The Crystal Structure of *trans*-Diiodo-1-methyl-3-trifluoromethyl-1,3-propanedionatobis(triphenylphosphite)rhodium(III)

G. J. VAN ZYL, G. J. LAMPRECHT and J. G. LEIPOLDT

Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa

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Abstract

trans-Diiodo-1-methyl-3-trifluoromethyl-1,3-propanedionatobis(triphenylphosphite)rhodium(III) was synthesized by means of the oxidative addition of iodine to $[Rh(TFAA)(P(OPh)_3)_2]$ in petroleum ether. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 18.810$, $b = 23.462$, $c = 19.780$ Å, $\beta = 101.66°$ and $Z = 8$. The coordination polyhedron has a slightly distorted octahedral configuration with the two iodide ligands in the *trans* positions. It is proposed that the *cis*-addition of iodine is followed by an isomerization reaction to give the final *trans*-diiodo complex.

Introduction

It is generally believed that the oxidative addition reactions of homonuclear molecules in non-polar solvents proceed via a concerted three-centre mechanism, which result in *cis*-addition if there is no subsequent rearrangement [1]. Kuwae *et al.* [2] studied the kinetics of the oxidative addition reaction $[Rh(EE)(L)_2] + I_2 \rightarrow [Rh(EE)(L)_2(I)_2]$ where EE = $S_2CN(CH_3)_2$ and acac and L = $2,4,6\text{-}(CH_3)_3C_6H_2NC$. They proposed that the reaction proceeds via two consecutive reactions. The first step involves the *cis*-addition of I_2, while the second step is an isomerization reaction to give the final product with the iodide ligands in the *trans* positions. This reaction scheme was based on the supposition that the final product is the *trans*-diiodo complex. The proposed retention of the two isocyanide ligands in the mutual *cis*-positions on going from reactant to product was based on the ground of H^1 NMR study of the product and the upward shift of the $\nu(N{\equiv}C)$ frequencies in the infra-red spectrum. This observation, however, merely confirmed that oxidative addition took place [3] and not that the two iodide ligands are in the *trans*-positions.

The reaction between $[Rh(TFAA)(P(OPh)_3)_2]$ and iodine was investigated as part of a program for the study of the oxidative addition reactions of rhodium(I) complexes. The H^1 NMR-spectrum of the reaction product of the corresponding acetylacetone (acac) complex, $[Rh(acac)(P(OPh)_3)_2(I)_2]$, shows only one signal for the methyl protons of the symmetrical β-diketone ligand ($\delta = 1.50$ ppm in $(CD_3)_2CO$) suggesting that they are magnetically equivalent. Two octahedral isomers are thus possible, *i.e.* the *cis*- and *trans*-diiodo complexes. To enable the derivation of a suitable reaction mechanism for this reaction, the crystal structure of the title compound was determined, whereby it was possible to ascertain whether *cis*- or *trans*-addition took place.

Experimental

The compound $[Rh(TFFA)(P(OPh)_3)_2]$ was prepared as described earlier [4]. 5 cm^3 of a solution of 0.0032 g (0.013 mmol) I_2 in petroleum–ether was added to 5 cm^3 of a solution of 0.010 g (0.011 mmol) $[Rh(TFAA)(P(OPh)_3)_2]$ in the same solvent. A few drops of acetone prevented the immediate precipitation of the reaction product, $[Rh(TFAA)(P(OPh)_3)_2(I)_2]$, A. Well shaped dark red–brown crystals were obtained after a few hours.

Crystal data: $RhC_{41}H_{34}O_8F_3P_2I_2$, $M = 1130.4$, monoclinic, space group $P2_1/n$, $a = 18.810(3)$, $b = 23.462(6)$, $c = 19.780(4)$ Å, $\beta = 101.66(1)°$, $Z = 8$, $D_{exp} = 1.827$ g cm^3 and μ(Mo Kα) = 20.8 cm^{-1}.

The three dimensional intensity data were collected for θ values between 3 and 23°, using graphite monochromated Mo Kα radiation. A crystal with dimensions 0.15 × 0.13 × 0.25 mm was used for the data collection. No decomposition of the crystal took place during the data collection. A total of 12 224 reflections were measured, of which 5666 were considered as observed, $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization effects.

