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Tris[bis(diphenylphosphino)methane-κ^2P,P']-rhenium(I) perrhenate

Kenton H. Whitmire,[a]* Daniel R. Derringer[b] and Kimberly R. Kongkasuwan[b]

[a]Chemistry Department MS-60, Rice University, 6100 Main Street, Houston, TX 77005-1892, USA, and [b]Chemistry Department, Hollins University, Roanoke, VA 24020-1607, USA

Correspondence e-mail: whitmir@rice.edu

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A reaction was carried out to make *trans*-[$Re_2\{O_2C$-3,5-$(OH)_2C_6H_3\}_2Br_2(dppm)_2$] (dppm is $Ph_2PCH_2PPh_2$). No *trans*-[$Re_2\{O_2C$-3,5-$(OH)_2C_6H_3\}_2Br_2(dppm)_2$] was isolated, however, and a very small quantity of crystalline [$Re(dppm)_3$]-[ReO_4] was obtained after several months. A product of decomposition by disproportionation of a complex of dirhenium, [$Re(dppm)_3$]ReO_4 is an ionic compound that contains a complex cation of Re^I bonded to three chelating dppm ligands. Although complexes that contain three chelating dppm ligands are very rare, this is the second time [$Re(dppm)_3$]$^+$ has been observed and characterized structurally. In 2000, [$Re(dppm)_3$]$^+$, with I^- as the counter-ion, was structurally characterized [Rivero *et al.* (2000). *Polyhedron*, **19**, 2249–2254]. The Re—P distances in the compound we characterized range from 2.408 (3) to 2.473 (3) Å, and the P—Re—P angles, associated with the chelate rings, range from 68.22 (12) to 70.04 (12)°. These values are very similar to those reported by Rivero *et al.* (2000).

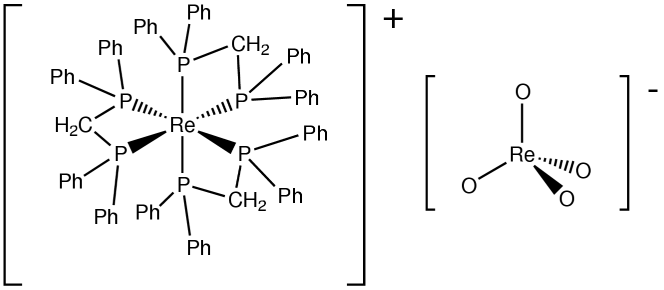
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.020 Å
Disorder in main residue
R factor = 0.046
wR factor = 0.115
Data-to-parameter ratio = 19.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Crystals of the title compound, (I), suitable for structure determination by single-crystal X-ray diffraction, were isolated from a mixture that the authors hoped would yield the dirhenium(II) compound, *trans*-[$Re_2\{O_2C$-3,5-$(OH)_2C_6H_3\}_2$-$Br_2(dppm)_2$] (dppm is $Ph_2PCH_2PPh_2$), but never did (see *Experimental*).



(I)

The IR spectrum of [$Re(dppm)_3$][ReO_4] shows a strong absorbance at 902 cm^{-1}, which is assignable to an IR active normal mode of ReO_4^-. Bands characteristic of the dppm ligands were observed at the following wavenumbers (in cm^{-1}): 1434 (*vs*), 1310 (*w*), 1091 (*s*), 742 (*vs*), 734 (*vs*), 721 (*vs*), and 698 (*vs*). The positions and intensities of these bands are in excellent agreement with those reported by Rivero *et al.* (2000). The electronic absorption spectrum of [$Re(dppm)_3$]ReO_4 exhibits an intense absorption at 302 nm in dichloromethane solution. This band tails into the visible and is responsible for the yellow color of the compound.

Experimental

The dirhenium(II) starting material, $Re_2Br_4(dppm)_2$, was prepared by a method described elsewhere (Cutler *et al.*, 1988). Triethylamine and 3,5-dihydroxybenzoic acid were obtained from commercial sources and used without further purification. Absolute ethanol (the reaction solvent) and triethylamine (a liquid reactant) were deaerated prior to use, and the reaction was carried out in an atmosphere of dinitrogen. No special precautions were taken to protect reaction products from oxygen during work-up.

