Low-Temperature Structures of fac-Trichloro(tetrahydrofuran)(D,L-tetrahydrofurfuranol)titanium(III) and fac-Trichloro(tetrahydrofuran)(D,L-tetrahydrofurfuroxide)titanium(IV)

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Abstract

The title compounds, (I) [TiCl$_3$(C$_5$H$_{10}$O$_2$)(C$_4$H$_8$O)] [IUPAC name: fac-trichloro(tetrahydrofuran)(D,L-tetrahydrofuran-2-methanol-O,O')titanium(III)], and (II) [TiCl$_3$(C$_5$H$_9$O$_2$)(C$_4$H$_8$O)] [IUPAC name: fac-trichloro-(tetrahydrofuran)(D,L-tetrahydrofuran-2-methanolato-O,O')titanium(III)], are pseudo-octahedral metal complexes of similar structure. The molecule of tetrahydrofurfuryl alcohol in (I) and its alkoxide anion in (II) act as chelating ligands. Disorder of the two enantiomers of the chelating ligand occurs in both structures.

Comment

High-activity titanium catalysts for ethylene polymerization frequently show an increase in reaction rate in the presence of an α-olefin. Addition of certain electron-donor compounds to these catalysts lowers the comonomer effect (Karol, Kao & Cann, 1993). Among the classes of Lewis-base compounds are ether alcohols. Hence, the interactions between tetrahydrofurfuryl alcohol and TiCl$_3$ and TiCl$_4$ were the subject of our studies.
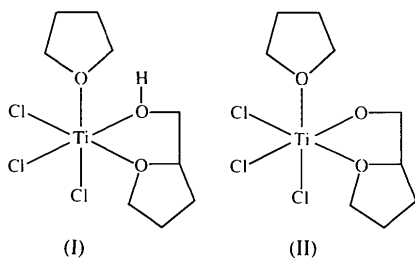
Compound (I) is an adduct of TiCl$_3$ with one bidentate molecule of ether alcohol and one molecule of thf. In contrast, TiCl$_4$ reacts with the hydroxy group of the ether alcohol with loss of HCl giving the compound (II) [of a very similar composition and structure to (I)] in which the tetrahydrofurfuroxide anion acts as a chelating ligand. Ti atoms are surrounded by three Cl atoms

and three O atoms which form significantly distorted fac-octahedral coordination geometries. Deformation of coordination spheres is mainly due to constraints arising from the five-membered chelate ring system and repulsion of the Cl atoms. Essential differences between both compounds involve the shortening (by 0.3 Å) of the Ti—O2 distance and the small lengthening of the O2—C5 distance in the alkoxide ligand of (II) compared with those in the molecule of ether alcohol of (I). A similar shortening of the Ti—O distance has been observed for [TiCl$_2$(OCH$_2$CH$_2$Cl)$_2$HOCH$_2$CH$_2$Cl]$_2$ (Winter, Sheridon & Hegg, 1991), which is the only titanium compound with the coordinated alcohol we have found in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) and which also contains the alkoxide ion.

