Inorganica Chimica Acta, 99 (1985) 13–17

The Crystal Structure of N-*o*-Tolylsalicylaldiminatocarbonyltriphenylphosphinerhodium(I)

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Received June 26, 1984

Abstract

N-*o*-tolylsalicylaldiminatocarbonyltriphenylphosphinerhodium(I) was prepared by means of the reaction

$$\mathrm{Rh(sal\text{-}NR)(CO)_2 + PPh_3 \longrightarrow Rh(sal\text{-}NR)(CO)(PPh_3) + CO}$$

The crystal structure of this compound was determined from 3196 unique observed reflections obtained with a computer-automated diffractometer. The compound crystallizes in the space group Pbca with $a = 25.236$ Å, $b = 19.354$ Å and $c = 11.365$ Å. The refinement with anisotropic thermal parameters converged to $R = 0.059$.

This structure determination shows that the carbonyl group *trans* to the nitrogen atom of the Schiff base was substituted by the PPh_3 ligand, which indicates that the nitrogen atom of the chelate ring has a larger thermodynamic *trans* effect than does the oxygen atom.

Introduction

An obvious way to distinguish between the thermodynamic *trans*-effect of two bonded atoms in a square planar configuration is to determine the bond distance between the central atom and two identical atoms *trans* to these atoms. The success of this method was illustrated by the determination of the relative *trans* influence of the oxygen and nitrogen atoms of 8-hydroxyquinoline in the compound 8-hydroxyquinolinato(1,5-cyclooctadiene)rhodium(I), [Rh(oxine)(COD)], [1]. The two Rh–S bond distances (S is the centre of the carbon–carbon double bonds in 1,5-cyclooctadiene) in this compound differ significantly, indicating that the nitrogen atom has a larger *trans* influence than does the oxygen atom. The two Rh–S bond distances in [Rh(acac)(COD)] [2] were as expected the same within experimental error, since the two oxygen atoms of the acac ligand are chemical equivalent. The relative *trans* influence of the two oxygen atoms of the β-diketone trifluorobenzoylacetone (TFBA) was also determined in this way [3].

The fact that only one of the carbonyl groups in complexes of the type [Rh(LL′)(CO)$_2$] (where LL′ = monocharged bidentate ligands such as β-diketones and 8-hydroxyquinoline) can be substituted by neutral ligands like triphenylphosphine [4] makes it possible to determine the relative *trans* influence of the two bonded atoms of LL′, since it may be assumed that the carbonyl group *trans* to the atom with the largest *trans* influence will be substituted by PPh$_3$. The relative *trans* influence of the bonded oxygen atoms in a number of monocharged bidentate ligands was determined in this way [5–7]. The results concerning the relative *trans* influence of the nitrogen and oxygen atoms in oxine as determined by means of the structure determination of [Rh(oxine)(COD)] was also confirmed by the structure determination of [Rh(oxine)(CO)(PPh$_3$)] [8].

The results obtained so far indicate that the most electronegative atom of LL′ or, in the case of β-diketones, the oxygen atom nearest to the most electronegative groups, has the smallest *trans* influence. This is in agreement with the polarization theory [9] and the σ-*trans*-effect [10], since the most electronegative atom or the atom nearest to the most electronegative group will be the least polarizable and also a weaker σ-donor.

Bonnaire *et al.* [11] determined the crystal structure of [Ir(sal-NR)(COD)], (sal-NR = N-*o*-tolylsalicylaldiminato ligand) but were unable to distinguish between the relative *trans* influence of the oxygen and nitrogen atoms of the sal-NR ligand, as the Ir–S bond distances did not differ significantly. In order to determine the relative *trans* influence of the oxygen and nitrogen atoms of sal-NR we solved the crystal structure of [Rh(sal-NR)(CO)(PPh$_3$)], obtained by means of the reaction:

$$\mathrm{[Rh(sal\text{-}NR)(CO)_2] + PPh_3 \longrightarrow [Rh(sal\text{-}NR)(CO)(PPh_3)] + CO.}$$

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0020-1693/85/$3.30

This work was done as part of a program for the study of the relative thermodynamic and kinetic *trans*-effects in square planar complexes of rhodium-(I).

