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Fast Ortho-Metalation Reactions in Binuclear Dirhodium Compounds. Syntheses and Molecular Structures of a Monometalated Compound and Two Doubly Metalated Compounds with Head-to-Head Configurations

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The reactions of $Rh_2(O_2CCH_3)_4(MeOH)_2$ and triphenylphosphine, in 1:4, 1:2, and 1:1 molar ratios, have been spectroscopically studied using different reaction conditions. Very reactive intermediate products, $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$ ($\mathbf{1}(HO_2CCH_3)_2$) and $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2][PPh_3](HO_2CCH_3)$ ($\mathbf{2}(HO_2CCH_3)$) have been isolated. The structure of $\mathbf{1}(HO_2CCH_3)_2$ has been determined by X-ray diffraction. Crystal data: space group $P\bar{1}$, $a = 9.807$ (6) Å, $b = 19.822$ (10) Å, $c = 8.476$ (5) Å, $\alpha = 80.10$ (2)°, $\beta = 111.02$ (2)°, $\gamma = 93.67$ (2)°, $Z = 2$, 3374 reflections, $R = 0.0289$. $\mathbf{1}(HO_2CCH_3)_2$ readily reacts with an excess of triphenylphosphine at room temperature to form the already reported doubly metalated compound $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(PPh_3)_2$ ($\mathbf{3}(PPh_3)_2$) with a head-to-tail structure. However under thermal conditions $\mathbf{1}(HO_2CCH_3)_2$ reacts with excess of triphenylphosphine giving in addition to $\mathbf{3}(PPh_3)_2$, $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(PPh_3)(HO_2CCH_3)$ ($\mathbf{4}(PPh_3,HO_2CCH_3)$), a doubly metalated compound with the orthometalated ligands in a head-to-head configuration. The structure of the closely related bis(acetic acid) adduct $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$ ($\mathbf{4}(HO_2CCH_3)_2$) has been determined by X-ray diffraction. Crystal data: space group $C2/c$, $a = 23.443$ (9) Å, $b = 19.868$ (8) Å, $c = 20.158$ (9) Å, $\beta = 106.60$ (2)°, $Z = 8$, 4873 reflections, $R = 0.0451$. The same mixture of compounds is formed from the reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$ and a 4-mol excess of PPh_3 in refluxing acetic acid. Para-substituted triarylphosphines $P(p\text{-}XC_6H_4)_3$ ($X = CH_3$, Cl) behave in a similar way, yielding a mixture of compounds with head-to-tail and head-to-head configurations. The structure of the compound $Rh_2(O_2CCH_3)_2[(ClC_6H_3)P(p\text{-}ClC_6H_4)_2]_2(HO_2CCH_3)_2$ ($\mathbf{8}(HO_2CCH_3)_2$), having a head-to-head configuration, has been determined by X-ray diffraction. Crystal data: space group $C2/c$, $a = 36.063$ (9) Å, $b = 16.558$ (6) Å, $c = 23.531$ (8) Å, $\beta = 125.34$ (2)°, $Z = 8$, 4316 reflections, $R = 0.0525$. Two different reaction pathways are proposed to justify this chemical behavior.

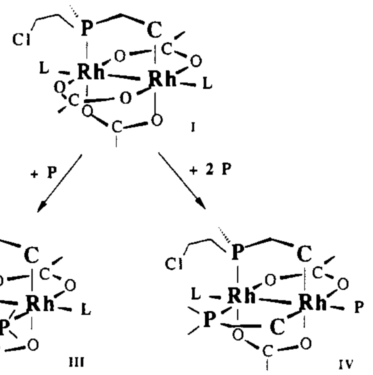
Introduction

Very few examples of compounds with orthometalated phosphines bridging a bimetallic unit have been reported in the literature.[1,2] After the report that dirhodium tetraacetate and triphenylphosphine react in refluxing acetic acid giving a doubly metalated product[2] of composition $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$, we have been investigating this particular reaction in order to gain insight into the mechanistic aspects. Using the (*o*-haloaryl)phosphines $P(o\text{-}BrC_6F_4)Ph_2$[3,4] and $P(o\text{-}ClC_6H_4)Ph_2$,[5] several intermediates were isolated and structurally characterized. The monometalated $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)Ph](HO_2CCH_3)_2$ was shown to react with $P(p\text{-}XC_6H_4)_3$, ($X = H$, CH_3) to selectively give doubly metalated compounds with head-to-tail (H-T) structures (III) by using a stoichiometric amount of phosphine or compounds with head-to-head (H-H) structures (IV) by using an excess of phosphine (Scheme I).[6] These results have been interpreted by assuming that the orthometalation can occur according to two different reaction pathways. Both pathways involve (i) axial coordination of one phosphine to the dirhodium unit, (ii) rearrangement of the phosphine from axial to equatorial coordination, with partial displacement of one acetate group and (iii) proton transfer from the phenyl ring of the phosphine to the acetate. The rearrangement of the axial phosphine, step ii, can occur from each of two different axial positions, so forming H-T (path A) or H-H compounds (path B). The proposed pathways were supported by the spectroscopic detection in solution of some intermediates. The ortho chlorine atom of the metalated phosphine was suggested to influence the selectivity of these reactions.

These observations prompted us to investigate the reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$ with different para-substituted phosphines $P(p\text{-}XC_6H_4)_3$ ($X = H$, CH_3, Cl) in order to see if the same intermediate compounds could be observed and if the metalation pathway leading to compounds with head-to-head structures can also occur with non-ortho-functionalized phosphines.

We report here the preparation and reactivity of two intermediate compounds $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$ ($\mathbf{1}(HO_2CCH_3)_2$)[7] and $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2][PPh_3](HO_2CCH_3)$ ($\mathbf{2}(HO_2CCH_3)$), as well as the crystal structure of the first one. We also present evidence of the two pathways in the reaction of $\mathbf{1}(HO_2CCH_3)_2$ with triphenylphosphine leading

Scheme I



L = CH_3CO_2H ; $\widehat{ClPC}$ = $(C_6H_4)P(o\text{-}ClC_6H_4)Ph$

P = PPh_3 ; $\widehat{PC}$ = $P(C_6H_4)Ph_2$

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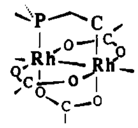
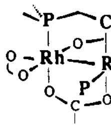
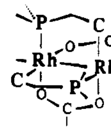
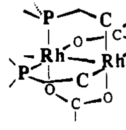
Table I. List of the Described Compounds with the Structure Type and Axial Ligands

structure type	structure	compound	metalated phosphine	axial phosphine
I		$\mathbf{1}(HO_2CCH_3)_2$	$P(C_6H_5)_3$	
		$\mathbf{1}(P)(HO_2CCH_3)$	$P(C_6H_5)_3$	$P(C_6H_5)_3$
		$\mathbf{1}(H_2O)_2$	$P(C_6H_5)_3$	
		$\mathbf{1}(P)(H_2O)$	$P(C_6H_5)_3$	$P(C_6H_5)_3$
II		$\mathbf{2}(HO_2CCH_3)$	$P(C_6H_5)_3$	
		$\mathbf{2}(H_2O)$	$P(C_6H_5)_3$	
III		$\mathbf{3}(HO_2CCH_3)_2$	$P(C_6H_5)_3$	
		$\mathbf{3}(P)_2$	$P(C_6H_5)_3$	$P(C_6H_5)_3$
		$\mathbf{3}(H_2O)_2$	$P(C_6H_5)_3$	
		$\mathbf{5}(HO_2CCH_3)_2$	$P(p\text{-}CH_3C_6H_4)$	
		$\mathbf{5}(P)_2$	$P(p\text{-}CH_3C_6H_4)_3$	$P(p\text{-}CH_3C_6H_4)_3$
		$\mathbf{5}(H_2O)_2$	$P(p\text{-}CH_3C_6H_4)_3$	
		$\mathbf{7}(HO_2CCH_3)_2$	$P(p\text{-}ClC_6H_4)_3$	
		$\mathbf{7}(P)_2$	$P(p\text{-}ClC_6H_4)_3$	$P(p\text{-}ClC_6H_4)_3$
		$\mathbf{7}(H_2O)_2$	$P(p\text{-}ClC_6H_4)_3$	
IV		$\mathbf{4}(P)(HO_2CCH_3)$	$P(C_6H_5)_3$	$P(C_6H_5)_3$
		$\mathbf{4}(HO_2CCH_3)_2$	$P(C_6H_5)_3$	
		$\mathbf{4}(H_2O)_2$	$P(C_6H_5)_3$	
		$\mathbf{6}(P)(HO_2CCH_3)$	$P(p\text{-}CH_3C_6H_4)_3$	$P(p\text{-}CH_3C_6H_4)_3$
		$\mathbf{6}(HO_2CCH_3)_2$	$P(p\text{-}CH_3C_6H_4)_3$	
		$\mathbf{6}(H_2O)_2$	$P(p\text{-}CH_3C_6H_4)_3$	
		$\mathbf{8}(P)(HO_2CCH_3)$	$P(p\text{-}ClC_6H_4)_3$	$P(p\text{-}ClC_6H_4)_3$
		$\mathbf{8}(HO_2CCH_3)_2$	$P(p\text{-}ClC_6H_4)_3$	
		$\mathbf{8}(H_2O)_2$	$P(p\text{-}ClC_6H_4)_3$	

to doubly metalated compounds with head-to-tail and head-to-head structures depending on the experimental conditions used; an unusually rapid metalation reaction is observed in the presence of excess of phosphine. We also report the isolation and the crystal structure of the compounds $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$ ($\mathbf{4}(HO_2CCH_3)_2$) and $Rh_2(O_2CCH_3)_2[(ClC_6H_3)P(p\text{-}ClC_6H_4)_2]_2(HO_2CCH_3)_2$ ($\mathbf{8}(HO_2CCH_3)_2$), both having the metalated phosphines in a head-to-head configuration. Part of these results has been published in a preliminary communication.[8]

Experimental Section

Materials and Procedures. The starting compound $Rh_2(O_2CCH_3)_4(MeOH)_2$ was synthesized by reported methods.[9] The phosphines $P(p\text{-}CH_3C_6H_4)_3$ and $P(p\text{-}ClC_6H_4)_3$ (Strem) and pyridine (Aldrich) 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 and chloroform were previously distilled and degassed; acetic acid only was degassed before use.

