Synthesis, Properties, and Crystal and Molecular Structure of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$,† a Binuclear Rhenium(I) Complex containing a Diphenyl Diselenide Bridge

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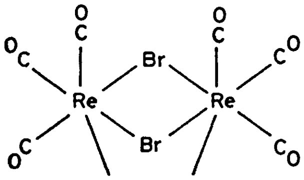
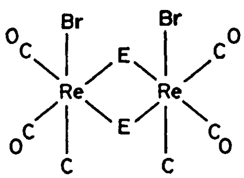
The tetrahydrofuran (thf) adduct, $[Re_2Br_2(CO)_6(thf)_2]$, reacts with diphenyl diselenide in toluene at room temperature to give the orange-red $[Re_2Br_2(CO)_6(Se_2Ph_2)]$. Three-dimensional *X*-ray analysis has shown this to be the first known example of a complex containing a Se_2R_2 unit bridging two metal atoms. The substance crystallises from toluene in the monoclinic system, space group *C*2/*c* with cell constants a = 11.813(3), b = 10.645(2), c = 19.593(5) Å, and β = 106.92(2)°, U = 2 357.15 Å^3, and D_c = 2.85 g cm^{-3}, M = 1 012.41 and Z = 4. Solution and refinement of the structure proved the compound to be isostructural with the diphenyl disulphide analogue reported previously and to consist of two Re^I atoms linked by two bromines and by a Se–Se 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 Re(2)–Br(1)–Br(2) intersect at an angle of 31°, a result which is similar to that found for the diphenyl disulphide, the dimethyl disulphide, and the tetraphenyldiphosphine derivatives. The Re–Se and Se–Se distances and the Re–Se–Se angle are 2.604(4) and 2.411(23) Å, and 106.2(1)°, respectively. The Re–Se–C(phenyl) angle is 109.9(8)°, while the Re ··· Re and Br ··· Br contacts are 3.90(4) and 3.462(20) Å. The Se(1) atom is 0.92 Å above the plane defined by Re(1)–Se(2)–C(phenyl) and the Re atoms are almost exactly in the plane defined by the two bromines and the two carbonyl carbon atoms; the torsional angle around the Se–Se bond is −121.4°. Similar to the dimethyl disulphide and the diphenyl disulphide derivatives, the diphenyl diselenide ligand of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ is displaced by thf.

AN important point in studying compounds of the type $[Re_2Br_2(CO)_6(E_2R_{2n})]$ (n = 1, E = S; n = 2, E = P) is that synthetic [1] and structural [2-4] studies carried out so far on these systems have shown that, independently of the synthetic procedure used, the product obtained is always (1) and no evidence was gathered for the formation of (2); *i.e.* the molecules contain bromine bridges and the R_nE–ER_n groups are also bridging; thus the reaction does not proceed *via* oxidative addition of the metal across the E–E bond. Inasmuch as the order of stability of such E–E bonds in the unco-ordinated molecule decreases in the order S > Se > Te,[5] one could hope to find reaction conditions leading to bond cleavage with formation of (2). In this report we give the results of such an attempt using diphenyl diselenide.

A further point of interest is that in the course of our structural investigations on complexes (1) with diphenyl disulphide,[2] tetraphenyldiphosphine,[3] and dimethyl disulphide,[4] we noted that the equatorial planes of the two metal atoms [*i.e.* $(OC)_2ReBr_2$] were not coplanar. In the case of the diphenyl disulphide derivative, for example, the normals to these planes make an angle of 33(1)° to one another. Since the Re ··· Re non-bonding distance [3.782(2) Å] was much larger than the S–S distance [2.140(9) Å], we indicated that the bending was possibly due to the short S–S distance in the bridging fragment. The synthesis of the corresponding diphenyl diselenide derivative would then offer the possibility of checking this specific point, in view of the longer Se–Se distance.



(1)



(2)

EXPERIMENTAL

Solvents were dried and purified by conventional methods. The i.r. spectra were measured with a Perkin-Elmer 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}.

