Journal of Organometallic Chemistry, 197 (1980) 345—355
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

FORMATION OF HALOGENOTRICARBONYL(*N*,*N*′-DIMETHYLETHANE-1,2-DIAMINE)RHENIUMS; AND THE CRYSTAL AND MOLECULAR STRUCTURE OF BROMOTRICARBONYL(*N*,*N*′-DIMETHYLETHANE-1,2-DIAMINE)RHENIUM(I)

EDWARD W. ABEL, MAQBOOL M. BHATTI,

Department of Chemistry, The University, Exeter EX4 4QD (Great Britain)

MICHAEL B. HURSTHOUSE, K.M. ABDUL MALIK,

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS (Great Britain)

and MOHAMED A. MAZID

Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX (Great Britain)

(Received March 19th, 1980)

Summary

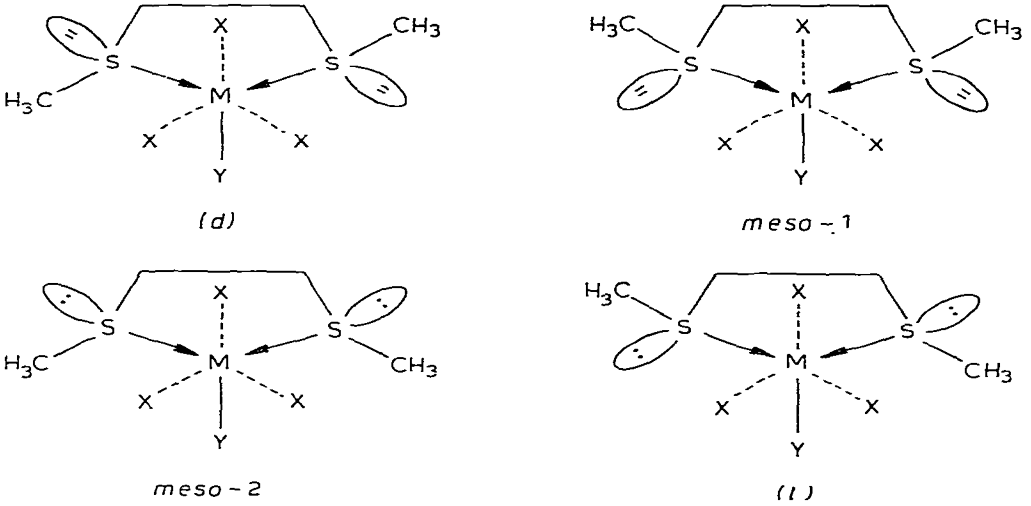
The complexes $[\mathrm{ReX(CO)_3\{Me(H)NCH_2CH_2N(H)Me\}}]$, (X = Cl, Br and I) have been prepared and characterised. The molecular structure of the bromotricarbonyl(*N*,*N*′-dimethylethane-1,2-diamine)rhenium(I) has been shown to have the bromine atom *cis* to both donor nitrogen atoms, and each of the methyl groups of the dmen ligand is positioned away from the bromine atom.

Introduction

In recent studies of the chelating ligand 2,5-dithiahexane we have noted [1,2] the existence of all the possible *fac* isomers in both $\mathrm{Pt^{IV}}$ and $\mathrm{Re^{I}}$ complexes as illustrated in Fig. 1.

These isomers interconvert by independent tetrahedral inversions at the two sulphur atoms, and whilst the proportion of each isomer present is largely temperature independent, the composition of the mixture is very dependent upon the nature of the halogen atom in both series of complexes.

N,*N*′-dimethylethane-1,2-diamine(dmen) is very closely analogous to 2,5-dithiahexane as a chelating group and some of the isomers analogous to



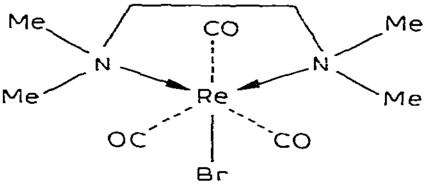
(d) meso-1

meso-2 (l)

Fig. 1. The observed isomers in the complexes [MX_3Y $MeSCH_2CH_2SMe$] where M = Pt^{IV}, X = Me, Y = Cl, Br or I; M = Re^I, X = CO, Y = Cl, Br or I.

those in Fig. 1 have been observed [3] and separated [4] by recrystallization for certain platinum complexes. In the absence of deprotonation, these isomers are non-interconverting [3], in contrast to the sulphur analogues.

