Preparation, Properties, and Crystal and Molecular Structures of Bis-(dialkylamine) Complexes of Rhenium(I)

By **Fausto Calderazzo, Dario Vitali, Ishwerlal P. Mavani,** and **Fabio Marchetti,** Istituto di Chimica Generale, University of Pisa, Via Risorgimento 35, 56100 Pisa, Italy
Ivan Bernal and **James D. Korp,** Chemistry Department, University of Houston, Houston, Texas 77004, U.S.A.
Jerry L. Atwood, Robin D. Rogers, and **M. Susan Dalton,** Chemistry Department, University of Alabama, University, Alabama 35486, U.S.A.

The crystal and molecular structures of the two bis(amine) complexes of rhenium(I), $[ReBr(CO)_3(NHR_2)_2]$ (R = Me or Et), have been studied by *X*-ray diffraction methods. The complexes crystallize in the monoclinic system, space group $P2_1/n$, with cell constants (R = Me) a = 9.023(3), b = 11.537(4), c = 12.199(4) Å, β = 97.28(3)°; and (R = Et) a = 7.340(2), b = 9.784(3), c = 22.742(6) Å, β = 95.05(2)°. The molecular structure in both cases consists of facially arranged ligands around six-co-ordinate rhenium(I); the two *cis* amine ligands do not interact appreciably either by intra- or inter-molecular hydrogen bonding. The ethyl derivative reacts with CO_2 to give the corresponding carbamato-complex $[Re(CO)_3(O_2CNEt_2)(NHEt_2)]$, the latter showing association in solution presumably due to intermolecular hydrogen bonding.

AMINE complexes of transition elements in low oxidation states stabilized by carbonyl groups are important since they are sometimes precursors to carbamoyl complexes,[1] they are believed to be involved in the catalytic dehydrogenative carbonylation of amines to dialkylureas,[2] and in the hydrogen bonding to nitrogen- and oxygen-containing Lewis bases, thus possibly explaining some of the kinetic features encountered in substitution reactions of six-co-ordinate metal complexes.[3-7] Hydrogen bonding also may be important in explaining the high amine : metal molar ratios found [8] in some amine complexes of transition elements and some spectroscopic features.[9]

In the course of our current studies on hetero-multiple-bridged (HMB) molecules of manganese and rhenium [10] of formula $[M_2Br_2(CO)_6(E_2R_{2n})]$ (M = Re, E = S, R = Me, n = 1; [10a] R = Ph; [10b] E = Se, R = Ph; [10c] E = Te, R = Ph; [10d] M = Mn, E = P, R = Ph, n = 2; [10e] M = Re [10f]), we have prepared some bis(dialkylamine) complexes of rhenium(II) starting from the tetrahydrofuran (thf) adduct $[Re_2Br_2(CO)_6(thf)_2]$. The methyl and the ethyl derivatives behave quite differently; in order to clarify these differences and in view of the general interest in amine complexes of transition metals, particularly when more than one amine group is present around the same metal atom, we decided to carry out *X*-ray structure investigations of both amine complexes. We also report the reaction of the diethylamine complex with CO_2 to give the corresponding carbamato-derivative, together with its spectroscopic properties.

EXPERIMENTAL

All of the operations described in this paper were carried out under an atmosphere of pre-purified nitrogen.

Solvents were purified and dried prior to use by conventional methods. I.r. spectra were measured with a Perkin-Elmer 283 instrument, usually on an expanded abscissa scale with CO as calibrant.

The bis(dimethylamine) complex $[ReBr(CO)_3(NHMe_2)_2]$ was prepared as previously described [11] from $[Re_2Br_2(CO)_6(thf)_2]$ with an excess of the amine in toluene as solvent. Purification of the complex was achieved by sublimation at *ca.* 100 °C (5×10^{-3} mmHg †). The i.r. spectra of the recrystallized and sublimed products in CCl_4 in the carbonyl stretching region were identical, within experimental error. The mass spectrum of both the recrystallised and the sublimed products showed an intense peak corresponding to $[Re_2Br_2(CO)_6(NHMe_2)_2]^+$ and the parent peak was not observed.

