1718 measured reflections
1718 independent reflections

3 standard reflections every 100 reflections intensity decay: 2.6%

Refinement

Refinement on F
$R = 0.0448$
$wR = 0.0324$
$S = 1.48$
1341 reflections
135 parameters
Only H-atom U's refined

$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\max} = 0.015$
$\Delta\rho_{\max} = 0.97$ e Å^{-3}
$\Delta\rho_{\min} = -0.99$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
Co1	0.5201 (1)	0.84488 (7)	0.8418 (2)	0.0214 (4)
Br2	0.5430 (1)	0.77576 (6)	1.1102 (2)	0.0359 (4)
Br3	0.2877 (1)	1.15424 (7)	0.9507 (2)	0.0494 (4)
Br4	0.5984 (1)	1.07330 (6)	0.6271 (2)	0.0388 (4)
N5	0.4519 (9)	0.7548 (4)	0.7220 (12)	0.028 (3)
N6	0.5676 (8)	0.9379 (4)	0.9672 (12)	0.024 (3)
N7	0.3191 (8)	0.8717 (4)	0.8905 (15)	0.035 (3)
N8	0.7225 (9)	0.8250 (4)	0.7958 (13)	0.031 (3)
N9	0.5217 (9)	0.8954 (4)	0.6124 (11)	0.030 (3)
C10	0.4385 (12)	0.9624 (6)	1.0671 (16)	0.041 (4)
C11	0.3100 (11)	0.9478 (6)	0.9555 (17)	0.037 (4)
C12	0.7740 (11)	0.8734 (6)	0.6507 (15)	0.035 (4)
C13	0.6530 (13)	0.8765 (6)	0.5188 (15)	0.039 (4)

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

Co1—Br2	2.407 (2)	N6—C10	1.494 (14)
Co1—N5	1.976 (9)	N7—C11	1.468 (14)
Co1—N6	1.988 (9)	N8—C12	1.491 (15)
Co1—N7	1.974 (8)	N9—C13	1.459 (15)
Co1—N8	1.956 (9)	C10—C11	1.495 (16)
Co1—N9	1.972 (9)	C12—C13	1.514 (17)
Br2—Co1—N9	173.3 (3)	N7—Co1—N8	176.3 (4)
N5—Co1—N6	174.1 (4)	N8—Co1—N9	85.4 (4)
N6—Co1—N7	85.0 (4)		

The $U_{\rm iso}$ parameters of the H7*A* and H9*A* atoms were fixed to avoid unreasonable values. The enantiomeric crystal structure gave $R = 0.0547$ and $wR = 0.0413$, which are significantly greater than those of the present structure.

Structure analysis was carried out using *CRYSTAN-GM* software (Edwards, Gilmore, Mackay & Stewart, 1995) on a SUN SPARC10 workstation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chelation of 2,6-Bis(hydroxymethyl)pyridine in *cis*-Dichloro(triphenylphosphine-*P*)[2-(oxymethylene-*O*)-6-(hydroxymethyl)pyridine-*N*]oxorhenium(V)–Water (2/1)

Thomas I. A. Gerber,[a] Joanne Perils,[a] Jan G. H. Du Preez[a] and Guiliano Bandoli[b]

[a]*Department of Chemistry, University of Port Elizabeth, PO Box 1600, 6000 Port Elizabeth, South Africa, and* [b]*Department of Pharmaceutical Science, University of Padova, Via Marzolo 5, 35131 Padova, Italy. E-mail: chajdp@upe.ac.za*

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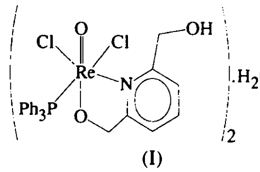
Abstract

The potentially terdentate dianionic ligand pyridine-2,6-bis(methanol) (H_2L) acts as a bidentate monoanionic N,O^--donor in the title compound, dichloro(oxo)[pyridine-2,6-bis(methanolato)(1−)-N,O](triphenylphosphine-P)rhenium(V)–water (2/1), $2[ReCl_2O\{C_5H_3N(CH_2O)(CH_2OH)\}(PPh_3)].H_2O$. The asymmetric unit contains two monomeric neutral independent and well separated $[ReOCl_2(HL)(PPh_3)]$ moieties per water molecule.

Comment

As part of a program to study the formation of oxorhenium(V) complexes containing mixed di- and terdentate N,O^--donor ligands (Du Preez, Gerber & Kemp, 1992; Gerber, Kemp, Du Preez & Bandoli, 1993; Bandoli, Gerber, Jacobs & Du Preez, 1994), we isolated the title compound, (I), in which the potentially terdentate 2,6-bis(hydroxymethyl)pyridine ligand (H_2L) acts as a bidentate N,O^--donor.



