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REACTIONS OF BROMO CARBONYL DERIVATIVES OF RHENIUM(I)

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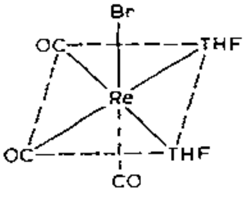
Dimeric tetrahydrofuran complexes of rhenium(I) were recently reported [1] to be obtained via carbon monoxide displacement from $ReBr(CO)_5$ with tetrahydrofuran (THF). Equilibria were shown to be operating in solution, together with the bridge-splitting reactions of the dimeric solid-state species with tetrahydrofuran (1)

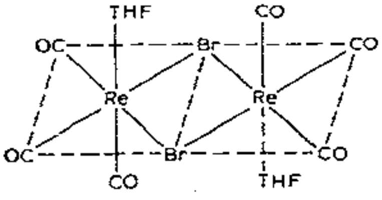
$$\begin{tikzcd}
\mathrm{ReBr(CO)_5} \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{ReBr(CO)_4THF} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, shift left, "-\mathrm{THF}"] & \mathrm{ReBr(CO)_3(THF)_2} \arrow[d, shift left, "-\mathrm{THF}"] \\
 & {[\mathrm{ReBr(CO)_4}]_2} \arrow[u, shift left, "+\mathrm{THF}"] & {[\mathrm{ReBr(CO)_3THF}]_2} \arrow[u, shift left, "+\mathrm{THF}"]
\end{tikzcd} \qquad (1)$$

The tricarbonyl-bistetrahydrofuran complex has an infrared spectrum in solution consistent with the *fac* configuration (I) of C_s symmetry for which three strong CO stretching vibrations are expected. It is interesting to note that the stable solid-state compound is the dimeric $[ReBr(CO)_3(THF)]_2$ reported previously by Hieber and co-workers [2], and obtained by a different route. The IR data suggest that the dimeric tricarbonyl has structure (II), of C_{2h} symmetry. The $ReBr_2Re$ bridge is regarded to be planar. No metal—metal bond is required in this case since the central metal atom, of d^6 configuration, acquires the EAN of the next inert gas, by considering the bromo ligand as a four-electron donor.



(I)

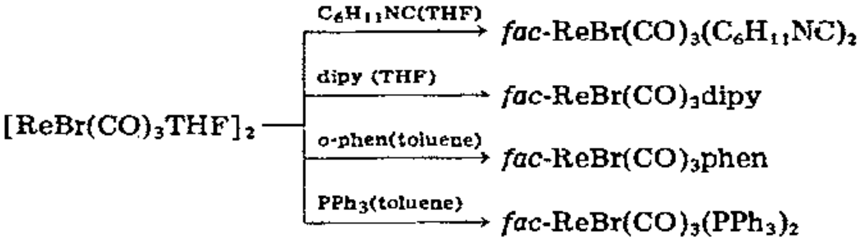
C_s, $2A' + A''$



(II)

C_{2h}, $A_u + 2B_u$

We have found that the THF groups from either $ReBr(CO)_3(THF)_2$ or $[ReBr(CO)_3THF]_2$ are, as expected, labile and can be replaced by lone pair donors, such as $C_6H_{11}NC$, 2,2′-dipyridyl, 9,10-phenanthroline and PPh_3. Products of hexacoordinate Re^I with a *facial* arrangement of the substituents (inferred from the IR spectra) are obtained. The reactions are usually very fast and are complete a few minutes after the mixing of the reagents at room temperature.



$$[\mathrm{ReBr(CO)_3THF}]_2 \left\{ \begin{array}{l} \xrightarrow{\mathrm{C_6H_{11}NC(THF)}} fac\text{-}\mathrm{ReBr(CO)_3(C_6H_{11}NC)_2} \\ \xrightarrow{\mathrm{dipy\ (THF)}} fac\text{-}\mathrm{ReBr(CO)_3dipy} \\ \xrightarrow{o\text{-}\mathrm{phen(toluene)}} fac\text{-}\mathrm{ReBr(CO)_3phen} \\ \xrightarrow{\mathrm{PPh_3(toluene)}} fac\text{-}\mathrm{ReBr(CO)_3(PPh_3)_2} \end{array} \right. \qquad (2)$$