Preparation of $[ReBr(CO)_3(NHEt_2)_2]$.—The thf adduct $[Re_2Br_2(CO)_6(thf)_2]$ (3.60 g, 4.26 mmol) was suspended in toluene (20 cm³) and treated with diethylamine (1.80 cm³, 17.2 mmol). Within about 20 min the solid dissolved to be then replaced by a colourless solid. The reaction mixture was stirred for 24 h; the solid was then collected by filtration and dried *in vacuo* (3.6 g, 85% yield). It was recrystallized from toluene (maximum temperature 70 °C) [Found: C, 26.4; H, 4.4; Br, 16.1; N, 5.3%; *M* (cryoscopy in benzene) 441. Calc. for $C_{11}H_{22}BrN_2O_3Re$: C, 26.6; H, 4.45; Br, 16.1; N, 5.65%; *M* 496.4].

In contrast to the corresponding methyl derivative,[11] which could be sublimed unchanged, the ethyl complex underwent sublimation at about 100 °C (*ca.* 5×10^{-2} mmHg) with formation of a colourless solid analysing for $[Re_2Br_2(CO)_6(NHEt_2)_2]$ [Found: C, 20.0; H, 2.6; Br, 20.2; N, 3.3%; *M* (cryoscopy in benzene) 822. Calc. for $C_{14}H_{22}Br_2N_4O_6Re_2$: C, 19.85; H, 2.6; Br, 18.9; N, 3.3%; *M* 846.5].

Preparation of $[Re(CO)_3(O_2CNEt_2)(NHEt_2)]$.—The bis-(amine) complex $[ReBr(CO)_3(NHEt_2)_2]$ (2.06 g, 4.16 mmol) in toluene (25 cm³) was treated with diethylamine (0.82 cm³, 7.85 mmol) and dry CO_2 at room temperature. After being stirred for about one day, the reaction mixture was filtered and the solution of the diethylcarbamato-complex was partially evaporated under reduced pressure and then treated with heptane (25 cm³). Upon cooling at 0 °C, the colourless compound which crystallized out was collected by filtration and dried *in vacuo* (0.97 g, 51% yield) [Found: C, 31.5; H, 4.8; N, 6.4%; *M* (cryoscopy in benzene) 785. Calc. for $C_{12}H_{21}N_2O_5Re$: C, 31.35; H, 4.6; N, 6.1%; *M* 459.5].

X-Ray Data Collection and Crystal Data.—$[ReBr(CO)_3(NHMe_2)_2]$. A crystal (dimensions 0.33 × 0.33 × 0.40

† Throughout this paper: 1 mmHg ≈ (101 325/760) Pa.

mm) of the dimethylamine derivative was sealed in a thin-walled capillary under a nitrogen atmosphere, due to its instability upon prolonged exposure to air. The *X*-ray data were collected in a manner described previously [10a] and corrected for Lorentz, polarization, and absorption effects. The crystal data and details of data collection are given in Table 1.

TABLE 1

Crystal data collection and refinement

Empirical formula	$C_{11}H_{22}BrN_2O_3Re$	$C_7H_{14}BrN_2O_3Re$
M	496.4	440.3
a/Å	7.340(2)	9.023(3)
b/Å	9.784(3)	11.537(4)
c/Å	22.742(6)	12.199(4)
β/°	95.05(2)	97.28(3)
U/Å^3	1 626.9	1 259.7
Z	4	4
Space group	$P2_1/n$	$P2_1/n$
D_c/g cm^{-3}	2.03	2.32
F(000)	944	816
μ(Mo-K_α)/cm^{-1}	105.2	135.4
λ(Mo-K_α)/Å	0.710 73	0.710 73
Scanning range for 2θ/°	$6.0 < 2\theta < 50.0$	$1.0 < 2\theta < 50.0$
Crystal orientation	Near [1,0,0]	Near [1,0,0]
Standards for intensity control (every 30 reflections)	[2,4̄,8̄] and [3,4,4]	[2,0,0] and [0,0,2]
Scan width for each reflection, Δθ	0.85 + 0.35tanθ	0.80 + 0.20tanθ
Maximum scan time/s	300	240
Minimum number of counts above background for prescan	40	40
Scan techniques	ω − 2θ	ω − 2θ
Total reflections collected	3 501	2 259
Contributing reflections in the last least-squares refinement	2 808	1 450
Variables	153	127
Weighting scheme	$w = 1/\sigma^2(F)$	unit weights
Final $R(F) = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.046	0.055
Final $R'(F) = [\Sigma w(\|\|F_o\| - \|F_c\|\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.043	0.056

$[ReBr(CO)_3(NHEt_2)_2]$. Suitable, transparent crystals of this complex were also sealed in thin-walled capillaries under a nitrogen atmosphere. The crystals were too fragile mechanically to allow pressure to be used in lodging them securely inside the walls of the capillary. Instead, we used silicone grease which produced the desired result but it did not allow us to determine the indices of the bounding faces nor to measure the crystal meaningfully for absorption correction. Since the absorption coefficient is relatively large ($\mu = 105.2$ cm^{-1}, see Table 1) and we could not correct for the undesirable effect absorption had on the measured structure factors, two of the carbon atoms [carbonyl, C(2) and C(3)] refined with non-positive definite anisotropic thermal parameters. This is an artifact of the uncorrected data and we eliminated it by refining these two atoms isotropically.

