Molecular Structure of *trans*-Methyliodo-*N*-benzoyl-*N*-phenylhydroxyaminobis(triphenylphosphite)rhodium(III)

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Abstract

trans-Methyliodo-*N*-benzoyl-*N*-phenylhydroxyaminobis(triphenylphosphite)rhodium(III) was synthesized by means of the oxidative addition of methyl iodide to *N*-benzoyl-*N*-phenylhydroxyaminobis(triphenylphosphite)rhodium(I) in an acetone medium. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.614(2)$, $b = 18.450(2)$, $c = 23.397(3)$ Å, $\beta = 114.91(1)^\circ$ and $Z = 4$. The structure was solved using 5412 observed reflections. The final R value was 0.080. The coordination polyhedron has an octahedral configuration with the iodide and methyl ligands in *trans* positions.

Introduction

Oxidative addition reactions play an important role in many homogeneous catalytic cycles, such as alkane activation, carbonylation, olefin hydrogenation, etc. [1–4]. Square planar Rh(I) complexes, being coordinatively unsaturated, undergo oxidative addition reactions with various organic and inorganic molecules [2, 5, 6]. Since oxidative addition reactions can proceed via different reaction pathways [3] and because the addition can be either *cis* or *trans*, it is imperative to know the molecular structures of reactants and products in order to propose suitable reaction mechanisms.

The crystal structure of *trans*-methyl-*N*-benzoyl-*N*-phenylhydroxyaminobis(triphenylphosphite)rhodium(III), $[Rh(BPHA)(P(OPh)_3)_2(CH_3)(I)]$, the final reaction product of the oxidative addition of CH_3I to $[Rh(BPHA)P(OPh)_3)_2]$, was determined as part of a program for the study of the structural and kinetic aspects of the oxidative addition reactions of Rh(I) complexes of type $[Rh(LL')(CO)(PPh_3)]$ and $Rh(LL')(P(OPh)_3)_2]$ where LL′ = monocharged bidentate ligands such as β-diketones and 8-hydroxyquinoline. The kinetic results for the oxidative addition of CH_3I to these types of complexes strongly favour an ionic S_N2 two-step operative mechanism which implies a *trans* geometry of addition [6–8]. In agreement with this the structure of the oxidative addition products $[Rh(\beta\text{-diketone})(P(OPh)_3)_2(CH_3)(I)]$ clearly indicates a *trans* addition [8].

A concerted three-centered *cis* addition is however a well known alternative especially in the case of homonuclear molecules like hydrogen. A recent high-pressure kinetic study of the oxidative addition of CH_3I to different Rh(I) complexes suggests the possibility of a three-centered *cis* addition of CH_3I [9]. In agreement with this possibility the crystal structure determination of $[Rh(cupf)(CO)(PPh_3)(CH_3)(I)]$ [10] (the methyl and iodide ligands are *cis* to one another) revealed a *cis* addition and thus also suggest the possibility of a three-centered transition state. This complex however contains a carbonyl ligand and it was found that the oxidative addition reactions with CH_3I are complicated by acyl–alkyl conversion reactions. For this reason we studied the addition of CH_3I to $[Rh(BPHA)(P(OPh)_3)_2]$, a complex without any carbonyl ligands.

Experimental

The dicarbonyl complex $[Rh(BPHA)(CO)_2]$ was prepared as previously described [11], while the complex $[Rh(BPHA)(P(OPh)_3)_2]$ was prepared by a method similar to that described for $[Rh(Qin)(P(OPh)_3)_2]$ [12]. The title compound was prepared by adding 0.9 g CH_3I to a solution of 0.3 of $[Rh(BPHA)(P(OPh)_3)_2]$ in 2 cm^3 acetone. After approximately two hours, dark yellow crystals, suitable for data collection, crystallized out of solution. A micro analyses (Mikroanalytisches Labor Pascher, Bonn) gave the following mass % results. Calculated: C, 55.73; H, 4.02; I, 11.77; Rh, 9.55; O, 11.88. Found C, 55.53; H, 4.10; I, 12.04; Rh, 9.50; O, 11.80%.

Crystal data. $C_{50}H_{43}INO_8P_2Rh$, molecular mass 1077.66, monoclinic space group $P2_1/c$, $a = 12.614(2)$, $b = 18.450(2)$, $c = 23.397(3)$ Å, $\beta = 114.91(1)^\circ$, $Z = 4$, $D_{calc} = 1.449$ g cm^{-3}, $D_{exp} = 1.440$ g cm^{-3}.

