Reactions of dirhodium(II) monometallated compounds with phosphines. Factors affecting the reactivity and the structure of the doubly-metallated compounds. Molecular structure of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2]\cdot(HO_2CCH_3)_2\cdot\frac{1}{2}(C_6H_6)$, a compound with two different metallated phosphines

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Abstract

Monometallated compounds of formula $Rh_2(O_2CCH_3)_3[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2](HO_2CCH_3)_2$ (X = CH_3, Cl) have been prepared in good yield. The reactions with *p*-substituted triarylphosphines $P(p\text{-}X'C_6H_4)_3$ (X' = CH_3, H, Cl) have been studied. For X = X' and [P]/[Rh_2] = 1 all the resulting doubly metallated compounds $Rh_2(O_2CCH_3)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2](HO_2CCH_3)_2$ (X = CH_3, Cl) have head-to-tail (H-T) structure. For [P]/[Rh_2] = 3 reaction progress is observed at room temperature. When X = X' a 1:1 mixture of H-T and H-H compounds is formed for X = Cl but only the H-H compound is obtained for X = CH_3. For X ≠ X' mixtures of H-T and H-H compounds are obtained. The entering phosphine, and to a less extent the phosphine in the monometallated compound, seems to influence the rate of the process and the product distribution. The crystal structure of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)][(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](HO_2CCH_3)_2\cdot\frac{1}{2}(C_6H_6)$ a doubly metallated compound with two different metallated phosphines in a head-to-tail configuration, is also described.

Introduction

It is known that dirhodium tetraacetate and triphenylphosphine undergo thermal reaction giving $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$, a compound that contains two acetates and two triphenylphosphine anions bridging the rhodium atoms [1]. The crystal structure indicated that the anionic phosphine ligands are in a head-to-tail configuration (II).

Later on we reported [2] that a monometallated compound of formula $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$ can be prepared in relatively high yield by using a modified synthetic procedure. This monometallated compound undergoes further reaction with triphenylphosphine giving the already described doubly metallated compound of formula $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$. The rate of the second metallation process as well as the structure of the reaction products depends on the experimental conditions used [3]; so the reaction of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$ with two moles of triphenylphosphine is very fast even at room temperature giving only the compound with the two metallated phosphines in a head-to-tail configuration. The same reaction performed at high temperature gives a mixture of the compounds with head-to-tail and head-to-head configurations.

These results prompted us to extend the studies to other related phosphines $P(m\text{-}CH_3C_6H_4)_3$ [4] and $P(p\text{-}XC_6H_4)_3$ (X = CH_3, Cl) in order to investigate whether this is or is not a general behavior, and what is the influence of the metallated and reacting phosphines on the reaction rate and product distribution. We describe here the preparation of monometallated compounds of formula $Rh_2(O_2CCH_3)_3[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2](HO_2CCH_3)_2$ (X = CH_3, Cl) and their reactivity with triarylphosphines. The crystal structure of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)][(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](HO_2CCH_3)_2\cdot\frac{1}{2}(C_6H_6)$ a doubly-metallated com-

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pound with two different metallated phosphines in a head-to-tail configuration, is also described.

Experimental

Materials

$Rh_2(O_2CCH_3)_4(MeOH)_2$ was prepared from $RhCl_3$ according to the literature procedures [5]. The phosphines $P(p\text{-}CH_3C_6H_4)_3$ and $P(p\text{-}ClC_6H_4)_3$ (Strem) were used as purchased. $P(C_6H_5)_3$ (Aldrich) was recrystallized from hot ethanol prior to use. All solvents were of analytical grade. Toluene, chloroform and acetic acid were degassed before use.

Preparation of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$

A green suspension of $Rh_2(O_2CCH_3)_4(MeOH)_2$ (100 mg, 0.198 mmol) in 50 cm^3 of a 3:1 toluene/acetic acid mixture, under an argon atmosphere, was taken to reflux until total solution of the green solid. $P(C_6H_5)_3$ (52 mg, 0.198 mmol), dissolved in 5 cm^3 of a 1:3 $CHCl_3$/toluene mixture was added to the green solution, which turned to brown–orange. The resulting solution was refluxed for 30 min; the solution turned to deep violet. The solvent was removed under vacuum and the crude product redissolved in a mixture of CH_2Cl_2/hexane (5 cm^3/5 cm^3). The solution was transferred to a chromatography column (30×2 cm) packed with silica gel in hexane. Elution with CH_2Cl_2/hexane (1:1) separated one minor yellow band that was discarded. Further elution with hexane/CH_2Cl_2/acetic acid (10:10:1) separated two purple and violet bands. The purple fraction was concentrated to dryness under reduced pressure and dissolved in the minimum amount of CH_2Cl_2. Addition of hexane yielded $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$ in the H-T configuration (16%). Analogous manipulation of the violet fraction gave $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$ (yield 65%): ^1H NMR ($CDCl_3$) spectrum (in ppm): 1.23 (CH_3, 6H, s), 2.15 (CH_3, 6H, s), 2.26 (CH_3, 3H, s), 6.6–8.1 (aromatics, 13H, m), 8.6 (aromatic, 1H, m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\delta p = 17.6$ ppm, $^1J_{Rh-P} = 150$ Hz, $^2J_{Rh-P} = 6$ Hz. $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum (in ppm): 21.73 (CH_3, s), 25.81 (CH_3, s), 26.32 (CH_3, s), 125–145 (aromatics, m), 179.13 (OCO, s), 183.34 (OCO, s), 191.14 (OCO, s).

