Inorganica Chimica Acta, 50 (1981) 121–124
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The Crystal Structure of 8-Hydroxyquinolinatocarbonyltriphenylphosphinerhodium(I)

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Received December 18, 1980

The crystal structure of 8-hydroxyquinolinatocarbonyltriphenylphosphine, $C_{28}H_{21}O_2NPRh$, was determined from 2995 unique observed reflections obtained with a computer automated diffractometer. The unit cell is triclinic with $a = 14.154$ Å, $b = 9.984$ Å, $c = 9.409$ Å, $\alpha = 116.16°$, $\beta = 90.09°$, $\gamma = 99.60°$, $Z = 2$ *with space group* $P\bar{1}$. *Refinement of the data with anisotropic thermal parameters converged to* $R = 4.9\%$. *The compound was prepared by the reaction between [Rh(oxine)(CO)$_2$] and triphenylphosphine. The structure determination shows that the carbonyl group* trans *to the nitrogen atom of the 8-hydroxyquinolinato ligand was substituted by the triphenylphosphine ligand, which indicate that the nitrogen atom of the chelate ring has a larger* trans *influence than the oxygen atom.*

Introduction

The fact that only one of the carbonyl groups in complexes of the type [Rh(LL′)(CO)$_2$] (where LL′ = bidentate ligands such as β-diketones, tropolone and 8-hydroxyquinoline) can be substituted by ligands like triphenylphosphine and triphenylarsine [1, 2] makes it possible to determine the relative *trans* influence of the two atoms of ligand LL′ which are bonded to the rhodium atom as it can be assumed that the carbonyl group which is situated *trans* to the atom which has the largest *trans* influence will be displaced by PPh$_3$ or AsPh$_3$.

The carbonyl groups in complexes where LL′ are symmetrical bidentate ligands are chemical equivalent as was indicated by the bond lengths in [Rh(acac)(CO)$_2$], [3]. In cases where LL′ are not symmetrical like non-symmetrical β-diketones (such as thenoyltrifluoroacetone (TTA) and benzoyltrifluoroacetone (TFBA)) and 8-hydroxyquinoline (oxine) it is however necessary to have a knowledge about the relative reactivities of the two carbonyl groups and thus of the relative *trans* effect of the two atoms of ligand LL′ which are bonded to the rhodium atom. The crystal structure determination of [Rh(TTA)(CO)(PPh$_3$)], [4], showed that the oxygen atom nearest to the strong electron-attracting CF$_3$-group has the smallest *trans* effect since it was the CO-group *trans* to this oxygen atom that was not displaced during the reaction

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

This effect of the CF$_3$-group was also observed in the bond distances in [Rh(TFBA)(COD)], [5]. These results are in agreement with the polarization theory [6] and the σ-*trans* effect [7] 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.

The crystal structure determination of [Rh(acac)(CO)(PPh$_3$)], [8], and [Rh(TROP)(CO)(PPh$_3$)], [9], showed that the PPh$_3$-group has a larger *trans* effect than the CO-group since the Rh–O bond distance (oxygen atom *trans* to the PPh$_3$-group) is significant longer than the other Rh–O bond distance in both structures. This was also proved by the synthesis of [Rh(TTA)(CO)(PPh$_3$)] from [Rh(acac)(CO)(PPh$_3$)] [10].

The crystal structure of [Rh(oxine)(CO)(PPh$_3$)] was determined as part of a program for the study of the relative *trans* effects in square planar rhodium(I) complexes.

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 [11]. An equivalent amount of sodium 8-hydroxyquinolate was added to the resulting yellow solution. About 30 cm^3 cold water was added to precipitate the [Rh(oxine)(CO)$_2$]. The precipitate was removed by centrifuging and washed with water, ethanol and ether and recrystallized from chloroform.

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[Rh(oxine)(CO)(PPh$_3$)] was prepared by adding an equivalent amount of triphenylphosphine to a solution of [Rh(oxine)(CO)$_2$] in a minimum acetone and the solution allowed to crystallize. The product was recrystallized from acetone. Well formed yellow-orange crystals were obtained.

