Finally, it was necessary to establish the relationship of this new aryldiazene complex **4** with respect to the diazenide **1** and the aryldiazene complex **3**. We observed separately that, provided the supply of HCl is restricted (e.g., by stirring under an atmosphere of HCl rather than bubbling), then compound **4** is indeed obtained from **1** by HCl addition.

Not only is complex **4** formed in the two above ways but it is also produced by the careful removal of one chloride from the neutral aryldiazene complex **3** by reaction with $AgBF_4$ (eq 5).

$$\underset{\mathbf{3}}{[RhCl_3(PPh_3)_2(p\text{-}NHNC_6H_4OMe)]} \xrightarrow[CH_2Cl_2]{AgBF_4} \underset{\mathbf{4}}{[RhCl_2(PPh_3)_2(p\text{-}NHNC_6H_4OMe)][BF_4]} \quad (5)$$

The reaction is reversed with HCl, and therefore application of an excess of HCl to compound **1** drives the reaction beyond the intermediate **4** to give **3**. It is therefore understandable that neither **1** nor **4** has been previously recognized in reactions of $RhCl(PPh_3)_3$ with arenediazonium salts in $CHCl_3$, especially in the presence of additional HCl.[1]

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Registry No. **1**, 112793-51-8; **1**·$2CH_2Cl_2$, 112793-52-9; **2**, 36581-28-9; **3**, 112837-81-7; **4**, 112817-43-3; $[RhCl(PPh_3)_2]_2$, 14653-50-0; $RhCl(PPh_3)_3$, 14694-95-2; $[RhCl(PPh_3)_3(p\text{-}N_2C_6H_4OMe)][BF_4]$, 112793-54-1.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom coordinates (3 pages); a table of observed and calculated structure amplitudes (30 pages). Ordering information is given on any current masthead page.

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(32) (a) Robinson et al. reported that $RhCl_2(PPh_3)_2(N_2Ar)$ complexes (e.g., complex **2**) abstract the elements of HCl from $CHCl_3$ to give the aryldiazene complexes $RhCl_3(PPh_3)_2(NHNAr)$ (e.g., complex **3**).[2a] The aryldiazene complex **4** is conveniently synthesized for comparison by addition of HBF_4 to $RhCl_2(PPh_3)_2(p\text{-}N_2C_6H_4OMe)$ (**2**). (b) With acetone as the solvent, HCl abstraction is circumvented; further **1**·$2Me_2CO$ has quite low solubility in acetone and is precipitated from this reaction (1:1 or 1:2 stoichiometry) in reasonable yield.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Departamento de Química Inorgánica, Universitat de Valencia, 46100 Burjassot, Valencia, Spain

Ortho-Metalation Reactions in Binuclear Dirhodium Compounds. Synthesis and Molecular Structure of an Unsymmetrical Rh_2^{4+} Compound with Two Different Ortho-Metalated Phosphines

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The complex $Rh_2(O_2CCH_3)_4\cdot 2PCCl$ [$PCCl = P(o\text{-}ClC_6H_4)Ph_2$] undergoes ortho metalation in refluxing chloroform to give a new dirhodium compound $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)]\cdot PCCl$; when this compound is stirred with PPh_3 (1:2 molar ratio) in CH_2Cl_2 at room temperature, it yields a new product $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2]\cdot P(C_6H_5)_3$, which has been characterized by X-ray crystallography. This first example of a Rh_2^{4+} unit with two different ortho-metalated phosphines bridging the two rhodium atoms also presents a nonsymmetrical coordination and might be formally described as a Rh(I)–Rh(III) dimer. It crystallizes in space group $P2_1/n$ with unit cell dimensions of $a = 13.905$ (3) Å, $b = 19.825$ (1) Å, $c = 21.742$ (3) Å, $\beta = 102.77$ (5)°, $V = 5845$ (3) Å^3, and $Z = 4$. Some important distances (Å) are as follows: Rh–Rh, 2.558 (1); Rh(1)–P, 2.222 (2), 2.215 (2); Rh(1)–O, 2.124 (5), 2.074 (6); Rh(2)–C, 2.041 (7), 2.044 (8); Rh(2)–O, 2.186 (5), 2.177 (6); Rh(2)–P(of $P(C_6H_5)_3$), 2.370 (2).

