Studies on Organometallic Hetero-multiple-bridged Molecules. Part 7.† Synthesis and Properties of Dichalcogenide-bridged Complexes of Rhenium(I) and the Crystal and Molecular Structures of the Diphenyl Ditelluride-bridged Complex, $[Re_2Br_2(CO)_6(Te_2Ph_2)]$ ‡

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By reaction of halogeno-carbonyl derivatives of rhenium(I) with the appropriate dichalcogenide E_2Ph_2 (E = S, Se, or Te), the dimeric rhenium(I) complexes $[Re_2X_2(CO)_6(E_2Ph_2)]$ (X = Br, E = Te; X = I, E = S, Se, or Te) have been prepared in good yields. The preparation of the tetrahydrofuran (thf) adduct $[Re_2I_2(CO)_6(thf)_2]$ is also reported. The crystal and molecular structures of one of these compounds, $[Re_2Br_2(CO)_6(Te_2Ph_2)]$, was solved by *X*-ray diffraction methods. The crystals are monoclinic, space group $P2_1/n$, with $a = 13.238(4)$, $b = 11.035(4)$, $c = 16.615(5)$ Å, $\beta = 91.29(3)°$, $U = 2\,426.5$ Å^3, $D_c = 3.04$ g cm^{-3} for $Z = 4$, and μ(Mo-K_α) = 165.2 cm^{-1}. Data collection yielded 1 782 observed reflections, $R = 0.079$. The molecular structure is of the hetero-multiple-bridged type, *i.e.* it consists of two pseudo-octahedral rhenium(I) centres joined by both bromide and Te_2Ph_2 bridges. Average distances are: Re–Br, 2.64(6), Te · · · Br, 3.674(6) Å, while Re · · · Re is 3.945(2) Å and Te–Te is 2.794(5) Å. Infrared spectra in the carbonyl stretching region have been compared for the two families of dichalcogenide derivatives $[Re_2X_2(CO)_6(E_2Ph_2)]$ and possible explanations for the observed decrease of $\tilde{\nu}$(CO) in the sequence S > Se > Te are discussed.

We have recently reported the preparation and crystal and molecular structure of E_2R_{2n}- and bromide-bridged complexes $[M_2Br_2(CO)_6(E_2R_{2n})]$ (M = Re, n = 1, E = S, R = Me,[1] Ph,[2] E = Se, R = Ph;[3] M = Mn,[4] Re,[5] n = 2, E = P, R = Ph). All of these compounds are characterized by bridging ligands of different nature and denticity and thus they belong to the category of hetero-multiple-bridged (h.m.b.) molecules. In the meantime a further case of organometallic h.m.b. molecules having Br and Se_2Me_2 units bridging two platinum(IV) centres has been reported.[6]

It was of interest to attempt the reaction of rhenium(I) with Te_2Ph_2 for two main reasons. Firstly, in view of the lower strength[7] of the Te–Te single bond it was conceivable that the reaction would proceed *via* oxidative addition across the Te–Te bond of Te_2Ph_2 rather than the simple co-ordinative addition observed until now; secondly, either one of the two reaction pathways would have produced new compounds having rhenium–tellurium bonds. These bonds are rare in the co-ordination chemistry of low-valent transition elements.[8]

This paper reports the preparation and the crystal and molecular structures of the product resulting from the co-ordinative addition of Te_2Ph_2 to rhenium(I), which represents the first example known in the literature of a molecule containing a Te_2Ph_2 bridge. Furthermore, we describe the iodo-analogues $[Re_2I_2(CO)_6(E_2Ph_2)]$ and the i.r. spectra in the carbonyl stretching region are presented.

EXPERIMENTAL

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were dried and purified by conventional methods. The i.r. spectra were measured with a Perkin-Elmer model 283 instrument. Each solution spectrum was recorded on an expanded abscissa scale and calibrated with CO; the wavenumber values are believed to be accurate to ±1 cm^{-1}.

The compound Te_2Ph_2 was prepared according to the literature method[9] by the reaction of MgPhBr with elemental tellurium and then with dry oxygen.