Thermal reactions were carried out in an argon atmosphere, using appropriate Schlenk-tube techniques. Silica gel (70–230 mesh, 60 Å, Aldrich) was used to pack the chromatography columns.

^{31}P NMR spectra were measured on a Bruker AC-200 FT spectrometer (81.015 MHz), operating at 300 K with broad-band decoupling. For all the measurements, the products were dissolved in CH_2Cl_2, using 85% H_3PO_4 in D_2O as external reference.

Table I lists the described compounds with their structural type and identity of the phosphine ligand used. Spectroscopic data, chemical shifts and coupling constants corresponding to the described compounds are listed in Table II.

Synthesis of $\mathbf{1(HO_2CCH_3)_2}$. To 400 mg of $Rh_2(O_2CCH_3)_4(MeOH)_2$ (0.79 mmol) in 120 mL of a hot (5:1) toluene/acetic acid mixture, 207 mg of $P(C_6H_5)_3$ (0.79 mmol) dissolved in 10 mL of toluene/$CHCl_3$ (1:1) was added with vigorous stirring. The color of the solution immediately changed from blue to blue-purple. After the solution was refluxed for 0.5 h, the solvent was evaporated under vacuum. The resulting crude oil was chromatographed in a column (1 × 50 cm) packed with silica gel suspended in hexane. After the column was washed with hexane/CH_2Cl_2/acetic acid (40:20:1), elution with hexane/CH_2Cl_2/acetic acid (40:40:3) separated a purple band. From this fraction, 92 mg (12% yield) of compound $\mathbf{3}(HO_2CCH_3)_2$ was isolated (see later). Elution with hexane/CH_2Cl_2/acetic acid (40:40:10) separated a blue band. The solvent was evaporated and the crude product was redissolved in CH_2Cl_2; addition of hexane precipitated $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$ ($\mathbf{1}(HO_2CCH_3)_2$) as a blue solid (structure type I, 440 mg, yield 73%).

By exchange reactions, the axial acetic acid molecules in compound $\mathbf{1}(HO_2CCH_3)_2$ are replaced by H_2O or PPh_3. The compounds so formed were identified on the basis of the spectroscopic data (see Table II). For simplicity they are named as $\mathbf{1}(L)(L')$, L and L′ being the axial ligands replacing the acetic acid molecules.

Synthesis of $\mathbf{1(PPh_3)(HO_2CCH_3)}$. A 200-mg (0.26-mmol) sample of $\mathbf{1}(HO_2CCH_3)_2$ was dissolved in CH_2Cl_2 (20 mL). A stoichiometric amount of PPh_3 (69 mg, 0.26 mmol) was added, and the solution changed to red-brown. Concentration under reduced pressure and addition of hexane gave 243 mg (96%) of the compound $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](PPh_3)(HO_2CCH_3)$, of structure type I.

Synthesis of $\mathbf{1(H_2O)_2}$. A 100-mg sample of compound $\mathbf{1}(HO_2CCH_3)_2$ (0.13 mmol) was dissolved in CH_2Cl_2/hexane (5 mL/5 mL) and the solution was chromatographed (1.5 × 30 cm, silica gel/hexane). After the column was washed with an acetone/hexane (1:10) mixture, higher polarity solvents (acetone/hexane, 1:1) eluted a blue band, which contained the water adduct $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](H_2O)_2$. Concentration under reduced pressure and addition of hexane yielded a blue powder (structure type I, 86 mg, 97%).

Synthesis of $\mathbf{1(PPh_3)(H_2O)}$. A 100-mg sample of $\mathbf{1}(H_2O)_2$ (0.15 mmol) was dissolved in CH_2Cl_2; addition of $P(C_6H_5)_3$ (38 mg, 0.15 mmol) produced a color change to red-brown. Concentration under reduced pressure and addition of hexane gave a brown-red solid, compound $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](PPh_3)(H_2O)$, which was separated by filtration (structure type I, 129 mg, 95%).

Synthesis of $\mathbf{2(HO_2CCH_3)}$ and $\mathbf{2(H_2O)}$. A 100-mg sample of $Rh_2(O_2CCH_3)_4(MeOH)_2$ (0.20 mmol) and 207 mg of PPh_3 (0.40 mmol) were refluxed in toluene (20 mL) for 1 h in an argon atmosphere. After evaporation to dryness under vacuum, the crude product was chromato-

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(7) In the full notation, the number indicates the composition and structure of the Rh_2X_8 core of the compound, showing the nature of the axial ligands in parentheses; sometimes, a short notation is used for simplicity without including the axial ligands.

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Table II. $^{31}P\{^1H\}$ NMR Data for the Described Compounds[a]

compound	δ^b	^1J(Rh–P)	^2J(Rh–P)	δ^c	^1J(Rh–P)	^2J(Rh–P)	^3J(P–P)
$1(HO_2CCH_3)_2$	17.6	150	6	...	...	...	...
$1(P)(HO_2CCH_3)$	24.1	160	...	−9.0	119	27	12
$1(H_2O)_2$	17.8	150	6	...	...	...	...
$1(P)(H_2O)$	23.7	157	...	−10.4	112	29	10
$2(HO_2CCH_3)$	16.0	139	10	41.1	187	5	...
$2(H_2O)$	15.7	138	10	41.6	188	5	...
$3(HO_2CCH_3)_2$	19.3	167	...				
$3(P)_2$	17.0	162	−11.9				
$3(H_2O)_2$	18.9	161	...				
$3(py)_2$	21.8	166	...				
$5(HO_2CCH_3)_2$	18.2	161	...				
$5(P)_2$	16.2	162	−15.8				
$5(H_2O)_2$	17.3	158	...				
$7(HO_2CCH_3)_2$	20.4	163	...				
$7(P)_2$	16.7	166	−10.1				
$7(H_2O)_2$	21.5	159	...				
$4(P)(HO_2CCH_3)$	25.3	152	3	5.2	132	28	7
$4(HO_2CCH_3)_2$	17.7	151	8	...	...	...	...
$4(H_2O)_2$	21.6	148	5	...	...	...	...
$6(P)(HO_2CCH_3)$	23.6	153	3	3.7	131	28	7
$6(HO_2CCH_3)_2$	15.0	149	5	...	...	...	...
$6(H_2O)_2$	16.0	149	6	...	...	...	...
$8(P)(HO_2CCH_3)$	23.6	153	3	1.6	124	28	8
$8(HO_2CCH_3)_2$	17.6	149	7	...	...	...	...
$8(H_2O)_2$	17.0	151	8	...	...	...	...

[a] Chemical shifts in ppm; coupling constants in Hz. [b] Chemical shift from orthometalated phosphine. [c] Compounds of type I, III, and IV, chemical shift for axial phosphine; compounds of type II, chemical shift for equatorial phosphine.

graphed (1.5 × 30 cm, silica gel/hexane). After elution with acetone/hexane (1:7), a minor orange band was separated and discarded. Increasing the polarity of the solvent mixture (acetone/hexane, 1:4) separated two bands; the first band contained compound $\mathbf{1}(H_2O)_2$. The second band, of green color, was concentrated under reduced pressure. The residue was dissolved in the minimum amount of a 1:1 CH_2Cl_2/acetic acid mixture. Addition of hexane yielded $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2][PPh_3](HO_2CCH_3)$ ($\mathbf{2}(HO_2CCH_3)$) as a green powder (structure type II, 4 mg, 1%). ^1H NMR ($CDCl_3$, δ): 0.93 (3 H, s), 1.04 (3 H, s), 1.66 (3 H, s), 2.15 (3 H, s), 6.2–7.5 (29 H, m). ^{13}C NMR ($CDCl_3$, δ): 21.4, 22.6, 23.3, 23.8 (*C*H_3, s), 122.0–143.7 (aromatic *C*–H), 187.6, 183.7, 183.9, 184.1 (*C*OO). The water adduct $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2][PPh_3](H_2O)$ ($\mathbf{2}(H_2O)$) was obtained by concentrating the fraction from the chromatography and precipitating the product with hexane, in the absence of acetic acid.

Synthesis of $\mathbf{3(HO_2CCH_3)_2}$ and $\mathbf{4(HO_2CCH_3)_2}$. A 400-mg sample of $Rh_2(O_2CCH_3)_4(MeOH)_2$ (0.79 mmol) and 829 mg of PPh_3 (3.16 mmol) were refluxed in toluene (30 mL) in argon atmosphere for 2 h. After evaporation to dryness under vacuum, the crude product was chromatographed (2 × 30 cm, silica gel/hexane). The column was first washed with CH_2Cl_2/hexane (1:1) and was later eluted with mixtures of acetone/hexane of increasing polarity (from 1:10 to 1:3). A red-orange band, which was collected and stored, eluted first followed by a blue band, which was also collected. Elution with acetone/hexane (1:1), separated an additional purple band. The orange-red band was reduced to dryness and chromatographed again using the previous method. Again, a blue and a purple band were collected after a minor red-orange band was discarded. The four blue and purple bands were recombined into one blue and one purple fraction. The purple one was concentrated to dryness under reduced pressure and dissolved in a minimum amount of acetic acid/CH_2Cl_2 (1:1). Addition of hexane yielded $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$ ($\mathbf{3}(HO_2CCH_3)_2$) (structure type III, determined by X-ray diffraction,[2a] 314 mg, 45%). Analogous treatment of the blue fraction gave $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$ ($\mathbf{4}(HO_2CCH_3)_2$) (structure type IV, 307 mg, 45%). Anal. Calcd (found): for $Rh_2P_2O_8C_{44}H_{42}$: C, 54.66 (54.45); H, 4.39 (4.35).

