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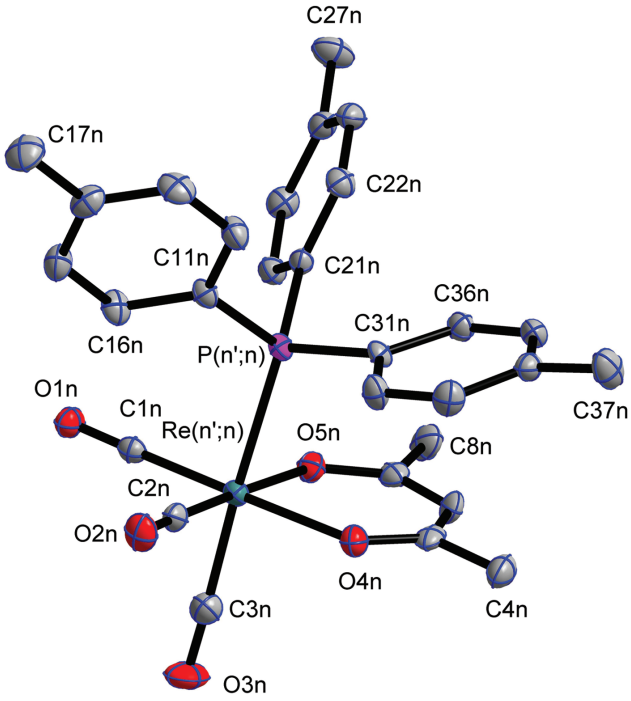
Crystal structure of *fac*-(acetylacetonato-κ^2O,O') tricarbonyl(tri(*p*-tolyl)phosphine-κ*P*)rhenium(I), $C_{29}H_{28}O_5PRe$



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Abstract

$C_{29}H_{28}O_5PRe$, triclinic, $P\bar{1}$ (no. 2), $a = 12.733(7)$ Å, $b = 18.668(11)$ Å, $c = 24.779(15)$ Å, $\alpha = 101.442(20)°$, $\beta = 100.844(18)°$, $\gamma = 104.240(19)°$, $V = 5419(9)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0307$, $wR_{ref}(F^2) = 0.0772$, $T = 100$ K.

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One representative complex is shown (Z′ = 4) n = A, B, C, D and n′ = 1–4 for the four respective molecules. 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:	Colourless cuboid
Size:	0.44 × 0.34 × 0.24 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	45.8 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	56.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	108469, 26855, 0.068
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 22905
$N(param)_{refined}$:	1298
Programs:	Bruker programs [1], SHELX [2], SIR97 [3], DIAMOND [4], ORTEP [5]

Source of materials

The starting complex *fac*-[Re(CO)$_3$(H$_2$O)(acac)] was prepared according to a published procedure [1]. *fac*-[Re(Acac)(CO)$_3$(H$_2$O)] (39 mg; 0.1 mmol) was dissolved in methanol (3 mL) and P(*p*-tolyl)$_3$ (31 mg; 0.1 mmol) dissolved in 3 mL methanol was added. The solution was stirred for 8 hours at room temperature and then left to crystallize. Yield = 49 mg, 72%. **IR** (KBr, cm^{-1}): ν_{CO} = 2020, 1887.

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$_{methyl}$ = 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.

