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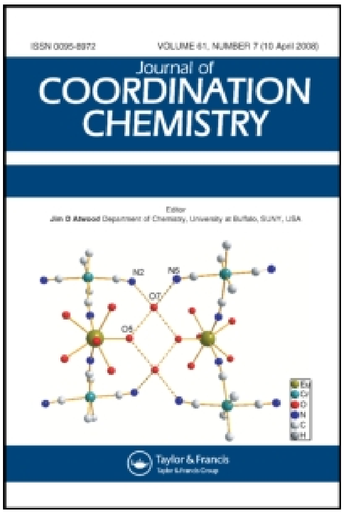

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE CHLORIDE-BRIDGED FACE-SHARING BIOCTAHEDRAL DIRHODIUM COMPLEX $[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)2]$

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To cite this Article Mura, Pasquale(1999) 'SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE CHLORIDE-BRIDGED FACE-SHARING BIOCTAHEDRAL DIRHODIUM COMPLEX $[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)2]$', Journal of Coordination Chemistry, 48: 4, 503 — 511
To link to this Article: DOI: 10.1080/00958979908023590
URL: http://dx.doi.org/10.1080/00958979908023590

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J. Coord. Chem., 1999, Vol. 48, pp. 503–511
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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE CHLORIDE-BRIDGED FACE-SHARING BIOCTAHEDRAL DIRHODIUM COMPLEX [HP-*i*-Pr$_3$][Rh$_2$Cl$_7$(P-*i*-Pr$_3$)$_2$]

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(Received 15 December 1998)

The reaction of an ethanolic suspension of $[NH_4]_3[RhCl_6]$ and P-*i*-Pr$_3$, in the presence of concentrated HCl, for 24 h, gives [HP-*i*-Pr$_3$][Rh$_2$Cl$_7$(P-*i*-Pr$_3$)$_2$], **1**, in 18.5% yeild and a small amount of Rh(H)(Cl)$_2$(P-*i*-Pr$_3$)$_2$, **2**. The dinuclear complex **1** was characterized by elemental analyses, IR, ^{1}H, ^{31}P NMR spectroscopy, and single crystal X-ray analysis. However, when the above reaction is continued for 48 h one obtains only **2**, in good yield. It is proposed that complex **1** is a reaction intermediate leading to **2**. Crystallographic data for **1** (at 298 K) are $a = 15.944(3)$, $b = 22.413(4)$, $c = 11.500(4)$ Å, space group $Pna2_1$ ($Z = 4$).

Keywords: Crystal structure; rhodium complex; tertiary phosphine complex; dinuclear complex

INTRODUCTION

Earlier publications described the isolation of the rhodium complex Rh(H)(Cl)$_2$(P-*i*-Pr$_3$)$_2$, **2**,[1–3] and the corresponding isomorphous iridium complex Ir(H)(Cl)$_2$(P-*i*-Pr$_3$)$_2$, **3**.[1,2] These were obtained by reacting an ethanolic suspension of $[NH_4]_3[RhCl_6]$ and $[NH_4]_2[IrCl_6]$, respectively, and the phosphine, in the presence of concentrated HCl.[1–3] However, these complexes were formulated as the paramagnetic hydrides M(H)$_2$(Cl)$_2$(P-*i*-Pr$_3$)$_2$.

A reinvestigation of **3**[1] as well as of **2**, shows that, in fact, both complexes are diamagnetic monohydrides and that the observed paramagnetic moments are due to cooperative surface phenomena.[1]

Recently, Harlow *et al.*[4] reported the preparation of a complex of composition $Rh(H)(Cl)_2(P\text{-}i\text{-}Pr_3)_2$, starting from a rhodium(I) complex. They also determined its X-ray crystal structure, which proves to be identical with that of **2**, obtained using our method[3] (see Experimental).

