The Structure of 2-Carboxyquinolinatobis(triphenylphosphite)rhodium(I)

G. J. LAMPRECHT, J. H. BEETGE, J. G. LEIPOLDT and D. R. DE WAAL

Department of Chemistry, University of the Orange Free State, Bloemfontein, 9301, South Africa

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Abstract

2-Carboxyquinolinatobis(triphenylphosphite)rhodium(I) was prepared by means of the following reaction:

$$[Rh(Qin)(CO)_2] + 2P(OPh)_3 \longrightarrow [Rh(Qin)(P(OPh)_3)_2] + 2CO$$

It crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.406$, $b = 18.702$, $c = 9.547$ Å, $\alpha = 76.36$, $\beta = 111.35$, $\gamma = 97.88°$ and $Z = 2$. The structure was determined from 4520 observed reflections. The final R value was 0.051. The Rh–P bond distances may indicate (although the difference is only about 3σ) that the nitrogen atom of the chelate ring has the largest *trans* influence. The chelate ring is significantly folded along the N–––O axis.

Introduction

In previous papers [1, 2] which dealt with preparations and structures of 2-carboxypyridinatocarbonyltriphenylphosphinerhodium(I) and 2-carboxyquinolinatocarbonyltriphenylphosphinerhodium(I), it was reported that in the respective complexes $[RhPic(CO)_2]$ and $[RhQin(CO)_2]$ the carbonyl group *trans* to the nitrogen atom was substituted by PPh_3. These results were in agreement with the polarization theory [3] and the *σ-trans* effect [4], since they indicated that the nitrogen atom of the chelate ring has a larger *trans*-influence than does the oxygen atom because, relative to a nitrogen atom, an oxygen atom is a weaker σ-electron donor due to its higher electronegativity.

Another obvious way to distinguish between the thermodynamic *trans* influence of two bonded atoms is to determine the metal–ligand bond distances of two identical atoms *trans* to these atoms. In complexes of the type $[Rh(\beta\text{-diketone})(CO)_2]$, both carbonyl groups are substituted by triphenylphosphite to form the corresponding bistriphenylphosphite complexes [5–8]. A small, but significant, difference in the two Rh–P bond distances in the trifluorobenzoylacetone (TFBA) complex was observed, indicating that the oxygen atom nearest to the electron-withdrawing CF_3 group has the smallest *trans* influence [6]. The two Rh–P bond distances in the trifluoroacetylacetone (TFAA) complex were, however, the same within experimental error [8]. No conclusion about the relative *trans* influence of the two oxygen atoms of TFAA could thus be made.

The fact that the different oxygen atoms of the β-diketone result in only a small difference in the two Rh–P bonds may be explained in two ways: (i) the difference in the thermodynamic *trans* influence of the two oxygen atoms of the β-diketone may be small; and (ii) the Rh–P bonds are very strong as a result of the π-acceptor properties of the triphenylphosphite [9].

The crystal structure determination of several complexes of the type $[Rh(LL')(CO)(PPh_3)]$ (where LL′ = β-diketones, picolinic acid, 8-hydroxyquinoline, etc.) indicate that the difference in the *trans* influence of an oxygen and a nitrogen atom is much greater than between the two oxygen atoms of a non-symmetrical β-diketone. The mean Rh–P bond length (phosphorus atom *trans* to an oxygen atom) is 2.238(2) Å [10–12], whereas the mean Rh–P bond *trans* to a nitrogen atom is 2.266(2) Å [1, 2, 13, 14]. It is thus expected that the greater difference in the *trans* influence of the nitrogen and oxygen atoms in 2-carboxyquinoline may be observed in the Rh–P bond lengths.

Experimental

An equivalent amount of solid quinaldic acid (2-carboxyquinoline) was added to a solution of $[Rh_2Cl_2(CO)_4]$ [15] in dimethylformamide. Addition of cold water to the reaction mixture precipitated 2-carboxyquinolinatodicarbonylrhodium(I), $[RhQin(CO)_2]$, which was centrifuged and purified by recrystallization from warm methanol. The title compound $[RhQin(P(OPh)_3)_2]$ was prepared by dissolving 0.25 g red crystals of $[RhQin(CO)_2]$ in 5 cm^3 acetone solution of $P(OPh)_3$ (0.47 g, 1.2 mole ratio). The resulting yellow crystals were recrystal-

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lized from acetone to yield well-formed crystals, suitable for X-ray data collection.