The structure was solved, using the X-ray 72 system of programs on a Univac 1100 computer. The two rhodium and four iodine atoms of the crystallographic independent molecules were located by means of the direct method. The positional parameters of the other non-hydrogen atoms were deduced

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TABLE I. Population Parameters of the F-atoms in the Two Orientation Positions

	Molecule 1		Molecule 2	
	Position 1	Position 2	Position 1	Position 2
	0.90(9)	0.17(5)	0.47(6)	0.69(8)
	0.70(9)	0.47(8)	0.52(7)	0.60(7)
	1.1(1)	0.13(5)	0.43(7)	0.73(8)
Average	0.90	0.26	0.47	0.67
Total	1.1(1)		1.1(1)	

from successive Fourier maps. A full matrix least squares refinement, using all the observed reflections and anisotropic thermal parameters for all the atoms, resulted in the residual factor $R = 10.6\%$.

A difference-Fourier synthesis revealed that there were three peaks within 1.4 Å from C_1. The presence of these peaks, together with the high temperature factors of the fluoride atoms, suggested a disorder in the crystal. Fluoride atoms were placed in these positions. The final population parameters of the fluoride atoms in the two crystallographic independent molecules are given in Table I. The final R value

TABLE II. Fractional Atomic Coordination of the Two Crystallographic Independent Molecules

Atom	Molecule 1			Molecule 2		
	x	y	z	x	y	z
Rh	0.2272(1)	0.3300(1)	0.1548(1)	0.3300(1)	0.5636(1)	0.8314(1)
I_1	0.1102(1)	0.2637(1)	0.1255(1)	0.2150(1)	0.4943(1)	0.8144(1)
I_2	0.3383(1)	0.4013(1)	0.1675(1)	0.4549(1)	0.6183(1)	0.8654(1)
P_1	0.2111(4)	0.3541(3)	0.2576(4)	0.3307(4)	0.5571(3)	0.7206(4)
P_2	0.2954(5)	0.2567(3)	0.1976(4)	0.2668(4)	0.6441(3)	0.8147(4)
O_1	0.248(1)	0.307(1)	0.059(1)	0.324(1)	0.566(1)	0.933(1)
O_2	0.159(1)	0.396(1)	0.107(1)	0.388(1)	0.489(1)	0.849(1)
C_1	0.257(3)	0.308(2)	−0.059(1)	0.437(2)	0.405(1)	0.901(2)
C_2	0.22-(2)	0.337(2)	0.003(2)	0.404(2)	0.464(1)	0.908(2)
C_3	0.182(2)	0.384(2)	−0.006(2)	0.391(2)	0.481(2)	0.966(2)
C_4	0.156(2)	0.411(1)	0.047(2)	0.349(2)	0.531(1)	0.977(2)
C_5	0.099(2)	0.455(2)	0.020(2)	0.340(2)	0.545(2)	1.048(2)
O_{11}	0.151(1)	0.319(1)	0.283(1)	0.384(1)	0.601(1)	0.696(1)
O_{12}	0.192(1)	0.420(1)	0.267(1)	0.350(1)	0.497(1)	0.693(1)
O_{13}	0.282(1)	0.348(1)	0.314(1)	0.255(1)	0.569(1)	0.667(1)
O_{21}	0.303(1)	0.208(1)	0.144(1)	0.186(1)	0.632(1)	0.773(1)
O_{22}	0.262(1)	0.224(1)	0.254(1)	0.299(1)	0.690(1)	0.770(1)
O_{23}	0.374(1)	0.273(1)	0.235(1)	0.260(1)	0.678(1)	0.881(1)
C_{111}	0.146(2)	0.306(2)	0.353(1)	0.387(2)	0.609(2)	0.626(2)
C_{112}	0.132(2)	0.345(2)	0.397(2)	0.337(2)	0.648(2)	0.590(2)
C_{113}	0.130(2)	0.328(2)	0.466(2)	0.342(2)	0.660(2)	0.520(2)
C_{114}	0.139(2)	0.271(2)	0.490(2)	0.393(2)	0.631(2)	0.489(2)
C_{115}	0.158(2)	0.231(2)	0.444(2)	0.442(2)	0.593(2)	0.528(2)
C_{116}	0.161(2)	0.248(2)	0.371(2)	0.442(2)	0.584(2)	0.600(2)
C_{121}	0.121(2)	0.443(2)	0.261(2)	0.416(2)	0.464(1)	0.704(1)
C_{122}	0.126(2)	0.490(2)	0.307(2)	0.404(2)	0.409(2)	0.681(2)
C_{123}	0.059(2)	0.519(2)	0.307(3)	0.464(2)	0.369(2)	0.683(2)
C_{124}	−0.004(2)	0.505(2)	0.258(2)	0.532(2)	0.395(2)	0.711(2)
C_{125}	−0.003(2)	0.459(2)	0.216(2)	0.542(2)	0.451(2)	0.744(2)
C_{126}	0.059(2)	0.428(2)	0.216(2)	0.479(2)	0.485(2)	0.737(2)
C_{131}	0.312(2)	0.384(2)	0.372(2)	0.208(1)	0.536(1)	0.619(1)
C_{132}	0.337(2)	0.436(2)	0.363(2)	0.137(2)	0.533(2)	0.630(2)
C_{133}	0.364(2)	0.466(2)	0.425(2)	0.085(2)	0.504(1)	0.581(2)
C_{134}	0.371(2)	0.439(2)	0.489(2)	0.113(2)	0.479(2)	0.523(2)
C_{135}	0.344(2)	0.387(2)	0.494(2)	0.185(2)	0.482(2)	0.518(2)
C_{136}	0.312(2)	0.357(2)	0.436(2)	0.235(2)	0.511(2)	0.564(2)
C_{211}	0.354(2)	0.201(2)	0.102(2)	0.137(1)	0.673(1)	0.738(1)
C_{212}	0.345(2)	0.146(2)	0.074(2)	0.080(2)	0.687(1)	0.773(2)
C_{213}	0.396(2)	0.136(2)	0.030(2)	0.030(2)	0.726(2)	0.736(2)