We have previously reported [5] the complex bromotricarbonyl (*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)rhenium(I) (I), which can have only one *fac*-isomer, and whose structure has recently been reported [6].



(I)

We were interested to extend our investigation of this type of complex to the *N*,*N*′-dimethylethane-1,2-diamine (dmen) ligand, where the corresponding *fac*-[$Re(CO)_3X$dmen] species has the possibility to form four different isomers.

Results and discussion

The dimeric carbonyl halides of rhenium and *N*,*N*′-dimethylethane-1,2-diamine react smoothly to produce the three complexes in good yield. (Table 1).

$$[\{Re(CO)_4X\}_2] + 2\,Me(H)NCH_2CH_2N(H)Me \rightarrow 2[Re(CO)_3X\ dmen] + 2\,CO$$

(X = Cl, Br and I)

The infrared spectra in the metal carbonyl stretching region (Table 1), indicated a *fac* structure for the products.

The four possible isomers for such complexes are illustrated in Fig. 2 (ignoring ring conformation).

In the cases of the chloride, bromide and iodide products the infrared spectra in the metal carbonyl region ($2A' + A''$) showed no extra bands due to isomers, but the local symmetry about the metal atom for all of the isomers in Fig. 2 would be similar; and solution infrared spectra would thus be unlikely to be sufficiently sensitive to detect isomers of this particular type.

The ^{1}H NMR spectra of these complexes are reported in Table 2, with the predictable broad signal for H—N, and poorly resolved methylene protons. Notable, however, are two sharp signals of equal intensity for the methyl protons. Such a very simple spectrum precludes the presence of a mixture of the isomers illustrated in Fig. 2, and has two likely explanations. Either the product is the racemate (a + c), where the two signals are due to the two methyl groups in each isomer having quite different chemical environments, or the product is one or other of the two *meso* forms (b and d), but in which, despite the identical environments of their respective methyl groups the doublet has been caused by a ^3J coupling with the H—N proton. A value of ca. 6 Hz for ^3J (between CH_3N and HN) has already been noted in some dmen metal complexes [3,4], and we have ourselves by decoupling the H—N resonance reduced the ^{1}H signals for CH_3N in our three compounds to a sharp singlet. Thus the chloro, bromo and iodo complexes all appear to be of one isomeric form, which is one or other of the *meso* isomers in Fig. 2.

The existence of bromotricarbonyl(*N*,*N*,*N'*,*N'*-tetramethylethane-1,2-diamine)rhenium(I) (I) demonstrates [5,6] that there would be no actual steric restriction to the formation of either *meso* isomer b or *meso* isomer d, but in

