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

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It was reported in a previous paper [1] that dealt with the crystal structure of 1-phenyl-3-trifluoromethyl-1,3-propanedionatobis(triphenylphosphite)rhodium(I), $[Rh(TFBA)(P(OPh)_3)_2]$, that the small but significant difference in the two Rh–P bond lengths may be attributed to a difference in the relative thermodynamic *trans*-influence [2] of the oxygen atoms of the β-diketone TFBA. A more recent paper [3] in which the structure of $[Rh(acac)(P(OPh)_3)_2]$ was reported (acac = 1,3-dimethyl-1,3-propanedione) dealt with determining whether the difference in the Rh–P bond lengths observed in $[Rh(TFBA)(P(OPh)_3)_2]$ [1] was significant or not. In $[Rh(acac)(P(OPh)_3)_2]$ [3] the two oxygen atoms in the bidentate ligand acac are chemical equivalent, and an insignificant difference in the Rh–P bond lengths was found.

This letter reports the crystal structure of 1-methyl-3-trifluoromethyl-1,3-propanedionatobis(triphenylphosphite)rhodium(I), $[Rh(TFAA)(P(OPh)_3)_2]$. The β-diketones TFAA, TFBA and acac have CH_3, CF_3 and C_6H_5 as terminal groups with electronegativities of 2.3, 3.35 and 3.0, respectively [4]. In the case of the ligand TFBA the difference in the electronegativities of the two terminal groups is 0.3 and in TFAA the difference is 1.0. It is thus expected that the bigger difference in the electronegativity in TFAA would result in a larger difference in the relative thermodynamic *trans*-influence of the two oxygen atoms of the β-diketone TFAA, compared to the β-diketone TFBA. Hence a larger difference in Rh–P bond distances is expected.

Experimental

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

Crystal Data

$RhC_{41}H_{34}O_8F_3P_2$, molecular mass = 877.57, triclinic space group $P\bar{1}$, $a = 20.741$ Å, $b = 20.953$ Å, $c = 10.109$ Å, $\alpha = 105.99°$, $\beta = 96.26°$, $\gamma = 68.16°$, $Z = 4$, $d_{calc} = 1.487$ g cm^{-3}, $\mu(MoK_\alpha) = 5.90$ cm^{-1}.

The three dimensional intensity data were collected with a Philips PW 1100 four circle single crystal X-ray diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.7107$ 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 10494 reflections were measured of which 5391 were considered as observed reflections. The data were corrected for Lorentz and polarization effects. A crystal with dimensions $0.25 \times 0.11 \times 0.10$ 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 the residual factor R of 10.1%. 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 perspective view of one of the two crystallographic independent $[Rh(TFAA)(P(OPh)_3)_2]$ molecules as well as the numbering system of the atoms is shown in Fig. 1. Selective bond distances and bond angles are given in Tables II and III respectively. The structure consists of well separated discrete molecular units.

The rhodium 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 5.9° and 4.1° with their respective polyhedra. The Rh–P bond lengths in the two independent $[Rh(TFAA)(P(OPh)_3)_2]$ molecules are 2.148(4), 2.136(6) and 2.145(6), 2.138(6) Å, respectively. The differences in these Rh–P bond lengths are of such magnitude (1–2 times the standard deviation) that they are considered to be insignificant and no conclusion