We recently proposed that the dinuclear complex $[HP\text{-}i\text{-}Pr_3][Ir_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$, **4**, is a reaction intermediate leading to the formation of $Ir(H)(Cl)_2(P\text{-}i\text{-}Pr_3)_2$, **3**.[2] As it is likely that $Rh(H)(Cl)_2(P\text{-}i\text{-}Pr_3)_2$, **2**, is formed by a reaction pathway involving the formation of the possible precursor $[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$, **1**,[5] we attempted to isolate this salt. This attempt was successful and **1** has now been fully characterized and its X-ray crystal structure determined.

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EXPERIMENTAL

Material and Equipment

All starting materials and solvents were obtained commercially and used as received. The syntheses were carried out under oxygen-free nitrogen. The infrared spectra were recorded using a Perkin-Elmer 16PC Fourier-transform spectrometer. Solution ^1H and ^{31}P NMR spectra were recorded on a Bruker AMX 600.* They are referenced ^1H relative to TMS and ^{31}P relative to external H_3PO_4.

Synthesis of $[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$, 1

Some 1 g of $[NH_4]_3[RhCl_6]$ was suspended in 12 cm^3 of degassed ethanol containing 1.6 cm^3 of concentrated HCl. The suspension was refluxed for 2 h. Afterward, 1.4 cm^3 of $P\text{-}i\text{-}Pr_3$ in 6 cm^3 of degassed ethanol were added. The suspension was refluxed for 24 h, then filtered. The red-brown mother liquor was left overnight. An appreciable quantity of orange crystals formed; the mother liquor was again filtered (yield of orange crystals: 0.1 g (8.1%)†) and after a few days a good quantity of brown-red crystals was

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* NMR spectra were collected at "Servizio NMR" of the Research Area of Rome.

† The orange crystals were analyzed: They proved to be the compound $Rh(H)(Cl)_2(P\text{-}i\text{-}Pr_3)_2$, **2**; IR and NMR spectra, elemental analyses, cell parameters and space group are the same as those of the original complex **2**.[3,4]

formed; the crystals were washed with cold ethanol, ether and dried under vacuum. Yield 0.45 g (18.5%). *Anal.* Calcd. for $C_{27}H_{64}Cl_7P_3Rh_2$ (%): C, 34.65; H, 6.91; Cl, 26.52; P, 9.93. Found:[‡] C, 34.52; H, 6.80; Cl, 26.35; P, 9.78.

Synthesis of $Rh(H)(Cl)_2(P\text{-}i\text{-}Pr_3)_2$, 2[3]

Some 1 g of $[NH_4]_3[RhCl_6]$ was suspended in 12 cm^3 of degassed ethanol containing 1.6 cm^3 of concentrated HCl. The suspension was refluxed for 2 h. Afterward, 1.4 cm^3 of P-*i*-Pr_3 in 6 cm^3 of degassed ethanol were added. The suspension was refluxed for 48 h, then filtered. The solid was washed with water several times to remove unreacted $[NH_4]_3[RhCl_6]$. The residual on the filter was dried under vacuum; 0.6 g of orange microcrystals of **2** were obtained (Yield: 48.9%). *Anal.* Calcd. for $C_{18}H_{43}Cl_2P_2Rh$ (%): C, 43.64; H, 8.77; Cl, 14.15; P, 12.50. Found: C, 43.49; H, 8.61; Cl, 14.03; P, 12.37. The IR spectrum of **2** shows a band at 1938 cm^{-1} which may be attributed to ν_{Rh-H}; we are not sure of this attribution considering that the sample may be contaminated by small quantities of carbonyl complexes as already observed for $Ir(H)(Cl)_2(P\text{-}i\text{-}Pr_3)_2$, **3**.[1] In the far IR spectrum **2** shows a strong band at 342 cm^{-1} attributed to ν_{Rh-Cl}. ^1H NMR spectra ($C_6D_5CD_3$ solution, room temperature) of **2** show sharp well resolved multiplets: $\delta(PCH) = 3.01$ ppm (m), $\delta(PCHCH_3) = 1.48$ ppm (d,vt) and $\delta(RhH) = -30.96$ ppm (d,t) of relative intesities 6 : 36 : 1 respectively; $J(HH) = 7.0$ Hz, $J(PH) = 12.8$ Hz and $J(RhH) = 33.8$ Hz. The broad band decoupled $^{31}P\{^1H\}$-spectrum ($C_6D_5CD_3$ solution, room temperature) shows a doublet at $\delta = 45.2$ ppm, $J(RhP) = 97$ Hz; selective decoupling of the signal due to the protons in the region 1–3 ppm converted this doublet into a doublet of doublets, confirming that **2**, as present in solution, is a monohydride with the stereochemistry shown by Harlow *et al.*[4] and ourselves.[3] The X-ray data obtained for the samples, obtained by these two groups, are summarized below:

