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The Crystal Structure of Tropolonatocarbonyltriphenylphosphinerhodium(I)

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Tropolonatocarbonyltriphenylphosphinerhodium(I) crystallizes in the triclinic space group P$\bar{1}$ *with* a = *8.843,* b = *10.555,* c = *13.575* Å, α = *88.95,* β = *103.12 and* γ = *96.06°. The compound was prepared by the reaction between* [*Rh(TROP)(CO)$_2$*] *and triphenylphosphine. 3030 Observed reflections were used for the structure determination. The final* R *value was 0.058. The rhodium–oxygen bond lengths were 2.034 and 2.081* Å. *The results indicate that the triphenylphosphine ligand has a larger* trans-*influence than the carbonyl group.*

Introduction

It is well known that one of the carbonyl groups in complexes of the type [Rh(LL)(CO)$_2$] (LL = bidentate ligands such as β-diketones, 8-hydroxyquinoline and tropolone) can be substituted by triphenylphosphine (PPh$_3$) and triphenylarsine [1, 2] to yield compounds of the type [Rh(LL)(CO)(PPh$_3$)]. To examine these reactions a knowledge of the relative *trans*-effect of the different ligands is necessary. As the two oxygen atoms of the tropolonato ligand are chemically equivalent it is expected that the two Rh–O bond distances in [Rh(TROP)(CO)$_2$] should be the same as was found [3] in the case of [Rh(acac)(CO)$_2$]. Any difference in the Rh–O bond distances in [Rh(TROP)(CO)(PPh$_3$)] could thus be attributed to the difference in the relative *trans*-influence of the CO and PPh$_3$ groups. The results of the crystal structure determination of [Rh(TTA)(CO)(PPh$_3$)] indicated that the oxygen atom nearest to the CF$_3$ group has a smaller *trans*-effect than the other oxygen atom of the TTA ligand [4]. The results of the crystal structure determination of [Rh(TROP)(CO)(PPh)$_3$] may also be used to confirm this conclusion about the relative *trans*-effect of the two oxygen atoms in the β-diketone TTA.

Experimental

A solution of [Rh$_2$Cl$_2$(CO)$_4$] was prepared by refluxing a solution of 0.5 g RhCl$_3$·3H$_2$O in 15 cm^3 dimethylformamide for approximately 30 minutes [5]. An equivalent amount of tropolone dissolved in methanol was added to the resulting yellow solution. About 50 cm^3 distilled water was added to precipitate the [Rh(TROP)(CO)$_2$]. The precipitate was removed by centrifuging and washed with water. [Rh(TROP)(CO)(PPh$_3$)] was prepared by dissolving equivalent quantities of [Rh(TROP)(CO)$_2$] and PPh$_3$ in a minimum acetone and allow the solution to crystallize. The product was recrystallized from acetone. Well formed orange crystals were obtained.

Crystal data: C$_{26}$H$_{20}$O$_3$PRh, molecular weight 514.3, triclinic space group *P$\bar{1}$*, *a* = 8.843, *b* = 10.555, *c* = 13.575 Å, α = 88.95, β = 103.12, γ = 96.06°, *z* = 2, μ(MoK$_\alpha$) = 8.12 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$_\alpha$ radiation (λ = 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 crystals was detectable. A total of 3415 independent reflections were measured, of which 3030 were considered as observed. Only Lorentz and polarization corrections were applied. A crystal with dimensions 0.1 × 0.2 × 0.2 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 atom was located from a three dimensional Patterson function. All the other non-hydrogen atoms were located from successive Fourier analyses. Five cycles of full matrix least squares refinement of all the positional and isotropic thermal parameters resulted in a *R* value of 8.6%. Four more cycles of refinement with anisotropic thermal parameters converged to *R* = 5.8%. In the final cycle no positional parameter exhibited shifts of more than 0.3 times its standard deviation.