The axial acetic acid molecules in $\mathbf{3}(HO_2CCH_3)_2$ and $\mathbf{4}(HO_2CCH_3)$ are exchanged by water using the procedure above described for $\mathbf{1}(HO_2CCH_3)_2$; this forms respectively the isomers $\mathbf{3}(H_2O)_2$ and $\mathbf{4}(H_2O)_2$ with the molecular formula $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(H_2O)_2$. Compound $\mathbf{3}(HO_2CCH_3)_2$ reacts with 2 equiv of PPh_3 giving $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(PPh_3)_2$ ($\mathbf{3}(PPh_3)_2$). Compound $\mathbf{4}(HO_2CCH_3)_2$ reacts with 1 equiv of PPh_3 giving $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(PPh_3)(HO_2CCH_3)$ ($\mathbf{4}(PPh_3)(HO_2CCH_3)$).

Synthesis of Compounds 5–8. Doubly metalated compounds of structural types III and IV were prepared with the phosphines $P(p\text{-}CH_3C_6H_4)_3$ and $P(p\text{-}ClC_6H_4)_3$ by the method described for PPh_3. The reaction times were 1 and 5 h respectively. After chromatography and crystallization in the presence of acetic acid compounds of formulation $Rh_2(O_2CCH_3)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]_2(HO_2CCH_3)_2$ were obtained. For X = CH_3, compounds $\mathbf{5}(HO_2CCH_3)_2$ (type III, 69%. Anal. Calcd (found) for $Rh_2P_2O_8C_{50}H_{54}$: C, 57.15 (57.45); H, 5.19 (5.03)) and $\mathbf{6}(HO_2CCH_3)_2$ (type IV, 28%. Anal. Calcd (found) for $Rh_2P_2O_8C_{50}H_{54}$: C, 57.15 (56.89); H, 5.19 (5.20)) were obtained; for X = Cl, $\mathbf{7}(HO_2CCH_3)_2$ (type III, 30%. Anal. Calcd (found) for $Rh_2P_2Cl_6O_8C_{44}H_{36}$: C, 45.04 (45.51); H, 3.10 (3.42)) and $\mathbf{8}(HO_2CCH_3)_2$ (type IV, 65%. Anal. Calcd (found) for $Rh_2P_2Cl_6O_8C_{44}H_{36}$: C, 45.04 (44.63); H, 3.10 (3.31)) were obtained. Exchange reactions of the axial acetic acid molecules were achieved in practically quantitative yields by the methods described for $\mathbf{3}(HO_2CCH_3)_2$ and $\mathbf{4}(HO_2CCH_3)_2$.

X-ray Crystallography. Approximately prismatic crystals suitable for X-ray studies were obtained by slow evaporation of a concentrated chloroform/acetic acid solution of the corresponding compound (**1** and **4**; minor amounts of acetonitrile were also added for **8**). A blue-gray crystal of approximate dimensions 0.20 × 0.25 × 0.33 mm (**1**) and pink-brown crystals of dimensions 0.25 × 0.25 × 0.35 mm (**4**) and 0.15 × 0.25 × 0.30 mm (**8**) were used for the analyses. The crystallographic data for $\mathbf{1}(HO_2CCH_3)_2$, $\mathbf{4}(HO_2CCH_3)_2$, and $\mathbf{8}(HO_2CCH_3)_2$ are summarized in Table III. Unit cell parameters were determined from the setting angles of 30 carefully centered reflections, having $12 < \theta < 17°$ (**1**), $13 < \theta < 20°$ (**4**), and $23 < \theta < 33°$ (**8**). Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using niobium-filtered Mo Kα (**1** and **4**) and nickel-filtered Cu Kα radiation (**8**) and the $\theta/2\theta$ scan type. All reflections with θ in the ranges 3–25° (**1**), 2.5–26° (**4**), and 3–60° (**8**) were measured; of 5364 (**1**), 8881 (**4**) and 8547 (**8**) independent reflections, 3374, having $I > 2\sigma(I)$ (**1**), 4873, having $I > 3\sigma(I)$ (**4**) and 4316, having $I > 2\sigma(I)$ (**8**), were considered observed and used in the analysis. The reflections were collected with a variable scan speed of 3–12° min^{-1} and a scan width from $(\theta - 0.6)°$ to $(\theta + 0.6 + 0.346 \tan\theta)°$ (**1** and **4**) and from $(\theta - 0.6)°$ to $(\theta + 0.6 + 0.142 \tan\theta)°$ (**8**). One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles were analyzed by following Lehmann and Larsen.[10] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied to (**8**) (maximum and minimum values for the transmission factors were 1.197 and 0.835).[11] Only the observed reflections were used in the structure solution and refinement.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares methods first with isotropic thermal parameters and then with anisotropic thermal parameters for all the

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(10) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580.
(11) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158. Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109.

Table III. Experimental Data for the X-ray Diffraction Studies

	$\mathbf{1}(HO_2CCH_3)_2$	$\mathbf{4}(HO_2CCH_3)_2$	$\mathbf{8}(HO_2CCH_3)_2$
mol formula	$C_{28}H_{31}O_{10}PRh_2$	$C_{44}H_{42}O_8P_2Rh_2$	$C_{44}H_{36}Cl_6O_8P_2Rh_2$
mol wt	764.33	966.57	1173.24
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$
radiatn	Nb-filtered Mo Kα (λ = 0.71073 Å)	Nb-filtered Mo Kα (λ = 0.71073 Å)	Ni-filtered Cu Kα (λ = 1.54184 Å)
a, Å	9.807 (6)	23.443 (9)	36.063 (9)
b, Å	19.822 (10)	19.868 (8)	16.558 (6)
c, Å	8.476 (5)	20.158 (9)	23.531 (8)
α, deg	80.10 (2)	90	90
β, deg	111.02 (2)	106.60 (2)	125.34 (2)
γ, deg	93.67 (2)	90	90
V, Å^3	1515 (2)	8998 (6)	11462 (7)
Z	2	8	8
D_{calcd}, g cm^{-3}	1.675	1.427	1.360
$F(000)$	768	3920	4688
μ, cm^{-1}	11.75	8.38	83.01
R^a	0.0289	0.0451	0.0525
$R_w{}^b$	0.0388	0.0605	0.0677

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

non-hydrogen atoms of **1** and for all the non-hydrogen atoms except those of the phenyl rings (not the metalated ones) for **4** and **8**. Some peaks were found in the final ΔF map of **8** probably due to the presence of a disordered molecule of acetonitrile of solvation, but it was not possible to find among the peaks an acceptable image of it. The 10 largest peaks, practically of the same height, were introduced as carbon atoms of different occupancy factors, but not refined. Being sure of neither the nature nor the number of molecules, the data for this structure are given without the presence of the solvent. All hydrogen atoms of **1** were clearly located in the final ΔF map and refined isotropically, only the two carboxylic hydrogen atoms of the axial acetic acid molecules of **4** and **8** were located in the ΔF map and refined isotropically, the remaining ones were placed at their geometrically calculated positions (C–H = 1.00 Å) and introduced in the final structure factor calculations. The final cycles of refinement were carried out on the basis of 467 (**1**), 403 (**4**) and 457 (**8**) variables; after the last cycles, no parameters shifted by more than 0.74 (**1**), 2.02 (**4**) and 0.52 (**8**) esd. The largest remaining peak in the final difference map was equivalent to about 0.78 (**1**), 1.05 (**4**) and 0.94 (**8**) e/Å^3. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o{}^2]^{-1}$ was used; at convergence the K and g values were 0.5178 and 0.0076 for **1**, 1.0 and 0.0056 for **4** and 0.4912 and 0.0035 for **8**, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 12. All calculations were carried out on the Cray Y-MP8/432 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna, Italy) and on the Gould Powernode 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[13] The final atomic coordinates for the non-hydrogen atoms for **1**, **4**, and **8** are given in Tables IV–VI, respectively. The atomic coordinates of the hydrogen atoms are given in Tables SI (**1**), SII (**4**), SIII (**8**); the thermal parameters are given in Tables SIV (**1**), SV (**4**), and SVI (**8**).

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of $\mathbf{1}(HO_2CCH_3)_2$

atom	x/a	y/b	z/c	U^a
Rh(1)	2753 (1)	2963 (1)	1652 (1)	297 (1)
Rh(2)	105 (1)	3013 (1)	703 (1)	319 (2)
P	2684 (1)	1876 (1)	2763 (2)	301 (4)
O(1)	2470 (1)	2705 (2)	−655 (4)	418 (13)
O(2)	35 (4)	2544 (2)	−1278 (4)	440 (15)
O(3)	2802 (3)	3351 (2)	3792 (4)	374 (13)
O(4)	373 (3)	3539 (2)	2671 (4)	378 (13)
O(5)	2768 (4)	4026 (2)	508 (5)	449 (15)
O(6)	377 (4)	3997 (2)	−853 (5)	470 (17)
O(7)	5295 (4)	3032 (2)	2498 (5)	526 (18)
O(8)	5546 (5)	4149 (2)	2663 (8)	895 (25)
O(9)	−2344 (4)	3275 (2)	−415 (5)	573 (19)
O(10)	−2392 (5)	4256 (3)	−2176 (6)	775 (21)
C(1)	982 (5)	1684 (2)	3102 (6)	324 (18)
C(2)	−165 (5)	2140 (2)	2138 (6)	353 (19)
C(3)	−1521 (6)	1975 (3)	2302 (7)	460 (23)
C(4)	−1729 (6)	1395 (3)	3322 (8)	578 (27)
C(5)	−590 (6)	944 (3)	4266 (8)	536 (25)
C(6)	770 (6)	1092 (3)	4159 (7)	432 (21)
C(7)	1212 (7)	2527 (3)	−1582 (6)	433 (22)
C(8)	1117 (8)	2254 (3)	−3168 (7)	633 (26)
C(9)	1627 (5)	3607 (2)	3741 (7)	384 (22)
C(10)	1752 (6)	4023 (3)	5107 (8)	591 (26)
C(11)	1593 (6)	4297 (3)	−555 (7)	416 (22)
C(12)	1668 (7)	4993 (3)	−1521 (8)	607 (27)
C(13)	6024 (6)	3516 (3)	3053 (8)	558 (28)
C(14)	7583 (7)	3428 (4)	4259 (9)	703 (32)
C(15)	−3002 (7)	3746 (4)	−1457 (8)	571 (26)
C(16)	−4622 (7)	3816 (5)	−2036 (11)	911 (38)
C(17)	2749 (5)	1289 (2)	1344 (7)	381 (20)
C(18)	1582 (6)	879 (3)	600 (7)	459 (23)
C(19)	1652 (8)	465 (3)	−525 (8)	629 (29)
C(20)	2904 (10)	448 (3)	−885 (8)	721 (37)
C(21)	4053 (8)	859 (4)	−199 (9)	693 (31)
C(22)	3992 (6)	1285 (3)	928 (8)	527 (26)
C(23)	4233 (5)	1607 (2)	4732 (6)	339 (19)
C(24)	4824 (7)	954 (3)	5168 (8)	628 (27)
C(25)	6054 (8)	785 (3)	6583 (8)	752 (32)
C(26)	6732 (7)	1266 (4)	7601 (8)	656 (29)
C(27)	6142 (7)	1903 (3)	7205 (8)	670 (28)
C(28)	4918 (6)	2074 (3)	5811 (7)	526 (24)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results

