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Note

First structural confirmation of different geometrical isomers in the same crystal lattice: the crystal structure of benzoylacetonatocarbonyltriphenylphosphinerhodium(I)

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Abstract

The first structural confirmation of two different [Rh(BA)(CO)(PPh$_3$)] isomers (BA = benzoylacetonate, $CH_3(CO)CH(CO)C_6H_5$), namely one with PPh$_3$ *cis* to the oxygen atom nearest to the phenyl group and the second isomer with PPh$_3$ *trans* to the oxygen nearest to the phenyl group, in the same crystal lattice is reported. The small influence of the different substituents is illustrated by the near equal Rh–O, Rh–P and Rh–C bond distances in the two different isomers. The structure crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 15.625(2)$, $b = 19.138(2)$, $c = 8.891(2)$ Å, $\alpha = 95.66(1)$, $\beta = 74.43(1)$, $\gamma = 90.52(1)°$ and $Z = 4$. The Rh–P, Rh–CO and Rh–O bond distances for isomer I are 2.249(3), 1.739(14), 2.032(8) and 2.079(8) Å, respectively, while the corresponding bond distances for isomer II are 2.248(3), 1.768(14), 2.018(8) and 2.057(7) Å, respectively.

Keywords: Crystal structures; Geometrical isomers; Rhodium complexes; Carbonyl complexes

1. Introduction

The substitution of one of the carbonyl groups in complexes of the type [Rh(LL′)(CO)$_2$] (when LL′ = monoanionic bidentate ligands such as β-diketonate, cupferrate, 8-hydroxyquinolate etc.) with a phosphorus ligand allows in principle the formation of two isomers. Crystal structure determinations of [Rh(TTA)(CO)(PPh$_3$)] [1] (TTA = 2-thenoyltrifluoroacetonate), [Rh(pic)(CO)(PPh$_3$)] [2] (pic = 2-carboxypyridinate) and [Rh(Sacac)(CO)(PPh$_3$)] [3] (Sacac = thioacetylacetonate) revealed that substitution takes place *trans* to the donor atom of the bidentate ligand exerting the larger *trans* influence. Bulky substituents and comparative electronegative substituent groups on a bidentate ligand alter the choice as illustrated by the structure determinations of [Rh(MACSM)(CO)(PPh$_3$)] [4] (MACSM = methyl(2-methylamino-1-cyclopentene-1-dithiocarboxylate) and [Rh(TFTMAA)(CO)(PPh$_3$)] [5] (TFTMAA = 1,1,1-trifluoro-5,5,5-trimethylpentanedionate). All the above mentioned studies, contrary to what one would expect, point to the existence of one isomer.

Recently some of the above-mentioned Rh(I) complexes as well as some Rh(I)–aminovinylketonato complexes were subjected to ^{13}C and ^{31}P NMR studies [6–9]. These studies clearly showed that only one [Rh(Oxq)(CO)(PPh$_3$)] (Oxq = 8-hydroxyquinolate) isomer is produced during the substitution reaction while all the aminovinylketonato complexes ([Rh(RC(NH)CH(CO)R′)(CO)(PPh$_3$)]) as well as the β-diketonato complexes of general formula [Rh(CF$_3$(CO)CH(CO)R)(CO)(PPh$_3$)] (R = CH$_3$, C$_6$H$_5$ and 2-thienyl) confirm the existence of two isomers in solution. It was shown that the predominant isomer in solution corresponds to the same isomer that was isolated in the solid state. It was also found that the isomer ratio of some of the Rh(I)–aminovinylketonato complexes are sensitive to the type of solvent used and proved the existence of a dynamic equilibrium between the two isomers in solution. We have recently shown [10] through successful TLC separation of an [Rh(CO)(AnMetha)(P(OCH$_2$)$_3$CCH$_3$)] isomer pair (AnMetha = *N*-methyl-*p*-methoxyphenylthiohydroxa-

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mato ligand) that the isomerization is a slow dissociatively activated process involving a rate determining chelate ring-opening step and that the reaction rate can be increased in more polar solvents.

We isolated the [Rh(BA)(CO)(PPh$_3$)] complex (BA = benzoylacetonate, CH$_3$(CO)CH(CO)C$_6$H$_5$) as part of our ongoing research on the solid state and kinetic behaviour of Rh(I) systems and hereby report the first structure determination of an Rh(I) complex which has both the isomers present in the same unit cell.

