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The Crystal Structure of the Methanol Solvate of 2-Carboxypyridinatocarbonyltriphenylphosphinerhodium(I)

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Abstract

2-Carboxypyridinatocarbonyltriphenylphosphinerhodium(I) was synthesized by means of the reaction [Rh(Pic)$(CO)_2$] + PPh_3 → [Rh(Pic)(CO)(PPh_3)] + CO. The crystal structure of this compound was determined from 3031 unique observed reflections obtained with an automated diffractometer. It crystallizes in the triclinic space group $P\bar{1}$ with a = 12.835 Å, b = 11.800 Å, c = 10.020 Å, α = 113.71°, β = 103.55°, γ = 61.19° and with two molecules per unit cell. The final R-value was 4.1%. The carbonyl group *trans* to the nitrogen atom of the carboxypyridinato ligand was substituted by the PPh_3 ligand. This indicates that the nitrogen atom of the chelate ring has a larger thermodynamic *trans* effect than does the oxygen atom.

Introduction

It is well known that only one of the carbonyl groups in complexes of the type [RhLL'$(CO)_2$] can be substituted by neutral ligands such as triphenylphosphine [1]. The two carbonyl groups in these complexes are chemically equivalent when LL' is a symmetrical bidentate ligand such as acac and tropolone, and only one isomer is possible during the reaction

$$[\mathrm{RhLL'(CO)_2}] + \mathrm{PPh_3} \longrightarrow [\mathrm{RhLL'(CO)(PPh_3)}] + \mathrm{CO} \qquad (1)$$

Two isomers are however possible when LL' are nonsymmetrical bidentate ligands such as 1,1,1-trifluoromethyl-3-methyl-1,3-propanedione, 8-hydroxyquinoline and picolinic acid. The determination of the specific isomer that forms during reaction (1) makes it possible to determine the relative *trans*-influence of the two atoms of LL' which are bonded to the rhodium atom as it can be assumed that the carbonyl group, which is situated trans to the atom with the largest *trans*-influence, will be substituted by PPh_3 or $AsPh_3$.

The result of the structure determination of [Rh(oxine)(CO)(PPh_3)], [Rh(oxine)(COD)] and [Rh(Sal-NR)(CO)(PPh_3)], indicated that the nitrogen atom of the chelate ring has a larger *trans*-influence than does the oxygen atom [2–4]. This is in agreement with the polarization theory [5] and the *σ-trans*-effect [6] since the oxygen atom is a weaker σ-electron donor due to its higher electronegativity. The crystal structure of [Rh(Pic)(CO)(PPh_3)], synthesized according to eqn. (1), was determined as part of a program for the study of the relative kinetic and thermodynamic *trans*-effect in square planar complexes of rhodium(I).

Experimental

A solution of [$Rh_2Cl_2(CO)_4$] was prepared by refluxing a solution of 0.5 g $RhCl_3 \cdot 3H_2O$ in 20 cm^3 dimethylformamide for approximately 30 min [7]. An equivalent amount of picolinic acid was added to the resulting yellow solution. About 40 cm^3 cold water was added to precipitate [Rh(Pic)$(CO)_2$]. The precipitate was removed by centrifuging and washed twice with cold water. The wet precipitate was used directly to prepare [Rh(Pic)(CO)(PPh_3)] by adding the precipitate to a solution containing an equivalent amount of triphenylphosphine in methanol, as the violet dicarbonyl compound decomposes during drying in the atmosphere. The [Rh(Pic)(CO)(PPh_3)] precipitated as fine lemon-green crystals after a few min. The precipitate was filtered off and dried in the atmosphere; it was recrystallized from a methanol-acetone mixture. Well-formed yellow crystals, suitable for X-ray analysis, were obtained. An examination of the crystals indicated that only one isomer formed during the reaction. The infra-red spectrum of these crystals shows the presence of one or more methanol molecules.

Crystal data: $C_{25}H_{19}O_3NPRh \cdot CH_3OH$, molecular mass 547.4, triclinic space group $P\bar{1}$ with a = 12.835

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TABLE I. Fractional Atomic Coordinates and Thermal Parameters ($\times 10^3$) with e.s.d.s in Parentheses.