We now have sufficient examples of structurally characterized ortho-metalated dirhodium compounds[3-7] to allow the $^{31}P\{^1H\}$ NMR spectroscopic parameters to be diagnostic of a particular structure. We will summarize the correlation between the spectroscopic data and coordination mode of the phosphorus ligands described elsewhere.[6] $^{31}P\{^1H\}$ chemical shift values in the range 14–26 ppm correspond to ortho-metalated triarylphosphines and are sensitive to the nature of the axial ligand. Non-metalated phosphines occupying equatorial coordination sites appear at lower fields, ca. 40–55 ppm, while axially coordinated phosphines appear at higher fields, +5 to −16 ppm. In doubly metalated compounds of type IV, the resonances corresponding to axially coordinated phosphines appear at about +5 ppm and are coupled to the two rhodium and to the two phosphorus nuclei of the metalated phosphines; this set of signals can be used as diagnostic for head-to-head configuration. The values of ^1J(Rh–P) for metalated phosphines are in the range 138–167 Hz, while for axial phosphines

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(12) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(13) Sheldrick, G. M. SHELX-76. Program for crystal structure determination. University of Cambridge, England, 1976; SHELXS-86 Program for the solution of crystal structures. University of Göttingen, 1986.

Table V. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of **4**(HO_2CCH_3)$_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*
Rh(1)	2493 (1)	643 (1)	2177 (1)	303 (2)[a]
Rh(2)	2532 (1)	1695 (1)	2863 (1)	335 (2)[a]
P(1)	1509 (1)	602 (1)	2013 (1)	325 (5)[a]
P(2)	2437 (1)	1296 (1)	1265 (1)	317 (5)[a]
O(1)	2646 (2)	119 (2)	3142 (2)	409 (16)[a]
O(2)	2935 (2)	1055 (2)	3749 (2)	466 (17)[a]
O(3)	3435 (2)	710 (2)	2504 (2)	430 (17)[a]
O(4)	3457 (2)	1780 (2)	2832 (3)	480 (18)[a]
O(5)	2761 (3)	−419 (3)	1676 (3)	768 (30)[a]
O(6)	3740 (4)	−350 (5)	1983 (5)	1201 (49)[a]
O(7)	2778 (2)	2564 (2)	3561 (2)	500 (18)[a]
O(8)	3393 (4)	2095 (3)	4481 (3)	1308 (41)[a]
C(1)	1350 (3)	1040 (3)	2721 (3)	345 (21)[a]
C(2)	1744 (3)	1562 (3)	3027 (3)	368 (21)[a]
C(3)	1576 (3)	1952 (4)	3519 (4)	517 (28)[a]
C(4)	1066 (4)	1844 (4)	3697 (4)	589 (33)[a]
C(5)	689 (4)	1326 (4)	3401 (4)	587 (30)[a]
C(6)	838 (3)	931 (4)	2911 (4)	485 (26)[a]
C(7)	1218 (3)	−260 (3)	2013 (3)	405 (15)
C(8)	1608 (3)	−791 (3)	2233 (4)	459 (17)
C(9)	1397 (4)	−1443 (4)	2247 (4)	597 (21)
C(10)	813 (4)	−1563 (4)	2061 (4)	633 (22)
C(11)	411 (4)	−1056 (4)	1853 (4)	664 (22)
C(12)	608 (3)	−385 (4)	1819 (4)	495 (17)
C(13)	965 (3)	982 (3)	1265 (3)	415 (15)
C(14)	730 (3)	614 (4)	652 (4)	538 (19)
C(15)	334 (4)	908 (5)	80 (5)	773 (26)
C(16)	185 (4)	1578 (5)	117 (5)	778 (27)
C(17)	396 (4)	1941 (5)	701 (4)	644 (22)
C(18)	791 (3)	1646 (4)	1287 (4)	482 (17)
C(19)	2104 (3)	2095 (3)	1361 (3)	361 (21)[a]
C(20)	2172 (3)	2286 (3)	2052 (3)	365 (22)[a]
C(21)	1957 (3)	2925 (3)	2153 (4)	476 (23)[a]
C(22)	1708 (4)	3346 (4)	1617 (4)	580 (33)[a]
C(23)	1632 (3)	3144 (3)	947 (4)	519 (28)[a]
C(24)	1829 (3)	2520 (3)	812 (3)	426 (25)[a]
C(25)	2107 (3)	940 (3)	407 (3)	395 (15)
C(26)	1898 (3)	289 (4)	339 (4)	497 (18)
C(27)	1658 (4)	3 (4)	−324 (4)	640 (22)
C(28)	1641 (4)	367 (4)	−899 (5)	648 (22)
C(29)	1873 (4)	1011 (4)	−834 (4)	601 (20)
C(30)	2110 (3)	1297 (4)	−195 (4)	451 (16)
C(31)	3164 (3)	1539 (3)	1169 (3)	385 (15)
C(32)	3502 (3)	1050 (4)	947 (4)	503 (17)
C(33)	4046 (4)	1231 (4)	852 (4)	617 (21)
C(34)	4251 (4)	1872 (4)	954 (4)	659 (22)
C(35)	3923 (4)	2359 (4)	1174 (4)	680 (23)
C(36)	3371 (3)	2193 (4)	1279 (4)	495 (17)
C(37)	2892 (3)	416 (4)	3695 (3)	413 (24)[a]
C(38)	3164 (4)	11 (4)	4329 (4)	665 (35)[a]
C(39)	3703 (3)	1262 (4)	2731 (3)	441 (26)[a]
C(40)	4367 (3)	1255 (5)	2866 (5)	730 (37)[a]
C(41)	3218 (5)	−626 (5)	1631 (6)	782 (45)[a]
C(42)	3299 (7)	−1175 (6)	1163 (8)	1374 (87)[a]
C(43)	3139 (4)	2621 (4)	4105 (4)	741 (39)[a]
C(44)	3350 (5)	3282 (5)	4444 (5)	1069 (51)[a]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

lower values are usually found. In the compound with structure type III, the steric crowding produced by the phenyl rings from the metalated phosphines weakens the axial rhodium–phosphorus bond, and broad ^{31}P NMR signals are absent due to some rapid dissociation occurring in solution. In compounds of type I or IV, one axial site is not sterically crowded, and the rhodium–axial phosphorus couplings are usually well resolved.

Because of the lability of the axial Rh–L bonds, rapid exchange of ligands occurs in solution, especially during the chromatographic separation. The presence of one molecule of water in an axial position is not easily detected by spectroscopy and in some cases can be assumed according to previous crystallographic identifications,[3,4] when all the possible ligands, acetic acid, and phosphine are not spectroscopically detected.