Comment

In recent years, rhenium has become one of the most studied transition metals due to the development of the *fac*-[Re(CO)$_3$(H$_2$O)$_3$]$^+$ cation, which bears the possibility of developing radiopharmaceuticals. The coordinated *β*-diketone type ligand, acetylacetone (Acac), is one of the most frequently used ligands to coordinate to the *fac*-[Re(CO)$_3$]$^+$ synthon, because the possibility exists to link biomolecules

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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}
C1A	0.8610(3)	0.4638(2)	0.06053(15)	0.0215(7)
C1B	0.1405(3)	0.1967(2)	0.21517(15)	0.0236(8)
C1C	0.7777(3)	−0.09041(19)	0.24114(14)	0.0175(7)
C1D	1.3331(3)	−0.3686(2)	0.40066(15)	0.0211(7)
C2A	0.6893(3)	0.36545(19)	0.08047(14)	0.0196(7)
C2B	0.2517(3)	0.1190(2)	0.27255(15)	0.0216(7)
C2C	0.8896(3)	−0.1711(2)	0.29682(14)	0.0211(7)
C2D	1.1544(3)	−0.4750(2)	0.39997(15)	0.0228(7)
C3A	0.6554(3)	0.4456(2)	0.00131(15)	0.0268(8)
C3B	0.0652(3)	0.0409(2)	0.18988(15)	0.0248(8)
C3C	0.9625(3)	−0.0141(2)	0.32562(16)	0.0265(8)
C3D	1.3439(3)	−0.4620(2)	0.47095(16)	0.0277(8)
C4A	0.4951(3)	0.1825(2)	−0.11948(15)	0.0239(8)
H4A1	0.4616	0.168	−0.0893	0.036*
H4A2	0.5169	0.1397	−0.1392	0.036*
H4A3	0.4406	0.1954	−0.1466	0.036*
C4B	0.3412(3)	−0.0594(2)	0.11076(16)	0.0304(9)
H4B1	0.3706	−0.0645	0.1488	0.046*
H4B2	0.4034	−0.0427	0.0937	0.046*
H4B3	0.2909	−0.1088	0.087	0.046*
C4C	0.8849(3)	−0.0739(2)	0.50317(15)	0.0294(8)
H4C1	0.9265	−0.1114	0.4973	0.044*
H4C2	0.8208	−0.0949	0.5177	0.044*
H4C3	0.9341	−0.0268	0.5307	0.044*
C4D	1.1549(3)	−0.4244(3)	0.61471(18)	0.0382(10)
H4D1	1.0942	−0.4692	0.5909	0.057*
H4D2	1.1235	−0.3884	0.636	0.057*
H4D3	1.2058	−0.4405	0.6414	0.057*
C5A	0.5970(3)	0.2509(2)	−0.09391(14)	0.0201(7)
C5B	0.2779(3)	−0.00123(19)	0.11499(15)	0.0212(7)
C5C	0.8442(3)	−0.0566(2)	0.44757(15)	0.0233(7)
C5D	1.2181(3)	−0.3860(2)	0.57760(16)	0.0265(8)
C6A	0.6577(3)	0.2819(2)	−0.12914(15)	0.0251(8)
H6A	0.6321	0.2581	−0.1687	0.03*
C6B	0.2288(3)	0.0162(2)	0.06637(15)	0.0252(8)
H6B	0.2358	−0.0112	0.0312	0.03*
C6C	0.7827(3)	−0.0041(2)	0.44570(14)	0.0251(8)
H6C	0.7693	0.0189	0.4805	0.03*
C6D	1.3086(3)	−0.3203(2)	0.60350(15)	0.0292(9)
H6D	1.3247	−0.3024	0.6437	0.035*
C7A	0.7527(3)	0.3448(2)	−0.11150(15)	0.0238(8)
C7B	0.1699(3)	0.0702(2)	0.06393(15)	0.0226(7)
C7C	0.7394(3)	0.01749(19)	0.39798(15)	0.0213(7)