Crystal data: $C_{28}H_{21}O_2NPRh$, molecular weight 537.4, triclinic space group $P\bar{1}$, a = 14.154Å, b = 9.984Å, c = 9.409Å, α = 116.16°, β = 90.09°, γ = 99.60°, Z = 2, $\mu(MoK_\alpha)$ = 8.1 cm^{-1}. The three dimensional intensity data were collected on a Philips PW 1100 four circle single crystal X-ray diffractometer. Graphite monochromated MoK_α radiation (λ = 0.7107Å) was used for the data collection. Three reflections were used as standards and remeasured after every 60 reflections to check possible crystal decay. No decomposition of the crystal was detectable during the data collection. A total of 3249 independent reflections were measured for θ values between 3° and 23°, of which 2995 were considered as observed. A crystal with dimensions 0.4 × 0.3 × 0.2 mm^3 was used for the data collection. The data were corrected for Lorentz and polarization effects but not for absorption due to the low value of μ (8.1 cm^{-1}). In the structure solution and refinement the space group was assumed to be $P\bar{1}$. This assumption was proved to be correct by the completeness of refinement.

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 three successive Fourier analyses. A full matrix least squares refinement, using all the observed reflections and anisotropic thermal parameters for all the atoms gave R = 0.049 after five cycles.

The atomic scattering factors used were those tabulated by Cromer and Waber, [12]. A table of the observed and calculated structure factors may be obtained from the authors. The final positional and thermal parameters with their standard deviations are given in Table I.

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

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	2026.3(4)	1942.5(7)	2689.1(8)	50(1)	61(1)	98(1)	10(0)	0(0)	51(0)
P	3192(1)	1248(2)	3719(2)	45(1)	42(1)	54(1)	8(1)	1(1)	25(1)
N	1001(4)	2355(9)	1392(11)	49(4)	95(5)	148(7)	8(4)	3(4)	98(5)
O(1)	2105(3)	255(6)	472(6)	69(3)	87(4)	80(4)	13(3)	−8(3)	56(3)
O(2)	1837(6)	4542(8)	5715(10)	157(7)	85(5)	144(7)	57(5)	24(5)	35(5)
C(1)	1929(6)	3494(10)	4561(13)	87(6)	73(6)	123(8)	34(5)	13(6)	52(6)
C(2)	471(6)	3469(11)	1964(15)	51(5)	122(8)	231(12)	26(5)	18(6)	140(9)
C(3)	−201(8)	3546(17)	849(21)	63(6)	166(13)	248(16)	28(7)	21(9)	167(13)
C(4)	−300(7)	2515(18)	−722(20)	55(6)	188(14)	232(15)	18(8)	12(9)	181(13)
C(5)	179(7)	203(18)	−2916(17)	72(7)	191(13)	135(10)	−26(7)	−23(7)	130(10)
C(6)	746(7)	−885(15)	−3356(13)	79(7)	184(12)	125(9)	−20(7)	−15(6)	123(9)
C(7)	1421(6)	−908(12)	−2225(11)	84(6)	131(8)	87(6)	−24(5)	−21(5)	81(6)
C(8)	1490(5)	179(10)	−640(11)	50(4)	99(6)	106(7)	−9(4)	−11(4)	82(6)
C(9)	899(5)	1300(12)	−180(13)	49(4)	118(8)	136(8)	−6(5)	−5(5)	109(7)
C(10)	243(6)	1334(14)	−1327(16)	45(5)	157(10)	169(11)	−4(5)	−4(6)	141(9)
C(11)	4342(4)	1610(6)	2962(7)	51(4)	45(3)	42(3)	6(3)	−1(3)	26(3)
C(12)	4936(5)	543(7)	2350(8)	56(4)	56(4)	58(4)	13(3)	3(3)	28(3)
C(13)	5832(5)	909(8)	1846(8)	59(4)	70(5)	56(4)	9(4)	7(3)	31(4)
C(14)	6136(5)	2382(9)	2002(8)	67(5)	77(5)	53(4)	7(4)	10(3)	37(4)
C(15)	5550(6)	3449(9)	2620(9)	74(5)	71(5)	80(5)	6(4)	13(4)	52(4)
C(16)	4644(5)	3076(8)	3086(8)	71(5)	54(4)	68(5)	6(3)	5(4)	38(4)
C(17)	3477(5)	2134(6)	5868(7)	60(4)	33(3)	50(4)	8(3)	9(3)	18(3)
C(18)	2704(5)	2286(7)	6827(9)	80(5)	39(4)	64(5)	5(3)	21(4)	16(3)
C(19)	2906(6)	2845(8)	8486(9)	102(6)	39(4)	69(5)	1(4)	29(5)	18(4)
C(20)	3851(7)	3239(8)	9152(9)	111(7)	47(4)	57(5)	13(4)	13(5)	22(4)
C(21)	4617(6)	3089(7)	8180(8)	88(5)	46(4)	57(4)	20(4)	2(4)	21(3)
C(22)	4424(5)	2532(7)	6531(8)	64(4)	41(3)	52(4)	10(3)	−3(3)	21(3)
C(23)	2986(4)	−772(6)	3232(7)	45(3)	40(3)	51(4)	5(3)	2(3)	24(3)
C(24)	2754(5)	−1848(7)	1638(8)	65(4)	45(4)	53(4)	14(3)	−4(3)	19(3)
C(25)	2604(5)	−3400(8)	1226(8)	65(4)	55(4)	61(4)	18(3)	−2(3)	22(4)
C(26)	2667(5)	−3898(7)	2379(9)	64(4)	48(4)	66(4)	8(3)	15(4)	26(4)
C(27)	2895(6)	−2845(8)	3959(9)	105(6)	56(4)	69(5)	11(4)	19(4)	40(4)
C(28)	3061(6)	−1269(7)	4395(8)	95(5)	51(4)	51(4)	8(4)	6(4)	30(3)