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

Atom	Molecule 1				Molecule 2			
	x	y	z	U^*_{eq} [a]	x	y	z	U^*_{eq} [a]
Rh	0.25567(8)	0.40863(8)	0.4298(1)	0.0396	0.81073(8)	0.08162(8)	0.5468(1)	0.0348
P(1)	0.2842(3)	0.3093(3)	0.2753(5)	0.0414	0.7120(3)	0.0725(3)	0.4847(5)	0.0347
P(2)	0.2859(3)	0.3535(3)	0.5885(5)	0.0367	0.7816(2)	0.1804(3)	0.4915(5)	0.0363
O(1)	0.2196(7)	0.5063(6)	0.5749(12)	0.0476	0.9102(7)	0.0817(6)	0.6082(12)	0.0471
O(2)	0.2234(7)	0.4631(7)	0.2782(12)	0.0529	0.8384(6)	−0.0143(7)	0.6006(13)	0.0560
C(1)	0.1750(18)	0.5544(16)	0.1620(25)	0.1080	1.0244(10)	0.0528(12)	0.7048(22)	0.0412
C(2)	0.1902(11)	0.5300(11)	0.2961(23)	0.0598	0.9585(10)	0.0351(10)	0.6524(17)	0.0563
C(3)	0.1700(12)	0.5792(12)	0.4215(23)	0.0655	0.9586(9)	−0.0328(9)	0.6564(17)	0.0475
C(4)	0.1842(11)	0.5631(10)	0.5458(21)	0.0637	0.9000(10)	−0.0496(10)	0.6311(20)	0.0576
C(5)	0.1569(13)	0.6208(12)	0.6741(24)	0.0724	0.9079(13)	−0.1218(13)	0.6415(28)	0.1084
F(1)	0.1072(12)	0.6816(10)	0.6480(20)	0.1610	0.9702(9)	−0.1634(8)	0.6616(24)	0.1758
F(2)	0.2019(10)	0.6421(10)	0.7512(18)	0.0683	0.8811(15)	−0.1548(10)	0.5472(28)	0.1489
F(3)	0.1237(11)	0.6035(10)	0.7526(20)	0.1799	0.8745(14)	−0.1168(10)	0.7476(27)	0.3427
O(11)	0.2481(7)	0.3135(7)	0.1279(11)	0.0474	0.7080(6)	−0.0049(7)	0.4383(13)	0.0490
O(12)	0.3618(7)	0.2693(7)	0.2210(14)	0.0602	0.6734(6)	0.1074(7)	0.3608(13)	0.0562
O(13)	0.2711(7)	0.2455(6)	0.3098(12)	0.0501	0.6515(7)	0.1012(7)	0.5969(14)	0.0523
O(21)	0.3546(7)	0.2840(7)	0.5619(12)	0.0662	0.8342(6)	0.2235(6)	0.5379(12)	0.0393
O(22)	0.2334(7)	0.3228(6)	0.6353(12)	0.0526	0.7705(6)	0.1847(6)	0.3351(12)	0.0512
O(23)	0.2961(7)	0.3999(7)	0.7411(12)	0.0502	0.7088(6)	0.2398(6)	0.5493(12)	0.0435
C(111)	0.1757(11)	0.3417(11)	0.1113(18)	0.0516	0.7514(9)	−0.0640(10)	0.3397(17)	0.0358
C(112)	0.1275(12)	0.3347(12)	0.1943(21)	0.0732	0.8028(12)	−0.0587(13)	0.2704(24)	0.0705
C(113)	0.0582(11)	0.3615(12)	0.1664(22)	0.0716	0.8440(11)	−0.1223(13)	0.1752(21)	0.0526
C(114)	0.0345(12)	0.3930(13)	0.0564(27)	0.0613	0.8295(13)	−0.1840(11)	0.1545(23)	0.0350
C(115)	0.0845(16)	0.3979(13)	−0.0266(24)	0.0577	0.7760(12)	−0.1863(12)	0.2209(23)	0.0398
C(116)	0.1546(12)	0.3712(12)	−0.0005(22)	0.0517	0.7346(12)	−0.1231(10)	0.3181(18)	0.0108
C(121)	0.4070(11)	0.3086(10)	0.2365(20)	0.0666	0.6148(9)	0.1051(10)	0.2840(19)	0.0429
C(122)	0.4017(14)	0.3480(11)	0.1451(21)	0.0788	0.5750(10)	0.0691(11)	0.3120(20)	0.0583
C(123)	0.4512(14)	0.3818(14)	0.1600(27)	0.0989	0.5131(10)	0.0708(10)	0.2238(20)	0.0507
C(124)	0.5031(14)	0.3725(16)	0.2604(29)	0.0960	0.5004(13)	0.1039(14)	0.1172(24)	0.0951
C(125)	0.5072(15)	0.3294(18)	0.3471(29)	0.1063	0.5455(13)	0.1369(14)	0.0959(23)	0.0981
C(126)	0.4609(13)	0.2914(14)	0.3317(25)	0.0678	0.5995(11)	0.1408(12)	0.1837(20)	0.0701
C(131)	0.2924(9)	0.1731(9)	0.2434(17)	0.0448	0.6449(11)	0.1537(10)	0.7176(18)	0.0516
C(132)	0.2969(13)	0.1327(11)	0.3281(23)	0.0912	0.5839(12)	0.2121(11)	0.7299(26)	0.0944
C(133)	0.3167(14)	0.0588(14)	0.2695(25)	0.0951	0.5750(13)	0.2673(13)	0.8526(28)	0.1010
C(134)	0.3290(13)	0.0292(13)	0.1284(29)	0.1178	0.6287(16)	0.2583(15)	0.9544(25)	0.0883
C(135)	0.3227(12)	0.0743(11)	0.0480(22)	0.0505	0.6859(15)	0.2009(15)	0.9352(24)	0.0779
C(136)	0.3066(11)	0.1472(12)	0.1037(20)	0.0458	0.6973(14)	0.1465(13)	0.8163(19)	0.0591
C(211)	0.3838(9)	0.2322(11)	0.6341(18)	0.0443	0.8644(12)	0.2369(10)	0.6660(20)	0.0301
C(212)	0.3743(10)	0.2468(10)	0.7749(19)	0.0448	0.8320(12)	0.2408(10)	0.7855(21)	0.0508
C(213)	0.4067(13)	0.1908(12)	0.8402(22)	0.0574	0.8674(13)	0.2557(13)	0.9118(25)	0.0616
C(214)	0.4507(16)	0.1261(12)	0.7682(27)	0.0807	0.9318(15)	0.2626(12)	0.9137(22)	0.0467
C(215)	0.4587(13)	0.1137(13)	0.6220(24)	0.0715	0.9630(14)	0.2580(13)	0.7965(28)	0.0405
C(216)	0.4226(11)	0.1675(10)	0.5550(23)	0.0811	0.9302(13)	0.2446(11)	0.6698(26)	0.0553
C(221)	0.1627(10)	0.3540(11)	0.6161(19)	0.0591	0.8182(9)	0.1384(10)	0.2267(17)	0.0464
C(222)	0.1287(10)	0.3076(11)	0.5630(22)	0.0575	0.8737(10)	0.1531(11)	0.2057(17)	0.0669
C(223)	0.0578(13)	0.3319(13)	0.5473(25)	0.0806	0.9160(12)	0.1087(14)	0.0959(21)	0.1131
C(224)	0.0195(13)	0.4074(16)	0.5819(26)	0.1295	0.8993(14)	0.0544(15)	0.0043(20)	0.1243
C(225)	0.0553(12)	0.4548(14)	0.6349(27)	0.1062	0.8408(12)	0.0391(13)	0.0303(22)	0.0826
C(226)	0.1268(10)	0.4278(10)	0.6557(20)	0.0730	0.7984(13)	0.0840(12)	0.1447(18)	0.0377
C(231)	0.3439(13)	0.4359(11)	0.7725(21)	0.0402	0.6862(10)	0.3138(9)	0.5524(19)	0.0544
C(232)	0.3204(24)	0.4983(18)	0.8779(28)	0.0497	0.6678(13)	0.3583(12)	0.6797(21)	0.0587
C(233)	0.3630(24)	0.5385(22)	0.9178(31)	0.0760	0.6439(14)	0.4333(12)	0.6918(28)	0.0931
C(234)	0.4265(20)	0.5097(20)	0.8658(35)	0.0651	0.6393(11)	0.4569(11)	0.5747(25)	0.0996
C(235)	0.4537(17)	0.4489(18)	0.7500(41)	0.1580	0.6575(12)	0.4078(12)	0.4523(23)	0.0959
C(236)	0.4034(14)	0.4128(16)	0.7039(37)	0.1119	0.6831(12)	0.3335(22)	0.4335(22)	0.0630