Preparation of $Rh_2(O_2CCH_3)_3[(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2](HO_2CCH_3)_2$ and $Rh_2(O_2CCH_3)_3[(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](HO_2CCH_3)_2$

These compounds were prepared in a manner analogous to that described above for $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$.

$Rh_2(O_2CCH_3)_3[(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2](HO_2CCH_3)_2$ (yield 73%): *Anal.* Calc.: C, 46.12; H, 4.34. Found: C, 45.13; H, 4.40%. ^1H NMR ($CDCl_3$) spectrum (in ppm): 1.32 (CH_3, 6H, s), 2.23 (CH_3, 15H, s), 2.42 (CH_3, 3H, s), 6.8–8.0 (aromatics, 10H, m), 8.4 (aromatic, 1H, m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\delta_P = 15.79$ ppm, $^1J_{Rh-P} = 143.4$ Hz, $^2J_{Rh-P} = 6$ Hz.

$Rh_2(O_2CCH_3)_3[(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](HO_2CCH_3)_2$ (yield 67%): *Anal.* Calc.: C, 38.72; H, 2.91. Found: C, 38.13; H, 2.91%. ^1H NMR ($CDCl_3$) spectrum (in ppm): 1.33 (CH_3, 6H, s), 2.30 (CH_3, 6H, s), 2.33 (CH_3, 3H, s), 6.3–8.1 (aromatics, 10H, m), 8.6 (aromatic, 1H, d). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\delta_P = 17.72$ ppm, $^1J_{Rh-P} = 151.15$ Hz, $^2J_{Rh-P} = 6$ Hz. $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum (in ppm): 22.44 (CH_3, s), 23.74 (CH_3, s), 23.92 (CH_3, s), 124–138 (aromatics, m), 181.46 (OCO, s), 182.62 (OCO, s), 191.50 (OCO, s).

Reaction of compounds of type $Rh_2(O_2CCH_3)_3[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2](HO_2CCH_3)_2$ with $P(p\text{-}X'C_6H_4)_3$

$X = H, CH_3, Cl$, $X' = H, CH_3$; $X = CH_3$, $X' = Cl$

All these reactions were performed by dissolving 0.198 mmol of $Rh_2(O_2CCH_3)_3[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2](HO_2CCH_3)_2$ and 0.594 mmol of $P(p\text{-}X'C_6H_4)_3$ in 10 ml of $CHCl_3$. The resulting brown–orange solution was stirred at room temperature and the evolution of the reactions was followed by ^{31}P NMR. All the reaction times are summarized in Table 1. When the reactions were completed the resulting red–brown solutions were concentrated to dryness under vacuum and the crude solids were redissolved in 5 ml of a mixture of CH_2Cl_2/hexane 1:1. For unsymmetrical reactions type (1b) ($X \neq X'$) the solution was transferred to a chromatography column (30×2 cm) packed with silica gel in hexane. Elution with CH_2Cl_2/hexane (1:1) separated one minor yellow band that was discarded. Further elution with hexane/CH_2Cl_2/CH_3COCH_3 (10:10:1) separated two violet and purple bands. The violet fraction was concentrated to dryness under reduced pressure and dissolved in the minimum amount of CH_2Cl_2. Addition of hexane yielded $Rh_2(O_2CCH_3)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]_2(H_2O)_2$ in the H-H configuration. Analogous manipulation of the purple fraction gave $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(H_2O)_2$ in the H-T configuration. Due to the high solubility of the compounds with different metallated phosphines, the reaction yields were calculated from the integral values of the ^{31}P NMR spectra. These values are summarized in Table 2.

TABLE 1. Product distribution and approximate time rates for reactions of type (1a) and (1b)

P[a]	P[b]	Reaction conditions	H-H (%)	H-T (%)	Reaction time (h)
PPh_3	PPh_3	1/3, r.t.		100	$\approx 10^{-4}$
$P(p\text{-}CH_3C_6H_4)_3$	$P(p\text{-}CH_3C_6H_4)_3$		100		12
$P(p\text{-}ClC_6H_4)_3$	$P(p\text{-}ClC_6H_4)_3$	1/3, Δtoluene	48	52	2
PPh_3	$P(p\text{-}CH_3C_6H_4)_3$	1/3, r.t.	71	29	20
PPh_3	$P(p\text{-}ClC_6H_4)_3$	1/3, $\Delta CHCl_3$	30	70	4
$P(p\text{-}CH_3C_6H_4)_3$	PPh_3	1/3, r.t.	60	40	18
$P(p\text{-}CH_3C_6H_4)_3$	$P(p\text{-}ClC_6H_4)_3$		35	65	80
$P(p\text{-}ClC_6H_4)_3$	PPh_3		31	69	72
$P(p\text{-}ClC_6H_4)_3$	$P(p\text{-}CH_3C_6H_4)_3$		60	40	50

[a]P = metallated phosphine. [b]P′ = reacting phosphine.

$Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2](H_2O)_2$ (H-T). We had difficulties in obtaining this compound in a crystalline pure state because of its solubility in all non-polar solvents. Due to that, good elemental analysis could not be obtained. ^1H NMR ($CDCl_3$) spectrum (in ppm): 1.2 (CH_3, 3H, s), 1.24 (CH_3, 3H, s), 2.15 (CH_3, 3H, s) 2.22 (CH_3, 3H, s) 2.32 (CH_3, 3H, s), 6.2–7.8 (aromatics, 25H, m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\delta_{Pa} = 19.33$ ppm, $\delta_{Pb} = 16.46$ ppm, $^1J_{Rh-Pa} = 173.0$ Hz, $^1J_{Rh-Pb} = 164.7$ Hz $^2J_{Rh-Pa} = 8.1$ Hz, $^2J_{Rh-Pb} = 7.8$ Hz.

$Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2](H_2O)_2$ (H-H). Only isolated as an oily product. $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\nu_{Pa} = 1566.23$ Hz, $\nu_{Pb} = 1436.21$ Hz, $^1J_{Rh-Pa} = 146.13$ Hz, $^1J_{Rh-Pb} = 145.25$ Hz, $^2J_{Rh-Pa} = 8.2$ Hz, $^2J_{Rh-Pb} = 7.8$ Hz, $^2J_{Pa-Pb} = 43.3$ Hz.

$Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](H_2O)_2 \cdot CH_2Cl_2$ (H-T). Anal. Found: C, 47.80; H, 3.08. Calc.: C, 47.78; H, 3.11%. ^1H NMR ($CDCl_3$) spectrum (in ppm): 1.2 (CH_3, 3H, s), 1.23 (CH_3, 3H, s), 6.6–7.4 (aromatics, 25H, m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\delta_{Pa} = 20.37$ ppm, $\delta_{Pb} = 16.46$ ppm, $^1J_{Rh-Pa} = 174.39$ Hz, $^1J_{Rh-Pb} = 167.65$ Hz, $^2J_{Rh-Pa} = 7.3$ Hz, $^2J_{Rh-Pb} = 7.3$ Hz.

$Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](H_2O)_2$ (H-H). Anal. Calc.: C, 48.69; H, 3.34. Found: C, 48.12; H, 3.30%. ^1H NMR ($CDCl_3$) spectrum (in ppm): 1.42 (CH_3, 3H, s), 1.65 (CH_3, 3H, s), 6.4–7.8 (aromatics, 25H, m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\nu_{Pa} = 1731.2$ Hz, $\nu_{Pb} = 1583.4$ Hz, $^1J_{Rh-Pa} = 143.4$ Hz, $^1J_{Rh-Pb} = 151.7$ Hz, $^2J_{Rh-Pa} = 8.1$ Hz, $^2J_{Rh-Pb} = 7.8$ Hz, $^2J_{Pa-Pb} = 39.4$ Hz.

$Rh_2(O_2CCH_3)_2[(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2][(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](H_2O)_2$ (H-T). Anal. Calc.: C, 50.32; H, 3.98. Found: C, 50.87; H, 4.02%. ^1H NMR ($CDCl_3$) spectrum (in ppm): 1.25 (CH_3, 3H, s), 1.29 (CH_3, 3H, s) 2.20 (CH_3, 3H, s), 2.27 (CH_3, 3H, s), 2.35 (CH_3, 3H, s), 6.4–7.7 (aromatics, 25H, m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\delta_{Pa} = 20.9$ ppm, $\delta_{Pb} = 16.7$ ppm, $^1J_{Rh-Pa} = 170.2$ Hz, $^1J_{Rh-Pb} = 162.7$ Hz, $^2J_{Rh-Pa} = 8.3$ Hz, $^2J_{Rh-Pb} = 8.2$ Hz.

$Rh_2(O_2CCH_3)_2[(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2][(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2](H_2O)_2$ (H-H). Anal. Calc.: C, 50.32; H, 3.98. Found: C, 49.98; H, 3.77%. ^1H NMR ($CDCl_3$) spectrum (in ppm): 1.39 (CH_3, 3H, s), 1.54 (CH_3, 3H, s), 2.08 (CH_3, 3H, s), 2.18 (CH_3, 3H, s), 2.20 (CH_3, 3H, s), 6.4–7.8 (aromatics, 25H, m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\nu_{Pa} = 1624.75$ Hz, $\nu_{Pb} = 1429.9$ Hz, $^1J_{Rh-Pa} = 150.75$ Hz, $^1J_{Rh-Pb} = 149.8$ Hz, $^2J_{Rh-Pa} = 6.3$ Hz, $^2J_{Rh-Pb} = 6.1$ Hz, $^2J_{Pa-Pb} = 38.6$ Hz.

