The Crystal Structure of 1,3-Dimethyl-1,3-propanedionatobis(triphenylphosphite)rhodium(I)

J. G. LEIPOLDT*, G. J. LAMPRECHT and G. J. VAN ZYL

Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa

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A previous paper [1] dealt with the preparation and crystal structure of 1-phenyl-3-trifluoromethyl-1,3-propanedionatobis(triphenylphosphite)rhodium(I), $[Rh(TFBA)(P(OPh)_3)_2]$ where TFBA is the singly charged non-symmetrical bidentate ligand, 1-phenyl-3-trifluoromethyl-1,3-propanedione. A possible explanation for the small but significant difference in the two Rh–P bond lengths (2.161(2) and 2.150(2) Å), was based on a difference in the relative thermodynamic *trans*-influence [2] of the two oxygen atoms of the *β*-diketone TFBA.

In an attempt to justify the above mentioned explanation for the difference in the Rh–P bond lengths, the crystal structure of the title compound 1,3-dimethyl-1,3-propanedionatobis(triphenylphosphite)rhodium(I), $[Rh(acac)(P(OPh)_3)_2]$, was determined. The two oxygen atoms in the bidentate ligand acac are chemical equivalent, so that any difference in Rh–P bond lengths in the present case cannot be attributed to a difference in *trans*-influence of the last mentioned two oxygen atoms.

With regard to this it may be noted that the two Rh–C bond lengths in $[Rh(acac)(CO)_2]$ [3] and the two Rh–S bond lengths in [Rh(acac)(COD)] (S is the centre of the carbon–carbon double bonds in 1,5-cyclooctadiene) [4] were as expected the same within experimental error.

Experimental

The title compound, $[Rh(acac)(P(OPh)_3)_2]$, was prepared by methods described [1]. The resulting yellow precipitate was filtered, washed with methanol and recrystallized from an acetone–water solution. Well formed needle-like light-yellow crystals suitable for data collection were obtained.

Crystal Data

$RhC_{41}H_{37}O_8P_2$, molecular mass = 822.59, triclinic space group $P\bar{1}$, $Z = 4$, $a = 18.673$ Å, $b = 10.661$ Å, $c = 20.307$ Å, $\alpha = 87.92°$, $\beta = 110.09°$, $\gamma = 90.74°$, $\mu(MoK_\alpha) = 5.71$ cm^{-1}, $d_{exp} = 1.441$ g cm^{-3}.

The three dimensional intensity data were collected with a Philips PW1100 four circle single crystal X-ray diffractometer using graphite monochromated MoK_α radiation ($\lambda = 7107$ Å) for θ values between 3° and 23°. Three reflections were used as standards and remeasured after every 60 reflections. No decomposition of the crystal was detectable during the data collection. A total of 10564 reflections were measured of which 8185 were considered as observed. The data were corrected for Lorentz and polarization effects. A crystal with dimensions 0.25 × 0.20 × 0.23 mm^3 was used for the data collection. The structure was solved using the X-ray 72 system of programs on a Univac 1100 computer. The rhodium atoms of the two crystallographic independent molecules were located from a three dimensional Patterson synthesis. The positional parameters of the other non-hydrogen atoms were deduced from successive Fourier and difference-Fourier synthesis. A full matrix least square refinement using all the observed reflections and anisotropic temperature parameters for all the atoms resulted in a residual factor R = 5.8%. The atomic scattering factors were those tabulated by Cromer and Waber [5]. The final positional and thermal parameters with their standard deviations are listed in Table I.

Results and Discussion

A stereoscopic view of the two crystallographic independent $[Rh(acac)(P(OPh)_3)_2]$ molecules is shown in Fig. 1. The numbering system of the atoms in the molecule are shown in Fig. 2. Selective bond distances and bond angles are given in Tables II and III respectively. The structure consists of well-separated discrete molecular units.

The Rh atom in each molecule has approximately a square planar coordination as proved by calculation of the best plane through the atoms of the coordination polyhedra. The two chelate rings are also planar and make angles of 3.4° and 3.9° with their respective polyhedra.

