Journal of Organometallic Chemistry, 247 (1983) 345–350
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE CRYSTAL AND MOLECULAR STRUCTURE OF *trans*-CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)RHODIUM(I) IN ITS MONOCLINIC FORM

A. CERIOTTI, G. CIANI and A. SIRONI*

Centro del C.N.R. di Studio sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Via G. Venezian 21, 20133 Milano (Italy)

(Received November 16th, 1982)

Summary

The structure of the title compound, $RhCl(CO)(PPh_3)_2$, has been investigated in its monoclinic modification. It belongs to space group $P2_1/n$ (No. 14), with cell constants a 12.182(3), b 24.285(5), c 11.894(3) Å, β 113.10(2)°, $Z = 4$. The structure was solved by conventional Patterson and Fourier methods, on the basis of 4295 significant counter data, by least-squares methods to a final conventional R value of 0.051. The complex exhibits a square planar coordination, with the two bulky phosphine ligands in mutually *trans* positions. The mean value of the Rh–P bond lengths is 2.326 Å. The Rh–Cl, Rh–C and C–O bond lengths are 2.371(2), 1.810(7), and 1.144(8) Å, respectively. The structure is compared with those of similar species and the small differences observed between the monoclinic and triclinic modifications of this compound are discussed.

Introduction

As a part of a structural investigation of carbonylrhodium(I) complexes we describe here the structure of the well known compound $RhCl(CO)(PPh_3)_2$ in its monoclinic form. The compound was prepared as previously reported [1], washed with ethanol and recrystallized by slow diffusion of isopropanol into a THF solution. The crystalline material showed the presence of two types of crystals, different in morphology, in colour and in the frequencies of the carbonyl stretching bands in their IR spectra in Nujol mulls. One of the two types of crystals, dark-orange and giving a single ν(CO) band at 1980 cm^{-1}, was found to be monoclinic and isomorphous with the analagous thiocarbonyl species $RhCl(CS)(PPh_3)_2$ [2], while the other type, yellow and giving a single ν(CO) band at 1965 cm^{-1}, was triclinic.

We began a crystallographic study on both species, in order to determine the structural differences, but after the appearance of a report of the structure of the

0022-328X/83/$03.00

triclinic form [3], we decided to not complete the detailed analysis of this form. We present below the complete structural results of the X-ray analysis of the monoclinic form of RhCl(CO)(PPh$_3$)$_2$, together with a comparison with the more relevant bond parameters of the triclinic modification.

TABLE 1 [a]

POSITIONAL PARAMETERS FOR *trans*-RhCl(CO)(PPh$_3$)$_2$ IN ITS MONOCLINIC FORM

Atom	*x*	*y*	*z*
Rh	134(1)	1477(1)	1826(1)
P(1)	2047(1)	1639(1)	1911(1)
P(2)	−1771(1)	1254(1)	1684(1)
Cl	572(1)	522(1)	2052(1)
C	−179(4)	2207(2)	1792(5)
O	−370(4)	2667(2)	1810(5)
CP111	2570(4)	2355(2)	2137(4)
CP112	2084(5)	2724(2)	1158(5)
CP113	2453(6)	3269(3)	1316(6)
CP114	3258(6)	3455(3)	2414(6)
CP115	3719(5)	3098(3)	3388(6)
CP116	3377(4)	2548(2)	3238(5)
CP121	2224(4)	1434(2)	505(4)
CP122	3051(5)	1687(2)	128(5)
CP123	3120(6)	1527(3)	−978(6)
CP124	2405(6)	1124(3)	−1664(6)
CP125	1607(5)	858(2)	−1293(5)
CP126	1512(5)	1019(2)	−214(5)
CP131	3216(4)	1286(2)	3160(5)
CP132	4241(5)	1103(2)	3047(6)
CP133	5179(7)	849(3)	4073(7)
CP134	5008(7)	806(3)	5174(7)
CP135	4024(7)	1009(3)	5296(7)
CP136	3089(6)	1245(3)	4284(6)
CP211	−2775(4)	1828(2)	1603(4)
CP212	−3164(5)	2147(3)	562(6)
CP213	−3944(6)	2587(3)	429(6)
CP214	−4318(6)	2711(3)	1349(6)
CP215	−3932(6)	2405(3)	2387(6)
CP216	−3159(5)	1955(2)	2526(5)
CP221	−1681(4)	858(2)	3020(4)
CP222	−888(5)	1037(2)	4154(6)
CP223	−768(6)	745(3)	5213(6)
CP224	−1396(6)	281(3)	5115(6)
CP225	−2152(6)	91(3)	4020(7)
CP226	−2301(5)	379(2)	2948(5)
CP231	−2703(4)	847(2)	364(4)
CP232	−3930(5)	814(2)	54(5)
CP233	−4644(6)	495(3)	−941(6)
CP234	−4147(6)	218(3)	−1625(6)
CP235	−2946(5)	244(2)	−1327(6)
CP236	−2211(4)	560(2)	−333(5)