C7D	1.3768(3)	−0.2789(2)	0.57595(15)	0.0230(7)
C8A	0.8099(3)	0.3691(2)	−0.15599(15)	0.0345(9)
H8A1	0.875	0.414	−0.1377	0.052*
H8A2	0.7573	0.382	−0.1841	0.052*
H8A3	0.8343	0.3272	−0.175	0.052*
C8B	0.1227(3)	0.0833(2)	0.00765(15)	0.0310(9)
H8B1	0.0846	0.1227	0.0136	0.047*
H8B2	0.0693	0.0356	−0.0171	0.047*
H8B3	0.1836	0.1001	−0.0103	0.047*
C8C	0.6729(3)	0.0743(2)	0.40238(16)	0.0305(9)
H8C1	0.649	0.0831	0.3649	0.046*
H8C2	0.7196	0.1227	0.4292	0.046*
H8C3	0.6069	0.0539	0.4159	0.046*
C8D	1.4706(3)	−0.2093(2)	0.61028(16)	0.0298(8)
H8D1	1.5109	−0.1866	0.5849	0.045*
H8D2	1.5221	−0.2239	0.6377	0.045*
H8D3	1.44	−0.172	0.6307	0.045*
C11A	0.9796(3)	0.34911(19)	0.10138(14)	0.0184(7)
C11B	0.4316(3)	0.30111(19)	0.24776(14)	0.0200(7)
C11C	0.6094(3)	−0.28057(19)	0.26070(14)	0.0182(7)
C11D	1.0342(3)	−0.35206(19)	0.36933(14)	0.0187(7)
C12A	1.0891(3)	0.3813(2)	0.10062(16)	0.0268(8)
H12A	1.1102	0.375	0.0656	0.032*
C12B	0.5157(3)	0.3609(2)	0.24207(16)	0.0284(8)
H12B	0.544	0.3547	0.2091	0.034*
C12C	0.5417(3)	−0.3467(2)	0.26843(15)	0.0251(8)
H12C	0.5171	−0.3451	0.3024	0.03*
C12D	0.9190(3)	−0.36788(19)	0.36152(14)	0.0206(7)
H12D	0.8889	−0.3555	0.3932	0.025*
C13A	1.1686(3)	0.4230(2)	0.15099(16)	0.0310(9)
H13A	1.2436	0.4448	0.1497	0.037*
C13B	0.5586(3)	0.4291(2)	0.28400(16)	0.0286(8)
H13B	0.6156	0.4693	0.2792	0.034*
C13C	0.5098(3)	−0.4150(2)	0.22671(16)	0.0275(8)
H13C	0.464	−0.4596	0.2329	0.033*
C13D	0.8478(3)	−0.4015(2)	0.30800(15)	0.0255(8)
H13D	0.7693	−0.4117	0.3035	0.031*
C14A	1.1414(3)	0.4334(2)	0.20260(15)	0.0269(8)
C14B	0.5196(3)	0.4400(2)	0.33298(15)	0.0259(8)
C14C	0.5428(3)	−0.4200(2)	0.17632(15)	0.0242(8)
C14D	0.8887(3)	−0.4207(2)	0.26055(15)	0.0248(8)
C15A	1.0309(3)	0.4013(2)	0.20307(16)	0.0288(8)
H15A	1.01	0.4076	0.2381	0.035*
C15B	0.4352(3)	0.3804(2)	0.33813(15)	0.0261(8)
H15B	0.4065	0.3866	0.3709	0.031*
C15C	0.6112(3)	−0.3530(2)	0.16883(15)	0.0258(8)
H15C	0.6355	−0.3546	0.1348	0.031*
C15D	1.0049(3)	−0.4030(2)	0.26833(15)	0.0270(8)
H15D	1.0351	−0.4144	0.2365	0.032*
C16A	0.9516(3)	0.3607(2)	0.15361(15)	0.0245(8)
H16A	0.8763	0.3402	0.1549	0.029*
C16B	0.3920(3)	0.3118(2)	0.29634(15)	0.0240(8)
H16B	0.3347	0.2718	0.301	0.029*
C16C	0.6434(3)	−0.2851(2)	0.21032(14)	0.0218(7)
H16C	0.6899	−0.2406	0.2044	0.026*
C16D	1.0752(3)	−0.3697(2)	0.32123(15)	0.0246(8)
H16D	1.1537	−0.3582	0.3255	0.03*
C17A	1.2290(3)	0.4776(3)	0.25685(17)	0.0427(11)