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TABLE I. Fractional Atomic Coordinates and Thermal Parameters. Positional Parameters $(\times 10^4)$ and Thermal Parameters $(\times 10^3)$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	3667.9(9)	4225.8(7)	2290.8(6)	34(1)	38(1)	48(1)	−1(0)	6(0)	−1(0)
P	2181(3)	2592(3)	1422(2)	26(1)	33(1)	47(2)	0(1)	8(1)	1(1)
O(1)	4890(8)	3171(6)	3402(5)	53(4)	44(4)	47(4)	−1(3)	0(4)	3(3)
O(2)	5136(8)	5619(6)	3209(6)	54(5)	40(4)	55(5)	−6(3)	5(4)	0(3)
O(3)	2244(12)	5946(8)	695(8)	116(8)	54(6)	88(7)	20(5)	−10(6)	14(5)
C(1)	2751(13)	5261(11)	1323(9)	47(7)	45(7)	67(8)	−6(5)	−4(6)	−5(6)
C(2)	5956(13)	3802(11)	4087(8)	47(6)	61(7)	46(7)	5(5)	12(5)	2(6)
C(3)	6083(12)	5188(11)	3988(8)	43(6)	61(7)	48(7)	−2(5)	17(5)	−4(6)
C(4)	7099(14)	6096(13)	4644(9)	52(7)	94(10)	57(8)	−21(7)	8(6)	−23(7)
C(5)	8253(16)	5846(16)	5527(11)	59(8)	116(13)	62(9)	−12(8)	9(7)	−24(9)
C(6)	8713(18)	4750(19)	5977(11)	73(10)	120(14)	65(10)	6(10)	−9(8)	−17(10)
C(7)	8096(19)	3559(19)	5651(11)	83(11)	142(16)	60(9)	35(11)	−12(8)	13(10)
C(8)	6872(16)	3115(14)	4836(9)	79(9)	91(10)	49(8)	8(8)	−12(7)	7(7)
C(11)	176(11)	2355(9)	1596(7)	33(5)	46(6)	45(6)	−1(4)	7(4)	−5(5)
C(12)	−565(12)	3422(11)	1736(8)	38(6)	64(7)	59(7)	15(5)	20(5)	−9(6)
C(13)	−2108(13)	3237(13)	1887(10)	36(6)	85(9)	82(9)	53(6)	18(6)	−16(7)
C(14)	−2866(14)	2029(14)	1881(10)	42(7)	102(11)	77(9)	−4(7)	23(6)	−16(8)
C(15)	−2129(15)	966(13)	1748(12)	50(8)	76(9)	123(12)	−2(7)	39(8)	−8(8)
C(16)	−598(13)	1124(11)	1586(10)	43(7)	60(7)	96(10)	−10(6)	28(6)	0(7)
C(21)	1957(11)	2678(8)	55(7)	47(6)	27(5)	47(6)	13(4)	14(5)	3(4)
C(22)	3275(13)	3163(10)	−313(9)	55(7)	43(6)	64(8)	8(5)	25(6)	7(5)
C(23)	3149(14)	3243(11)	−1351(9)	61(8)	60(7)	59(8)	9(6)	18(6)	3(6)
C(24)	1738(16)	2870(11)	−2034(9)	80(9)	57(7)	55(7)	18(6)	15(7)	10(6)
C(25)	428(14)	2393(12)	−1660(9)	61(8)	70(8)	59(8)	−4(6)	4(6)	5(6)
C(26)	547(12)	2295(10)	−610(8)	44(6)	47(6)	52(7)	2(5)	−3(5)	1(5)
C(31)	2912(10)	1052(9)	1749(8)	24(5)	30(5)	62(7)	−3(4)	0(4)	0(5)
C(32)	3212(12)	246(9)	1020(9)	46(6)	35(6)	81(8)	8(5)	16(6)	−13(6)
C(33)	3791(14)	−922(11)	1314(11)	53(7)	44(7)	106(11)	13(6)	12(7)	5(7)
C(34)	4063(14)	−1285(12)	2322(13)	55(8)	46(7)	116(12)	3(6)	3(8)	15(8)
C(35)	3771(15)	−492(12)	3059(11)	64(8)	52(8)	91(10)	1(6)	10(7)	12(7)
C(36)	3188(13)	692(10)	2770(9)	50(7)	45(7)	77(9)	−2(5)	13(6)	12(6)

TABLE II. Interatomic Distances (A) with Estimated Standard Deviations in Parentheses.

Rh–O(1)	2.034(7)	C(11)–C(12)	1.398(16)
Rh–O(2)	2.081(7)	C(12)–C(13)	1.418(16)
Rh–C(1)	1.797(12)	C(13)–C(14)	1.377(19)
Rh–P	2.232(2)	C(14)–C(15)	1.390(21)
P–C(11)	1.832(10)	C(15)–C(16)	1.412(19)
P–C(21)	1.823(10)	C(16)–C(11)	1.401(15)
P–C(31)	1.823(10)	C(21)–C(22)	1.415(16)
O(1)–C(2)	1.299(12)	C(22)–C(23)	1.390(17)
O(2)–C(3)	1.299(12)	C(23)–C(24)	1.399(16)
O(3)–C(1)	1.151(15)	C(24)–C(25)	1.410(19)
C(2)–C(3)	1.461(16)	C(25)–C(26)	1.408(17)
C(3)–C(4)	1.417(16)	C(26)–C(21)	1.389(13)
C(4)–C(5)	1.427(17)	C(31)–C(32)	1.403(16)
C(5)–C(6)	1.356(25)	C(32)–C(33)	1.401(16)
C(6)–C(7)	1.356(26)	C(33)–C(34)	1.389(22)
C(7)–C(8)	1.409(18)	C(34)–C(35)	1.401(22)
C(8)–C(2)	1.392(17)	C(35)–C(36)	1.417(17)
		C(36)–C(31)	1.404(16)

The atomic scattering factors used were those tabulated by Cromer and Waber [6]. A list of the observed and calculated structure factors may be obtained from the authors. The final positional and thermal parameters are listed in Table I. The estimated standard deviations in the last significant figure are given in parentheses.