Preparation of $[Re_2Br_2(CO)_6(Te_2Ph_2)]$.—The tetrahydrofuran (thf) adduct $[Re_2Br_2(CO)_6(thf)_2]$ (2.0 g, 2.37 mmol) in toluene (20 cm^3) was treated with diphenyl ditelluride (0.98 g, 2.39 mmol) at room temperature: the addition of the ditelluride resulted in the prompt formation of a red solid suspended in a solution of the same colour. The mixture was stirred for *ca.* 10 h and then filtered. The precipitate of the crude $[Re_2Br_2(CO)_6(Te_2Ph_2)]$ was dried *in vacuo* (2.29 g, 87% yield). The compound was recrystallyzed from a benzene–heptane mixture. It is slightly soluble in CCl_4 and other halogenated solvents and sparingly soluble in aromatic and saturated hydrocarbons at room temperature. It reacts with tetrahydrofuran forming the thf adduct.[10,11] Molecular-weight determinations could not be carried out due to the low solubility.

Preparation of $[Re_2I_2(CO)_6(E_2Ph_2)]$.—The three complexes were prepared by the reaction of $[ReI(CO)_5]$[12] with a slight excess (see Table 1) of the dichalcogenide ligand, in toluene as solvent, at the reflux temperature of the solvent under slightly reduced pressure (temperature of the bath *ca.* 120 °C) to remove the evolved carbon monoxide. In the case of $[Re_2I_2(CO)_6(S_2Ph_2)]$, its preparation was also successfully carried out *via* thf displacement from $[Re_2I_2(CO)_6(thf)_2]$, see Table 1. The reactions were monitored by i.r. in the carbonyl stretching region. At intermediate stages, the presence of $[Re_2I_2(CO)_8]$ was substantiated by its typical $\tilde{\nu}$(CO) values. At the end of the reaction (S_2Ph_2 : 32 h; Se_2Ph_2: 19 h; Te_2Ph_2 : 12 h), the hot solution was filtered and $[Re_2I_2(CO)_6(S_2Ph_2)]$ and $[Re_2I_2(CO)_6(Se_2Ph_2)]$ were obtained as crystalline solids by cooling down to

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† Part 6 is ref. 3.

‡ Di-μ-bromo-μ-diphenyl ditelluride-bis[tricarbonylrhenium(I)].

room temperature. In the case of the sparingly soluble $[Re_2I_2(CO)_6(Te_2Ph_2)]$ no recrystallization was attempted and the compound was recovered from the reaction mixture by filtration after cooling to room temperature.

The three iodo-derivatives react with neat thf with displacement of the dichalcogenide ligand (see Results and Discussion section). The three compounds are not significantly affected by air in the solid state. The Nujol mull spectra of the three iodo-derivatives in the 400—4 000 cm^{-1} region are similar to each other and to those of the three bromo-complexes $[Re_2Br_2(CO)_6(E_2Ph_2)]$ for the bands of higher intensity.

TABLE 1

Preparation and analytical data of $[Re_2X_2(CO)_6(E_2Ph_2)]$ (X = Br or I; E = S, Se, or Te)

Compound	Method [a]	$[E_2Ph_2]/[Re]$ [b]	Yield (%)	Analysis (%) [c] C	H	X	E
$[Re_2Br_2(CO)_6(Te_2Ph_2)]$	A	0.50	87	20.0 (19.5)	0.95 (0.90)	14.1 (14.4)	n.d.
$[Re_2I_2(CO)_6(S_2Ph_2)]$ [d]	A,B	0.52 (A) 0.62 (B)	55 (A) 22 (B)	21.5 (21.35)	1.20 (1.0)	25.2 (25.05)	6.55 (6.35)
$[Re_2I_2(CO)_6(Se_2Ph_2)]$	B	0.66	54	19.7 (19.55)	0.95 (0.90)	22.7 (22.95)	15.0 (14.25)
$[Re_2I_2(CO)_6(Te_2Ph_2)]$	B	0.68	65	18.6 (17.95)	1.2 (0.85)	21.3 (21.1)	n.d.

[a] The complexes are deep red or red-brown. Method A.: from $[Re_2X_2(CO)_6(thf)_2]$; method B: from $[ReI(CO)_5]$. [b] Molar ratio. [c] Calculated values are given in parentheses. n.d. = Not determined. [d] Molecular weight (by cryoscopy in benzene) for a 1.33×10^{-2} *m* solution: 914 (1 012.6).