The Rh–P bond lengths in the two independent $[Rh(acac)(P(OPh)_3)_2]$ molecules are 2.147(2), 2.156(2) and 2.142(2), 2.150(2) Å, respectively. Although the difference in the two Rh–P bond lengths in each molecule is about four times the standard deviation, it is not considered as significant since it is expected that the two Rh–P bonds are equivalent, as the two oxygen atoms *trans* to the Rh–P bonds are chemical equivalent. The difference in the Rh–P bond distances in $[Rh(TFBA)(P(OPh)_3)_2]$ is about 5 times the standard deviation [1] and it may thus be just significant. It is important to note that there is not a large difference between the electronegativities of a

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*Author to whom all correspondence should be addressed.

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TABLE I. Atomic Coordinates (with e.s.d.'s in parentheses) and Equivalent Isotropic Thermal Parameters (Å^2).

Molecule 1					Molecule 2			
Atom	x	y	z	U_{eq}*^{a}	x	y	z	U_{eq}*^{a}
Rh	0.01901(3)	0.44414(5)	0.29128(3)	0.0450	0.50600(3)	0.07367(5)	0.28659(3)	0.0493
P_1	−0.0138(1)	0.2503(2)	0.2781(1)	0.0480	0.4760(1)	0.2685(2)	0.2752(1)	0.0503
P_2	−0.0780(1)	0.5091(2)	0.2039(1)	0.0541	0.4020(1)	0.0167(2)	0.2074(1)	0.0483
O_1	0.0531(3)	0.6274(5)	0.3144(3)	0.0520	0.5382(3)	−0.1136(5)	0.3090(3)	0.0657
O_2	0.1179(3)	0.3845(5)	0.3688(3)	0.0513	0.6109(3)	0.1263(5)	0.3560(3)	0.0530
O_{11}	0.0240(3)	0.1562(4)	0.3455(3)	0.0657	0.3884(3)	0.3010(4)	0.2604(3)	0.0517
O_{12}	0.0108(4)	0.1628(5)	0.2271(3)	0.1043	0.4964(4)	0.3617(5)	0.2196(3)	0.1313
O_{13}	−0.1028(3)	0.2213(4)	0.2569(3)	0.0593	0.5205(3)	0.3537(4)	0.3403(3)	0.0467
O_{21}	−0.1058(3)	0.4162(5)	0.1406(3)	0.0590	0.4054(3)	−0.1096(5)	0.1672(3)	0.0547
O_{22}	−0.1570(3)	0.5497(6)	0.2113(3)	0.1013	0.3291(3)	−0.0315(5)	0.2268(3)	0.0580
O_{23}	−0.0679(3)	0.6430(5)	0.1677(3)	0.0863	0.3646(3)	0.1162(5)	0.1432(3)	0.0457
C_1	0.2371(5)	0.3796(10)	0.4593(5)	0.0670	0.7374(5)	0.1198(9)	0.4346(5)	0.0630
C_2	0.1690(5)	0.4549(8)	0.4082(4)	0.0537	0.6662(5)	0.0529(8)	0.3906(4)	0.0690
C_3	0.1695(5)	0.5855(8)	0.4073(5)	0.0503	0.6644(5)	−0.0788(8)	0.3885(4)	0.0827
C_4	0.1137(5)	0.6637(7)	0.3607(4)	0.0497	0.6035(5)	−0.1533(7)	0.3491(4)	0.0850
C_5	0.1254(6)	0.8058(8)	0.3634(6)	0.0663	0.6135(6)	−0.2948(8)	0.3516(5)	0.1050
C_{121}	0.0354(5)	0.2050(7)	0.1732(4)	0.0717	0.5179(4)	0.3264(7)	0.1644(4)	0.0593
C_{122}	0.0991(5)	0.2769(8)	0.1866(5)	0.0883	0.5840(5)	0.2606(8)	0.1766(5)	0.0647
C_{123}	0.1253(6)	0.3114(10)	0.1311(6)	0.1527	0.6060(6)	0.2393(10)	0.1164(6)	0.0873
C_{124}	0.0853(8)	0.2732(12)	0.0648(6)	0.1807	0.5593(8)	0.2844(11)	0.0490(6)	0.1427
