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The Crystal Structure of N-benzoyl-N-phenylhydroxylaminocarbonyltriphenylphosphinerhodium(I)

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N-Benzoyl-N-phenylhydroxylaminocarbonyltriphenylphosphinerhodium(I), [Rh(BPHA)(CO)(PPh$_3$)], was prepared by the reaction between [Rh(BPHA)(CO)$_2$] and triphenylphosphine and recrystallized from acetone. The crystal structure of the compound was determined from 4572 unique observed reflections obtained with a computer automated diffractometer. The unit cell is triclinic with a = *14.723* Å, b = *9.567* Å, c = *10.328* Å, *α* = *107.8°, β = 97.2°, γ = 82.9°,* Z = *2 and space group* P$\bar{1}$. *The final* R-*value was 0.042. The structure determination showed that the carbonyl group* trans *to the oxygen atom bonded to the nitrogen atom of the chelate ring was not substituted during the reaction. This result indicates that this oxygen atom of BPHA has a smaller* trans *influence than the other oxygen atom. The Rh–O bond distances indicate that the triphenylphosphine ligand has a larger* trans *influence than the carbonyl group.*

Introduction

The crystal structure of [Rh(BPHA)(CO)(PPh$_3$)], BPHA = N-Benzoyl-N-phenylhydroxylamine and PPh$_3$ = triphenylphosphine, was determined as part of a program for the study of the relative *trans* effects of the atoms L and L′ in complexes of the type [Rh(LL′)(CO)$_2$] and [Rh(LL′)(CO)(PPh$_3$)] (LL′ = bidentate ligands such as β-diketones, 8-hydroxyquinoline, tropolone and BPHA) and the factors that have an influence on the *trans* effect of L and L′. The fact that only one carbonyl group in complexes of the type [Rh(LL′)(CO)$_2$] is substituted by ligands like PPh$_3$ and AsPh$_3$ during the reaction [1]

$$[\mathrm{Rh(LL')(CO)_2}] + \mathrm{PPh_3} \rightarrow [\mathrm{Rh(LL')(CO)(PPh_3)}] + \mathrm{CO} \qquad (1)$$

makes it possible to determine the relative *trans* influence of L and L′ 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 structure determination of [Rh(TTA)(CO)(PPh$_3$)] and [Rh(TFBA)(COD)] (TTA = thenoyltrifluoroacetone, TFBA = benzoyltrifluoroacetone and COD = 1,5-cyclooctadiene) showed that the oxygen atom nearest to the strong electron-attracting CF$_3$–group has the smallest *trans* effect [2, 3]. The crystal structure determination of [RhQ(CO)(PPh$_3$)] (Q = 8-hydroxyquinoline) showed that the nitrogen atom has a larger *trans* effect than the more electronegative oxygen atom as it was the carbonyl group *trans* to the nitrogen atom that was substituted by the triphenylphosphine ligand according to reaction (1) [4].

The Rh–O and Rh–C bonds in the dicarbonyl complexes should be chemical equivalent when L = L′ (as in the case of symmetrical β-diketones like acetylacetone, acac) as was indicated by the results of the crystal structure determination of [Rh(acac)(CO)$_2$] [5]. The significant difference in the Rh–O bond lengths in [Rh(acac)(CO)(PPh$_3$)] and [Rh(TROP)(CO)(PPh$_3$)] (TROP = tropolone) was thus attributed to the difference in the *trans* effect of the CO and PPh$_3$ ligands [6, 7].

Experimental

A solution of [Rh$_2$Cl$_2$(CO)$_4$] was prepared by refluxing a solution of 0.3 g RhCl$_3$·3H$_2$O in 20 cm^3 dimethylformamide for approximately 30 minutes [8]. The colour of the solution changed from red to light yellow during this time. An equivalent amount of N-benzoyl-N-phenylhydroxylamine was added to the resulting yellow solution. About 50 cm^3 cold water was added to precipitate the reaction product [Rh(BPHA)(CO)$_2$]. The precipitate was removed by centrifuging and washed with water, a little ethanol