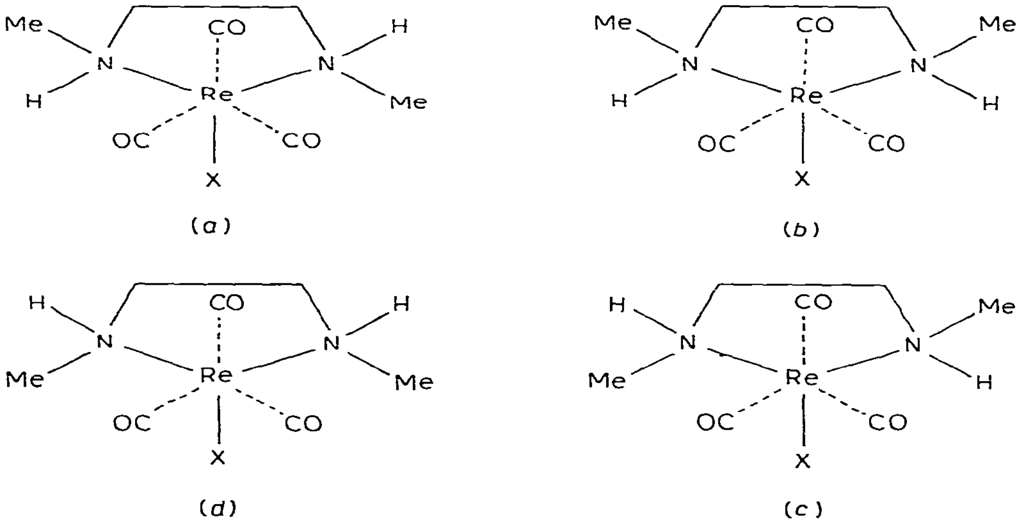


Fig. 2. Possible isomers of *fac*-[ReX(CO)$_3$ dmen]. a and c represent the *d* and *l* forms of a racemic mixture, and b and d are the two (different) *meso* isomers.

TABLE 1

HALOGENOTRICARBONYL (*N*,*N*′-DIMETHYLETHANE-1,2-DIAMINE)RHENIUMS

Compound	Colour	Yield (%)	m.p. (°C)	Analyses (Found (Calc.)%) C	H	N	ν(CO)cm^{-1} [a]
[ReCl(CO)$_3$(Me(H)NCH$_2$CH$_2$N(H)Me)]	White	70	210—213	20.8(21.3)	2.95(3.07)	6.98(7.10)	2030s, 1924s, 1888s.
[ReBr(CO)$_3$(Me(H)NCH$_2$CH$_2$N(H)Me)]	White	70	228—230	19.5(19.2)	2.70(2.75)	6.34(6.38)	2034s, 1926s, 1890s.
[ReI(CO)$_3$(Me(H)NCH$_2$CH$_2$N(H)Me)]	White	65	220—222	[b]			2034s, 1924s, 1890s.

[a] In chloroform solution.

[b] C, H, N analyses always slightly high, apparently due to small traces of excess amine ligand.

TABLE 2

^{1}H NMR DATA FOR HALOGENOTRICARBONYL (*N*,*N*′-DIMETHYLETHANE-1,2-DIAMINE) RHENIUMS

Compound	Solvent	Temp.	δ (ppm) relative to TMS (internal)		
			H—N	CH$_2$—N	CH$_3$—N [a]
[ReCl(CO)$_3$Me(H)NCH$_2$CH$_2$N(H)Me]	(CD$_3$)$_2$SO	30°C	4.87 (broad)	~3.0 (multiplet)	2.854, 2.800
[ReBr(CO)$_3$Me(H)NCH$_2$CH$_2$N(H)Me]	(CD$_3$)$_2$SO	30°C	4.90 (broad)	~3.0 (multiplet)	2.847, 2.788
[ReI(CO)$_3$Me(H)NCH$_2$CH$_2$N(H)Me]	(CD$_3$)$_2$SO	30°C	4.87 (broad)	~3.0 (multiplet)	2.844, 2.785

[a] These equal intensity doublets collapsed to sharp singlets upon irradiation with H—N frequency.

the actual reactions one isomer has been formed exclusively, as far as we can detect.

In our studies [1,2] on the analogous sulphur isomers (Fig. 1) we found that with increasing size of halogen atom the proportion of isomer *meso*-2 fell. With the steric requirement of chlorine, bromine or iodine being larger than the carbonyl group we felt that the most likely structure for our products was the *meso* structure b in Fig. 2, where both methyl groups have avoided the bulky halogen atom. We have determined the crystal and molecular structure of [ReBr(CO)$_3$(dmen)] by X-ray methods, and find this conclusion to be substantiated.

The molecular structure of bromotricarbonyl(*N*,*N'*-dimethylethane-1,2-diamine)rhenium(I) is shown in Figure 3 together with the atom numbering system. Selected bond lengths and bond angles are presented in Table 3. The rhenium atom has a distorted octahedral coordination with the dmen ligand forming a chelate ring. The bromine atom is *cis* with respect to both of the donor nitrogen atoms, and the three carbonyls are in a *facial* configuration. Both methyl groups of the dmen ligand are positioned away from the bromine atom, and have very similar environments, confirming the structure b from the alternatives in Figure 2.