Cryst. syst. *Space group*	*Rh(H)(Cl)$_2$(P-i-Pr$_3$)$_2$,* **2**, *Ref.* [4] *Monoclinic* *P* $2_1/c$	*Rh(H)(Cl)$_2$(P-i-Pr$_3$)$_2$,* **2**, *Refs.* [1,3] *Monoclinic* *P* $2_1/c$
a, Å	8.092(1)	8.221(1)
b, Å	8.961(1)	8.965(1)

[‡] Elemental analyses were made by "Servizio di Microanalisi" of the Research Area of Rome.

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(Continued)

Cryst. syst. *Space group*	*Rh(H)(Cl)$_2$(P-i-Pr$_3$)$_2$*, **2**, *Ref.* [4] *Monoclinic* *P* 2$_1$/*c*	*Rh(H)(Cl)$_2$(P-i-Pr$_3$)$_2$*, **2**, *Refs.* [1,3] *Monoclinic* *P* 2$_1$/*c*
c, Å	16.270(3)	16.417(2)
β, °	92.56(1)	92.26(1)
Rh(1)–Cl(1)	2.342(1) Å	2.329(1) Å
Rh(1)–P(1)	2.367(1) Å	2.363(1) Å
Rh(1)–H(1)	1.54(6) Å	1.47(9) Å
Cl(1)–Rh(1)–P(1)	90.05(2)°	89.78(3)°
Cl(1)–Rh(1)–H(1)	91(2)°	74(3)°
P(1)–Rh(1)–H(1)	88(2)°	90(3)°

Thus our crystal data for **2** are in good agreement with those reported by Harlow *et al.*[4] if one takes into account the fact that our data were collected at room temperature and those of Harlow *et al.* at −100°C.

X-ray Structure Solution and Refinement of [HP-*i*-Pr$_3$][Rh$_2$Cl$_7$(P-*i*-Pr$_3$)$_2$], 1[5]

Brown-red prisms of **1** were obtained from the mother liquor. Data collection was performed by a Syntex P2$_1$ automatic diffractometer (room temperature); no decay correction was applied. The data were corrected for Lorenz and polarization effects. An empirical absorption correction, based on azimuthal scans of several reflections, was applied to intensities.[6] The structure was solved by direct methods, using programs SIR88,[7] which provided the complete structure. The latter was refined using full-matrix least-squares calculations using local programs.[8] The number of observations was 2907 ($Io > 3\sigma(Io)$), and the number of the variable parameters was 351 (8.28 observations for each parameter). The final R values of the observed reflections (full-matrix refinement), after the introduction of the fixed contribution of 58 H atoms of the P-*i*-Pr$_3$ groups, are $R = 0.042$ and $R_w = 0.058$ (five H atoms were not introduced because of being bonded to the slightly disordered C atoms, i.e.: C(21), C(212), C(32) and C(322)). Additional details of the crystallographic experiments concerning complex **1** are given in Table I.