Preparation of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$.—The tetrahydrofuran adduct $[Re_2Br_2(CO)_6(thf)_2]$ (2.93 g; 3.47 mmol) was suspended in toluene (20 ml) and treated with Se_2Ph_2 (1.12 g; 3.59 mmol) at room temperature. The solution immediately became orange and an orange-red solid precipitated out. The reaction mixture was stirred for *ca.* 22 h and the complex was filtered off, washed with toluene, and dried *in vacuo* (91% yield). The *compound* was recrystallised from toluene, the maximum temperature of the external bath being *ca.* 80 °C (Found: C, 21.8; H, 1.1; Br, 15.4. $C_{18}H_{10}Br_2O_6Re_2Se_2$ requires C, 21.35; H, 1.00; Br, 15.8). The compound was found to be stable in air in the solid state for several hours, whereas slow decomposition occurred in solution. Due to its low solubility, the molecular weight in solution could not be determined. The i.r. solution spectrum in the carbonyl stretching region showed the following bands (CCl_4): 2 057m, 2 041s, 1 963s, 1 960sh, and 1 936s cm^{-1}. Treatment of the complex with neat tetrahydrofuran resulted in the appearance of the carbonyl bands typical [6] of $[ReBr(CO)_3(thf)_2]$.

X-*Ray Diffraction Study*.—The crystals of di-μ-bromo-μ-diphenyl diselenide-bis[*fac*-tricarbonylrhenium(I)] used in this study were obtained by recrystallisation from toluene. Single crystals were glued to a glass fibre attached to an

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† Di-μ-bromo-μ-diphenyl diselenide-bis[*fac*-tricarbonylrhenium(I)].

XYZ translation head and mounted on a computer-controlled Enraf–Nonius CAD–4 diffractometer. Preliminary cell constants, space group, and orientation matrix were determined using standard routines of the CAD–4 system.[7] Since the space group was found to be the same as that of the sulphur analogue ($C2/c$) and the cell constants were little changed, a few reflections known to be little affected by changing Se for S were checked and from here on we assumed the two compounds to be isomorphous and isostructural. Subsequent solution of the structure bore this out (see below). Before data collection, twenty-four strong reflections having $30 \leqslant 2\theta \leqslant 40°$ were automatically centred by the diffractometer and the cell constants and orientation matrix obtained in the least-squares fit were subsequently used for intensity-data collection.