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TABLE I. Fractional Atomic Coordinates and Thermal Parameters. Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^3$). Estimated Standard Deviations in Parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	2736.8(2)	2654.3(4)	4466.3(4)	36(1)	33(1)	36(1)	1(0)	3(0)	9(0)
P	3509(1)	1456(1)	2661(1)	36(1)	29(1)	35(1)	−1(1)	3(1)	7(1)
C(1)	3146(4)	1188(6)	5217(5)	49(3)	47(3)	42(3)	1(2)	3(2)	11(2)
O(1)	3386(3)	258(5)	5697(4)	97(3)	61(3)	69(3)	12(2)	1(2)	38(2)
O(2)	2233(2)	4362(4)	3717(3)	55(2)	41(2)	42(2)	13(2)	17(2)	16(2)
O(3)	1999(2)	4016(3)	6057(3)	44(2)	41(2)	39(2)	5(1)	10(1)	14(1)
C(2)	1584(3)	5183(5)	5769(4)	34(2)	35(2)	35(2)	−3(2)	4(2)	10(2)
N	1708(3)	5400(4)	4613(4)	45(2)	39(2)	43(2)	3(2)	8(2)	13(2)
C(3)	1288(3)	6595(5)	4097(5)	44(3)	38(3)	45(3)	0(2)	13(2)	17(2)
C(4)	707(4)	6233(6)	2892(6)	53(3)	58(3)	54(3)	−1(3)	2(3)	31(3)
C(5)	259(4)	7364(7)	2387(7)	60(4)	71(4)	78(4)	−1(3)	4(3)	45(3)
C(6)	423(5)	8828(7)	3087(8)	69(4)	65(4)	94(5)	12(3)	24(4)	49(4)
C(7)	1040(5)	9163(6)	4263(7)	77(4)	40(3)	87(5)	3(3)	33(4)	24(3)
C(8)	1488(4)	8040(6)	4790(6)	63(3)	39(3)	63(3)	−4(2)	22(3)	15(3)
C(9)	1010(3)	6219(5)	6793(5)	41(3)	33(2)	43(3)	−5(2)	9(2)	13(2)
C(10)	128(3)	6813(5)	6448(5)	37(3)	36(2)	59(3)	−2(2)	10(2)	15(2)
C(11)	−403(4)	7695(5)	7485(6)	58(3)	32(3)	68(4)	−4(2)	22(3)	13(2)
C(12)	−39(4)	8011(6)	8856(6)	64(4)	52(3)	64(4)	1(3)	24(3)	8(3)
C(13)	849(5)	7428(7)	9185(6)	77(4)	79(4)	45(3)	−1(3)	17(3)	10(3)
C(14)	1377(4)	6515(6)	8161(5)	58(3)	64(4)	42(3)	−3(3)	9(3)	15(3)
C(15)	3808(3)	−520(5)	2365(5)	49(3)	32(2)	36(2)	2(2)	6(2)	8(2)
C(16)	3096(4)	−1392(6)	2328(6)	74(4)	36(3)	60(3)	−12(3)	15(3)	7(3)
C(17)	3290(5)	−2904(6)	2147(7)	98(5)	39(3)	75(4)	−12(3)	24(4)	11(3)
C(18)	4192(6)	−3537(7)	2002(7)	110(6)	41(3)	79(5)	6(4)	17(4)	20(3)
C(19)	4913(5)	−2684(7)	2043(7)	78(4)	45(3)	86(5)	12(3)	4(4)	23(3)
C(20)	4711(4)	−1158(6)	2224(6)	60(3)	39(3)	56(3)	10(2)	3(3)	12(2)
C(21)	2935(3)	1595(5)	1015(5)	42(3)	45(3)	37(2)	−1(2)	4(2)	13(2)
C(22)	2757(6)	379(7)	−82(6)	127(6)	57(4)	44(3)	−6(4)	−18(4)	1(3)
C(23)	2377(7)	567(10)	−1338(7)	176(9)	93(6)	52(4)	−14(6)	−40(5)	11(4)
C(24)	2159(5)	1941(10)	−1496(7)	78(5)	116(6)	49(4)	17(4)	0(3)	33(4)
C(25)	2309(5)	3147(8)	−400(7)	95(5)	88(5)	60(4)	21(4)	12(4)	37(4)
C(26)	2688(5)	2972(6)	874(6)	94(5)	50(3)	50(3)	9(3)	6(3)	18(3)
C(27)	4601(3)	2225(5)	2743(5)	35(2)	31(2)	46(3)	0(2)	3(2)	7(2)
C(28)	4967(4)	2239(6)	1569(6)	49(3)	58(3)	56(3)	−6(3)	15(3)	13(3)
C(29)	5774(4)	2934(7)	1681(7)	49(3)	77(4)	79(4)	−9(3)	17(3)	23(4)
C(30)	6211(4)	3578(7)	2973(8)	43(3)	69(4)	93(5)	−11(3)	9(3)	15(4)
C(31)	5863(4)	3531(7)	4141(7)	49(3)	71(4)	74(4)	−15(3)	0(3)	7(3)
C(32)	5051(4)	2851(6)	4038(6)	43(3)	57(3)	56(3)	−11(2)	−3(2)	9(3)