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TABLE I Crystal data for $[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$, **1**

Formula	$C_{27}H_{64}Cl_7P_3Rh_2$
Mol. wt.	935.79
Cryst. dimens., mm	0.09 × 0.22 × 0.25
Cryst. syst.	Orthorhombic
Space group	$Pna2_1$
Cell dimens.[a]	
a, Å	15.944(3)
b, Å	22.413(4)
c, Å	11.500(4)
V, Å^3	4110(2)
Z	4
Calcd. density, g cm^{-3}	1.513
Scan method	$\theta/2\theta$
Radiation	MoKα ($\lambda = 0.71069$ Å)
Monochromator	Graphite crystal
2θ range, deg	3–56
No. of total data	5116
Variable scan speed range, deg min^{-1}	1.2–29.3
No. of obsd. data, $Io > 3\sigma(Io)$	2907
R value for equiv. reflns.	0.016
μ, cm^{-1}	13.647
$F(000)$	1920.0
Final residuals (for 2907 data)	
R, R_w[b]	0.0417, 0.0575
a, b, c values in the weight function $w = 1.0/(a + bF_o + cF_o^2)$	10.42409, 0.00001, 0.00056
Goodness of fit for last cycle	1.02
Max. Δ/σ for last cycle	0.00

[a] Lattice parameters calculated from 15 high-angle reflections measured at $\pm 2\theta$ (2θ interval 18.11–27.75°).

[b] $R = \sum|F_o - F_c|/\sum|F_o|$; $R_w = \{\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

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RESULTS AND DISCUSSION

$[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$[5]

The IR spectrum of **1** shows a band at 2384 cm^1 (m) assigned to the ν_{P-H} vibration of the phosphonium cation[1,9] and a very strong band at 338 cm^{-1} assigned to a ν_{Rh-Cl} stretch.[1,9] The $^{31}P\{^1H\}$ NMR spectrum ($C_6D_5CD_3$ solution, 298 K) of **1** shows two resonances at 68.31 ppm and 26.19 ppm attributed to the two coordinated P-i-Pr_3 groups and to the $(HP(3)\text{-}i\text{-}Pr_3)^+$ counterion respectively, see Figure 1; the ratio of the two bands is ≅ 2 : ≅ 1. ^1H NMR spectrum ($C_6D_5CD_3$ solution, 298 K) shows a doublet at $\delta(PH) = 7.75$ ppm assigned to the proton of the phosphonium counterion,[1,9] two broad multiplets at $\delta(PCH) = 3.19$ ppm (m) and $\delta(PCH) = 2.68$ ppm (m) attributed to the two coordinated P-i-Pr_3 groups and to the $(HP(3)\text{-}i\text{-}Pr_3)^+$ counterion, respectively; at $\delta(PCHCH_3) = 1.69$ ppm and $\delta(PCHCH_3) = 1.27$ ppm a multiplet and a doublet of doublets attributed to the two

