Acta Cryst. (1995). C**51**, 201–203

$[ReCl_3(C_8H_{11}P)_2(C_7H_{11}N)_2].C_6H_4Cl_2$

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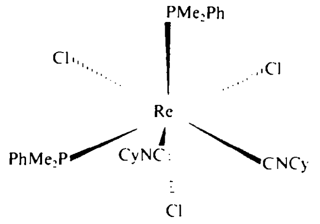
(*Received* 15 *February* 1994; *accepted* 27 *June* 1994)

Abstract

Trichlorobis(cyclohexyl isocyanide)bis(dimethylphenylphosphine)rhenium(III) has been synthesized from $[ReOCl_3(CNCy)_2]$ (Cy = cyclohexyl) by the removal of oxygen with excess dimethylphenylphosphine. The structure of its 1,2-dichlorobenzene adduct, determined by single-crystal X-ray methods, has a monocapped octahedral arrangement (idealized C_s symmetry) of the seven ligands about the Re atom; the three Cl atoms adopt a *fac* geometry, opposite the face capped by one isocyanide ligand.

Comment

Although many mononuclear complexes of rhenium with seven or more ligands have been characterized structurally, only a few non-hydridic structures have been reported so far. They have been shown to possess a variety of geometries, *e.g.* monocapped octahedral (Drew, Davis, Edwards & Marshalsea, 1978; Treichel, Williams, Freeman & Gelder, 1979; Drew, Brisdon & Watts, 1984), monocapped trigonal prismatic (Jurisson, Francesconi, Linder, Treher, Malley, Gougoutas & Nunn, 1991; Warner, Cheatham, Tulip, Williams & Lippard, 1991) and pentagonal bipyramidal (Fletcher & Skapski, 1974; Ara, Fanwick & Walton, 1991, 1992; Che, Wang, Yeung, Wong & Peng, 1992; Leeaphon, Fanwick & Walton, 1991). From the few known structures, it is observed that Re^V complexes typically possess pentagonal bypiramidal geometry, while Re^{III} complexes are more flexible, examples of all three above-mentioned geometries being found in this set. However, when only monodentate ligands are present, the capped octahedral or trigonal prismatic arrangements seem to be preferred (Treichel, Williams, Freeman & Gelder, 1979; Drew, Brisdon & Watts, 1984, Warner, Cheatham, Tulip, Williams & Lippard, 1991).



(I)

The structure of $[ReCl_3(PMe_2Ph)_2(CNCy)_2]$ (Cy = cyclohexyl), (I), an Re^{III} complex containing only monodentate ligands, shows monocapped octahedral geometry (see Fig. 1), with the three Cl atoms adopting a *fac* geometry. The *trans* axes through the metal atom show remarkable deviations from linearity [Cl(3)—Re—P(1) 157.6 (3), Cl(2)—Re—P(2) 158.5 (2), Cl(1)—Re—C(24) 162.3 (8)°] caused by flattening of the [P(1),P(2),C(24)] face which is capped by the seventh ligand (CNCy). Very similar coordination geometry was found for $[ReBr_3(PMe_2Ph)_2(CO)_2]$ (Drew, Brisdon & Watts, 1984). The geometry about the metal atom is fairly regular (*cis L*—Re—*L* angles in the octahedron lie in the range 71–89°), in contrast to the uneven angular distribution of the ligands found in other known seven-coordinate rhenium complexes, where polydentate ligands typically require smaller bite angles, as low as 59.8° (Leeaphon, Fanwick & Walton, 1991).

Although the short Re—CNCy bond distances of 1.94 (2) and 1.95 (3) Å [Re—CN*R* values in seven-coordinate rhenium complexes have been found in the range 1.94–2.01 Å (Treichel, Williams, Freeman & Gelder, 1979; Warner, Cheatham, Tulip, Williams & Lippard, 1991)] suggest that in $[ReCl_3(PMe_2Ph)_2(CNCy)_2]$ there is little or no steric crowding about the metal atom, the bending of both C—N—Cy angles to 160 (3)° indicates significant interligand repulsion. The use of ligands with small cone angles (cyclohexyl isocyanide and dimethylphenylphosphine) and the remarkable size of the Re atom certainly favour the formation of highly coordinated metal complexes. However, repeated crystallizations with excess dimethylphenylphosphine failed to afford eight-coordinate rhenium complexes.