2. Experimental

[Rh(BA)(CO)(PPh$_3$)], formula weight = 1108.72, triclinic, space group $P\bar{1}$ with $a = 15.625(2)$, $b = 19.138(2)$, $c = 8.891(2)$ Å, $\alpha = 95.66(1)$, $\beta = 74.43(1)$, $\gamma = 90.52(1)$°, $Z = 4$ (two independent molecules), $D_{calc} = 1.45$ g cm^{-3} and μ(Mo Kα) = 0.761 mm^{-1}.

A crystal (thin plate) with dimensions 0.25 × 0.1 × 0.03 mm was used for the data collection. The three-dimensional intensity data, using an Enraf-Nonius CAD4 diffractometer, were collected at 298 K for θ values between 3 and 20° using Mo Kα radiation. The index ranges were $-14 < h < 14$, $-18 < k < 18$ and $0 < l < 8$. A total of 4481 independent reflections was measured of which 3079 were considered as observed ($I > 2\sigma I$). The data were corrected for Lorentz, polarization, decay and absorption effects. The final R was 0.060 using all observed reflections, and refinement of all the non-hydrogen atoms anisotropically. The hydrogen atom positions were calculated (phenyl hydrogen C–H = 0.93 Å; methyl group C–H = 0.96 Å) riding on the adjacent carbon atom and refined with an overall isotropic thermal parameter. The structure was solved and parameters refined using the SHELXS86 and SHELXL93 program systems [16,17]. The final difference Fourier showed no sign of disorder. Atomic coordinates and equivalent isotropic displacement parameters are given in Table 1.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for [Rh(BA)(CO)(PPh$_3$)]

	x	y	z	U_{eq} [a]
Rh(1) [b]	3359(1)	4271(1)	516(1)	50(1)
P(1)	2069(2)	4566(2)	2319(4)	53(1)
C(11)	3250(8)	3421(7)	1068(17)	64(4)
O(11)	3160(7)	2866(5)	1514(14)	99(4)
O(13)	3510(5)	5253(4)	−191(8)	49(2)
O(12)	4524(6)	3975(4)	−1200(10)	67(2)
C(12)	5019(8)	4351(7)	−2203(15)	59(4)
C(13)	4814(9)	4987(7)	−2312(16)	70(4)
C(14)	4122(8)	5438(7)	−1332(12)	49(3)
C(15)	5780(9)	3942(7)	−3371(15)	66(4)
C(141)	4070(12)	6214(9)	−1786(17)	72(4)
C(142)	4759(14)	6532(8)	−2494(23)	98(5)
C(143)	4617(11)	7228(10)	−2842(21)	109(6)
C(144)	3789(10)	7570(8)	−2355(24)	110(7)
C(145)	3087(12)	7116(10)	−1785(22)	111(6)
C(146)	3232(17)	6476(12)	−1342(24)	130(7)
C(111)	1521(7)	5342(5)	2061(13)	37(3)
C(112)	1917(8)	5953(7)	2272(13)	60(4)
C(113)	1502(11)	6576(8)	2015(18)	87(5)
C(114)	685(10)	6584(9)	1688(16)	71(4)
C(115)	355(10)	5972(9)	1472(19)	87(5)
C(116)	756(11)	5340(8)	1665(15)	80(4)
C(121)	1219(8)	3915(6)	2466(14)	49(3)
C(122)	1200(8)	3465(6)	1092(14)	54(4)
C(123)	608(8)	2948(7)	926(20)	75(4)
C(124)	1(8)	2864(6)	2285(14)	54(3)
C(125)	−47(7)	3244(6)	3769(15)	55(3)
C(126)	548(8)	3752(7)	3784(16)	63(4)
C(131)	2116(8)	4701(6)	4311(14)	52(3)
C(132)	2736(10)	4374(8)	4788(16)	84(5)
C(133)	2801(12)	4373(8)	6378(20)	83(5)
C(134)	2246(13)	4838(10)	7352(20)	93(6)
C(135)	1607(10)	5261(8)	7030(16)	78(4)
C(136)	1568(10)	5135(7)	5468(15)	67(4)
Rh(2)	8352(1)	1067(1)	6107(1)	47(1)
P(2)	7088(2)	650(2)	5643(3)	42(1)
C(21)	8101(7)	1859(7)	5434(15)	55(3)
O(21)	7904(7)	2409(7)	5014(13)	100(3)
O(22)	8675(6)	175(4)	6880(8)	51(2)
O(23)	9505(5)	1464(4)	6519(9)	58(2)
C(22)	9400(8)	34(7)	7132(15)	57(3)
C(23)	10059(8)	423(7)	7190(12)	52(3)
C(24)	10152(8)	1128(6)	6904(13)	52(3)
C(25)	9461(9)	−721(8)	7590(17)	82(5)
C(241)	10888(8)	1584(6)	7050(14)	51(3)
C(242)	11014(9)	2187(8)	6279(18)	74(4)
C(243)	11722(12)	2604(7)	6335(19)	87(5)
C(244)	12290(10)	2433(11)	7211(26)	93(6)
C(245)	12170(10)	1861(12)	7963(21)	97(7)
C(246)	11498(9)	1420(8)	7849(16)	68(4)
C(211)	6671(6)	−131(5)	6568(11)	27(2)
C(212)	5831(7)	−142(6)	7602(11)	40(3)
C(213)	5546(7)	−733(7)	8262(13)	52(3)
C(214)	6074(10)	−1331(6)	7955(20)	73(4)
C(215)	6911(10)	−1311(7)	6928(14)	62(4)
C(216)	7210(8)	−729(6)	6192(13)	49(3)
C(221)	7160(8)	441(6)	3566(14)	54(3)
C(222)	7747(8)	740(6)	2428(13)	54(3)
C(223)	7749(10)	590(8)	824(16)	85(5)
C(224)	7245(11)	63(7)	406(17)	85(5)
C(225)	6657(9)	−249(6)	1539(15)	55(3)
C(226)	6626(7)	−89(5)	3091(12)	39(3)
C(231)	6147(7)	1263(5)	6295(12)	39(3)
C(232)	5473(7)	1271(5)	5634(14)	39(3)
C(233)	4749(10)	1734(6)	6224(18)	77(5)
C(234)	4722(9)	2191(5)	7578(14)	58(4)
C(235)	5363(9)	2181(8)	8358(18)	76(4)
C(236)	6065(1)	1708(7)	7728(17)	74(4)