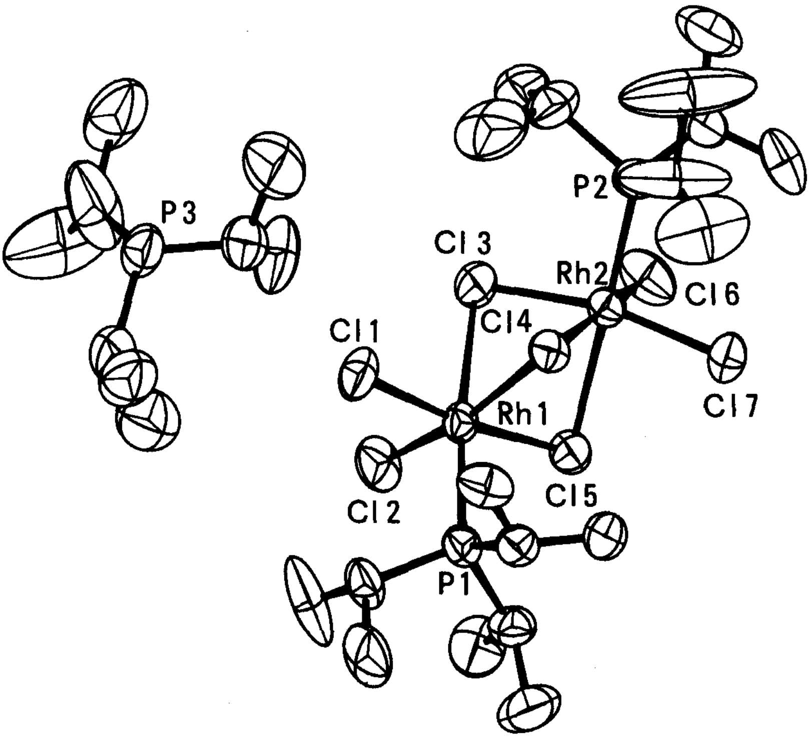

FIGURE 1 Geometry[8] of $[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$, **1**, with hydrogen atoms of $P\text{-}i\text{-}Pr_3$ groups omitted for clarity. Thermal ellipsoids are drawn at the 30% probability levels.

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coordinated $P\text{-}i\text{-}Pr_3$ groups and to the $(HP(3)\text{-}i\text{-}Pr_3)^+$ phosphonium group respectively, see Figure 1, appear; the relative intensities of the bands are 1 : 6 : 3 : 36 : 18. The ^1H NMR spectrum of **1** is broader of that of the analogous iridium compound, $[HP\text{-}i\text{-}Pr_3][Ir_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$;[1] this suggests, together with the imperfect ratio of the $^{31}P\{^1H\}$ bands, that complex **1** is dynamic in solution.

Molecular Structure of $[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$[5]

Figure 1 shows a perspective view of **1** and defines the atom numbering scheme for the heavy atoms. A listing of final positional parameters for non-hydrogen atoms is given in Table II. Selected bond lengths and angles are given in Tables III and IV respectively; thermal parameters, hydrogen atomic parameters and observed and calculated structure factors are available as supplementary material, upon request.

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TABLE II Atomic coordinates and isotropic thermal parameters, U_{eq} (Å^2)*, of non-hydrogen atoms (E.S.D.s in parentheses) for $[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$, **1**