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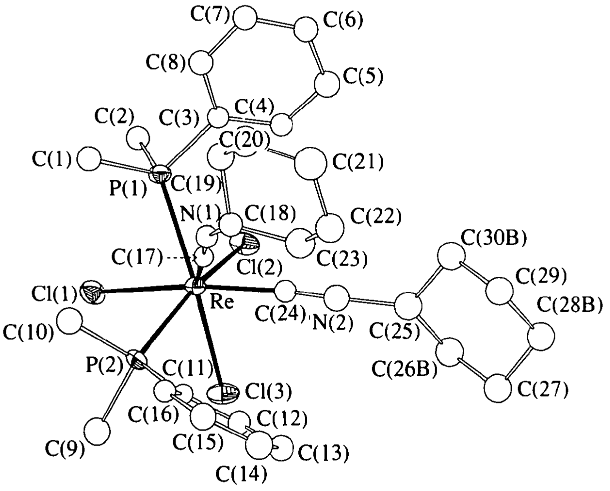

Fig. 1. Molecular structure and atomic labelling scheme for $[ReCl_3(PMe_2Ph)_2(CNCy)_2]$. Displacement ellipsoids are drawn at the 30% probability level. Only one set of the disordered cyclohexyl ligand atoms is drawn. H atoms have been omitted for clarity.

Experimental

$[ReCl_3(PMe_2Ph)_2(CNCy)_2]$ was obtained as a yellow insoluble product from $[ReOCl_3(CNCy)_2]$ (Cy = cyclohexyl) (Bryan, Stenkamp, Tulip & Mayer, 1987) by removal of oxygen with excess dimethylphenylphosphine in benzene at 323 K. IR data: ν(NC) 2152 (*s*), 2074 (*sh*), 2033 (*br*) and 1993 (*sh*) cm^{-1}; ν(P—C$_{ar}$) 912 cm^{-1}. M.p. 479 K (dec.). Analysis: calculated for $[ReCl_3(PMe_2Ph)_2(CNCy)_2].C_6H_6$, C 49.97, H 5.78, N 3.24%; found, C 49.71, H 5.71, N 3.06%. Crystals of $[ReCl_3(PMe_2Ph)_2(CNCy)_2].C_6H_4Cl_2$ were obtained by slow diffusion of *n*-heptane into a 1,2-dichlorobenzene solution of the complex. Crystallization of $[ReCl_3(PMe_2Ph)_2(CNCy)_2]$ from a number of other organic solvents (CH_2Cl_2, 1,2-dichloroethane) proved to be unsuccessful.

Crystal data

$[ReCl_3(C_8H_{11}P)_2$-
$(C_7H_{11}N)_2].C_6H_4Cl_2$
$M_r = 934.15$
Orthorhombic
$P2_1cn$
$a = 9.197$ (2) Å
$b = 17.323$ (4) Å
$c = 25.841$ (7) Å
$V = 4117$ (2) Å^3
$Z = 4$
$D_x = 1.507$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–11°
$\mu = 3.380$ mm^{-1}
$T = 293$ (2) K
Prism
0.25 × 0.10 × 0.10 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{min} = 0.96$, $T_{max} = 1.00$
3832 measured reflections
3832 independent reflections

1639 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 25°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 30$
3 standard reflections
frequency: 60 min
intensity decay: 48%

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.112$
$S = 1.101$
1639 reflections
229 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0735P)^2 + 8.9961P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.96$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