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of **8**(HO_2CCH_3)$_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*
Rh(1)	1877 (1)	429 (1)	1746 (1)	443 (4)[a]
Rh(2)	2022 (1)	135 (1)	843 (1)	449 (5)[a]
Cl(1)	690 (1)	−306 (3)	−2020 (2)	1149 (24)[a]
Cl(2)	51 (2)	2900 (3)	1005 (3)	1663 (40)[a]
Cl(3)	477 (2)	−3489 (3)	1216 (3)	1454 (38)[a]
Cl(4)	1996 (2)	−3027 (2)	−73 (2)	1166 (33)[a]
Cl(5)	1789 (2)	−2350 (3)	4240 (2)	1280 (36)[a]
Cl(6)	4331 (1)	−413 (3)	4619 (2)	1373 (29)[a]
P(1)	1168 (1)	−46 (2)	1006 (1)	509 (17)[a]
P(2)	2222 (1)	−738 (2)	2245 (1)	467 (17)[a]
O(1)	1613 (2)	1564 (4)	1252 (4)	528 (43)[a]
O(2)	1899 (3)	1428 (4)	619 (4)	586 (54)[a]
O(3)	2516 (2)	1054 (4)	2302 (3)	490 (41)[a]
O(4)	2717 (2)	448 (4)	1661 (3)	514 (39)[a]
O(5)	1856 (3)	943 (5)	2676 (4)	619 (53)[a]
O(6)	1613 (3)	2195 (5)	2286 (5)	782 (68)[a]
O(7)	2252 (2)	99 (4)	147 (4)	525 (43)[a]
O(8)	2979 (4)	405 (7)	872 (5)	1286 (75)[a]
C(1)	1016 (4)	−115 (6)	128 (5)	487 (56)[a]
C(2)	1376 (4)	−64 (6)	50 (5)	518 (61)[a]
C(3)	1260 (4)	−124 (7)	−637 (5)	596 (63)[a]
C(4)	825 (4)	−244 (8)	−1171 (6)	697 (77)[a]
C(5)	476 (4)	−337 (7)	−1091 (5)	763 (69)[a]
C(6)	577 (4)	−272 (7)	−444 (5)	702 (70)[a]
C(7)	791 (4)	732 (7)	967 (6)	558 (30)
C(8)	573 (4)	1262 (7)	411 (7)	733 (37)
C(9)	342 (5)	1934 (9)	433 (8)	912 (45)
C(10)	328 (5)	2042 (8)	984 (7)	864 (42)
C(11)	538 (4)	1530 (8)	1554 (7)	884 (43)
C(12)	778 (4)	870 (7)	1540 (6)	680 (34)
C(13)	961 (4)	−1020 (7)	1081 (5)	549 (29)
C(14)	695 (4)	−1111 (8)	1349 (6)	747 (37)
C(15)	564 (5)	−1894 (8)	1410 (7)	858 (41)
C(16)	678 (4)	−2534 (8)	1187 (7)	773 (38)
C(17)	910 (5)	−2475 (8)	908 (7)	833 (41)
C(18)	1060 (4)	−1686 (7)	860 (6)	738 (37)
C(19)	2167 (3)	−1437 (6)	1596 (5)	475 (59)[a]
C(20)	2082 (4)	−1071 (6)	996 (5)	492 (64)[a]
C(21)	2042 (4)	−1587 (7)	489 (5)	579 (74)[a]
C(22)	2068 (5)	−2414 (7)	581 (6)	691 (85)[a]
C(23)	2147 (4)	−2756 (7)	1176 (6)	692 (80)[a]
C(24)	2195 (4)	−2274 (7)	1683 (6)	559 (69)[a]
C(25)	2079 (4)	−1251 (6)	2783 (5)	474 (27)
C(26)	1736 (4)	−954 (7)	2822 (6)	564 (31)
C(27)	1630 (4)	−1292 (7)	3245 (6)	693 (35)
C(28)	1894 (4)	−1936 (7)	3669 (6)	668 (34)
C(29)	2229 (4)	−2256 (7)	3643 (6)	640 (33)
C(30)	2338 (4)	−1906 (6)	3209 (5)	568 (31)
C(31)	2837 (4)	−629 (6)	2901 (5)	492 (28)
C(32)	3002 (4)	−210 (6)	3541 (5)	494 (28)
C(33)	3446 (5)	−95 (8)	4022 (7)	791 (38)
C(34)	3746 (4)	−479 (8)	3942 (7)	782 (38)
C(35)	3618 (5)	−913 (8)	3366 (7)	767 (39)
C(36)	3160 (4)	−969 (7)	2847 (6)	589 (32)
C(37)	1692 (4)	1818 (7)	808 (5)	591 (72)[a]
C(38)	1499 (5)	2650 (7)	494 (6)	787 (90)[a]
C(39)	2806 (4)	898 (6)	2163 (6)	551 (76)[a]
C(40)	3277 (4)	1248 (7)	2630 (6)	651 (66)[a]
C(41)	1747 (4)	1595 (9)	2750 (6)	610 (78)[a]
C(42)	1742 (5)	1857 (8)	3368 (7)	939 (110)[a]
C(43)	2602 (4)	239 (7)	241 (6)	553 (75)[a]
C(44)	2699 (5)	256 (7)	−303 (7)	839 (94)[a]

[a] *Equivalent isotropic U defined as one-third of the trace of the or*thogonalized $\mathbf{U}_{ij}$ tensor.

Reactivity of $Rh_2(O_2CCH_3)_4(MeOH)_2$ with an Excess of Phosphine $P(\mathit{p}\text{-}XC_6H_4)_3$ (X = H, CH_3, Cl). We have reacted $Rh_2(O_2CCH_3)_4(MeOH)_2$ with a 4 molar equiv excess of PPh_3 in refluxing toluene for 2 h. The $^{31}P\{^1H\}$ NMR spectrum of the solution shows signals centered around 20 ppm, due to metalated phosphines, together with a well-resolved signal centered at ca. 5 ppm. All the observed signals were assigned to the new compound $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(PPh_3)(HO_2CCH_3)$ (**4**-(PPh_3)(HO_2CCH_3)), having the H–H structure, as well as the already described[2] **3**$(PPh_3)_2$, having the H-T structure. These two compounds were separated by chromatographic methods and were isolated as acetic acid adducts in ca. 45 yield. The crystal structure of **4**$(HO_2CCH_3)_2$ confirms that the phosphines are in a head-to-head configuration.

The same reaction with the para-substituted triarylphosphines gave analogous doubly metalated compounds in different ratios depending on the phosphine used. The yield of the compound with the head-to-head structure was higher for the less basic phosphine: $P(p\text{-}ClC_6H_4)_3$ (65%), $P(C_6H_5)_3$ (45%), $P(p\text{-}CH_3C_6H_4)_3$ (28%). These values did not change substantially by increasing the excess of phosphine used, but they showed some dependence on the reaction temperature. We found that the reaction rate roughly decreases in the order $P(p\text{-}CH_3C_6H_4)_3 > P(C_6H_5)_3 > P(p\text{-}ClC_6H_4)_3$.

Reactivity of $Rh_2(O_2CCH_3)_4(MeOH)_2$ with PPh_3. We have confirmed that rhodium tetraacetate and triphenylphosphine (1:2 molar ratio) react in refluxing acetic acid for 1 h to give $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$ (**3**$(HO_2CCH_3)_2$) as the only isolable product. The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture showed additional signals of low intensity, indicating the presence of the monometalated compound $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$ (**1**$(HO_2CCH_3)_2$) as a minor reaction product.

If an aprotic solvent such as toluene is used, a mixture of three products is obtained, compound **3**$(HO_2CCH_3)_2$ being the major one. These three compounds were separated by column chromatography and isolated as water adducts. Further recrystallization in the presence of acetic acid gave the adducts with acetic acid **1**$(HO_2CCH_3)_2$ (10%), $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2][PPh_3](HO_2CCH_3)$ (**2**(HO_2CCH_3)) (1%), and **3**$(HO_2CCH_3)_2$ (75%). The ^{31}P NMR data for these compounds are given in Table II.

Compound **2**(HO_2CCH_3) shows one resonance at 16.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum corresponding with the metalated phosphine and an additional low-field resonance (δ = 41.1 ppm), which is diagnostic of an equatorial-bound phosphorus. This equatorial phosphine, unlike those occupying axial positions, is not exchanged by other ligands during the chromatography; however, the axial acetic acid is easily replaced by water giving **2**(H_2O). Additionally **2**(HO_2CCH_3) slowly metalates at room temperature forming **3**$(HO_2CCH_3)_2$. The reaction is considerably faster if an excess of acetic acid is added.

The reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$ with PPh_3 in a 1:2 molar ratio in refluxing chloroform over 90 min gave **1** and **2** in 35% and 5% yields respectively, together with unreacted rhodium acetate. These yields did not improve with longer reaction times in chloroform or with lower reaction temperatures.

Preparation and Reactivity of Compound 1. When $Rh_2(O_2CCH_3)_4(MeOH)_2$ and PPh_3 (1:1) were thermally reacted in acetic acid, compound **3** and dirhodium tetraacetate were obtained as the main reaction products. We obtained the highest **1**:**3** concentration ratio when the phosphine is added to a hot solution of $Rh_2(O_2CCH_3)_4(MeOH)_2$ in a (5:1) toluene/acetic acid mixture with efficient stirring (see Experimental Section). These conditions help to prevent the formation of the bis(phosphine) adduct and help to facilitate a rapid metalation of the phosphine. From this reaction mixture we isolated **1**$(HO_2CCH_3)_2$ in fairly good yield (ca. 70%).

The availability of compound **1** in a reasonable yield allowed us to undergo a detailed study of a single metalation process under very controlled conditions. By reacting **1**$(HO_2CCH_3)_2$ and triphenylphosphine in CH_2Cl_2 or $CHCl_3$ solution (1:1 molar ratio) one of the axial ligands is readily replaced by phosphine giving **1**$(PPh_3)(HO_2CCH_3)$. This compound, identified by the ^{31}P NMR spectrum, gives only **3**$(HO_2CCH_3)_2$ under thermal conditions. However **1**$(HO_2CCH_3)_2$, in the presence of a 3 molar equiv of PPh_3, metalates immediately at room temperature in chloroform, yielding **3**$(PPh_3)_2$.

As a final experiment we added an excess of triphenylphosphine to a solution of **1**$(HO_2CCH_3)_2$ in refluxing toluene. In these conditions compounds **3**$(PPh_3)_2$ and **4**$(PPh_3)(HO_2CCH_3)$ were formed in approximately equal amounts.

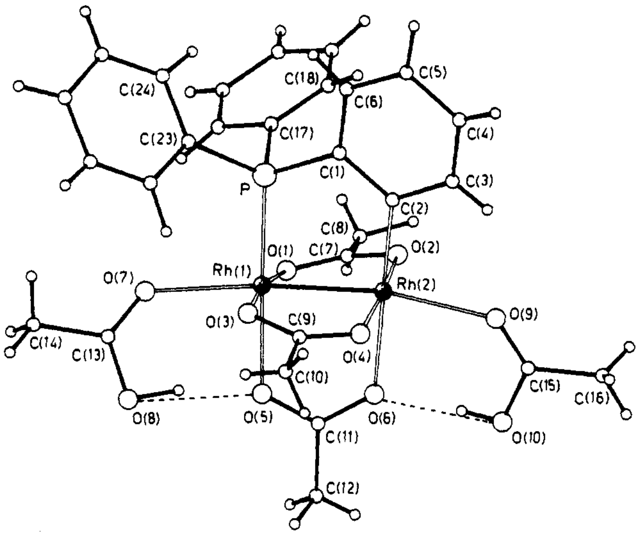

Figure 1. View of the molecular structure of the complex $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$ (**1**$(HO_2CCH_3)_2$), with the atomic numbering scheme.