Preparation of $[Re_2I_2(CO)_6(thf)_2]$.—The thf adduct was prepared by treating $[ReI(CO)_5]$ with thf at its reflux temperature under slightly reduced pressure, removing the CO evolved, and monitoring the reaction by i.r. At the end of the reaction (63 h), the solution was concentrated to a small volume and the colourless compound precipitated with heptane, filtered off, and dried *in vacuo* (67% yield). Recrystallization was carried out by dissolving the crude product in thf and reprecipitating it with iso-octane (Found: C, 17.7; H, 1.2; I, 26.3. Calc. for $C_{14}H_{16}I_2O_6Re_2$: C, 17.9; H, 1.70; I, 27.05%). Infrared spectra in the carbonyl stretching region (values for the bromo-analogue, in parentheses): 2 027m (2 030m), 1 914s (1 916s), and 1 895s (1 895s) in thf solution; 2 029m and 1 925s cm^{-1} in CCl_4 solution. Formation of the thf adduct was also observed when $[ReI(CO)_5]$ was treated with neat thf under u.v. irradiation at temperatures not higher than 20 °C. Under these conditions, after 42 h irradiation and by intermittently removing the CO evolved, the resulting solution consisted of almost pure $[ReI(CO)_3(thf)_2]$, as evidenced by the i.r. spectrum. In both methods the intermediate formation of $[Re_2I_2(CO)_8]$ was observed spectroscopically.

X-*Ray Data Collection, Structure Determination and Refinement for* $[Re_2Br_2(CO)_6(Te_2Ph_2)]$.—Single crystals of the compound were difficult to obtain. The crystals for the *X*-ray diffraction study were prepared by heating the compound (0.22 g) in toluene (10 cm^3) at 118 °C in a stainless-steel autoclave and then slowly cooling down the system to room temperature.

Crystal data. $C_{18}H_{10}Br_2O_6Re_2Te_2$, $M = 1\,109.7$, Monoclinic, $a = 13.238(4)$, $b = 11.035(4)$, $c = 16.615(5)$ Å, $\beta = 91.29(3)°$, $U = 2\,426.5$ Å^3, $Z = 4$, $D_c = 3.04$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 165.2$ cm^{-1}, space group $P2_1/n$, $F(000) = 1\,960$. The lattice parameters were determined for a least-squares refinement of the angular settings of 15 reflections ($2\theta > 34°$) accurately centred on an Enraf-Nonius CAD-4 diffractometer. A crystal of dimensions $0.22 \times 0.45 \times 1.00$ mm was sealed in a thin-walled capillary under a nitrogen atmosphere. Data were collected on the diffractometer with graphite-crystal monochromated molybdenum radiation ($\lambda = 0.710\,69$ Å). The diffracted intensities were collected by the ω—2θ scan technique in a manner similar to that described previously.[13] All reflections in one independent quadrant out to $2\theta \leqslant 50°$ were measured; 1 782 were considered observed [$I \geqslant 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Full-matrix least-squares refinement was carried out 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, Te, Br, O, and C were taken from Cromer and Waber,[14a] and the scattering for Re, Te, and Br converted for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[14b] Scattering factors for hydrogen were from ref. 15.

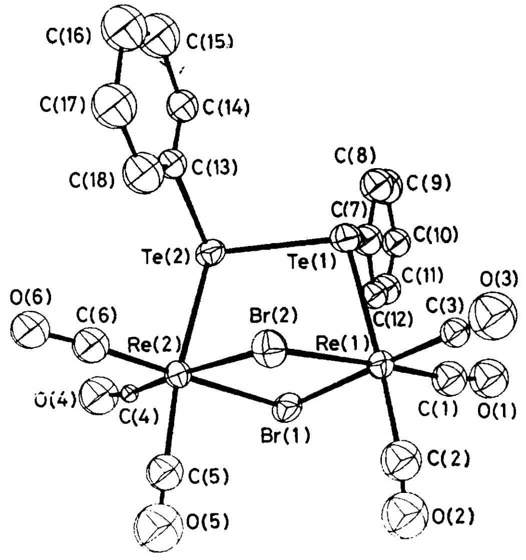

FIGURE 1 View of the molecule showing the folding along the Br · · · Br vector and the numbering system employed in the crystallographic study

The structure was solved by the application of the direct

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* 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).