Atom	*x*	*y*	*z*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Rh(1)	0.1882(0)	0.3473(1)	0.0377(1)	37(1)	40(1)	33(1)	−2(0)	0(0)	14(0)
P(1)	0.3061(1)	0.4284(2)	0.2147(2)	34(1)	35(1)	34(1)	−17(1)	0(0)	10(0)
O(1)	0.1901(4)	0.2339(5)	0.1514(5)	71(3)	52(3)	39(3)	−42(3)	−14(2)	22(2)
O(2)	0.1219(5)	0.0904(5)	0.1439(5)	89(4)	71(4)	55(3)	−56(3)	−10(3)	31(3)
O(3)	0.1599(7)	0.5084(8)	−0.1388(7)	142(6)	149(7)	91(5)	−102(6)	−41(4)	88(5)
O(4)	0.2049(7)	0.1092(9)	0.4358(8)	136(7)	169(8)	87(5)	−99(6)	−22(5)	72(5)
N(1)	0.0942(4)	0.2404(5)	−0.1108(5)	37(3)	43(3)	34(3)	−18(3)	0(2)	12(2)
C(1)	0.1343(6)	0.1590(7)	0.0901(7)	55(4)	42(4)	39(4)	−27(3)	0(3)	12(3)
C(2)	0.1733(7)	0.4476(9)	−0.0677(8)	69(5)	83(6)	48(4)	−50(5)	−14(4)	33(4)
C(3)	0.0510(6)	0.2432(7)	−0.2482(7)	44(4)	54(4)	38(4)	−16(3)	1(3)	16(3)
C(4)	−0.0065(6)	0.1619(7)	−0.3374(8)	44(4)	53(5)	45(4)	−17(4)	1(3)	8(4)
C(5)	−0.0216(7)	0.0785(8)	−0.2859(8)	54(5)	55(5)	48(4)	−25(4)	0(4)	0(4)
C(6)	0.0234(6)	0.0752(7)	−0.1442(7)	53(4)	45(4)	43(4)	−27(4)	0(3)	0(3)
C(7)	0.0810(5)	0.1573(6)	−0.0620(7)	40(4)	36(4)	37(4)	−17(3)	0(3)	1(3)
C(8)	0.4361(5)	0.2814(6)	0.2475(7)	30(3)	32(3)	46(4)	−15(3)	0(3)	1(3)
C(9)	0.4972(6)	0.1777(7)	0.1264(8)	45(4)	43(4)	51(4)	−15(3)	1(3)	0(3)
C(10)	0.5987(7)	0.0600(8)	0.1449(9)	54(5)	49(5)	83(6)	−21(4)	1(4)	1(4)
C(11)	0.6338(7)	0.0495(8)	0.2847(10)	50(5)	53(5)	91(6)	−21(4)	−1(4)	28(5)
C(12)	0.5709(6)	0.1550(8)	0.4050(9)	45(4)	51(5)	74(5)	−15(4)	0(4)	26(4)
C(13)	0.4720(6)	0.2712(7)	0.3865(7)	46(4)	47(4)	50(4)	−22(3)	0(3)	20(3)
C(14)	0.2400(5)	0.5341(6)	0.3919(6)	34(3)	32(3)	36(3)	−11(3)	0(3)	11(3)
C(15)	0.1496(6)	0.5172(7)	0.4240(7)	52(4)	50(4)	46(4)	−25(3)	16(3)	10(3)
C(16)	0.0995(7)	0.5969(8)	0.5604(8)	76(5)	64(5)	56(5)	−38(4)	21(4)	10(4)
C(17)	0.1377(7)	0.6927(7)	0.6629(8)	61(5)	50(4)	46(4)	−21(4)	11(4)	13(3)
C(18)	0.2277(6)	0.7091(7)	0.6288(7)	51(4)	52(4)	43(4)	−19(4)	0(3)	1(3)
C(19)	0.2790(6)	0.6299(7)	0.4931(7)	40(4)	49(4)	40(4)	−20(3)	0(3)	1(3)
C(20)	0.3687(6)	0.5287(7)	0.1898(7)	51(4)	43(4)	33(3)	−28(3)	10(3)	1(3)
C(21)	0.4904(6)	0.4933(8)	0.2122(7)	55(5)	68(5)	43(4)	−40(4)	1(3)	1(4)
C(22)	0.5337(8)	0.5784(10)	0.2016(9)	84(6)	91(7)	54(5)	−63(6)	14(4)	1(5)
C(23)	0.4537(10)	0.6983(11)	0.1708(9)	13(9)	90(7)	55(5)	−79(7)	23(5)	1(5)
C(24)	0.3309(9)	0.7341(9)	0.1469(9)	106(8)	59(5)	67(6)	−43(5)	21(5)	16(4)
C(25)	0.2880(7)	0.6478(7)	0.1554(8)	73(5)	40(4)	58(5)	−22(4)	16(4)	15(3)
C(26)	0.2867(12)	0.1625(14)	0.4801(14)	156(12)	169(12)	131(10)	−121(11)	−63(9)	100(10)