The Ti—Cl1 distance in (I) is longer by 0.1 Å than the mean value of 2.31 (3) Å observed for the remaining Ti—Cl distances, which is probably a consequence of the hydrogen bonding formed by this Cl
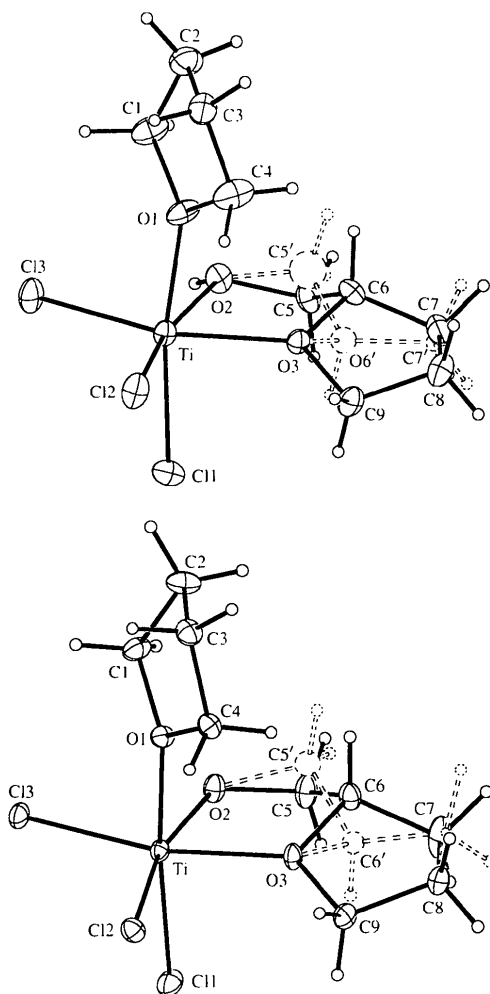
Fig. 1. Molecular structure of (I) (top) and (II) (bottom). Displacement ellipsoids are drawn at the 50% probability level. The minor component is shown by dashed lines.

atom with the hydroxy group of the adjacent molecule [H2···Cl1^i 2.32 (4), O2···Cl1^i 3.032 (3) Å, O2—H2···Cl1^i 168 (4)°; symmetry code: (i) $1 - x, -y, 2 - z$]. Numerous intramolecular C—H···Cl and C—H···O close contacts, with C···Cl and C···O distances in the ranges 3.32–3.43 and 3.09–3.32 Å, respectively, exist between the thf molecules and the donor (O, Cl) atoms in both crystals.

The same type of disorder occurs in both structures. It was modelled (see *Experimental*) as a 5:1 mixture of enantiomers of the chelating ligands and is shown in Fig. 1. It is evident that the disordered D- and L-forms of the chelate ligand on the same site must adopt different conformations. Significant conformational similarity is observed between the main ligand components of both compounds and between their minor components. In Table 3 only the torsion angles for the major component are given.

The enantiomer disorder has already been observed in the crystal structures of other compounds; the first example was reported by Furberg & Jensen (1968). The structures presented here are an unusual case of stereochemical disordering because, although an equal number of D- and L-enantiomers of the chelating ligand exist in the unit cell, the main and minor components of the entire metal complex molecule are not antipodes of each other. This implies that the crystals are a mixture of four diastereoisomers that may exist for the six-coordinate metal complexes with both a chiral centre on the metal (four distinguishable ligating atoms) and a chiral ligand. A racemic pair of configuration C-(S) and A-(R) constitutes the main component of the crystals (ca 85%) and another racemic pair of configurations C-(R) and A-(S) is their minor component.

The crystal packing of (I) is dominated by the above-mentioned hydrogen bonding which leads to the formation of centrosymmetric dimers. The dimers in (I) and the monomers in (II) are packed by van der Waals forces. Kunz, Pregosin, Camalli, Caruso & Zambonelli (1983) have found tetrahydrofurfuryl alcohol as a disordered solvent molecule in an HgI₂ complex but did not propose a model for the disorder.
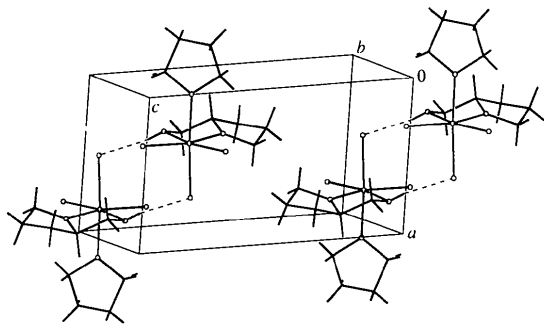

Fig. 2. Packing diagram of (I). Hydrogen bonds are marked by dashed lines. The minor component is omitted.

