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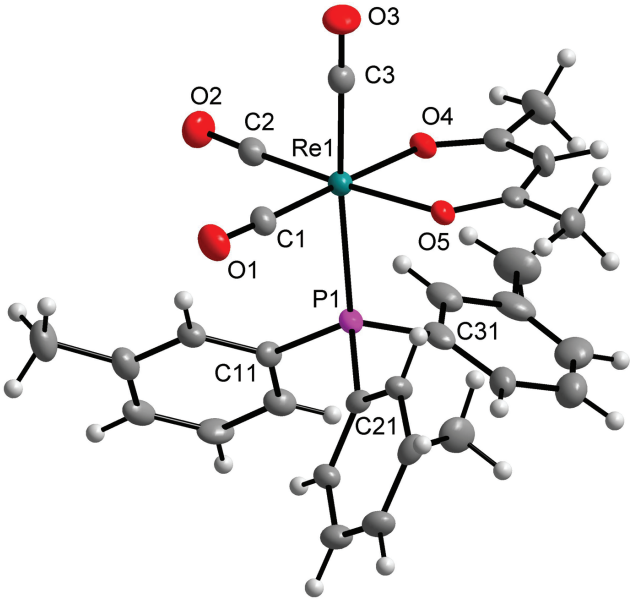
Crystal structure of *fac*-(acetylacetonato-κ²*O*,*O*′)tricarbonyl(tri-*m*-tolyl phosphane-κ*P*)rhenium(I), $C_{29}H_{28}O_5PRe$



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Abstract

$C_{29}H_{28}O_5PRe$, monoclinic, $P2_1/n$ (no. 14), $a = 10.548(5)$ Å, $b = 22.996(5)$ Å, $c = 11.022(5)$ Å, $\beta = 98.011(5)°$, $V = 2647.4(18)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0306$, $wR_{ref}(F^2) = 0.0911$, $T = 100$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Cuboid, colorless
Size:	0.36 × 0.27 × 0.21 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.69 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
$2\theta_{max}$, completeness:	56°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	50865, 6391, 0.082
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5316
$N(param)_{refined}$:	325
Programs:	Bruker programs [1], SHELX [2], SIR97 [3], DIAMOND [4], WinGX [5]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Re1	0.706991(15)	0.170970(6)	0.256785(13)	0.01742(7)
O1	0.9057(4)	0.16411(13)	0.4870(3)	0.0342(8)
O2	0.5565(3)	0.08446(15)	0.3919(3)	0.0377(8)
O3	0.5695(3)	0.27169(14)	0.3702(3)	0.0376(8)
O4	0.5679(3)	0.16952(11)	0.0977(3)	0.0218(6)
O5	0.7997(3)	0.23508(12)	0.1597(3)	0.0214(6)
P1	0.83375(10)	0.09770(4)	0.15523(9)	0.0186(2)
C1	0.8335(5)	0.16813(16)	0.3993(4)	0.0236(9)
C2	0.6141(4)	0.11564(18)	0.3387(4)	0.0250(9)
C3	0.6168(4)	0.23388(18)	0.3269(4)	0.0243(9)
C4	0.4433(5)	0.1908(2)	−0.0902(4)	0.0342(10)
H4A	0.3942	0.1585	−0.0622	0.051*
H4B	0.4713	0.1806	−0.1686	0.051*
H4C	0.3893	0.2256	−0.1007	0.051*
C5	0.5583(4)	0.20262(19)	0.0033(4)	0.0256(9)
C6	0.6439(4)	0.24690(19)	−0.0163(4)	0.0278(9)
H6	0.6218	0.2705	−0.0868	0.033*
C7	0.7583(4)	0.25962(17)	0.0578(4)	0.0244(9)
C8	0.8457(5)	0.3054(2)	0.0190(4)	0.0323(10)
H8A	0.9216	0.3089	0.0809	0.048*
H8B	0.8007	0.3428	0.0105	0.048*
H8C	0.8721	0.2945	−0.0597	0.048*
C11	0.8270(4)	0.02294(16)	0.2084(4)	0.0207(8)
C12	0.8265(4)	−0.02442(17)	0.1298(4)	0.0269(9)
H12	0.8225	−0.0182	0.0442	0.032*
C13	0.8318(4)	−0.08041(18)	0.1754(4)	0.0291(10)
H13	0.832	−0.1125	0.1211	0.035*
C14	0.8368(4)	−0.09002(18)	0.3000(5)	0.0295(10)
H14	0.841	−0.1287	0.3303	0.035*
C15	0.8356(4)	−0.04386(19)	0.3817(4)	0.0291(10)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C16	0.8293(4)	0.01236(18)	0.3333(4)	0.0224(8)
H16	0.8266	0.0444	0.3871	0.027*
C17	0.8373(5)	−0.0532(2)	0.5162(4)	0.0386(12)
H17A	0.8363	−0.0155	0.5574	0.058*
H17B	0.9149	−0.0745	0.5491	0.058*
H17C	0.7618	−0.0757	0.5301	0.058*
C21	1.0074(4)	0.11092(17)	0.1702(3)	0.0198(8)
C22	1.0524(4)	0.16796(16)	0.1721(4)	0.0214(8)
H22	0.9935	0.1992	0.1721	0.026*
C23	1.1832(4)	0.18000(19)	0.1742(4)	0.0246(9)
C24	1.2681(4)	0.1333(2)	0.1798(4)	0.0289(9)
H24	1.3572	0.1404	0.1827	0.035*
C25	1.2237(4)	0.0764(2)	0.1811(4)	0.0286(9)
H25	1.2829	0.0451	0.186	0.034*
C26	1.0937(4)	0.06492(18)	0.1751(4)	0.0224(8)
H26	1.0639	0.0259	0.1745	0.027*
C27	1.2307(5)	0.2419(2)	0.1729(5)	0.0351(11)
H27A	1.1579	0.2687	0.1686	0.053*
H27B	1.275	0.2478	0.1014	0.053*
H27C	1.29	0.2495	0.2479	0.053*
C31	0.7870(4)	0.09353(18)	−0.0110(4)	0.0280(9)
C32	0.6679(5)	0.07091(19)	−0.0564(4)	0.0330(10)
H32	0.6128	0.0571	−0.0015	0.04*
C33	0.6276(5)	0.0683(2)	−0.1869(5)	0.0375(11)
C34	0.7116(5)	0.0900(2)	−0.2605(5)	0.0391(12)
H34	0.687	0.0883	−0.3467	0.047*
C35	0.8276(5)	0.1138(2)	−0.2181(5)	0.0401(12)
H35	0.8808	0.1291	−0.2731	0.048*
C36[a]	0.8665(5)	0.1150(2)	−0.0918(4)	0.0290(10)
H36[a]	0.9479	0.1306	−0.0605	0.035*
C37	0.5014(5)	0.0425(2)	−0.2328(5)	0.0478(14)
H37A	0.459	0.0304	−0.1632	0.072*
H37B	0.5133	0.0086	−0.2839	0.072*
H37C	0.4484	0.0714	−0.2815	0.072*

