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Synthesis, Reactivity and Crystal Structure of $[Rh(C_6H_5Me)\{P(OPh)_3\}_2]ClO_4$

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The complex $[Rh(C_6H_5Me)\{P(OPh)_3\}_2]ClO_4$ *undergoes reactions which give rise to the replacement of the toluene by N- or P-donor ligands, diolefin or arenes and lead to cationic or neutral rhodium(I) complexes.*

The title compound is monoclinic $P2_1/c$ *with* a = *14.9559(10),* b = *10.1843(5),* c = *26.6971(40)* Å, β = *92.49(1)*° *and* Z = *4. The structure has been determined from three-dimensional data collected by X-rays counter methods. Final* R *value is 0.034 for 5524 observed independent reflections. The Rh atom appears* π*-bonded to the arene ring which is puckered, to some extent, as to give a distorted boat-like conformation.*

Introduction

The synthesis of cationic rhodium(I) complexes of the type $[Rh(arene)\{P(OPh)_3\}_2]^+$ (arene = C_6H_6, $C_6H_3Me_3$, C_6Me_6) has been reported in two communications [1, 2]. Furthermore, other arene complexes of the general formula $[Rh(arene)(diolefin)]^+$ have also been prepared [3, 4] and their reactivity shows them as coordinatively unsaturated species [3].

In the present paper we describe the synthesis, reactivity and crystal structure of the complex $[Rh(C_6H_5Me)\{P(OPh)_3\}_2]ClO_4$.

Results and Discussion

Synthesis and Reactivity

The dimeric complex $[RhCl\{P(OPh)_3\}_2]_2$ (I) [5] reacts in dichloromethane–toluene (1:2) with silver perchlorate, according to eqn. (1)

$$1/2[RhCl\{P(OPh)_3\}_2]_2 + AgClO_4 + C_6H_5Me \longrightarrow [Rh(C_6H_5Me)\{P(OPh)_3\}_2]ClO_4 + AgCl \quad (1)$$

to give $[Rh(C_6H_5Me)\{P(OPh)_3\}_2]ClO_4$ (II), which after removal of the precipitated silver chloride and concentration of the solution can be isolated as yellow crystals. Complex (II) has been identified by elemental analysis and its n.m.r. spectrum confirms the coordination of the toluene (τ8.15 (3H, Me), 4.25 (5H, aromatic)).

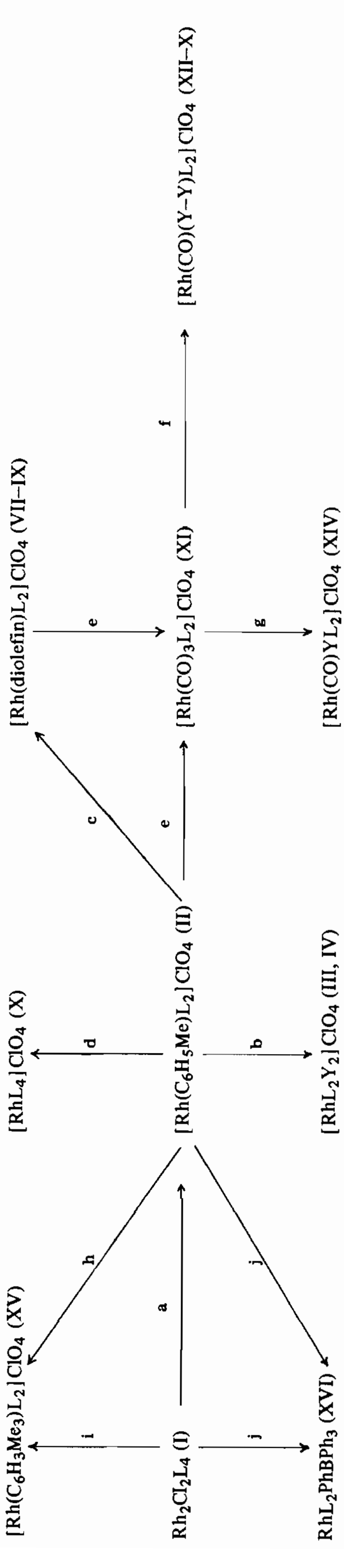
Complex (II) reacts readily with different ligands as may be seen from the Scheme. Thus, addition of *p*-methoxybenzonitrile, *o*-chlorobenzonitrile 2-ethylpyridine or 4-methylpyridine gives rise to the substitution of the toluene and formation of $[Rh(p\text{-}MeO{-}C_6H_4{-}CN)_2\{P(OPh)_3\}_2]ClO_4$ (III), $[Rh(o\text{-}Cl{-}C_6H_4{-}CN)_2\{P(OPh)_3\}_2]ClO_4$ (IV), $[Rh(2\text{-}Et\text{-}py)_2\{P(OPh)_3\}_2]ClO_4$ (V) or, respectively, $[Rh(4\text{-}Me\text{-}py)_2\{P(OPh)_3\}_2]ClO_4$ (VI). Complexes (III) and (IV) show vibrations in the 2270–2250 cm^{-1} range (KBr), which being assignable to the coordinated nitrile are shifted towards higher energies ($\Delta\nu \simeq$ 15–30 cm^{-1}) with respect to the free ligand. This indicates coordination of the nitrile groups to the rhodium atom *via* σ-donation of the lone pair on the nitrogen atom [6–9].

Similarly, complex (II) reacts readily with diolefins such as 1,5-cyclooctadiene (COD), 2,5-norbornadiene (NBD) to give the previously described [10] complexes $[Rh(COD)\{P(OPh)_3\}_2]ClO_4$ (VII) and $[Rh(NBD)\{P(OPh)_3\}_2]ClO_4$ (VIII) and with tetrafluorobenzobicyclo(2,2,2)octatriene (tetrafluorobenzobarrelene, TFB), which behaves as a diolefin ligand, to give the complex $[Rh(TFB)\{P(OPh)_3\}_2]ClO_4$ (IX). Complex (IX) can also be prepared by reaction (2)

$$1/2[RhCl(TFB)]_2 + AgClO_4 + 2P(OPh)_3 \longrightarrow [Rh(TFB)\{P(OPh)_3\}_2]ClO_4 + AgCl \quad (2)$$

The reaction of complex (II) with an excess of triphenylphosphite in dichloromethane solution leads to the previously described [5] coordinatively unsaturated compound $[Rh\{P(OPh)_3\}_4]ClO_4$ (X).