(continued)

TABLE II. *(continued)*

Atom	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
C_{214}	0.446(2)	0.169(2)	0.017(2)	0.037(2)	0.749(2)	0.673(2)
C_{215}	0.449(2)	0.226(2)	0.049(2)	0.095(2)	0.733(2)	0.643(2)
C_{216}	0.397(2)	0.242(2)	0.091(2)	0.148(2)	0.695(2)	0.676(2)
C_{221}	0.267(2)	0.165(2)	0.274(2)	0.311(2)	0.748(1)	0.786(2)
C_{222}	0.307(2)	0.152(2)	0.337(2)	0.382(2)	0.765(1)	0.806(2)
C_{223}	0.310(2)	0.097(2)	0.358(2)	0.401(2)	0.823(2)	0.818(3)
C_{224}	0.280(2)	0.055(2)	0.317(2)	0.344(2)	0.864(1)	0.813(2)
C_{225}	0.238(2)	0.066(2)	0.252(2)	0.274(2)	0.846(2)	0.789(2)
C_{226}	0.235(2)	0.125(2)	0.225(2)	0.255(2)	0.787(1)	0.779(2)
C_{231}	0.428(2)	0.243(2)	0.282(2)	0.201(2)	0.177(1)	0.913(1)
C_{232}	0.445(2)	0.190(2)	0.271(2)	0.174(2)	0.731(2)	0.927(2)
C_{233}	0.500(2)	0.163(2)	0.328(2)	0.117(2)	0.733(2)	0.961(2)
C_{234}	0.531(2)	0.194(2)	0.384(2)	0.078(2)	0.682(2)	0.975(2)
C_{235}	0.508(2)	0.252(2)	0.392(2)	0.109(2)	0.626(2)	0.959(2)
C_{236}	0.453(2)	0.278(2)	0.341(2)	0.169(2)	0.620(2)	0.929(2)
$F_1{}^a$	0.091(3)	0.488(2)	0.067(2)	0.385(3)	0.516(2)	1.098(2)
$F_2{}^a$	0.033(2)	0.435(2)	0.004(4)	0.277(3)	0.524(2)	1.050(3)
$F_3{}^a$	0.108(3)	0.480(2)	−0.025(3)	0.344(4)	0.597(2)	1.062(3)
$F_1'{}^b$	0.264(6)	0.251(4)	−0.047(6)	0.394(3)	0.376(2)	0.852(2)
$F_2'{}^b$	0.236(5)	0.339(3)	−0.103(5)	0.432(3)	0.372(2)	0.957(2)
$F_3'{}^b$	0.330(5)	0.327(4)	−0.035(4)	0.494(3)	0.411(2)	0.896(4)