Results and discussion

The system of numbering of the atoms in the molecule is shown in Fig. 1. The bond lengths and angles with their standard deviations are given in Tables II and III respectively.

If the pseudo-twofold symmetry of the tropolonato ligand is taken into account, the bond distances could be divided into pairs. The average bond lengths

TABLE III. Bond Angles (degrees) with Estimated Standard Deviations in Parentheses.

O(1)–Rh–O(2)	77.8(3)
O(1)–Rh–P	96.6(2)
O(2)–Rh–C(1)	97.7(4)
C(1)–Rh–P	87.9(4)
Rh–O(1)–C(2)	116.1(7)
O(1)–C(2)–C(3)	115.9(9)
C(2)–C(3)–O(2)	115.2(8)
C(3)–O(2)–Rh	114.9(6)
C(3)–C(2)–C(8)	126.0(10)
C(2)–C(8)–C(7)	129.4(14)
C(8)–C(7)–C(6)	132.1(16)
C(7)–C(6)–C(5)	125.3(13)
C(6)–C(5)–C(4)	132.5(14)
C(5)–C(4)–C(3)	127.1(13)
C(4)–C(3)–C(2)	127.5(10)
Rh–P–C(11)	114.9(3)
Rh–P–C(21)	115.0(3)
Rh–P–C(31)	113.9(3)
Rh–C(1)–O(3)	176.2(11)

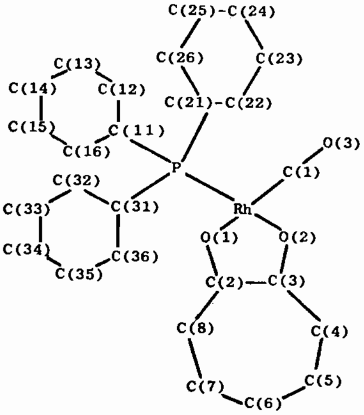

Fig. 1. The system of numbering of the atoms in the molecule.

TABLE IV. Bond Lengths in the Tropolonato Ligand in NaTROP and [Rh(TROP)(CO)(PPh$_3$)].

Bond Type	Bond Length (A)	
	NaTROP	[Rh(TROP(CO)(PPh$_3$)]
C–O[a]	1.278	1.299
C(2)–C(3)[b]	1.487	1.461
C(3)–C(4)	1.426	1.417
C(4)–C(5)[c]	1.390	1.427
C(5)–C(6)[d]	1.388	1.356

[a]Average of C(3)–O(2) and C(2)–O(1). [b]Average of C(2)–C(3) and C(2)–C(8). [c]Average of C(4)–C(5) and C(8)–C(7). [d]Average of C(5)–C(6) and C(6)–C(7).

of the five bond types thus obtained are given in Table IV. The deviation of the individual bond distances from the average value is smaller than the standard deviation for each of the five bond types. The comparison of the bond lengths in [Rh(TROP)(CO)(PPh$_3$)] and in sodium tropolonate [7] indicates (see Table IV) that a strong metal–oxygen bond is accompanied by an increase in the C–O bond lengths and a decrease in the C(2)–C(3) bond length. Hamor and Watkin [8] pointed out that a pure σ bond between trigonally hybridized carbon atoms is never shorter than 1.48 Å. The data in Table IV therefore do suggest that the Rh–O bonds are involved in the delocalization of the π electron density of the seven-membered ring. The C–C–C bond angles vary between 126.0° and 132.5°. The sum of these seven angles is 899.9°. The calculation of the best planes through the atoms of the seven-membered ring and the five-membered chelate ring showed no significant deviation from a plane. These rings are at an angle of 2.1° to one another and are thus nearly co-planar.

The phosphorous atom is approximately tetrahedrally surrounded by the rhodium atom and three carbon atoms of the three phenyl rings. The Rh–P distance is 2.232 Å and the mean P–C distance is 1.826 Å. These bond distances compare well with those found in [Rh(TTA)(CO)(PPh$_3$)] and [Rh(acac)(CO)(PPh$_3$)] [3, 4]. The calculation of the best planes through the atoms of the phenyl rings showed that they are planar within the experimental error. The average C–C bond distance in the phenyl rings (1.401 Å) is in good agreement with the normal value (1.394 Å) for the aromatic C–C bond [9]. All the bond angles are 120° within the experimental error.