U_{iso} for C and N; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	U_{iso}/U_{eq}
Re	1/4	−0.20890 (4)	−0.72003 (3)	0.0510 (3)
Cl(1)	0.2911 (8)	−0.2195 (4)	−0.8143 (2)	0.084 (3)
Cl(2)	0.5056 (8)	−0.1648 (4)	−0.7102 (3)	0.084 (2)
Cl(3)	0.3615 (8)	−0.3386 (4)	−0.7110 (3)	0.086 (2)
P(1)	0.2279 (10)	−0.0747 (3)	−0.7476 (3)	0.061 (2)
P(2)	0.0484 (8)	−0.2913 (4)	−0.7453 (3)	0.060 (2)
C(1)	0.070 (3)	−0.053 (2)	−0.7885 (9)	0.077 (9)
C(2)	0.369 (3)	−0.036 (2)	−0.7849 (9)	0.070 (8)
C(3)	0.217 (3)	−0.0054 (12)	−0.6953 (9)	0.061 (7)
C(4)	0.292 (3)	−0.0157 (12)	−0.6503 (9)	0.066 (7)
C(5)	0.279 (3)	0.0344 (14)	−0.6092 (10)	0.088 (9)
C(6)	0.194 (3)	0.101 (2)	−0.6161 (11)	0.078 (9)
C(7)	0.118 (3)	0.116 (2)	−0.6588 (11)	0.079 (8)
C(8)	0.128 (3)	0.062 (2)	−0.6984 (11)	0.079 (8)
C(9)	0.086 (4)	−0.377 (2)	−0.7847 (10)	0.095 (9)
C(10)	−0.084 (3)	−0.243 (2)	−0.7861 (9)	0.090 (9)
C(11)	−0.058 (3)	−0.3274 (13)	−0.6914 (9)	0.050 (6)
C(12)	0.014 (3)	−0.3620 (14)	−0.6522 (10)	0.068 (7)
C(13)	−0.060 (3)	−0.389 (2)	−0.6064 (11)	0.079 (8)
C(14)	−0.208 (4)	−0.381 (2)	−0.6063 (11)	0.099 (10)
C(15)	−0.275 (4)	−0.3469 (14)	−0.6462 (11)	0.093 (10)
C(16)	−0.209 (3)	−0.3196 (12)	−0.6877 (10)	0.063 (7)
C(17)	0.071 (3)	−0.1683 (14)	−0.6897 (10)	0.053 (7)
N(1)	−0.033 (2)	−0.1410 (11)	−0.6732 (8)	0.064 (6)
C(18)	−0.150 (3)	−0.1226 (14)	−0.6375 (9)	0.073 (8)
C(19)	−0.194 (3)	−0.040 (2)	−0.6400 (11)	0.098 (10)
C(20)	−0.310 (4)	−0.018 (2)	−0.6035 (13)	0.121 (13)
C(21)	−0.275 (6)	−0.045 (2)	−0.5519 (13)	0.140 (14)
C(22)	−0.204 (4)	−0.123 (2)	−0.5444 (10)	0.110 (11)
C(23)	−0.097 (4)	−0.145 (2)	−0.5842 (12)	0.117 (12)
C(24)	0.277 (3)	−0.2142 (12)	−0.6457 (8)	0.064 (6)
N(2)	0.278 (3)	−0.2215 (11)	−0.6015 (8)	0.091 (7)
C(25)	0.3345 (2)	−0.23151 (11)	−0.54656 (5)	0.236 (11)
C(26*A*)	0.3588 (5)	−0.31774 (11)	−0.53495 (7)	0.236 (11)
C(26*B*)	0.4492 (3)	−0.28845 (14)	−0.52586 (7)	0.236 (11)
C(27)	0.3899 (4)	−0.32791 (10)	−0.47679 (7)	0.236 (11)
C(28*A*)	0.3948 (2)	−0.24796 (14)	−0.45079 (8)	0.236 (11)
C(28*B*)	0.3595 (3)	−0.2661 (2)	−0.43535 (6)	0.236 (11)
C(29)	0.2449 (3)	−0.2091 (2)	−0.45606 (6)	0.236 (11)
C(30*A*)	0.2062 (3)	−0.2018 (3)	−0.51384 (8)	0.236 (11)
C(30*B*)	0.3041 (4)	−0.16968 (12)	−0.50512 (9)	0.236 (11)
Cl(1*S*)	0.993 (2)	−0.4756 (8)	−0.4668 (5)	0.230 (8)
Cl(2*S*)	0.881 (2)	−0.3040 (7)	−0.4734 (4)	0.211 (6)
C(1*S*)	0.876 (4)	−0.438 (2)	−0.4238 (14)	0.114 (11)
C(2*S*)	0.829 (4)	−0.366 (2)	−0.4292 (14)	0.127 (13)
C(3*S*)	0.729 (4)	−0.341 (2)	−0.3894 (12)	0.108 (11)
C(4*S*)	0.680 (4)	−0.381 (2)	−0.3499 (14)	0.116 (12)
C(5*S*)	0.732 (5)	−0.461 (2)	−0.3481 (13)	0.127 (12)
C(6*S*)	0.826 (3)	−0.486 (2)	−0.3855 (12)	0.104 (11)