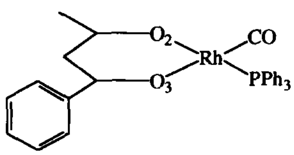
[a] $U_{eq} = 1/3\ \Sigma_i \Sigma_j U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* (a_i a_j)$.

[b] The first digit refers to the isomer.

3. Results and discussion

Reaction of the dinuclear complex, $[Rh(CO)_2Cl]_2$, with 2 equiv. BA in DMF at room temperature affords the $[Rh(BA)(CO)_2]$ complex. Slow addition of H_2O precipitated bright orange crystals. Reaction between $[Rh(BA)(CO)_2]$ and equimolar PPh_3 afforded the title complex ($\nu(CO) = 2074$ and 1998 cm^{-1}, KBr matrix). Yellow plate like crystals were obtained from an acetone/water solution at ~293 K.

The structure of $[Rh(BA)(CO)(PPh_3)]$ was determined by X-ray diffraction methods. The space group $P\bar{1}$ required two independent molecules ($Z = 4$) in the unit cell which turned out to be the two different isomers, namely the isomer with PPh_3 *cis* to the oxygen nearest to the phenyl group (I) and the second isomer with PPh_3 *trans* to the oxygen nearest to the phenyl group (II).



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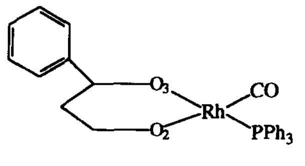
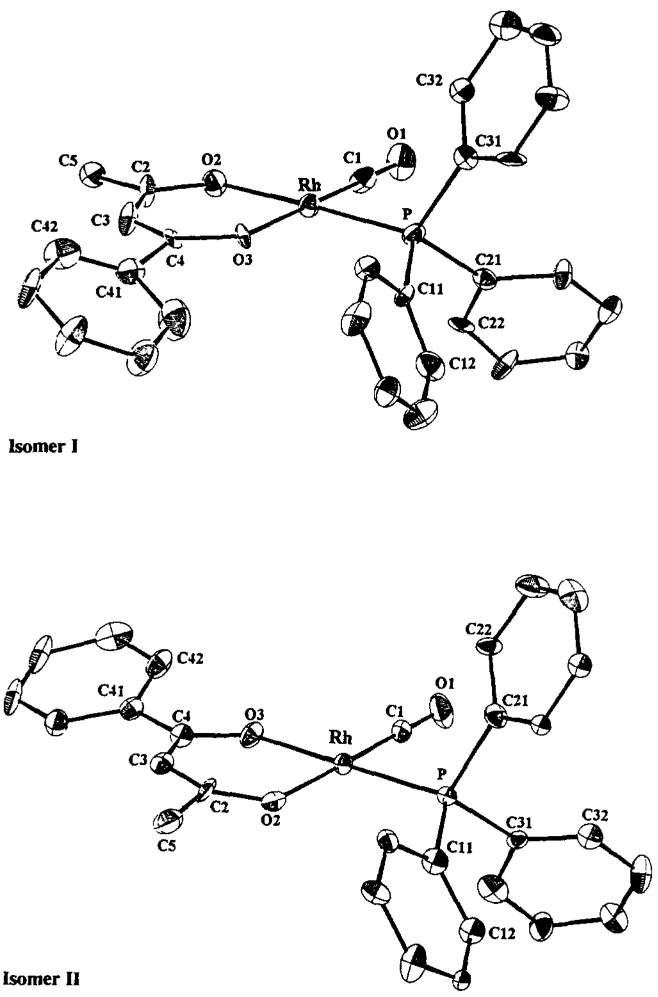


II

^1H NMR spectra ($CDCl_3$ at 296 K) clearly showed the existence of both isomers in solution (two methine peaks; $\delta_I = 6.15$, $\delta_{II} = 6.06$; methyl groups: $\delta_I = 2.25$, $\delta_{II} = 1.68$ ppm, average integrated peak ratio $I_I/I_{II} = 2.22$) with a mole ratio of 2:1. This was also verified with ^{31}P NMR spectra in $CDCl_3$ ($\delta_I = 49.6$, $\delta_{II} = 49.3$ ppm; $^1J(P\text{–}Rh)_I = 175.6$; $^1J(P\text{–}Rh)_{II} = 174.3$ Hz; average integrated peak ratio $I_I/I_{II} = 2.02$) and deuteroacetone ($\delta_I = 50.47$; $\delta_{II} = 49.73$ ppm; $^1J(P\text{–}Rh)_I = 172.6$; $^1J(P\text{–}Rh)_{II} = 175.2$ Hz; average integrated peak ratio $I_I/I_{II} = 1.99$). These doublets in the ^{31}P NMR spectra could not be verified in a related study [6] on the