Crystal Data

$RhC_{46}H_{36}O_8P_2N$, molecular mass 895.65, triclinic space group $P\bar{1}$, $a = 12.406$, $b = 18.702$, $c = 9.547$ Å, $\alpha = 76.36$, $\beta = 111.35$, $\gamma = 97.88°$, $Z = 2$, $D_{exp} = 1.472$ g cm^{-3}, μ(Mo Kα) = 5.5 cm^{-1}.

The structure was solved from three-dimensional intensity data as described earlier [1]. No decomposition of the crystal was detectable during the data collection. A total of 5566 reflections were measured, of which 4520 were considered as observed. Six cycles of full matrix least-squares refinement using all the observed reflections and anisotropic thermal parameters for all the non-hydrogen atoms resulted in a *R*-value of 0.051. Final positional and thermal parameters are given in Table I.

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

Atom	x	y	z	U_{eq} [a]
Rh(1)	0.4416(0)	0.1973(0)	0.2348(1)	36(3)
P(1)	0.3434(1)	0.2759(1)	0.0410(2)	30(3)
P(2)	0.4092(1)	0.2506(1)	0.3906(2)	30(3)
O(1)	0.3055(4)	0.2255(3)	0.4589(5)	58(6)
O(2)	0.5048(4)	0.2456(3)	0.5602(5)	47(12)
O(3)	0.3950(4)	0.3371(2)	0.3267(5)	50(16)
O(4)	0.3057(4)	0.2511(2)	−0.1221(5)	44(7)
O(5)	0.2266(4)	0.3017(2)	0.0421(5)	45(6)
O(6)	0.4036(4)	0.3548(2)	−0.0080(5)	45(2)
O(7)	0.4972(4)	0.1585(2)	0.0869(5)	49(10)
O(8)	0.6665(5)	0.1309(3)	0.0887(6)	78(29)
N(1)	0.5596(4)	0.1160(3)	0.3904(6)	36(1)
C(1)	0.5820(6)	0.0827(3)	0.5434(7)	38(8)
C(2)	0.4947(6)	0.0794(3)	0.6092(8)	48(16)
C(3)	0.5182(7)	0.0463(4)	0.7617(8)	55(21)
C(4)	0.6270(8)	0.0148(4)	0.8521(9)	62(24)
C(5)	0.7093(7)	0.0153(4)	0.7888(8)	59(19)
C(6)	0.6879(6)	0.0490(4)	0.6310(8)	45(8)
C(7)	0.7715(6)	0.0500(4)	0.5599(8)	53(5)
C(8)	0.7438(6)	0.0792(4)	0.4065(8)	49(4)
C(9)	0.6363(6)	0.1104(3)	0.3257(7)	42(4)
C(10)	0.6002(6)	0.1361(4)	0.1535(7)	47(7)
C(11)	0.1896(6)	0.2095(4)	0.3736(8)	53(18)
C(12)	0.1098(8)	0.2477(6)	0.3953(12)	97(40)
C(13)	−0.0092(11)	0.2275(10)	0.3162(17)	128(64)
C(14)	−0.0379(10)	0.1749(10)	0.2266(15)	116(77)
C(15)	0.0443(10)	0.1386(7)	0.2089(12)	96(3)
C(16)	0.1628(7)	0.1553(5)	0.2857(9)	68(13)
C(17)	0.6234(6)	0.2530(4)	0.5931(8)	43(3)
C(18)	0.6880(7)	0.2213(4)	0.7438(8)	55(6)
C(19)	0.8085(8)	0.2268(5)	0.7838(11)	75(10)
C(20)	0.8616(8)	0.2619(6)	0.6788(13)	87(20)
C(21)	0.7950(7)	0.2936(5)	0.5297(11)	75(20)
C(22)	0.6734(6)	0.2888(4)	0.4860(9)	55(4)
C(23)	0.3719(6)	0.3917(3)	0.3903(8)	43(6)
C(24)	0.3377(6)	0.4564(4)	0.2845(9)	55(6)
C(25)	0.3177(8)	0.5152(4)	0.3385(10)	70(15)
C(26)	0.3318(7)	0.5075(4)	0.4931(10)	66(20)
C(27)	0.3663(7)	0.4421(4)	0.5944(9)	65(4)
C(28)	0.3873(7)	0.3826(4)	0.5441(8)	60(13)
C(29)	0.2427(6)	0.1852(4)	−0.1523(7)	41(9)
C(30)	0.2841(7)	0.1466(4)	−0.2265(8)	60(14)
C(31)	0.2193(8)	0.0829(5)	−0.2717(10)	72(4)
C(32)	0.1180(8)	0.0612(5)	−0.2416(11)	80(16)
C(33)	0.0783(8)	0.0994(6)	−0.1635(12)	88(15)
C(34)	0.1435(7)	0.1645(5)	−0.1178(10)	69(15)
C(35)	0.1499(5)	0.3537(4)	−0.0651(8)	41(6)
C(36)	0.0748(7)	0.3765(5)	−0.0109(10)	75(8)
C(37)	−0.0065(8)	0.4270(6)	−0.1116(13)	89(19)
C(38)	−0.0125(8)	0.4521(5)	−0.2622(12)	78(20)
C(39)	0.0639(7)	0.4271(5)	−0.3128(10)	66(10)
C(40)	0.1463(6)	0.3770(4)	−0.2149(9)	55(5)
C(41)	0.5249(6)	0.3660(3)	0.0331(7)	40(7)
C(42)	0.5862(7)	0.3239(4)	−0.0107(9)	60(10)
C(43)	0.7069(7)	0.3398(5)	0.0305(10)	74(9)
C(44)	0.7605(7)	0.3958(5)	0.1074(10)	73(8)
C(45)	0.6946(8)	0.4382(5)	0.1471(10)	69(7)
C(46)	0.5754(6)	0.4220(4)	0.1101(8)	52(6)