Crystal data. $[Re_2Br_2(CO)_6(Se_2Ph_2)]$, $M = 1\,012.41$, Monoclinic, $a = 11.813(3)$, $b = 10.645(2)$, $c = 19.593(5)$ Å, $\beta = 106.92(2)°$, $U = 2\,357.15$ Å^3, $D_m = 2.84(2)$ g cm^{-3}, $Z = 4$, $D_c = 2.85$ g cm^{-3}, $F(000) = 1\,816$. Space group $C2/c$. Mo-K_α radiation, $\lambda = 0.710\,73$ Å. Throughout this study, Mo-K_α radiation was used in conjunction with a high-density graphite monochromator set at a take-off angle of 5.85°. Data were collected using the $\theta - 2\theta$ technique and with a scan rate determined by a fast pre-scan (20.116 6° min^{-1}). Reflections having more than 70 net counts above background were measured at a new rate such that a minimum of 2 000 counts above background was achieved. The scan rates for data collection varied from 0.2 to 3.4° min^{-1}. All reflections having less than 70 counts above background in the pre-scan were assumed to be unobserved. Experience with previous measurements showed that these weak reflections have intensities $I < 3\sigma(I)$, which is always our cut-off criterion. For any given intensity measurement, the width of the scan range was determined with the equation scan range $= A + B \tan\theta$ with $A = 1.20°$ and $B = 0.40°$. Backgrounds were collected for 25% of the total scan time at each end of the scan range. A horizontally variable aperture was used during data collection; its width was also determined using the above equation and in this case $A = 5.20$ mm and $B = 2.11$ mm. A manual slit, inserted to define the vertical width in front of the counter, was set at 4 mm. The crystal-to-source distance was 216 mm, while the crystal-to-counter distance was set at 176 mm and the upper and lower discriminators for the pulse-height analyser were set to obtain 95% of the Mo-K_α peak. As a check for reliability of the electronic system and in order to monitor crystal stability, three reflections (5,5,10; 3,9,2; and 2,6,12) were measured every 30 data points. No significant variation in the intensity of these standards was noted during the course of data collection. A total of 3 287 reflections were collected in the range $4 \leqslant 2\theta \leqslant 60°$, of which 2 032 had intensities $I > 3\sigma(I)$, with $\sigma(I) = (I)^{\frac{1}{2}}$. These data were corrected for Lorentz and polarisation effects (including the effect of the monochromatising crystal[8] and for absorption †). The crystal used during data collection was a diamond-shaped parallelepiped of dimensions $0.27 \times 0.27 \times 0.09$ mm, with the [1,0,0] direction across two corners of the diamond and mounted, approximately, along this direction. The faces defining the crystal were the families of {1,1,0} and {0,0,1}. The distance between the (0,0,1) and $(0,0,\bar{1})$ faces was 0.09 mm; between (1,1,0) and $(\bar{1},\bar{1},0)$ 0.27 mm, and between $(1,\bar{1},0)$ and $(\bar{1},1,0)$ also 0.27 mm. Using this information and the calculated value of the absorption coefficient[9] ($\mu = 178$ cm^{-1}), the intensities were corrected, with the resulting transmission coefficient ranging from 4.8 to 21.7%. Data decollation and reduction was performed with a local program for the CAD–4 System. Absorption corrections were obtained from a local variation of ORABS.† The rest of the calculations were performed by the *X*-RAY 1972 program system.[9] Finally, the stereo-plots are from Johnson's program ORTEP 2.[10]

Solution and refinement of structure. Since we knew that the selenium derivative was isomorphous with the diphenyl disulphide analogue,[2] we assumed that it was isostructural as well. Refinement of our selenium data using the disulphide co-ordinates with refined, individual, isotropic thermal parameters for all the atoms led to a discrepancy index $R\{=\Sigma|(F_o - F_c)|/\Sigma|F_o|\}$ of 0.090. Conversion to anisotropic parameters (omitting the hydrogen atoms) gave R of 0.081. Finally, anisotropic reffnement of the heavy atoms, and inclusion of the hydrogens at their idealised positions and with isotropic thermal parameters of 6.33 Å^2 (the mean isotropic thermal parameter of the six carbon atoms of the relevant phenyl rings) gave an R of 0.076 and a $R' = 0.091$ $\{=[\Sigma w(F_o - F_c)^2/\Sigma(F_o)^2]^{\frac{1}{2}}\}$. The weights were set to unity in the refinement.

Unobserved reflections were not included in the final refinement, and a difference-Fourier map showed only random noise <0.5 e Å^{-3}. The final shifts in the parameters were generally <0.07 of their estimated standard deviations.

TABLE 1

Positional parameters ($\times 10^4$) with estimated standard deviations in parentheses. Hydrogen atom positions are idealised values calculated just before the last cycle of refinement

Atom	*x*	*y*	*z*
Re	1 588(1)	1 661(1)	3 167(1)
Br	0 599(3)	2 139(3)	1 792(1)
Se	1 029(2)	−0 676(2)	2 844(1)
O(1)	3 993(25)	1 019(25)	3 004(13)
O(2)	2 326(27)	4 433(23)	3 414(17)
O(3)	2 627(23)	1 086(23)	4 765(11)
C(1)	3 086(24)	1 258(29)	3 059(13)
C(2)	1 935(41)	3 376(32)	3 275(14)
C(3)	2 227(29)	1 314(28)	4 176(15)
C(4)	0 875(22)	−1 565(26)	3 678(12)
C(5)	0 244(30)	−1 067(29)	4 104(16)
C(6)	0 144(33)	−1 770(36)	4 686(16)
C(7)	0 678(37)	−2 904(35)	4 823(16)
C(8)	1 323(35)	−3 385(35)	4 392(19)
C(9)	1 417(26)	−2 692(27)	3 807(16)
H(5)	−0 126	−0 249	4 000
H(6)	−0 298	−1 435	4 992
H(7)	0 590	−3 386	5 224
H(8)	1 733	−4 193	4 500
H(9)	1 857	−3 012	3 501

