Crystal structure of fac-(acetylacetonato κ2#) tricarbonyl(benzyldiphenylphosphine-κP) rhenium(I), C27H24O5PRe.

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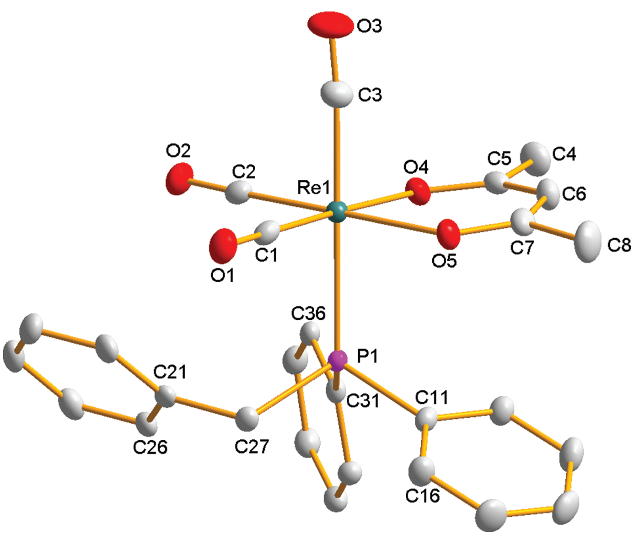

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Abstract

$C_{27}H_{24}O_5PRe$, triclinic, $P\bar{1}$ (no. 2), $a = 9.0305(17)$ Å, $b = 12.084(2)$ Å, $c = 12.403(2)$ Å, $\alpha = 89.688(6)°$, $\beta = 70.083(6)°$, $\gamma = 76.315(6)°$, $V = 1232.2(4)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0180$, $wR_{ref}(F^2) = 0.0432$, $T = 100(2)$ K.

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

Table 1: Data collection and handling.

Crystal:	Yellow cuboid
Size:	0.36 × 0.19 × 0.11 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	50.3 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	56.8°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6098, 6098, 0.052
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5829
$N(param)_{refined}$:	325
Programs:	Bruker programs [1], SHELX [2], SIR97 [3], DIAMOND [4], ORTEP [5], OLEX2 [6]

Source of materials

The starting complex *fac*-[Re(CO)$_3$(H$_2$O)(acac)] was prepared according to a published procedure [6]. *fac*-[Re(CO)$_3$(H$_2$O)(acac)] (39 mg; 0.1 mmol) was dissolved in MeOH (3 mL) and benzyldiphenylphosphine (PPh$_2$Bz) (0.028 g; 0.1 mmol) dissolved in methanol (2 mL) was added. The solution was stirred for 6 h at room temperature. The light yellow solution was left to crystallise and yellow crystals of the title complex were collected. Yield = 40 mg, 62%.

Experimental details

In the structure, all the H atoms were positioned geometrically and refined discemible using a riding model, with C—H$_{methine}$ = 0.98 Å; C—H$_{methylene}$ = 0.99 Å; C—H$_{methyl}$ = 0.96 Å; C—H$_{aromatic}$ = 0.93 Å. The U_{iso} parameters of the H atoms were fixed; $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and methine and $U_{iso}(H) = 1.5U_{eq}(C)$.

A limited number of inner reflections, which are cut by the primary beam stop have been omitted manually.

Comment

Some radionuclides of some metals are of significat interest for its rich coordination abilities and nuclear properties. The radiometal that has received significant attention is ^{99m}Tc, because it is easily accessible and possesses almost near perfect nuclear properties; ($t_{1/2}$ = 6.02 h; γ = 140 keV, 100%).