SCHEME



L = P(OPh)$_3$. ^{a}AgClO$_4$(CH$_2$Cl$_2$:C$_6$H$_5$Me); ^{b}Y = p-MeO–C$_6$H$_4$–CN, o-Cl–C$_6$H$_4$–CN, 2Et-py or 4-Me-py; ^{c}diolefin = TFB, NBD, COD; ^{d}L; ^{e}CO; ^{f}(Y–Y) = bipy or phen; ^{g}Y = p-MeO–C$_6$H$_4$–CN; ^{h}C$_6$H$_3$Me$_3$; ^{i}AgClO$_4$(CH$_2$Cl$_2$:C$_6$H$_3$Me$_3$); ^{j}NaBPh$_4$.

Both complex (II) and also the complexes of the type [Rh(diolefin){P(OPh)$_3$}$_2$]ClO$_4$ react with carbon monoxide to form [Rh(CO)$_3${P(OPh)$_3$}$_2$]-ClO$_4$ (XI). The single band due to ν(CO) at 2015 cm^{-1} observed in chloroform solution suggest a trigonal bipyramidal structure with the three CO groups on the equatorial plane. Moreover in potassium bromide discs it shows three bands at 2140(m), 2070(s) and 2040(s) cm^{-1} which indicate a noticeable distorsion in the solid state [11]. The reaction of complex (XI) with bidentate ligands, such as bipyridine or phenanthroline gives rise to the displacement of two CO groups and to the formation of the novel pentacoordinated complexes [Rh(CO)(bipy)-{P(OPh)$_3$}$_2$]ClO$_4$ (XII) and [Rh(CO)(phen){P-(OPh)$_3$}$_2$]ClO$_4$ (XIII) which exhibit a strong absorption due to ν(CO) at 2020 cm^{-1}. Similarly, addition of the monodentate ligand (p-MeO–C$_6$H$_4$–CN) to complex (XI) renders the tetracoordinated complex [Rh(CO)(p-MeO–C$_6$H$_4$–CN){P(OPh)$_3$}$_2$]ClO$_4$ (XIV) [ν(CN) = 2255 cm^{-1} and ν(CO) = 2014 cm^{-1}] (CH$_2$Cl$_2$ solution).

On the other hand, reaction of 1,3,5-C$_6$H$_3$Me$_3$ with solutions of complex (II) gives [Rh(C$_6$H$_3$Me$_3$)-{P(OPh)$_3$}$_2$]ClO$_4$ (XV) which can also be obtained by reacting complex (I) with silver perchlorate in dichloromethane–trimethylbenzene solution [2]. Another interesting reaction is that of complex (II) with sodium tetraphenylborate which gives rise to the precipitation of the neutral complex Rh{P-(OPh)$_3$}$_2$PhBPh$_3$ (XVI) which is also obtainable from complex (I). It seems noteworthy that the crystal structure of the analogous complex Rh{P-(OMe)$_3$}$_2$PhBPh$_3$ shows a boat-like conformation of the arene ring [12, 13].

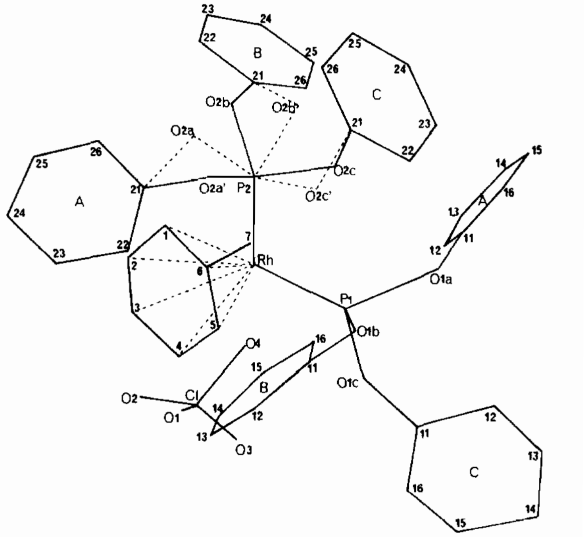


Fig. 1. A projection of the compound viewed down the (100) axis.

The analytical data of the complexes confirm the proposed formulation. As previously observed for analogous complexes [5, 10] some of them crystallize with dichloromethane molecules. All the complexes are yellow or orange-coloured crystals and exhibit the bands which are characteristic of the perchlorate anion (T_d) at approx. 1100 and 620 cm^{-1} [14]. Conductance studies in acetone show them as uni-univalent electrolytes.

Crystal Structure

The crystal data, together with the experimental conditions and the solution and refinement procedures and parameters are given in Table I.

Atomic parameters, from the last refinement cycle are given in Table II. In the Figure 1, a projection of the structure along (100), together with the atomic numbering, is shown. The main geometrical characteristics of the structure are shown in Tables III and IV. A schematic view of the Rh neighbourghood is presented in Fig. 2.

A.- *The phenyl rings*

The six rings are planar within experimental error. Atomic deviations from the best least squares plane through each of them range from 0 to 0.013 Å, in absolute value, with an average of 0.004 Å. The fit, as measured by the χ^2_5 (X-Ray System 1970)