H17A	1.1944	0.4794	0.289	0.064*
H17B	1.2619	0.5297	0.2544	0.064*
H17C	1.2877	0.4523	0.2624	0.064*
C17B	0.5686(4)	0.5141(2)	0.37821(17)	0.0384(10)
H17D	0.5317	0.5121	0.4094	0.058*
H17E	0.5574	0.5563	0.3621	0.058*
H17F	0.6489	0.5223	0.3927	0.058*
C17C	0.5085(3)	−0.4945(2)	0.13160(17)	0.0352(9)
H17G	0.5391	−0.4866	0.0991	0.053*
H17H	0.4266	−0.5135	0.1191	0.053*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H17I	0.5373	−0.532	0.1475	0.053*
C17D	0.8114(3)	−0.4596(3)	0.20221(16)	0.0390(10)
H17J	0.8558	−0.4681	0.1746	0.059*
H17K	0.7656	−0.4271	0.1913	0.059*
H17L	0.7626	−0.5088	0.2029	0.059*
C21A	0.8087(3)	0.20825(18)	0.05539(13)	0.0177(7)
C21B	0.5125(3)	0.17775(19)	0.20704(14)	0.0185(7)
C21C	0.5145(3)	−0.16280(19)	0.29751(13)	0.0167(7)
C21D	1.1984(3)	−0.21424(19)	0.43085(14)	0.0191(7)
C22A	0.8785(3)	0.1720(2)	0.08264(14)	0.0228(7)
H22A	0.9573	0.1946	0.0934	0.027*
C22B	0.6087(3)	0.2137(2)	0.19256(15)	0.0241(8)
H22B	0.6072	0.252	0.1725	0.029*
C22C	0.4135(3)	−0.2079(2)	0.30319(15)	0.0221(7)
H22C	0.4127	−0.2515	0.3176	0.026*
C22D	1.3141(3)	−0.1799(2)	0.44813(14)	0.0205(7)
H22D	1.3615	−0.2063	0.4644	0.025*
C23A	0.8321(3)	0.1028(2)	0.09390(15)	0.0282(8)
H23A	0.8802	0.0783	0.1122	0.034*
C23B	0.7067(3)	0.1943(2)	0.20693(16)	0.0266(8)
H23B	0.7712	0.2194	0.1964	0.032*
C23C	0.3148(3)	−0.1897(2)	0.28808(14)	0.0226(7)
H23C	0.2476	−0.2207	0.2928	0.027*
C23D	1.3601(3)	−0.1078(2)	0.44170(15)	0.0247(8)
H23D	1.4389	−0.0854	0.4539	0.03*
C24A	0.7168(3)	0.0682(2)	0.07908(15)	0.0261(8)
C24B	0.7122(3)	0.1387(2)	0.23663(15)	0.0232(7)
C24C	0.3122(3)	−0.1269(2)	0.26605(14)	0.0219(7)
C24D	1.2938(3)	−0.0676(2)	0.41784(15)	0.0240(8)
C25A	0.6485(3)	0.1056(2)	0.05262(15)	0.0238(8)
H25A	0.5697	0.0833	0.0425	0.029*
C25B	0.6158(3)	0.1026(2)	0.25096(15)	0.0236(8)
H25B	0.6175	0.0643	0.271	0.028*
C25C	0.4115(3)	−0.0827(2)	0.25981(14)	0.0218(7)
H25C	0.4112	−0.0399	0.2446	0.026*
C25D	1.1787(3)	−0.1022(2)	0.40055(15)	0.0267(8)
H25D	1.1315	−0.076	0.3839	0.032*
C26A	0.6929(3)	0.1743(2)	0.04071(14)	0.0213(7)
H26A	0.6445	0.1985	0.0225	0.026*
C26B	0.5172(3)	0.12169(19)	0.23653(14)	0.0199(7)
H26B	0.4525	0.0964	0.2468	0.024*
C26C	0.5121(3)	−0.0996(2)	0.27539(14)	0.0205(7)
H26C	0.5792	−0.0681	0.271	0.025*
C26D	1.1312(3)	−0.1744(2)	0.40712(15)	0.0247(8)
H26D	1.0524	−0.1966	0.3953	0.03*
C27A	0.6670(4)	−0.0067(2)	0.09175(19)	0.0398(10)