It has now been found that $[\mathrm{ReBr(CO)_3THF}]_2$ also reacts in toluene with dialkyl- and diaryldisulphides, R_2S_2, giving oxidative coordination due to cleavage of the sulphur—sulphur bond of the disulphide:

$$[\mathrm{ReBr(CO)_3THF}]_2 + \mathrm{R_2S_2} \rightarrow [\mathrm{ReBr(CO)_3SR}]_2 + 2\ \mathrm{THF} \qquad (3)$$

$(\mathrm{R} = \mathrm{CH_3}, \mathrm{Ph}, p\text{-}\mathrm{CH_3C_6H_4})$

The reactions are fast at room temperature. The products of the reactions, which analyse correctly for the formulations given, are yellow (CH_3) to orange (Ph, p-$CH_3C_6H_4$) solids soluble in organic solvents, somewhat reactive with $CHCl_3$ to give still unknown products. The dimeric formula was established by cryoscopy in benzene (M.W. found 761; calculated for $[\mathrm{ReBr(CO)_3SR}]_2$ 794.46) and by mass spectrometry [3] (found mass 789.7033; calculated for the lowest isotopes of $C_8H_6Br_2O_6Re_2S_2$ 789.7033). The compounds are diamagnetic as shown by bulk magnetic susceptibility measurements for the methyl derivative ($\chi_M = -155 \cdot 10^{-6}$ cgsu at room temperature) and suggested by the sharpness of the ^{1}H-NMR peaks). Some insight into the problem of the molecular structure of these compounds came from the IR data in the terminal CO stretching region, which are reported in Table 1. The complexes show four main bands and the effect of the R group attached to sulphur on the CO stretchings is rather limited.

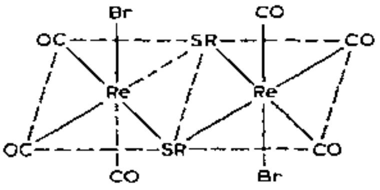
Several structures are in principle possible for these compounds and some of them are indicated below (III—VI). No effect of the orientation of the R group on the molecular symmetry has been considered for the moment.

TABLE 1

CO stretching vibrations of $[\mathrm{ReBr(CO)_3SR}]_2$ complexes*

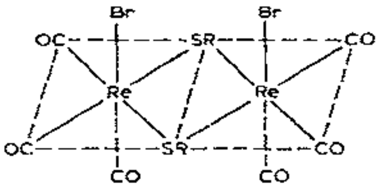
R	ν_{CO} (cm^{-1})			
CH_3	2058m	2042vs	1962s	1930s—m
C_6H_5	2056m	2040vs	1962s	1932s—m
p-$C_6H_4CH_3$	2055m	2040vs	1960s	1932s—m

* CCl_4 solutions. Spectra recorded on expanded abscissa scale, calibration with $CO_{(g)}$.



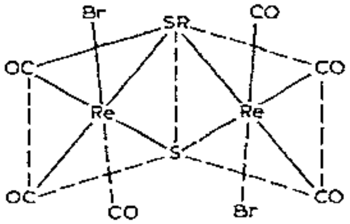
(III)

C_{2h} : $A_u + 2B_u$



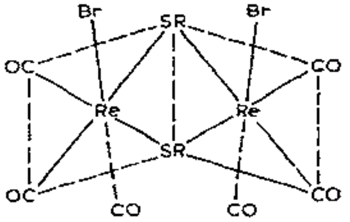
(IV)

C_{2v}: $2A_1 + 2B_1 + B_2$



(V)

C_s : $3A' + 3A''$



(VI)