Experimental

The air- and moisture-sensitive title compounds were prepared under dried N₂. Anhydrous TiCl₄ and D,L-tetrahydrofurfuryl alcohol were obtained commercially and TiCl₃(thf)₃ was prepared according to the literature method (Manzer, 1982). For (I), a solution of TiCl₃(thf)₃ (11.11 g, 30 mmol) and D,L-tetrahydrofurfuryl alcohol (2.91 ml, 30 mmol) in CH₂Cl₂ (80 ml) was stirred over four weeks. The solution containing a microcrystalline product was concentrated to 40 ml and the solid was then filtered off, washed with CH₂Cl₂ and dried *in vacuo*; yield 57%. Analysis: found C 32.8, H 5.4, Cl 32.5, Ti 14.6%; calculated for C₉H₁₈O₃Cl₃Ti C 32.9, H 5.5, Cl 32.4, Ti 14.6%. A portion of the compound (3.28 g) was dissolved in thf (60 ml) at 323 K and concentrated to 40 ml. Crystals suitable for X-ray experiments formed after 2 d. For (II), to a vigorously stirred solution of TiCl₄ (3.8 g, 20 ml) in *n*-hexane (80 ml) was added D,L-tetrahydrofurfuryl alcohol dropwise (1.94 ml, 20 mmol). After evolution of HCl had finished, the yellow solid TiCl₃(C₅H₉O₂) was collected by filtration, washed with *n*-hexane and dried *in vacuo*; yield 97%. Analysis: found C 23.67, H 3.48, Cl 41.38, Ti 18.81%; calculated for C₅H₉Cl₃OTi C 23.52, H 3.55, Cl 41.65, Ti 18.75%. A portion of the TiCl₃(C₅H₉O₂) (3.83 g) was dissolved in thf (25 ml). The resulting solution was concentrated and left at 277 K. After two weeks, crystals had formed; yield 47.9%. Analysis: found C 32.8, H 5.2, Cl 32.6, Ti 14.6%; calculated for C₉H₁₇Cl₃O₃Ti C 33.0, H 5.2, Cl 32.5, Ti 14.6%. The crystal densities D_m were measured at room temperature by flotation in CCl₄/CH₂Cl₂.

Compound (I)

Crystal data

[TiCl₃(C₅H₁₀O₂)(C₄H₈O)]	Mo $K\alpha$ radiation
$M_r = 328.48$	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 39
$P\bar{1}$	reflections
$a = 7.502\,(5)$ Å	$\theta = 8$–12°
$b = 8.320\,(6)$ Å	$\mu = 1.190$ mm^{-1}
$c = 11.809\,(6)$ Å	$T = 80\,(2)$ K
$\alpha = 87.00\,(5)°$	Irregular
$\beta = 89.76\,(5)°$	$0.4 \times 0.3 \times 0.2$ mm
$\gamma = 69.65\,(6)°$	Pale blue
$V = 690.0\,(8)$ Å³	
$Z = 2$	
$D_x = 1.581\,(3)$ Mg m^{-3}	
$D_m = 1.525$ Mg m^{-3}	

Data collection

Kuma KM4 computer-controlled four-circle diffractometer	$R_{int} = 0.0202$
	$\theta_{max} = 26°$
$\omega/2\theta$ scans	$h = -9 \rightarrow 0$
Absorption correction: none	$k = -9 \rightarrow 8$
2542 measured reflections	$l = -14 \rightarrow 14$
2396 independent reflections	3 standard reflections
2067 observed reflections	monitored every 100
$[I > 2\sigma(I)]$	reflections
	intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0267$
$wR(F^2) = 0.0689$
$S = 1.091$
2395 reflections
215 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.58P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.101$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Refinement