The reaction products when $X = X' = H$, CH_3 were manipulated as described above. Recrystallization from a CH_2Cl_2/acetic acid mixture allowed the isolation of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$ (H-T) and $Rh_2(O_2CCH_3)_2[(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2]_2(HO_2CCH_3)_2$ (H-H) in each case. The preparation of these two compounds has already been described in the literature [1, 3].

$X = X' = Cl$

100 mg of $Rh_2(O_2CCH_3)_3[(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](HO_2CCH_3)_2$ (0.115 mmol) and 126 mg of $P(p\text{-}ClC_6H_4)_3$ (0.346 mmol) were refluxed in 10 ml of toluene for 1 h in an argon atmosphere. The resulting red–brown solution was evaporated to dryness under vacuum and the crude product was chromatographed as described above. The two compounds so obtained were crystallized in a CH_2Cl_2/acetic acid mixture yielding the two conformations, H-T (52%) and H-H (48%), of $Rh_2(O_2CCH_3)_2[(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2]_2(HO_2CCH_3)_2$.

$X = H$, $X' = Cl$

100 mg of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$ (0.131 mmol) and 143 mg of $P(p\text{-}ClC_6H_4)_3$

TABLE 2. Fractional positional and thermal parameters with e.s.d.s in parentheses

Atom	x	y	z	U_{eq} (×100)[a]
Rh1	0.33409(2)	−0.13243(3)	0.05444(3)	2.69(1)
Rh2	0.27268(2)	0.08685(3)	0.22350(3)	2.75(1)
O1	0.3105(2)	−0.0476(3)	−0.0782(3)	3.8(1)
O2	0.2912(2)	0.1480(3)	0.0825(3)	3.6(1)
C1	0.3032(2)	0.0732(4)	−0.0331(4)	3.8(2)
C2	0.3067(3)	0.1277(5)	−0.1259(5)	6.4(3)
O3	0.3821(1)	0.1043(3)	0.2747(3)	3.7(1)
C3	0.4346(2)	0.0381(4)	0.1872(4)	3.9(2)
O4	0.4317(1)	−0.0600(3)	0.0899(3)	3.8(1)
C4	0.5029(3)	0.0840(6)	0.2080(6)	7.7(3)
O5	0.4059(2)	−0.3093(3)	−0.1173(3)	4.5(1)
C5	0.4046(3)	−0.3351(5)	−0.2315(5)	4.8(2)
O6	0.3654(2)	−0.2553(3)	−0.2764(3)	6.3(2)
C6	0.4479(3)	−0.4589(5)	−0.3319(5)	7.2(3)
O7	0.2348(2)	0.3070(3)	0.3575(3)	4.9(1)
C7	0.2722(3)	0.3791(4)	0.4187(5)	5.1(2)
O8	0.3447(2)	0.3421(3)	0.4199(4)	6.6(2)
C8	0.2393(4)	0.5190(5)	0.5003(7)	8.2(3)
P1	0.35189(6)	−0.19663(9)	0.2087(1)	3.10(4)
C10	0.2969(2)	−0.0829(4)	0.3547(4)	3.5(2)
C15	0.2893(3)	−0.1162(4)	0.4529(4)	4.5(2)
C14	0.2493(3)	−0.0239(5)	0.5667(5)	5.4(2)
C13	0.2198(3)	0.0990(5)	0.5811(5)	5.2(2)
C12	0.2267(2)	0.1305(4)	0.4832(4)	4.3(2)
C11	0.2639(2)	0.0406(4)	0.3648(4)	3.1(2)
C20	0.3306(3)	−0.3453(4)	0.1818(4)	4.2(2)
C21	0.3852(3)	−0.4577(4)	0.1563(5)	5.6(2)
C22	0.3645(4)	−0.5658(5)	0.1430(6)	7.8(3)
C23	0.2915(5)	−0.5604(6)	0.1563(6)	8.1(4)
C24	0.2375(4)	−0.4500(6)	0.1804(5)	7.2(3)
C25	0.2567(3)	−0.3425(5)	0.1927(5)	5.4(2)
C30	0.4486(2)	−0.2182(4)	0.2542(4)	3.6(2)
C31	0.5043(2)	−0.2908(5)	0.1585(5)	4.6(2)
C32	0.5785(3)	−0.3090(5)	0.1915(5)	5.6(2)
C33	0.5970(3)	−0.2520(5)	0.3146(6)	5.9(3)
C34	0.5424(3)	−0.1772(5)	0.4095(6)	6.1(3)
C35	0.4681(3)	−0.1608(4)	0.3798(5)	5.0(2)
C40	0.1732(2)	−0.1209(4)	0.0521(4)	3.4(2)
C45	0.1113(2)	−0.1708(4)	0.0222(5)	4.5(2)
C44	0.1193(2)	−0.2993(4)	−0.0541(5)	4.9(2)
C43	0.1893(2)	−0.3754(4)	−0.0999(5)	4.5(2)
C42	0.2512(2)	−0.3293(4)	−0.0713(4)	4.1(2)
C41	0.2451(2)	−0.1994(3)	0.0075(4)	3.2(2)
Cl1	0.20089(8)	−0.5394(1)	−0.1966(2)	7.79(7)
P2	0.16566(5)	0.04772(9)	0.1477(1)	3.15(4)
C50	0.0847(2)	0.0996(4)	0.2563(4)	3.8(2)
C51	0.0895(2)	0.0517(4)	0.3463(5)	4.4(2)
C52	0.0310(2)	0.0890(5)	0.4321(5)	5.2(2)
C53	−0.0346(3)	0.1690(4)	0.4222(5)	5.1(2)
C54	−0.0425(3)	0.2130(4)	0.3314(5)	5.3(2)
C55	0.0175(2)	0.1806(4)	0.2492(5)	4.6(2)
Cl2	−0.10940(8)	0.2097(2)	0.5266(2)	8.74(9)
C60	0.1302(2)	0.1228(4)	0.0417(4)	3.6(2)
C61	0.1218(2)	0.2538(4)	0.0877(5)	4.5(2)
C62	0.0918(3)	0.3161(4)	0.0133(5)	5.2(2)
C63	0.0718(3)	0.2487(5)	−0.1085(5)	5.1(2)
C64	0.0816(3)	0.1182(5)	−0.1587(5)	5.5(2)
C65	0.1112(2)	0.0560(4)	−0.0823(4)	4.5(2)
Cl3	0.03221(9)	0.3271(2)	−0.2014(2)	8.35(8)
C71	0.0344(8)	0.473(1)	0.584(1)	21.1(4)*
C72	0.0678(8)	0.436(1)	0.465(1)	21.1(4)*
C73	0.0382(8)	0.503(1)	0.392(1)	21.1(4)*