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

can be made from it. The Rh–P bond distances in [Rh(TFAA)(P(OPh)$_3$)$_2$] are, as in the case of [Rh(TFBA)(P(OPh)$_3$)$_2$] [1] and [Rh(acac)(P(OPh)$_3$)$_2$] [3] significantly shorter than the Rh–P bond distances in similar Rh(I)–phosphine complexes. The Rh–P bond distances in [Rh(TTA)(CO)(PPh$_3$)] [6] and [Rh(TFDMAA)(CO)(PPh$_3$)] [7] are 2.245(4) and 2.239(2) Å, respectively. The significantly shorter Rh–P bond distances in the case of the phosphite complexes are probably the result of the strong π-electron acceptor properties of the phosphite ligand [4], resulting in a relative stronger Rh–P bond and hence a shorter bond length.

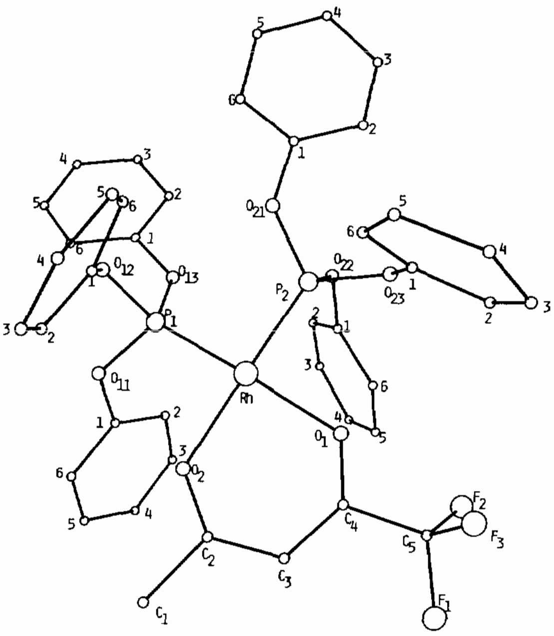

Fig. 1. Perspective view of a Rh(TFAA)(P(OPh)$_3$)$_2$ molecule. The numbering system of the atoms of the phenyl rings of the phosphite groups is as follow (see Table I): the first digit refers to the phosphorous atom, the second digit refers to the oxygen atoms bonded to the phosphorous atom and the third digit refers to the carbon atoms of the phenyl ring bonded to the oxygen atom.