method program MULTAN-74. The Re, Te, and Br atoms were refined anisotropically. The ten hydrogen atoms were placed at their calculated positions and not refined. Several cycles of refinement led to final values of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.079$ and $R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma(F_o)^2 = 0.096$. The standard deviation of an observation of unit weight was 14.6. Unit weights were used at all stages; no systematic variation of $w|F_o| - |F_c|)$ *vs.* $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 2. The observed and calculated structure factor amplitudes and thermal parameters are given in Supplementary Publication No. SUP 22990 (15 pp.).*

TABLE 2

Final fractional co-ordinates for $[Re_2Br_2(CO)_6(Te_2Ph_2)]$

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Re(1)	0.018 4(2)	0.261 0(2)	0.596 4(1)
Re(2)	−0.133 6(2)	0.489 6(2)	0.730 3(1)
Te(1)	0.147 8(3)	0.293 3(3)	0.727 5(2)
Te(2)	0.051 4(2)	0.480 0(4)	0.809 6(2)
Br(1)	−0.020 3(4)	0.495 0(6)	0.602 6(3)
Br(2)	−0.123 4(4)	0.253 3(5)	0.708 0(3)
O(1)	0.185(3)	0.274(4)	0.470(3)
O(2)	−0.140(4)	0.240(4)	0.463(3)
O(3)	0.049(4)	0.008(6)	0.590(3)
O(4)	−0.129(3)	0.753(4)	0.750(3)
O(5)	−0.321(4)	0.502(6)	0.621(3)
O(6)	−0.270(3)	0.478(3)	0.880(2)
C(1)	0.116(5)	0.272(6)	0.514(4)
C(2)	−0.081(5)	0.242(6)	0.507(4)
C(3)	0.033(4)	0.082(4)	0.594(3)
C(4)	−0.132(3)	0.658(3)	0.735(2)
C(5)	−0.256(4)	0.497(6)	0.660(3)
C(6)	−0.213(4)	0.482(5)	0.824(3)
C(7)	0.274(4)	0.410(5)	0.689(3)
C(8)	0.358(5)	0.396(6)	0.733(4)
C(9)	0.441(5)	0.476(7)	0.713(4)
C(10)	0.431(4)	0.542(5)	0.635(3)
C(11)	0.343(5)	0.547(5)	0.600(4)
C(12)	0.261(4)	0.478(5)	0.619(3)
C(13)	0.041(4)	0.385(4)	0.922(3)
C(14)	0.125(4)	0.382(5)	0.966(3)
C(15)	0.122(5)	0.312(6)	1.044(4)
C(16)	0.036(5)	0.251(6)	1.067(4)
C(17)	−0.054(5)	0.264(6)	1.008(4)
C(18)	−0.049(5)	0.325(7)	0.935(4)
H(1)[C(8)]	0.363	0.341	0.782
H(2)[C(9)]	0.504	0.474	0.757
H(3)[C(10)]	0.490	0.581	0.613
H(4)[C(11)]	0.330	0.611	0.558
H(5)[C(12)]	0.197	0.477	0.591
H(6)[C(14)]	0.190	0.481	0.949
H(7)[C(15)]	0.182	0.330	1.087
H(8)[C(16)]	0.035	0.205	1.113
H(9)[C(17)]	−0.114	0.212	1.025
H(10)[C(18)]	−0.110	0.336	0.899

Table 3 lists the bond lengths and angles. Figure 1 shows the packing of the molecule in the unit cell.

RESULTS AND DISCUSSION

The complexes reported in this paper have been prepared by reactions (1) and (2) in toluene. A reaction of type (1) was also carried out between S_2Ph_2 and $[Re_2I_2(CO)_6(thf)_2]$. The observation of an intermediate colourless precipitate and the i.r. spectra in the carbonyl stretching region in the course of the reactions between $[ReI(CO)_5]$ and E_2Ph_2 clearly indicate the presence of the sparingly soluble complex $[Re_2I_2(CO)_8]$.