[a] $U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$. Starred item = U_{iso}(×100).

(0.393 mmol) were refluxed in 10 ml of $CHCl_3$ for 4 h. The resulting red–orange solution was concentrated to dryness and the crude solid was chromatographed as described above. The compounds obtained were the two conformations, H-T (70%) and H-H (30%), of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}ClC_6H_3)P(p\text{-}Cl\text{-}C_6H_4)_2](H_2O)_2$.

Measurements

NMR spectra were measured on a Brucker AC-200 FT spectrometer, operating at 300 K. In $^{31}P\{^1H\}$ NMR spectra, chemical shifts were referred to external 85% H_3PO_4 in D_2O. In ^1H and $^{13}C\{^1H\}$ NMR spectra, chemical shifts were referred to TMS and $CDCl_3$, respectively.

Crystal data

The structure of the title compound, $C_{44}H_{37}Cl_3O_8P_2Rh_2 \cdot \frac{1}{2}C_6H_6$, was determined by X-ray diffraction. $M_r = 1093.9$, triclinic, space group $P\bar{1}$, $a = 18.719(1)$, $b = 12.078(1)$, $c = 11.607(1)$ Å, $\alpha = 116.13(1)$, $\beta = 94.59(1)$, $\gamma = 74.24(1)°$, $V = 2265.2(1)$ Å^3, $Z = 2$, $D_x = 1.62$ Mg/m^3. Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å), μ(Mo Kα) = 10.16 cm^{-1}, $F(000) = 1114$, $T = 293$ K. Final conventional R factor = 0.034 for 6212 observed reflections and 541 variables.

X-ray crystallographic procedures

Dark red crystal, 0.33×0.23×0.22 mm size. Mo Kα radiation, graphite crystal monochromator, Nonius CAD4 single crystal diffractometer ($\lambda = 0.71073$ Å). Unit cell dimensions determined from the angular settings of 25 reflections $20° < \theta < 30°$. Space group $P\bar{1}$ from structure determination. 8583 reflections measured, *hkl* range (−22, −14, 0) to (22, 14, 13), θ limits ($0° < \theta < 25°$). ω–2θ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. Intensity checked monitoring three standard reflections every 60 min. Final drift corrections between 0.99 and 1.02. Profile analysis performed on all reflections [6, 7]; empirical absorption correction applied, using Ψ-scans [8]. μ(Mo Kα) = 10.16 cm^{-1} (correction factors in the range 0.77 to 0.99). Some double measured reflections averaged $R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I = 0.012$, resulting in 7969 unique reflections of which 6212 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections applied. Structure was solved by Patterson interpretation using the program SHELX86 [9] and Fourier synthesis. Isotropic least-squares refinement, using SHELX76 [10], converged to $R = 0.098$. At this stage, additional empirical absorption correction was applied [11], resulting in a further decrease of R to 0.070. The maximum and minimum absorption correction factors were 0.81 and 1.02, respectively. Further anisotropic refinements fol-

lowed by a difference Fourier synthesis allowed the location of some hydrogen atoms.