The overall geometry of this type of molecule has been reported previously [6] for the structure of the corresponding [ReBr(CO)$_3$tmen] complex. Notable, however, is the significantly shorter Re—Br bond length [2.609(1) Å] in

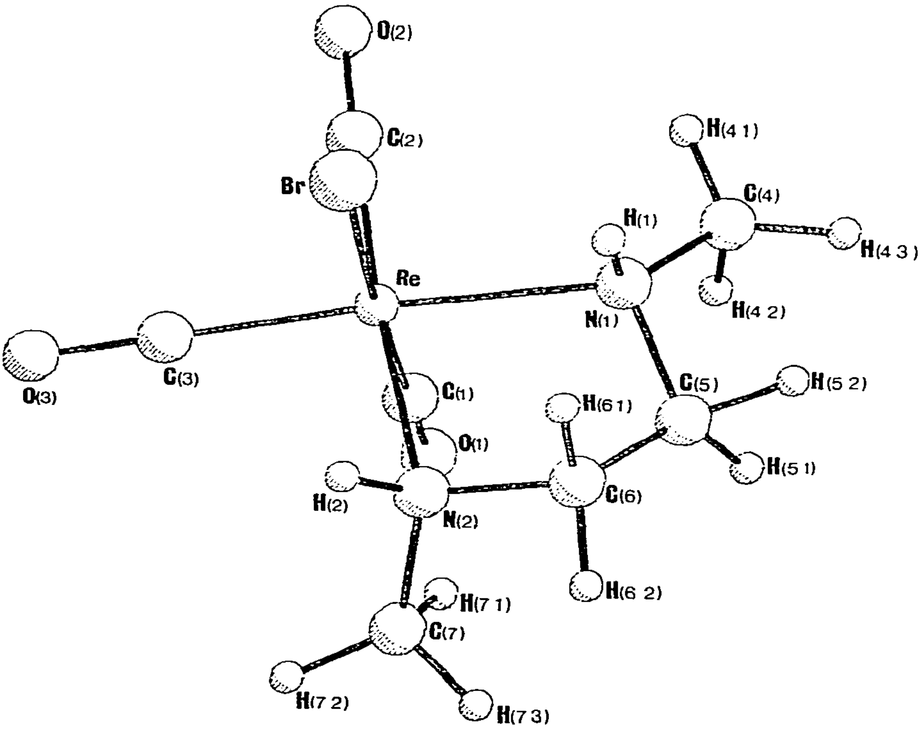


Fig. 3. The molecular structure of bromotricarbonyl(*N*,*N'*-dimethylethane-1,2-diamine)rhenium(I).

TABLE 3

INTRAMOLECULAR INTERATOMIC DISTANCES (Å) AND INTERBOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bond lengths			
Re—Br	2.609 (1)	Re—C(1)	1.898 (9)
Re—N(1)	2.213 (6)	Re—C(2)	1.893(10)
Re—N(2)	2.236 (7)	Re—C(3)	1.894(10)
C(1)—O(1)	1.136(10)	N(1)—C(4)	1.492(10)
C(2)—O(2)	1.143(11)	N(1)—C(5)	1.494(12)
C(3)—O(3)	1.182(12)	N(2)—C(6)	1.498(11)
		N(2)—C(7)	1.504(13)
		C(5)—C(6)	1.483(13)
(b) Bond angles			
Br—Re—C(1)	177.2 (2)	C(1)—Re—N(2)	94.1 (4)
Br—Re—C(2)	91.8 (3)	C(2)—Re—C(3)	88.6 (4)
Br—Re—C(3)	93.4 (3)	C(2)—Re—N(1)	97.4 (3)
Br—Re—N(1)	83.4 (2)	C(2)—Re—N(2)	174.2 (3)
Br—Re—N(2)	84.1 (2)	C(3)—Re—N(1)	173.3 (3)
C(1)—Re—C(2)	89.8 (4)	C(3)—Re—N(2)	95.8 (3)
C(1)—Re—C(3)	88.9 (3)	N(1)—Re—N(2)	78.1 (3)
C(1)—Re—N(1)	94.1 (3)		
Re—N(1)—C(5)	108.4 (5)	Re—N(2)—C(6)	109.8 (6)
Re—N(1)—C(4)	118.8 (5)	Re—N(2)—C(7)	116.3 (6)
Re—N(1)—H(1)	95 (5)	Re—N(2)—H(2)	96 (6)
C(4)—N(1)—C(5)	109.6 (7)	C(6)—N(2)—C(7)	111.9 (8)
C(4)—N(1)—H(1)	122 (6)	C(6)—N(2)—H(2)	112 (5)
C(5)—N(1)—H(1)	100 (6)	C(7)—N(2)—H(2)	110 (6)
Re—C(1)—O(1)	179.4 (9)	N(1)—C(5)—C(6)	109.4 (7)
Re—C(2)—O(2)	178.1 (8)	N(2)—C(6)—C(5)	108.3 (7)
Re—C(3)—O(3)	177.9 (8)		