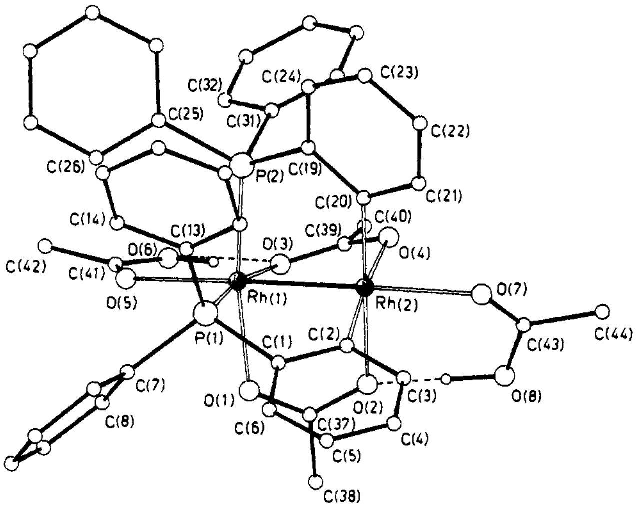

Figure 2. View of the molecular structure of the complex $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$ (**4**$(HO_2CCH_3)_2$), with the atomic numbering scheme.

Molecular Structures of $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$ (1$(HO_2CCH_3)_2$), $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(HO_2CCH_3)_2$, (4$(HO_2CCH_3)_2$), and $Rh_2(O_2CCH_3)_2[(ClC_6H_3)P(p\text{-}ClC_6H_4)]_2(HO_2CCH_3)_2$ (8$(HO_2CCH_3)_2$). Views of the structures of **1**, **4**, and **8** are shown in Figures 1–3, respectively. Important bond distances and angles of **1** are listed in Table VII; important bond distances and angles of **4** and **8** are listed and compared in Table VIII, as the structures of the two complexes are very similar. In the structure of **1**, the two Rh atoms are bridged by three acetate groups and by a triphenylphosphine metalated in one phenyl ring; two oxygens of two acetic acid molecules, occupying the axial positions, complete the slightly distorted octahedral coordination [angles in the range 84.0 (1)–96.7 (2)°] around the metals. The value of the Rh–Rh bond distance, 2.430 (2) Å, falls within the lowest range reported for dirhodium compounds of comparable structure[14a] and is slightly longer than that found (2.410 (1) Å) in the previously reported monometalated dirhodium complex $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)Ph](HO_2CCH_3)_2$.[6] The bridge involving the metalated PPh_3 shows an "envelope" conformation with Rh(1) deviating by 0.538 (2) Å from the mean plane defined by the other four atoms;

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[14] Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982: (a) p 311; (b) pp 192–198.

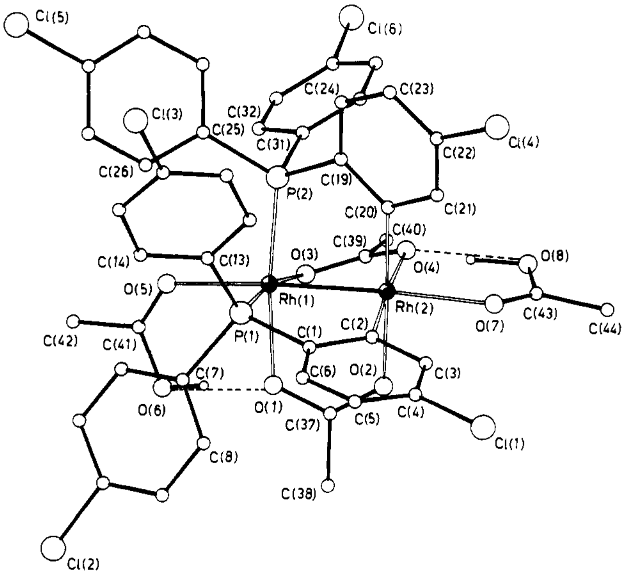


Figure 3. View of the molecular structure of the complex $Rh_2(O_2CCH_3)_2[(ClC_6H_3)P(p\text{-}ClC_6H_4)]_2(HO_2CCH_3)_2$ (**8**$(HO_2CCH_3)_2$) with the atomic numbering scheme.

Table VII. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for **1**$(HO_2CCH_3)_2$

Distances

Rh(1)–Rh(2)	2.430 (2)	O(5)–C(11)	1.264 (6)
Rh(1)–P	2.206 (2)	O(6)–C(11)	1.259 (7)
Rh(1)–O(1)	2.025 (4)	O(7)–C(13)	1.216 (7)
Rh(1)–O(3)	2.073 (4)	O(8)–C(13)	1.313 (8)
Rh(1)–O(5)	2.163 (3)	O(9)–C(15)	1.206 (7)
Rh(1)–O(7)	2.336 (4)	O(10)–C(15)	1.313 (9)
Rh(2)–O(2)	2.034 (4)	C(1)–C(2)	1.402 (6)
Rh(2)–O(4)	2.045 (4)	C(1)–C(6)	1.402 (7)
Rh(2)–O(6)	2.218 (4)	C(2)–C(3)	1.398 (8)
Rh(2)–O(9)	2.301 (4)	C(3)–C(4)	1.366 (8)
Rh(2)–C(2)	1.999 (5)	C(4)–C(5)	1.388 (8)
P–C(1)	1.800 (6)	C(5)–C(6)	1.378 (9)
P–C(17)	1.830 (6)	C(7)–C(8)	1.504 (9)
P–C(23)	1.832 (4)	C(9)–C(10)	1.499 (9)
O(1)–C(7)	1.268 (6)	C(11)–C(12)	1.490 (7)
O(2)–C(7)	1.273 (8)	C(13)–C(14)	1.505 (8)
O(3)–C(9)	1.273 (7)	C(15)–C(16)	1.493 (9)
O(4)–C(9)	1.254 (5)		

Angles

O(5)–Rh(1)–O(7)	85.5 (2)	Rh(1)–P–C(1)	110.2 (2)
O(3)–Rh(1)–O(7)	91.1 (2)	Rh(1)–O(1)–C(7)	119.3 (4)
O(3)–Rh(1)–O(5)	85.1 (2)	Rh(2)–O(2)–C(7)	117.4 (4)
O(1)–Rh(1)–O(7)	94.5 (2)	Rh(1)–O(3)–C(9)	117.4 (3)
O(1)–Rh(1)–O(5)	88.2 (2)	Rh(2)–O(4)–C(9)	119.7 (4)
O(1)–Rh(1)–O(3)	170.9 (2)	Rh(1)–O(5)–C(11)	119.2 (4)
P–Rh(1)–O(7)	95.7 (1)	Rh(2)–O(6)–C(11)	121.9 (4)
P–Rh(1)–O(5)	178.5 (2)	Rh(1)–O(7)–C(13)	124.7 (4)
P–Rh(1)–O(3)	95.8 (1)	Rh(2)–O(9)–C(15)	131.1 (5)
P–Rh(1)–O(1)	90.9 (1)	P–C(1)–C(6)	122.7 (4)
Rh(2)–Rh(1)–O(7)	174.4 (1)	P–C(1)–C(2)	115.7 (4)
Rh(2)–Rh(1)–O(5)	89.0 (1)	C(2)–C(1)–C(6)	121.4 (5)
Rh(2)–Rh(1)–O(3)	87.2 (1)	Rh(2)–C(2)–C(1)	122.9 (4)
Rh(2)–Rh(1)–O(1)	86.6 (1)	C(1)–C(2)–C(3)	116.5 (5)
Rh(2)–Rh(1)–P	89.8 (1)	Rh(2)–C(2)–C(3)	120.4 (4)
Rh(1)–Rh(2)–C(2)	96.7 (2)	O(1)–C(7)–O(2)	126.3 (5)
Rh(1)–Rh(2)–O(9)	169.0 (1)	O(2)–C(7)–C(8)	117.3 (6)
Rh(1)–Rh(2)–O(6)	84.0 (1)	O(1)–C(7)–C(8)	116.5 (6)
Rh(1)–Rh(2)–O(4)	87.3 (1)	O(3)–C(9)–O(4)	126.3 (5)
Rh(1)–Rh(2)–O(2)	87.6 (1)	O(4)–C(9)–C(10)	116.9 (5)
O(9)–Rh(2)–C(2)	94.0 (2)	O(3)–C(9)–C(10)	116.8 (5)
O(6)–Rh(2)–C(2)	178.5 (2)	O(5)–C(11)–O(6)	122.6 (5)
O(6)–Rh(2)–O(9)	85.2 (12)	O(6)–C(11)–C(12)	119.1 (6)
O(4)–Rh(2)–C(2)	90.5 (2)	O(5)–C(11)–C(12)	118.3 (6)
O(4)–Rh(2)–O(9)	90.2 (2)	O(7)–C(13)–O(8)	124.1 (6)
O(4)–Rh(2)–O(6)	88.3 (2)	O(8)–C(13)–C(14)	114.4 (6)
O(2)–Rh(2)–C(2)	93.7 (2)	O(7)–C(13)–C(14)	121.5 (6)
O(2)–Rh(2)–O(9)	94.1 (2)	O(9)–C(15)–O(10)	124.6 (7)
O(2)–Rh(2)–O(6)	87.7 (2)	O(10)–C(15)–C(16)	112.7 (6)
O(2)–Rh(2)–O(4)	173.8 (2)	O(9)–C(15)–C(16)	122.7 (7)

it is nearly coplanar with the acetate bridge and almost perpendicular to the other two acetate bridges (the dihedral angles between the mean planes are 4.9 (1), 89.2 (1) and 83.5 (1)°, respectively). The Rh(1)–P and Rh(2)–C(2) bond distances, 2.206 (2) and 1.999 (5) Å respectively, are comparable to those found in the other monometalated dirhodium complex, 2.209 (2) and 2.026 (7) Å.[6] The Rh–O bond trans to the carbon atom, 2.218 (4) Å, is longer than that trans to the P atom, 2.163 (3) Å, in agreement with the expected order of trans influence of M–C and M–P bonds, and both bonds are much longer than the other four involving acetate ligands [in the range 2.025 (4)–2.073 (4) Å]. The rather long Rh–O bond distances involving the axial acetic acid molecules, 2.301 (4) and 2.336 (4) Å, are indicative of the high trans effect of the metal–metal bond. The Rh–Rh–O_{axial} angles, 169.0 (1) and 174.4 (1)° deviate slightly from linearity, unlike the doubly metalated complexes, for which the deviations are significant. This suggests that steric interactions between the non-metalated phenyl rings and the axial ligands are responsible for these deviations.[2a]

The two OH groups of the axial acetic acid molecules interact with the two oxygen atoms of the same bridging acetate, opposite to the metalated bridge, through intramolecular hydrogen bonds [O(8)···O(5) = 2.705 (5) and O(10)···O(6) = 2.586 (6) Å; O(8)H(8)O(5) = 168 (8) and O(10)H(10)O(6) = 169 (9)°].