Introduction

Following the isolation of the doubly metalated compound $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot 2HO_2CCH_3$ by thermal reaction of $Rh_2(O_2CCH_3)_4\cdot 2PPh_3$ in refluxing acetic acid, we have acquired further knowledge about the mechanism of this type of ortho-metalation reaction.[1,2] By heating the adduct $Rh_2(O_2CCH_3)_4\cdot 2P(C_6F_4Br)(C_6H_5)_2$ in different reaction conditions (Scheme I), we have isolated three intermediate reaction products (I–III), in addition to the doubly metalated compound $Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2$ (IV), analogous to the one previously reported.[2,3]

From all these data we proposed that the important step in the metalation reaction is the I → III conversion, where a proton-transfer process from one phenyl group of the phosphine to one acetate takes place. Compound IV, as well as the homologous one with triphenylphosphine, contains a dirhodium unit with two ortho-metallated phosphines acting as bridging ligands. In each case the molecules have a head-to-tail relationship of the two ortho-metalated ligands and lie on a crystallographic 2-fold axis perpendicular to the metal–metal bond.

Experimental Section

Synthesis of Compounds 1–6. $Rh_2(O_2CCH_3)_4\cdot 2CH_3OH$[4] and PCCl[5] were prepared according to literature procedures. Commercially available $P(C_6H_5)_3$ (Aldrich) was recrystallized from hot ethanol prior to use.

Compound 1. An orange suspension of $Rh_2(O_2CCH_3)_4\cdot 2PCCl$ in 100 mL of $CHCl_3$ was refluxed under an atmosphere of nitrogen for 80 min to yield a brown-red solution. The solution was concentrated under reduced pressure to one-third of its initial volume, and hexane was added to precipitate a brown-red solid (240 mg). Yield: 85%. Anal. Calcd for $Rh_2C_{42}H_{36}Cl_2P_2O_6$: C, 51.71, H, 3.64. Found: C, 51.27; H, 3.73. ^{31}P NMR: $\delta_1 = 23.2$ ($^1J_{Rh-P} = 168$ Hz), $\delta_2 = 9.8$ ($^1J_{Rh-P} = 111$ Hz). ^1H

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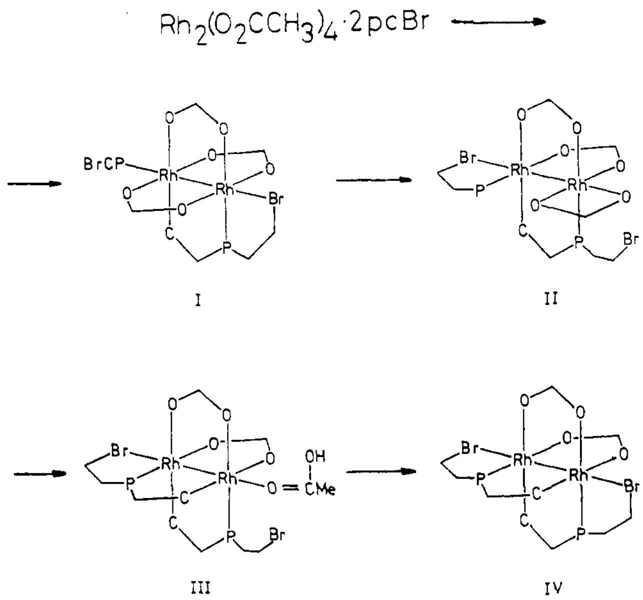
0020-1669/88/1327-1010$01.50/0

Scheme I



NMR: δ 2.01 (s, CH_3, 3 H), 1.18 (s, CH_3, 3 H), 1.52 (s, CH_3, 3 H), 6.3–7.6 (m, aromatics, 27 H).

Compound 2. Compound **1** (200 mg, 0.205 mmol) and PPh_3 (108 mg, 0.41 mmol) were dissolved in 10 mL of CH_2Cl_2 under nitrogen. The resulting solution was stirred for 24 h at room temperature. During this time, the solution color, initially brown-red, changed to deep red. Part of the solvent (ca. 8 mL) was removed under reduced pressure and hexane added to precipitate a red solid (212 mg). Yield: 90%. ^{31}P NMR: $\delta_1 = 24.8$ ($^1J_{Rh-P} = 152$ Hz), $\delta_2 = 23.6$ ($^1J_{Rh-P} = 152$ Hz), $\delta_3 = 5.4$ ($^1J_{Rh-P} = 129$ Hz).