Refinement on F^2
$R(F) = 0.0233$
$wR(F^2) = 0.0629$
$S = 1.107$
3233 reflections
211 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.6656P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.172$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}/U_{iso}
Ti	0.34105 (5)	0.18842 (5)	0.79488 (3)	0.01331 (12)
Cl1	0.65508 (7)	−0.02442 (7)	0.82696 (4)	0.02010 (14)
Cl2	0.43067 (8)	0.30011 (7)	0.62734 (4)	0.02184 (15)
Cl3	0.36967 (8)	0.37422 (7)	0.92688 (4)	0.02246 (15)
O1	0.0558 (3)	0.3379 (2)	0.76338 (12)	0.0199 (4)
O2	0.2321 (3)	0.0596 (2)	0.92426 (14)	0.0175 (4)
O3	0.2635 (2)	0.0014 (2)	0.71315 (12)	0.0144 (4)
C1	−0.0803 (4)	0.4375 (4)	0.8465 (2)	0.0240 (6)
C2	−0.2674 (4)	0.5109 (4)	0.7830 (3)	0.0278 (6)
C3	−0.2118 (4)	0.5179 (3)	0.6596 (2)	0.0219 (5)
C4	−0.0430 (4)	0.3563 (4)	0.6540 (3)	0.0294 (6)
C5†	0.2204 (7)	−0.1056 (5)	0.8971 (2)	0.0175 (8)
C6†	0.1468 (4)	−0.0818 (3)	0.7768 (2)	0.0168 (8)
C7†	0.1654 (12)	−0.2413 (9)	0.7167 (4)	0.022 (2)
C8	0.2149 (4)	−0.2003 (3)	0.5963 (2)	0.0224 (5)
C9	0.3354 (4)	−0.0895 (3)	0.6107 (2)	0.0194 (5)
C5'‡	0.158 (4)	−0.069 (3)	0.897 (2)	0.037 (9)
C6'‡	0.262 (3)	−0.145 (2)	0.7969 (11)	0.017 (4)
C7'‡	0.197 (6)	−0.255 (4)	0.7223 (17)	0.006 (7)

† Site occupancy = 0.840. ‡ Site occupancy = 0.160; U_{iso}.

Table 2. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}/U_{iso}
Ti	0.49213 (3)	0.23758 (2)	0.65869 (2)	0.00976 (7)
Cl1	0.24008 (5)	0.34546 (3)	0.60750 (3)	0.01755 (9)
Cl2	0.61110 (5)	0.37657 (3)	0.61963 (3)	0.01389 (8)
Cl3	0.32595 (5)	0.14477 (3)	0.49388 (3)	0.01509 (8)
O1	0.74813 (14)	0.15370 (7)	0.71990 (8)	0.0117 (2)
O2	0.45839 (14)	0.14488 (8)	0.73289 (8)	0.0140 (2)
O3	0.67928 (14)	0.29751 (8)	0.82536 (8)	0.0125 (2)
C1	0.7518 (3)	0.03669 (11)	0.71573 (13)	0.0166 (3)
C2	0.9650 (3)	0.00676 (12)	0.80805 (14)	0.0198 (3)
C3	1.0732 (3)	0.10256 (12)	0.81184 (12)	0.0163 (3)
C4	0.9494 (2)	0.19481 (11)	0.79613 (11)	0.0136 (3)
C5†	0.5161 (5)	0.1650 (2)	0.8409 (2)	0.0168 (5)
C6†	0.7082 (3)	0.2242 (2)	0.9086 (2)	0.0143 (5)
C7†	0.7684 (9)	0.2962 (5)	1.0035 (5)	0.026 (2)
C8	0.8807 (3)	0.38533 (12)	1.00201 (12)	0.0157 (3)
C9	0.7677 (3)	0.40130 (11)	0.87616 (12)	0.0159 (3)
C5'‡	0.5770 (19)	0.1439 (9)	0.8568 (9)	0.016 (3)
C6'‡	0.6138 (13)	0.2607 (7)	0.8896 (7)	0.011 (3)
C7'‡	0.779 (3)	0.2928 (14)	1.0121 (16)	0.002 (5)

† Site occupancy = 0.827. ‡ Site occupancy = 0.173; U_{iso}.