During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined. Positions for most hydrogen atoms were calculated geometrically and included in the refinement. All hydrogens refined as rigid groups with a common isotropic thermal parameter. The final conventional agreement factors were $R=0.034$ and $R_w=0.037$ for the 6212 'observed' reflections and 541 variables. Function minimized $\Sigma w(F_o-F_c)^2$, $w=1/(\sigma^2(F_o)+0.00020F_o^2)$ with $\sigma(F_o)$ from counting statistics. Maximum shift over error ratio in the last full matrix least-squares cycle was less than 0.28. Final difference Fourier map showed no peaks higher than 0.61 e/Å^3 nor deeper than -0.74 e/Å^3. Atomic scattering factors from the International Tables for X-ray Crystallography (1974). Geometrical calculations made with PARST [12]. All calculations made on an IBM 3090 computer of the University of Oviedo.

Results

The two monometallated compounds $Rh_2(O_2CCH_3)_3[(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2](HO_2CCH_3)_2$ and $Rh_2(O_2CCH_3)_3[(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](HO_2CCH_3)_2$ can be prepared in quite good yield following the synthetic procedure already described for the analogous compound with $P(m\text{-}CH_3C_6H_4)_3$ [4]. They have been characterized by ^1H, ^{13}C and ^{31}P NMR.

Reactivity of the monometallated compounds

The reaction of these monometallated compounds with triarylphosphines $P(p\text{-}XC_6H_4)_3$ (X = CH_3, H, Cl) yields doubly-metallated compounds of the type $Rh_2(O_2CCH_3)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]_2(P(p\text{-}XC_6H_4)_3)_n$ in reaction (1a) or $Rh_2(O_2CCH_3)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2][(p\text{-}X'C_6H_3)P(p\text{-}X'C_6H_4)_2](P(p\text{-}X'C_6H_4)_3)_n$ in reaction (1b), depending on the type of phosphine used.

In all cases a three molar excess of the corresponding phosphines was used in order to make the metallation faster. Due to that the obtained doubly-metallated compounds coordinate phosphine in the axial positions; during the chromatographic purification, this phosphine is exchanged by water.

$$Rh_2(O_2CCH_3)_2(X, PC)(X', PC)(P)_n \xrightarrow[(CH_3)_2CO\ (H_2O)]{\text{chromatography}} Rh_2(O_2CCH_3)_2(X, PC)(X', PC)(H_2O)_2$$

$n=1$ for H-H configuration
$n=2$ for H-T configuration

We already have enough spectroscopic data to allow the ^{31}P NMR spectroscopic results to have diagnostic value [3, 4, 13]. Two spectroscopic details are important in order to determine the configuration (H-T or H-H) of these doubly-metallated compounds: $^2J_{P-P'}$ between equatorial phosphines and δ_P, $^3J_{P-Paxial}$. For the non-symmetrical compounds the observation of a $^2J_{P-P'}$ with an approximate value of 40 Hz is diagnostic for H-H configuration. This coupling is not observed for compounds with H-T configuration. Besides, the chemical shift for the axial phosphine shows characteristic values of *c.* 5 ppm when the compound has H-H configuration, with very clear couplings to the rhodium nuclei ($^1J_{Rh-Pax}$, $^2J_{Rh-Pax}$) and even to the phosphorous nuclei ($^3J_{Peq-Pax}$). However, in compounds with H-T configuration the resonance for the axial position appears at higher field (0 to -15 ppm) and all or part of the couplings are lost due to partial dissociation. Because of steric repulsion of the four aromatic rings, the compounds with H-H conformation only have one axial site available to coordinate one phosphine. However, less sterically demanding ligands such as water or acetic acid can form bis-adduct compounds [3].

The reactions can be performed in the NMR tube and chemical evolution was followed by ^{31}P NMR spectroscopy. We observed a wide range of reaction activity for the different experiences that were tested. While the reaction of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$ with triphenylphosphine is practically instantaneous those involving $P(p\text{-}ClC_6H_4)_3$ require thermal conditions in high boiling point solvents.