H27A	0.7272	−0.0244	0.1103	0.06*
H27B	0.6238	−0.0447	0.0562	0.06*
H27C	0.6177	0.0004	0.117	0.06*
C27B	0.8192(3)	0.1181(2)	0.25245(17)	0.0336(9)
H27D	0.8774	0.1491	0.2388	0.05*
H27E	0.8065	0.0638	0.235	0.05*
H27F	0.8432	0.1281	0.2939	0.05*
C27C	0.2042(3)	−0.1082(2)	0.24890(17)	0.0325(9)
H27G	0.1433	−0.1455	0.2564	0.049*
H27H	0.188	−0.1104	0.2083	0.049*
H27I	0.2111	−0.0568	0.2708	0.049*
C27D	1.3449(3)	0.0108(2)	0.41083(18)	0.0358(10)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H27J	1.2856	0.0303	0.3936	0.054*
H27K	1.3965	0.0077	0.3863	0.054*
H27L	1.386	0.0454	0.4481	0.054*
C31A	0.9373(3)	0.26878(19)	−0.01782(14)	0.0183(7)
C31B	0.3794(3)	0.23526(19)	0.12813(14)	0.0188(7)
C31C	0.6471(3)	−0.21734(19)	0.37949(13)	0.0167(7)
C31D	1.0556(3)	−0.2951(2)	0.49070(14)	0.0199(7)
C32A	0.9962(3)	0.3251(2)	−0.03973(15)	0.0221(7)
H32A	1.0011	0.3771	−0.025	0.027*
C32B	0.3264(3)	0.2901(2)	0.11822(15)	0.0247(8)
H32B	0.2953	0.3129	0.1466	0.03*
C32C	0.7144(3)	−0.2628(2)	0.39317(14)	0.0229(8)
H32C	0.7578	−0.2776	0.3681	0.028*
C32D	0.9880(3)	−0.3586(2)	0.50176(15)	0.0240(8)
H32D	0.9767	−0.4082	0.4785	0.029*
C33A	1.0476(3)	0.3056(2)	−0.08286(15)	0.0256(8)
H33A	1.0883	0.3445	−0.097	0.031*
C33B	0.3185(3)	0.3117(2)	0.06750(15)	0.0261(8)
H33B	0.2828	0.3497	0.0619	0.031*
C33C	0.7193(3)	−0.2869(2)	0.44278(15)	0.0250(8)
H33C	0.7652	−0.3184	0.4511	0.03*
C33D	0.9370(3)	−0.3501(2)	0.54645(16)	0.0298(9)
H33D	0.8893	−0.394	0.5526	0.036*
C34A	1.0403(3)	0.2292(2)	−0.10578(15)	0.0236(8)
C34B	0.3616(3)	0.2788(2)	0.02480(15)	0.0219(7)
C34C	0.6575(3)	−0.2653(2)	0.48048(14)	0.0211(7)
C34D	0.9544(3)	−0.2788(3)	0.58233(16)	0.0335(10)
C35A	0.9801(3)	0.1736(2)	−0.08430(15)	0.0234(7)
H35A	0.973	0.1214	−0.0998	0.028*
C35B	0.4101(3)	0.2219(2)	0.03401(15)	0.0246(8)
H35B	0.4381	0.1974	0.005	0.03*
C35C	0.5952(3)	−0.2163(2)	0.46820(14)	0.0221(7)
H35C	0.5557	−0.1987	0.4944	0.026*
C35D	1.0192(3)	−0.2157(3)	0.57058(16)	0.0336(9)
H35D	1.03	−0.1662	0.594	0.04*
C36A	0.9301(3)	0.19315(19)	−0.04068(14)	0.0198(7)
H36A	0.8904	0.1542	−0.0263	0.024*
C36B	0.4185(3)	0.2000(2)	0.08456(14)	0.0212(7)
H36B	0.4514	0.1605	0.0895	0.025*
C36C	0.5896(3)	−0.1927(2)	0.41858(14)	0.0198(7)
H36C	0.5463	−0.1594	0.4111	0.024*
C36D	1.0694(3)	−0.2230(2)	0.52489(15)	0.0274(8)
H36D	1.1129	−0.1787	0.5173	0.033*
C37A	1.0964(3)	0.2081(2)	−0.15229(16)	0.0343(9)
H37A	1.1346	0.2545	−0.1618	0.052*