The calculation of the best plane through Rh, O(1), O(2), C(1) and P showed that the coordination polyhedron is approximately planar. The ligand–Rh–ligand bond angles however, deviate significantly from 90°, see Table III. This large distortion is due to the small 'bite' angle (77.8°) of the five-membered chelate ring. The sum of the four ligand–Rh–ligand bond angles is 360.0°. The Rh–C(1)–O(3) chain is approximately linear (176.2). The Rh–C(1) and C(1)–O(3) bond lengths (1.797 Å and 1.151 Å respectively) are in good agreement with the bond distances found in [Rh(acac)(CO)(PPh$_3$)] [3].

Since the two oxygen atoms in the tropolonate ion are chemically equivalent, it could be assumed that the two Rh–O bond distances in a symmetrical molecule, such as [Rh(TROP)(CO)$_2$], would be the same. This is the case in the similar molecule [Rh(acac)(CO)$_2$] where the two Rh–O bond distances were found to be 2.040 and 2.044 Å [3]. The Th–O bond distances (oxygen atoms of the tropolonate ions) in Th(TROP)$_4$·DMF were also the same within the experimental error [10]. The significant difference in the two Rh–O bond lengths in [Rh-TROP)(CO)(PPh$_3$)] (Rh–O(1) = 2.034(7) Å and Rh–O(2) = 2.081(7) Å) therefore indicates that the triphenylphosphine ligand has a larger *trans*-effect than the carbonyl ligand.

The crystal structure determination of [Rh(TTA)(CO)(PPh_3)] [4] showed that the oxygen atom nearest to the CF_3 group has the smallest *trans*-effect, as it was the CO group *trans* to this oxygen atom that was not displaced in the reaction [Rh(TTA)($CO)_2$] + PPh_3 → [Rh(TTA)(CO)(PPh_3)] + CO. This is in agreement with the polarization theory [11] and the σ *trans*-effect [12] since the oxygen atom nearest to the CF_3 group will be least polarizable and a weaker σ donor as a result of the electron attracting power of the CF_3 group. Further support for this observation is also found in the comparison of the Rh–C bond distances in [Rh(TTA)(CO)(PPh_3)] [4] and in [Rh(TROP)(CO)(PPh_3)]. The Rh–C bond distances in these compounds are 1.780 and 1.797 Å respectively. Although this difference is only about 1½ times the standard deviation it indicates that the oxygen atom nearest to a CF_3 group has a smaller *trans*-effect than the oxygen atom of the tropolone ligand. This is in agreement with the relative polarizability of the two oxygen atoms due to the electron-attracting power of the CF_3 group.

The relative *trans*-effect of the PPh_3 and CO ligands was verified by means of the following reaction:

$$[\mathrm{Rh(TROP)(CO)(PPh_3)}] + \mathrm{TTA} \rightleftharpoons [\mathrm{Rh(TTA)(CO)(PPh_3)}] + \mathrm{TROP} \qquad (1)$$

The specific isomer which would be obtained would depend on (*i*) which Rh–O bond in [Rh(TROP)(CO)(PPh_3)] will break first (thus the relative *trans*-effect of PPh_3 and CO) and (*ii*) which of the two oxygen atoms of the TTA group will bond first (thus the effect of the CF_3 and thenoyl groups on the *trans*-effect of the two oxygen atoms). According to the results of the structure determination of [Rh(TTA)(CO)(PPh_3)] [4] the oxygen atom nearest to the thenoyl group (which has the largest *trans*-effect) will bond first, since a good *trans* labilizer is also a good entering group in square planar substitution reactions.

According to this and the fact that the PPh_3 group has a larger *trans*-effect than the CO group the isomer obtained by reaction (1) should be the same as obtained by the following reaction:

$$[\mathrm{Rh(TTA)(CO)_2}] + \mathrm{PPh_3} \rightarrow [\mathrm{Rh(TTA)(CO)(PPh_3)}] + \mathrm{CO} \qquad (2)$$

[Rh(TTA)(CO)(PPh_3)] (according to reaction (2)) was obtained by the published method [1]. [Rh(TTA)(CO)(PPh_3)] (according to reaction (1)) was prepared by mixing 0.2 g TTA (an excess) with 0.2 g [Rh(TROP)(CO)(PPh_3)] in 30 cm^3 methanol. The solution was evaporated and chromatographed on an alumina column to remove the excess TTA. The X-ray powder patterns of [Rh(TTA)(CO)(PPh_3)] obtained by these two methods were identical which showed that the same isomer was obtained. This experimental results thus confirm the proposals based on the structure determination about the relative *trans*-effect of the different ligands in this type of compounds.

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