The data were collected in exactly the manner described previously for the other compounds of this series.[10a] Those crystallographic parameters and data collection and processing details which are unique to this study are summarized in Table 1.

Solution of the Structure and Refinement.—The position of the Re atom was deduced from the inspection of a Patterson map for $[ReBr(CO)_3(NHMe_2)_2]$ and the subsequent calculation of difference-Fourier maps allowed the location of the remaining non-hydrogen atoms. Refinement with isotropic temperature factors led to a reliability index

TABLE 2

Fractional atomic co-ordinates

Atom	x/a	y/b	z/c
	$[ReBr(CO)_3(NHEt_2)_2]$		
Re	0.089 8(1)	0.096 0(1)	0.139 3(0)
Br	0.247 1(4)	0.055 0(2)	0.039 8(1)
O(1)	−0.087(3)	0.121(2)	0.257(1)
O(2)	0.425(2)	−0.035(2)	0.207(1)
O(3)	0.267(3)	0.372(2)	0.164(1)
N(1)	−0.049(3)	−0.101(2)	0.112(1)
N(2)	−0.145(2)	0.197(2)	0.084(1)
C(1)	−0.008(5)	0.112(2)	0.214(1)
C(2)	0.291(4)	0.010(2)	0.184(1)
C(3)	0.189(3)	0.265(2)	0.154(1)
C(11)	−0.244(3)	−0.120(2)	0.129(1)
C(12)	−0.342(3)	−0.243(3)	0.103(1)
C(13)	0.052(3)	−0.226(2)	0.124(1)
C(14)	0.070(4)	−0.272(2)	0.190(1)
C(21)	−0.099(4)	0.312(2)	0.047(1)
C(22)	−0.256(4)	0.374(3)	0.007(1)
C(23)	−0.308(3)	0.242(2)	0.121(1)
C(24)	−0.249(4)	0.369(2)	0.160(1)
H(11A)	−0.248	−0.120	0.175
H(11B)	−0.326	−0.032	0.113
H(12A)	−0.475	−0.254	0.116
H(12B)	−0.339	−0.243	0.056
H(12C)	−0.259	−0.333	0.120
H(13A)	0.173	−0.224	0.107
H(13B)	−0.034	−0.307	0.100
H(14A)	0.137	−0.369	0.197
H(14B)	0.148	−0.195	0.217
H(14C)	−0.065	−0.280	0.209
H(21A)	0.009	0.276	0.020
H(21B)	−0.030	0.392	0.074
H(22A)	−0.213	0.454	−0.020
H(22B)	−0.318	0.292	−0.020
H(22C)	−0.357	0.411	0.035
H(23A)	−0.356	0.163	0.148
H(23B)	−0.431	0.275	0.093
H(24A)	−0.345	0.407	0.188
H(24B)	−0.123	0.337	0.190
H(24C)	−0.200	0.452	0.133
	$[ReBr(CO)_3(NHMe_2)_2]$		
Re	0.960 88(7)	0.883 30(6)	0.757 97(5)
Br	0.938 8(2)	1.089 6(2)	0.850 5(2)
O(1)	0.982(2)	0.649(2)	0.647(2)
O(2)	0.699(2)	0.917(2)	0.602(1)
O(3)	1.137(2)	0.982(2)	0.578(1)
N(1)	0.844(2)	0.821(2)	0.901(1)
N(2)	1.173(1)	0.862(2)	0.876(1)
C(1)	0.968(2)	0.736(2)	0.700(2)
C(2)	0.781(2)	0.903(2)	0.664(2)
C(3)	1.060(2)	0.948(2)	0.647(2)
C(4)	0.681(2)	0.853(2)	0.886(2)
C(5)	0.857(2)	0.700(2)	0.926(2)
C(6)	1.289(2)	0.951(2)	0.867(2)
C(7)	1.248(2)	0.748(2)	0.877(2)
H(1)[N(1)]	0.898	0.861	0.968
H(2)[N(2)]	1.147	0.909	0.952
H(3)[C(4)]	0.640	0.809	0.868
H(4)[C(4)]	0.602	0.823	0.955
H(5)[C(4)]	0.673	0.952	0.895
H(6)[C(5)]	0.843	0.682	1.013
H(7)[C(5)]	0.775	0.649	0.863
H(8)[C(5)]	0.956	0.720	0.995
H(9)[C(6)]	1.328	0.918	0.816
H(10)[C(6)]	1.246	1.029	0.852
H(11)[C(6)]	1.362	0.959	0.939
H(12)[C(7)]	1.166	0.657	0.881
H(13)[C(7)]	1.338	0.746	0.960
H(14)[C(7)]	1.263	0.730	0.819