Experimental

The N-*o*-tolylsalicylaldiminato ligand was prepared by the reaction of equivalent amounts of salicylaldehyde and *o*-toluidine in hot methanol [11]. Clear yellow crystals were obtained from the concentrated cooled solution. The crystals were washed with cold methanol and dried under vacuum.

A solution of $[Rh_2Cl_2(CO)_4]$ was prepared by refluxing a solution of 0.4 g $RhCl_3 \cdot 3H_2O$ in 15 cm^3 dimethylformamide for approximately 30 minutes until the colour of the solution changed from red to yellow [12]. An equivalent amount of the Schiff base was added to the resulting yellow solution. This was followed by about 0.1 g sodium bicarbonate. The addition of an excess of water resulted in the separation of a thick oil. The water was decantated and the oil was dissolved in acetone. The slow addition of water to this solution resulted in a fine yellow precipitate. An equivalent amount of PPh_3 was added to a solution of $Rh(sal\text{-}NR)(CO)_2$ in acetone. Well-formed yellow crystals, suitable for data collection, were obtained.

Crystal Data

$C_{33}H_{27}O_2NPRh$, molecular weight 603.5, orthorhombic space group Pbca with a = 25.236 Å, b = 19.354 Å, c = 11.365 Å, z = 8, $\mu(MoK\alpha)$ = 6.51 cm^{-1}.

A crystal with dimensions 0.25 × 0.20 × 0.30 mm^3 was used for the data collection. The three dimensional intensity data were collected on a Philips PW 1100 four circle single crystal X-ray diffractometer using graphite monochromated MoKα radiation (λ = 0.7107 Å) for θ values between 3° and 23°. A total of 4149 reflections were measured, of which 3196 were considered as observed. Three reflections were used as a standard and remeasured after every 60 reflections to check for any decomposition. The data were corrected only for Lorentz and polarization effects.

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 and all the 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 the residual factor R = 0.082. Five cycles of refinement with anisotropic thermal parameters converged to R = 0.059. The atomic scattering factors were those tabulated by Waber [13]. A list of the observed and calculated structure factors may be obtained from the authors. The final positional and thermal parameters with their standard deviations are listed in Table I.

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 are given in Tables II and III respectively. The structure consists of well-separated discrete molecular units.

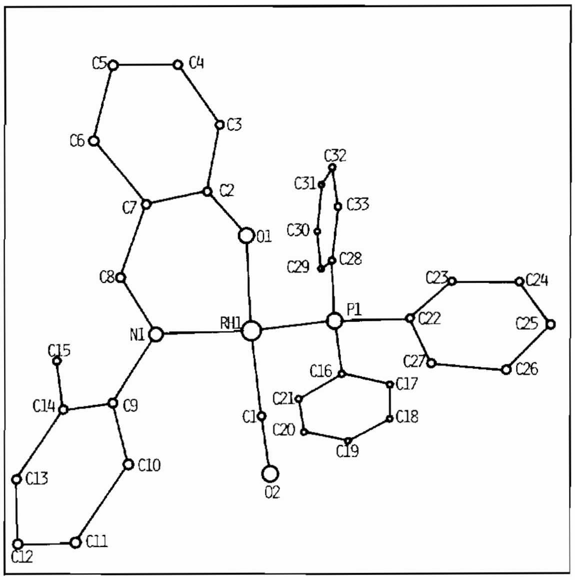

Fig. 1. A perspective view of the molecule showing also the system of numbering of the atoms in the molecule.

The calculation of the best plane through the atoms of the coordination polyhedron showed it to be planar, within experimental error, and all the ligand–rhodium–ligand bond angles are near 90°, as expected from a square planar dsp^2 hybridization in which the 5s, $4p_x$, $4p_y$ and $4d_{x^2-y^2}$ metal orbitals take part. The Rh–N and Rh–O bond lengths (2.092-(7) and 2.027(6) respectively) are about the same as those found in [Ir(sal-NR)(COD)] [11], [Rh(oxine)-(COD)] [1] and $[Rh(oxine)(CO)(PPh_3)]$ [8]. The Pd–O bond lengths in [Pd(dmba)(sal-NH)] [14] (dmba = N,N-dimethylbenzylamine-2-C,N) are however about the same as the Pd–N bond length. The relative large Pd–O bond length in this structure is probably due to the large thermodynamic *trans*-effect of the σ-carbon bond. The N–Rh–O(1) 'bite' angle (88.7(3)°) is in agreement with similar angles found in related complexes with the salicylaldiminato group, presenting an approximately square planar configuration at the central atom. The calculation of the best