$$[Re_2Br_2(CO)_6(thf)_2] + Te_2Ph_2 \longrightarrow 2\ thf + [Re_2Br_2(CO)_6(Te_2Ph_2)] \quad (1)$$

$$2\ [ReI(CO)_5] + E_2Ph_2 \longrightarrow 4\ CO + [Re_2I_2(CO)_6(E_2Ph_2)] \quad (2)$$

$$(E = S, Se, or Te)$$

TABLE 3

Interatomic bond distances (Å) and angles (°) for $[Re_2Br_2(CO)_6(Te_2Ph_2)]$

(*a*) Bonds

Re(1)–Br(1)	2.634(7)	Re(2)–Br(1)	2.627(5)
Re(1)–Br(2)	2.668(6)	Re(2)–Br(2)	2.638(6)
Re(1)–Te(1)	2.763(4)	Re(2)–Te(2)	2.756(4)
Re(1)–C(1)	1.91(6)	Re(2)–C(4)	1.86(3)
Re(1)–C(2)	1.97(7)	Re(2)–C(5)	1.98(5)
Re(1)–C(3)	1.99(5)	Re(2)–C(6)	1.90(5)
Te(1)–Te(2)	2.794(5)	Te(2)–C(13)	2.15(5)
Te(1)–C(7)	2.21(6)	C(4)–O(4)	1.08(5)
C(1)–O(1)	1.18(7)	C(5)–O(5)	1.07(6)
C(2)–O(2)	1.06(7)	C(6)–O(6)	1.21(6)
C(3)–O(3)	0.84(7)	C(13)–C(14)	1.31(7)
C(7)–C(8)	1.33(8)	C(14)–C(15)	1.50(8)
C(8)–C(9)	1.45(9)	C(15)–C(16)	1.38(9)
C(9)–C(10)	1.48(8)	C(16)–C(17)	1.52(9)
C(10)–C(11)	1.30(7)	C(17)–C(18)	1.39(9)
C(11)–C(12)	1.36(7)	C(18)–C(13)	1.38(7)
C(12)–C(7)	1.39(7)		
Re(1) · · · Re(2)	3.945(4)	Br(2) · · · Te(1)	3.624(7)
Br(1) · · · Te(1)	3.742(7)	Br(2) · · · Te(2)	3.780(7)
Br(1) · · · Te(2)	3.551(7)	Br(1) · · · Br(2)	3.485(8)

(*b*) Angles

Br(1)–Re(1)–Br(2)	82.2(2)	Br(1)–Re(2)–Br(2)	82.9(2)
Br(1)–Re(1)–C(1)	96(2)	Br(1)–Re(2)–C(4)	91(1)
Br(1)–Re(1)–C(2)	90(2)	Br(1)–Re(2)–C(5)	90(1)
Br(1)–Re(1)–C(3)	174(1)	Br(1)–Re(2)–C(6)	178(2)
Br(1)–Re(1)–Te(1)	87.7(1)	Br(1)–Re(2)–Te(2)	82.5(1)
Br(2)–Re(1)–C(1)	177(2)	Br(2)–Re(2)–C(4)	173(1)
Br(2)–Re(1)–C(2)	93(2)	Br(2)–Re(2)–C(5)	90(2)
Br(2)–Re(1)–C(3)	93(1)	Br(2)–Re(2)–C(6)	96(2)
Br(2)–Re(1)–Te(1)	83.7(1)	Br(2)–Re(2)–Te(2)	88.9(2)
C(1)–Re(1)–Te(1)	98(2)	C(4)–Re(2)–Te(2)	90(1)
C(2)–Re(1)–Te(1)	176(2)	C(5)–Re(2)–Te(2)	172(1)
C(3)–Re(1)–Te(1)	95(1)	C(6)–Re(2)–Te(2)	96(2)
C(1)–Re(1)–C(2)	85(3)	C(4)–Re(2)–C(5)	90(2)
C(1)–Re(1)–C(3)	86(2)	C(4)–Re(2)–C(6)	90(2)
C(2)–Re(1)–C(3)	87(2)	C(5)–Re(2)–C(6)	91(2)
Re(1)–Te(1)–C(7)	107(1)	Re(2)–Te(2)–C(13)	111(1)
Re(1)–Te(1)–Te(2)	101.4(1)	Re(2)–Te(2)–Te(1)	101.9(1)
C(7)–Te(1)–Te(2)	94(1)	C(13)–Te(2)–Te(1)	96(1)
Re(1)–Br(1)–Re(2)	97.1(2)	Re(1)–Br(2)–Re(2)	96.0(2)
Re(1)–C(1)–O(1)	171(5)	Re(2)–C(4)–O(4)	169(4)
Re(1)–C(2)–O(2)	172(6)	Re(2)–C(5)–O(5)	178(5)
Re(1)–C(3)–O(3)	171(7)	Re(2)–C(6)–O(6)	176(4)
Te(1)–C(7)–C(8)	114(4)	Te(2)–C(13)–C(14)	115(4)
Te(1)–C(7)–C(12)	119(4)	Te(2)–C(13)–C(18)	116(4)
C(12)–C(7)–C(8)	126(6)	C(18)–C(13)–C(14)	128(5)
C(7)–C(8)–C(9)	116(6)	C(13)–C(14)–C(15)	117(5)
C(8)–C(9)–C(10)	117(5)	C(14)–C(15)–C(16)	122(6)
C(9)–C(10)–C(11)	118(6)	C(15)–C(16)–C(17)	114(6)
C(10)–C(11)–C(12)	126(6)	C(16)–C(17)–C(18)	124(6)
C(11)–C(12)–C(7)	115(5)	C(17)–C(18)–C(13)	115(5)