[a] Position 1 (Table 1). [b] Position 2 (Table 1).

was 9.7%. The final positional parameters are listed in Table II. See also 'Supplementary Material'.

Discussion

A perspective view of one of the two crystallographic independent $[Rh(TFAA)(P(OPh)_3)_2(I)_2]$ molecules (the stereochemistry of the two is identical), as well as the numbering system of the atoms, is shown in Fig. 1. Selected bond distances and angles are given in Tables III and IV, respectively. The structure consists of well separated discrete molecular units.

The coordination polyhedron has a slightly distorted octahedral geometry. The two $P(OPh)_3$ ligands and the bidentate ligand (TFAA) are located in an equatorial plane with the two iodide ligands in the axial positions. The equatorial planes of the octahedra O_1, O_2, P_1, P_2 and O_1, P_1, I_1, I_2 and O_2, P_2, I_1, I_2 are planer within the experimental error. The angles between these planes range from 88.6 to 90.0°. The chelate rings are also planar and the angle between the plane through the chelate ring and the equatorial plane O_1, O_2, P_1, P_2 is 2.0 and 7.0° for the two polyhedra.

The mean Rh–P bond distances (2.206(11) Å) is significantly shorter than the average Rh–P bond distance (2.395(7) Å) in *cis*-diiodo(2,4-pentane-

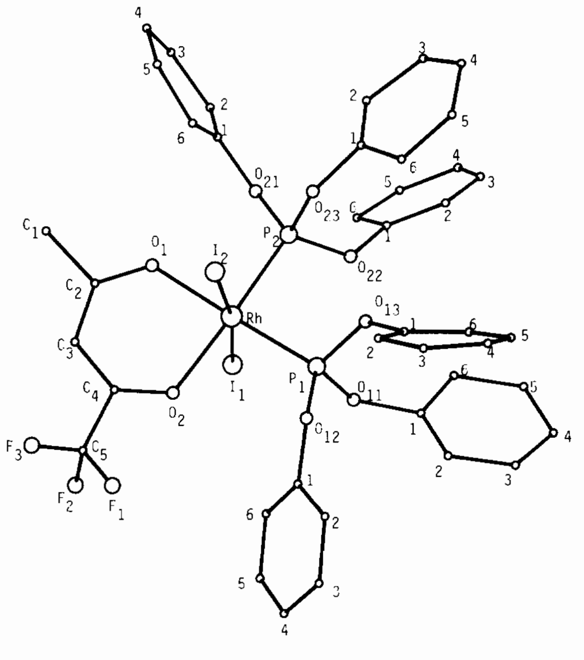

Fig. 1. Perspective view of a $[Rh(TFAA)(P(OPh)_3)_2(I)_2]$ molecule. The numbering system of the atoms of the phenyl rings of the phosphite groups is as follows (see Table II): the first digit refers to the phosphorous atom, the second digit refers to the oxygen atoms bonded to the phosphorous atom and the third digit refers to the carbon atoms of the phenyl ring bonded to the oxygen atom.