[a] All parameters × 10^4.

Experimental

Crystal data. $C_{37}H_{30}ClOP_2Rh$, $M = 691.0$, monoclinic, space group $P2_1/n$ (No.14), a 12.182(3), b 24.285(5), c 11.894(3) Å, β 113.10(2)°, V 3236.6 Å^3, D_c 1.42 g cm^{-3}, $Z = 4$, $F(000) = 1408$. Mo-K_α radiation (λ 0.7107 Å), μ(Mo-K_α) 7.3 cm^{-1}.

Intensity measurements. The crystal sample, of dimensions 0.20 × 0.30 × 0.36 mm, was mounted on the BASIC diffractometer [4]. The intensity data were collected with Mo-K_α graphite monochromated radiation, by the ω-scan method, within the limits $3° < \vartheta < 25°$. Three reflections were measured at regular intervals and revealed no crystal decay. The integrated intensities were corrected for Lorentz and polarization effects but not for absorption.

After removing all data having $I < 2.5\sigma(I)$ a set of 4295 independent reflections was obtained, and used in the structure solution and refinement.

Structure solution and refinement. The structure solution was based on Patterson and Fourier methods. The refinements were carried out by block-matrix least-squares. The atoms were refined anisotropically, except for the phenyl carbon atoms. The phenyl hydrogen atoms were located in their ideal geometry (C–H 1.0 Å), with an isotropic thermal factor of 5.0 Å^2. They were not refined, but their contribution to the structure factors was taken into account. The final reliability indices R and R_w were 0.051 and 0.062, respectively.

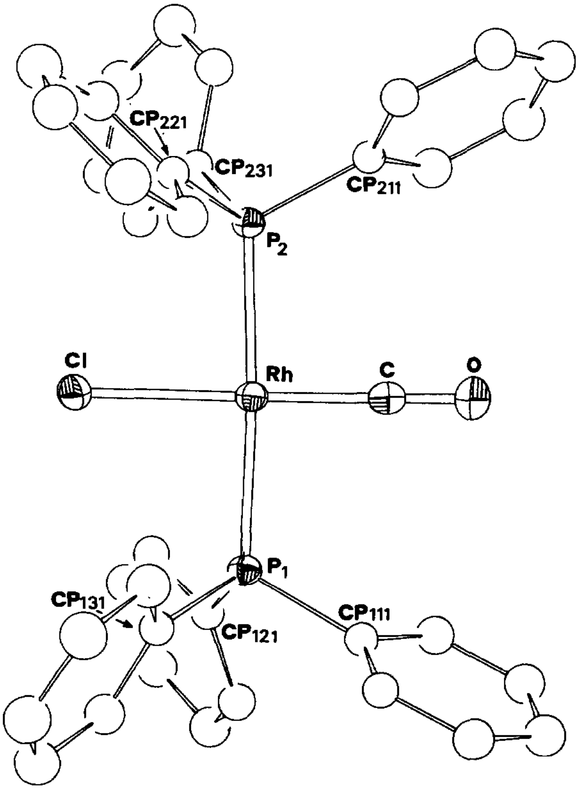

Fig. 1. A view of the complex *trans*-RhCl(CO)(PPh$_3$)$_2$ in its monoclinic form.