our dimethyl ligand complex in contrast to the Re—Br bond [2.636(2) Å] in the tetramethyl ligand complex [6].

In $[\mathrm{ReBr(CO)_3(tmen)}]$ the chelate ring is disordered and two crystallographically independent conformations are found for the molecule, differing in the way in which the carbon—carbon bond in the chelate ring twists to achieve an unstrained conformation. In the case of our complex $[\mathrm{ReBr(CO)_3dmen}]$, there is no hint of disorder present in the dmen ligand. Table 4 lists the dihedral angle between the plane containing the rhenium and ring carbon atoms and that which contains the metal and the ring nitrogen atoms (29.0°), and also the torsional angle between the nitrogen atoms across the ligand C—C bond (57.3°).

These angles are significantly different from the corresponding values (23.5° and 51.4°), found in the λ configuration of $[\mathrm{ReBr(CO)_3(tmen)}]$ [6], but the comparison should be made with caution, since in the tmen complex the ring carbons are disordered, and the parameters of these atoms are rather less precise. Figure 4 shows a view of the molecular structure of our complex looking down the line joining the midpoints of the ring carbon atoms and the rhenium atom. This illustrates the puckering of the dmen ligand and adoption of the λ-*gauche* configuration. Bond lengths and angles related to the rest of the molecule are as expected. The shortest intermolecular (non-hydrogen) contact is 3.04 Å

TABLE 4

LEAST-SQUARES PLANES IN THE FORM $Ax + By + Cz = D$, WHERE x, y, z ARE FRACTIONAL CO-ORDINATES

Deviations (Å) of relevant atoms are given in square brackets.

Plane (1)	through Re, N(1) and N(2) atoms $7.8268x - 3.0460y + 4.2672z = 1.7416$
	[C(4) −0.766, C(5) −0.444, C(6) 0.271, C(7) −1.199, H(1) 0.942, H(2) 0.755]
Plane (2)	through Re, C(5) and C(6) atoms $4.9225x + 1.6262y + 6.5245z = 1.5744$
	Angle between plane (1) and (2) = 29.0°

Torsion angle between the N atoms across the C(5)—C(6) bond = 57.3°.

involving N(1) and O(1) $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$. The packing of molecules in the unit cell looking approximately down the *a* axis is shown in Figure 5.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer and ^{1}H NMR spectra were recorded on either a Jeol MH100 or a Jeol JNM-PS100 instrument. Melting points are uncorrected, and reactions were performed routinely under an atmosphere of dry nitrogen. *N*,*N*′-dimethylethane-1,2-diamine was used as supplied and rhenium carbonyl halides were prepared by literature methods [7,8].

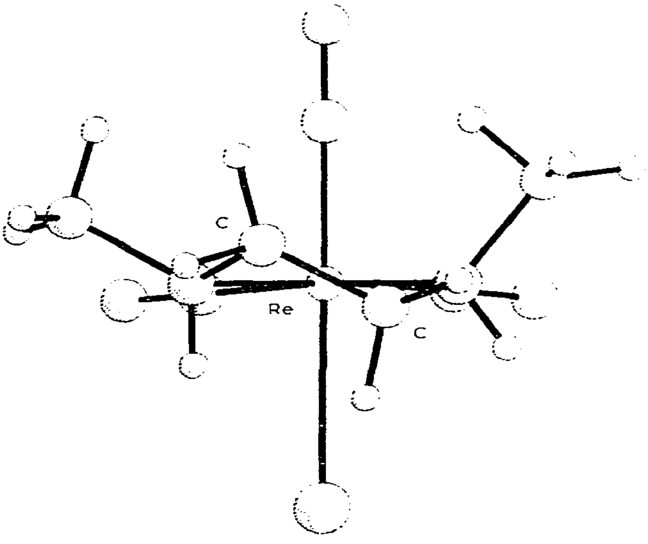


Fig. 4. View of the molecular structure of bromotricarbonyl(*N*,*N*′-dimethylethane-1,2-diamine)rhenium(I) illustrating the puckering of the dmen ligand.