An attempt was made to synthesize *trans*-$[Re_2\{O_2C\text{-}3,5\text{-}(OH)_2C_6H_3\}_2Br_2(dppm)_2]$: a mixture containing $Re_2Br_4(dppm)_2$ (0.1031 g, 0.07058 mmol), 3,5-dihydroxybenzoic acid (0.0239 g, 0.1551 mmol), and triethylamine (0.1 ml, 0.7 mmol) was refluxed in ethanol (20 ml) for 1 h, and then cooled to room temperature. Diethyl ether (*ca* 10 ml) was added, in an effort to cause the desired product to precipitate from solution. No precipitation occurred, so the mixture was cooled to *ca.* 268 K in a laboratory freezer and kept there for 1 d. After a day at 268 K, the mixture was still clear. It was transferred to an evaporating dish and allowed to warm to room temperature. As the solvent evaporated from the mixture, some precipitation occurred, but because the quantity of solid was very small, no attempt was made to isolate it. Instead, the compound was redissolved by adding to the mixture a small volume (*ca* 10 ml) of 95% ethanol. After a short time (a few minutes), a white compound precipitated from solution. The white compound, whose identity was never determined, was filtered off. To the filtrate, another quantity (*ca* 20 ml) of 95% ethanol was added. This mixture, from which crystals of $[Re(dppm)_3]ReO_4$ were ultimately obtained, was returned to the laboratory freezer, where it remained for nearly eight months before it was removed to allow solvent to evaporate slowly at room temperature. After approximately one month at room temperature, crystals of $[Re(dppm)_3]ReO_4$ (not more than one dozen in number) formed in the mixture. The crystals were collected and dried.

An IR spectrum of $[Re(dppm)_3]ReO_4$ as a mineral oil (Nujol) mull was recorded in the region 4000–600 cm^{-1} with a Nicolet Magna–IR System 550 spectrometer. An electronic absorption spectrum from 200–800 nm was obtained with an HP 8452A Diode Array spectrophotometer on a dichloromethane solution in a 1 cm quartz cell.

Crystal data

$[Re(C_{25}H_{22}P_2)_3][ReO_4]$
$M_r = 1589.50$
Orthorhombic, *Pbca*
$a = 17.805$ (4) Å
$b = 37.831$ (14) Å
$c = 19.3318$ (18) Å
$V = 13022$ (6) Å^3
$Z = 8$
$D_x = 1.622$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 3.5$–5.9°
$\mu = 3.91$ mm^{-1}
$T = 293$ (2) K
Irregular cut block, yellow
0.3 × 0.3 × 0.2 mm

Data collection

Rigaku AFC-5*S* diffractometer
$2\theta-\omega$ scans
Absorption correction: none
5937 measured reflections
5937 independent reflections
4208 reflections with $I > 2\sigma(I)$
$\theta_{max} = 20.0°$