$R(F) = 0.084$. Conversion to anisotropic thermal parameters and further refinement gave $R(F) = 0.060$. The hydrogen-atom positions were determined from a difference-Fourier map but their parameters were not refined. Additional cycles of refinement led to final values of $R(F) = 0.055$ and $R'(F) = 0.056$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations (σ). A final difference-Fourier showed no feature greater than 0.3 e Å^{-3}. The standard deviation of an observation of unit weight was 1.62. 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. A total of 1 450 reflections, with $I > 3\sigma(I)$, were used in the refinement. Refinement was carried out using the ORFLS program of Busing and Levy.*

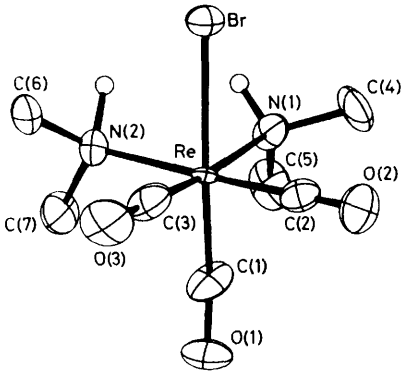


FIGURE 1 ORTEP view of $[ReBr(CO)_3(NHMe_2)_2]$ with the numbering scheme

The structure of $[ReBr(CO)_3(NHEt_2)_2]$ was solved by Patterson methods for the Re and Br atoms. The non-hydrogen atoms came out in the first difference map computed. The hydrogen atoms were added at ideal positions with fixed thermal parameters. Under these conditions,

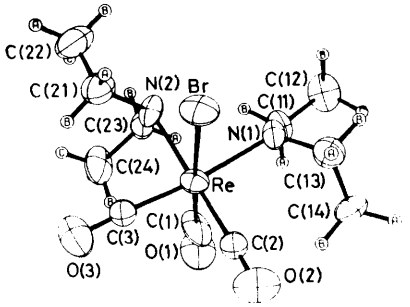


FIGURE 2 ORTEP view of $[ReBr(CO)_3(NHEt_2)_2]$ with the numbering scheme

the refinement converged to conventionally defined $R(F) = 0.046$ and $R'(F) = 0.043$. The weights used were $w = 1/\sigma^2(F)$, where the values of $\sigma(F)$ were obtained assuming that Poisson statistics are obeyed. A total of 2 808 reflections with $I > 3\sigma(I)$ were used in the refinement. All data processing was done with a Honeywell 66/60 computer using the SHELX system of programs by G. M. Sheldrick.[12] The final values of position parameters for both compounds are given in in Table 2. Anisotropic thermal parameters, observed and calculated structure factor amplitudes, and relevant least-squares planes for both compounds are given in Supplementary Publication No. SUP 23120 (25 pp.).†

The molecular structure and atom-numbering scheme for $[ReBr(CO)_3(NHMe_2)_2]$ is given in Figure 1 and that for $[ReBr(CO)_3(NHEt_2)_2]$ in Figure 2.[13] Bond distances and angles are listed in Table 3.