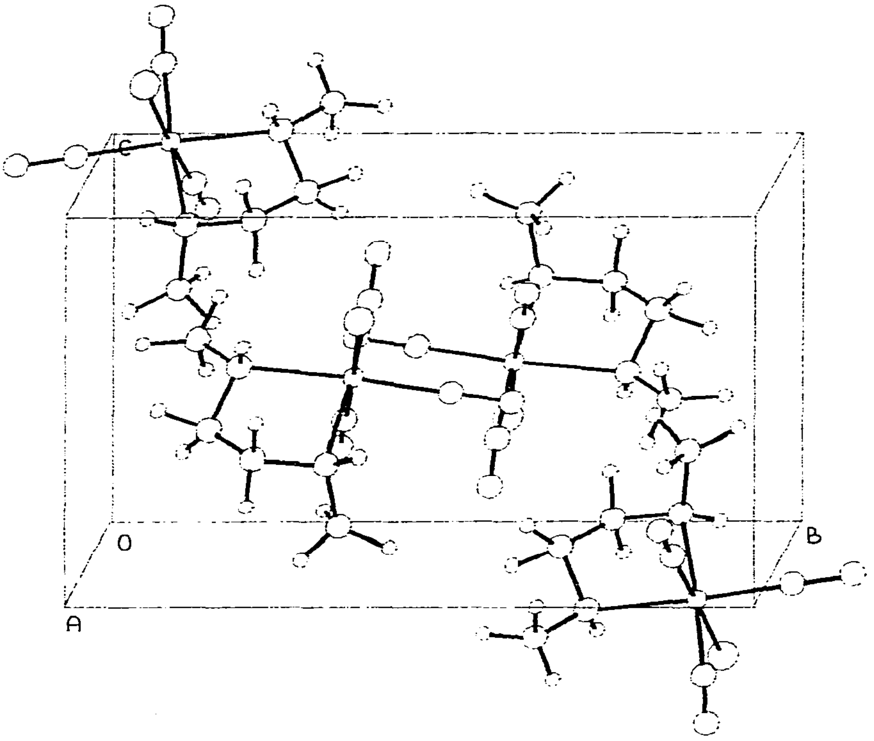


Fig. 5. Packing of the molecules within the unit cell of crystals of bromotricarbonyl(N,N'-dimethylethane-1,2-diamine)rhenium(I) looking approximately down the a axis.

Preparation of bromotricarbonyl(N,N'-dimethylethane-1,2-diamine)rhenium(I)

To [{ReBr(CO)$_4$}$_2$] (0.300 g, 0.396 mmol) in chloroform (10 cm^3) was added N,N'-dimethylethane-1,2-diamine (0.075 g, 0.850 mmol), and the mixture heated under reflux (3 days). Solvent and volatiles were removed (30°C/0.001 mm), and the residue dissolved in chloroform. After filtration the solution was cooled to —20°C, yielding white crystals of the product. The analogous chloro and iodo complexes were prepared in the same way (Table 1).

Crystal data

$C_7H_{12}BrN_2O_3Re$, mol. wt. 438.2, monoclinic, space group $P2_1/n$ (No. 14), a = 10.791(2), b = 13.264(3), c = 8.232(1) Å, β = 99.64(1)°, U = 1161.6 Å^3, Z = 4, D_c = 2.50 g cm^{-3}, $F(000)$ = 808, μ(Mo-K_α) = 139.7 cm^{-3}, λ(Mo-K_α) = 0.71069 Å.