Compound 3. Compound **1** (200 mg, 0.205 mmol) was dissolved in 5 mL of CH_2Cl_2. Hexane (5 mL) was added and the solution chromatographed (1.5 × 30 cm, silica gel/hexane). After a washing of the column with an acetone/hexane (1:10) mixture, the band on the top changed color from brown-red to blue. Increasing polarity (acetone/hexane (1:2)) eluted a blue band. The solvent was removed under vacuum, and the pale blue solid was recrystallized from CH_2Cl_2/hexane. Addition of a stoichiometric amount of PPh_3 (54 mg, 0.205 mmol), after redissolving the solid in 5 mL of CH_2Cl_2, changed the solution color to brown-red. Hexane was used to precipitate the brown-red solid (216 mg). Yield: 80%. ^{31}P NMR: $\delta_1 = 23.8$ ($^1J_{Rh-P} = 161$ Hz), $\delta_2 = 9.8$ ($^1J_{Rh-P} = 113$ Hz).

Compound 4. Compound **3** (200 mg, 0.212 mmol) was boiled under reflux in 15 mL of toluene for 1 h. The solvent was removed under vacuum and the crude product redissolved in a mixture of CH_2Cl_2/hexane (5 mL/5 mL). The solution was transferred to a chromatography column (30 × 2 cm) packed with silica gel in hexane. Elution with CH_2Cl_2/hexane (1:2) separated two minor bands, yellow and green, which were discarded. Further elution with acetone/hexane (1:1) separated a blue band. The solution was evaporated to dryness and the product redissolved in 5 mL of CH_2Cl_2. After the addition of 3 drops of acetic acid, the resulting solution was precipitated with hexane to give a blue solid (120 mg). Yield 60%. ^{31}P NMR: $\delta_1 = 23.4$ ($^1J_{Rh-P} = 167$ Hz), $\delta_2 = 15.4$ ($^1J_{Rh-P} = 161$ Hz).

Compound 5. An orange suspension of $Rh_2(O_2CCH_3)_4 \cdot 2PCCl$ in 15 mL of toluene was refluxed under an atmosphere of nitrogen for 1 h to yield a green suspension. The suspension was concentrated under reduced pressure to one-third of its initial volume, yielding a green solid (150 mg). Yield: 80%. Anal. Calcd for $Rh_2C_{42}H_{36}Cl_2P_2O_6$: C, 51.71; H, 3.64. Found: C, 52.55; H, 3.97. ^{31}P NMR: $\delta_1 = 51.2$ ($^1J_{Rh-P} = 178$ Hz), $\delta_2 = 14.6$ ($^1J_{Rh-P} = 150$ Hz).

Compound 6. An orange suspension of $Rh_2(O_2CCH_3)_4 \cdot 2PCCl$ in 15 mL of toluene was refluxed under an atmosphere of nitrogen for 3 h. The solvent was removed under vacuum and the crude product redissolved in a mixture of CH_2Cl_2/hexane (5 mL/5 mL). The solution was transferred to a chromatography column (30 × 2 cm) packed with silica gel in hexane. Elution with acetone/hexane (1:4) separated a blue-violet band. The solution was evaporated to dryness and the product redissolved in 5 mL of CH_2Cl_2. The solution was precipitated with hexane to give a pale violet solid (30 mg). Yield: 16%. ^{31}P NMR: $\delta = 18.6$ ($^1J_{Rh-P} = 148$ Hz).

X-ray Crystallography for Compound 2. Experimental and computational methods employed were those used routinely in this laboratory.[6]

Table I. Crystal Data for $Rh_2(CH_3COO)_2(PC)(PCCl) \cdot PPh_3 \cdot 2C_6H_6$

formula	$Rh_2ClP_3O_4C_{58}H_{48} \cdot 2C_6H_6$
fw	1299.44
space group	$P2_1/n$
systematic absences	$0k0$, $k \neq 2n$; $h0l$, $h + l \neq 2n$
a, Å	13.905 (3)
b, Å	19.825 (1)
c, Å	21.742 (3)
α, deg	90
β, deg	102.77 (5)
γ, deg	90
V, Å^3	5845 (3)
Z	4
d_{calcd}, g/cm^3	1.477
cryst size, mm	0.1 × 0.2 × 0.3
μ(Mo Kα), cm^{-1}	28.2
data colln instrument	CAD-4
radiation (monochromated in incident beam)	Mo Kα ($\lambda_\alpha = 0.71073$ Å)
orientation reflcns: no.; range (2θ), deg	25; 20–30
temp, °C	20
scan method	ω–2θ
data colln range (2θ), deg	4–45
unique data: total no.; no. with $F_o^2 > 3\sigma(F_o^2)$	6103; 4645
no. of params refined	730
transmission factors: max; min	0.9986; 0.929
R^a	0.0440
$R_w{}^b$	0.0562
quality-of-fit indicator^c	1.44
largest shift/esd, final cycle	0.04
largest peak, e/Å^3	0.761

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table I summarizes the pertinent information. The crystal was attached to a glass fiber with epoxy cement and mounted on a CAD-4 diffractometer. Three reflections monitored regularly throughout the data collection gave no indication of decomposition. With $Z = 4$ in space group $P2_1/n$, the dinuclear molecule was expected to reside on a general position. The MULTAN direct-methods program provided positions for the two independent rhodium atoms, and the rest of the molecule was developed by an alternating series of least-squares refinements and difference electron density maps.