TABLE 3

Bond distances (Å) and angles (°) for $[ReBr(CO)_3(NHR_2)_2]$

	R = Et	R = Me
(*a*) Distances		
Re–Br	2.660(2)	2.652(2)
Re–N(1)	2.24(2)	2.27(1)
Re–N(2)	2.27(2)	2.26(1)
Re–C(1)	1.90(2)	1.85(2)
Re–C(2)	1.90(2)	1.88(2)
Re–C(3)	1.82(2)	1.87(2)
C(1)–O(1)	1.20(3)	1.21(3)
C(2)–O(2)	1.16(3)	1.20(2)
C(3)–O(3)	1.20(3)	1.22(3)
N(1)–C(11)/N(1)–C(4)	1.53(3)	1.52(2)
N(1)–C(13)/N(1)–C(5)	1.45(3)	1.44(3)
N(2)–C(21)/N(2)–C(6)	1.46(3)	1.48(3)
N(2)–C(23)/N(2)–C(7)	1.58(3)	1.48(3)
C(11)–C(12)	1.50(3)	
C(13)–C(14)	1.57(3)	
C(21)–C(22)	1.52(4)	
C(23)–C(24)	1.56(3)	
(*b*) Angles		
Br–Re–C(1)	174.5(8)	176.0(7)
Br–Re–C(2)	90.5(7)	92.5(6)
Br–Re–C(3)	95.2(7)	91.0(7)
Br–Re–N(1)	81.4(4)	83.5(5)
Br–Re–N(2)	87.7(4)	86.1(4)
Re–C(1)–O(1)	173(2)	168(2)
Re–C(2)–O(2)	173(2)	178(2)
Re–C(3)–O(3)	175(2)	173(2)
Re–N(1)–C(11)/Re–N(1)–C(4)	116(1)	112(1)
Re–N(1)–C(13)/Re–N(1)–C(5)	118(1)	116(1)
Re–N(2)–C(21)/Re–N(2)–C(6)	117(1)	115(1)
Re–N(2)–C(23)/Re–N(2)–C(7)	114(1)	117(1)
N(1)–Re–C(1)	97.1(9)	92.5(9)
N(1)–Re–C(2)	94.7(8)	93.3(7)
N(1)–Re–C(3)	173.0(7)	174.4(9)
N(1)–Re–N(2)	85.2(6)	85.1(6)
N(2)–Re–C(1)	97.4(1)	94.2(8)
N(2)–Re–C(2)	178.2(8)	178.0(7)
N(2)–Re–C(3)	88.6(8)	93.4(8)
C(1)–Re–C(2)	84.0(1)	87.0(9)
C(1)–Re–C(3)	87(1)	93(1)
C(2)–Re–C(3)	91(1)	88.0(9)
N(1)–C(11)–C(12)	115(2)	
N(1)–C(13)–C(14)	115(2)	
N(2)–C(21)–C(22)	116(2)	
N(2)–C(23)–C(24)	110(2)	
C(11)–N(1)–C(13)/C(4)–N(1)–C(5)	109(2)	108(2)
C(21)–N(2)–C(23)/C(6)–N(2)–C(7)	108(2)	107(1)

RESULTS AND DISCUSSION

The dialkylamine complexes described in this paper were prepared by the reaction of the thf adduct with the appropriate amine [equation (1)]. The methyl deriv-

* Crystallographic programs used on a Univac 1110 include ORFLS (structure factor calculation and least-squares refinement), by W. R. Busing, K. O. Martin, and H. A. Levy; ORFFE (distances and angles with e.s.d.s), by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP (thermal ellipsoid drawings), by C. K. Johnson; FOURIER (D. J. Hodgson's version of Dellaca and Robinson's program); and BPL (least-squares planes), by W. E. Hunter.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 4

Spectral data for some rhenium(I) complexes

Complex	Medium	$\tilde{\nu}$(CO)/cm^{-1}			$\tilde{\nu}$(NH)/cm^{-1}	Ref.
$[Re_2Br_2(CO)_6(thf)_2]$	$CHCl_3$	2 032m	1 924s			*a*
$[ReBr(CO)_3(thf)_2]$	thf	2 030m	1 914s	1 891ms		*a*
$[ReBr(CO)_3(NH_2CH_2CH_2NH_2)]$	thf	2 018s	1 903s	1 876s		*a*
$[ReBr(CO)_3(NHMe_2)_2]$ [c]	CCl_4	2 032s	1 926s	1 896s		*a*
	Benzene	2 026s	1 915s	1 887s		*a*
	thf	2 023s	1 912s	1 887s		*a*
	Nujol	2 030s	1 920s	1 870s	3 210	*b*
$[ReBr(CO)_3(NHMe_2)_2]$ [d]	CCl_4	2 031s	1 927s	1 896s		*b*
$[ReBr(CO)_3(NHEt_2)_2]$ [b,e]	Nujol	2 020s		1 890s, br	3 210 3 190	*b*
$[Re_2Br_2(CO)_6(NHEt_2)_2]$ [d]	CCl_4	2 031s	1 924s			*b*
	Nujol	2 020s		1 900s, br	3 250	*b*
$[Re(CO)_3(O_2CNEt_2)(NHEt_2)]$	CH_2Cl_2	2 016m	1 899ms	1 876s		*b*
	thf	2 016m	1 904ms	1 886s		*b*
	Toluene	2 018m	1 904ms	1 883s		*b*
	CCl_4 [f]	2 020m	1 906ms	1 886		*b*
	Heptane [f]	2 018m	1 906ms	1 897s		*b*
	Nujol	2 020m	1 895s	1 875s	3 260	*b*