same complex. It is also interesting to note that for similar complexes, $[Rh(quin)(CO)(P(R\text{-}C_6H_4)_3]$, (quin = 2-quinaldinate anion; R = 4-Me, 3-Me, 4-MeO, 4-F, 4-Cl), it was only in the case of the halo-substituted phosphine ligands where two isomers could be detected in the ^{31}P NMR [11] spectra.

A perspective drawing, indicating the numbering scheme for the two isomers, is shown in Fig. 1 while the most important bond distances and angles are reported in Table 2. The Rh–P and Rh–CO bond distances in both the isomers are in agreement with those found in other β-diketone complexes. The Rh–P bond distances in the two isomers are the same within experimental error, 2.248(3) and 2.249(3) Å for isomers I and II, respectively. The complex has an approximate square-planar geometry with the Rh, P, carbonyl carbon and the two BA oxygen atoms in the same plane.



Isomer I

Isomer II

Fig. 1. Perspective drawing and numbering scheme of the two different isomers in $[Rh(BA)(CO)(PPh_3)]$.

Table 2
Selected bond distances and angles for the different isomers in $[Rh(BA)(CO)(PPh_3)]$

	Isomer I	Isomer II
Rh–P	2.249(3)	2.248(3)
Rh–C(1)	1.739(14)	1.768(14)
Rh–O(2)	2.079(8)	2.018(8)
Rh–O(3)	2.032(8)	2.057(7)
C(1)–O(1)	1.16(2)	1.22(2)
Rh–C(1)–O(1)	176.6(13)	177.8(11)
C(1)–Rh–O(2)	90.3(5)	178.2(4)
C(1)–Rh–O(3)	178.3(5)	92.1(4)
O(2)–Rh–O(3)	88.1(3)	86.2(3)
O(2)–Rh–P	177.8(3)	94.8(2)
O(3)–Rh–P	92.6(2)	179.0(2)
O(1)–Rh–P	88.9(4)	87.0(4)

The fact that both isomers are found in the same crystal lattice, in contrast to what has been observed for other β-diketone complexes, is rare and a somewhat fortuitous phenomenon. Factors like thermodynamic control, ligand basicity, metal type and especially solvent polarities are among those studied for a number of geometrical isomers of d^8 complex ions [12]. These often act in concert so that an unequivocal explanation for a specific isomer choice in the solid state is seldom at hand.