Toward the end of this process it became evident that the two ortho-metalated ligands $P(C_6H_5)_2(o\text{-}C_6H_4)$ (PC) and $P(C_6H_5)(o\text{-}ClC_6H_4)(o\text{-}C_6H_4)$ were not ordered. This was manifested in the appearance of the chlorine atom with partial occupancies at two positions; Cl(1) was attached to C(52) and Cl(1a) was attached to C(26). Refinement was continued for all atoms, including both Cl(1) and Cl(1a). These were initially given equal occupancies, but the occupancies were then treated as variables, subject to the constraint that their sum be unity. The final value for Cl(1) was very close to 0.70. The two Cl positions are by no means equivalent in their relationship to Rh(1), with the distances from Rh(1) to Cl(1) and Cl(1a) being 3.012 (4) and 3.819 (8) Å, respectively.

After the structure of the complex had been well refined, a difference electron density map showed that there are also two benzene molecules in the asymmetric unit, each on a general position and well-defined. The entire structure including the interstitial benzene molecules was then refined anisotropically to convergence, with the occupancy number for Cl(1) fixed at 0.700.

A perspective drawing of compound **2** is shown in Figure 1. Table II contains the list of positional parameters. Important bond distances and angles are listed in Table III.

Results and Discussion

The unexpected results of our investigation using the phosphine $P(o\text{-}ClC_6H_4)(C_6H_5)_2$ (PCCl) are summarized in Scheme II. We have obtained a new compound of molecular formula Rh_2-

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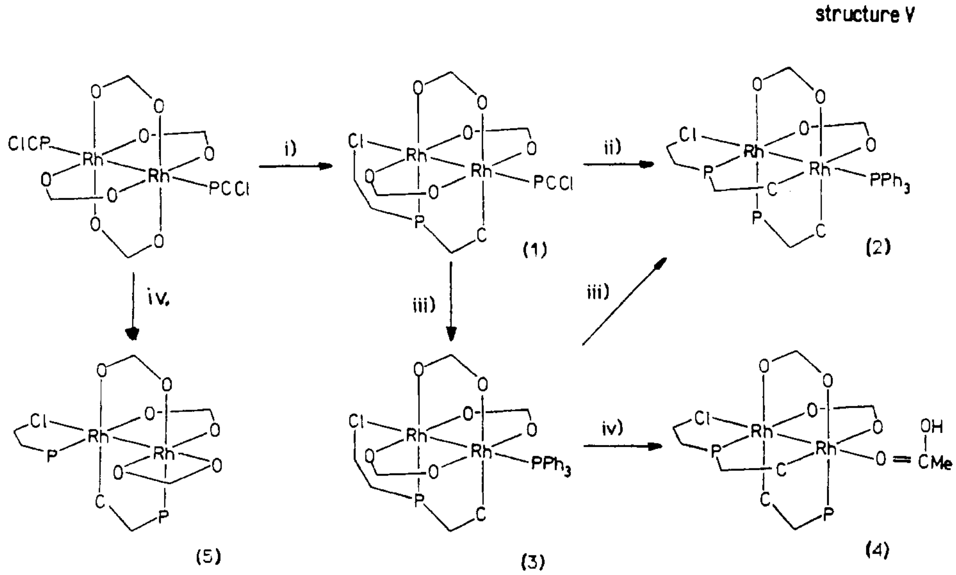
Table II. Positional Parameters and Their Estimated Standard Deviations for $Rh_2(PC)(PCCl)(CH_3CO_2)_2{\cdot}PPh_3{\cdot}2C_6H_6$