H37B	1.0401	0.1737	−0.186	0.052*
H37C	1.1511	0.1824	−0.1393	0.052*
C37B	0.3565(3)	0.3052(2)	−0.02864(16)	0.0317(9)
H37D	0.3193	0.3455	−0.0269	0.048*
H37E	0.3142	0.2621	−0.0614	0.048*
H37F	0.4326	0.3254	−0.0326	0.048*
C37C	0.6571(3)	−0.2946(2)	0.53295(16)	0.0331(9)
H37G	0.7054	−0.3281	0.5346	0.05*
H37H	0.5806	−0.3234	0.5315	0.05*
H37I	0.6852	−0.2513	0.5668	0.05*
C37D	0.9076(4)	−0.2705(3)	0.63470(17)	0.0485(13)
H37J	0.8639	−0.321	0.6362	0.073*
H37K	0.8593	−0.237	0.6327	0.073*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H37L	0.9694	−0.2483	0.669	0.073*
O1A	0.9307(2)	0.51703(14)	0.08670(11)	0.0319(6)
O1B	0.0997(2)	0.24427(17)	0.22686(12)	0.0380(7)
O1C	0.74866(19)	−0.08874(14)	0.19430(10)	0.0232(5)
O1D	1.3778(2)	−0.35750(15)	0.36545(10)	0.0276(6)
O2A	0.6562(2)	0.35904(14)	0.12002(10)	0.0274(6)
O2B	0.2779(2)	0.12048(16)	0.32028(11)	0.0310(6)
O2C	0.9300(2)	−0.21903(15)	0.28540(11)	0.0296(6)
O2D	1.0945(2)	−0.52600(15)	0.36482(11)	0.0323(6)
O3A	0.6113(3)	0.49184(19)	−0.00153(13)	0.0492(9)
O3B	−0.0171(2)	−0.00089(16)	0.18877(12)	0.0359(7)
O3C	1.0441(2)	0.03077(16)	0.32850(13)	0.0388(7)
O3D	1.3856(2)	−0.51004(18)	0.47353(13)	0.0425(8)
O4A	0.61673(18)	0.27630(13)	−0.03988(9)	0.0191(5)
O4B	0.27709(19)	0.02853(14)	0.16623(10)	0.0209(5)
O4C	0.87074(19)	−0.09210(14)	0.40541(10)	0.0228(5)
O4D	1.1838(2)	−0.41809(15)	0.52454(10)	0.0242(6)
O5A	0.79732(19)	0.38462(14)	−0.06084(10)	0.0207(5)
O5B	0.1534(2)	0.11241(14)	0.10691(10)	0.0229(5)
O5C	0.74901(19)	−0.00613(14)	0.34744(10)	0.0217(5)
O5D	1.37022(18)	−0.29578(14)	0.52267(10)	0.0211(5)
P1A	0.86810(7)	0.29695(5)	0.03730(4)	0.01593(17)
P2B	0.38580(7)	0.20841(5)	0.19499(4)	0.01696(17)
P3C	0.64372(7)	−0.18889(5)	0.31314(4)	0.01565(17)
P4D	1.13523(7)	−0.30956(5)	0.43782(4)	0.01733(17)
Re1A	0.742490(10)	0.375516(7)	0.014352(5)	0.01548(4)
Re2B	0.205511(11)	0.116401(8)	0.194413(6)	0.01708(4)
Re3C	0.822697(10)	−0.092164(8)	0.318269(5)	0.01607(4)
Re4D	1.258990(11)	−0.391199(8)	0.458099(6)	0.01742(4)

to its backbone. The main reason for the use of a phosphine ligand is because they form robust bonds with organometallic fragments. This study is part of a investigation where the electronic and steric properties of the mono- and bidentate ligands are altered and coordinated to various transition metals to explore their chelating behaviour and reactivity [6–13].