[a] $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$. Estimated standard deviations are given in parentheses.

Results and Discussion

The molecular structure of $[Rh(Qin)(P(OPh)_3)_2]$ and the system of numbering the atoms is shown in Fig. 1. Selected bond lengths and angles are given in Tables II and III, respectively.

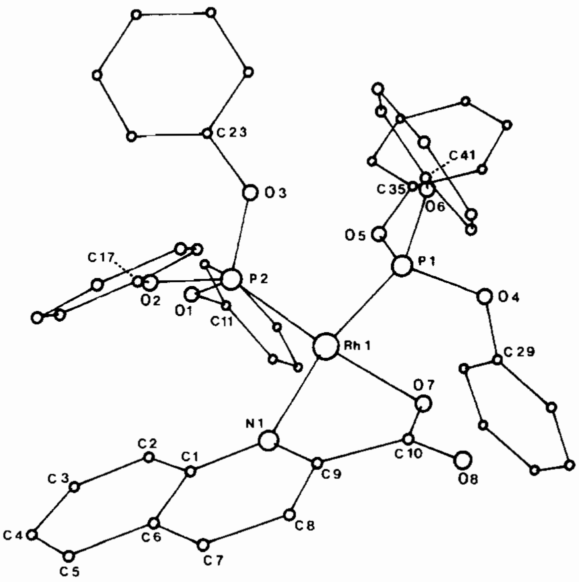

Fig. 1. A perspective view of the molecule together with the system of numbering all the non-phenyl atoms.

TABLE II. Selected Interatomic Distances (Å)^a

Rh(1)–N(1)	2.150(5)	O(7)–C(10)	1.282(8)
Rh(1)–O(7)	2.079(6)	C(10)–O(8)	1.221(11)
Rh(1)–P(1)	2.153(1)	C(10)–C(9)	1.511(9)
Rh(1)–P(2)	2.147(2)	N(1)–C(9)	1.337(10)
P(1)–O(4)	1.614(5)	C(9)–C(8)	1.403(9)
P(1)–O(5)	1.593(6)	C(8)–C(7)	1.367(10)
P(1)–O(6)	1.606(5)	C(7)–C(6)	1.428(13)
P(2)–O(1)	1.613(6)	C(6)–C(1)	1.414(9)
P(2)–O(2)	1.612(4)	C(1)–N(1)	1.386(8)
P(2)–O(3)	1.598(5)		

^{a}e.s.d.s given in parentheses.