and ether. It was recrystallized from acetone. [Rh(BPHA)(CO)(PPh$_3$)] was prepared by adding an equivalent amount of triphenylphosphine to a solution of [Rh(BPHA)(CO)$_2$] in acetone. The product was crystallized from acetone. Well formed yellow crystals were obtained.

Crystal data: $C_{32}H_{25}O_3NPRh$, molecular weight 605.4, triclinic space group $P\bar{1}$, a = 14.723 Å, b = 9.567 Å, c = 10.328 Å, α = 107.8°, β = 97.2°, γ = 82.9°, Z = 2, μ(MoKα) = 6.99 cm^{-1}.

The three dimensional intensity data were collected on a Philips PW1100 four circle single crystal X-ray diffractometer. Graphite monochromated MoKα radiation (λ = 0.7107 Å) was used for the data collection for θ values between 3 and 25 °C. Three reflections were used as standards and remeasured after every 60 reflections to monitor possible crystal decay. No decomposition of the crystal was detectable during the data collection. A total of 4801 reflections were measured of which 4572 were considered as observed. Only Lorentz and polarization corrections were applied. A crystal with dimensions 0.8 × 0.5 × 0.4 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 coordinates of the rhodium atom were determined from a three dimensional Patterson function. All the other non-hydrogen atoms were located from two successive Fourier functions. A full matrix least-

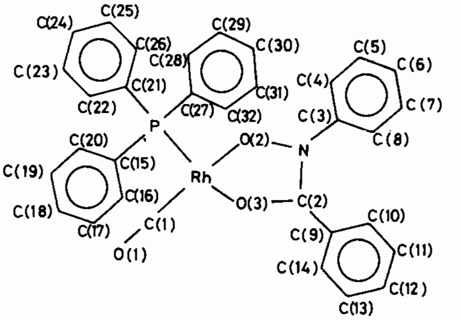

Fig. 1. The numbering system of the atoms of the molecule.

squares refinement, using all the observed reflections and anisotropic temperature parameters for all the atoms gave $R = 0.042$. In the final cycle no positional parameter exhibited shifts of more than 0.3 times its standard deviation.

The atomic scattering factors used were those tabulated by Cromer and Waber [9]. 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 bond angles with their standard deviations are given in Tables II and III respectively.

The calculation of the best plane through the atoms Rh, O(2), O(3), P and C(1) showed that the coordination polyhedron is planar within the experimental error. The various ligand–rhodium–ligand bond angles however deviate significantly from the expected 90° for a dsp^2 hybridization, see Table III. These large deviations from 90° can be attributed to the small 'bite' angle of the five-membered chelate ring (78.4°). The five-membered chelate ring is also planar within the experimental error. This plane makes an angle of 0.6° with the plane through the coordination polyhedron. The two phenyl rings which are bonded to the chelate ring are however not co-planar with the chelate ring – they make angles of 61.1° and 45.2° with the chelate ring. The angle between these two phenyl rings is 58.8°.