C_{125}	0.0214(8)	0.2040(14)	0.0504(5)	0.1357	0.4943(8)	0.3497(12)	0.0411(5)	0.0957
C_{126}	−0.0074(6)	0.1634(11)	0.1055(5)	0.0827	0.4711(6)	0.3736(9)	0.0982(5)	0.0803
C_{131}	−0.1392(4)	−0.1050(7)	0.2562(4)	0.0433	0.5215(4)	0.3308(7)	0.4090(4)	0.0507
C_{132}	−0.1036(5)	−0.0095(7)	0.2563(5)	0.0727	0.4681(5)	0.2605(9)	0.4253(4)	0.0767
C_{133}	−0.1482(5)	−0.1209(8)	0.2542(5)	0.0750	0.4724(6)	0.2492(10)	0.4970(5)	0.0877
C_{134}	−0.2221(6)	−0.1142(9)	0.2540(5)	0.082	0.5308(6)	0.3113(10)	0.5484(5)	0.0880
C_{135}	−0.2561(6)	0.0041(10)	0.2549(6)	0.0977	0.5841(6)	0.3829(10)	0.5299(5)	0.0720
C_{136}	−0.2129(5)	0.1150(8)	0.2565(5)	0.0830	0.5814(5)	0.3936(9)	0.4592(5)	0.0563
C_{111}	0.0225(4)	0.1770(7)	0.4125(4)	0.0603	0.3557(4)	0.4173(6)	0.2641(4)	0.0547
C_{112}	−0.0302(5)	0.2486(9)	0.4246(4)	0.1023	0.2867(5)	0.4104(8)	0.2733(5)	0.0960
C_{113}	−0.0284(7)	0.2598(6)	0.4952(6)	0.1453	0.2474(6)	0.5221(9)	0.2755(6)	0.1187
C_{114}	0.0286(7)	0.1974(11)	0.5502(5)	0.0933	0.2805(5)	0.6374(8)	0.2684(5)	0.0917
C_{115}	0.0814(6)	0.1250(11)	0.5353(5)	0.0993	0.3520(6)	0.6435(8)	0.2633(5)	0.1100
C_{116}	0.0813(5)	0.1127(9)	0.4657(5)	0.0827	0.3916(5)	0.5324(7)	0.2615(5)	0.0877
C_{211}	−0.1690(5)	0.4213(8)	0.0781(4)	0.0643	0.4693(4)	−0.1433(7)	0.1517(4)	0.0500
C_{212}	−0.2006(6)	0.3075(10)	0.0562(5)	0.0713	0.4895(5)	−0.2694(8)	0.1618(4)	0.0823
C_{213}	−0.2614(7)	0.3038(13)	−0.0109(7)	0.0803	0.5533(6)	−0.3099(9)	0.1481(5)	0.1070
C_{214}	−0.2841(7)	0.4157(14)	−0.0509(6)	0.1150	0.5962(6)	−0.2241(10)	0.1229(6)	0.0903
C_{215}	−0.2536(7)	0.5277(13)	−0.0262(6)	0.1297	0.5728(6)	−0.1001(10)	0.1107(6)	0.1027
C_{216}	−0.1936(6)	0.5372(12)	0.0417(5)	0.1007	0.5087(5)	0.0563(9)	0.1252(5)	0.0827
C_{221}	−0.1803(5)	0.5197(7)	0.2674(5)	0.0880	0.3172(4)	−0.0019(7)	0.2888(4)	0.0650
C_{222}	−0.2525(5)	0.4688(9)	0.2528(6)	0.0540	0.2507(5)	0.0615(8)	0.2816(5)	0.0827
C_{223}	−0.2788(6)	0.4409(9)	0.3096(6)	0.1213	0.2338(5)	0.0879(8)	0.3427(5)	0.1050
C_{224}	−0.2326(7)	0.4652(10)	0.3776(6)	0.1610	0.2853(6)	0.0500(9)	0.4085(5)	0.0983
C_{225}	−0.1608(6)	0.5218(10)	0.3910(6)	0.1300	0.3506(6)	−0.0170(9)	0.4137(5)	0.0900
C_{226}	−0.1331(5)	0.5485(8)	0.3354(5)	0.0967	0.3686(5)	−0.0443(8)	0.3534(4)	0.0707
C_{231}	−0.0031(5)	0.6786(7)	0.1528(4)	0.0740	0.3058(4)	0.0915(7)	0.0802(4)	0.0487
C_{232}	0.0195(5)	0.8013(9)	0.1663(5)	0.0793	0.3213(7)	0.1080(16)	0.0202(5)	0.1073
C_{233}	0.0855(6)	0.8454(11)	0.1521(6)	0.1060	0.2631(7)	0.0886(17)	−0.0460(5)	0.1127
C_{234}	0.1235(6)	0.7645(11)	0.1238(6)	0.1403	0.1926(5)	0.0585(10)	−0.0490(5)	0.0793
C_{235}	0.0984(6)	0.6413(11)	0.1084(6)	0.1807	0.1773(6)	0.0430(13)	0.0115(5)	0.0900
C_{236}	0.0333(6)	0.5984(9)	0.1240(6)	0.1510	0.2352(6)	0.0598(13)	0.0777(5)	0.0833