Structure determination

The crystals were colourless transparent blocks, and the specimen chosen had dimensions 0.26 × 0.18 × 0.09 mm, and was bounded by the six intersecting faces (011), (0$\bar{1}\bar{1}$), (01$\bar{1}$), (0$\bar{1}$1), ($\bar{1}$01), and (101). The space group and preliminary cell dimensions were determined from oscillation and Weissenberg photographs. Accurate cell dimensions were calculated by least squares refinement of setting angles for twenty-five reflections within 17° ⩽ θ(Mo-K_α) ⩽ 20°, auto-

TABLE 5

FRACTIONAL COORDINATES (Re $\times 10^5$, OTHERS $\times 10^4$) OF THE NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atoms	x/a	y/b	z/c
Re	24333 (3)	9958(2)	3290 (4)
Br	4596 (1)	766(1)	2251 (1)
O(1)	—33 (6)	1355(5)	—1970(10)
O(2)	1021 (7)	749(5)	3198(10)
O(3)	2156 (8)	—1280(5)	—358(10)
N(1)	2860 (6)	2619(5)	704 (9)
N(2)	3609 (7)	1302(5)	—1609(10)
C(1)	888 (8)	1224(6)	—1103(12)
C(2)	1549 (8)	824(6)	2111(12)
C(3)	2239 (8)	—402(7)	—108(12)
C(4)	1880 (8)	3295(7)	1191(14)
C(5)	3276 (9)	3021(7)	—812(13)
C(6)	4205 (8)	2322(7)	—1338(14)
C(7)	2979(12)	1156(9)	—3366(13)

matically centred on a Nonius CAD 4 diffractometer. Intensity data were recorded on the same instrument using Mo-K_α radiation in conjunction with a graphite monochromator and an ω—2θ scanning mode. All reflections in the range $1.5° \leqslant \theta \leqslant 25°$ and with $k \geqslant 0$, $l \geqslant 0$ and h positive and negative, were measured in the manner described in reference [9]. Two standard reflections were used as intensity controls, and were remeasured every 50 reflections; these showed insignificant variations in intensity during the entire period of the data collection. The data were corrected for Lorentz and polarization and absorption effects and merged to obtain 2034 unique reflections. Of these 1714 satisfied the condition $|F_0| \geqslant 4\sigma(|F_0|)$, and considered as observed.

TABLE 6

ANISOTROPIC TEMPERATURE FACTORS (Re $\times 10^4$, OTHERS $\times 10^3$, Å^2) OF THE NON-HYDROGEN ATOMS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

The temperature factor exponent takes the form:

$-2\pi^2 (U_{11}h^2a^{*2} + - - - 2U_{12}hka^*b^*)$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re	285(2)	246(2)	260(2)	—2(1)	—13(1)	8(1)
Br	49(1)	56(1)	53(1)	—4(1)	—10(1)	14(1)
O(1)	41(4)	57(4)	77(6)	12(4)	—36(4)	—7(3)
O(2)	71(5)	56(4)	52(5)	1(4)	18(4)	3(4)
O(3)	116(6)	34(4)	66(6)	—6(4)	28(5)	—8(4)
N(1)	29(3)	24(3)	33(4)	—1(3)	0(3)	5(3)
N(2)	37(4)	36(3)	39(4)	1(3)	10(3)	2(3)
C(1)	47(5)	30(4)	43(6)	1(4)	1(4)	—5(4)
C(2)	47(5)	35(4)	34(5)	2(4)	11(4)	2(4)
C(3)	49(5)	38(5)	42(6)	2(4)	2(4)	6(4)
C(4)	42(5)	43(5)	56(7)	—12(5)	8(4)	11(4)
C(5)	51(5)	36(4)	51(6)	6(4)	15(5)	—5(4)
C(6)	34(4)	46(5)	62(7)	7(5)	15(4)	—6(4)
C(7)	83(8)	65(6)	25(6)	4(5)	2(5)	14(5)