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

Bond	Molecule 1	Molecule 2
Rh–P(1)	2.148(4)	2.145(6)
Rh–P(2)	2.136(6)	2.138(6)
Rh–O(1)	2.085(10)	2.089(13)
Rh–O(2)	2.068(14)	2.084(15)
P(1)–O(11)	1.602(13)	1.589(16)
P(1)–O(12)	1.591(14)	1.612(15)
P(1)–O(13)	1.591(17)	1.611(15)
P(2)–O(21)	1.596(12)	1.615(15)
P(2)–O(22)	1.605(18)	1.594(13)
P(2)–O(23)	1.620(13)	1.602(11)
C(1)–C(2)	1.539(38)	1.549(33)
C(2)–C(3)	1.386(27)	1.434(30)
C(3)–C(4)	1.363(33)	1.366(31)
C(4)–C(5)	1.500(27)	1.493(36)
C(2)–O(2)	1.280(24)	1.254(21)
C(4)–O(1)	1.240(23)	1.268(21)
C(5)–F(1)	1.381(29)	1.293(28)
C(5)–F(2)	1.278(34)	1.226(37)
C(5)–F(3)	1.304(40)	1.300(42)

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

Angle	Molecule 1	Molecule 2
P(1)–Rh–P(2)	90.6(2)	92.3(2)
P(2)–Rh–O(1)	91.1(4)	92.4(4)
P(1)–Rh–O(2)	90.1(4)	87.4(4)
O(2)–Rh–O(1)	88.0(5)	87.9(5)
Rh–P(1)–O(11)	115.0(5)	118.1(5)
Rh–P(1)–O(12)	121.0(6)	116.0(7)
Rh–P(1)–O(13)	116.9(5)	119.7(6)
Rh–P(2)–O(21)	116.5(6)	116.7(5)
Rh–P(2)–O(22)	119.8(5)	121.9(5)
Rh–P(2)–O(23)	116.4(6)	116.3(6)

The two P–Rh–P bond angles of 90.6(2)° and 92.3(2)° in the present structure are, as in the case of [Rh(TFBA)(P(OPh)$_3$)$_2$] [1] and [Rh(acac)(P(OPh)$_3$)$_2$] [3] significantly larger than the P–Rh–C bond angles of 87.1(4)° and 87.8(2)° in Rh–phosphine complexes like [Rh(TTA)(CO)(PPh$_3$)] [6] and [Rh(acac)(CO)(PPh$_3$)] [8], respectively. This relative large P–Rh–P bond angle may be explained by the fact that the two P(OPh)$_3$ groups *cis* two 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 relatively large cone angle (128°) of the P(OPh)$_3$ group [9].

There is a good comparison between the average Rh–O bond distance of 2.082 Å and the averages of 2.069 and 2.069 Å found in [Rh(acac)(P(OPh)$_3$)$_2$] [3] and [Rh(TFBA)(P(OPh)$_3$)$_2$] [1], respectively. This correlation is also good with the Rh–O bond distance (oxygen atom *trans* to the phosphine group) in Rh–phosphine complexes like [Rh(TTA)(CO)(PPh$_3$)] [6] (2.085(7) Å) and [Rh(acac)(CO)(PPh$_3$)] [8] (2.087(4) Å).

Each of the four P atoms are tetrahedrally surrounded by the Rh-atom and three oxygen atoms. The average P–O bond distance of 1.602 Å compares well with the averages of 1.606 and 1.609 Å found in [Rh(TFBA)(P(OPh)$_3$)$_2$] [1] and [Rh(acac)(P(OPh)$_3$)$_2$] [3], respectively. The average C–O bond length of 1.404 Å in the four P(OPh)$_3$-groups, is also in good agreement with the values of 1.389 Å and 1.394 Å found in the above-mentioned two complexes, respectively.

The twelve phenyl rings are planar within experimental error and the average C–C bond distance and bond angle in the phenyl rings are within experimental error identical to the accepted values of 1.399 Å and 120° for phenyl rings [10]. The average C–F bond length of 1.297 Å is in good agreement with the average (1.303 Å) found in [Rh(TFBA)(P(OPh)$_3$)$_2$] [1].

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