The doubly metalated complexes **4** and **8** differ only in the phosphine ligands, those of **8** being *p*-Cl substituted triphenylphosphines, so that their structures are quite comparable. The two Rh atoms are bridged by two acetate groups and by two triphenylphosphine ligands in which metalation has occurred at one of the phenyl rings of each phosphine; as for **1** two oxygens of two acetic acid molecules occupy the axial positions. Because of the presence of the two metalated bridges, the octahedral coordination around the Rh atoms is more distorted than in **1** [angles in the range 79.5 (2)–106.1 (2)° in **4** and 82.1 (3)–102.1 (3)° in **8**]. The Rh–Rh–O_{axial} angles, 163.6 (2) and 167.2 (2)° in **4** and 167.4 (2) and 167.6 (2)° in **8**, deviate significantly from linearity, in a manner different from that observed in **1**. The Rh–Rh bond distances, 2.493 (1) in **4** and 2.511 (2) Å in **8**, are longer than those in **1** in agreement with the values found in the other doubly metalated complexes.[2-5]

The two bridges involving the metalated phosphines, in a head-to-head configuration, are nearly perpendicular to one another as well as the two acetate bridges (the dihedral angles between the mean planes are 85.8 (2) and 81.6 (1)° in **4** and 83.0 (1) and 85.6 (1)° in **8**). The metalated bridges, as in **1**, show "envelope" conformations with Rh(1) deviating from the mean planes through the other four atoms by 0.693 (1) and 0.761 (1) Å in **4** and 0.451 (1) and 0.793 (2) Å in **8**. The Rh–P bond distances, 2.237 (2) and 2.221 (2) Å in **4** and 2.244 (3) and 2.230 (3) Å in **8**, are slightly longer than those in monometalated **1**, whereas the Rh–C bond distances, 1.986 (7) and 1.994 (6) Å in **4** and 1.997 (9) and 2.019 (10) Å in **8**, are comparable to that found in **1**. The Rh–O bonds trans to the carbon atoms, 2.193 (5) and 2.176 (4) Å in **4** and 2.163 (6) and 2.188 (7) Å in **8**, are longer than those trans to the P atoms, 2.120 (4) and 2.145 (4) Å in **4** and 2.147 (7) and 2.122 (7) Å in **8**. The Rh–O bond distances involving the axial acetic acid molecules, 2.198 (5) and 2.498 (7) Å in **4** and 2.224 (11) and 2.390 (10) Å in **8**, are rather long, especially that involving O(5), whereas in **1** they were practically equal. It is not clear if the lengthening of one axial Rh–O bond and the shortening of one axial Rh–O bond in both **4** and **8** with respect to **1** are due to steric or electronic (or both) factors. We assume that steric interactions between the four non-metalated phenyl rings and the axial ligand should be responsible for the lengthening of one of the two axial Rh–O bonds in **4** and **8**. The shortening of the axial Rh–O bond could be attributed to the presence of a weakly bonded axial ligand at the other side of the metal–metal bond.

Unlike in **1**, the two OH groups of the axial acetic acid molecules are hydrogen-bonded to two oxygen atoms of different

Table VIII. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for **4**$(HO_2CCH_3)_2$ and **8**$(HO_2CCH_3)_2$

	4$(HO_2CCH_3)_2$	**8**$(HO_2CCH_3)_2$		**4**$(HO_2CCH_3)_2$	**8**$(HO_2CCH_3)_2$
		Distances			
Rh(1)–Rh(2)	2.493 (1)	2.511 (2)	O(8)–C(43)	1.328 (11)	1.341 (13)
Rh(1)–P(1)	2.237 (2)	2.244 (3)	C(1)–C(2)	1.408 (9)	1.415 (22)
Rh(1)–P(2)	2.221 (2)	2.230 (3)	C(1)–C(6)	1.376 (10)	1.386 (13)
Rh(1)–O(1)	2.145 (4)	2.122 (7)	C(2)–C(3)	1.400 (11)	1.420 (18)
Rh(1)–O(3)	2.120 (4)	2.147 (7)	C(3)–C(4)	1.360 (13)	1.340 (14)
Rh(1)–O(5)	2.498 (7)	2.390 (10)	C(4)–C(5)	1.375 (11)	1.385 (25)
Rh(2)–O(2)	2.176 (4)	2.188 (7)	C(5)–C(6)	1.383 (12)	1.348 (20)
Rh(2)–O(4)	2.193 (5)	2.163 (6)	C(19)–C(20)	1.408 (9)	1.398 (17)
Rh(2)–O(7)	2.198 (5)	2.224 (11)	C(19)–C(24)	1.395 (9)	1.395 (15)
Rh(2)–C(2)	1.986 (7)	1.997 (9)	C(20)–C(21)	1.402 (9)	1.404 (18)
Rh(2)–C(20)	1.994 (6)	2.019 (10)	C(21)–C(22)	1.359 (10)	1.381 (16)
P(1)–C(1)	1.799 (7)	1.810 (13)	C(22)–C(23)	1.370 (11)	1.378 (21)
P(1)–C(7)	1.843 (7)	1.837 (14)	C(23)–C(24)	1.378 (10)	1.361 (20)
P(1)–C(13)	1.836 (6)	1.829 (13)	C(37)–C(38)	1.491 (10)	1.528 (16)
P(2)–C(19)	1.804 (6)	1.834 (13)	C(39)–C(40)	1.503 (10)	1.505 (15)
P(2)–C(25)	1.823 (7)	1.829 (15)	C(41)–C(42)	1.489 (19)	1.528 (25)
P(2)–C(31)	1.835 (7)	1.837 (10)	C(43)–C(44)	1.498 (13)	1.512 (26)
O(1)–C(37)	1.247 (7)	1.301 (19)	Cl(1)–C(4)		1.764 (15)
O(2)–C(37)	1.275 (8)	1.250 (19)	Cl(2)–C(10)		1.753 (18)
O(3)–C(39)	1.281 (8)	1.290 (20)	Cl(3)–C(16)		1.757 (15)
O(4)–C(39)	1.226 (9)	1.270 (15)	Cl(4)–C(22)		1.733 (15)
O(5)–C(41)	1.174 (15)	1.195 (17)	Cl(5)–C(28)		1.735 (18)
O(6)–C(41)	1.344 (13)	1.342 (17)	Cl(6)–C(34)		1.762 (12)
O(7)–C(43)	1.182 (9)	1.172 (19)			
		Angles			
O(3)–Rh(1)–O(5)	79.5 (2)	82.1 (3)	Rh(1)–P(2)–C(19)	110.5 (2)	110.5 (3)
O(1)–Rh(1)–O(5)	87.7 (2)	86.8 (3)	Rh(1)–O(1)–C(37)	119.7 (4)	119.3 (8)
O(1)–Rh(1)–O(3)	81.8 (2)	83.7 (3)	Rh(2)–O(2)–C(37)	120.4 (4)	119.9 (7)
P(2)–Rh(1)–O(5)	97.0 (2)	97.5 (2)	Rh(1)–O(3)–C(39)	121.7 (4)	119.4 (6)
P(2)–Rh(1)–O(3)	91.8 (1)	91.2 (2)	Rh(2)–O(4)–C(39)	117.1 (5)	120.4 (9)
P(2)–Rh(1)–O(1)	171.4 (1)	172.9 (3)	Rh(1)–O(5)–C(41)	131.9 (7)	129.9 (8)
P(1)–Rh(1)–O(5)	106.1 (2)	102.1 (3)	Rh(2)–O(7)–C(43)	131.0 (5)	132.6 (7)
P(1)–Rh(1)–O(3)	170.6 (1)	169.0 (2)	P(1)–C(1)–C(6)	122.6 (5)	122.8 (10)
P(1)–Rh(1)–O(1)	90.9 (1)	86.4 (2)	P(1)–C(1)–C(2)	116.4 (5)	116.8 (8)
P(1)–Rh(1)–P(2)	94.8 (1)	98.2 (1)	C(2)–C(1)–C(6)	120.6 (6)	120.2 (11)
Rh(2)–Rh(1)–O(5)	163.6 (2)	167.4 (2)	Rh(2)–C(2)–C(1)	123.4 (5)	123.3 (7)
Rh(2)–Rh(1)–O(3)	84.5 (1)	86.2 (3)	C(1)–C(2)–C(3)	115.8 (6)	117.1 (11)
Rh(2)–Rh(1)–O(1)	86.2 (1)	87.4 (2)	Rh(2)–C(2)–C(3)	120.5 (5)	119.5 (11)
Rh(2)–Rh(1)–P(2)	87.4 (1)	87.2 (1)	P(2)–C(19)–C(24)	124.3 (5)	122.8 (8)
Rh(2)–Rh(1)–P(1)	89.2 (1)	88.7 (1)	P(2)–C(19)–C(20)	114.4 (5)	115.0 (8)
Rh(1)–Rh(2)–C(20)	95.7 (2)	95.4 (3)	C(20)–C(19)–C(24)	121.2 (6)	122.2 (9)
Rh(1)–Rh(2)–C(2)	95.3 (2)	97.0 (4)	Rh(2)–C(20)–C(19)	123.6 (5)	123.1 (8)
Rh(1)–Rh(2)–O(7)	167.2 (2)	167.6 (2)	C(19)–C(20)–C(21)	116.4 (6)	116.7 (9)
Rh(1)–Rh(2)–O(4)	85.9 (1)	84.4 (2)	Rh(2)–C(20)–C(21)	120.0 (5)	120.2 (8)
Rh(1)–Rh(2)–O(2)	84.5 (1)	84.4 (2)	O(1)–C(37)–O(2)	123.5 (6)	125.0 (10)
C(2)–Rh(2)–C(20)	91.1 (3)	87.1 (4)	O(2)–C(37)–C(38)	117.4 (6)	119.5 (11)
O(7)–Rh(2)–C(20)	92.0 (2)	93.3 (4)	O(1)–C(37)–C(38)	119.1 (6)	115.5 (11)
O(7)–Rh(2)–C(2)	94.9 (2)	92.1 (4)	O(3)–C(39)–O(4)	124.9 (7)	123.2 (13)
O(4)–Rh(2)–C(20)	96.9 (2)	97.4 (4)	O(4)–C(39)–C(40)	119.4 (7)	118.5 (12)
O(4)–Rh(2)–C(2)	171.8 (2)	175.1 (4)	O(3)–C(39)–C(40)	115.7 (7)	118.3 (11)
O(4)–Rh(2)–O(7)	82.9 (2)	85.8 (3)	O(5)–C(41)–O(6)	122.0 (10)	123.0 (13)
O(2)–Rh(2)–C(20)	179.3 (2)	175.5 (4)	O(6)–C(41)–C(42)	111.8 (11)	111.5 (11)
O(2)–Rh(2)–C(2)	89.6 (2)	88.4 (4)	O(5)–C(41)–C(42)	126.1 (12)	125.5 (12)
O(2)–Rh(2)–O(7)	87.8 (2)	87.6 (3)	O(7)–C(43)–O(8)	122.6 (8)	122.8 (14)
O(2)–Rh(2)–O(4)	82.4 (2)	87.1 (3)	O(8)–C(43)–C(44)	113.2 (8)	110.5 (13)
Rh(1)–P(1)–C(1)	107.7 (2)	111.4 (5)	O(7)–C(43)–C(44)	124.2 (8)	126.7 (12)