$^a U_{eq}^* = 1/3\ (U_{11} + U_{22} + U_{33} + 2U_{23} + 2U_{13} + 2U_{12})$.

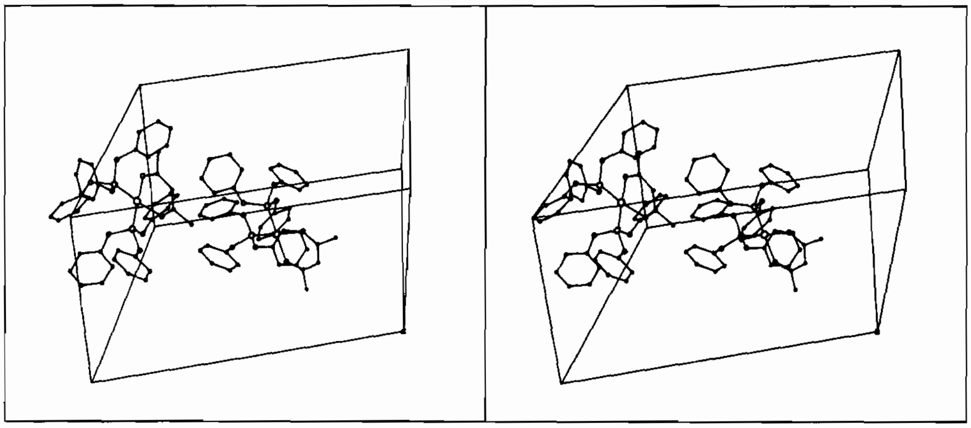

Fig. 1. A stereoview showing the orientation and position of the two crystallographic independent [Rh(acac)(P(OPh)$_3$)$_2$] molecules in the unit cell. The symmetry related molecules are omitted for clarity.