	x/a	y/b	z/c	U_{eq}
Rh(1)	0.2326(1)	0.0045(1)	−0.0268	0.0429(3)
Rh(2)	0.1963(1)	−0.13205(4)	−0.0968(1)	0.0438(3)
Cl(1)	0.3124(3)	0.0288(2)	0.1365(4)	0.071(1)
Cl(2)	0.3135(3)	0.0664(2)	−0.1435(4)	0.075(2)
Cl(3)	0.3280(2)	−0.0821(2)	−0.0847(5)	0.061(1)
Cl(4)	0.1699(2)	−0.0768(2)	0.0749(3)	0.048(1)
Cl(5)	0.1582(3)	−0.0332(2)	−0.1880(3)	0.056(1)
Cl(6)	0.2306(4)	−0.1718(2)	−0.2774(4)	0.082(2)
Cl(7)	0.0582(3)	−0.1617(2)	−0.1191(5)	0.078(2)
P(1)	0.1348(2)	0.0767(2)	0.0150(4)	0.049(1)
P(2)	0.2295(3)	−0.2188(2)	−0.0027(4)	0.058(1)
P(3)	0.6144(3)	0.0611(2)	0.0680(5)	0.076(2)
C(11)	0.177(1)	0.1460(6)	0.088(2)	0.064(6)
C(111)	0.238(2)	0.1820(9)	0.014(2)	0.14(1)
C(112)	0.112(1)	0.1871(9)	0.136(2)	0.104(9)
C(12)	0.0535(8)	0.0518(6)	0.120(2)	0.057(5)
C(121)	0.090(1)	0.0343(8)	0.239(2)	0.069(6)
C(122)	−0.005(1)	0.0032(8)	0.070(2)	0.064(5)
C(13)	0.071(1)	0.0968(7)	−0.115(2)	0.065(6)
C(131)	0.119(1)	0.124(1)	−0.217(2)	0.094(9)
C(132)	−0.008(1)	0.1369(9)	−0.090(3)	0.107(9)
C(21)	0.159(2)	−0.235(1)	0.119(3)	0.19(2)
C(211)	0.183(2)	−0.289(2)	0.197(3)	0.27(2)
C(212)	0.091(2)	−0.219(1)	0.147(3)	0.17(2)
C(22)	0.337(1)	−0.219(1)	0.062(2)	0.092(8)
C(221)	0.405(1)	−0.2155(9)	−0.035(3)	0.11(1)
C(222)	0.351(2)	−0.174(1)	0.152(2)	0.14(1)
C(23)	0.232(1)	−0.2837(7)	−0.098(2)	0.086(7)
C(231)	0.277(2)	−0.3387(8)	−0.053(3)	0.12(1)
C(232)	0.146(2)	−0.3014(9)	−0.142(3)	0.13(1)
C(31)	0.537(1)	0.0068(8)	0.023(2)	0.076(7)
C(311)	0.544(2)	−0.051(1)	0.091(2)	0.13(1)
C(312)	0.537(2)	−0.004(1)	−0.105(3)	0.12(1)
C(32)	0.710(2)	0.057(1)	−0.003(5)	0.20(2)
C(321)	0.747(1)	−0.005(1)	0.012(3)	0.16(2)
C(322)	0.738(2)	0.094(2)	−0.073(3)	0.22(2)
C(33)	0.570(1)	0.1345(9)	0.070(2)	0.088(8)
C(331)	0.511(1)	0.142(1)	0.169(2)	0.11(1)
C(332)	0.526(2)	0.153(1)	−0.044(2)	0.12(1)

*$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_j \cdot \mathbf{a}_j$.

Complex **1** is a dinuclear species, a $(\mu_2\text{-}Cl)_3$-bridged, face-sharing bioctahedral compound. The distances (see Table III), both of terminal[1,3,10] and bridging[1,11] chloride ligands, are in the range of those reported in the literature; this does not hold for Rh–Cl(3) and Rh–Cl(5) of 2.554(4) Å and 2.526(4) Å, respectively, which are longer than all others, in agreement with a greater *trans*-influence of P atoms than of Cl.[1,11] Also in this structure, as in the analogous $[HP\text{-}i\text{-}Pr_3][Ir_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$[1] complex, is present a

TABLE III Relevant bond distances (Å) for [HP-*i*-Pr_3][Rh_2Cl_7(P-*i*-Pr_3)$_2$], **1**, with E.S.D.s in parentheses; P(3)H–Cl hydrogen bond distances (Å)

Rh(1)–Cl(1)	2.332(5)	Rh(2)–Cl(4)	2.368(4)
Rh(1)–Cl(2)	2.321(5)	Rh(2)–Cl(5)	2.526(4)
Rh(1)–Cl(3)	2.554(4)	Rh(2)–Cl(6)	2.325(5)
Rh(1)–Cl(4)	2.385(4)	Rh(2)–Cl(7)	2.314(4)
Rh(1)–Cl(5)	2.358(4)	Rh(2)–P(2)	2.287(4)
Rh(1)–P(1)	2.298(4)	P(3)–Cl(3)[a]	4.125
Rh(2)–Cl(3)	2.384(3)	P(3)–Cl(6)[a]	3.928

[a] Symmetry code: $(1-x;\ -y;\ \frac{1}{2}+z)$.