(I)

The asymmetric unit contains two monomeric neutral independent and well separated $[ReOCl_2(HL)(PPh_3)]$ molecules (*A* and *B*) per water molecule (Fig. 1). There is no intermolecular bonding of significance and in both molecules the coordination geometry about the metal atom is distorted octahedral. Molecules *A* and *B* are well superimposable; in fact, the weighted r.m.s. deviation [derived from the *BMFIT* program (Nyburg, 1974)] is only 0.048 Å when the fitting is performed using the coordination geometry atoms. No bond distances and angles differ by more than two standard deviations, apart from the Re=O(1) distance which is 1.68 (1) in molecule *A* and 1.64 (1) Å in *B*. The Re atom is out of the mean equatorial plane [by 0.15 (1) and 0.16 (1) Å in *A* and *B*, respectively, towards the oxo O(1) atom] and the five-membered metallocycle assumes a twist-envelope conformation, with the Re atom out of the O(2)—C(6)—C(5)—N(1) ring by 0.09 (1) and 0.10 (1) Å in *A* and *B*, respectively. The structural properties (Table 2) are a common feature for numerous six-coordinate octahedral monooxo complexes of rhenium(V) and do not deserve any comment (Bandoli *et al.*, 1994, and references therein). The water molecule engages in hydrogen bonding with the O(3*A*) atom at (*x*, *y*, *z* − 1) and no other interaction less than 3.3 Å can be observed in the packing.

Experimental

The synthesis of (I) was carried out by reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ and $C_5H_3N(CH_2OH)_2$ (molar ratio 1:1) in an ethanolic solution for 1 h under refluxing conditions. Recrystallization was from acetonitrile.

Crystal data

$2[ReCl_2O(C_7H_8NO_2)$-$(C_{18}H_{15}P)].H_2O$
$M_r = 1365.0$
Orthorhombic
$Pna2_1$
$a = 16.331\ (6)$ Å
$b = 29.61\ (1)$ Å
$c = 10.854\ (5)$ Å
$V = 5249\ (4)$ Å^3
$Z = 4$
$D_x = 1.727$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 8$–$14°$
$\mu = 4.923$ mm^{-1}
$T = 296$ K
Parallelepiped
0.30 × 0.20 × 0.15 mm
Violet

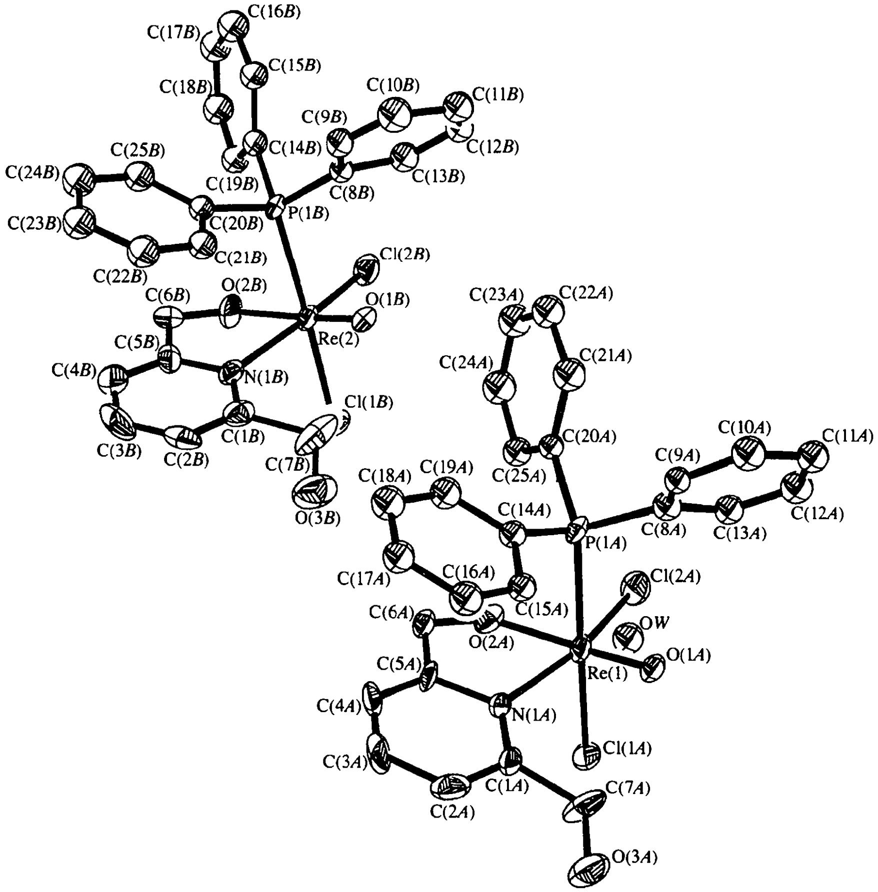


Fig. 1. The molecular structure of molecules *A* and *B* (*ORTEP*II; Johnson, 1976) and the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.