[a] Data from ref. 11. [b] This work. [c] Recrystallized product. [d] Sublimed. [e] No solution spectra could be measured because of low solubility and alteration with time of the soluble species. [f] Three less intense bands are observable (in heptane) at 2 030, 1 923, and 1 911 cm^{-1}.

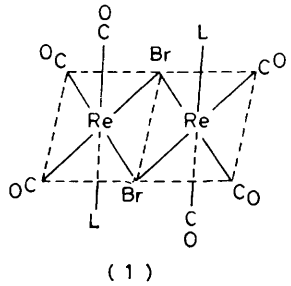
ative is thermally stable and it sublimes unchanged

$$[Re_2Br_2(CO)_6(thf)_2] + 4NHR_2 \longrightarrow 2[ReBr(CO)_3(NHR_2)_2] + 2thf \quad (1)$$

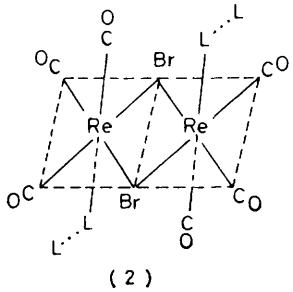
[*ca.* 100 °C (5×10^{-3} mmHg)] as shown by the spectral data, see Table 4. The complex shows a spectral pattern in the carbonyl stretching region with three bands [11] which is typical of the class of rhenium(I) compounds of the type $[ReBr(CO)_3L_2]$ or $[ReBr(CO)_3(LL)]$ (LL = bidentate ligand) with nitrogen containing-ligands in a *fac* stereochemistry. The ethyl derivative $[ReBr(CO)_3(NHEt_2)_2]$ behaved differently from its methyl analogue in many respects. I.r. spectra (Nujol mulls) had the three-band pattern typical of $[ReBr(CO)_3L_2]$ complexes; however, dilute solutions of the compound in CCl_4 showed signs of alteration with time and moreover, sublimation *in vacuo* modified the original analytical composition, one amine group per rhenium being lost, thus suggesting the gas-phase reaction (2).

$$2[ReBr(CO)_3(NHEt_2)_2] \longrightarrow 2NHEt_2 + [Re_2Br_2(CO)_6(NHEt_2)_2] \quad (2)$$

Consistent with this hypothesis, the carbonyl pattern in the i.r. spectrum of the sublimed product was that typical of $[Re_2Br_2(CO)_6L_2]$ complexes of *trans* structure (2), with two main bands at 2 031ms and 1 924s cm^{-1} (CCl_4), to be compared with the bands at 2 032 and 1 924 cm^{-1} (in chloroform) found for $[Re_2Br_2(CO)_6(thf)_2]$, which is known [11] to have the solid-state structure (1; L = thf). However, the possibility existed that both the amine complexes had structure (2) with more (L = $NHMe_2$) or less (L = $NHEt_2$) tightly hydrogen-bonded amine and this, in addition to the general interest for amine complexes of low-valent transition elements outlined in the Introduction, justifies the undertaking of the *X*-ray investigation of both complexes.



(1)



(2)

The structure of both amine complexes consists of six-co-ordinate rhenium(I) bonded to the three carbonyl groups in *fac* geometry, to the two nitrogen atoms of the amine, and to the bromine atom. In spite of the difficulties with absorption and refinement, the Re–C and C–O distances are near those found in the dimeric members of the $[Re_2Br_2(CO)_6(E_2R_{2n})]$ series; [10] in the latter cases the donor set of atoms is *fac*-$ReBr_2(CO)_3E$ for each individual six-co-ordinate rhenium atom. For comparison of the data, see Table 5. Also, the molecular parameters of our compounds compare favourably with those obtained by Tsutsui and co-workers [14] for $[\{Re(CO)_3\}_2(tpp)]$ (tpp = *meso*-tetraphenylporphinate).