The observations were weighted according to the formula $w = 1/(A + BF_0 + CF_0^2)$, where, in the final cycles of refinements, A, B and C had values 5.5, -0.10 and 0.0018, respectively and were chosen on the basis of an analysis of $\Sigma w\Delta^2$.

Atomic scattering factors were taken from ref. 5 for Rh, Cl, P, O and C and from ref. 6 for H. The effects of the anomalous dispersion were taken into account [7]. The final difference Fourier map was flat, except for some residual peaks not exceeding 0.8 $e^-/\text{Å}^3$.

The positional parameters are listed in Table 1. Tables of thermal parameters and observed and calculated structure factors, and final coordinates of the phenyl hydrogen atoms, can be obtained on application to the authors.

All the computations were performed on an UNIVAC 1100/80 computer at the computing center of Milan University.

Discussion

The structure of the complex *trans*-$RhCl(CO)(PPh_3)_2$, in its monoclinic form, is illustrated in Fig. 1.

Bond distances and angles are reported in Table 2. The metal atom exhibits the expected square-planar coordination, with slight distortion, reflected in the values of the bond angles at rhodium. The two phoshine ligands are *trans* to one another.

The Rh–Cl, Rh–P and Rh–C bond lengths are comparable with the parameters in similar complexes [2,3,8,9]. The Rh–C–O angle of 177.7(6)° shows that this interaction is linear. The Rh, P(1), P(2), Cl, C and O atoms are almost coplanar, the maximum deviation from the "best plane" being of 0.023 Å for the rhodium atom.

The bond parameters are very similar to those obtained for the same compound in the triclinic form. The crystal data are: *a* 9.202(3), *b* 10.416(3), *c* 9.678(3) Å, *α*

TABLE 2

INTERATOMIC DISTANCES AND ANGLES IN *trans*-$RhCl(CO)(PPh_3)_2$ (MONOCLINIC FORM)

Distances (Å)			
Rh–P(1)	2.327(1)	P(2)–CP(211)	1.831(6)
Rh–P(2)	2.324(1)	P(2)–CP(221)	1.823(6)
Rh–Cl	2.371(2)	P(2)–CP(231)	1.827(5)
Rh–C	1.810(7)	C–O	1.144(8)
P(1)–CP(111)	1.834(6)	C–C (phenyl)	1.34(1)–1.44(1) (mean 1.39)
P(1)–CP(121)	1.837(6)	Cl...H(126)	2.69
P(1)–CP(131)	1.819(5)	Cl...H(236)	2.72
Angles (deg.)			
P(1)–Rh–P(2)	176.0(1)	Rh–P(2)–CP(211)	117.0(2)
P(1)–Rh–Cl	89.1(1)	Rh–P(2)–CP(221)	110.0(2)
P(1)–Rh–C	91.9(2)	Rh–P(2)–CP(231)	117.1(2)
P(2)–Rh–Cl	87.4(1)	CP(111)–P(1)–CP(121)	103.5(3)
P(2)–Rh–C	91.7(2)	CP(111)–P(1)–CP(131)	102.2(2)
Cl–Rh–C	175.1(2)	CP(121)–P(1)–CP(131)	106.4(3)
Rh–C–O	177.7(6)	CP(211)–P(2)–CP(221)	104.9(3)
Rh–P(1)–CP(111)	116.8(2)	CP(211)–P(2)–CP(231)	100.9(2)
Rh–P(1)–CP(121)	112.8(2)	CP(221)–P(2)–CP(231)	105.5(2)
Rh–P(1)–CP(131)	113.9(2)		