Table 2. *Selected geometric parameters* (Å, °)

Re—C(24)	1.94 (2)	Re—Cl(2)	2.485 (7)
Re—C(17)	1.95 (3)	C(17)—N(1)	1.15 (3)
Re—P(2)	2.429 (6)	N(1)—C(18)	1.45 (3)

Re—P(1)	2.439 (6)	C(24)—N(2)	1.15 (2)
Re—Cl(1)	2.472 (7)	N(2)—C(25)	1.52 (2)
Re—Cl(3)	2.481 (6)		
C(24)—Re—C(17)	74.2 (11)	P(1)—Re—Cl(3)	157.6 (3)
C(24)—Re—P(2)	109.7 (7)	Cl(1)—Re—Cl(3)	87.8 (2)
C(17)—Re—P(2)	71.2 (8)	C(24)—Re—Cl(2)	78.0 (8)
C(24)—Re—P(1)	110.2 (6)	C(17)—Re—Cl(2)	130.1 (7)
C(17)—Re—P(1)	72.8 (8)	P(2)—Re—Cl(2)	158.5 (2)
P(2)—Re—P(1)	114.7 (3)	P(1)—Re—Cl(2)	79.4 (3)
C(24)—Re—Cl(1)	162.3 (8)	Cl(1)—Re—Cl(2)	88.8 (3)
C(17)—Re—Cl(1)	123.5 (8)	Cl(3)—Re—Cl(2)	83.0 (2)
P(2)—Re—Cl(1)	78.9 (2)	N(1)—C(17)—Re	177 (2)
P(1)—Re—Cl(1)	78.2 (2)	C(17)—N(1)—C(18)	160 (3)
C(24)—Re—Cl(3)	79.0 (7)	N(2)—C(24)—Re	172 (3)
C(17)—Re—Cl(3)	129.5 (8)	C(24)—N(2)—C(25)	160 (3)
P(2)—Re—Cl(3)	79.0 (2)		

Systematic absences: $l = 2n + 1$ in $h0l$; $h + k = 2n + 1$ in $hk0$. Data were corrected for crystal decay and Lp effects. Since our sample suffered extremely fast decay (48% in I by the end of data collection) we collected data using the constant-precision method, prescanning all reflections and not remeasuring those which were found to be 'unobservable' [$I < \sigma(I)$ in prescan]; all reflections for which the counting statistics are obviously poor have therefore been omitted from the final cycles and refinement, in which only 1639 observed data were used. The structure was solved by direct methods (*SIR*92; Altomare, Cascarano, Giacovazzo, Guagliardi, Burla, Polidori & Camalli, 1994) and refined by full-matrix least squares with anisotropic displacement parameters for the Re, P and Cl atoms. H atoms were included at calculated positions and given a common isotropic displacement parameter [refined $U_H = 0.12(2)$ Å^2]. One of the cyclohexyl rings was found to be disordered; the two half-occupancy moieties were given a common displacement parameter and had their bond lengths constrained (C—C = 1.54 Å), and H atoms omitted. The 1,2-dichlorobenzene solvent molecule was found to have full occupancy.

Calculations were carried out on a Silicon Graphics Personal Indigo computer, running IRIX 4.01 with *SHELXL*93 (Sheldrick, 1993). Molecular graphics were produced using *ORTEP*II (Johnson, 1971).

We thank the Italian CNR (Progetto Finalizzato Chimica Fine II) for financial support. The technical support by G. Mezza is also acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1095). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 203–205

[3,10-Diethyl-5,8-diazadodecane-3,10-dithiolato(3–)-*N*,*N*′,*S*,*S*′]oxorhenium(IV) Chloroform Solvate

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(*Received* 5 *May* 1994; *accepted* 30 *June* 1994)

Abstract

The structural analysis of the title compound $[Re(C_{14}H_{29}N_2S_2)O].CHCl_3$ was undertaken in order to determine whether the high solubility of the complex in chloroform was due to disruption of the hydrogen bonding between complexes. The N—H···O hydrogen-bonding scheme previously observed in the non-solvated material was found to persist in the chloroform solvate. The chloroform molecules occupy hydrophobic pockets created by the ethyl substituents and are involved in close contacts with the coordinated S atoms.

Comment

Rhenium complexes involving radioactive ^{186}Re and ^{188}Re have potential as tumour-targetting radiotherapeu-