The Re–Br distances for the amine complexes agree well with each other, but are among the longest observed in the related compounds of rhenium(I), see Table 5. In $[Re_2Br_2(CO)_6(S_2Ph_2)]$ [10b] the Re–Br length is 2.607(3) Å, while in the corresponding dimethyl disulphide derivative [10a] the separation is 2.599(2) Å. In the case of $[Re_2Br_2(CO)_6(P_2Ph_4)]$,[10f] the Re–Br bond distances are in the range 2.632(2)—2.679(2) Å [average 2.650(6) Å]. In $[Re_2Br_2(CO)_6(thf)_2]$,[11] in which the Re_2Br_2 fragment is planar, the Re–Br distance is 2.643(4) Å. If one takes into consideration that all the compounds of the $[Re_2Br_2(CO)_6(E_2R_{2n})]$ series and $[Re_2Br_2(CO)_6(thf)_2]$ itself are bromide-bridged dimers, for which longer Re–Br distances are to be expected, the long Re–Br bond found for the present amine complexes becomes particularly significant. Bearing this in mind, it is im-

TABLE 5

Interatomic distances (Å) in some rhenium complexes [a]

Compound	Oxidation number of rhenium	Re–Br	Re–N	Re–C	Ref
(*a*) With nitrogen ligands					
$[ReBr(CO)_3(Me_2NCH_2CH_2NMe_2)]$	I	2.636(2)	2.28(1) 2.27(2)	1.95(2) 1.91(2) 1.89(2)	15
$[ReBr(CO)_3(MeNHCH_2CH_2NHMe)]$	I	2.609(1)	2.213(6) 2.236(7)	1.898(9) 1.893(10) 1.894(10)	16
$[\{Re(CO)_3\}_2(tpp)]$ [b]	I		2.168(9)	1.869(16) 1.854(16) 1.847(19)	14
$[ReBr(CO)_3(NHMe_2)_2]$	I	2.652(2)	2.27(1) 2.26(1)	1.85(2) 1.88(2) 1.87(2)	This work
$[ReBr(CO)_3(NHEt_2)_2]$	I	2.660(2)	2.24(2) 2.27(2)	1.90(2) 1.90(2) 1.82(2)	This work
$[ReO_2(en)_2Cl]$	V		2.16(2) [c]		*d*
$[ReO_2(py)_4Cl]\cdot 2H_2O$	V		2.15(1) [c]		*d*
$[ReN(S_2CNEt_2)_2]$	V		1.656		*e*
(*b*) Without nitrogen ligands					
$[Re_2Br_2(CO)_6(S_2Ph_2)]$	I	2.607(3)		1.915(22) 1.903(31) 1.858(22)	10*b*
$[Re_2Br_2(CO)_6(Se_2Ph_2)]$	I	2.656(20)		1.89(3) 1.87(3) 1.94(3)	10*c*
$[Re_2Br_2(CO)_6(Te_2Ph_2)]$	I	2.634(7)		1.935(50)	10*d*

[a] In all of the complexes of rhenium(I) the stereochemistry around the metal is *fac*. [b] tpp = *meso*-Tetraphenylporphinate. [c] Average value. [d] C. J. L. Lock, and G. Turner, *Acta Crystallogr., Sect. B*, 1978, **34**, 923. [e] S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1972, 1079.

portant also to note that in the two other rhenium(I) compounds with a nitrogen ligand, namely $[ReBr(CO)_3(Me_2NCH_2CH_2NMe_2)]$ [15] and $[ReBr(CO)_3(MeNHCH_2CH_2NHMe)]$,[16] whose molecular parameters are available in the literature, the observed Re–Br distances [2.636(2) and 2.609(1) Å respectively] can be compared with the average distances of 2.652(2) and 2.660(2) Å in $[ReBr(CO)_3(NHMe_2)_2]$ and $[ReBr(CO)_3(NHEt_2)_2]$ respectively.

The reason for the exceedingly longer Re–Br distances in our compounds is uncertain. These data suggest, however, that caution must be taken in relating bond distances to other properties of a molecule, such as the '*trans* influence.'