atom	*x*	*y*	*z*	*B*, Å$^{2\,a}$	atom	*x*	*y*	*z*	*B*, Å$^{2\,a}$
Rh(1)	0.03495 (4)	0.34075 (3)	0.23425 (3)	2.50 (1)	C(53)	-0.2116 (7)	0.2832 (6)	0.3572 (5)	5.5 (3)
Rh(2)	0.20061 (4)	0.40137 (3)	0.26821 (3)	2.27 (1)	C(54)	-0.2132 (8)	0.3127 (6)	0.4151 (5)	6.4 (3)
Cl(1)	-0.1502 (2)	0.2724 (2)	0.2525 (2)	4.20 (8)	C(55)	-0.1579 (8)	0.3686 (6)	0.4364 (5)	5.9 (3)
Cl(1a)	-0.0749 (6)	0.2523 (4)	0.0785 (4)	4.3 (2)	C(56)	-0.0987 (7)	0.3985 (5)	0.3992 (4)	4.4 (2)
P(1)	0.0141 (2)	0.3945 (1)	0.1426 (1)	2.75 (5)	C(61)	-0.1306 (6)	0.4771 (4)	0.2488 (4)	2.9 (2)
P(2)	-0.0343 (2)	0.4169 (1)	0.2852 (1)	2.57 (5)	C(62)	-0.1016 (7)	0.5338 (4)	0.2196 (4)	3.6 (2)
P(3)	0.3733 (2)	0.4185 (1)	0.2985 (1)	2.65 (5)	C(63)	-0.1741 (7)	0.5804 (5)	0.1884 (5)	4.5 (2)
O(1)	0.0721 (4)	0.2869 (3)	0.3207 (3)	3.2 (1)	C(64)	-0.2722 (7)	0.5692 (5)	0.1906 (5)	5.2 (3)
O(2)	0.2299 (4)	0.3166 (3)	0.3340 (3)	3.2 (1)	C(65)	-0.3007 (7)	0.5129 (5)	0.2197 (5)	4.7 (3)
O(3)	0.1100 (4)	0.2643 (3)	0.1995 (3)	3.5 (1)	C(66)	-0.2311 (6)	0.4660 (5)	0.2489 (4)	3.7 (2)
O(4)	0.2372 (4)	0.3330 (3)	0.1984 (3)	3.2 (1)	C(71)	0.4214 (5)	0.4938 (4)	0.2688 (4)	2.7 (2)
C(1)	0.1624 (6)	0.2829 (4)	0.3469 (4)	2.9 (2)	C(72)	0.4058 (6)	0.5012 (4)	0.2038 (4)	3.0 (2)
C(2)	0.1916 (7)	0.2297 (5)	0.3991 (4)	4.4 (2)	C(73)	0.4300 (6)	0.5631 (5)	0.1774 (4)	4.0 (2)
C(3)	0.1939 (6)	0.2781 (4)	0.1866 (4)	3.1 (2)	C(74)	0.4671 (7)	0.6165 (5)	0.2165 (5)	4.5 (2)
C(4)	0.2371 (7)	0.2231 (5)	0.1520 (5)	4.9 (3)	C(75)	0.4822 (6)	0.6093 (5)	0.2818 (5)	4.6 (3)
C(11)	-0.1132 (6)	0.4089 (4)	0.0958 (4)	3.2 (2)	C(76)	0.4602 (6)	0.5477 (4)	0.3086 (4)	3.6 (2)
C(12)	-0.1275 (6)	0.4316 (5)	0.0333 (4)	3.7 (2)	C(81)	0.4341 (6)	0.4155 (4)	0.3830 (4)	2.8 (2)
C(13)	-0.2240 (7)	0.4351 (5)	-0.0030 (5)	4.5 (2)	C(82)	0.3807 (6)	0.4047 (5)	0.4290 (4)	3.6 (2)
C(14)	-0.3052 (7)	0.4169 (5)	0.0210 (5)	4.9 (3)	C(83)	0.4307 (7)	0.4024 (5)	0.4936 (4)	4.4 (2)
C(15)	-0.2880 (7)	0.3927 (5)	0.0843 (5)	4.8 (3)	C(84)	0.5326 (7)	0.4095 (5)	0.5095 (4)	4.3 (2)