Å, b = 11.800 Å, c = 10.020 Å, α = 113.71°, β = 103.55°, γ = 61.19°, z = 2, d_{exp} = 1.494 g cm^{-3}, d_{calc} = 1.495 g cm^{-3} and $\mu(MoK_\alpha)$ = 8.2 cm^{-1}.

The three dimensional intensity data were collected on a Philips PW1100 single crystal X-ray diffractometer. Graphite monochromated MoK_α radiation (λ = 0.7107 Å) was used for the data collection. Three reflections were used as standards and were re-measured after every 60 reflections. No decomposition of the crystal was detectable during the data collection. A total of 3337 independent reflections were measured for θ between 3° and 26°, of which 3031 were considered as observed. A crystal with dimensions 0.30 × 0.23 × 0.35 mm^3 was used for the data collection. The data were corrected only for Lorentz and polarization effects, μ = 8.2 cm^{-1}.

The structure was solved by using the X-ray 72 systems 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. A full matrix least squares refinement, using all the observed reflections and anisotropic thermal parameters for all the atoms, gave R = 0.041. The atomic scattering factors were those tabulated by Cromer and Waber [8]. 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.

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.

The calculation of the best plane through the atoms of the co-ordination polyhedron showed it to be planar, within experimental error. The ligand–

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

Rh(1)–P(1)	2.262(2)	C(8)–C(9)	1.386(8)
Rh(1)–O(1)	2.066(7)	C(9)–C(10)	1.424(10)
Rh(1)–N(1)	2.088(6)	C(10)–C(11)	1.404(14)
Rh(1)–C(2)	1.802(11)	C(11)–C(12)	1.395(10)
P(1)–C(8)	1.827(6)	C(12)–C(13)	1.399(9)
P(1)–C(14)	1.829(6)	C(13)–C(8)	1.396(10)
P(1)–C(20)	1.829(10)	C(14)–C(15)	1.392(13)
O(1)–C(1)	1.278(10)	C(15)–C(16)	1.402(10)
O(2)–C(1)	1.219(13)	C(16)–C(17)	1.391(12)
O(2)–O(4)	2.825(9)	C(17)–C(18)	1.393(15)
C(2)–O(3)	1.134(15)	C(18)–C(19)	1.402(9)
C(3)–N(1)	1.365(9)	C(19)–C(14)	1.391(10)
C(7)–N(1)	1.347(12)	C(20)–C(21)	1.398(10)
C(1)–O(2)	1.219(13)	C(21)–C(22)	1.406(18)
C(1)–C(7)	1.513(9)	C(22)–C(23)	1.403(14)
C(3)–C(4)	1.394(12)	C(23)–C(24)	1.410(17)
C(4)–C(5)	1.383(15)	C(24)–C(25)	1.405(17)
C(5)–C(6)	1.410(10)	C(25)–C(20)	1.414(10)
C(6)–C(7)	1.385(11)	C(26)–O(4)	1.372(22)

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, 79.0°, of the five-membered chelate ring. This angle may be compared with the 'bite' angle (80.0°) in [Rh(oxine)(CO)(PPh$_3$)], [2].

The calculation of the best plane through the atoms of the 2-carboxypyridinato ligand showed it to be planar, within experimental error, and approximately co-planar (2.25°) with the co-ordination polyhedron. The rhodium–ligand bond lengths compare well with those found in [Rh(oxine)(CO)(PPh$_3$)] and [Rh(SAL-NR)(CO)(PPh$_3$)], [2, 4].