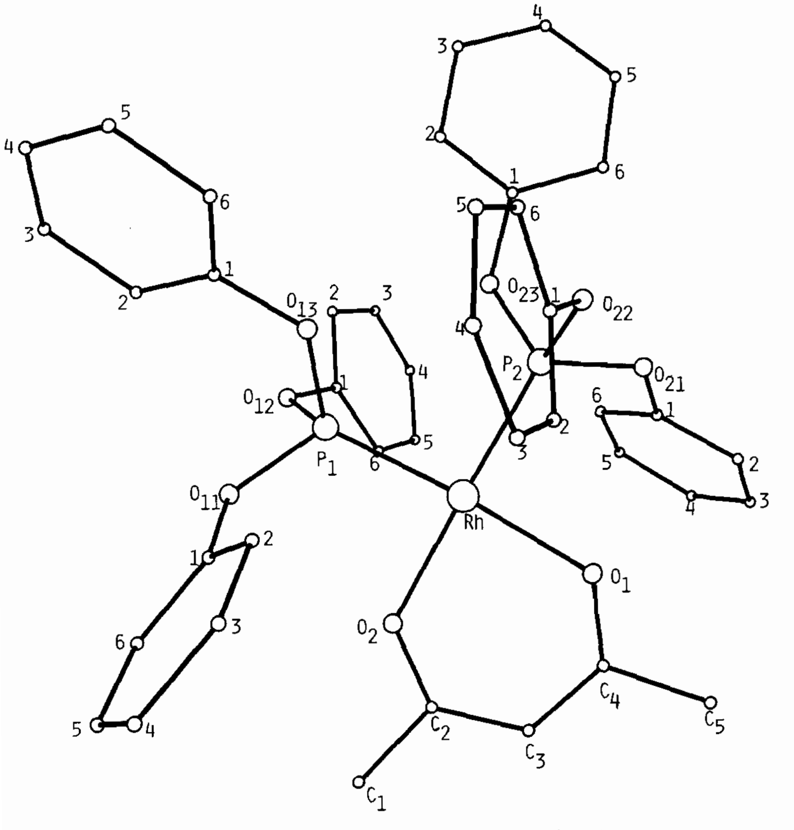

Fig. 2. Perspective view of a [Rh(acac)(P(OPh)$_3$)$_2$] molecule. The numbering system of the atoms of the phenyl rings of the phosphite groups is as follow (see Table I): the first digit refers to the phosphorous atom, the second digit refers to the oxygen atoms bonded to the phosphorous atom and the third digit refers to the carbon atoms of the phenyl ring bonded to the oxygen atom.

CF_3 and a phenyl group [6]. A large difference in the relative *trans* influence of the oxygen atoms of the β-diketone and consequently a large difference in the two Rh–P bond distances is thus not expected.

The Rh–P bond distances in the present structure are, as in the case of [Rh(TFBA)(P(OPh)$_3$)$_2$], significantly shorter than the Rh–P bond distances in similar Rh(I)–phosphine complexes. The Rh–P bond distances in [Rh(acac)(CO)(PPh$_3$)] [7] and [Rh(TFDMAA)(CO)(PPh$_3$)] [8] are 2.244(2) and 2.239(2) Å respectively. The significantly shorter Rh–P bond distances in the case of the phosphite complex are probably the result of the strong π-electron acceptor properties of the phosphite ligand

TABLE II. Selected Interatomic Distances (Å) with e.s.d. s in Parentheses.

Bond	Molecule 1	Molecule 2
$Rh-P_1$	2.147(2)	2.142(2)
$Rh-P_2$	2.156(2)	2.150(2)
$Rh-O_1$	2.067(5)	2.081(5)
$Rh-O_2$	2.061(5)	2.065(5)
P_1-O_{11}	1.623(5)	1.600(5)
P_1-O_{12}	1.600(7)	1.615(7)
P_1-O_{13}	1.596(5)	1.606(5)
P_2-O_{21}	1.590(5)	1.613(6)
P_2-O_{22}	1.597(7)	1.614(6)
P_2-O_{23}	1.622(6)	1.616(5)
C_1-C_2	1.551(12)	1.508(11)
C_2-C_3	1.400(12)	1.405(12)
C_3-C_4	1.404(11)	1.402(11)
C_4-C_5	1.528(12)	1.522(12)
C_2-O_2	1.267(9)	1.286(9)
C_4-O_1	1.261(9)	1.278(9)

TABLE III. Selected Bond Angles (degrees) with e.s.d. s in Parentheses.

Angle	Molecule 1	Molecule 2
P_1-Rh-P_2	93.75(7)	94.15(7)
O_1-Rh-O_2	88.8(2)	87.2(1)
O_1-Rh-P_2	90.3(1)	89.9(1)
O_2-Rh-P_1	87.5(2)	89.3(2)
$Rh-P_1-O_{11}$	116.3(2)	116.1(2)
$Rh-P_1-O_{12}$	122.4(3)	122.0(3)
$Rh-P_1-O_{13}$	116.3(2)	116.3(2)
$Rh-P_2-O_{21}$	114.7(2)	116.8(2)
$Rh-P_2-O_{22}$	123.4(2)	121.9(2)
$Rh-P_2-O_{23}$	116.0(2)	116.4(2)

[6], resulting in a relatively stronger Rh–P bond and hence a shorter bond length.