C(16)	-0.1919 (6)	0.3885 (4)	0.1219 (4)	3.4 (2)	C(85)	0.5863 (7)	0.4209 (5)	0.4637 (4)	4.4 (2)
C(21)	0.0594 (6)	0.3526 (4)	0.0779 (4)	3.2 (2)	C(86)	0.5377 (6)	0.4216 (5)	0.4004 (4)	4.1 (2)
C(22)	0.1320 (6)	0.3813 (5)	0.0531 (4)	4.1 (2)	C(91)	0.4441 (5)	0.3502 (4)	0.2721 (4)	2.7 (2)
C(23)	0.1537 (8)	0.3556 (6)	-0.0040 (5)	5.6 (3)	C(92)	0.5199 (6)	0.3632 (5)	0.2396 (4)	4.0 (2)
C(24)	0.1022 (7)	0.2994 (6)	-0.0313 (5)	5.8 (3)	C(93)	0.5761 (7)	0.3091 (5)	0.2240 (4)	4.5 (2)
C(25)	0.0301 (8)	0.2690 (5)	-0.0062 (5)	5.5 (3)	C(94)	0.5554 (7)	0.2432 (5)	0.2378 (5)	4.6 (3)
C(26)	0.0102 (7)	0.2947 (5)	0.0503 (4)	4.3 (2)	C(95)	0.4829 (7)	0.2304 (5)	0.2721 (5)	4.9 (3)
C(31)	0.0800 (5)	0.4739 (4)	0.1545 (4)	2.5 (2)	C(96)	0.4266 (6)	0.2839 (5)	0.2884 (4)	4.1 (2)
C(32)	0.0475 (6)	0.5301 (5)	0.1146 (4)	3.4 (2)	C(101)	0.6763 (9)	0.0718 (7)	0.0266 (6)	9.0 (4)
C(33)	0.0935 (6)	0.5926 (5)	0.1269 (4)	3.7 (2)	C(102)	0.652 (1)	0.1374 (8)	0.0124 (6)	9.6 (4)
C(34)	0.1702 (6)	0.6004 (4)	0.1806 (4)	3.3 (2)	C(103)	0.676 (1)	0.1883 (8)	0.0536 (8)	11.7 (5)
C(35)	0.2014 (5)	0.5443 (4)	0.2193 (4)	2.8 (2)	C(104)	0.724 (1)	0.1714 (9)	0.1131 (7)	11.5 (5)
C(36)	0.1590 (5)	0.4796 (4)	0.2071 (4)	2.3 (2)	C(105)	0.7498 (9)	0.1092 (8)	0.1306 (6)	9.0 (4)
C(41)	0.0571 (6)	0.4728 (4)	0.3316 (4)	2.8 (2)	C(106)	0.7318 (9)	0.0575 (7)	0.0919 (7)	8.9 (4)
C(42)	0.0219 (6)	0.5269 (5)	0.3637 (4)	3.6 (2)	C(201)	0.4460 (8)	0.3544 (6)	0.9515 (6)	7.1 (4)
C(43)	0.0883 (6)	0.5742 (5)	0.3965 (4)	3.6 (2)	C(202)	0.4166 (8)	0.4122 (7)	0.9765 (6)	7.2 (3)
C(44)	0.1887 (6)	0.5660 (4)	0.3984 (4)	2.9 (2)	C(203)	0.4023 (9)	0.4139 (7)	1.0381 (6)	8.1 (4)
C(45)	0.2210 (6)	0.5139 (4)	0.3653 (4)	2.8 (2)	C(204)	0.413 (1)	0.3542 (8)	1.0752 (6)	8.8 (4)
C(46)	0.1561 (5)	0.4664 (4)	0.3293 (3)	2.1 (2)	C(205)	0.4452 (9)	0.2971 (7)	1.0506 (6)	8.2 (4)
C(51)	-0.0973 (6)	0.3724 (4)	0.3391 (4)	3.1 (2)	C(206)	0.4586 (8)	0.2959 (6)	0.9890 (6)	7.2 (3)
C(52)	-0.1519 (6)	0.3144 (5)	0.3201 (5)	4.1 (2)					