TABLE III. Selected Bond Angles (°)^a

P(1)–Rh(1)–P(2)	91.0(1)	C(6)–C(7)–C(8)	119.0(6)
P(2)–Rh(1)–N(1)	101.7(2)	C(7)–C(8)–C(9)	118.9(8)
N(1)–Rh(1)–O(7)	77.9(2)	C(8)–C(9)–N(1)	124.0(6)
O(7)–Rh(1)–P(1)	88.6(1)	C(9)–N(1)–C(1)	118.2(5)
P(1)–Rh(1)–N(1)	166.1(2)	O(7)–C(10)–O(8)	125.4(6)
P(2)–Rh(1)–O(7)	170.2(2)	C(9)–C(10)–O(8)	119.1(6)
Rh(1)–N(1)–C(9)	107.3(4)	P(1)–O(4)–C(29)	123.6(4)
N(1)–C(9)–C(10)	116.8(5)	P(1)–O(5)–C(35)	130.2(5)
C(8)–C(10)–O(7)	115.3(7)	P(1)–O(6)–C(41)	121.6(4)
C(10)–O(7)–Rh(1)	111.6(4)	P(2)–O(1)–C(11)	125.7(5)
N(1)–C(1)–C(6)	120.4(7)	P(2)–O(2)–C(17)	125.0(5)
C(1)–C(6)–C(7)	119.1(6)	P(2)–O(3)–C(23)	131.0(4)

^{a}e.s.d.s given in parentheses.

The rhodium atom has approximately a square planar co-ordination as proved by calculation of the best plane through the atoms P(1), P(2), N(1) and O(7) of the co-ordination polyhedron. The deviation of the ligand–rhodium–ligand bond angles from 90° (Table III) may be attributed to the small 'bite' angle of 77.9 of the five membered chelate ring. In contrast to two other identical chelate rings [1, 2], the chelate ring Rh(1), N(1), O(7), C(9) and C(10) is not planar.

The equation for the best plane through the chelate ring is $0.4798x + 0.8275y + 0.2915z = 5.6128$. The deviations of the individual atoms from this plane are 0.168, −0.214, 0.124, 0.116 and −0.194 Å for Rh(1), O(7), C(10), C(9) and N(1), respectively. The chelate ring is folded along the N(1)·····O(7) axis. The angle between the plane formed by Rh, O(7), N(1) and the least squares plane through N(1), C(9), C(10), O(7) (this fragment is planar within experimental error) is 29.2°. The corresponding angle [2] is only 4.5° in [Rh(Qin)(CO)(PPh$_3$)]. The large angle in the present stucture may be explained by the large *trans* influence of the phosphite ligands as a result of the strong Rh–P bonds; this weakens the Rh–N and, especially, the Rh–O bonds. The Rh–O bond lengths are 2.034 Å in [Rh(Qin)(CO)(PPh$_3$)] [2] and 2.079 Å in the present structure.

The quinoline system is almost planar, as shown by an angle of 3.3° between the two six-membered rings N(1), C(1), C(6), C(7), C(8), C(9) and C(1), C(2), C(3), C(4), C(5), C(6). The angle between the same planes in [Rh(Qin)(CO)(PPh$_3$)] [2] was 2.1°.

Each of the two phosphorous atoms are tetrahedrally surrounded by the rhodium atom and three oxygen atoms (see Table III). The average P–O bond distance of 1.606 Å is the same as found in [Rh(TFBA)(P(OPh)$_3$)$_2$] [6]. The average C–O bond distance of 1.401 Å in the P(OPh$_3$)$_2$-group is in good agreement with the value of 1.389 Å in [Rh(TFBA)(P(OPh)$_3$)$_2$] [6].

The six phenyl rings are planar, within experimental error; the average C–C bond distances and bond angles in the phenyl rings are, within experimental error, identical to the accepted values of 1.339 Å and 120° for phenyl rings [16].

The Rh–P bond lengths indicate (although the difference in the two Rh–P bond lengths is only about three times the standard deviation) that the nitrogen atom of the chelate ring has a greater *trans* influence than the oxygen atom. This is in agreement with the result of the structure determination of [Rh(Qin)(CO)(PPh$_3$)] [2] and with the σ-*trans* effect [4] since the nitrogen atom is the better σ-donor.

The *trans* influence of nitrogen, relative to oxygen, in these type of ligands is more dramatic in the complex [Rh(Oxine)(COD)] [17], where the difference in bond lengths was 0.024 Å, due to the larger *trans* influence of the nitrogen atom. The small effect of the difference in the *trans* influence in the phosphite complexes can be explained to be a result of the strong Rh–P bonds, as discussed in the introduction. The Rh–P bond distances in phosphine complexes [1, 2] similar to the present phosphite complex were about 0.11 Å longer than the Rh–P bond distance in the present structure.

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