TABLE 2

Bond lengths (in Å) in $[Re_2Br_2(CO)_6(Se_2Ph_2)]$ with estimated standard deviations in parentheses

Re–Br	2.656(20)	C(4)–C(9)	1.35(4)
Re–C(1)	1.89(3)	C(1)–O(1)	1.14(4)
Re–C(2)	1.87(3)	C(2)–O(2)	1.22(4)
Re–C(3)	1.94(3)	C(3)–O(3)	1.14(4)
Re–Re*	3.899(43)	Se–Se*	2.411(23)
C(4)–C(5)	1.38(5)	Se–C(4)	1.94(3)
C(5)–C(6)	1.40(5)	Br–Br*	3.462(20)
C(6)–C(7)	1.35(5)	Se–Br	3.587(6)
C(7)–C(8)	1.39(6)	Se*–Br	3.739(8)
C(8)–C(9)	1.406(5)	Re–Se	2.604(4)

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† Absorption corrections were carried out using our local version (UNIVAC 1108) of the program ORABS, obtained from the Crystallographic Program Library of Brookhaven National Laboratory.

TABLE 3

Bond angles (°)

C(2)–Re–Br	86.8(8)	Se–Re–Br	86.0(1)
C(2)–Re–Br*	90(1)	Se–Re–Br*	90.6(1)
C(2)–Re–C(1)	93(2)	Se–Re–C(1)	86.3(9)
C(2)–Re–C(3)	94(1)	Se–Re–C(3)	93.6(9)
C(1)–Re–Br	94.6(8)	Br–Re–Br*	81.3(1)
C(1)–Re–Br*	175.0(8)	Br–Re–C(3)	177.0(9)
C(1)–Re–C(3)	88(1)	Br*–Re–C(3)	95.7(10)
Re–Br–Re*	94.4(1)	Re–Se–Se*	106.2(1)
Re–C(1)–O(1)	179(2)	Re–Se–C(4)	109.9(8)
Re–C(2)–O(2)	170(3)	C(4)–Se–Se*	98.3(7)
Re–C(3)–O(3)	178(3)	Se–C(4)–C(5)	121(2)
Se–C(4)–C(9)	116(2)	C(5)–C(4)–C(9)	122(3)
C(4)–C(5)–C(6)	118(3)	C(5)–C(6)–C(7)	120(4)
C(6)–C(7)–C(8)	121(3)	C(7)–C(8)–C(9)	120(3)
C(4)–C(9)–C(8)	119(3)	C(2)–Re–Se	172.7(8)

TABLE 4

Selected least-squares planes with deviations of atoms (in Å) from them in parentheses

(*a*) Plane defined by C(4)—C(9) (phenyl ring)

$$0.689\,74x + 0.437\,94y + 0.576\,60z = 2.516\,70$$

[C(4) −0.005 0, C(5) 0.006 0, C(6) −0.002 5, C(7) −0.002 1, C(8) 0.003 2, C(9) 0.000 3, Se −0.038 4]

(*b*) Plane defined by Br, Br*, C(1), and C(3)

$$0.212\,51x + 0.963\,37y + 0.163\,59z = 2.656\,62$$

[Re 0.0328]