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Scheme II[a]



[a] Key: (i) reflux in $CHCl_3$ for 80 min; (ii) 2 mol of PPh_3, at room temperature in CH_2Cl_2; (iii) 1 mol of PPh_3, at room temperature in $CHCl_3$; (iv) reflux in toluene for 1 h.

$(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2]{\cdot}P(C_6H_5)_3$ (**2**), in which two different metalated phosphines bridge the two rhodium atoms in a head-to-head fashion (structure V).

The thermal reaction of $Rh_2(O_2CCH_3)_4{\cdot}2PCCl$ in refluxing chloroform for 80 min yielded a new compound, **1**. The spectroscopic and analytical data found for **1** are consistent with the

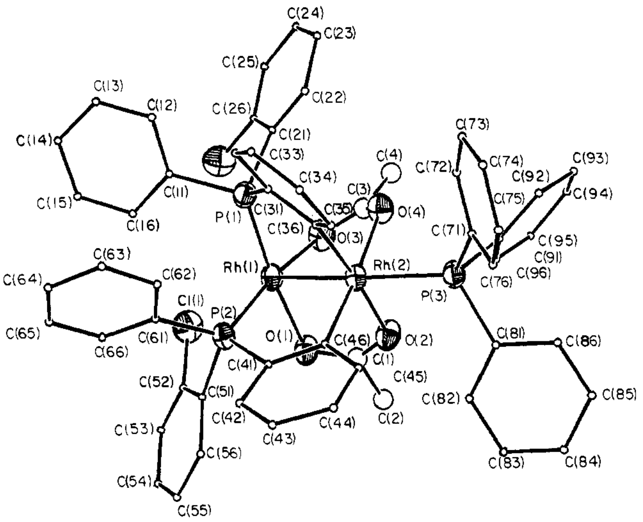


Figure 1. ORTEP drawing of compound **2**. Carbon atoms were drawn with arbitrary radii for clarity.

stoichiometry $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)]\cdot PCCl$. We assume for this compound a structure analogous to that of I in Scheme I, with three acetate groups and one ortho-metalated phosphine bridging the two rhodium atoms. One phosphine and the chlorine atom from the ortho-metalated one occupy the axial positions. This is the first case in which an intermediate monometalated compound with this type of structure is obtained as the major product of the reaction. In the systems, with $P(C_6H_5)_3$[1] or $P(BrC_6F_5)_2$,[2,3] the corresponding intermediate product either was not detected or was obtained in only low yield (5–10%).

When a mixture of compound **1** and $P(C_6H_5)_3$ (1:2) was stirred in CH_2Cl_2 at room temperature for 24 h, a new product $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2]\cdot P(C_6H_5)_3$ (**2**) was obtained in practically quantitative yield. Compound **2** has been characterized by elemental analysis, ^1H and ^{31}P NMR spectroscopy, and a crystal structure determination.

The molecular structure of **2** shows a binuclear dirhodium unit with a Rh–Rh bond distance of 2.5580 (8) Å. The two rhodium atoms are bridged by two acetate anions as well as by one PCCl and one PPh_3, which have each undergone ortho metalation in one phenyl ring. A second $P(C_6H_5)_3$ ligand and the chlorine atom of the metalated PCCl ligand occupy the two axial positions.

The molecule **2** is unusually interesting for two reasons: (i) It is the first example of a Rh_2^{4+} unit with two different ortho-metalated phosphines bridging the two rhodium atoms. (ii) The two metalated carbon atoms are bonded to the same rhodium atom, and therefore the second rhodium atom coordinates the two P atoms from the two ortho-metalated phosphines. As a result of this head-to-head coordination, the two rhodium atoms have different environments, RhO_2P_2Cl for Rh(1) and RhO_2C_2P for Rh(2). This compound can be formally described as a Rh(I)–Rh(III) dimer.

Further studies of the reactivity of compound **1** have been carried out. The axial phosphine PCCl can be easily displaced from compound **1** by triphenylphosphine, giving $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)]\cdot P(C_6H_5)_3$ (**3**). This compound does not undergo chemical change after stirring in $CHCl_3$ at room temperature for 48 h, but ortho metalation of the PPh_3 ligand in compound **3** does occur in refluxing toluene. It proceeds even faster when acetic acid is present in the reaction medium. However, the doubly metalated compound $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2]\cdot HO_2CCH_3$ (**4**) that can be isolated has a ^{31}P NMR spectrum that is consistent with a symmetrical structure (like IV in Scheme I) rather than the one shown for compound **2**.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Rh_2(PC)(PCCl)(CH_3CO_2)_2\cdot PPh_3\cdot 2C_6H_6$[a]

Rh(1)–Rh(2)	2.558 (1)	P(1)–C(31)	1.810 (8)
Rh(1)–P(1)	2.222 (2)	P(2)–C(41)	1.815 (8)
Rh(1)–P(2)	2.215 (2)	P(2)–C(51)	1.835 (9)
Rh(1)–O(1)	2.124 (5)	P(2)–C(61)	1.837 (8)
Rh(1)–O(3)	2.074 (6)	P(3)–C(71)	1.812 (9)
Rh(2)–P(3)	2.370 (2)	P(3)–C(81)	1.847 (8)
Rh(2)–O(2)	2.186 (5)	P(3)–C(91)	1.839 (8)
Rh(2)–O(4)	2.177 (6)	O(1)–C(1)	1.260 (9)
Rh(2)–C(36)	2.041 (7)	O(2)–C(1)	1.234 (10)
Rh(2)–C(46)	2.044 (8)	O(3)–C(3)	1.289 (11)
Cl(1)–C(52)	1.692 (10)	O(4)–C(3)	1.242 (10)
Cl(1a)–C(26)	1.674 (13)	C(31)–C(36)	1.404 (9)
P(1)–C(11)	1.858 (8)	C(41)–C(46)	1.394 (11)
P(1)–C(21)	1.859 (9)		