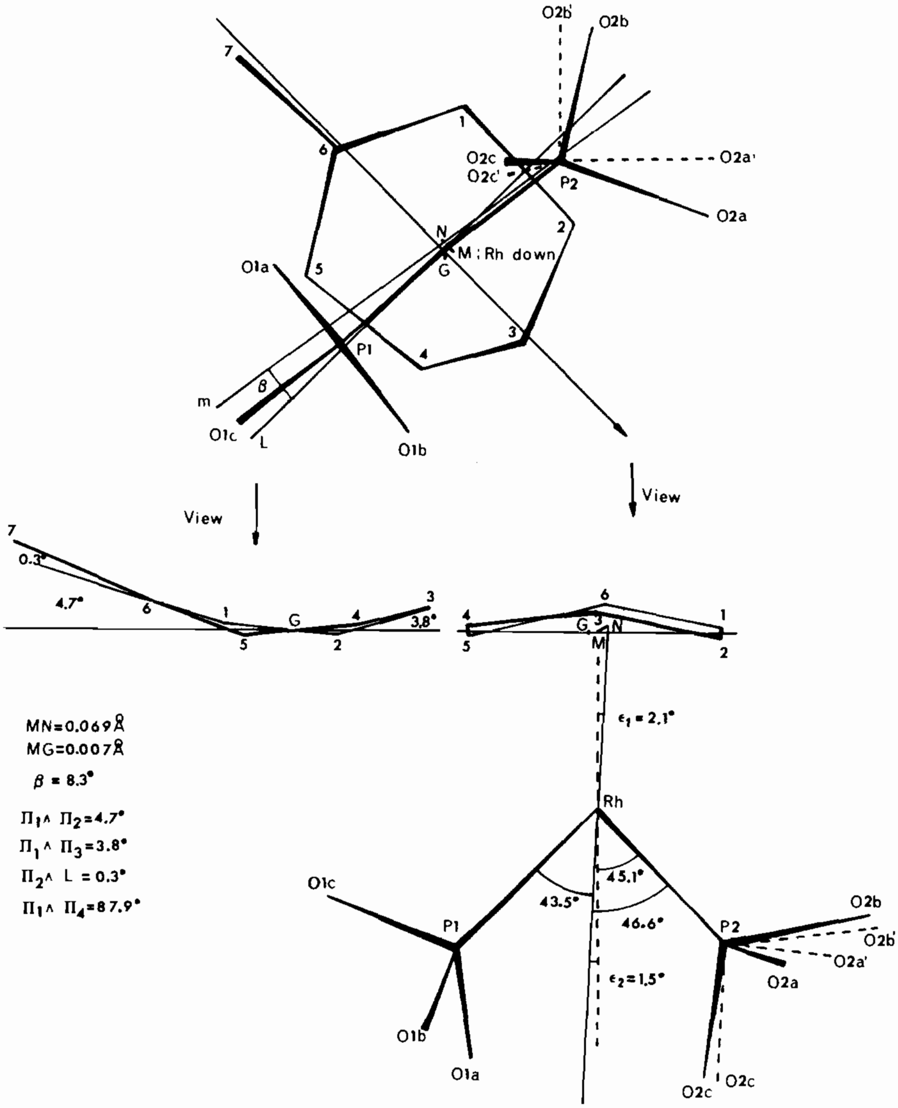


Fig. 2. Schematic views of the Rh bonding and arene ring deformation. Π stands for "plane", L for "line". G is the C(1), C(2), C(4), C(5) centroid. L is drawn through G and parallel to the midpoints of C(1)–C(2) and C(3)–C(4), which define the reference plane and its normal n. Π_1 is through C(1), C(2), C(4), C(5), Π_2 through C(1), C(5), C(6), Π_3 through C(2), C(3), C(4), Π_4 through Rh, P(1), P(2) and L C(7), C(8). m is the intersection of Π_1 and Π_4. M is the projection of Rh along n onto Π_1 and N is the orthogonal projection of Rh along Π_4 onto Π_1.

TABLE I. Crystal Analysis Parameters for $[Rh(C_6H_5Me)\{P(OPh)_3\}_2]ClO_4$ at Room Temperature.

a) *Crystal Data*

Crystal size and habit: 0.14 × 0.30 × 0.45 mm; yellow, transparent, prismatic deformed hexagonal basis, elongated on the axis.
Symmetry: Monoclinic 2/m. $P2_1/c$.
Unit cell determination: Least squares fit from 78 reflections up $\theta < 25°$.
Unit cell dimensions: $a = 14.9559(10)$, $b = 10.1843(5)$, $c = 26.6971(40)$ Å, $\beta = 92.49(1)°$.
Packing: $V = 4062.5(5)$ Å^3, $Z = 4$, $D_c = 1.496$ Mg m^{-3}, Mr = 915.1, $F(000) = 1872$ e.

b) *Experimental Data*

Technique: 4-circle Philips PW 1100 diffractometer, bisecting geometry.
Orientation: $(h0h)$ with $\chi \sim 0.3°$, $\phi \sim 106.6°$; $(0k0)$, $\chi \sim 84.8°$, $\phi \sim 12.0°$.
Monochromator: Graphite oriented for MoK$_{\bar{\alpha}}$ ($\bar{\lambda} = 0.71069$ Å).
Collection mode: ω-2θ up to 25°; $(\sin\theta/\lambda)_{max} = 0.595$ Å^{-1}. Scan width 0.8°. Detector windows 1° × 1°. 1 min. per reflexion.
Number of data independent: 7343.
Number of data observed: 5526 with $I_{obs} > 2\sigma_c(I)$ criterion.
Stability: 2 standards monitored every 90 min. No variation detected.
Absorption: $\mu = 6.157$ cm^{-1}. Crystal faces (010) (001) (100) (102)
Maximum and minimum transmission factors 0.929, 0.847.

c) *Solution and Refinement*

Solution mode: Patterson techniques.
Refinement mode: Least square on Fs. Observed reflections only. 14 blocks for the final. Mixed thermal model with H isotropic. Final shift/error 0.14.
Parameters: Number of variables 693, degrees of freedom: 4831, ratio of freedom: 8.
Extinction: Two reflections ($\bar{1}02$) (102) omitted.
W-scheme: Empirical to give no trends in $\langle w\Delta^2\rangle$ *vs.* $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$
Thermal values: U_{22} C(7) = 0.164, U_{11} C(15c) = 0.176 Å^2 maximum values.
Disorder: For one PO$_3$ group in the O's. Population parameters refined.
ΔF: Revealed the disorder with peaks of 2 eÅ^{-3}. Gave all H-atoms. Final with noise of −0.26 to 0.30 eÅ^{-3}.
R and R_w (final): 0.034 and 0.038.
Atomic scattering factors from International Tables for X-ray Crystallography [15]. Neutral atoms.
Real part of anomalous dispersion applied for Rh, Cl and P (International Tables).
Computing: X-System of Stewart *et al.* [16] on a UNIVAC 1100/80.

estimator range from 0.1, for ring 1A, to 10.7, for ring 1C, with an average of 6.6. The average geometries for the rings are given in Table IV.

B.- *The ClO_4^- group*

It does not present any special feature, as compared with the literature.

C.- *The PO_3 groups*

Two of them are present in the molecule. The one involving P2 (see Fig. 1) appeared doubled in one of the final ΔF syntheses, with hights of about 2 eÅ^{-3}. So a disordered model was included in the refinement, with population parameters for each oxygen pairs constrained to sum unity. The final populations were 0.24(1) and 0.76(1) for each set. The disorder is somehow particular in that each pair of disordered oxygen share the same Ph-ring, which have no much higher thermal parameters than the other three rings.