From the ^{31}P NMR spectra, we can calculate the relative concentration of the compounds with H-H or H-T conformation in solution. The ratio H-H/H-T depends very much on the phosphine used. In symmetrical reaction (1a) with triphenylphosphine the compound with H-T conformation is quantitatively obtained while in the reaction with tris-*p*-tolylphosphine only the corresponding H-H compound is formed. With $P(p\text{-}ClC_6H_4)_3$ reaction (1a) yields a mixture of H-H and H-T compounds approximately of 1:1 ratio. This reaction

$$Rh_2(O_2CCH_3)_3(X, PC) \xrightarrow{+3P(p\text{-}XC_6H_4)_3} Rh_2(O_2CCH_3)_2(X, PC)_2P_n \quad (1a)$$

$$Rh_2(O_2CCH_3)_3(X, PC) \xrightarrow{+3P(p\text{-}X'C_6H_4)_3} Rh_2(O_2CCH_3)_2(X, PC)(X', PC)P'_n \quad (1b)$$

$(X, PC) = (p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2)$
$(X', PC) = (p\text{-}X'C_6H_3)P(p\text{-}X'C_6H_4)_2)$

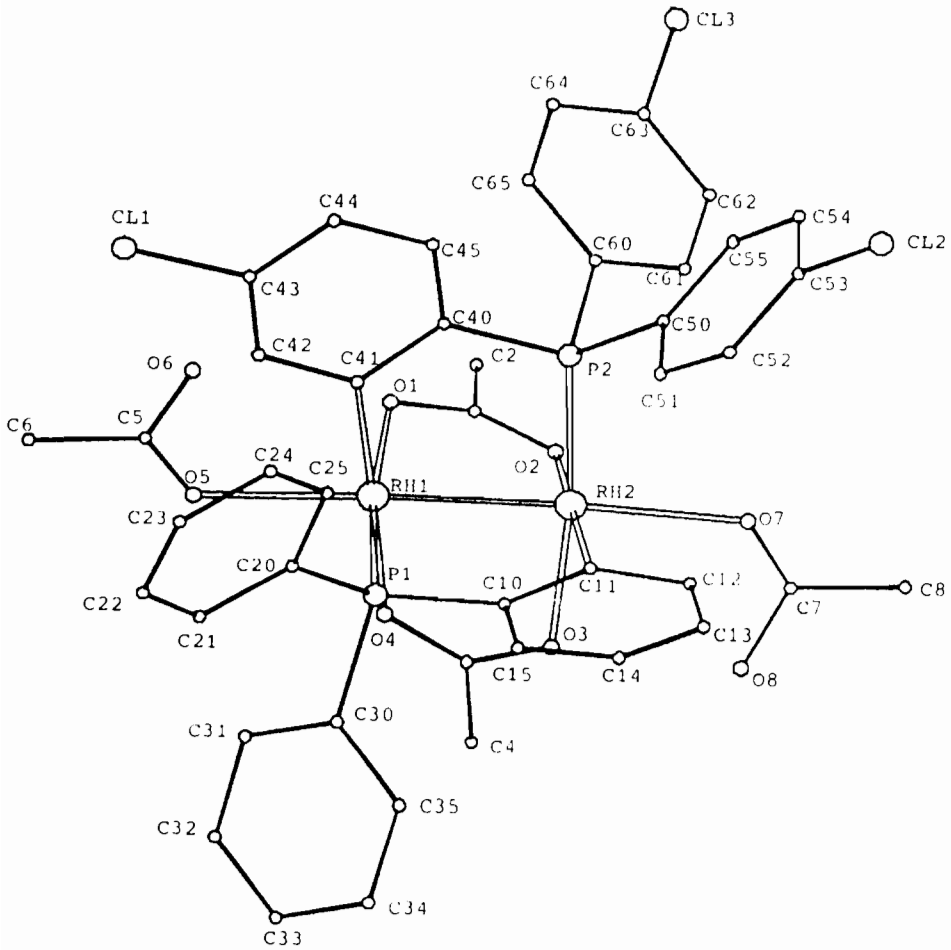

Fig. 1. Perspective view and atomic numbering scheme for $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)][(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](HO_2CCH_3)_2 \cdot \frac{1}{2}(C_6H_6)$.

only runs in boiling toluene while the two above-mentioned reactions occur at room temperature.

The unsymmetrical reactions (1b) with these three phosphines always give a mixture of the compounds $Rh_2(O_2CCH_3)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2][(p\text{-}X'C_6H_3)P(p\text{-}X'C_6H_4)_2] \cdot P_n$ with H-H and H-T conformations ($P = P(C_6H_5)_3$, $P(p\text{-}CH_3C_6H_4)_3$ or $P(p\text{-}ClC_6H_4)_3$; $n = 2$ for H-T; $n = 1$ for H-H; X, X' = H, CH_3, Cl, $X \neq X'$). Table 1 summarizes the approximate reaction time for all the experiences and the product distribution for reactions of type (1a) and (1b). The Table also shows the percentage of H-H compound in the reaction mixture calculated from the integral values obtained in ^{31}P NMR spectra. In all cases these spectra did not show additional signals that could be attributed to side reaction products.

Discussion

Previous investigations had already shown that the second metallation process can follow two different reaction pathways [2, 3, 13], that yield doubly-metallated compounds with H-H or H-T conformations. The results presented above give additional information about the influence of the reacting and metallated phosphine on the occurrence of each of these pathways. For the symmetrical reactions (1a), we can find a systematic behavior in the fact that PPh_3 favors the formation of H-T compounds while tris-*p*-tolylphosphine favors the H-H compounds. Both reaction pathways seem to be equally favored in the case of $P(p\text{-}ClC_6H_4)_3$.