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

Bond	Molecule 1	Molecule 2
$Rh-P_1$	2.194(9)	2.200(9)
$Rh-P_2$	2.208(8)	2.222(8)
$Rh-I_1$	2.663(3)	2.672(3)
$Rh-I_2$	2.649(3)	2.644(3)
$Rh-O_1$	2.08(2)	2.04(2)
$Rh-O_2$	2.11(2)	2.05(2)
P_1-O_{11}	1.56(2)	1.59(2)
P_1-O_{12}	1.60(2)	1.58(2)
P_1-O_{13}	1.57(2)	1.61(2)
P_2-O_{21}	1.57(2)	1.58(2)
P_2-O_{22}	1.57(2)	1.60(2)
P_2-O_{23}	1.57(2)	1.57(2)
C_1-C_2	1.62(5)	1.53(4)
C_2-C_3	1.41(5)	1.30(6)
C_3-C_4	1.37(6)	1.45(5)
C_4-C_5	1.51(5)	1.47(5)
O_1-C_2	1.26(4)	1.29(4)
O_2-C_4	1.24(4)	1.24(4)
C_5-F_1	1.22(6)	1.35(6)
C_5-F_2	1.19(7)	1.30(8)
C_5-F_3	1.23(8)	1.25(7)
$C_1-F'_1$	1.31(10)	1.32(6)
$C_1-F'_2$	1.17(9)	1.37(6)
$C_1-F'_3$	1.47(10)	1.12(7)

TABLE IV. Selected Bond Angles (°) with e.s.d.s in Parentheses

Angle	Molecule 1	Molecule 2
I_1-Rh-I_2	172.5(1)	169.5(1)
P_1-Rh-O_1	176.9(7)	176.8(7)
P_2-Rh-O_2	175.6(6)	178.7(6)
P_1-Rh-P_2	91.3(3)	91.2(3)
O_1-Rh-O_2	89.4(9)	89.8(8)
I_1-Rh-P_1	95.2(2)	90.1(2)
I_1-Rh-P_2	91.1(2)	95.9(2)
I_1-Rh-O_1	87.6(6)	86.8(6)
I_1-Rh-O_2	86.1(6)	84.1(5)
I_2-Rh-P_1	90.2(2)	95.9(2)
I_2-Rh-P_2	94.0(2)	92.6(2)
I_2-Rh-O_1	87.2(6)	87.3(6)
I_2-Rh-O_2	88.5(6)	87.2(5)
P_2-Rh-O_1	87.1(6)	88.9(7)
P_1-Rh-O_2	92.3(7)	90.0(6)
$F_1-C_5-F_2$	103(5)	104(4)
$F_1-C_5-F_3$	105(4)	108(5)
$F_2-C_5-F_3$	107(5)	112(6)
$F'_1-C_1-F'_2$	142(7)	100(4)
$F'_1-C_1-F'_3$	101(6)	116(5)
$F'_2-C_1-F'_3$	99(6)	111(5)

dionato-*O,O'*)bistriphenylphosphinerhodium(III) (**B**) [5]. The significant shorter Rh–P bond distance in the case of the phosphite complex, is probably the result of the strong π-electron acceptor properties of the phosphite ligand compared to the phosphine ligand [6], as well as the *trans*-arrangement of the two PPh_3 ligands in **B**, resulting in a weakening of the Rh–P bond due to the *trans* influence of the PPh_3 ligand. The mean Rh–P bond distance in the present structure is significantly longer than the average Rh–P bond length (2.145(4) Å) in [Rh(TFAA)-$(P(OPh)_3)_2$] [7] and [Rh(acac)$(P(OPh)_3)_2$] [8]. This longer Rh–P bond distance in the present structure can be attributed to the fact that there is less electron density available for strong π-bonding in the case of Rh(III) compared to Rh(I).

The I–Rh–I bond angles (average 171°), as well as the I–Rh–O bond angles, which are significantly smaller than 90°, and the I–Rh–P bond angles, which are all greater than 90°, indicate that there is a significant amount of steric repulsion between the iodide ligands and the $P(OPh)_3$ groups.

The average Rh–I distance in **A** is 2.657 Å, compared to 2.621 Å in **B** [5]. The reason for this difference may be found in the different geometrical arrangements of the iodide ligand in these complexes. The iodide ligands are *trans* to one another in **A** and *trans* to an oxygen atom of the β-diketone in **B**. The difference between the Rh–I bond distances in **A** and **B** can thus be attributed to the difference in the relative thermodynamic *trans* influence between an iodide and an oxygen atom of the β-diketone.