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

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	1311.1(3)	171.7(3)	486.8(6)	44(1)	31(1)	35(1)	5(1)	−1(1)	−1(1)
O(1)	1263(3)	114(3)	2264(5)	54(4)	59(4)	35(3)	12(3)	0(3)	1(3)
C(2)	1531(4)	−267(5)	2989(8)	46(5)	53(6)	36(5)	3(5)	0(4)	2(5)
C(3)	1440(4)	−152(6)	4229(9)	64(7)	84(8)	43(6)	−3(6)	6(5)	8(6)
C(4)	1740(5)	−522(7)	5046(10)	73(8)	101(9)	48(6)	9(7)	2(6)	10(7)
C(5)	2123(5)	−1012(7)	4705(9)	96(9)	85(9)	40(6)	16(7)	−10(6)	8(6)
C(6)	2192(5)	−1153(6)	3508(9)	81(8)	62(7)	42(6)	9(6)	−10(6)	11(5)
C(7)	1895(4)	−784(5)	2642(8)	52(6)	46(5)	42(5)	0(5)	−11(5)	7(5)
C(8)	1973(4)	−999(5)	1443(8)	50(6)	48(6)	39(5)	2(5)	−6(5)	4(5)
N	1771(3)	−727(3)	505(6)	42(4)	34(4)	38(4)	7(3)	−5(4)	−3(3)
C(9)	1904(5)	−1099(5)	−586(9)	86(8)	35(5)	57(6)	26(5)	−37(6)	−2(5)
C(10)	2330(4)	−792(6)	−1294(9)	71(7)	79(8)	39(6)	34(6)	16(5)	8(6)
C(11)	2476(6)	−1173(7)	−2279(11)	96(10)	87(9)	67(8)	11(8)	−3(8)	12(7)
C(12)	2219(6)	−1806(7)	−2554(11)	123(12)	91(10)	55(8)	23(9)	−14(8)	12(8)
C(13)	1803(6)	−2080(7)	−1897(10)	122(11)	80(9)	47(7)	42(8)	−12(7)	−2(6)
C(14)	1651(5)	−1703(6)	−809(11)	88(9)	58(7)	75(8)	10(7)	−25(7)	2(6)
C(15)	1232(5)	−1993(7)	−88(12)	67(8)	112(11)	96(10)	−21(8)	4(7)	9(9)
C(1)	1368(4)	290(4)	−1071(9)	50(6)	32(5)	64(6)	17(4)	−7(5)	−1(4)
O(2)	1427(3)	386(4)	−2086(6)	103(6)	69(5)	39(4)	30(4)	3(4)	12(3)
P	793(1)	1135(1)	608(2)	40(1)	26(1)	38(1)	1(1)	0(1)	−1(1)
C(16)	344(3)	1281(4)	−635(8)	34(5)	32(4)	45(5)	0(4)	6(4)	5(4)
C(17)	175(3)	1952(4)	−938(8)	41(5)	38(5)	49(5)	0(4)	2(4)	4(4)
C(18)	−174(4)	2033(5)	−1894(9)	45(6)	56(6)	56(6)	3(5)	1(5)	8(5)
C(19)	−354(4)	1459(6)	−2540(9)	42(6)	73(7)	57(6)	−5(5)	−4(5)	−5(6)
C(20)	−185(4)	805(6)	−2221(9)	60(7)	66(7)	59(7)	−2(6)	−11(6)	−2(6)
C(21)	162(4)	719(5)	−1268(9)	51(6)	40(5)	57(6)	−13(4)	−9(5)	−11(5)
C(22)	1154(3)	1947(4)	700(8)	35(5)	38(5)	44(5)	0(4)	0(4)	−2(4)
C(23)	980(4)	2485(5)	1404(10)	70(7)	33(5)	75(7)	−13(5)	14(6)	−9(5)
C(24)	1245(5)	3134(5)	1385(11)	82(8)	52(6)	80(8)	−16(6)	5(7)	−14(6)
C(25)	1674(5)	3223(6)	648(12)	64(7)	59(7)	99(9)	−12(6)	−15(7)	9(7)
C(26)	1846(5)	2687(6)	−73(12)	61(7)	68(8)	112(10)	−19(6)	18(7)	7(8)
C(27)	1585(4)	2046(6)	−34(10)	55(7)	61(7)	79(8)	−8(5)	20(6)	4(6)
C(28)	353(4)	1146(4)	1897(8)	50(6)	22(4)	43(5)	4(4)	13(4)	−1(4)
C(29)	−197(4)	1050(4)	1756(8)	48(6)	30(5)	57(6)	−2(4)	13(5)	2(4)
C(30)	−519(4)	1011(5)	2752(10)	69(7)	46(6)	63(7)	−11(5)	18(6)	−8(5)
C(31)	−307(5)	1060(5)	3863(10)	74(8)	49(6)	66(7)	−2(6)	25(6)	−13(6)
C(32)	250(5)	1163(5)	4027(9)	89(8)	49(6)	49(6)	4(6)	18(6)	0(5)
C(33)	574(4)	1203(5)	3033(9)	66(7)	34(5)	52(6)	7(5)	5(5)	−6(4)

