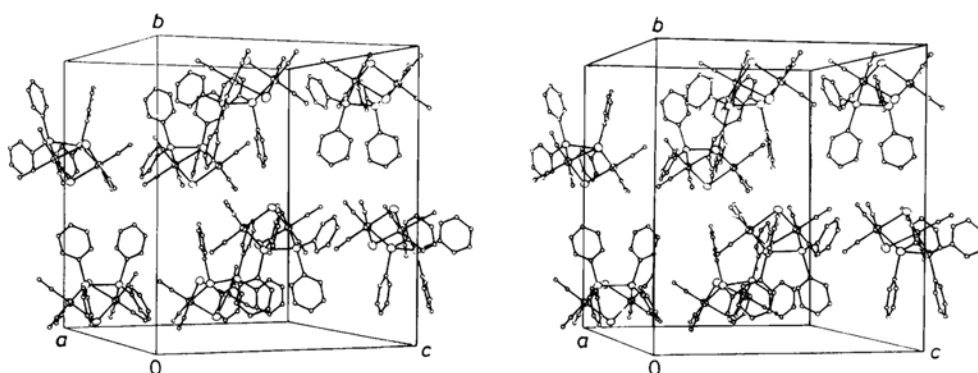
\* Averages of the values in the two independent molecules.

shown to be  $P2_1/n$ , an alternative setting of the conventional  $P2_1/c$ . Intensities in the range  $4 \leq 2\theta \leq 32^\circ$  were measured using the  $\theta$ — $2\theta$  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  $0.4$ — $5.0^\circ$  min<sup>-1</sup>) 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 3640 data were collected, 2197 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,<sup>10</sup> 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  $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.040$  using the weighting scheme  $w = \sigma(F)^{-2}$ . The atomic scattering factors used were computed from numerical Hartree-Fock wavefunctions;<sup>11</sup> for hydrogen, those of Stewart *et al.*<sup>12</sup> were used. The anomalous dispersion coefficients of Cromer and Liber-



**Figure 3.** Stereoscopic comparison of the two independent molecular geometries of  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Sb}_2\text{Ph}_4)]$ . The  $\text{Re}_2\text{Br}_2\text{Sb}_2$  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

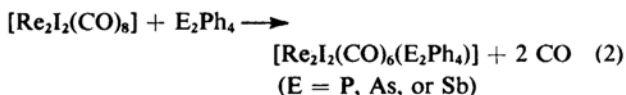
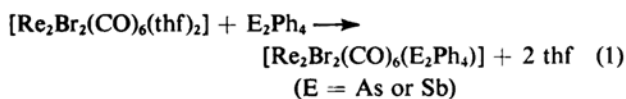


**Figure 4.** Stereoscopic view of the molecular packing in the unit cell. Note how pairs of molecules along  $c$  show oppositely twisted phenyls

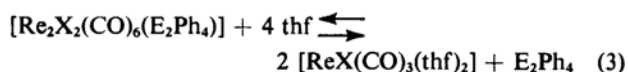
man<sup>13</sup> were used for Re, Br, and Sb. Bond lengths and angles are given in Table 3, based on the positional parameters of Table 2. Figure 1 shows one of the two molecules of the asymmetric unit, together with the numbering scheme used. Other views of the compound and of the crystal packing are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



The complex  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{P}_2\text{Ph}_4)]$  reported in an earlier publication<sup>1b</sup> has also been obtained according to equation (1). The products, which may be regarded as arising from the co-ordinative addition of  $\text{E}_2\text{Ph}_4$  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).



Complete reaction to the thf adduct was found in the case of X = Br, E = Sb, while both the thf and the  $\text{E}_2\text{Ph}_4$  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  $\text{E}_2\text{Ph}_4$  was observed with X = Br, E = P and with X = I, E = P or As. That the failure of the  $\text{P}_2\text{Ph}_4$  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  $\text{P} > \text{As} > \text{Sb} > \text{Bi}$  have usually been found for transition metal complexes,<sup>14</sup> thus our results seem to conform to this Group trend. In agreement with this, no stable complex could be obtained from  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{thf})_2]$  and the newly prepared<sup>6</sup>  $\text{Bi}_2\text{Ph}_4$ . The decomposition of the latter, presumably to  $\text{BiPh}_3$  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  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Bi}_2\text{Ph}_4)]$  containing an ever looser Bi–Bi bond as a result of electron donation to the metal. Disproportionation to  $\text{BiR}_3$  and elemental bismuth is the usually observed decomposition path for  $\text{Bi}_2\text{R}_4$  (R = Me or Et) complexes.<sup>15</sup> Although a few complexes of  $\text{Sb}_2\text{Ph}_4$  have been reported in the literature,<sup>16</sup> structural information

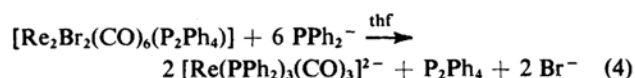
Table 4. Mass spectra of the complexes  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{E}_2\text{Ph}_4)]$  (E = P, As, or Sb)