The presence of two *cis* monodentate nitrogen ligands in our complexes offers the unique possibility of investigating the hydrogen-bonding interactions in this specific case. The intermolecular N · · · Br contacts for $[ReBr(CO)_3(NHMe_2)_2]$ are 3.55 and 3.65 Å, which are higher than the van der Waals radii (3.45 Å [17]). For the ethyl derivative, the corresponding N · · · Br contacts are 3.65 and 3.77 Å. These findings, together with the observation that the band at about 3 200 cm^{-1} associated with the N–H stretching vibration is very little changed on going from the solid-state spectra in Nujol to those in solution, excludes any important intermolecular hydrogen bonding being present in these complexes. The problem remains whether intramolecular hydrogen bonding is present, which may occur between the two co-ordinated amine groups or between the amine hydrogens and the filled metal t_{2g} orbitals.[9,18] The analysis of the internal parameters of the two molecules led us to conclude that the two N–H bonds do not greatly interact either with themselves or with the filled *d* orbitals of the metal, which is not unexpected because of the π back-donation to the CO groups.

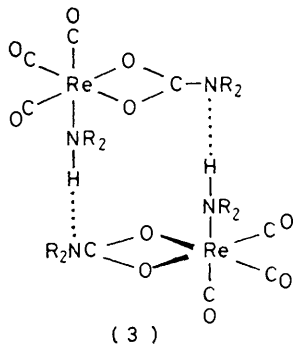
The alkyl groups in $[ReBr(CO)_3(NHR_2)_2]$ are not equivalent, as shown by the C–N–Re–Br dihedral angles [R = Me: C(4)–N(1)–Re–Br 74(1), C(5)–N(1)–Re–Br −161(1), C(6)–N(2)–Re–Br −59(1), C(7)–N(2)–Re–Br 174(1); R = Et: C(13)–N(1)–Re–Br 80(2), C(11)–N(1)–Re–Br −148(1), C(21)–N(2)–Re–Br −56(1), C(23)–N(2)–Re–Br 176(1)°]. The non-equivalence of the amine groups is evidenced by the spectra [Nujol or $(CClF_3)_n$ mulls] of the diethylamine complex showing two N–H stretches separated by *ca.* 20 cm^{-1}; the dimethylamine derivative has only one N–H stretching vibration, which is in agreement with its smaller dihedral angle as specified above.

In view of the paucity of the data concerning amine complexes of rhenium,[19] which is in contrast with the well established Re–N multiple bonds,[20] we decided to investigate the reactivity of the present amine complexes with CS_2 [11] and CO_2. The reaction of the bis(dimethylamine) complex with CO_2 gave the corresponding carbamato-complex [equation (3)]. The diethylcarbamato-complex could not be isolated in a pure form.

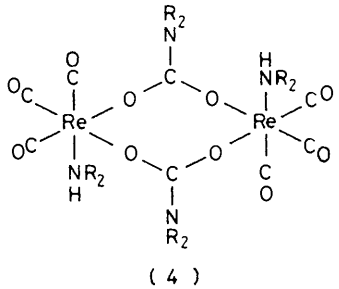
$$[ReBr(CO)_3(NHEt_2)_2] + CO_2 + NHEt_2 \longrightarrow [NH_2Et_2]Br + [Re(CO)_3(O_2CNEt_2)(NHEt_2)] \quad (3)$$

This complex has an i.r. spectrum in the carbonyl

stretching region which is similar to that [11] of the corresponding dithiocarbamato-derivatives $[Re(CO)_3(S_2CNR_2)(NHR_2)]$ (R = Me or Et), see Table 4, with three carbonyl absorptions, typical of the monomeric *fac*-$Re(CO)_3$ pattern. However, by looking at the details of the i.r. spectrum under high resolution and in a non-polar solvent such as heptane, three more bands of lower intensity are observable at 2 030, 1 923, and 1 911 cm^{-1} in addition to the intense main bands at 2 018, 1 906, and 1 897 cm^{-1}. Moreover, the molecular weight by cryoscopy in benzene lies between that calculated for the monomer and that of the dimer. We believe that these observations in solution can be accommodated by assuming that the carbamato-complex is undergoing some kind of molecular association in solution, forming dimers of the hydrogen-bonded type, structure (3), or of the carbamato-bonded type, (4). In view of the fact that the formation of (3) does not require bond-breaking, that the extra $\tilde{\nu}$(CO) bands are at higher wavenumbers,



(3)



(4)

and that the carbamato-nitrogen is a site of high electron density, this is the preferred structure. The *O*-carbamato-complex shows an intense band at 1 520 cm^{-1} which is attributed [21] to the C–N stretching vibration of a bidentate carbamato-group. Infrared bands around 1 700 cm^{-1} which are typical of monodentate carbamato-groups are absent, thus confirming the structural assignment for this compound as a monomeric complex of six-co-ordinate rhenium(I), two co-ordination sites being occupied by the two oxygens of the carbamato-group.

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