The Rh–O bond distances (2.067(5), 2.061(5), 2.081(5) and 2.065(5) Å) compare well with those found in [Rh(TPBA)(OPh)$_3$)$_2$] [1] (2.067(6) and 2.070(6) Å). There is also a good correlation with the Rh-O distances (oxygen atom *trans* to the phosphine group) in Rh–phosphine complexes like [Rh(acac)-(CO)(PPh$_3$)] [7] (2.087(4) Å) and [Rh(TTA)(CO)-(PPh$_3$)] [9] (2.085(7) Å). The average (1.394 Å) O–C bond lengths in the phosphite groups compare well with the average of 1.389 Å and 1.40 Å found in [Rh(TFBA)(P(OPh)$_3$)$_2$] [1] and [RhBr$_2$(NO)(P-(OPh)$_3$)$_2$] [10], respectively.

The two P–Rh–P bond angles of 93.75(7)° and 94.15(7)° in the present structure are, as in the case of [Rh(TPBA)(P(OPh)$_3$)$_2$] significantly larger than the P–Rh–C bond angles of 87.8(2)° and 87.1(4)° in Rh(I)–phosphine complexes like [Rh(acac)(CO)-(PPh$_3$)] [7] and [Rh(TTA)(CO)(PPh$_3$)] [9], respectively. The relative large P–Rh–P bond angle may be explained by the fact that the two P(OPh)$_3$ groups *cis* to one another experience a larger steric hindrance than a PPh$_3$-group and a CO-group *cis* to each other. This is due to the relative large cone angle (128°) of the P(OPh)$_3$ group [11]. The large cone angle of the PPh$_3$ group (145°) may explain the fact that even in the presence of a large excess of PPh$_3$ only one carbonyl group is substituted by PPh$_3$ [12].

Each of the four P atoms are tetrahedrally surrounded by the Rh atom and three oxygen atoms. The average P–O bond distance of 1.609 Å compares well with the average bond distance (1.606 Å) in Rh(TFBA)(P(OPh)$_3$)$_2$ [1].

The twelve phenyl rings in the two molecules are planar within experimental error and the C–C bond distances and bond angles in the phenyl rings are within experimental error identical to the accepted values of 1.399 Å and 120° for phenyl rings [13].

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References

1 G. J. Lamprecht, J. G. Leipoldt and G. J. van Zyl, *Inorg. Chim. Acta, 97* (1985).
2 C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York, 1965.
3 F. Huq and A. C. Skapski, *J. Cryst. Mol. Struct., 4,* 411 (1974).
4 P. H. Tucker, W. Scutcher and D. R. Russel, *Acta Crystallogr., Sect. B:, 31,* 592 (1975).
5 D. T. Cromer and J. T. Waber, *Acta Crystallogr., 18,* 704 (1965).
6 J. E. Huheey, 'Inorganic Chemistry Principles of Structure and Reactivity', Harper and Row, New York, 1972.
7 J. G. Leipoldt, L. D. C. Bok, S. S. Basson and T. I. A. Gerber, *Inorg. Chim. Acta, 26,* L38 (1978).
8 J. G. Leipoldt, S. S. Basson and J. T. Nel, *Inorg. Chim. Acta, 74,* 85 (1972).
9 J. G. Leipoldt, L. D. C. Bok, J. S. van Vollenhoven and A. I. Pieterse, *J. Inorg. Nucl. Chem., 40,* 61 (1978).
10 R B. English and L. R. Nassimbeni, *Acta Crystallogr., Sect. B:, 32,* 3299 (1976).
11 C. A. Tolman, *Chem. Rev., 77,* 313 (1977).
12 F. Bonati and G. Wilkinson, *J. Chem. Soc.,* 3156 (1964).
13 L. E. Sutin, 'Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959', The Chemical Society, London, 1965, p. 5165.