D.- *The Rh-arene bonding*

The Rh atom appears π-bonded to the arene ring (Nolte *et al.* [13]), in agreement with some Mo compounds (Atwood *et al.* [18]). From the distances of the Rh atom to the arene ring, from the torsion angles within the arene ring (Table IV) and from the least squares planes calculations, the boat-like distortion of the ring is apparent.

Rh distances to C(3) and to C(6) are higher than the rest, which vary in a pairwise fashion: to C(2) and to C(5) are the shortest and to C(1) and C(4) are in between. Torsion angles on C(4)–C(5) and on C(1)–C(2) are the lowest and moreover, as compared with the planes of the Ph-rings, the best least squares plane through the arene ring has a χ_3^2 of 153.9 (see Table IV). The atomic deviations to the plane show pairwise relations analogous to the Rh–C distances. Matching the torsion angles values, the ring can be divided into the two 4-membered parts with lowest χ^2 values, namely those formed by C(6), C(1), C(2), C(3) and C(3) to C(6), to describe the boat. Both parts make a dihedrical angle of 5.2°. Thus the best least squares plane through C(1), C(2), C(4) and C(5) is taken as reference plane through the ring, see Fig. 2, with χ_3^2 of 14.3 versus 69.6 and 140.1 for the other two possibilities. It makes angles of 0.2°, 2.6° and 2.6° with

TABLE II. Atomic Parameters.

Final Fractional coordinates and temperature factors in the expression exp $10^{-5}[-2\pi^2(\sum_{j=1}^{3} U_{ij}a_i^*a_j^*h_ih_j)]$, while for hydrogen the isotropic expression is: exp 10^{-3}. $(-8\pi^2U\sin^2\theta/\lambda^2)$. (see output from computer). Table of observed structure factors compared with the calculated ones is available either from the authors or the editor.

Atom		X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
Rh		0.190592(14)	0.165928(23)	0.095851(7)	3142(11)	4241(13)	3331(11)	108(10)	−128(1)	135(11)
P	1	0.243832(46)	0.250518(79)	0.165995(27)	2850(34)	4292(43)	3373(37)	108(31)	−239(21)	−13(32)
O	1A	0.245272(130)	0.170993(232)	0.217817(73)	3313(99)	5792(130)	3560(101)	−18(101)	−311(79)	577(104)
C	11A	0.172273(201)	0.105794(329)	0.237281(109)	4060(165)	4793(176)	3473(152)	−363(141)	487(125)	−184(137)
C	12A	0.084973(224)	0.134675(380)	0.222135(137)	4155(175)	6405(239)	5359(198)	−298(156)	187(146)	178(167)
C	13A	0.016321(273)	0.069853(480)	0.245164(164)	4742(232)	8080(289)	6959(256)	−1295(205)	805(192)	248(226)
C	14A	0.035251(332)	−0.020261(517)	0.282030(181)	6886(286)	8477(320)	7196(278)	−2545(249)	1481(228)	1542(249)
C	15A	0.121636(345)	−0.047547(490)	0.296447(176)	8689(326)	7879(307)	6883(266)	−1025(242)	753(229)	3035(231)
C	16A	0.191214(308)	0.015913(435)	0.274012(151)	5934(226)	6995(257)	5645(220)	120(201)	−372(179)	1820(194)
O	1B	0.346460(130)	0.290389(216)	0.173371(76)	3209(99)	5250(127)	3655(105)	−710(90)	−166(82)	67(93)
C	11B	0.398787(194)	0.347341(317)	0.136729(114)	3610(145)	4173(175)	4038(155)	−640(136)	123(121)	−842(143)
C	12B	0.364929(238)	0.435802(358)	0.102182(130)	4337(187)	5165(198)	4896(189)	−363(157)	−89(146)	−312(161)
C	13B	0.423342(296)	0.489847(456)	0.068448(162)	6645(260)	5932(239)	5615(226)	−738(204)	281(192)	976(205)
C	14B	0.512457(299)	0.457195(437)	0.071132(170)	6505(256)	6707(268)	6620(246)	−2078(213)	2022(209)	86(211)
C	15B	0.544537(256)	0.369945(450)	0.106015(183)	4566(197)	7428(278)	8594(287)	−566(185)	1855(194)	600(234)
C	16B	0.487901(233)	0.313329(411)	0.139519(158)	4117(180)	5754(228)	6636(230)	333(166)	566(163)	573(201)
O	1C	0.190947(140)	0.383554(224)	0.178331(78)	4313(114)	5310(129)	3822(112)	1009(101)	−657(89)	−807(99)
C	11C	0.216705(211)	0.467540(342)	0.218988(122)	4163(168)	5348(199)	4347(182)	1418(147)	−324(136)	−763(150)
C	12C	0.203317(239)	0.431255(402)	0.267600(137)	5128(193)	6518(231)	5196(204)	−135(174)	574(156)	−685(176)
C	13C	0.226333(284)	0.519827(527)	0.305573(178)	6539(252)	8604(338)	4783(236)	1227(231)	79(188)	−1411(228)
C	14C	0.260827(367)	0.639790(493)	0.295225(206)	9734(341)	6247(300)	7895(329)	600(243)	−389(256)	−3276(255)
C	15C	0.274316(506)	0.671795(496)	0.246912(196)	17755(571)	5164(256)	7040(307)	−1230(317)	838(315)	−1017(242)
C	16C	0.250871(387)	0.586647(409)	0.207632(178)	12660(392)	4326(219)	5937(252)	368(234)	1102(253)	−569(195)
P	2	0.281243(50)	−0.001544(84)	0.105925(29)	3759(40)	4295(43)	3859(40)	287(33)	−862(31)	−302(35)
O	2A	0.371841(196)	−0.001071(346)	0.074989(111)	4002(154)	6353(198)	4398(160)	573(159)	−176(128)	−176(154)
O	2A′	0.315231(668)	−0.077127(892)	0.058794(318)	6487(745)	3714(618)	3467(558)	752(463)	529(410)	−456(390)
C	21A	0.368750(266)	0.018494(454)	0.022138(141)	6232(225)	7813(290)	4582(192)	2877(218)	1038(162)	710(189)
C	22A	0.401984(381)	0.137386(579)	0.009300(263)	8305(337)	7056(362)	10329(451)	−1436(256)	−243(289)	−3732(338)
C	23A	0.408051(502)	0.161876(754)	−0.042049(295)	13091(524)	8363(405)	12358(579)	−4059(386)	4244(409)	1607(417)
C	24A	0.381879(469)	0.071836(686)	−0.076252(221)	14182(507)	10266(430)	6020(312)	−957(378)	2579(304)	−66(304)
C	25A	0.352504(416)	−0.042380(579)	−0.062524(206)	11176(391)	9056(360)	6703(307)	−147(300)	−865(269)	−2290(275)
C	26A	0.343949(320)	−0.072758(509)	−0.013959(200)	7969(295)	5402(259)	8801(344)	−196(218)	1326(238)	−506(238)
O	2B	0.243016(207)	−0.138982(304)	0.087805(137)	5242(181)	4605(186)	6260(226)	−277(138)	−503(152)	−1159(150)
O	2B′	0.237165(565)	−0.138276(807)	0.132347(377)	4007(448)	3677(501)	5216(593)	−682(362)	−1672(384)	1136(393)
C	21B	0.156583(266)	−0.188334(372)	0.100312(187)	5290(200)	4134(205)	9990(312)	−122(159)	−1935(200)	626(209)
C	22B	0.120676(370)	−0.260517(437)	0.063091(229)	8547(339)	4925(247)	8162(326)	230(234)	1059(287)	278(234)

