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Di-μ-oxo-bis{[tris(2-pyridylmethyl)amine-*N*,*N*′,*N*″,*N*‴]rhenium(IV)} Tetrakis(hexafluorophosphate) Diacetone Tetrahydrate

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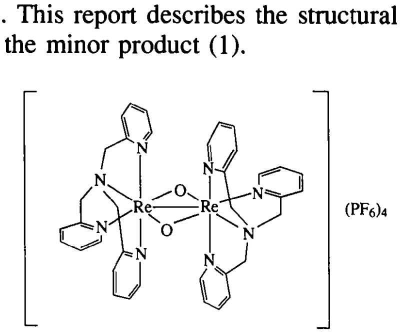
Abstract

The title compound, $[Re_2(\mu\text{-}O)_2(C_{18}H_{18}N_4)_2](PF_6)_4.2(CH_3)_2CO.4H_2O$, was structurally characterized. The structure of the complex cation consists of a binuclear unit, (tpa)Re(μ-O)$_2$Re(tpa) [tpa = tris(2-pyridylmethyl)amine], having a crystallographically imposed centre of symmetry at the midpoint of the Re≡Re triple bond. Each Re ion is in a pseudo-octahedral coordination environment comprising two bridging O atoms and four N atoms of tpa, in which the tertiary amine and one of the pyridine N atoms are *trans* to the oxo bridge. The Re≡Re distance, average Re—O distance and Re—N distances are 2.364 (1), 1.950 (6) and 2.105 (7)–2.150 (6) Å, respectively.

Comment

The reaction of $Re^{V}OCl_3(PPh_3)_2$ with tris(2-pyridylmethyl)amine (tpa) gave a μ-oxo Re^{III} dimer, $[Re^{III}_2(\mu\text{-}O)Cl_2(tpa)_2](PF_6)_2$, as a major product (Takahira, Umakoshi & Sasaki, 1994). An Re^{IV} dimer, $[Re_2(\mu\text{-}O)_2(tpa)_2]^{4+}$, was obtained as a minor product on one occasion during the repeated preparation of the Re^{III} dimer. Although the Re^{IV} dimer was not obtained reproducibly and in sufficient quantity to study its properties further, its structure was successfully determined. This report describes the structural characteristics of the minor product (1).



(1)

Fig. 1 shows the configuration of the complex cation with the atomic numbering scheme. The structure of the complex cation consists of a binuclear unit, (tpa)Re(μ-O)$_2$Re(tpa), having a crystallographically imposed centre of symmetry at the midpoint of the Re≡Re bond. Each Re ion is in a pseudo-octahedral coordination environment comprising two bridging O atoms and four N atoms of tpa, in which the tertiary amine and one of the pyridine N atoms are *trans* to the oxo bridge. The distance between the Re atoms [2.364 (1) Å] is comparable to those of $Ba_2[Re_2(\mu\text{-}O)_2(edta)_2].4.5H_2O$ [2.3621 (8) Å; Ikari *et al.*, 1993], $K_4[Re_2(\mu\text{-}O)_2(C_2O_4)_4].3H_2O$ [2.362 (1) Å; Lis, 1975], $[Re_2(\mu\text{-}O)_2Cl_2(tacn)_2]I_2.2H_2O$ (tacn = 1,4,7-triazacyclononane) [2.376 (2) Å; Böhm, Wieghardt, Nuber & Weiss, 1990] and $[Re_2(\mu\text{-}O)_2I_2(tacn)_2]I_2.2H_2O$ [2.381 (1) Å; Böhm, Wieghardt, Nuber & Weiss, 1991], and an Re≡Re triple bond is indicated. The average Re—O distance [1.950 (6) Å] is also comparable to that of these complexes. The bond lengths between Re and N that are *trans* to bridging O are *ca* 0.04 Å longer than those *cis* to bridging O.

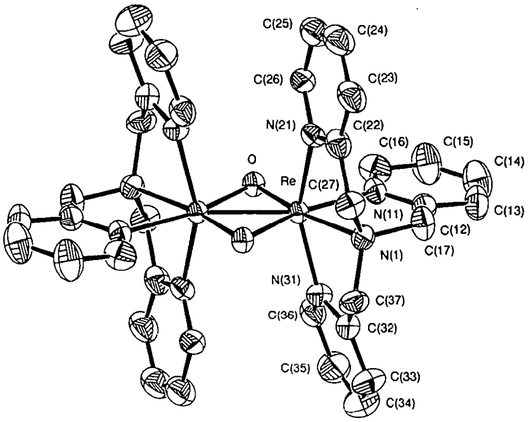


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the $[Re_2(\mu\text{-}O)_2(tpa)_2]^{4+}$ ion with the atomic numbering scheme.