(*c*) Plane defined by Br*, Br, C(1)*, and C(3)*

$$-0.212\,51x + 0.963\,37y - 0.163\,57z = 1.729\,38$$

(*d*) Plane defined by Re, C(4), and Se

$$-0.769\,04x + 0.394\,10y + 0.503\,26z = 3.631\,02$$

Angle between the normals to planes (*b*) and (*c*), 31.11°

The positional and thermal parameters obtained in the last cycle of refinement are listed in Tables 1 and 2. Tables 3 and 4 give the bond lengths and bond angles, and the equations of least-squares planes passing through relevant groups of atoms. Table 5 lists the torsional angles for the Re–Se–Se–Re fragment. Observed and calculated structure factors and anisotropic thermal parameters are deposited as Supplementary Publication No. SUP 22539 (15 pp.).†

Figure 1 is a diagrammatic representation of the molecule in which the numbering system employed in the crystallographic study is shown. Figure 2 is a stereo-pair in which the molecule is shown with the atoms represented by 50% probability ellipsoids and Figure 3 is a stereo-packing diagram.

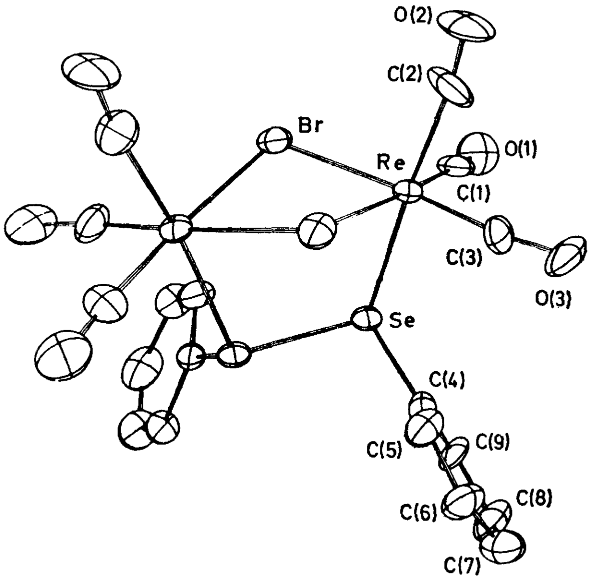

FIGURE 1 View of the molecule showing the folding along the Br ··· Br* vector and the numbering system employed in the crystallographic study

RESULTS AND DISCUSSION

The tetrahydrofuran adduct $[Re_2Br_2(CO)_6(thf)_2]$ is a convenient starting material for the preparation of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$. The results of the *X*-ray investigation have shown that, as we have found in the case of S_2Ph_2,[2] here also the co-ordination to rhenium is *via* the bridging Se_2Ph_2 and no cleavage of the Se–Se bond takes place. The mild conditions of the reaction might suggest that we are dealing with a kinetically controlled product rather than one which is thermodynamically stable. That this is not so is indicated by

$$[Re_2Br_2(CO)_6(thf)_2] + Se_2Ph_2 \longrightarrow [Re_2Br_2(CO)_6(Se_2Ph_2)] + 2\ thf$$

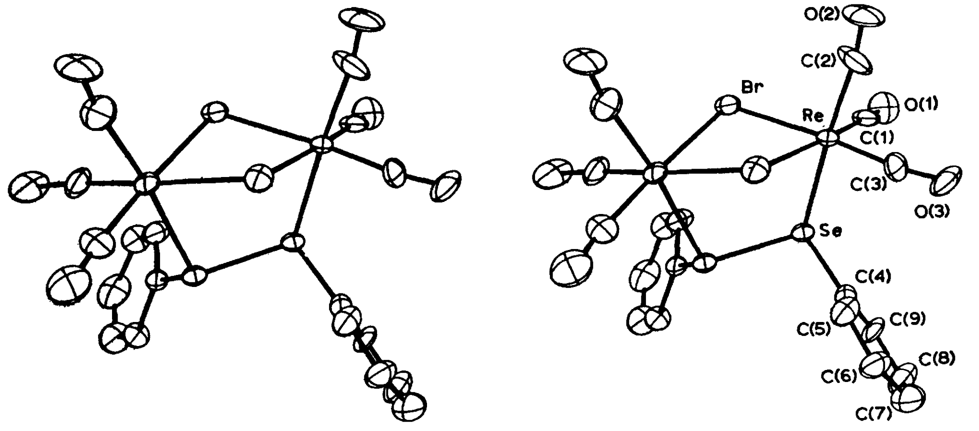

FIGURE 2 Stereo-plot of the configuration and conformation of the molecule. The anisotropic thermal motion of the atoms is given in the form of 50% probability ellipsoids