Three dimensional intensity data were collected and corrected as previously described [10]. A total of

0020-1693/89/$3.50

TABLE 1. Fractional atomic coordinates with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Rh	0.1070(1)	0.2753(1)	0.5051(0)	C(115)	0.6548(13)	0.3303(9)	0.5242(7)
I(1)[a]	0.2017(1)	0.1447(1)	0.4926(1)	C(116)	0.5664(11)	0.3361(8)	0.5462(6)
I(2)[b]	−0.0462(6)	0.3678(4)	0.4866(3)	C(121)	0.3909(11)	0.4409(7)	0.5938(6)
P(1)	0.2595(3)	0.3407(2)	0.5165(1)	C(122)	0.4207(13)	0.4953(8)	0.5625(6)
P(2)	0.1745(3)	0.2615(2)	0.6082(1)	C(123)	0.5298(13)	0.5290(8)	0.5911(7)
O(1)	0.0372(8)	0.2827(6)	0.4087(4)	C(124)	0.6038(13)	0.5082(9)	0.6521(7)
O(2)	−0.0460(8)	0.2182(6)	0.4820(4)	C(125)	0.5728(13)	0.4538(8)	0.6848(7)
C	0.0171(14)	0.3725(11)	0.5079(8)	C(126)	0.4650(11)	0.4205(7)	0.6544(5)
C(0)	−0.0996(11)	0.2113(8)	0.4213(5)	C(131)	0.1759(10)	0.4141(7)	0.4051(5)
N	−0.0581(10)	0.2396(7)	0.3844(5)	C(132)	0.1550(12)	0.3897(8)	0.3447(6)
C(1)	−0.2020(10)	0.1620(7)	0.3975(5)	C(133)	0.0764(14)	0.4306(10)	0.2929(6)
C(2)	−0.1877(13)	0.0943(8)	0.4271(7)	C(134)	0.0260(16)	0.4923(11)	0.3037(8)
C(3)	−0.2859(14)	0.0487(9)	0.4060(8)	C(135)	0.0468(16)	0.5158(11)	0.3654(8)
C(4)	−0.3918(12)	0.0695(8)	0.3556(7)	C(136)	0.1243(14)	0.4744(9)	0.4177(7)
C(5)	−0.4019(11)	0.1368(8)	0.3293(6)	C(211)	0.1674(11)	0.3373(7)	0.7029(5)
C(6)	−0.3079(11)	0.1843(8)	0.3493(6)	C(212)	0.2387(11)	0.3971(8)	0.7239(6)
C(7)	−0.1085(11)	0.2366(8)	0.3155(5)	C(213)	0.2756(13)	0.4167(9)	0.7874(7)
C(8)	−0.1258(13)	0.1704(9)	0.2850(7)	C(214)	0.2388(12)	0.3761(9)	0.8264(6)
C(9)	−0.1780(15)	0.1735(10)	0.2160(7)	C(215)	0.1672(12)	0.3170(8)	0.8033(6)
C(10)	−0.2038(16)	0.2398(12)	0.1861(7)	C(216)	0.1269(12)	0.2964(8)	0.7402(6)
C(11)	−0.1804(16)	0.3041(12)	0.2187(8)	C(221)	0.0552(11)	0.1451(7)	0.6183(5)
C(12)	−0.1326(14)	0.3019(10)	0.2839(6)	C(222)	−0.0557(11)	0.1744(7)	0.5998(6)
O(11)	0.3825(6)	0.3026(4)	0.5418(3)	C(223)	−0.1492(14)	0.1263(10)	0.5858(7)
O(12)	0.2810(7)	0.4065(4)	0.5641(4)	C(224)	−0.1309(16)	0.0504(9)	0.5908(8)
O(13)	0.2612(7)	0.3736(4)	0.4543(4)	C(225)	−0.0192(17)	0.0242(10)	0.6088(9)
O(21)	0.1261(8)	0.3221(5)	0.6386(3)	C(226)	0.0746(15)	0.0705(8)	0.6243(8)
O(22)	0.1540(7)	0.1874(5)	0.6362(4)	C(231)	0.3893(11)	0.2163(7)	0.6863(6)
O(23)	0.3119(7)	0.2679(5)	0.6488(3)	C(232)	0.4044(14)	0.2078(10)	0.7486(6)
O(111)	0.4663(11)	0.3000(7)	0.5159(5)	C(233)	0.4901(16)	0.1569(11)	0.7854(8)
C(112)	0.4403(15)	0.2569(9)	0.4630(7)	C(234)	0.5547(16)	0.1195(9)	0.7614(10)
C(113)	0.5264(21)	0.2508(11)	0.4416(10)	C(235)	0.5392(18)	0.1295(11)	0.6990(10)
C(114)	0.6346(16)	0.2879(10)	0.4724(9)	C(236)	0.4559(14)	0.1799(8)	0.6617(8)

[a] Population parameter 0.877(3). [b] Population parameter 0.154(3). See also 'Supplementary Material'.