[a]Occupancy: 0.95.

Source of material

The starting complex *fac*-$[Re(CO)_3(H_2O)(acac)]$ was prepared according to a published procedure [7]. *fac*-$[Re(acac)(CO)_3(H_2O)]$ (39 mg; 0.1 mmol) was dissolved in methanol (3 mL) and P(*m*-tolyl)$_3$ (31 mg, 0.1 mmol) dissolved in 3 mL methanol was added. The solution was stirred for 10 hours at room temperature and the slighty yellow solution that formed was left to crystallize. Crystals suitable for X-ray diffraction formed. Yield = 65 mg, 96%. **IR** (KBr, cm^{-1}): νCO = 2013, 1911, 1881.

Experimental details

In the structure all the H atoms were positioned geometrically and refined discernible using a riding model, with C—$H_{methine}$ = 0.98 Å; C—H_{methyl} = 0.96 Å; C—$H_{aromatic}$ = 0.93 Å. The H atom isotropic displacement parameters were fixed; $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and methine and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl protons, allowing them to ride on the parent atom.

Discussion

The use of the '2 + 1' mixed ligand model (where a bidentate ligand is coordinated in the equatorial position and a monodentate ligand in the sixth position) on the *fac*-$[M(CO)_3(H_2O)_3]^+$ (M = Tc(I), Re(I)) complex is frequently utilized in the design of new potential radiopharmaceuticals and is due to the lability of the three aqua ligands that the precursor possesses. The said model has been greatly explored in our group for the coordination of different types of ligands, with altered electronic, steric and biological properties [6–11]. This investigation forms part of a perpetual research project of which the objective is to determine structure and reactivity relations of different transition metal complexes [12–15].

The title complex displays typical octahedral geometry around the rhenium(I) metal center, which is slightly distorted and can be seen in the O5—Re1—C2 (176.39(15)°), O4—Re1—C1 (177.10(14)°) and P1—Re1—C3 (174.24(12)°) bond angles that deviate from 180°. A bite angle of 84.79(11)° is noted from the coordination of the acetylacetonato (acac) ligand to the metal and corresponds well with similar structures [16, 17]. Bond distances of the phosphine coordination to the rhenium(I) metal center is typically around the same value of 2.5093(11) Å, as noted in the title compound [16–18]. The molecules pack in horizontal layers, in a head-to-head fashion, when viewed along the *c*-axis.

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