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

Rh–O(1)	2.027(6)	P–C(16)	1.834(9)
Rh–N	2.092(7)	C(16)–C(17)	1.409(12)
Rh–P	2.281(2)	C(17)–C(18)	1.408(13)
Rh–C(1)	1.791(10)	C(18)–C(19)	1.407(15)
O(1)–C(2)	1.297(11)	C(19)–C(20)	1.385(15)
C(2)–C(7)	1.415(13)	C(20)–C(21)	1.403(14)
C(7)–C(8)	1.438(13)	C(21)–C(16)	1.381(12)
N–C(8)	1.293(12)	P–C(22)	1.819(8)
N–C(9)	1.471(12)	C(22)–C(23)	1.384(13)
C(1)–O(2)	1.177(12)	C(23)–C(24)	1.424(15)
C(2)–C(3)	1.444(13)	C(24)–C(25)	1.379(17)
C(3)–C(4)	1.394(16)	C(25)–C(26)	1.393(18)
C(4)–C(5)	1.410(18)	C(26)–C(27)	1.404(16)
C(5)–C(6)	1.399(14)	C(27)–C(22)	1.386(14)
C(6)–C(7)	1.428(14)	P–C(28)	1.839(9)
C(9)–C(10)	1.469(15)	C(28)–C(29)	1.409(13)
C(10)–C(11)	1.392(17)	C(29)–C(30)	1.396(14)
C(11)–C(12)	1.421(20)	C(30)–C(31)	1.374(16)
C(12)–C(13)	1.393(20)	C(31)–C(32)	1.432(17)
C(13)–C(14)	1.486(17)	C(32)–C(33)	1.397(15)
C(14)–C(15)	1.450(18)	C(33)–C(28)	1.411(13)
C(14)–C(9)	1.357(15)		

plane through the atoms of the chelate ring showed it to be planar, within experimental error. This plane makes an angle of 8.6° with the plane through the coordination polyhedron and an angle of 6.5° with the plane through the phenyl fragment C(2)–C(7).

The *o*-tolyl group shows no significant deviation from planarity and forms an angle of 77.7° with the remainder of the salicylaldiminato residue. This large angle is not unexpected since the corresponding angle in the case of [Ir(sal-NR)(COD)] [11] is 85.7°. The bond lengths and angles in the salicyladiminato ligand are equal (within experimental error) to those found in [Ir(sal-NR)(COD)].

The phosphorous atom is surrounded tetrahedrally by the rhodium atom and three carbon atoms of the phenyl rings. The mean P–C bond distance (1.831 Å) and the Rh–P bond distance (2.281 Å) compare well with those found in [Rh(oxine)(CO)(PPh$_3$)] [8]. The average C–C bond length within the phenyl rings (1.399 Å) is in good agreement with the normal value (1.399 Å) for the aromatic C–C bond [15]. All the bond angles are 120° and all the rings are planar, within experimental error.