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 5

Torsional angles (°) for the chalcogenide ligands as bound and free molecules [a]

Molecule	Re–E–E–Re	C–E–E–C	Ref.
$[Re_2Br_2(CO)_6(S_2Me_2)]$	+11.43	−121.24	4
$[Re_2Br_2(CO)_6(S_2Ph_2)]$	+8.26	−116.94	2
$[Re_2Br_2(CO)_6(Se_2Ph_2)]$	+12.59	−121.44	This study
Me–S–S–Me		83.9(9)	*b*
Ph–S–S–Ph		96.2(1.0)	*c*
Ph–Se–Se–Ph		98(3)	*d*

[a] The torsional angle of a fragment ABCD about the bond BC is that angle which the fragment AB has to be turned so as to eclipse CD while the observer views the system along BC. If the angle is positive the motion is clockwise. [b] B. Beagley and M. T. McAloon, *Trans. Faraday Soc.*, 1971, **67**, 3216. [c] J. D. Lee and M. W. R. Bryan, *Acta Cryst.*, 1969, **B25**, 2094. [d] R. E. Marsh, *Acta Cryst.*, 1952, **5**, 458.

the fact that the same substance was obtained when the starting material was $[ReBr(CO)_5]$ and more forcing conditions had to be used * to displace the co-ordinated CO groups (reflux temperature of benzene).

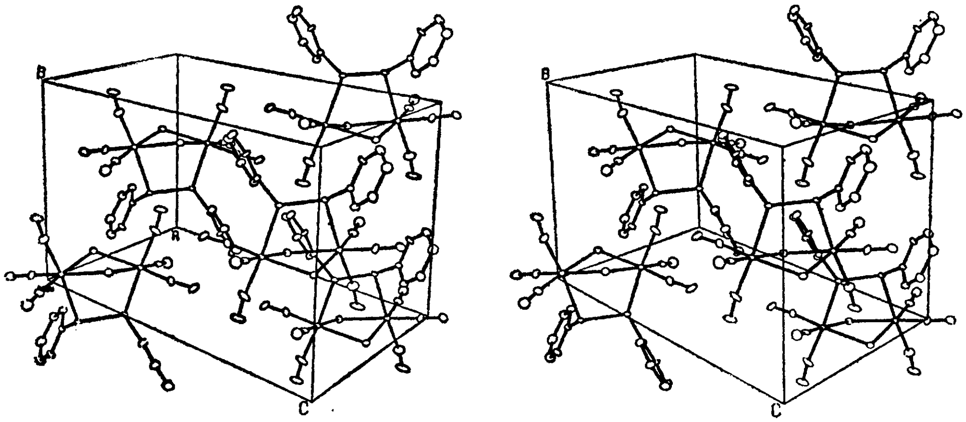

FIGURE 3 Stereo-plot showing the packing of the molecules in the unit cell

To the best of our knowledge, our diphenyl diselenide complex represents the first crystallographically determined example of a molecule containing an Se_2R_2 unit bridging two metal atoms. Although still limited to a small number of examples, the existence of S_2R_2 bridges in metal complexes is now well-established.[2,11-15]

As in the case of the diphenyl disulphide analogue,[2] the molecule has a crystallographic 2-fold axis. In the discussion that follows, all the atoms at positions x,y,z have axially related counterparts (labelled with an asterisk) at positions $x,y,\frac{1}{2}-z$. Within the quoted standard deviations, the bonding parameters of the $Re(CO)_3$ fragments are the same as those found in the case of the other molecules of the same series, both with sulphur-[2,4] and phosphorus-containing[3] bridging systems. Thus, this part of the molecule seems little affected by the changes in bonding associated with the bidentate ligand.