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

about them is still limited.<sup>16b</sup> It was then decided to study the complex  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Sb}_2\text{Ph}_4)]$  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  $\text{P}_2\text{Ph}_4$ ,<sup>1b</sup>  $\text{S}_2\text{Ph}_2$ ,<sup>1c</sup>  $\text{Se}_2\text{Ph}_2$ ,<sup>1d</sup> and  $\text{Te}_2\text{Ph}_2$ .<sup>1e</sup> The Sb-Sb distance of 2.826(4) Å (see Table 3) is somewhat shorter than in the uncomplexed molecule<sup>17</sup> [2.837(1) Å] and in the complex  $[\{\text{Cr}(\text{CO})_5\}_2(\text{Sb}_2\text{Ph}_4)]$  [2.866(1) Å].<sup>16b</sup> This is somewhat unusual for complexes of  $\text{E}_2\text{Ph}_n$  ligands, for which a lengthening of the E-E bond upon complexation was regularly observed both for  $\text{P}_2\text{Ph}_4$ <sup>1b</sup> and for chalcogenides.<sup>1c-e</sup>

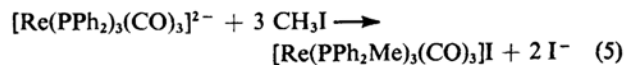
Of considerable interest is the folding angle, *i.e.* the angle between the normals to the Re-Br-Br planes (10.7°, averaged over the two independent molecules). This finding confirms that the major factor in determining the folding angle is the E-E distance of the bridge. As a matter of fact, the folding angle in this antimony derivative is the same, within experimental error, as that of the  $\text{Te}_2\text{Ph}_2$  derivative<sup>1d</sup> [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<sup>19</sup> ( $r_M = r_{\text{Re-E}} - \frac{1}{2}r_{\text{E-E}}$ ) 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  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{P}_2\text{Ph}_4)]$  has been found to undergo nucleophilic attack by  $\text{PPh}_2^-$ , according to the stoichiometry of equation (4). The dianion has not been

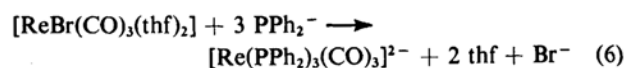


isolated and the i.r. spectrum in solution shows more bands than expected for the  $C_{3v}$  symmetry ( $A_1 + E$ ) of the *fac* structure. The existence of intermediate solvated products of lower substitution, such as  $[\text{Re}(\text{PPh}_2)_2(\text{CO})_3(\text{thf})]^-$ , or of the *mer* isomer, 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,<sup>18</sup> in addition to the unperturbed one. Whatever the nature of the carbonyl species in solution is, it must contain terminal  $\text{PPh}_2$  groups of sufficiently high nucleophilicity to react with methyl iodide [equation (5)]. The same product was obtained



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



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  $\text{cm}^{-1}$  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*  $\text{PR}_2$  groups have been reported in the literature<sup>19</sup> 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  $[\text{Re}_2\text{Br}_2(\text{CO})_6(\text{E}_2\text{Ph}_4)]$  complexes in the carbonyl stretching region confirm the earlier findings<sup>19</sup> concerning the i.r. activity of the carbonyl stretching vibration as a function of the folding angle. As was the case with the  $\text{Te}_2\text{Ph}_2$ -bridged complexes of both manganese<sup>1e</sup> and rhenium,<sup>1e</sup> the fifth stretching vibration expected for compounds having  $C_{2v}$  symmetry ( $2A_1 + 2B_1 + B_2$ ) is found for the  $\text{Sb}_2\text{Ph}_4$  derivative as a well separated band at *ca.* 1 955  $\text{cm}^{-1}$ . It is notable that the  $\text{Sb}_2\text{Ph}_4$  compound shares with the  $\text{Te}_2\text{Ph}_2$  derivatives mentioned above<sup>1e,1e</sup> a small folding angle of the  $\text{Re}_2\text{Br}_2$  moiety along the line of the  $\text{Br} \cdots \text{Br}$  vector. Relevant to this point is the observation that the compound  $[\text{Re}_2\text{Cl}_2(\text{CO})_6(\text{Ph}_2\text{AsCH}_2\text{AsPh}_2)]$ , whose  $\text{Re}_2\text{Cl}_2$  fragment is only slightly distorted from planarity,<sup>20</sup> shows five well defined i.r.

carbonyl stretching vibrations<sup>21</sup> in n-heptane at 2 058m, 2 040m, 1 966m, 1 951m, and 1 928s cm<sup>-1</sup>.

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<sub>2</sub> group, in agreement with the alleged lower stability of the Re-E bond.

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We wish to thank the National Research Council (C.N.R., Roma), the Robert A. Welch Foundation, and the U.S. National Science Foundation for support of this work. We also thank Dr. A. Morvillo, Istituto Chimica Analitica, University of Padova, for the mass spectral measurements.