(Continued overleaf)

TABLE II. *(Continued)*

C	23B	0.038275(383)	−0.313026(507)	0.066505(245)	8918(382)	5929(286)	8747(355)	−715(253)	−3701(320)	−812(258)
C	24B	−0.009373(338)	−0.293491(497)	0.106728(284)	6563(278)	6326(291)	14632(536)	−2151(224)	413(316)	569(311)
C	25B	0.027324(569)	−0.220697(612)	0.145787(267)	14825(622)	7510(347)	8898(401)	−369(369)	4785(424)	1130(305)
C	26B	0.112965(420)	−0.167432(514)	0.142595(211)	11761(441)	5690(258)	8055(312)	−1860(286)	−4080(307)	214(252)
O	2C	0.325062(189)	−0.023063(298)	0.159680(108)	4532(157)	4925(168)	4595(164)	992(133)	−1111(126)	−288(131)
O	2C′	0.360557(471)	0.015992(756)	0.145302(325)	2031(357)	2595(402)	5647(500)	−347(311)	−1774(338)	−550(367)
C	21C	0.409035(238)	−0.087874(367)	0.171894(131)	5740(202)	4912(204)	5109(193)	1755(166)	−2002(158)	−30(162)
C	22C	0.463697(266)	−0.029952(421)	0.207706(142)	6653(236)	4427(220)	5133(206)	231(179)	−1810(173)	−144(171)
C	23C	0.538141(273)	−0.096230(448)	0.225893(160)	5618(218)	6624(269)	6189(229)	−188(203)	−2178(193)	946(208)
C	24C	0.556598(253)	−0.219398(435)	0.207870(151)	5268(206)	6951(263)	6160(227)	1426(187)	−1042(170)	2003(199)
C	25C	0.501297(284)	−0.275321(442)	0.172412(164)	7111(255)	4661(222)	6894(248)	1560(194)	−843(194)	398(204)
C	26C	0.426522(301)	−0.209554(406)	0.153546(174)	7078(253)	5192(222)	7303(260)	1433(191)	−2735(217)	−1558(195)
Cl		−0.212722(57)	0.431461(93)	0.062741(35)	4696(43)	5993(52)	6145(50)	−677(39)	−118(37)	531(43)
O	1	−0.121518(185)	0.438510(364)	0.052224(141)	4873(147)	10217(241)	10785(239)	−1058(155)	515(151)	1170(200)
O	2	−0.264079(237)	0.417378(484)	0.017622(144)	7772(208)	14385(337)	9127(236)	−495(224)	−2743(178)	933(237)
O	3	−0.237783(323)	0.549232(427)	0.086113(181)	13190(325)	9379(268)	12437(323)	1825(238)	2346(261)	−2222(234)
O	4	−0.229520(243)	0.324348(392)	0.094530(159)	8281(209)	9524(245)	12157(287)	−1832(190)	135(194)	4625(225)
C	1	0.079128(298)	0.087104(487)	0.040705(169)	7328(260)	5779(271)	8078(285)	1470(216)	−5418(224)	−1634(217)
C	2	0.150370(340)	0.136864(756)	0.012738(158)	7197(280)	14664(584)	4043(213)	5306(350)	−2321(194)	−2456(276)
C	3	0.174675(345)	0.265651(814)	0.016072(196)	6381(279)	13623(563)	5476 (265)	1470(326)	−893(225)	3597(340)
C	4	0.135236(302)	0.341558(576)	0.048937(202)	6068(260)	6435(294)	8928(341)	−535(235)	−3269(263)	3233(274)
C	5	0.066571(293)	0.294808(437)	0.078104(175)	5739(237)	6504(276)	5969(235)	2774(222)	−2461(197)	−872(208)
C	6	0.033115(224)	0.167901(432)	0.072980(146)	3884(171)	6914(246)	6446(217)	294(181)	−1937(153)	1099(203)
C	7	−0.046923(347)	0.124352(1125)	0.100390(362)	4022(251)	16358(832)	14153(616)	−1062(323)	−1420(294)	7186(541)

Atom		X/A	Y/B	Z/C	U
H	12A	0.073(2)	0.203(4)	0.199(1)	49(12)
H	13A	−0.045(4)	0.098(5)	0.236(2)	63(14)
H	14A	−0.005(3)	−0.064(4)	0.299(1)	43(12)
H	15A	0.131(4)	−0.114(6)	0.323(2)	85(17)
H	16A	0.247(3)	0.005(4)	0.282(1)	37(0)
H	12B	0.301(2)	0.468(3)	0.100(1)	21(8)
H	13B	0.398(2)	0.544(4)	0.048(1)	29(11)
H	14B	0.554(3)	0.489(5)	0.049(1)	50(13)
H	15B	0.606(3)	0.349(4)	0.107(1)	51(12)
H	16B	0.512(2)	0.255(4)	0.162(1)	23(9)
H	12C	0.175(2)	0.353(3)	0.276(1)	18(8)
H	13C	0.216(2)	0.491(4)	0.334(1)	25(10)
H	14C	0.272(4)	0.695(6)	0.320(2)	77(18)