8591 reflections were measured of which 5412 were considered as observed reflections. The structure was solved, using the X-ray 72 system of programmes.

The rhodium and iodine atoms were located by means of the direct method. The positional parameters of the other non-hydrogen atoms were deduced from successive Fourier maps. A least-squares refinement, using all the observed reflections and anisotropic thermal parameters for all the non-hydrogen atoms, resulted in an R value of 0.095. A difference-Fourier synthesis revealed a peak *trans* with respect to I(1) and about 2.5 Å from the central Rh atom. Because the chemical analysis was in full agreement with the structural analysis at this point, the presence of the mentioned peak suggested a disorder in the crystal. An iodine atom, I(2), was placed in this position and a final population parameter refinement yielded the following values for the population parameters for the iodine atoms: I(1) = 0.877(3) and I(2) = 0.154(3). The refinement of the population parameters of the iodine atom was not subjected to the condition that their sum equals unity to observe the effect of any other possible disorder on the refinement. Since this sum is nearly unity (1.03) the above-mentioned condition was not implemented. Because of the relatively high electron density round I(1), the expected similar population parameters for the carbon atom of the methyl ligand, *trans* to iodine atom, could not be determined. The final R value was 0.080. Final positional parameters are given in Table 1.

Results and Discussion

The molecular structure of [Rh(BPHA)(P(OPh)$_3$)$_2$-(CH$_3$)(I)] and the system of numbering the atoms, is shown in Fig. 1, while selected bond distances and bond angles are listed in Tables 2 and 3, respectively.

The Rh–I bond distance (2.759(2) Å) is in agreement with the Rh–I bond distance (also *trans* to a CH$_3$-ligand) found in [RhI(CH$_3$)(C$_2$(DO)(DOBF$_2$))],

TABLE 2. Selected interatomic distances (Å) with e.s.d.s in parentheses

Rh–I(1)	2.759(2)	N–C(0)	1.292(20)
Rh–I(2)[a]	2.477(8)	N–C(7)	1.464(15)
Rh–C	2.137(20)	C(0)–C(1)	1.483(18)
Rh–O(1)	2.051(8)	P(1)–O(11)	1.575(8)
Rh–O(2)	2.060(10)	P(1)–O(12)	1.590(9)
Rh–P(1)	2.190(4)	P(1)–O(13)	1.586(10)
Rh–P(2)	2.208(3)	P(2)–O(21)	1.580(11)
O(1)–N	1.352(5)	P(2)–O(22)	1.584(10)
O(2)–C(0)	1.296(3)	P(2)–O(23)	1.592(8)

[a] Population parameter 0.154(3) – see 'Discussion'.

TABLE 3. Selected bond angles (°) with e.s.d.s in parentheses

I(1)–Rh–C	174.2(4)	I(1)–Rh–P(1)	95.6(1)
P(1)–Rh–O(2)	172.3(3)	P(2)–Rh–C	91.6(5)
P(2)–Rh–O(1)	176.4(3)	C–Rh–O(1)	89.4(6)
P(1)–Rh–P(2)	90.9(1)	O(1)–Rh–I(1)	86.9(3)
P(2)–Rh–O(2)	96.6(3)	I(1)–Rh–P(2)	91.7(1)
O(2)–Rh–O(1)	79.9(4)	Rh–O(1)–N	108.4(8)
O(1)–Rh–P(1)	92.6(3)	O(1)–N–C(0)	119.8(9)
P(1)–Rh–C	89.1(5)	N–C(0)–O(2)	121.3(11)
C–Rh–O(2)	89.2(6)	C(0)–O(2)–Rh	109.7(9)
O(2)–Rh–I(1)	85.7(3)		