From the observed results in the unsymmetrical reactions (1b), we can conclude that both the metallated and the reacting phosphine have some influence in the product distribution although, in some cases, the second has a slightly stronger effect. $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$ reacts with $P(p\text{-}CH_3C_6H_4)_3$ giving the H-H conformation as the major product while $Rh_2(O_2CCH_3)_3[p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2](HO_2CCH_3)_2$ reacts with $P(C_6H_5)_3$ giving approximately equal amounts of both conformations.

Even though we do not have yet a detailed interpretation for this behavior the results seem to be quite systematic and reproducible.

TABLE 3. Selected bond distances (Å) and angles (°) and their e.s.d.s for $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}ClC_6H_3)P(p\text{-}Cl\text{-}C_6H_4)](HO_2CH_3)_2$

Bond distances			
Rh(1)–Rh(2)	2.513(1)	Rh(1)–O(9)	2.169(3)
Rh(1)–O(5)	2.338(2)	Rh(1)–C(41)	1.981(4)
Rh(1)–P(1)	2.214(1)	Rh(1)–O(1)	2.513(1)
Rh(2)–O(2)	2.153(4)	Rh(2)–O(3)	2.126(3)
Rh(2)–O(7)	2.346(3)	Rh(2)–P(2)	2.208(1)
Rh(2)–C(11)	1.982(5)	P(1)–C(10)	1.811(4)
P(1)–C(20)	1.832(6)	P(1)–C(30)	1.826(4)
P(2)–C(40)	1.810(4)	P(2)–C(50)	1.837(5)
P(2)–C(60)	1.817(5)	C(1)–O(1)	1.286(5)
C(1)–O(2)	1.240(5)	C(2)–O(3)	1.286(5)
C(2)–O(4)	1.237(5)		
Bond angles			
O(4)–Rh(1)–C(41)	175.2(2)	O(1)–Rh(1)–P(1)	173.2(1)
Rh(1)–Rh(2)–O(7)	165.7(1)	O(2)–Rh(2)–C(11)	173.6(1)
Rh(2)–Rh(1)–O(5)	166.2(1)	O(3)–Rh(2)–P(2)	172.7(1)
O(1)–Rh(1)–C(41)	92.0(2)	O(4)–Rh(1)–P(1)	95.5(1)
P(1)–Rh(1)–C(41)	89.0(1)	O(1)–Rh(1)–O(4)	83.8(1)
O(3)–Rh(2)–C(11)	90.9(2)	O(2)–Rh(2)–P(2)	94.1(1)
P(2)–Rh(2)–C(11)	91.9(1)	O(2)–Rh(2)–O(3)	83.3(1)
P(1)–C(10)–C(11)	116.8(4)	P(2)–C(40)–C(41)	116.0(3)
O(1)–C(1)–O(2)	123.6(5)	O(3)–C(3)–O(4)	124.2(4)

It is reasonable to assume that the values reported in Table 2 correspond to the product distribution under kinetic control. We already know that if the H-H compound is boiled in acetic acid it changes to the thermodynamically more stable H-T compound but in the present experiments there is no excess of acetic acid in solution and the reactions are performed at room temperature. When a mixture of H-H and H-T compounds is refluxed in chloroform no change in the relative concentration of these compounds can be observed even after many hours.

The structure of the compound was solved by X-ray crystallographic procedures. The atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. A perspective view of the molecule with the atomic labelling is shown in Fig. 1. Important bond distances and angles are listed in Table 3.

The structure consists of a Rh_2^{4+} unit bridged by two cisoid acetate groups, one triphenylphosphine and one tris-*p*-chlorophenylphosphine in which orthometallation has occurred at one of the phenyl rings of each phosphine. The metallated phosphines are in a head-to-tail configuration. The axial sites are occupied by molecules of acetic acid. The geometry around each rhodium atom is distorted octahedral.

The rhodium–rhodium distance at 2.513(1) Å is similar to that observed for other doubly-metallated compounds of rhodium(II) with oxygen donor axial ligands [1, 3, 4, 14].

The equatorial Rh–O distances are relatively long, in the range 2.169(3)–2.126(3) Å, those *trans* to carbon being longer than the rest. No significant differences are found for the Rh–P, Rh–C and Rh–O distances around each rhodium atom.

The axial Rh–O distances are considerably longer, 2.337(3) and 2.345(3) Å, than the equatorial one, with slight deviations from linearity Rh(2)–Rh(1)–O(5) 166.2(1)° and Rh(1)–Rh(2)–O(7) 165.7(1)°.

The crystal packing includes one solvent molecule at the symmetric center. This molecule was found more likely to be benzene and was included in the refinement as a idealized phenyl ring.

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