(Continued on facing page)

TABLE II. *(Continued)*

H	15C	0.292(4)	0.748(6)	0.240(2)	122(19)
H	16C	0.272(4)	0.613(7)	0.175(2)	87(20)
H	22A	0.415(4)	0.182(7)	0.026(2)	77(25)
H	23A	0.426(5)	0.224(8)	−0.053(3)	93(25)
H	24A	0.382(3)	0.081(5)	−0.112(2)	57(14)
H	25A	0.325(4)	−0.103(7)	−0.087(2)	86(19)
H	26A	0.330(4)	−0.154(8)	−0.004(2)	100(23)
H	22B	0.147(3)	−0.273(4)	0.039(2)	35(14)
H	23B	0.022(3)	−0.355(6)	0.045(2)	59(17)
H	24B	−0.069(4)	−0.326(6)	0.108(2)	79(17)
H	25B	0.004(4)	−0.206(6)	0.168(2)	60(19)
H	26B	0.138(3)	−0.127(5)	0.166(2)	64(16)
H	22C	0.453(2)	0.048(4)	0.219(1)	14(9)
H	23C	0.578(3)	−0.059(4)	0.248(1)	42(12)
H	24C	0.606(2)	−0.270(4)	0.221(1)	42(11)
H	25C	0.512(2)	−0.356(5)	0.160(1)	37(11)
H	26C	0.389(3)	−0.244(5)	0.129(2)	52(13)
H	1	0.058(3)	0.003(5)	0.043(1)	48(13)
H	2	0.186(4)	0.089(6)	−0.011(2)	77(18)
H	3	0.222(3)	0.293(5)	−0.010(2)	64(15)
H	4	0.148(3)	0.428(5)	0.051(1)	39(12)
H	5	0.041(3)	0.339(4)	0.098(1)	32(12)
H	7A	−0.036(6)	0.105(11)	0.134(4)	122(34)
H	7B	−0.045(5)	0.036(8)	0.100(3)	93(29)
H	7C	−0.096(4)	0.143(5)	0.079(2)	71(16)

TABLE III. Some Interatomic Distances (A) and Angles (°) with the Least-squares Estimates for the Standard Deviations in Parentheses.

a.- *Arene*			
C(1)–C(2)	1.421(7)	C(6)–C(1)–C(2)	121.0(5)
C(2)–C(3)	1.363(11)	C(1)–C(2)–C(3)	120.9(5)
C(3)–C(4)	1.327(8)	C(2)–C(3)–C(4)	118.6(5)
C(4)–C(5)	1.399(7)	C(3)–C(4)–C(5)	121.9(6)
C(5)–C(6)	1.391(6)	C(4)–C(5)–C(6)	122.1(4)
C(6)–C(1)	1.394(6)	C(5)–C(6)–C(1)	115.1(4)
C(6)–C(7)	1.497(8)	C(5)–C(6)–C(7)	121.3(5)
		C(1)–C(6)–C(7)	123.6(6)
b.- *Rh bonds*			
Rh–C(1)	2.319(4)	Rh–C(2)	2.293(4)
Rh–C(3)	2.362(6)	Rh–C(4)	2.316(6)
Rh–C(5)	2.305(4)	Rh–C(6)	2.407(3)
Rh–P(1)	2.180(1)	Rh–P(2)	2.188(1)
c.- *ClO_4-group*			
Cl–O(1)	1.406(3)	O(1)–Cl–O(2)	109.4(2)
Cl–O(2)	1.408(4)	O(1)–Cl–O(3)	108.9(3)
Cl–O(3)	1.410(5)	O(1)–Cl–O(4)	111.0(2)
Cl–O(4)	1.411(4)	O(2)–Cl–O(3)	108.6(3)
		O(2)–Cl–O(4)	109.3(3)
		O(3)–Cl–O(4)	109.5(3)

(Continued overleaf)

the six membered plane and with the planes through the above mentioned 4-membered halves.

The Rh situation is described in Fig. 2. Its distance to G (the geometrical centroid of the C(1), C(2), C(4), C(5) set) is 1.863(9) Å, to the center of the C(1)–C(2) bond is 2.194(6) Å and to the C(4)–C(5) center is 2.202(7) Å, with angles of P(2)–Rh–(1-2) = 101.7(2)°, P(1)–Rh–(4-5) = 104.6(2)°, (1-2)–Rh–(4-5) = 64.1(3)° and P(1)–Rh–P(2) = 90.07(3)°, all of which describe the square planar interpretation for the Rh bonding [13].

The three arene rings mentioned in the literature [13, 18] show the same type of deformations than the present one, but to a bit higher degree.

Further work on related rhodium complexes with more symmetrical arene ligands is in progress.

E.- *Packing*

No other significant distances between atomic groups, were found in the structure, so the packing is due to van der Waals forces.

Experimental

The C, H and N analyses were made with a Perkin-Elmer 240 microanalyzer. The i.r. spectra were recorded on a Perkin-Elmer 577 spectrophotometer using KBr discs or chloroform or dichloromethane solutions of the compounds. Conductivities were measured in ~5 × 10^{-4} *M* solutions with a Philips PW 9501/01 conductimeter.