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Experimental

A mixture of $ReOCl_3(PPh_3)_2$ (166 mg), tris(2-pyridylmethyl)-amine (90 mg) and NH_4PF_6 (550 mg) in ethanol/water (60/2 ml) was refluxed for 8 h and then cooled to room temperature. The black precipitate was dissolved in a minimum amount of acetone to remove white insoluble material. The filtrate was loaded onto a silica gel column (Sephadex LH-20, 3×13 cm) and eluted with acetone. Crystals of $[Re_2(\mu\text{-}O)_2(tpa)_2](PF_6)_4.2(CH_3)_2CO.4H_2O$ were obtained by concentrating the eluate of the deep red band.

Crystal data

$[Re_2(O)_2(C_{18}H_{18}N_4)_2]$-$(PF_6)_4.2C_3H_6O.4H_2O$
$M_r = 1753.23$
Triclinic
$P\overline{1}$
$a = 13.192$ (4) Å
$b = 13.865$ (6) Å
$c = 9.822$ (3) Å
$\alpha = 104.02$ (3)°
$\beta = 110.14$ (2)°
$\gamma = 106.22$ (3)°
$V = 1501$ (1) Å^3
$Z = 1$
$D_x = 1.94$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12.5\text{–}15°$
$\mu = 4.31$ mm^{-1}
$T = 296$ K
Parallelepiped
0.52 × 0.11 × 0.09 mm
Deep red

Data collection

Rigaku AFC-5*R* diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: none
6837 measured reflections
6008 independent reflections
5517 observed reflections [$F > 6\sigma(F)$]

$R_{int} = 0.017$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 16$
$k = -17 \rightarrow 17$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 150 reflections
intensity variation: none

Refinement

Refinement on *F*
$R = 0.045$
$wR = 0.051$
$S = 1.73$
5517 reflections
388 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(|F_o|) + (0.015|F_o|)^2]$

$(\Delta/\sigma)_{max} = 0.5$ for F(25), 0.1 for all other atoms
$\Delta\rho_{max} = 1.75$ e Å^{-3}
$\Delta\rho_{min} = -1.34$ 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)

B_{iso} for water O atoms; $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	B_{iso}/B_{eq}
Re(1)	0.00937 (3)	0.09092 (2)	0.03195 (3)	2.44 (1)
P(1)	−0.2791 (2)	−0.0742 (2)	−0.6457 (2)	4.3 (1)
P(2)	0.2262 (2)	0.5779 (2)	0.6176 (2)	3.1 (1)
F(11)	−0.1856 (7)	−0.0160 (8)	−0.4767 (9)	12.9 (5)
F(12)	−0.274 (1)	0.0314 (9)	−0.659 (1)	20.3 (8)
F(13)	−0.3796 (8)	−0.1392 (8)	−0.8171 (8)	12.8 (4)
F(14)	−0.288 (1)	−0.1814 (8)	−0.635 (1)	19.5 (7)
F(15)	−0.3754 (7)	−0.0690 (9)	−0.592 (1)	14.5 (5)
F(16)	−0.1887 (8)	−0.0721 (9)	−0.708 (1)	16.1 (6)
F(21)	0.1402 (8)	0.4603 (5)	0.577 (1)	12.9 (5)
F(22)	0.3256 (7)	0.6935 (6)	0.680 (1)	11.7 (4)
F(23)	0.1786 (9)	0.6180 (6)	0.739 (1)	15.2 (5)
F(24)	0.2711 (8)	0.5394 (6)	0.497 (1)	13.6 (5)
F(25)	0.168 (1)	0.5972 (8)	0.543 (2)	23.3 (9)
F(26)	0.317 (1)	0.562 (1)	0.743 (2)	23.3 (9)
O(1)	−0.0030 (4)	−0.0038 (4)	−0.1605 (5)	3.0 (2)
N(1)	0.0248 (5)	0.2190 (5)	0.2224 (7)	3.1 (2)
N(11)	0.0276 (5)	0.2179 (5)	−0.0580 (7)	3.3 (2)
N(21)	−0.1666 (5)	0.0725 (5)	−0.0339 (7)	3.1 (2)
N(31)	0.1933 (5)	0.1768 (5)	0.1576 (7)	3.1 (2)
C(12)	0.0490 (7)	0.3146 (6)	0.0424 (9)	3.5 (3)
C(13)	0.0792 (8)	0.4089 (7)	0.009 (1)	5.1 (3)
C(14)	0.083 (1)	0.4003 (8)	−0.132 (1)	6.8 (5)
C(15)	0.058 (1)	0.2988 (8)	−0.238 (1)	6.9 (5)
C(16)	0.0302 (8)	0.2072 (7)	−0.198 (1)	4.7 (3)
C(17)	0.0302 (8)	0.3193 (6)	0.1846 (9)	4.5 (3)
C(22)	−0.1865 (7)	0.1200 (6)	0.088 (1)	4.0 (3)
C(23)	−0.2989 (8)	0.1160 (7)	0.064 (1)	5.2 (4)
C(24)	−0.3901 (8)	0.0621 (8)	−0.089 (1)	5.7 (4)
C(25)	−0.3676 (7)	0.0169 (7)	−0.214 (1)	4.9 (3)
C(26)	−0.2545 (7)	0.0241 (6)	−0.1821 (9)	3.6 (3)
C(27)	−0.0834 (7)	0.1754 (6)	0.2486 (9)	3.7 (3)
C(32)	0.2289 (7)	0.2446 (6)	0.3057 (9)	3.6 (3)
C(33)	0.3477 (8)	0.3134 (8)	0.401 (1)	4.8 (3)
C(34)	0.4285 (8)	0.3140 (8)	0.338 (1)	6.0 (4)
C(35)	0.3905 (8)	0.2469 (8)	0.183 (1)	5.6 (4)
C(36)	0.2692 (7)	0.1776 (6)	0.092 (1)	4.3 (3)
C(37)	0.1373 (7)	0.2391 (7)	0.3634 (9)	3.7 (3)
O(2)	0.1966 (7)	−0.2955 (8)	0.115 (1)	10.0 (4)
C(1)	0.323 (2)	−0.212 (1)	0.390 (2)	11.7 (8)
C(2)	0.281 (1)	−0.2814 (9)	0.222 (1)	7.2 (5)
C(3)	0.363 (1)	−0.340 (1)	0.198 (2)	14 (1)
O*W*1	0.486 (2)	−0.490 (2)	0.193 (3)	26.6 (9)
O*W*2	0.593 (2)	−0.419 (1)	0.057 (2)	21.2 (7)