The most important aspect of this structure determination is the fact that the PPh$_3$ group is *trans* to the nitrogen atom. This means that the carbonyl group *trans* to the nitrogen atom of the Schiff base ligand was substituted by the triphenylphosphine ligand during the reaction

$$[\mathrm{Rh(sal\text{-}NR)(CO)_2}] + \mathrm{PPh_3} \longrightarrow [\mathrm{Rh(sal\text{-}NR)(CO)(PPh_3)}] + \mathrm{CO}.$$

This result indicates that the nitrogen atom of the salicylaldiminato ligand has a larger *trans* influence than does the oxygen atom. This is in agreement with the observed effect (crystal structure determination of [Ir(sal-NR)(COD)] [11]) of these two atoms on

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

N–Rh–O(1)	88.7(3)	C(12)–C(13)–C(14)	117.0(12)
Rh–O(1)–C(2)	129.3(6)	C(13)–C(14)–C(9)	117.2(11)
O(1)–C(2)–C(7)	124.3(8)	C(13)–C(14)–C(15)	117.9(11)
C(2)–C(7)–C(8)	123.9(8)	Rh–P–C(16)	115.7(3)
C(7)–C(8)–N	127.6(8)	Rh–P–C(28)	113.8(3)
C(8)–N–Rh	124.4(6)	C(21)–C(16)–C(17)	119.8(8)
N–Rh–C(1)	94.1(3)	C(16)–C(17)–C(18)	118.8(8)
C(1)–Rh–P	90.1(3)	C(17)–C(18)–C(19)	121.1(9)
P–Rh–O(1)	87.2(2)	C(18)–C(19)–C(20)	119.1(9)
Rh–N–C(9)	121.6(6)	C(19)–C(20)–C(21)	120.1(10)
C(8)–N–C(9)	113.9(7)	C(20)–C(21)–C(16)	121.1(9)
Rh–C(1)–O(2)	176.9(8)	C(16)–P–C(22)	102.8(4)
C(7)–C(2)–C(3)	118.9(9)	C(27)–C(22)–C(23)	119.6(8)
C(2)–C(3)–C(4)	119.0(10)	C(22)–C(23)–C(24)	120.4(9)
C(3)–C(4)–C(5)	122.2(10)	C(23)–C(24)–C(25)	119.2(10)
C(4)–C(5)–C(6)	119.0(10)	C(24)–C(25)–C(26)	120.6(10)
C(5)–C(6)–C(7)	120.5(10)	C(25)–C(26)–C(27)	119.6(11)
C(6)–C(7)–C(2)	120.1(9)	C(26)–C(27)–C(22)	120.6(10)
N–C(9)–C(10)	115.5(8)	C(22)–P–C(28)	104.2(4)
N–C(9)–C(14)	118.1(9)	C(33)–C(28)–C(29)	120.3(8)
C(14)–C(9)–C(10)	126.2(10)	C(28)–C(29)–C(30)	119.3(9)
C(9)–C(10)–C(11)	114.8(10)	C(29)–C(30)–C(31)	121.0(10)
C(10)–C(11)–C(12)	120.9(12)	C(30)–C(31)–C(32)	120.7(10)
C(11)–C(12)–C(13)	123.6(12)	C(31)–C(32)–C(33)	118.5(9)
		C(32)–C(33)–C(28)	120.2(9)

the Ir–S bond lengths (S are the centres of the C–C double bonds in cyclooctadiene), although the difference in the two Ir–S bond distances is not significant, only two times the standard deviation.

The fact that the nitrogen atom of sal-NR has a larger *trans* influence than does the oxygen atom is in agreement with the polarization theory [9] and the *σ-trans*-effect [10], since the oxygen atom is a weaker σ-donor due to its higher electronegativity. This conclusion about the relative *trans* influence of the nitrogen and oxygen atoms in these type of ligands was also confirmed by means of the structure determinations of [Rh(oxine)(COD)] [1] and [Rh(oxine)(CO)(PPh$_3$)] [2].

The Rh–P bond length is significantly longer in this compound (2.281(2) Å) and in [Rh(oxine)(CO)(PPh$_3$)] (2.261(2) Å) (in both cases are the phosphorous atom *trans* to the nitrogen atom) than in the corresponding β-diketone complexes (about 2.238 Å) with the phosphorous atom *trans* to an oxygen atom [5–7, 16, 17]. This is also an indication that the nitrogen atom has a larger *trans* influence than does the oxygen atom in these type of compounds.

Acknowledgements

We thank Mr. Jon Albain of the South African C.S.I.R. for the data collection and also the C.S.I.R. and the research fund of this University for financial support.

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