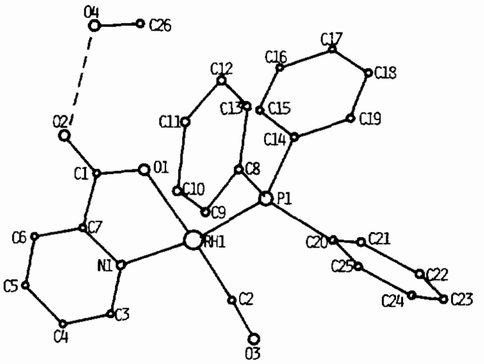

Fig. 1. Perspective view of the molecule with atom numbering scheme.

The methanol molecule is hydrogen bonded to the keto group of the carboxylic acid, O(4)–O(2) = 2.825 Å.

The phosphorus atom is surrounded approximately tetrahedrally by the rhodium atom and three carbon atoms of the three phenyl rings. The mean P–C bond distance, 1.829 Å, and the Rh–P bond distance compare well with those found in [Rh(oxine)(CO)(PPh$_3$)] and in [Rh(SAL-NR)(CO)(PPh$_3$)], [2, 4]. The average C–C bond length in the phenyl rings (1.402 Å) is in good agreement with the normal value (1.399 Å) for the aromatic C–C bond [9]. All the bond angles are 120°, and the rings are planar, within the experimental error.

This crystal structure determination shows that the carbonyl group *trans* to the nitrogen atom of the 2-carboxypyridinato ligand was substituted by the triphenylphosphine ligand during reaction (1). This result indicates that the nitrogen atom of the chelate ring has a larger *trans*-influence than

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

P(1)–Rh(1)–O(1)	90.9(1)	C(9)–C(10)–C(11)	119.6(6)
P(1)–Rh(1)–C(2)	93.5(3)	C(10)–C(11)–C(12)	120.1(7)
O(1)–Rh(1)–N(1)	78.9(2)	C(11)–C(12)–C(13)	120.1(8)
N(1)–Rh(1)–C(2)	96.9(3)	C(13)–C(8)–C(9)	120.9(5)
Rh(1)–C(2)–O(3)	176.5(8)	Rh(1)–P(1)–C(14)	114.6(2)
Rh(1)–O(1)–C(1)	116.5(5)	C(14)–C(15)–C(16)	119.0(7)
N(1)–C(3)–C(4)	120.9(9)	C(15)–C(16)–C(17)	121.3(9)
C(3)–C(4)–C(5)	119.7(7)	C(16)–C(17)–C(18)	119.0(7)
C(4)–C(5)–C(6)	119.3(8)	C(17)–C(18)–C(19)	120.4(7)
C(5)–C(6)–C(7)	117.9(9)	C(18)–C(19)–C(14)	119.9(8)
N(1)–C(7)–C(6)	122.9(6)	C(19)–C(14)–C(15)	120.4(6)
N(1)–C(7)–C(1)	115.1(6)	Rh(1)–P(1)–C(20)	121.0(2)
O(1)–C(1)–C(7)	115.7(8)	C(20)–C(21)–C(22)	119.4(7)
O(2)–C(1)–C(7)	118.9(7)	C(21)–C(22)–C(23)	119.3(9)
C(3)–N(1)–C(7)	119.1(6)	C(22)–C(23)–C(24)	121.6(13)
Rh(1)–N(1)–C(7)	113.5(4)	C(23)–C(24)–C(25)	119.0(9)
Rh(1)–P(1)–C(8)	107.7(2)	C(24)–C(25)–C(20)	119.2(8)
C(8)–C(9)–C(10)	119.3(7)	C(25)–C(20)–C(21)	121.5(9)
C(12)–C(13)–C(8)	120.0(6)		

does the oxygen atom. This is in agreement with the results of the structure determination of [Rh(oxine)(CO)(PPh_3)], [Rh(oxine)(COD)] and [Rh(SAL-NR)(CO)(PPh_3)], [2–4].

The Rh–P bond length in this compound (2.262(2)) and in the corresponding oxine and SAL-NR compounds (the phosphorus atom is in all these cases *trans* to the nitrogen atom) is significantly longer than in the corresponding β-diketone complexes (about 2.238 Å) with the phosphorus atom *trans* to an oxygen atom [10–14]. This result also indicates that the nitrogen atom has a larger *trans*-influence than does the oxygen atom in these type of compounds.

There is no rhodium–rhodium interaction, for steric reasons. Rhodium–rhodium interaction is however possible in the case of [Rh(Pic)($CO)_2$] and may explain its intense violet colour and dichroic behaviour in the solid state [15, 16].

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