TABLE III. *(Continued)*

d.- *PO_3-groups*

P(1)–O(1a)	1.602(2)	O(1a)–C(11a)	1.397(4)
P(1)–O(1b)	1.592(2)	O(1b)–C(11b)	1.404(4)
P(1)–O(1c)	1.610(2)	O(1c)–C(11c)	1.424(4)
P(2)–O(2a)	1.617(3)	O(2a)–C(21a)	1.424(5)
P(2)–O(2a′)	1.578(9)	O(2a′)–C(21a)	1.617(10)
P(2)–O(2b)	1.580(3)	O(2b)–C(21b)	1.440(5)
P(2)–O(2b′)	1.706(9)	O(2b′)–C(21b)	1.534(10)
P(2)–O(2c)	1.567(3)	O(2c)–C(21c)	1.444(5)
P(2)–O(2c′)	1.561(8)	O(2c′)–C(21c)	1.450(9)
Rh–P(1)–O(1a)	122.2(1)	P(1)–O(1a)–C(11a)	125.4(2)
Rh–P(1)–O(1b)	121.4(1)	P(1)–O(1b)–C(11b)	125.6(2)
Rh–P(1)–O(1c)	110.1(1)	P(1)–O(1c)–C(11c)	122.9(2)
Rh–P(2)–O(2a)	117.6(1)	P(2)–O(2a)–C(21a)	121.0(3)
Rh–P(2)–O(2a′)	120.1(3)	P(2)–O(2a′)–C(21a)	112.0(6)
Rh–P(2)–O(2b)	116.0(1)	P(2)–O(2b)–C(21b)	123.7(3)
Rh–P(2)–O(2b′)	116.0(3)	P(2)–O(2b′)–C(21b)	110.4(6)
Rh–P(2)–O(2c)	117.0(1)	P(2)–O(2c)–C(21c)	126.6(3)
Rh–P(2)–O(2c′)	116.3(3)	P(2)–O(2c′)–C(21c)	126.6(5)
O(1a)–P(1)–O(1b)	92.6(1)	C(22a)–C(21a)–O(2a)	112.2(4)
O(1a)–P(1)–O(1c)	103.7(1)	C(22a)–C(21a)–O(2a′)	152.3(5)
O(1b)–P(1)–O(1c)	103.9(1)	C(26a)–C(21a)–O(2a)	126.5(4)
O(2a)–P(2)–O(2b)	98.4(2)	C(26a)–C(21a)–O(2a′)	83.8(4)
O(2a)–P(2)–O(2c)	98.2(2)	C(22b)–C(21b)–O(2b)	110.9(4)
O(2b)–P(2)–O(2c)	106.7(2)	C(22b)–C(21b)–O(2b′)	151.9(5)
O(2a′)–P(2)–O(2b′)	94.3(5)	C(26b)–C(21b)–O(2b)	127.8(4)
O(2a′)–P(2)–O(2c′)	109.3(5)	C(26b)–C(21b)–O(2b′)	83.0(5)
O(2b′)–P(2)–O(2c′)	96.4(4)	C(22c)–C(21c)–O(2c)	116.7(3)
O(2a)–P(2)–O(2a′)	44.6(4)	C(22c)–C(21c)–O(2c′)	107.4(4)
O(2b)–P(2)–O(2b′)	42.5(4)	C(26c)–C(21c)–O(2c)	120.9(3)
O(2c)–P(2)–O(2c′)	28.8(3)	C(26c)–C(21c)–O(2c′)	126.0(5)

TABLE IV. Some Geometrical Characteristics for the Compound.

TABLE IVa. Average geometry in the phenyl rings. The range is given as the minimum–maximum values. In terms of the pooled e.s.d .s it is given as $|M_x\text{-min}|/(\sigma_{M_x}^2\text{-}\sigma_{min}^2)^{1/2}$. The average is calculated as $\Sigma x_i/\sigma_i^2/\Sigma\ 1/\sigma_i^2$. The internal and external e.s.d .s are given as $1/(\Sigma\ 1/\sigma_i^2)^{1/2}$ and $[\Sigma(x_i\text{-}\bar{x})^2/\sigma_i^2/(N\text{-}1)\Sigma(1/\sigma_i^2)]^{1/2}$ (Domenicano *et al.)* [17].

Parameter	Range	No. of data	Range in σp terms	Average	Internal and external e.s.d.
C–C bond (Å)	1.302(4)–1.400(11)	36	6.9	1.369	0.001, 0.003
C–C–C angle (°)	116.5(3)–122.1(3)	36	8.3	120.0	0.1, 0.2
C–H bond (Å)	0.65(8)–1.01(4)	30	4.0	0.90	0.01, 0.01
C–C–H angle (°)	113(3)–127(3)	60	3.3	120.0	0.4, 0.5

TABLE IVb. Some torsion angles in (°) with the corresponding e.s.d. s.

C(1)–C(2)–C(3)–C(4)	5.7(7)	G–Rh–P(1)–O(1a)	137.0(3)
C(2)–C(3)–C(4)–C(5)	–4.9(10)	G–Rh–P(1)–O(1b)	–133.0(3)
C(3)–C(4)–C(5)–C(6)	–3.0(7)	G–Rh–P(1)–O(1c)	3.9(3)
C(4)–C(5)–C(6)–C(1)	7.1(6)	G–Rh–P(2)–O(2a)/O(2a′)	60.2(4)/ 18.9(5)
C(6)–C(1)–C(2)–C(3)	–1.2(7)	G–Rh–P(2)–O(2b)/O(2b′)	–37.8(4)/–101.5(6)
C(5)–C(6)–C(1)–C(2)	–6.7(8)	G–Rh–P(2)–O(2c)/O(2c′)	–169.9(4)/ 163.8(5)

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TABLE IVb. *(Continued)*

P(1)–O(1a)–C(11a)–C(12a)	−20.1(4)	P(2)–O(2a)/O(2a')–C(21a)–C(22a)	109.2(4)/ −0.6(14)
P(1)–O(1a)–C(11a)–C(16a)	163.0(3)	P(2)–O(2a)/O(2a')–C(21a)–C(26a)	−76.8(5)/−155.8(6)
P(1)–O(1a)–C(11b)–C(12b)	35.6(4)	P(2)–O(2b)/O(2b')–C(21b)–C(22b)	146.7(4)/ 88.1(12)
P(1)–O(1a)–C(11b)–C(16b)	−147.6(3)	P(2)–O(2b)/O(2b')–C(21b)–C(26b)	−32.5(6)/−120.4(6)
P(1)–O(1a)–C(11c)–C(12c)	−72.3(4)	P(2)–O(2c)/O(2c')–C(21c)–C(22c)	137.3(3)/−171.3(5)
P(1)–O(1a)–C(11c)–C(16c)	110.8(4)	P(2)–O(2c)/O(2c')–C(21c)–C(26c)	−51.5(5)/ 33.3(9)

TABLE IVc. Arene planarity. χ^2, as calculated in the X-Ray 70 System. Δ s, in Å, are the atomic distances to the plane, with the corresponding atom number.

Atoms defining the plane	χ^2	Δ_1	Δ_2	Δ_3	Δ_4	Δ_5	Δ_6	Δ_7
C(1) to C(6)	153.9	0.011	0.024	−0.033	0.005	0.030	−0.037	−0.161
C(1), C(2), C(3), C(6)	1.9	−0.005	0.005	−0.002	0.088	0.119	0.002	−0.114
C(3), C(4), C(5), C(6)	10.6	0.099	0.115	0.005	−0.011	0.010	−0.005	−0.134
C(1), C(2), C(4), C(5)	14.3	−0.010	0.010	−0.045	−0.010	0.010	−0.061	−0.191

TABLE V. Analytical Results and Conductivities for the Novel Complexes (L = $P(OPh)_3$).