Results and Discussion

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

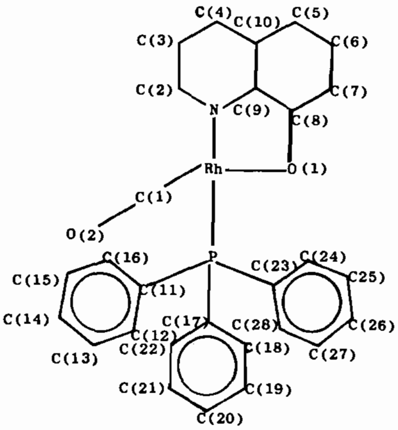

Fig. 1. The numbering system of the atoms of the molecule.

The calculation of the best plane through Rh, N, P, O(1) and C(1) showed that the coordination polyhedron is planar within the experimental error. The ligand-rhodium-ligand bond angles however deviate significantly from 90°, see Table III. This large deviation from 90° can be attributed to the small 'bite' angle (80.0°) of the five membered chelate ring. This angle may be compared with the bite angle (77.8°) of the five membered ring in [Rh(TROP)(CO)(PPh$_3$)], [9].

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

Rh–O(1)	2.042(5)	C(11)–C(12)	1.391(9)
Rh–N	2.098(9)	C(12)–C(13)	1.403(10)
Rh–C(1)	1.786(9)	C(13)–C(14)	1.403(12)
Rh–P	2.261(2)	C(14)–C(15)	1.383(12)
N–C(2)	1.356(13)	C(15)–C(16)	1.401(11)
C(2)–C(3)	1.451(22)	C(16)–C(11)	1.407(10)
C(3)–C(4)	1.369(21)	C(17)–C(18)	1.405(10)
C(4)–C(10)	1.421(19)	C(18)–C(19)	1.417(11)
C(10)–C(5)	1.412(17)	C(19)–C(20)	1.394(13)
C(5)–C(6)	1.374(20)	C(20)–C(21)	1.404(12)
C(6)–C(7)	1.440(18)	C(21)–C(22)	1.406(10)
C(7)–C(8)	1.396(12)	C(22)–C(17)	1.395(9)
C(8)–C(9)	1.424(14)	C(23)–C(24)	1.405(8)
C(9)–C(10)	1.437(19)	C(24)–C(25)	1.399(10)
C(9)–N	1.376(13)	C(25)–C(26)	1.386(13)
O(1)–C(8)	1.328(12)	C(26)–C(27)	1.388(9)
C(1)–O(2)	1.155(11)	C(27)–C(28)	1.417(11)
P–C(11)	1.822(16)	C(28)–C(23)	1.396(12)
P–C(17)	1.826(6)		
P–C(23)	1.830(7)		

The calculation of the best plane through the atoms of the 8-hidroxyquinolinato ligand showed it to be planar within the experimental error. This plane makes an angle of 0.9° with the plane through the coordination polyhedron. The Rh–N bond length is 0.05Å longer than the Rh–O bond distance. This difference may be attributed to the relative *trans* influence of the triphenylphosphine and carbonyl ligands since it is about the same as the difference in the two Rh–O bond distances in [Rh(TROP)(CO)(PPh$_3$)] and [Rh(acac)(CO)(PPh$_3$)] (0.047Å and 0.058Å respectively) which was interpreted in the