C_{2v}: $2A_1 + 2B_1 + B_2$

Structure (III) can be excluded since four infrared CO stretchings are observed instead of the expected three. Structure (V) is also unlikely in view of the IR results. The two possibilities (IV) and (VI), which are in closer agreement with the IR data, consist of molecules in which the Br groups are in *cis* positions. It is worth noting that the IR data cannot distinguish between the planar (IV) and the bent (VI) arrangements of the $Re(SR)_2Re$ system. The observed diamagnetism in these compounds of Re(II) (d^5 configuration) makes the formation of a metal—metal bond highly probable. The bent structure (VI) requires five bands. Some of the measured spectra in CCl_4 contain a weak shoulder on the low-frequency side of the band at about 1930 cm^{-1}. This might be a ^{13}CO satellite. However, it should be noted that the similar mercapto-bridged dimers of iron(I), $Fe_2(CO)_6(SR)_2$, which have been shown by X-ray diffraction methods [4] to be bent, also show four main bands, while the fifth CO stretching is sometimes not observed and is always very weak [5]. The ^{1}H-NMR spectrum of the methyl derivative at 60 Mc shows one proton resonance only at τ 7.77 (d_6-benzene). On the other hand, some of the infrared CO stretching bands are slightly asymmetric and this may suggest the presence of more than one isomer in solution. Again, it should be recalled that the CO stretching vibrations of the iron(I) mercapto-bridged dimers are not very sensitive [5] to the relative orientation of the SR groups, as expected. A more conclusive answer to this problem may be found from work now in progress involving chromatographic separations and ^{1}H-NMR spectra at 100 Mc.

Finally, it is worth noting that the rhenium(II) complexes are rather labile and react with some Lewis bases to give rhenium(I) complexes and the disulphide. This reaction has been found to be promoted by 2,2'-dipyridyl and by tetrahydrofuran:

$$[ReBr(CO)_3SR]_2 + 4\,THF \xrightarrow[\text{room temperature}]{THF} 2\,ReBr(CO)_3(THF)_2 + R_2S_2 \qquad (4)$$

Preliminary experiments have indicated that the rate of reaction (4) is much greater for R = Ph and p-$C_6H_4CH_3$ than for R = CH_3. Reaction (4), which strongly supports the suggested bis-mercapto-bridged structure, appears to be unprecedented among bis-mercapto-bridged complexes of transition elements and sets an example of a reversible electron transfer process assisted by rhenium and promoted by a purely σ-donor ligand such as tetrahydrofuran.

Experimental

The preparation and handling of compounds were carried out under an atmosphere of prepurified nitrogen. The IR spectra were measured with a Perkin—Elmer mod. 337 instrument.

The preparation of the methyl-mercapto derivative is described in detail. The other compounds of the same class are prepared in a strictly analogous manner.

To a suspension of $[ReBr(CO)_3THF]_2$ (1.53 g; 1.81 mmole) in toluene (12 ml), 0.33 g (3.50 mmole) of $(CH_3)_2S_2$ were added at room temperature. After about 10 min the solid initially present disappeared to give a yellow solution. After two days part of the solvent was evaporated under reduced pressure and then iso-octane (10 ml) was added to complete the precipitation of the complex, which was separated by filtration and dried in vacuo (1.26 g; 87.5 % yield).

Analytical

Calculated for $C_8H_6Br_2O_6S_2Re_2$: C, 12.09; H, 0.76; Br, 20.12; S, 8.07. Found: C, 12.33; H, 0.89; Br, 20.41; S, 7.85.

The compound is stable in air in the solid state, soluble in aromatic hydrocarbons and reacts with $CHCl_3$. Solutions in tetrahydrofuran are not stable and finally yield the typical spectrum of $ReBr(CO)_3(THF)_2$. On the other hand, treatment of the complex with 2,2'-dipyridyl (dipy) in d_6-benzene resulted in the formation of $ReBr(CO)_3$(dipy) and $(CH_3)_2S_2$ (^{1}H-NMR, singlet at τ 8.00).

Satisfactory analytical results were obtained for the other complexes reported in this paper.

ACKNOWLEDGEMENT

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