The title complex, *fac*-[Re(Acac)$(CO)_3$(P(*p*-tolyl)$_3$)] crystallizes with eight formula units in the unit cell (Z = 8) and the asymmetric unit contains four independent Re(I) complexes (A, B, C and D). The structure displays a typical octahedral geometry with the rhenium centre surrounded by three facial carbonyl ligands, a β-diketonato ligand and a monodentate tri(*p*-tolyl)phosphine ligand [14–20]. All four crystallographically independent complexes display distortion in its octahedral geometry, which is evident from the P1A-Re1A-C3A (174.45(12)°), P2B-Re2B-C3B (176.71(10)°), P3C-Re3C-C3C (177.44(11)°) and P4D-Re4D-C3D (175.15(12)°) bond angles. Intra- and intermolecular C—H···O interactions contribute to the supramolecular aggregation.

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References

1. Bruker. SADABS and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, (2004).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R.: SIR97: a new tool for crystal structure determination and refinement. J. Appl. Crystallogr. **32** (1999) 115–119.
4. Brandenburg, K.; Putz, H.: DIAMOND. Visual crystal structure information system. Version 3.2i. Crystal Impact, Bonn, Germany, (2012).
5. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
6. Manicum, A.; Schutte-Smith, M.; Kemp, G.; Visser, H. G.: Illustration of the electronic influence of coordinated β-diketone type ligands: A kinetic and structural study. Polyhedron **85** (2015) 190–195.
7. Manicum, A.; Schutte-Smith, M.; Visser, H. G.; Pretorius, C.; Roodt, A.: Crystal structure of *fac*-tricarbonyl(hexafluoro-acetylacetonato-κ^2*O*,*O*′)-(nitrato-κO)rhenium(I), $C_{16}H_{21}O_8N_2F_6Re$, Z. Kristallogr. -NCS **231** (2016) 263–266.
8. Visser, H. G.; Roodt, A.; Volmink, A.; Kemp, G.: *fac*-Tricarbonyl-(pyridine-κ*N*)(1,1,1-trifluoroacetylacetone-κ^2*O*,*O*′)-rhenium(I). Acta Crystallogr. **E67** (2011) m1631–m1631.
9. Schutte, M.; Roodt, A.; Visser, H. G.: Coordinated aqua *vs* methanol substitution kinetics in *fac*-Re(I) tricarbonyl tropolonato complexes. Inorg. Chem. **51** (2012) 11996–12006.
10. Schutte, M.; Kemp, G.; Visser, H. G.; Roodt, A.: Tuning the reactivity in classic low-spin d^6 rhenium(I) tricarbonyl radiopharmaceutical synthon by selective bidentate ligand variation (*L*,*L*′-Bid; *L*,*L*′ = *N*,*N*′, *N*,*O* and *O*,*O*′ donor atom sets) in *fac*-[Re$(CO)_3$(*L*,*L*′-Bid)(MeOH)]^n complexes. Inorg. Chem. **50** (2011) 12486–12498.
11. Brink, A.; Visser, H. G.; Roodt, A.: Novel imino rhenium(I) tricarbonyl complexes of salicylidene-derived ligands: Synthesis, X-ray crystallographic studies, spectroscopic characterization and DFT calculations. Polyhedron **52** (2013) 416–423.