Complex	Found (Calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})
	C	H	N	
$[Rh(C_6H_5Me)L_2]ClO_4$ (II)	56.21 (56.43)	4.12 (4.15)	–	128
$[Rh(p\text{-}MeO\text{–}C_6H_4\text{–}CN)_2L_2]ClO_4 \cdot 1/2Cl_2CH_2$ (III)	55.45 (55.71)	4.34 (3.98)	2.15 (2.48)	149
$[Rh(o\text{-}Cl\text{–}C_6H_4\text{–}CN)_2L_2]ClO_4 \cdot 1/2Cl_2CH_2$ (IV)	51.82 (51.06)	3.79 (3.42)	2.01 (2.46)	106
$[Rh(2\text{-}Et\text{-}py)_2L_2]ClO_4$ (V)	56.86 (57.86)	4.70 (4.63)	2.24 (2.70)	135
$[Rh(4\text{-}Me\text{-}py)_2L_2]ClO_4$ (VI)	56.77 (57.12)	4.37 (4.36)	2.09 (2.77)	113
$[Rh(TFB)L_2]ClO_4 \cdot Cl_2CH_2$ (IX)	51.36 (51.88)	3.69 (3.35)	–	149
$[Rh(CO)_3L_2]ClO_4 \cdot Cl_2CH_2$ (XI)	48.91 (48.41)	3.42 (3.22)	–	137
$[Rh(CO)(bipy)L_2]ClO_4 \cdot 1/2Cl_2CH_2$ (XII)	54.60 (54.34)	3.97 (3.73)	2.69 (2.67)	121
$[Rh(CO)(phen)L_2]ClO_4 \cdot 1/2Cl_2CH_2$ (XIII)	55.55 (55.36)	3.85 (3.63)	2.97 (2.62)	132
$[Rh(CO)(p\text{-}MeO\text{–}C_6H_4\text{–}CN)L_2]ClO_4$ (XIV)	54.81 (54.91)	3.97 (3.76)	1.50 (1.42)	142
$[Rh(C_6H_3Me_3)L_2]ClO_4$ (XV)	56.25 (57.30)	4.59 (4.46)	–	134
RhL_2PhBPh_3 (XVI)	70.10 (69.12)	4.95 (4.79)	–	0

Preparation of the Complexes

The starting complex $[RhCl\{P(OPh)_3\}_2]_2$ (I) was prepared as described by Haines [5]. All the reactions were carried out at room temperature.

$[Rh(C_6H_5Me)\{P(OPh)_3\}_2]ClO_4$ (II). To a solution of complex (I) (0.104 g, 0.068 mmol) in toluene–dichloromethane (2:1) was added $AgClO_4$ (0.028 g, 0.136 mmol) in the same solvent. After 20 min stirring under exclusion of light and filtration through kieselguhr the filtrate was concentrated to obtain complex (II), which was filtered and washed with hexane (90% yield).

Preparation of complexes of the type $[RhY_2\{P(OPh)_3\}_2]ClO_4$ (III–VI). In each case the stoichiometric amount of the respective ligand Y was added to a dichloromethane solution of complex (II). After 20 min stirring the solution was concentrated and the respective yellow complexes precipitated by addition of hexane, filtered and washed with hexane (Yields: (III) Y = *p*-MeO–C_6H_4–CN, 63%; (IV) Y = *o*-Cl–C_6H_4–CN, 57%; (V) Y = 2-Et-py, 43%; (VI) Y = 4-Me-py, 28%).

$[Rh(TFB)\{P(OPh)_3\}_2]ClO_4$ (IX). (IX) can be obtained by two different routes:

i) To a dichloromethane solution of complex (II) (0.030 g, 0.033 mmol) was added 0.007 g (0.033 mmol) of tetrafluorobenzobarrelene (TFB) in dichloromethane. After 30 min stirring the solution was concentrated and the orange-coloured complex was precipitated with hexane, filtered and washed with hexane (60% yield).

The previously described [10] complexes (VII) and (VIII) can also be obtained by this method.

ii) $AgClO_4$ (0.024 g, 0.114 mmol) was added to an acetone suspension of $[RhCl(TFB)]_2$ (0.041 g, 0.057 mmol) and stirred for 20 min under exclusion of light whereupon $P(OPh)_3$ (0.060 ml, 0.0228 mmol) in the same solvent was added. After 15 min stirring the solution was filtered through kieselguhr and the filtrate was evaporated to dryness. Extraction of the oily residue with dichloromethane and precipitation with hexane complex (IX).

$[Rh(CO)_3\{P(OPh)_3\}_2]ClO_4$ (XI). Bubbling of CO (atmospheric pressure, room temperature) for 45 min through dichloromethane solutions of complex (II) led to the required complex which was isolated by addition of hexane (30% yield).

Complex (XI) can also be obtained by carbonylation of the diolefin complexes (VII–IX).

Preparation of complexes of the type $[Rh(CO)(Y\text{-}Y)\{P(OPh)_3\}_2]ClO_4$ (XII, XIII) or $[Rh(CO)Y\{P(OPh)_3\}_2ClO_4$ (XIV). CO was bubbled for 45 min through the dichoromethane solution of complex (II) whereupon the corresponding ligands (bipy, phen or *p*-MeO–C_6H_4–CN) were added to the obtained solution of complex (XI). 30 min stirring, concentrating of the solution and precipitation with hexane rendered the respective complexes (XII, XIII or XIV).

$[Rh(C_6H_3Me_3)\{P(OPh)_3\}_2]ClO_4$ (XV). The synthesis was carried out as for (II) but in a mixture of Cl_2CH_2:$C_6H_3Me_3$ (1:2).

$Rh\{P(OPh)_3\}_2PhBPh_3$ (XVI). To a solution of complex (II) (0.023 g, 0.025 mmol) in methanol was added $NaBPh_4$ (0.008 g, 0.025 mmol) in the same solvent. After 48 h stirring the resulting precipitate was filtered off, washed with methanol and hexane (56% yield).

Crystal Structure

All the relevant data and procedures are collected in Table I.

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