In order to define conclusively both the molecular structure and the interatomic parameters, one of these complexes, namely $[Re_2Br_2(CO)_6(Te_2Ph_2)]$, was studied by *X*-ray diffraction methods. The molecular structure of the diphenyl ditelluride complex consists of two pseudo-octahedral rhenium(I) centres joined by a common edge, through bromide and Te_2Ph_2 bridges. As such, this is the first ditelluride-bridged molecule characterized by *X*-ray methods to be reported in the

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

literature. Thus, although $[Re_2Br_2(CO)_6(Te_2Ph_2)]$ is not isostructural in a crystallographic sense with the sulphur [2] and selenium [3] analogues, the three molecules do possess essentially the same structure (Figure 2). Relevant structural parameters (average values) are Re–Br, 2.642(6), Te · · · Br, 3.674(6) Å. The presence of the uncleaved Te_2Ph_2 moiety is shown by the Te–Te separation of 2.794(5) Å, close to the sum of the covalent radii,[16] 2.74 Å, and to the value found in Te_2Ph_2 itself, 2.712 Å.[17] The average Re–Te length of 2.760(5) Å is the first to be determined but fits in well with the general trend established for the Group 6 congeners. The Re · · · Re non-bonding distance is 3.945(2) Å.

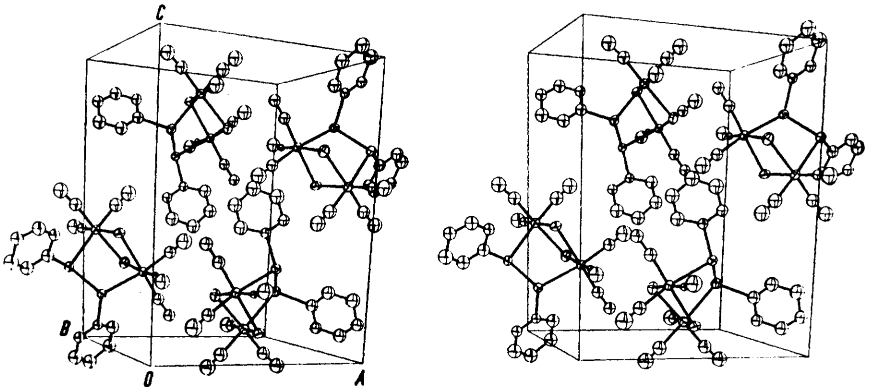

FIGURE 2 Packing of the molecule in the unit cell

Compared to the sulphur and selenium derivatives, the largest overall structural change in this molecule concerns the ' angle of fold ' about the Br · · · Br vector in the Re_2Br_2 fragment. Values of 33° for the sulphur derivative [2] and 31° for that of selenium [3] may be compared with 13.2° for the present compound, see Tables 4 and 5. This can be partially attributed to the decrease in strain of the bridging unit afforded by the larger E–E bond length {for the situation in which there is only a bromide bridge, $[Re_2Br_2(CO)_6(thf)_2]$,[10] the angle of fold is 0°}.