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

Rh–C(1)–O(2)	175.2(12)	Rh–P–C(11)	110.7(3)
N–Rh–O(1)	80.0(3)	Rh–P–C(17)	119.7(2)
N–Rh–C(1)	96.3(4)	Rh–P–C(23)	114.5(2)
P–Rh–C(1)	92.3(4)	C(11)–C(12)–C(13)	120.7(7)
P–Rh–O(1)	91.3(2)	C(12)–C(13)–C(14)	119.2(7)
Rh–O(1)–C(8)	114.4(5)	C(13)–C(14)–C(15)	120.2(7)
Rh–N–C(9)	111.0(7)	C(14)–C(15)–C(16)	120.7(8)
O(1)–C(8)–C(9)	117.5(7)	C(15)–C(16)–C(11)	119.4(7)
C(8)–C(9)–N	117.0(10)	C(16)–C(11)–C(12)	119.7(6)
N–C(2)–C(3)	117.7(10)	C(17)–C(18)–C(19)	118.5(7)
C(2)–C(3)–C(4)	120.7(13)	C(18)–C(19)–C(20)	120.7(8)
C(3)–C(4)–C(10)	121.9(16)	C(19)–C(20)–C(21)	120.1(7)
C(4)–C(10)–C(9)	115.4(11)	C(20)–C(21)–C(22)	119.6(7)
C(10)–C(5)–C(6)	120.6(13)	C(21)–C(22)–C(17)	120.1(6)
C(5)–C(6)–C(7)	121.4(10)	C(22)–C(17)–C(18)	121.0(6)
C(6)–C(7)–C(8)	119.4(10)	C(23)–C(24)–C(25)	120.1(7)
C(7)–C(8)–C(9)	119.2(10)	C(24)–C(25)–C(26)	120.8(6)
C(8)–C(9)–C(10)	120.9(9)	C(25)–C(26)–C(27)	119.7(7)
C(9)–C(10)–C(5)	118.5(11)	C(26)–C(27)–C(28)	120.3(9)
C(10)–C(9)–N	122.1(9)	C(27)–C(28)–C(23)	119.9(6)
C(2)–N–C(9)	122.1(10)	C(28)–C(23)–C(24)	119.3(6)

same way, [9, 8]. This difference in the Rh–N and Rh–O bond distance is small in comparison with that found (0.415Å and 0.284Å) in oxoisopropoxobis(8-hydroxyquinolinato)vanadium(V), [13]. This large difference is however probably due to the *trans* influence of the oxo and isopropoxo ligands. Large differences in the metal–nitrogen and metal–oxygen bond distances (as large as 0.13Å) were also observed in tetrakis(5-bromo-8-quinolinatotungsten(IV), [14]. These large differences are probably due to the fact that the coordination polyhedron have a dodecahedral geometry which with the nitrogen atoms in the A and the oxygen atoms in the B positions can accommodate larger differences in M–A and M–B bond lengths compared with square planar complexes, [15].

The C–C, C–N and C–O bond distances and the bond angles in [Rh(oxine)(CO)(PPh$_3$)] agree well with those found in other 8-hydroxyquinolinato complexes, [13, 14].

The phosphorous atom is approximately tetrahedrally surrounded by the rhodium atom and three carbon atoms of the three phenyl rings. The mean P–C distance is 1.826Å and the Rh–P distance is 2.261Å. These values compare well with those found in [Rh(acac)(CO)(PPh$_3$)], [8], and [Rh(TROP)(CO)(PPh$_3$)], [9]. The average C–C bond distance (1.400Å) in the phenyl rings is in good agreement with the normal value (1.394Å) for the aromatic C–C bond. All the bond angles are 120° within the experimental error. The calculation of the best planes through the atoms of the phenyl rings showed that they are planar within the experimental error.

This crystal structure determination shows that the carbonyl group *trans* to the nitrogen atom of the 8-hydroxyquinolinato ligand was substituted by the triphenylphosphine ligand in the reaction

$$[\text{Rh(oxine)(CO)}_2] + \text{PPh}_3 \rightarrow [\text{Rh(oxine)(CO)(PPh}_3)] + \text{CO}.$$

This result indicates that the nitrogen atom in oxine has a larger *trans* influence than the oxygen atom and is thus a better σ-electron donor.

Acknowledgement

We thank Dr. G. Gafner of the South African C.S.I.R. for the data collection, and the South African C.S.I.R. and the Sentrale Navorsingsfonds of this University for financial assistance.

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