We were most interested in the changes at the Re_2Br_2-E_2R_2 fragment introduced by changing from E = S to E = Se, thus lengthening the bridge between the rhenium atoms. The S–S distance in the diphenyl disulphide derivative[2] is 2.140(9) Å, while the corresponding Se–Se distance in the selenium analogue is 2.411(23) Å. The Re · · · Re non-bonding distances are 3.782(2) and 3.90(4) Å, respectively. The angles between the normals to the planes defined by Re, Br, Br* and by Re*, Br*, Br are 33° (E = S) and 31° (E = Se). At the same time, the Re–Br distance increases from 2.607(3) (E = S) to 2.656(20) Å (E = Se). Therefore, the introduction of a longer bridge in the molecule does not result in a major change of the folding angle along the Br · · · Br vector. Instead, the $Re_2Br_2(CO)_6$ fragment expands in such a way as to accommodate the increase, while preserving the folding angle essentially unchanged. The change in the distance S–S to Se–Se of 0.27 Å can readily be understood in terms of the difference in covalent radii of the two elements. According to Pauling,[5] this difference is 0.13 Å, which is thus confirmed, even though in this case the elements are also bound to a metal, while Pauling's data refer to divalent elements. This result is also consistent with the change in Re–E distance of 0.12 Å {Re–S is 2.487(6) Å in $[Re_2Br_2(CO)_6(S_2Ph_2)]$[2] and Re–Se is 2.604(4) Å in the compound of the present study}. Thus, while retaining its shape, the R–S–S*–Re fragment is simply enlarged to accommodate the increase in radius of the Se ligand. This result implies a preferred shape for the molecule, and one can conclude that the foldings originally reported for $[Re_2Br_2(CO)_6(S_2Ph_2)]$ (33°)[2] and for $[Re_2Br_2(CO)_6(S_2Me_2)]$ (28°)[4] are not determined by the relative lengths of the Re · · · Re and S–S distances. Rather, the folding seems to be an electronic effect dictated by the stereochemistry of the atomic orbitals involved.

It is worthwhile noting that the Re–Se distance in the present molecule is somewhat longer than that recently reported[16] [2.46(1) Å] for a cubane-like type of compound containing rhenium(IV). This is readily explained by the different oxidation states in the two cases.

Another quantity which is not seriously affected by the change from S to Se is the torsional angle about the E–E vector (defined according to the recommendations of the IUPAC–IUB Commission[17]). The values of the tor-

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† We thank Dr. I. P. Mavani for carrying out this experiment.

sional angles (see Table 5) for the C–S–S–C and C–Se–Se–C fragment do not vary in any systematic way and furthermore, the value for the S_2Me_2 derivative is identical, within experimental error, with that of $[Re_2Br_2(CO)_6(Se_2Ph_2)]$.

I.r. spectra in the carbonyl stretching region may be quite sensitive to subtle electronic changes that are not easily detected in the solid-state bonding parameters. Both the S_2Ph_2 and Se_2Ph_2 derivatives show four main bands in the carbonyl region (CCl_4 solution): 2 059 (2 057), 2 043 (2 041), 1 964 (1 963), and 1 937 (1 936) cm^{-1} (the values in parentheses are those for the selenium derivative; the relative intensity sequence is m,s,s,s; the selenium derivative shows an additional shoulder at about 1 960 cm^{-1}). Although the change is small, the selenium derivative shows a *decrease* of the carbonyl wavenumber values. The chemical literature still contains only a limited number of examples [18,19] for which a comparison of ν_{CO} values for related sulphur- and selenium-containing ligands can be made.

Further discussion of the structural, spectroscopic, and chemical properties of the whole series $[Re_2Br_2(CO)_6(E_2Ph_2)]$ (E = S, Se, or Te) will be reported later.

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