TABLE 4

Selected least-squares planes for $[Re_2Br_2(CO)_6(Te_2Ph_2)]$ *

Plane A: $-0.700x - 0.0874y - 0.7087z + 7.2381 = 0$
Plane B: $-0.8128x + 0.0369y - 0.5814z + 5.2041 = 0$
Plane C: $0.4124x + 0.7378y - 0.5345z + 3.3504 = 0$
Plane D: $-0.6882x - 0.1085y - 0.7174z + 7.4334 = 0$
Plane E: $-0.8077x + 0.0392y - 0.5882z + 5.2751 = 0$

Plane A		Plane B		Plane C	
Atoms	Deviation	Atoms	Deviation	Atoms	Deviation
Br(1)	0.012	Br(1)	−0.013	Re(1)	0.089
Br(2)	−0.012	Br(2)	0.012	Re(2)	−0.089
C(1)	−0.016	C(4)	0.017	Te(1)	−0.126
C(3)	0.016	C(6)	−0.016	Te(2)	0.126
Re(1)	−0.049	Re(2)	0.009		

Plane 1	Plane 2	Angle
A	B	12.09
C	D	88.88
C	E	89.42
D	E	13.19

* Deviations in Å and angles in degrees. Plane A is defined by Br(1), Br(2), C(1), and C(3); B by Br(1), Br(2), C(4), and C(6); C by Re(1), Re(2), Te(1), and Te(2); D by Re(1), Br(1), and Br(2); E by Re(2), Br(1), and Br(2).

The three iodo-complexes reported in this paper are very likely to have the same structure as their bromo-analogues, at least in solution: this is clearly suggested by the i.r. data in the carbonyl stretching region, see Table 6. For the more soluble S_2Ph_2 derivative it was possible to carry out cryoscopic measurements which showed the compound to be dimeric in benzene. Thus, once again in the series of these rhenium complexes, co-ordinative addition rather than oxidative addition is preferred, even with the weaker Te–Te bond of Te_2Ph_2. The three iodo-derivatives were obtained at the reflux temperature of toluene, thus suggesting that our compounds are not kinetically controlled products. Despite that, the dichalcogenide ligands are readily displaced by co-ordinating solvents. Equilibria (3) and (4) are predominantly displaced towards the monomeric

$$[Re_2X_2(CO)_6(E_2Ph_2)] + 2\ thf \rightleftharpoons E_2Ph_2 + [Re_2X_2(CO)_6(thf)_2] \quad (3)$$

$$[Re_2X_2(CO)_6(thf)_2] + 2\ thf \rightleftharpoons 2\ [ReX(CO)_3(thf)_2] \quad (4)$$

bis adducts in neat thf. From qualitative measurements it appears that the rate of displacement of the dichalcogen by thf and rupture of the halogen bridge decreases in the order S > Se > Te. Thus, for $[Re_2I_2(CO)_6(Te_2Ph_2)]$ it is possible to measure the i.r. spectrum in the carbonyl stretching region within the first 5 min from the preparation of the solution, while the other complexes are drastically changed upon contact with thf. Moreover, the i.r. measurements in the carbonyl stretching region for thf solutions of the complexes qualitatively indicate that the rate of reaction with thf decreases in the order Br > I.

The i.r. data of Table 6 are of particular interest. In contrast to the paucity of i.r. $\tilde{\nu}(CO)$ data existing in the literature for families of compounds containing chalcogens as ligands,[8,18] the data of Table 6 establish conclusively that the nature of the chalcogen has a pronounced effect on the carbonyl stretching vibrations. Some comments can be made about the spectroscopic data of Table 6. Firstly, all the compounds show four main bands; however, within the series of bromo-complexes, an additional shoulder is present for the selenium compound, and a fifth band becomes observable in the tellurium compound. This can be explained by considering that, with increasing size of the chalcogen, the expected spectrum for the C_{2v} symmetry of the $Re_2(CO)_6$ core of the molecule ($2A_1 + 2B_1 + B_2$) was approached (Se) and finally observed (Te). Secondly, within each family of chalcogen derivatives, a decrease in $\tilde{\nu}$(CO) is observed with increasing atomic number of the chalcogen. By assuming that mixing of the CO stretching vibrations with other vibrations within the molecule is negligible and therefore that mass effects do not affect the $\tilde{\nu}$(CO) values, their decrease must be due to the transmission of an electronic effect from the chalcogen through the metal. Back donation by a π mechanism from the metal to CO appears to increase in the order S < Se < Te. On the other hand, such a trend can be the result of either a change in σ-donor power, chalcogen to metal, see (5), or of a change in π-accepting power of the chalcogen, see (6). For the