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

Re(1)—Re(1^{i})	2.364 (1)	N(11)—C(12)	1.34 (1)
Re(1)—O(1)	1.947 (5)	N(11)—C(16)	1.36 (1)
Re(1)—O(1^{i})	1.953 (6)	N(21)—C(22)	1.37 (1)
Re(1)—N(1)	2.150 (6)	N(21)—C(26)	1.358 (8)
Re(1)—N(11)	2.146 (7)	N(31)—C(32)	1.36 (1)
Re(1)—N(21)	2.105 (7)	N(31)—C(36)	1.37 (1)
Re(1)—N(31)	2.107 (5)	C(12)—C(17)	1.49 (1)
N(1)—C(17)	1.51 (1)	C(22)—C(27)	1.509 (9)
N(1)—C(27)	1.52 (1)	C(32)—C(37)	1.49 (1)
N(1)—C(37)	1.54 (1)		
O(1)—Re(1)—O(1^{i})	105.3 (2)	C(27)—N(1)—C(37)	110.9 (7)
O(1)—Re(1)—N(1)	168.5 (3)	Re(1)—N(11)—C(12)	114.5 (6)
O(1)—Re(1)—N(11)	88.4 (2)	Re(1)—N(11)—C(16)	124.1 (6)
O(1)—Re(1)—N(21)	101.2 (2)	C(12)—N(11)—C(16)	121.0 (8)
O(1)—Re(1)—N(31)	100.7 (2)	Re(1)—N(21)—C(22)	113.6 (4)
O(1^{i})—Re(1)—N(1)	86.2 (2)	Re(1)—N(21)—C(26)	125.7 (6)
O(1^{i})—Re(1)—N(11)	166.1 (2)	Re(1)—N(31)—C(32)	113.6 (6)
O(1^{i})—Re(1)—N(21)	93.1 (3)	Re(1)—N(31)—C(36)	123.9 (4)
O(1^{i})—Re(1)—N(31)	93.6 (2)	C(32)—N(31)—C(36)	121.9 (6)
N(1)—Re(1)—N(11)	80.1 (3)	N(11)—C(12)—C(13)	121.2 (9)
N(1)—Re(1)—N(21)	77.7 (2)	N(11)—C(12)—C(17)	118.7 (8)
N(1)—Re(1)—N(31)	78.2 (3)	C(13)—C(12)—C(17)	119.9 (8)
N(11)—Re(1)—N(21)	86.3 (3)	N(1)—C(17)—C(12)	113.0 (8)
N(11)—Re(1)—N(31)	81.3 (3)	N(21)—C(22)—C(23)	120.7 (7)
N(21)—Re(1)—N(31)	154.4 (2)	N(21)—C(22)—C(27)	117.4 (8)
Re(1)—O(1)—Re(1^{i})	74.7 (2)	C(23)—C(22)—C(27)	121.9 (9)
Re(1)—N(1)—C(17)	111.3 (5)	N(1)—C(27)—C(22)	105.9 (7)
Re(1)—N(1)—C(27)	106.4 (4)	N(31)—C(32)—C(33)	120.7 (9)
Re(1)—N(1)—C(37)	105.1 (5)	N(31)—C(32)—C(37)	117.1 (6)
C(17)—N(1)—C(27)	110.4 (7)	C(33)—C(32)—C(37)	122.2 (8)
C(17)—N(1)—C(37)	112.4 (5)	N(1)—C(37)—C(32)	106.0 (7)