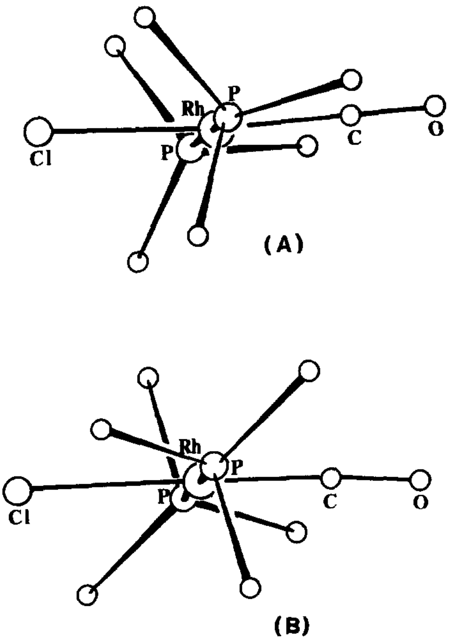

Fig. 2. A view of the complex approximately along the P... P direction, showing that the phosphine ligands are eclipsed in the monoclinic form (A) and staggered in the triclinic one (B).

72.34(3), β 69.43(3), γ 89.65(3)°, V 822.3 Å^3, $Z = 1$, and are comparable with those previously reported [3].

Whereas the previous structural analysis of the triclinic form was based on a non-centrosymmetric ordered model (space group $P1$, No. 1) [3], we have preferred to assume the centrosymmetric $P\bar{1}$ (No. 2) space group, which leads to a statistical disorder of the carbonyl group and of the chlorine atom, the Rh atom lying on an inversion centre. This assumption led to more satisfactory results and more acceptable bonding lengths.

The refinements were carried out on the basis of 2960 counter data ($I > 2.5\sigma(I)$) up to an R value of 0.083. Relevant bond parameters are as follows: Rh–P 2.330(2) Å, Rh–Cl 2.415(5) Å, Rh–C 1.76(2) Å, C–O 1.22(3) Å and Rh–C–O 173(2)°.

The main difference between the two modifications of *trans*-RhCl(CO)(PPh$_3$)$_2$ consists in the stereochemistry of the two phoshine ligands. In the monoclinic form the two phosphine groups are almost eclipsed, being related by an approximate mirror plane, as found in the analogous isomorphous complex *trans*-RhCl(CS)-(PPh$_3$)$_2$ [2]. In contrast, in the triclinic form the phosphine ligands are staggered, because of their centrosymmetric relationship. This difference is illustrated in Fig. 2, and may account for the different positions of the ν(CO) bands of the two forms, in the IR.

The bond parameters within the triphenylphosphine groups are normal, with P–C distances in the range 1.819(5)–1.837(6) Å, mean 1.828 Å, and average Rh–P–C and C–P–C angles of 114.9° and 103.9°, respectively.

We thank the Italian C.N.R. for financial support.

References

1 D. Evans, J.A. Osborn and G. Wilkinson, Inorg. Synth., 11 (1968) 99.

2 J.L. De Boer, D. Rogers, A.C. Skapski and P.G.H. Troughton, Chem. Commun., (1966) 756; in this paper a non-reduced monoclinic cell was used, with *a* 12.134, *b* 24.213, *c* 13.156 Å, *β* 123.03°, *V* 3242 Å^3, space group $P2_1/c$.

3 A. Del Pra, G. Zanotti and P. Segala, Cryst. Struc. Comm., 8 (1979) 959.

4 See footnote in: G. Ciani, M. Manassero and A. Sironi, J. Organometal. Chem., 199 (1980) 271.

5 D.T. Cromer and J.B. Mann, Acta Crystallogr. A, 24 (1968) 321.

6 J.B. Forsyth and M. Wells, Acta Crystallogr., 12 (1959) 412.

7 International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.

8 R. Mason, G. Scollary, B. Moyle, K.I. Hardcastle, B.L. Show and C.J. Moulton, J. Organometal. Chem., 113 (1976) C49.

9 T.R. Gaffney and J.A. Ibers, Inorg. Chem., 21 (1982) 2857.