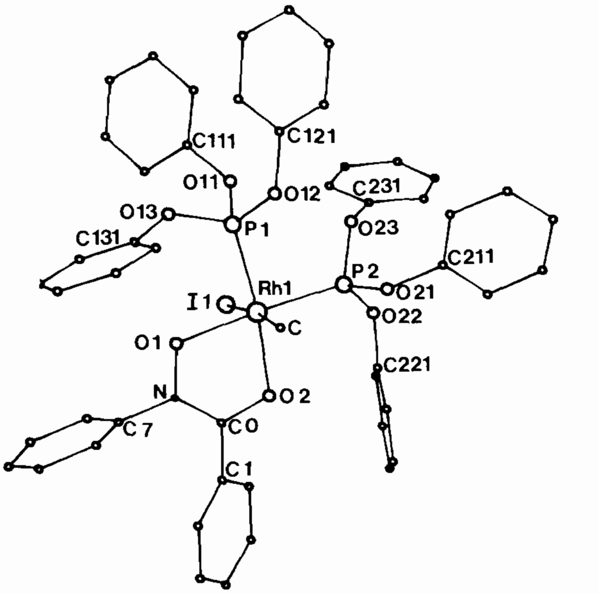

Fig. 1. A perspective view of the molecule together with the system of numbering all the non-phenyl atoms in the molecule.

(2.813(3) Å) [13] and [$RhI_3(CO)(CPh(NCH_3)(CPhNCH_3))$], (2.774(4) Å) [14]. The Rh–C bond distance (2.137(20) Å) is comparable to the Rh–C bond distances of 2.090(20) Å and significantly larger than the Rh–C bond length of 1.968(13) Å in the above-mentioned complexes, respectively. The strong *trans* influence of the methyl group [15], is reflected by the fact that the Rh–I(1) bond distance is significantly longer than the Rh–I bond distances of 2.606(3) and 2.637(4) Å *trans* to an oxygen atom [16] or 2.663(3) and 2.649(3) Å *trans* to an iodine atom [17]. The strong *trans* influence of the methyl group is also reflected by the large difference (0.135 Å) in the Rh–O bond lengths in [$Rh(cupf)(CO)(PPh_3)(CH_3)(I)$] [10]; the one oxygen atom is *trans* to a methyl group and the other *trans* to a carbonyl group. As a result of the low population parameter of 0.154(3) for I(2), the bond distance Rh–I(2) may be regarded as meaningless.

The central Rh atom is octahedrally surrounded by the six atoms P(1), P(2), O(1), O(2), I(1) and C. The bond angles between the atoms defining the coordination polyhedron (Table 3), as well as the average twist angle, ϕ, of 59.3°, proved an almost ideal octahedral geometry. The twist angle, ϕ, as defined and described by Muetterties and Guggenberger [18], has values of 60° and 0° for an ideal octahedron and an ideal trigonal prism, respectively. The three equatorial planes of the octahedron P(1), P(2), O(1), O(2) and P(1), I(1), O(2), C and O(1), P(2), I(1), C make angles of 85.7, 87.1 and 89.6° with each other and are planar within experimental error.

The crystal structure determination clearly indicates a *trans* addition of methyl iodide to [$Rh(BPHA)(P(OPh)_3)_2$]. This result strongly favours an ionic S_N2 two-step mechanism since a concerted three-centered mechanism should result in a *cis* addition of methyl iodide. This is in agreement with the results of a high-pressure kinetic study of the oxidative addition of CH_3I to [$Rh(LL')(P(OPh)_3)_2$] complexes [8] which strongly favours an ionic S_N2 addition mechanism with a linear transition state, Rh——CH_3——I, which implies a *trans* addition.

The kinetic results of the oxidative addition of CH_3I to [$Rh(cupf)(CO)(PPh_3)$] as well as the crystal structure determination of the final oxidative addition product [10] however point to a *cis* addition. A concerted three-centered transition state is thus not ruled out. In agreement with this, the kinetic and structural results of the oxidative addition of I_2 [19] and $Hg(CN)_2$ [20] to complexes of the type [$Rh(LL')(P(OPh)_3)_2$] also points to a *cis* addition. The final *cis* addition product [$Rh(cupf)(CO)(PPh_3)(CH_3)(I)$] could however have resulted via a fast isomerization of an original *trans* oxidative addition product although no isomerization reaction was observed. We must however point out that the *cis* → *trans* isomerization reaction of [$Rh(\beta\text{-diketone})(P(OPh)_3)_2(I)_2$] is fast with a half-life of only about 2 seconds [17]. Such a fast isomerization reaction would have been undetectable in comparison with the relatively slow oxidative addition reaction of [Rh(cupf)(CO)(PPh$_3$)] with CH$_3$I with a half-life of about 600 seconds [10].

Supplementary Material

A list of the thermal parameters is available from the authors.

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