Rh(2)–Rh(1)–P(1)	87.94 (6)	Rh(1)–P(1)–C(11)	118.9 (3)
Rh(2)–Rh(1)–P(2)	89.95 (6)	Rh(1)–P(1)–C(21)	117.7 (3)
Rh(2)–Rh(1)–O(1)	87.3 (1)	Rh(1)–P(1)–C(31)	109.1 (3)
Rh(2)–Rh(1)–O(3)	87.4 (2)	C(11)–P(1)–C(21)	95.5 (4)
P(1)–Rh(1)–P(2)	97.91 (9)	C(11)–P(1)–C(31)	109.6 (4)
P(1)–Rh(1)–O(1)	173.2 (2)	C(21)–P(1)–C(31)	104.6 (4)
P(1)–Rh(1)–O(3)	90.0 (2)	Rh(1)–P(2)–C(41)	111.4 (3)
P(2)–Rh(1)–O(1)	87.0 (2)	Rh(1)–P(2)–C(51)	108.3 (3)
P(2)–Rh(1)–O(3)	171.6 (2)	Rh(1)–P(2)–C(61)	125.7 (3)
O(1)–Rh(1)–O(3)	84.9 (2)	C(41)–P(2)–C(51)	108.2 (4)
Rh(1)–Rh(2)–P(3)	160.04 (6)	C(41)–P(2)–C(61)	101.4 (4)
Rh(1)–Rh(2)–O(2)	81.6 (1)	C(51)–P(2)–C(61)	100.5 (4)
Rh(1)–Rh(2)–O(4)	80.8 (1)	Rh(2)–P(3)–C(71)	116.7 (2)
Rh(1)–Rh(2)–C(36)	93.5 (2)	Rh(2)–P(3)–C(81)	119.0 (3)
Rh(1)–Rh(2)–C(46)	95.8 (2)	Rh(2)–P(3)–C(91)	112.8 (2)
P(3)–Rh(2)–O(2)	84.1 (1)	C(71)–P(3)–C(81)	104.9 (4)
P(3)–Rh(2)–O(4)	84.5 (1)	C(71)–P(3)–C(91)	103.4 (4)
P(3)–Rh(2)–C(36)	101.3 (2)	C(81)–P(3)–C(91)	97.4 (4)
P(3)–Rh(2)–C(46)	99.4 (2)	Rh(1)–O(1)–C(1)	117.0 (5)
O(2)–Rh(2)–O(4)	86.5 (2)	Rh(2)–O(2)–C(1)	121.6 (5)
O(2)–Rh(2)–C(36)	174.4 (3)	Rh(1)–O(3)–C(3)	118.4 (5)
O(2)–Rh(2)–C(46)	95.7 (3)	Rh(2)–O(4)–C(3)	120.8 (6)
O(4)–Rh(2)–C(36)	95.5 (3)	Rh(2)–C(36)–C(31)	121.8 (6)
O(4)–Rh(2)–C(46)	175.7 (2)	Rh(2)–C(46)–C(41)	121.6 (5)
C(36)–Rh(2)–C(46)	82.0 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

An understanding of the factors responsible for the two reaction pathways, one leading to the head-to-head and the other to the head-to-tail product, will require further investigation.

Additionally, $Rh_2(O_2CCH_3)_4\cdot 2PCCl$ reacts in refluxing toluene to yield the compounds $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)]\cdot P(o\text{-}ClC_6H_4)(C_6H_5)_2$ (**5**) and finally $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)]_2\cdot HO_2CCH_3$ (**6**) with structures of types II and IV (Scheme I), respectively. This reaction sequence is similar to the one we described for $Rh_2(O_2CCH_3)_4\cdot 2P(BrC_6F_5)(C_6H_5)_2$.[2,3]

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Registry No. **1**, 112841-24-4; **2**, 112841-25-5; **2**·$2C_6H_6$, 112924-69-3; **3**, 112841-26-6; **4**, 112841-29-9; **5**, 112841-27-7; **6**, 112863-46-4; $Rh_2(O_2CCH_3)_4\cdot 2PCCl$, 112841-28-8.

Supplementary Material Available: Complete tables of bond distances and angles and anisotropic displacement parameters (8 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.