The calculation of the best planes through all the phenyl rings showed that they are planar within the experimental error. The average C–C bond distance (1.397 Å) in the phenyl rings is in good agreement with the normal value (1.394 Å) for the aromatic C–C bond [10]. All the bond angles are 120° within the experimental error.

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

Rh–C(1)	1.809(6)
Rh–O(2)	2.037(4)
Rh–O(3)	2.089(3)
Rh–P	2.232(1)
C(1)–O(1)	1.145(8)
O(2)–N	1.366(5)
N–C(2)	1.311(7)
C(2)–O(3)	1.302(6)
N–C(3)	1.446(7)
C(3)–C(4)	1.394(7)
C(4)–C(5)	1.399(9)
C(5)–C(6)	1.402(9)
C(6)–C(7)	1.400(10)
C(7)–C(8)	1.407(9)
C(3)–C(8)	1.398(7)
C(2)–C(9)	1.479(6)
C(9)–C(14)	1.404(7)
C(9)–C(10)	1.401(6)
C(10)–C(11)	1.402(7)
C(11)–C(12)	1.404(8)
C(12)–C(13)	1.400(9)
C(13)–C(14)	1.399(8)
P–C(15)	1.826(5)
P–C(21)	1.837(5)
P–C(27)	1.831(5)
C(15)–C(16)	1.408(8)
C(16)–C(17)	1.399(8)
C(17)–C(18)	1.396(11)
C(18)–C(19)	1.406(11)
C(19)–C(20)	1.411(8)
C(20)–C(15)	1.399(7)
C(21)–C(22)	1.379(7)
C(22)–C(23)	1.402(11)
C(23)–C(24)	1.369(13)
C(24)–C(25)	1.365(10)
C(25)–C(26)	1.414(10)
C(26)–C(21)	1.369(8)
C(27)–C(28)	1.391(8)
C(28)–C(29)	1.408(9)
C(29)–C(30)	1.398(9)
C(31)–C(32)	1.408(9)
C(32)–C(27)	1.404(7)
C(30)–C(31)	1.383(11)

The Rh–C–O chain is approximately linear, 178.5(5)°, with the C–O bond distance 1.145 Å which is the same as found in [Rh(TROP)(CO)(PPh$_3$)] and [Rh(TTA)(CO)(PPh$_3$)] [2, 7].

The phosphorous atom is tetrahedrally surrounded by the rhodium atom and three carbon atoms of the phenyl rings. The mean P–C distance is 1.831 Å, the same as in [RhQ(CO)(PPh$_3$)], [Rh(TROP)(CO)(PPh$_3$)] and Rh(TTA)(CO)(PPh$_3$) [2, 4, 7]. The Rh–P bond distance, 2.232 Å, is the same as in the TTA and TROP complexes but is significantly shorter than the 8-hydroxyquinoline complex. The much

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

Rh–C(1)–O(1)	178.5(5)
C(1)–Rh–P	89.0(2)
P–Rh–O(2)	94.3(1)
O(2)–Rh–O(3)	78.4(1)
O(3)–Rh–C(1)	98.3(2)
Rh–O(2)–N	111.4(3)
Rh–O(3)–C(2)	112.1(3)
O(2)–N–C(2)	119.1(4)
O(3)–C(2)–N	118.9(4)
O(2)–N–C(3)	113.7(4)
N–C(3)–C(4)	117.4(4)
C(3)–C(4)–C(5)	119.1(5)
C(4)–C(5)–C(6)	119.2(6)
C(5)–C(6)–C(7)	120.7(6)
C(6)–C(7)–C(8)	120.7(5)
C(7)–C(8)–C(3)	117.3(5)
C(8)–C(3)–C(4)	122.8(5)
C(3)–N–C(2)	127.0(4)
O(3)–C(2)–C(9)	117.7(4)
N–C(2)–C(9)	123.3(4)
C(2)–C(9)–C(10)	122.8(4)
C(9)–C(10)–C(11)	119.5(5)
C(10)–C(11)–C(12)	119.9(5)
C(11)–C(12)–C(13)	120.0(5)
C(12)–C(13)–C(14)	120.7(5)
C(13)–C(14)–C(9)	118.9(5)
C(14)–C(9)–C(10)	121.0(4)
Rh–P–C(15)	117.3(2)
Rh–P–C(21)	114.8(2)
Rh–P–C(27)	111.7(1)
C(15)–C(16)–C(17)	120.0(6)
C(16)–C(17)–C(18)	119.5(7)
C(17)–C(18)–C(19)	121.4(6)
C(18)–C(19)–C(20)	118.8(6)
C(19)–C(20)–C(15)	120.0(6)
C(20)–C(15)–C(16)	120.4(5)
C(21)–C(22)–C(23)	119.8(7)
C(22)–C(23)–C(24)	121.3(6)
C(23)–C(24)–C(25)	118.9(7)
C(25)–C(26)–C(21)	120.6(5)
C(26)–C(21)–C(22)	119.0(5)
C(24)–C(25)–C(26)	120.3(7)
C(28)–C(29)–C(30)	119.5(7)
C(29)–C(30)–C(31)	120.8(6)
C(30)–C(31)–C(32)	120.0(6)
C(31)–C(32)–C(27)	119.5(6)
C(32)–C(27)–C(28)	120.4(5)
C(27)–C(28)–C(29)	119.8(5)