TABLE 7

FRACTIONAL COORDINATES ($\times 10^3$) AND ISOTROPIC TEMPERATURE FACTORS ($\times 10^3$ ($Å^2$)) OF THE HYDROGEN ATOMS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c	U_{iso}
H (1)	365 (4)	252 (7)	139 (9)	52 (26)
H (2)	420 (6)	78 (4)	—130 (1)	45 (26)
H(41)	144 (7)	301 (6)	219 (7)	47 (26)
H(42)	107 (5)	322 (6)	24 (7)	39 (22)
H(43)	220 (9)	407 (3)	117(16)	82 (36)
H(51)	251(13)	344(13)	—153(25)	220 (88)
H(52)	357(10)	374 (4)	—27(13)	70 (34)
H(61)	496 (5)	222 (5)	—31 (6)	30 (20)
H(62)	450 (7)	239 (6)	—252 (5)	38 (22)
H(71)	208(11)	143(10)	—315(12)	250 (90)
H(72)	286(19)	43(12)	—396(14)	292(140)
H(73)	337(14)	168(19)	—415(21)	170 (81)

The structure was solved by Patterson and successive electron density syntheses, and refined by full-matrix least-squares calculations. Isotropic refinement of the non-hydrogen atom parameters converged at $R(= \Sigma\ \Delta F/\Sigma F_0)$ = 0.068 for the 1714 reflections, with a further reduction to 0.042 with anisotropic temperature factors. All hydrogen atoms were then located from difference electron-density syntheses and refined isotropically with C—H and N—H vectors constrained at 1.08 and 0.95 Å respectively. After several more cycles the refinement was terminated at R = 0.031 and R_ω $[= (\Sigma\omega\ \Delta F^2/\Sigma\omega F_0^2)^{1/2}]$ = 0.033. The weighting scheme applied was $\omega = 1/[\sigma^2|F_0| + 0.0003|F_0|^2]$ and this gave nearly flat analysis of variance with sin θ and $(F_0/F_{max})^{1/2}$. A final difference electron-density map showed no anomalous peaks and no hints of disorder. Particular attention was paid to the region around the methylene carbon atoms, spurious peaks in the structure of the related tmen complex [6] had indicated the presence of disorder. The atomic scattering factors for Re and Br atoms were taken from reference 10, and corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ values from reference 11, while those for O, N and C atom were taken from reference 12 and for H from reference 13. The final atomic positional and thermal parameters are given in Tables 5—7. The lists of observed and calculated structure factors are available from the authors on request.

Calculations were performed on the Queen Mary College ICL 1904S and ICL 2980, and the University of London CDC 7600 computers, using the programs SHELX-76 [14] for structure determination and refinement, PLUTO [15] for drawing figures and XANADU [16] for least squares plane and torsion angle calculations.

Acknowledgement

We thank the Science Research Council for their support of this work.

References

1 E.W. Abel, A.R. Khan, K. Kite, K.G. Orrell and V. Sik, J. Organometal. Chem., 145 (1978) C18, and J. Chem. Soc. Dalton, (1980) in press.
2 E.W. Abel, M.A. Bhatti, K.G. Orrell and V. Sik, to be published.
3 P. Haake and P.C. Turley, J. Amer. Chem. Soc., 90 (1968) 2293.
4 D. Goldsworthy and K. Kite, to be published.
5 E.W. Abel and S.P. Tyfield, Canad. J. Chem., 47 (1969) 4627.
6 M.C. Couldwell and J. Simpson, J. Chem. Soc. Dalton, (1979) 1101.
7 E.W. Abel, G.B. Hargreaves and G. Wilkinson, J. Chem. Soc., (1958) 3149.
8 G. Dolcetti and J.R. Norton, Inorg. Synth., 16 (1976) 35.
9 M.B. Hursthouse, R.A. Jones, K.M.A. Malik and G. Wilkinson, J. Amer. Chem. Soc., 101 (1979) 4128.
10 D.T. Cromer and J.T. Waber, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974 Volume 4, p. 101.
11 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
12 D.T. Cromer and J.B. Mann, Acta Cryst. A, 24 (1968) 321.
13 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
14 SHELX, Crystallographic Calculation Program, G.M. Sheldrick, University of Cambridge, 1976.
15 XANADU, Programme for Least squares Planes and Torsion Angles Calculation, P. Roberts and G.M. Sheldrick, University of Cambridge.
16 PLUTO, Programme for Crystallographic Drawing, W.D.S. Motherwell, University of Cambridge.