A compilation of crystal structures for [Rh(LL′)(CO)(PPh$_3$)] complexes [13] has shown that the reaction of equimolar or excess PPh$_3$ on the precursor [Rh(LL′)(CO)$_2$)] complexes (LL′ = unsymmetrical β-diketones) gave substitution of only one CO group and that the preferred solid state isomer had a *cis*-like arrangement, that is, with PPh$_3$ *cis* to the more electronegative substituent of the β-diketone ring. Since most of these crystallizations were done in acetone or acetone/water media, the preferred *cis*-like isomer choice is in accord with the general finding that polar solvents favour *cis*-isomers as found in for example square-planar palladium(II)–phosphine complexes [14]. Although the NMR data show a 2:1 isomer ratio in different solvents, the effect of added water to promote crystallization in the acetone solution must have changed the solution polarity and perhaps the isomer composition ratio towards a 1:1 ratio. Such a change is however no pre-requisite towards similtaneous crystallization of these isomers since only one form usually dominates the solid state geometry.

Another equalizing factor between the *cis*- and *trans*-like forms should be the near equal group electronegativities [15] of 2.55 and 2.58 for the methyl and phenyl substituents, respectively. As a result of this there is within experimental error no meaningful difference between Rh–O, Rh–P and Rh–C bond distances (Fig. 1) for the two isomers. Furthermore, only one CO stretching frequency (1978 cm^{-1}; KBr matrix) is indicative of very similar bond orders for the CO ligands if compared to distinguishable differences in those of the [Rh(CO)(AnMetha)(P(OCH$_2$)$_3$CCH$_3$)] isomer pair. Given these similarities, we suggest that a fine balance of thermodynamic control over enthalpy and entropy related factors together with minimization of crystallization energy and associate packing effects are responsible for this unusual crystal composition.

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References

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

[2] J.G. Leipoldt, G.J. Lamprecht and D.E Graham, *Inorg. Chim. Acta, 101* (1985) 123.

[3] L.J. Botha, S.S. Basson and J.G. Leipoldt, *Inorg. Chim. Acta, 126* (1987) 25.

[4] G.J.J. Steyn, A. Roodt and J.G. Leipoldt, *Inorg. Chem., 31* (1992) 3477.

[5] J.G. Leipoldt, S.S. Basson and J.H. Potgieter, *Inorg. Chim. Acta, 117* (1986) L3.

[6] A.M. Trzeciak and J.J. Ziólkowski, *Inorg. Chim. Acta, 96* (1985) 15.

[7] T.G. Cherkasova, L.V. Osetrova and Yu.S. Varshavsky, *Rhodium Express, 1* (1993) 8.

[8] T.G. Cherkasova, Yu.S. Varshavsky, I.M. Podkorytov and L.V. Osetrova, *Rhodium Express, 0* (1993) 21.

[9] M.R. Galding, T.G. Cherkasova, L.V. Osetrova and Yu.S. Varshavsky, *Rhodium Express, 1* (1993) 14.

[10] S.S. Basson, J.G. Leipoldt, E.C. Steynberg and D.M.C. Smit, *Rhodium Express, 0* (1993) 16.

[11] M. Cano, J.V. Heras, M.A. Lobo and E. Pinilla, *Polyhedron, 11* (1992) 2679.

[12] (a) G.K. Anderson and R.J. Cross, *Chem. Soc. Rev., 9* (1980) 185; (b) R.J. Cross, *Adv. Inorg. Chem., 34* (1989) 219.

[13] D.E. Graham, G.J. Lamprecht, I.M. Potgieter, A. Roodt and J.G. Leipoldt, *Transition Met. Chem.,* (1991) 193.

[14] A.W. Verstuyft and J.H. Nelson, *Inorg. Chem., 14* (1975) 1501.

[15] R.J. Boyd and S.L. Boyd, *J. Am. Chem. Soc., 114* (1992) 1652.

[16] G.M. Sheldrick, *SHELXS86*, program for the solution of crystal structures, University of Göttingen, Germany, 1986.

[17] G.M. Sheldrick, SHELXL93, *J. Appl. Crystallogr.,* (1994) to be published.