### References

- (a) J. D. Korp, I. Bernal, J. L. Atwood, W. E. Hunter, F. Calderazzo, and D. Vitali, *J. Chem. Soc., Chem. Commun.*, 1979, 576; (b) J. L. Atwood, J. K. Newell, W. E. Hunter, I. Bernal, F. Calderazzo, I. P. Mavani, and D. Vitali, *J. Chem. Soc., Dalton Trans.*, 1978, 1189; (c) I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *Gazz. Chim. Ital.*, 1976, 106, 971; (d) J. Korp, I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *J. Chem. Soc., Dalton Trans.*, 1979, 1492; (e) F. Calderazzo, D. Vitali, R. Poli, J. L. Atwood, R. D. Rogers, J. M. Cummings, and I. Bernal, *ibid.*, 1981, 1004; (f) J. L. Atwood, I. Bernal, F. Calderazzo, L. G. Canada, R. Poli, R. D. Rogers, C. A. Veracini, and D. Vitali, *Inorg. Chem.*, 1983, 22, 1797; (g) F. Calderazzo, R. Poli, D. Vitali, J. D. Korp, I. Bernal, G. Pelizzi, J. L. Atwood, and W. E. Hunter, *Gazz. Chim. Ital.*, 1983, 113, 761.
- W. E. Dasent, 'Nonexistent Compounds,' Marcel Dekker, New York, 1965, p. 54.
- W. Kuchen and H. Buchwald, *Chem. Ber.*, 1958, 91, 2871.
- A. Tzschach and W. Lange, *Chem. Ber.*, 1962, 95, 1360.
- W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1962, 1490.
- F. Calderazzo, A. Morvillo, G. Pelizzi, and R. Poli, *J. Chem. Soc., Chem. Commun.*, 1983, 507.
- D. Vitali and F. Calderazzo, *Gazz. Chim. Ital.*, 1972, 102, 587.
- K. Moedritzer, *Synth. React. Inorg. Metal-Org. Chem.*, 1971, 1, 63.
- W. Kuchen and H. Buchwald, *Chem. Ber.*, 1959, 92, 227.
- G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, 27, 368.
- D. T. Cromer and S. B. Mann, *Acta Crystallogr., Sect. A*, 1968, 24, 321.
- R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, 42, 3175.
- D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, 53, 1891.
- (a) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1959, 1047; (b) R. J. Angelici and C. M. Ingemanson, *Inorg. Chem.*, 1969, 8, 83; (c) G. Innorta, G. Reichenbach, and A. Foffani, *J. Organomet. Chem.*, 1970, 22, 731; (d) L. E. Manzer and C. A. Tolman, *J. Am. Chem. Soc.*, 1975, 97, 1955; (e) R. R. Cordeman and J. L. Beauchamp, *ibid.*, 1976, 98, 3998; (f) S. Ahrlund, T. Berg, and P. Trinderup, *Acta Chem. Scand., Ser. A*, 1977, 31, 775; (g) G. Bellachioma, G. Reichenbach, and G. Cardaci, *J. Chem. Soc., Dalton Trans.*, 1980, 634.
- E. Wiberg and K. Mödritzer, *Z. Naturforsch., Teil B*, 1957, 12, 132; H. J. Breunig and D. Müller, *Angew. Chem.*, 1982, 94, 448; A. J. Ashe and E. G. Ludwig, *Organometallics*, 1982, 1, 1408; H. J. Breunig and D. Müller, *Z. Naturforsch., Teil B*, 1983, 38, 125.
- (a) H. Baumgarten, H. Johannsen, and D. Rehder, *Chem. Ber.*, 1979, 112, 2650; (b) J. Seyerl and G. Huttner, *Cryst. Struct. Commun.*, 1980, 9, 1099.
- K. Deuten and D. Rehder, *Cryst. Struct. Commun.*, 1980, 9, 167.
- W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Am. Chem. Soc.*, 1965, 87, 2563; W. F. Edgell and J. Lyford, *ibid.*, 1971, 93, 6407; M. Darensbourg and C. Borman, *Inorg. Chem.*, 1976, 15, 3121; M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *J. Am. Chem. Soc.*, 1976, 98, 3127; W. F. Edgell, S. Hedge, and A. Barbetta, *ibid.*, 1978, 100, 1406; M. Y. Darensbourg and J. M. Hanckel, *J. Organomet. Chem.*, 1981, 217, C9; F. Calderazzo, G. Pampaloni, and G. Pelizzi, *ibid.*, 1982, 233, C41.
- M. Cooke, M. Green, and D. Kirkpatrick, *J. Chem. Soc. A*, 1968, 1507; J. Grobe and R. Rau, *Z. Anorg. Allg. Chem.*, 1975, 414, 19.
- C. J. Commons and B. F. Hoskins, *Aust. J. Chem.*, 1975, 28, 1201.
- R. Colton and J. E. Garrard, *Aust. J. Chem.*, 1973, 26, 529.

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