12. Riondato, M.; Camporese, D.; Martín, D.; Suades, J.; Alvarez-Larena, A.; Mazzi, U.: Synthesis and characterisation of [Re$(CO)_3$(SS)(P)] complexes: a [2 + 1] concept for ^{99m}Tc- and ^{188}Re-radiopharmaceutical applications. Eur. J. Inorg. Chem. **44** (2005) 4048–4055.
13. Marmion, M. E.; Woulfe, S. R.; Neumann, W. L.; Nosco, D. L.; Deutsch, E.: Complexes of technetium-99g and -99m

with substituted acac2en and trialkyl phosphines (where acac2en = *N*,*N*′-ethylenebis[acetylacetone iminato]). Nucl. Med. Biol. **26** (1999) 755–770.
14. Manicum, A.; Visser, H. G.; Engelbrecht, I.; Roodt, A.: Crystal structure of *fac*-(acetylacetonato-κ^2*O*,*O*′) tricarbonyl(cyclohexyldiphenylphosphine-κ*P*) rhenium(I), $C_{26}H_{28}O_5PRe$, Z. Kristallogr. -NCS **230** (2015) 150–152.
15. Brink, A.; Visser, H. G.; Roodt, A.: Tetraethylammonium (acetylacetonenato)bromidotricarbonylrhenate(I). Acta Crystallogr. **E67** (2011) m34–m35.
16. Benny, P. D.; Fugate, G. A.; Barden, A. O.; Morley, J. E.; Silva-Lopez, E.; Twamley, B.: Metal-assisted in situ formation of a tridentate acetylacetone ligand for complexation of *fac*-$Re(CO)^{3+}$ for radiopharmaceutical applications. Inorg. Chem. Comm. **47** (2008) 2240–2242.
17. Sagnou, M.; Tsoukalas, C.; Triantis, C.; Raptopoulou, C. P.; Terzis, A.; Pirmettis, I.; Pelecanou, M.; Papadopoulos, M.: A new tricarbonyl *fac*-[M(acac)(isc)$(CO)_3$] complex (M = Re, ^{99m}Tc) with acetylacetonate (acac) and isocyanide (isc) in a 2 + 1 combination. Inorg. Chim. Acta **363** (2010) 1649–1653.
18. Triantis, C.; Tsotakos, T.; Tsoukalas, C.; Sagnou, M.; Raptopoulou, C.; Terzis, A.; Psycharis, V.; Pelecanou, M.; Pirmettis, I.; Papadopoulos, M.: Synthesis and characterization of *fac*-[$M(CO)_3$(P)(OO)] and *cis*-*trans*-[$M(CO)_2$(P)(OO)] complexes (M = Re, ^{99m}Tc) with acetylacetone and curcumin as OO donor bidentate ligands. Inorg. Chem. **52** (2013) 12995–13003.
19. Papagiannopoulou, D.; Triantis, C.; Vassileiadis, V.; Raptopoulou, C. P.; Psycharis, V.; Terzis, A.; Pirmettis, I.; Papadopoulous, M. S.: Synthesis, structural characterisation and radiochemistry of di- and tricarbonyl Re(I) and ^{99m}Tc(I) complexes with 8-hydroxy quinolone or 8-mercaptoquinoline and triphenylphosphine. Polyhedron **68** (2014) 46–52.
20. Vassileiadis, V.; Triantis, C.; Raptopoulou, C. P.; Psycharis, V.; Pirmettis, I.; Papadopoulous, M. S.; Papagiannopoulou, D.: Synthesis, structural characterisation and radiochemistry of '2 + 1' *fac*-[^{99m}Tc/$Re(CO)_3$(L)(2-mercaptopyridine)] complexes, where L is phosphine or isocyanide. Polyhedron **81** (2014) 511–516.