Compound (II)

Crystal data

[TiCl$_3$(C$_5$H$_9$O$_2$)(C$_4$H$_8$O)]
$M_r = 327.48$
Monoclinic
$P2_1/c$
$a = 9.074$ (8) Å
$b = 12.553$ (9) Å
$c = 15.65$ (2) Å
$\beta = 131.06$ (12)°
$V = 1344$ (3) Å^3
$Z = 4$
$D_x = 1.618$ (5) Mg m^{-3}
$D_m = 1.562$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8.5–11°$
$\mu = 1.222$ mm^{-1}
$T = 80$ (2) K
Irregular
$0.4 \times 0.4 \times 0.3$ mm
Green-yellow

Data collection

Kuma KM4 computer-controlled four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3747 measured reflections
3233 independent reflections
2955 observed reflections
  [$I > 2\sigma(I)$]

$R_{int} = 0.0237$
$\theta_{max} = 28°$
$h = -1 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = -20 \rightarrow 20$
3 standard reflections
  monitored every 100 reflections
  intensity decay: 2%

Table 3. *Selected geometric parameters (Å, °) for (I) and (II)*

	(I)	(II)
Ti—O1	2.091 (2)	2.121 (3)
Ti—O2	2.140 (2)	1.806 (2)
Ti—O3	2.117 (2)	2.106 (4)
Ti—Cl1	2.422 (2)	2.302 (2)
Ti—Cl2	2.337 (2)	2.335 (2)
Ti—Cl3	2.313 (2)	2.275 (4)
O1—C1	1.477 (3)	1.472 (2)
O1—C4	1.466 (3)	1.470 (3)
O2—C5	1.459 (4)	1.425 (3)
O3—C6	1.473 (3)	1.472 (2)
O3—C9	1.461 (3)	1.461 (2)
C1—C2	1.507 (4)	1.516 (4)
C2—C3	1.518 (4)	1.529 (2)
C3—C4	1.497 (4)	1.517 (2)
C5—C6	1.505 (4)	1.511 (3)
C6—C7	1.501 (6)	1.502 (5)
C7—C8	1.519 (6)	1.524 (6)
C8—C9	1.515 (3)	1.522 (4)
O1—Ti—O2	84.9 (1)	89.3 (1)
O1—Ti—O3	82.8 (1)	82.2 (2)
O2—Ti—O3	73.9 (1)	76.9 (1)
O1—Ti—Cl1	170.6 (1)	172.8 (1)
O1—Ti—Cl2	90.9 (1)	86.1 (1)
O1—Ti—Cl3	91.4 (1)	88.4 (2)
O2—Ti—Cl1	89.7 (1)	93.1 (1)
O2—Ti—Cl2	167.8 (1)	162.3 (1)
O2—Ti—Cl3	89.3 (1)	97.6 (1)
O3—Ti—Cl1	88.3 (1)	91.7 (1)
O3—Ti—Cl2	94.2 (1)	85.5 (1)
O3—Ti—Cl3	162.6 (1)	169.1 (1)