Data collection

Siemens *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (four ψ scans) (North, Phillips & Mathews, 1968)
$T_{\min} = 0.42$, $T_{\max} = 0.48$
5162 measured reflections
4880 independent reflections
3741 reflections with $F > 4\sigma(F)$
$R_{\rm int} = 0.0155$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 35$
$l = 0 \rightarrow 12$
2 standard reflections every 250 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0443$
$wR = 0.0597$
$S = 0.85$
3741 reflections
419 parameters
H atoms not refined
$w = 1/[\sigma^2(F) + 0.0049F^2]$
$(\Delta/\sigma)_{\max} = 0.48$
$\Delta\rho_{\max} = 1.87$ e Å^{-3}
$\Delta\rho_{\min} = -1.67$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute configuration: Flack (1983)
Flack parameter = −0.003 (19)

Table 1. *Selected bond lengths (Å) and angles (°)*

	Molecule *A*	Molecule *B*
Re—Cl(1)	2.418 (5)	2.428 (5)
Re—Cl(2)	2.355 (7)	2.345 (7)
Re—P(1)	2.468 (4)	2.461 (4)
Re—O(1)	1.680 (13)	1.639 (13)
Re—O(2)	1.923 (13)	1.862 (14)
Re—N(1)	2.205 (18)	2.206 (18)
Cl(1)—Re—Cl(2)	87.8 (3)	87.7 (3)
Cl(1)—Re—P(2)	177.8 (3)	177.4 (2)
Cl(1)—Re—O(1)	97.1 (4)	97.5 (5)
Cl(1)—Re—O(2)	94.4 (4)	92.3 (5)
Cl(1)—Re—N(1)	88.2 (5)	87.0 (5)
Cl(2)—Re—P(1)	89.9 (2)	91.9 (2)
Cl(2)—Re—O(1)	101.8 (6)	100.6 (5)
Cl(2)—Re—O(2)	90.2 (4)	92.0 (6)
Cl(2)—Re—N(1)	164.3 (5)	165.2 (5)
P(1)—Re—O(1)	83.4 (4)	85.1 (4)
P(1)—Re—O(2)	85.6 (4)	85.1 (5)
P(1)—Re—N(1)	93.9 (4)	92.8 (4)
O(1)—Re—O(2)	163.7 (6)	164.3 (7)
O(1)—Re—N(1)	93.8 (7)	93.9 (6)
O(2)—Re—N(1)	75.0 (6)	74.4 (7)

The H atoms, with the exception of the missing water H atoms, were included in calculated positions, but were not refined. Only a common variable displacement parameter was applied to them.

Data collection: *SHELXTL-Plus* (Sheldrick, 1987). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: AB1373). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Tetranuclear Iron Cluster Complex: $[\{Fe(CO)_3\}_3\{\mu_3\text{-}CC[Fe(CO)_2(\eta^5\text{-}C_5H_5)]\text{-}C(CF_3)\}]$

KENNETH W. MUIR,[a] LJUBICA MANOJLOVIĆ-MUIR,[a] FIONA MORRICE,[a] KARINE GUENNOU,[b] FRANÇOIS PÉTILLON[b] AND RENÉ RUMIN[b]

[a]*Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland, and* [b]*URA CNRS 322, Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences et Techniques, Université de Bretagne Occidentale, BP 452, 29275 Brest CEDEX, France. E-mail: ken@chem.gla.ac.uk*

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Abstract

Undecacarbonyl[4(η^5)-cyclopentadienyl]-μ_3-(4,4,4-trifluorobutaneheptayl)-tetrairon(3 *Fe—Fe*), $[\{Fe(CO)_3\}_3\{\mu_3\text{-}CC[Fe(CO)_2Cp]C(CF_3)\}]$ (Cp is η^5-C_5H_5) contains a triangular $\{Fe(CO)_3\}_3$ core [Fe—Fe distances 2.482 (1), 2.663 (1) and 2.693 (1) Å] linked *via* an unusual C_3CF_3 bridging unit to an $Fe(CO)_2Cp$ group.

Comment

The dinuclear complex $[\{Cp(CO)Fe\}_2\{\mu\text{-}C_2(CF_3)_2\text{-}SMe\}_2]$ (Cp is η^5-C_5H_5), (1), reacts with triiron dodecacarbonyl $[Fe_3(CO)_{12}]$ to give μ_3-η^2-alkyne