The phosphorous atoms are tetrahedrally surrounded by the rhodium and three oxygen atoms. The average P–O bond distance (1.58 Å) and Rh–P–O bond angle (114°) compares well with those found in [Rh(TFBA)$(P(OPh)_3)_2$] [9] and [Rh-(TFAA)$(P(OPh)_3)_2$] [7]. The twelve phenyl rings are planar within experimental error and the average C–C bond distance (1.39(4) Å) and bond angle (120(3)°) are within the experimental error identical to the accepted values of 1.399 Å and 120° for phenyl rings [10].

The most important feature of this structure is the *trans* arrangement of the two iodide atoms. The kinetic study of the oxidative addition of I_2 to [Rh(TFAA)$(P(OPh)_3)_2$] to give the final product, **A**, indicated that the reaction proceeds via two consecutive first-order reactions (to be published). Since it can be assumed that the oxidative addition of I_2 (a homonuclear molecule) proceeds via a concerted three-centre mechanism [1], the first step is probably the *cis*-addition and the second the isomerization reaction to give the final *trans*-diiodo complex. This proposed reaction scheme raised the question why the intermediate *cis*-diiodo complex, **C**, is thermodynamically unstable, while the *cis*-diiodo complex, **B** [5], is stable.

In complex **B** there must be a large steric repulsion between the two iodide ligands in the *cis* positions because the I–Rh–I bond angle (95.4(1)°) is significant greater than 90° and because the van der Waals radius of iodide (2.15 Å) [11] would predict a larger distance than the observed I–I distance of 3.877(4) Å. The large cone angle of PPh_3 (145°) [12] would, however, result in a very large steric repulsion (as indicated by the large distortion of the square planar geometry and large P–Rh–P bond angles (average 98.1(2)° in $[Rh(PPh_3)_3Cl]$ [13]) if the two PPh_3 ligands were *cis* to one another.

On the other hand, the relative small cone angle (128°) of $P(OPh)_3$ [12] resulted in an average P–Rh–P bond angle of only 91.3° in complex **A**. The steric repulsion will thus be much less with the two $P(OPh)_3$ ligands *cis* to one another and the intermediate *cis*-diiodo complex, **C**, would thus be relative unstable and isomerize to the final *trans*-diiodo complex, **A**.

Supplementary Material

A list of the experimental and calculated structure factors, as well as the anisotropic thermal parameters, may be obtained from the authors.

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References

1 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley, New York, 1980.
2 R. Kuwae, T. Tanaka and K. Kawakami, *Bull. Chem. Soc. Jpn., 52,* 437 (1979).
3 A. L. Balch, *J. Am. Chem. Soc., 98,* 8049 (1976).
4 A. M. Trzeciak and J. J. Ziółkowskii, *Inorg. Chim. Acta Lett., 64,* L267 (1982).
5 S. S. Basson, J. G. Leipoldt, I. M. Potgieter, A. Roodt and T. J. van der Walt, *Inorg. Chim. Acta,* 1986, submitted for publication.
6 J. E. Huheey, 'Inorganic Chemistry Principles of Structure and Reactivity', Harper and Row, New York, 1972.
7 G. J. van Zyl, G. J. Lamprecht and J. G. Leipoldt, *Inorg. Chim. Acta, 102,* L1 (1985).
8 J. G. Leipoldt, G. J. Lamprecht and G. J. van Zyl, *Inorg. Chim. Acta, 96,* L31 (1985).
9 G. J. Lamprecht, J. G. Leipoldt and G. J. van Zyl, *Inorg. Chim. Acta, 97,* 31 (1985).
10 L. E. Sutin, 'Tables of Interatomic Distances and Configuration in Molecules and Ions', Suppl. 1956–1959, The Chemical Society, London, 1965, p. S165.
11 F. A. Cotton and G. Wilkinson, 'Basic Inorganic Chemistry', Wiley, New York, 1976.
12 C. A. Tolman, *Chem. Rev., 77,* 313 (1977).
13 M. J. Bennet and P. B. Donaldson, *Inorg. Chem., 16,* 655 (1977).