Cl1—Ti—Cl2	92.8 (1)	89.6 (1)
Cl1—Ti—Cl3	96.2 (1)	98.0 (2)
Cl2—Ti—Cl3	102.3 (1)	99.3 (1)
C4—O1—C1	108.8 (2)	109.5 (2)
C4—O1—Ti	124.8 (2)	126.9 (2)
C1—O1—Ti	126.4 (2)	121.7 (1)
C5—O2—Ti	116.3 (2)	124.2 (2)
C9—O3—C6	110.1 (2)	111.2 (2)
C9—O3—Ti	131.0 (2)	134.4 (1)
C6—O3—Ti	117.7 (2)	113.8 (2)
O1—C1—C2	105.0 (2)	104.9 (2)
C1—C2—C3	104.2 (3)	103.1 (2)
C4—C3—C2	102.0 (3)	101.9 (2)
O1—C4—C3	104.8 (2)	104.9 (2)
O2—C5—C6	105.6 (3)	106.0 (2)
O3—C6—C7	106.0 (3)	103.7 (3)
O3—C6—C5	105.3 (2)	103.5 (2)
C7—C6—C5	117.0 (4)	119.5 (3)
C6—C7—C8	103.7 (4)	103.8 (4)
C9—C8—C7	104.2 (3)	103.1 (2)
O3—C9—C8	104.3 (2)	104.4 (2)
O3—Ti—O2—C5	17.2 (3)	16.1 (2)
O2—Ti—O3—C9	−153.1 (2)	−158.7 (2)
O2—Ti—O3—C6	12.8 (2)	11.3 (1)
Ti—O2—C5—C6	−41.9 (4)	−38.2 (3)
C9—O3—C6—C7	6.1 (4)	15.4 (3)
Ti—O3—C6—C7	−162.5 (4)	−156.9 (3)
C9—O3—C6—C5	130.7 (3)	140.9 (2)
Ti—O3—C6—C5	−38.0 (3)	−31.5 (2)
O2—C5—C6—O3	48.0 (4)	40.0 (3)
O2—C5—C6—C7	165.4 (4)	154.5 (3)
O3—C6—C7—C8	−25.0 (6)	−32.3 (5)
C5—C6—C7—C8	−142.0 (4)	−146.7 (3)
C6—C7—C8—C9	34.3 (6)	37.2 (4)
C6—O3—C9—C8	15.4 (2)	7.8 (2)
Ti—O3—C9—C8	−177.9 (2)	178.0 (1)
C7—C8—C9—O3	−30.6 (4)	−27.5 (3)

During the measurements the crystals were kept in a stream of cooled nitrogen. Refinement of the ordered model of both structures gave a final R of 0.0306 for (I) and 0.0307 for (II). In both cases, however, residual electron densities on the different Fourier maps (ca 1–2 e Å⁻³) in the vicinity of the chiral C6 atom were found. This may be explained by the assumption that enantiomers of the chelating ligand occupy the same crystallographic position. We refined a model in which only atoms C5, C6 and C7 (and attached H atoms) of both enantiomers had the different positions; the remaining atoms of ligands were assumed to overlap. Bonds for the disordered part of ligand enantiomers were restrained to be equal within 0.03 Å. The refined site-occupation factors for the major component were 0.84 for (I) and 0.83 for (II). Non-H atoms of the minor component were allowed isotropic motion; all other non-H atoms were refined anisotropically. H atoms were refined except for those attached to the disordered atoms, for which a riding model (with U_{iso} refined for the major component and fixed for the minor component) was used. For (II), an alternative cell ($P2_1/n$) with c = 11.862 Å and β = 95.83° was generated by the matrix 100/010/101.

For both compounds, data collection: *KM4 Software* (Kuma, 1989); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

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[Bis(diphenylphosphino)amine-P,P']bromotricarbonylrhenium(I), [ReBr(CO)₃{NH(PPh₂)₂}]

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Abstract

The structure of [ReBr(CO)₃(C₂₄H₂₁NP₂)] consists of discrete molecules in which the Re ion has a six-coordinate octahedral environment with the three carbonyl groups in facial positions.

Comment

The attention received by Tc compounds in view of the applications of new ⁹⁹ᵐTc radiopharmaceuticals is well known (Deutsch, Libson, Jurisson & Linday, 1983). As a result of the very similar chemical behaviour of the third-row Re congener, synthetic routes tested with Re may be usefully transferred to the preparation of analogous radioactive ⁹⁹Tc or ⁹⁹ᵐTc compounds. In addition, complexes of Re and Tc are often isomorphous (Rossi et al., 1989). This study is a continuation of a series of investigations of Re and Tc complexes. Crystals of [ReBr(CO)₃{NH(PPh₂)₂}], (I), were kindly supplied by the late Professor Magon.

The structure consists of discrete molecules in which the Re atom has a six-coordinate octahedral environ-