larger Rh–P bond distance in $[\mathrm{RhQ(CO)(PPh_3)}]$ (2.261 Å) can be attributed to the larger *trans* influence of the nitrogen atom (as a result of the lower electronegativity) in 8-hydroxyquinoline than the oxygen atom in β-diketones, tropolone and BPHA.

The two Rh–O bond distances differ by 0.052 Å. This difference is significantly as it is about 14 times the standard deviation in the Rh–O bond distances and may be attributed to the relative *trans* influence of the triphenylphosphine and carbonyl ligands since it is about the same as the difference in two Rh–O bond distances in $[\mathrm{Rh(TROP)(CO)(PPh_3)}]$ and $[\mathrm{Rh(acac)(CO)(PPh_3)}]$ [6, 7] (0.047 Å and 0.058 Å respectively) which was interpreted in the same way.

The crystal structure determination showed that the carbonyl group *trans* to the oxygen atom bonded to the nitrogen atom of BPHA (see Fig. 1) was not substituted by the $\mathrm{PPh_3}$ ligand in the reaction

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

This result indicated that this oxygen atom has a smaller *trans* influence than the oxygen atom bonded to the carbon atom of the five-membered chelate ring. This is in agreement with the polarization theory and the σ-*trans* effect [11, 12] since the oxygen atom nearest to the more electronegative nitrogen atom (than carbon atom) will be the least polarizable and a weaker σ-donor as a result of the greater electron attracting power of the more electronegative nitrogen atom.

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References

1 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).

2 J. G. Leipoldt, L. D. C. Bok, J. S. van Vollenhoven and A. I. Pieterse, *J. Inorg. Nucl. Chem., 40,* 61 (1978).

3 J. G. Leipoldt, S. S. Basson, G. J. Lamprecht, L. D. C. Bok and J. J. J. Schlebusch, *Inorg. Chim. Acta, 40,* 43 (1980).

4 J. G. Leipoldt, S. S. Basson and C. R. Dennis, *Inorg. Chim. Acta, 50,* 121 (1981).

5 F. Huq and A. C. Skapski, *J. Cryst. Mol. Struct., 4,* 411 (1974).

6 J. G. Leipoldt, S. S. Basson, L. D. C. Bok and T. I. A. Gerber, *Inorg. Chim. Acta, 26,* L35 (1978).

7 J. G. Leipoldt, L. D. C. Bok, S. S. Basson and H. Meyer, *Inorg. Chim. Acta, 42,* 105 (1980).

8 Yu. S. Varshavskii and T. G. Cherkasova, *Russ. J. Inorg. Chem., 12,* 1709 (1967).

9 D. T. Cromer and J. T. Waber, *Acta Cryst., 18,* 104 (1965).

10 L. E. Sutin (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions. Supplement 1956 - 1959,* p. S16s. London; *The Chemical Society.*

11 A. A. Grinberg, *Acta Phisicochim. U.S.S.R., 3,* 573 (1945).

12 C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York (1966).