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Re1	0.19351(2)	0.29170(2)	0.12807(2)	0.01370(3)
P1	0.18998(7)	0.20541(5)	0.30979(5)	0.01253(11)
O1	−0.1769(2)	0.38212(16)	0.22543(17)	0.0255(4)
O2	0.1399(3)	0.07837(17)	0.02860(17)	0.0271(4)
O3	0.1887(3)	0.3977(2)	−0.0991(2)	0.0434(6)
O5	0.2380(2)	0.43764(15)	0.19616(16)	0.0196(4)
O4	0.4521(2)	0.22899(15)	0.06561(15)	0.0187(3)
C24	−0.1320(3)	−0.0925(2)	0.2441(2)	0.0246(5)
H24	−0.1588	−0.1519	0.2103	0.029*
C25	−0.0147(3)	−0.1183(2)	0.2949(2)	0.0232(5)
H25	0.0388	−0.1958	0.2966	0.028*
C26	0.0252(3)	−0.0316(2)	0.3435(2)	0.0186(5)
H26	0.1055	−0.0505	0.3786	0.022*
C23	−0.2101(3)	0.0208(2)	0.2428(2)	0.0253(6)
H23	−0.2918	0.0391	0.2089	0.030*
C16	0.1095(3)	0.3554(2)	0.5081(2)	0.0219(5)
H16	−0.0008	0.3555	0.5227	0.026*
C21	−0.0506(3)	0.0828(2)	0.3417(2)	0.0162(4)
C22	−0.1693(3)	0.1078(2)	0.2908(2)	0.0210(5)
H22	−0.2230	0.1851	0.2888	0.025*
C27	−0.0077(3)	0.1770(2)	0.3957(2)	0.0171(5)
H27A	−0.0050	0.1562	0.4725	0.021*
H27B	−0.0944	0.2481	0.4072	0.021*
C35	0.4843(3)	−0.1168(2)	0.2006(2)	0.0199(5)
H35	0.5311	−0.1651	0.1312	0.024*
C36	0.3999(3)	−0.0040(2)	0.2010(2)	0.0157(4)
H36	0.3902	0.0246	0.1316	0.019*
C14	0.3090(4)	0.4196(2)	0.5622(2)	0.0259(6)
H14	0.3360	0.4617	0.6142	0.031*
C34	0.4997(3)	−0.1583(2)	0.3018(2)	0.0201(5)
H34	0.5554	−0.2356	0.3018	0.024*
C31	0.3297(3)	0.06701(19)	0.3030(2)	0.0140(4)
C32	0.3492(3)	0.0252(2)	0.4040(2)	0.0169(5)
H32	0.3044	0.0738	0.4732	0.020*
C33	0.4339(3)	−0.0871(2)	0.4034(2)	0.0187(5)
H33	0.4468	−0.1153	0.4722	0.022*
C5	0.5586(3)	0.2839(2)	0.0614(2)	0.0185(5)
C11	0.2311(3)	0.2923(2)	0.4111(2)	0.0160(4)
C12	0.3919(3)	0.2954(2)	0.3892(2)	0.0196(5)
H12	0.4755	0.2538	0.3228	0.023*
C8	0.3628(4)	0.5744(2)	0.2351(3)	0.0324(7)
H8A	0.2486	0.6115	0.2786	0.049*
H8B	0.4086	0.6240	0.1769	0.049*
H8C	0.4241	0.5606	0.2876	0.049*
C7	0.3735(3)	0.4622(2)	0.1767(2)	0.0205(5)
C6	0.5261(3)	0.3947(2)	0.1098(2)	0.0220(5)
H6	0.6162	0.4274	0.0959	0.026*
C4	0.7328(3)	0.2191(3)	−0.0006(3)	0.0272(6)
H4A	0.7354	0.1430	−0.0294	0.041*
H4B	0.7930	0.2113	0.0526	0.041*
H4C	0.7831	0.2607	−0.0654	0.041*
C3	0.1949(4)	0.3613(2)	−0.0148(2)	0.0254(6)
C15	0.1486(4)	0.4185(2)	0.5836(2)	0.0271(6)
H15	0.0651	0.4606	0.6498	0.033*
C2	0.1598(3)	0.1578(2)	0.0673(2)	0.0180(5)
C1	−0.0364(3)	0.3486(2)	0.1884(2)	0.0183(5)
C13	0.4306(3)	0.3592(2)	0.4645(2)	0.0244(5)
H13	0.5404	0.3614	0.4489	0.029*

The 3rd row congener and 5d analogue of technetium, namely rhenium has been a significant focus, due to its β-emitting isotopes ^{188}Re and ^{186}Re that have a potential use in radiotherapy. Since its development by Alberto *et al.* [7–9], the *fac*-$[M(H_2O)_3(CO)_3]^+$ (M = Tc, Re) has been extensively used because it opens innovative prospects for novel labelling strategies for the development of new diagnostic and therapeutic radiopharmaceutical drugs [7–13]. The primary reason for its popularity is because of the inert nature of the *fac*-$[M(CO)_3]^+$ core in aqueous media and also the lability of the aqua ligands to be substituted by combinations of various mono- and bidentate ligands (*OO'*–, *NO*–, *NN'*–, *NS*–donating, etc.) *via* the '2 + 1' mixed ligand approach [14–21].

The geometry around the title complex, *fac*-$[Re(Acac)(CO)_3(PPh_2Bz)]$ is typically octahedral and the central rhenium metal is bound to three *fac* carbonyl ligands, a chelate β-diketonato ligand, acetylacetonato (Acac) through its oxygen atoms and to a monodentate benzyldiphenylphosphine ligand (PPh_2Bz) through its phosphorus atom. In the coordination sphere, the Re1–P1 bond distance of 2.4718(7) Å is the longest and is consistent with those found in similar Re(I)-tricarbonyl complexes. All the bond distances and angles are considered to be within the normal range [11–24].

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