$h = -17 \rightarrow 0$
$k = 0 \rightarrow 36$
$l = 0 \rightarrow 16$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.115$
$S = 1.11$
5937 reflections
305 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 156.3064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.96$ e Å^{-3}
$\Delta\rho_{min} = -0.96$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Re1—P3	2.408 (3)	P4—C411	1.842 (7)
Re1—P4	2.416 (3)	P4—C2	1.846 (13)
Re1—P1	2.415 (3)	P4—C421	1.863 (7)
Re1—P6	2.439 (3)	P5—C3	1.829 (12)
Re1—P5	2.466 (3)	P5—C511	1.851 (7)
Re1—P2	2.473 (3)	P5—C521	1.851 (7)
P1—C111	1.853 (7)	P6—C611	1.807 (14)
P1—C121	1.862 (7)	P6—C3	1.836 (13)
P1—C1	1.850 (12)	P6—C621	1.843 (13)
P2—C1	1.831 (12)	P6—C601	1.901 (15)
P2—C211	1.852 (7)	Re2—O4	1.578 (15)
P2—C221	1.858 (8)	Re2—O2	1.645 (14)
P3—C321	1.834 (8)	Re2—O3	1.680 (17)
P3—C2	1.835 (13)	Re2—O1	1.709 (11)
P3—C311	1.861 (7)		
P3—Re1—P4	70.04 (12)	C321—P3—C311	96.3 (4)
P3—Re1—P1	91.41 (12)	C2—P3—C311	103.4 (5)
P4—Re1—P1	97.87 (12)	C321—P3—Re1	122.6 (3)
P3—Re1—P6	159.24 (12)	C2—P3—Re1	96.2 (4)
P4—Re1—P6	91.81 (12)	C311—P3—Re1	128.2 (3)
P1—Re1—P6	101.31 (12)	C411—P4—C2	103.0 (5)
P3—Re1—P5	101.64 (12)	C411—P4—C421	96.4 (4)
P4—Re1—P5	92.67 (12)	C2—P4—C421	103.7 (5)
P1—Re1—P5	165.45 (12)	C411—P4—Re1	127.2 (3)
P6—Re1—P5	68.22 (12)	C2—P4—Re1	95.6 (4)
P3—Re1—P2	95.38 (12)	C421—P4—Re1	126.6 (3)
P4—Re1—P2	160.78 (11)	C3—P5—C511	102.8 (5)
P1—Re1—P2	69.21 (11)	C3—P5—C521	106.1 (5)
P6—Re1—P2	104.42 (11)	C511—P5—C521	93.2 (4)
P5—Re1—P2	102.80 (12)	C3—P5—Re1	92.5 (4)
C111—P1—C121	98.4 (4)	C511—P5—Re1	134.5 (3)
C111—P1—C1	101.4 (5)	C521—P5—Re1	123.4 (3)
C121—P1—C1	105.2 (5)	C611—P6—C3	98.4 (8)
C111—P1—Re1	127.9 (3)	C611—P6—C621	92.2 (8)
C121—P1—Re1	124.1 (3)	C3—P6—C621	106.2 (6)
C1—P1—Re1	95.4 (4)	C3—P6—C601	108.2 (8)
C1—P2—C211	107.5 (5)	C621—P6—C601	96.6 (8)
C1—P2—C221	101.9 (5)	C611—P6—Re1	135.8 (7)
C211—P2—C221	92.3 (4)	C3—P6—Re1	93.2 (4)
C1—P2—Re1	94.0 (4)	C621—P6—Re1	125.0 (4)
C211—P2—Re1	125.9 (3)	C601—P6—Re1	125.7 (7)
C221—P2—Re1	131.7 (3)	P2—C1—P1	97.9 (5)
C321—P3—C2	107.6 (5)	P3—C2—P4	97.5 (6)

Data collection: *TEXSAN* (Molecular Structure Corporation, 1990); cell refinement: *TEXSAN*; data reduction: *TEXSAN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Siemens, 1992); software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

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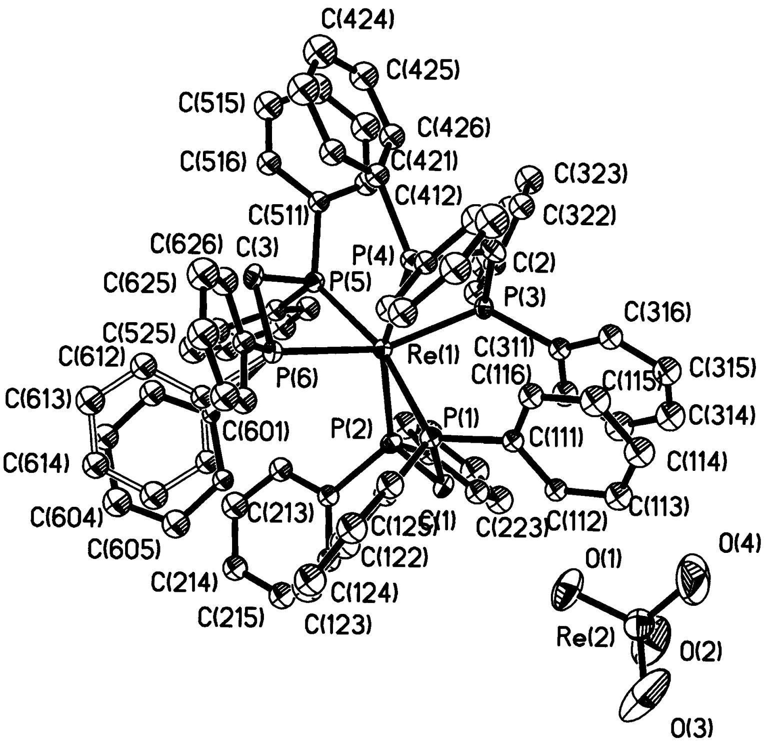

Figure 1

A view of [Re(dppm)$_3$][ReO$_4$], with the atomic numbering scheme. H atoms have been omitted in order to improve the clarity. Likewise, not all C atoms around each ring are labeled. The C atoms are numbered sequentially around a ring. Displacement ellipsoids are drawn at the 30% probability level. One of the phenyl rings was found to be disordered. Two sites were resolved, which were refined isotropically as rigid bodies.

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