bridging acetates, through the interactions O(6)···O(3) = 2.546 (11) and O(8)···O(2) = 2.588 (8) Å and O(6)H(6)O(3) = 172 (9) and O(8)H(8)O(2) = 178 (8)° in **4** and O(6)···O(1) = 2.65 (2) and O(8)···O(4) = 2.52 (2) Å and O(6)H(6)O(1) = 176 (13) and O(8)H(8)O(4) = 176 (11)° in **8**. As shown in Figures 2 and 3, the structures of **4** and **8** are very similar, also with regard to the orientations of the phenyl rings (excepting one); the only differences concern the disposition of the two acetic acid molecules (and the corresponding formed hydrogen bonds).

Finally, it is interesting to compare the structure of **4** (with a H-H structure) to that of the isomer **3**$(HO_2CCH_3)_2$ (with a H-T structure).[2a] In the H-T complex, having an imposed C_2 symmetry, the values of the Rh–Rh [2.508 (1) Å], Rh–P [2.210 (2) Å], Rh–C [1.996 (6) Å], and Rh–O [2.136 (4) Å, trans to Rh–P; 2.190 (4) Å, trans to Rh–C] bonds are quite comparable to the corresponding values found in **4**. The main differences are the values of the two Rh–O_{axial} bonds [2.342 (5) Å, equal for symmetry constraints], which are intermediate between the two found for the same bonds in **4** (and also in the similar complex **8**).

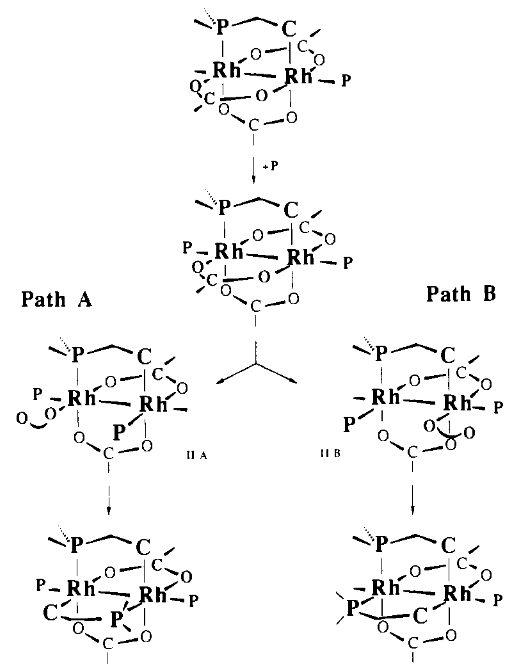
Discussion

The preparation of **1** in good yields requires the prevention of further metalation of **1**. This can be achieved by the procedure described in the Experimental Section. We have shown that the thermal reaction of a 1:1 mixture of rhodium tetraacetate and phosphine in acetic acid gives only rhodium tetraacetate and compound **3**. Apparently the low solubility of the bis(phosphine) adduct displaces the equilibrium to the right.

$$2[Rh_2](P)(CH_3OH) \rightarrow [Rh_2](P)_2 + [Rh_2](CH_3OH)_2$$

As described, **1** immediately metalates to give **3** when reacted with 2 equiv of triphenylphosphine. It seems remarkable to involve both electronic and steric effects to explain this high reactivity. The presence of two phosphines in the axial coordination sites

Scheme II



usually increases the rhodium–rhodium bond distance.[14b] It is reasonable to assume that longer metal–metal bond distances will facilitate the rearrangement of one acetate from bridging (compound **1**) to chelating coordination mode (compound **2**). In the reaction from **2** to **3**, where the same influence is observed, the steric effects produced by axial ligands could be important too.

Although the intermediate, compound **2**, is obtained in very low yield from the thermal reaction of rhodium tetraacetate and triphenylphosphine in chloroform, we have recently observed[15] that this compound can be easily obtained by photochemical reaction of the adduct **1**$(PPh_3)(HO_2CCH_3)$. The reaction **2** → **3** is rapid at room temperature in the presence of acetic acid and extremely rapid in the presence of triphenylphosphine. Kinetic studies are in progress in order to obtain additional information about the mechanisms of these two reactions.

We have previously[3] characterized the compound $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}BrC_6F_4)Ph][P(o\text{-}BrC_6F_4)Ph_2]$, which also has structure type II, and contains an *o*-bromo-substituted phosphine acting as a P, Br donor ligand and occupying one equatorial and one axial position of one rhodium atom. One of the acetate groups is also chelating the other metal atom. Because of this chelating coordination mode, this phosphine does not metalate unless strong reaction conditions are used. We assume a similar structure for compound **2**(HO_2CCH_3) with the only exception that the equatorial phosphine acts now as monodentate ligand, allowing one molecule of acetic acid to coordinate. The difference of reactivity must be related in principle to the capacity of the ortho-functionalized phosphines to act as chelating *P*-halogen donor ligands stabilizing the intermediate of structural type II.

It is worth noting the different thermal reactions of $Rh_2(O_2CCH_3)_4(MeOH)_2$ and various amounts of $P(C_6H_5)_3$; a 2 molar equiv excess of phosphine gives **3** while a 4 molar equiv excess gives **3** and **4**. The reaction of **1** and excess PPh_3 gives **3** at room temperature and, under thermal conditions, a mixture of **3** and **4**. We believe that a reasonable interpretation of these results is that the second metalation process can occur by two different ways, pathway A giving compounds with a head-to-tail structure and pathway B giving compounds with a head-to-head structure (see Scheme II).

These two reaction pathways have been described in detail in a recent paper.[6] In the present case, pathway B requires a higher reaction temperature, and thus the intermediate with an equatorial phosphine cannot be detected. However, in the reactions of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)Ph]$, (structure type I) and $PMePh_2$ in excess, a short-lived species was detected[6] which showed a $^{31}P\{^1H\}$ NMR spectrum in good agreement with the structure of the proposed intermediate IIB.

In this particular case, pathway A has a lower energy barrier and is the favored process at room temperature.

Rhodium electron-binding energies have been recorded for different rhodium compounds and the observed values decrease as the oxidation state of the rhodium atom decreases.[16] We have recorded the X-ray photoelectron spectra of **5**$(2H_2O)$, which has a head-to-head structure, in order to see if there is a certain degree of delocalization. The Rh(3d) spectrum shows two peaks at 308.1 ($d_{5/2}$) and 312.8 ($d_{3/2}$) eV without any evidence of further splitting due to the two different coordination environments of the rhodium atoms in this compound. These values are similar to the values reported for dirhodium(II) tetraacetate and some related compounds.[16]

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Registry No. **1**$(HO_2CCH_3)_2$, 138459-68-4; **1**$(H_2O)_2$, 138459-69-5; **2**(HO_2CCH_3), 138459-70-8; **2**(H_2O), 138459-71-9; **3**$(HO_2CCH_3)_2$, 91837-70-6; **3**$(P)_2$, 125505-48-8; **3**$(H_2O)_2$, 138459-72-0; **3**$(py)_2$, 92669-58-4; **4**$(HO_2CCH_3)_2$, 138459-78-6; **4**$(H_2O)_2$, 138459-79-7; **5**$(HO_2CCH_3)_2$, 138459-73-1; **5**$(P)_2$, 138488-61-6; **5**$(H_2O)_2$, 138459-74-2; **6**$(HO_2CCH_3)_2$, 138459-80-0; **6**$(H_2O)_2$, 138459-81-1; **7**$(HO_2CCH_3)_2$, 138459-75-3; **7**$(P)_2$, 138459-76-4; **7**$(H_2O)_2$, 138459-77-5; **8**$(HO_2CCH_3)_2$, 138459-82-2; **8**$(H_2O)_2$, 138459-83-3; $Rh_2(O_2CCH_3)_4(MeOH)_2$, 41772-64-9.

Supplementary Material Available: Tables of hydrogen atom coordinates (Tables SI–SIII), thermal parameters for the non-hydrogen atoms (Tables SIV–SVI), bond distances and angles (Tables SVII–SIX), and solvent atom coordinates of **8** (Table SX) (18 pages); listings of observed and calculated structure factors (75 pages). Ordering information is given on any current masthead page.

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