TABLE IV Relevant bond angles (°) for [HP-*i*-Pr_3][Rh_2Cl_7(P-*i*-Pr_3)$_2$], **1**, with E.S.D.s in parentheses

Cl(2)–Rh(1)–Cl(1)	91.3(2)	Cl(5)–Rh(2)–Cl(4)	81.0(1)
Cl(3)–Rh(1)–Cl(1)	93.6(2)	Cl(6)–Rh(2)–Cl(3)	91.4(2)
Cl(3)–Rh(1)–Cl(2)	88.4(1)	Cl(6)–Rh(2)–Cl(4)	170.7(1)
Cl(4)–Rh(1)–Cl(1)	90.7(1)	Cl(6)–Rh(2)–Cl(5)	91.3(2)
Cl(4)–Rh(1)–Cl(2)	166.7(1)	Cl(7)–Rh(2)–Cl(3)	168.4(1)
Cl(4)–Rh(1)–Cl(3)	78.3(1)	Cl(7)–Rh(2)–Cl(4)	94.2(2)
Cl(5)–Rh(1)–Cl(1)	172.4(2)	Cl(7)–Rh(2)–Cl(5)	88.7(1)
Cl(5)–Rh(1)–Cl(2)	92.2(2)	Cl(7)–Rh(2)–Cl(6)	90.8(2)
Cl(5)–Rh(1)–Cl(3)	79.8(1)	P(2)–Rh(2)–Cl(3)	99.6(1)
Cl(5)–Rh(1)–Cl(4)	84.3(1)	P(2)–Rh(2)–Cl(4)	95.2(1)
P(1)–Rh(1)–Cl(1)	92.2(2)	P(2)–Rh(2)–Cl(5)	176.3(2)
P(1)–Rh(1)–Cl(2)	94.4(1)	P(2)–Rh(2)–Cl(6)	92.5(2)
P(1)–Rh(1)–Cl(3)	173.5(1)	P(2)–Rh(2)–Cl(7)	91.6(2)
P(1)–Rh(1)–Cl(4)	98.7(1)	Rh(1)–Cl(3)–Rh(2)	81.2(1)
P(1)–Rh(1)–Cl(5)	94.3(1)	Rh(1)–Cl(4)–Rh(2)	85.2(1)
Cl(4)–Rh(2)–Cl(3)	82.1(1)	Rh(1)–Cl(5)–Rh(2)	82.4(1)
Cl(5)–Rh(2)–Cl(4)	79.8(1)		

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bifurcated hydrogen bond: P(3)–Cl(6) of 3.928 Å and P(3)–Cl(3) of 4.125 Å, see Table III; localization of the hydrogen bonded to P(3) atom was not possible. Some carbon atoms show higher isotropic thermal factors; this is probably due to unresolved disorder for corresponding phosphine groups. However, these atoms could be refined without any problem.

The results indicate that the dinuclear complex [HP-*i*-Pr_3][Rh_2Cl_7(P-*i*-Pr_3], **1**, is a likely intermediate leading to the formation of Rh(H)(Cl)$_2$(P-*i*-Pr_3)$_2$, **2**, obtained by reacting [NH_4]$_3$[$RhCl_6$] with P-*i*-Pr_3 in the presence of HCl. While the suggestion that dinuclear intermediates of the type $[Ir_2Cl_7(PR_3)_2]^-$ are precursors for the mononuclear complexes of the type $Ir(H)(Cl)_2(PR_3)_2$ (R = bulky substituent) was first proposed by Shaw and coworkers,[9] its validity for the corresponding rhodium complexes has now been evinced.

We are aware that other intermediates will certainly have preceded the formation of **1**, and others will have followed it, before **2** is finally produced. However, their lifetimes were probably much shorter or/and their solubility in the reaction medium higher than those of **1** and **2**, thus preventing their isolation.

Acknowledgments

I am indebted to Progetto Finalizzato "Chimica Fine II" del CNR, for financial support, and to Prof. L.M. Venanzi and Prof. A. Segre for discussion.

Supplementary Material

Anisotropic thermal parameters, hydrogen atom positions and parameters and structure factors for complex **1** are available as supplementary material, upon request.

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