$$E \xrightarrow{\sigma} M : Te > Se > S \qquad (5)$$

$$E \xleftarrow{\pi} M : S > Se > Te \qquad (6)$$

$$r_{Re} = r_{Re-E} - \tfrac{1}{2}\, r_{E-E} \qquad (7)$$

reasons which follow, we prefer the interpretation (5). By taking the data of Table 5 into account and considering that the covalent radius of rhenium in our complexes can be calculated from relationship (7) we obtain the following values for r_{Re}: $[Re_2Br_2(CO)_6(S_2Ph_2)]$, 1.417(10); $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ 1.398(15); $[Re_2Br_2(CO)_6(Te_2Ph_2)]$, 1.357(15) Å. These can be compared with 1.51 Å for rhenium(0) in $[Re_2(CO)_{10}]$,[19] with 1.283 Å in the metal itself,[20a] and with 1.48—1.50 Å in some complexes of rhenium(I).[20b] It thus appears that there is a tendency to Re–E bond contraction from S_2Ph_2 to Te_2Ph_2 through Se_2Ph_2, which is what one would expect for a sequence of stronger bonds in the order Re–S < Re–Se < Re–Te. This can, therefore, only be a consequence of the order of increasing σ-bond order from S to Te, (5).

TABLE 5

Interatomic distances and angles for $[Re_2Br_2(CO)_6(E_2Ph_2)]$ complexes and for E_2Ph_2 molecules (E = S, Se, or Te)

Compound	Re–E (Å)	Re · · · Re (Å)	E–E (Å)	Torsional angles (°) Re–E–E–Re	Torsional angles (°) C–E–E–C	Ref.
$[Re_2Br_2(CO)_6(S_2Ph_2)]$	2.487(6)	3.782(2)	2.140(9)	8.26	−116.94	2
$[Re_2Br_2(CO)_6(Se_2Ph_2)]$	2.604(4)	3.90(4)	2.411(23)	12.59	−121.44	3
$[Re_2Br_2(CO)_6(Te_2Ph_2)]$	2.760(5)	3.945(2)	2.794(5)	11.31	−126.6	This work
S_2Ph_2			2.030(5)		96.2	*a*
Se_2Ph_2			2.29(1)		98(3)	*b*
Te_2Ph_2			2.712(2)		88.5	17

[a] J. D. Lee and M. W. R. Bryant, *Acta Crystallogr.*, 1969, **B25**, 2094. [b] R. E. Marsh, *Acta Crystallogr.*, 1952, **5**, 458.

TABLE 6

Infrared spectra of $[Re_2X_2(CO)_6(E_2Ph_2)]$ complexes (X = Br or I; E = S, Se, or Te) in the carbonyl stretching region [a]

E	$\tilde{\nu}$(CO)/cm^{-1}										
	X = Br						X = I				
S	2.059	2 043	2 027w [b]	1 964 [c]		1 937	2 053	2 038	2 025w [b]	1 963	1 938
Se	2 057	2 041	2 024w [b]	1 963	*ca.* 1 960 (sh)	1 936	2 051	2 035	2 022w [b]	1 961 [c]	1 936
Te	2 054	2 039	2 019w [b]	1 962	1 957	1 932	2 049	2 034	2 015w [b]	1 960 [c]	1 933

[a] CCl_4 solution. Relative wavenumber shifts were verified for E = S or Te by measuring the spectra of solutions containing both compounds. The sequence of intensities of the four main bands is m,s,s,s. [b] Attributed to a ^{13}C–O stretching vibration. [c] Asymmetric band.

This conclusion is in agreement with the generally accepted view that metals in low oxidation states should be considered as class B [21] and should therefore form their more stable complexes with the heavier ligand atoms. The same conclusion can be obtained by the so-called hard–soft acid–base theory.[22] However, no quantitative data are available to substantiate this view and our complexes may possibly provide a simple system for checking this hypothesis. Work is now in progress aimed at clarifying this aspect of the problem.

Finally, it is interesting to note that chalcogens and halogens appear to behave similarly when linked to metal carbonyl moieties, *i.e.* $\tilde{\nu}$(CO) values decrease with increasing atomic number of the halogen. This is quite well substantiated by the numerous data existing in the literature for halogeno-metal carbonyls [23] and it is confirmed by the present study when comparing the i.r. data of the iodo-derivatives with those of the bromo-complexes, see Table 6.

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