Symmetry code: (i) $-x, -y, -z$.

The coordinates of the Re atom were found from a Patterson map and the remaining non-H atoms were found by successive structure-factor–Fourier calculations. All the non-H atoms were refined anisotropically except the water O atoms, but at the final stage of refinement F(25) had shifted abnormally towards P(2) to give a P(2)—F(25) distance of 1.01 Å. Although the difference Fourier calculation after refinement without F(25) shows a peak around 1.3 Å from P(2), succesive refinement including F(25) again converged with a shift of F(25) towards the former position, so refinement was terminated at this stage. No attempt was made to locate H atoms. All computations were performed using *UNICS*III (Sakurai & Kobayashi, 1979) and *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the IUCr (Reference: AS1122). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Cyclopalladated Complex, $[PdCl(C_{37}H_{32}N)]$

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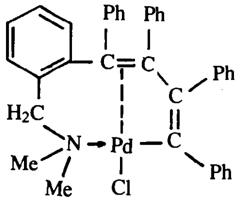
Abstract

In the structure of chloro{4-[2-(dimethylaminomethyl)phenyl]-1,2,3,4-tetraphenyl-(3,4-η)-buta-1,3-dienyl-C^1,N}palladium(II), (1), the Pd atom is surrounded by five atoms [C(1), C(3), C(4), Cl and N], but if the midpoint of the ligand C(3)=C(4) bond is considered as a coordination site, the environment around the Pd atom is nearly square planar.

Comment

Cyclopalladated compounds are an important part of modern organometallic chemistry and they have attracted much attention owing to their structural features (Dehand *et al.*, 1983; Caires, Mauro, Santos, Gambardella & Lechat, 1994) and applications in organic synthesis and catalysis (Ryabov, 1985). Insertion of alkynes into the Pd—C bond of cyclopalladated complexes has proved to be a very interesting route for the preparation of novel organometallic molecules. In the present paper we report the X-ray structure analysis of (1).



(1)

The compound was prepared by the interaction of diphenylacetylene with [Pd(N,N-dimethylbenzylamine)Cl]$_2$, as described in the literature (Bahsoun *et al.*, 1979). The results of this study are illustrated in

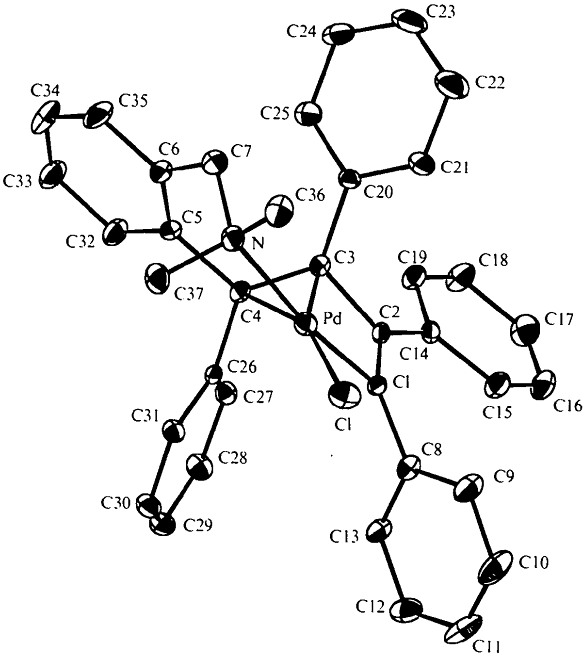


Fig. 1. View of the molecule showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% level.