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Contribution from the Departamento de Química Inorgánica, Universitat de Valencia, Dr. Moliner 50,
46100 Burjasot-Valencia, Spain, and Departamento de Cristalografía, Mineralogía y Depósitos Minerales,
Universitat de Barcelona, Martí y Franquis s/n, 08028 Barcelona, Spain

# Ortho-Metalation Reactions in Binuclear Dirhodium Compounds. Molecular Structure and Reactivity of a Monometalated Compound with the Phosphine $P(o\text{-}ClC_6H_4)(C_6H_5)_2$

Pascual Lahuerta,*[†] Jorge Payá,[†] Xavier Solans,[‡] and M. Angeles Ubeda[†]

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The complex $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)](HO_2CCH_3)_2$ [(**1**)$(HO_2CCH_3)_2$] has been characterized by X-ray crystallography. This is a new example of a fully characterized $Rh_4^{2+}$ unit with only one ortho-metalated phosphine bridging the two rhodium atoms. It crystallizes in space group $P\bar{1}$ with unit cell dimensions of $a = 14.324$ (3) Å, $b = 11.627$ (3) Å, $c = 11.105$ (3) Å, $\alpha = 65.25$ (2)°, $\beta = 112.57$ (3)°, $\gamma = 100.43$ (2)°, $V = 1551$ (1) Å$^3$, and $Z = 2$. Some important distances (Å) are as follows: Rh–Rh, 2.401 (1); Rh(1)–P, 2.209 (2); Rh(2)–C(2), 2.026 (7); Rh–O (trans to O), in the range of distances 2.009 (5)–2.051 (4); Rh(1)–O(27) (trans to P) 2.185 (6); Rh(2)–O(29) (trans to C) 2.241 (4). Compounds of formulation $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)](P(p\text{-}XC_6H_4)_3)$ (X = $CH_3$ (**2**), H (**3**), Cl (**4**)) can be obtained in solution from (**1**)$(HO_2CCH_3)_2$ by axial ligand exchange. Compounds **2–4** undergo thermal reactions in $CHCl_3/HO_2CCH_3$ (3:1 mixture) yielding doubly metalated compounds of formula $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(XC_6H_3)P(XC_6H_4)_2](HO_2CCH_3)$ (X = $CH_3$ (**5**), H (**6**), Cl (**7**)). If an excess of the corresponding $P(p\text{-}XC_6H_4)_3$ ligand is used, the metalation reaction is considerably faster, and adducts of molecular formula $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(XC_6H_3)P(XC_6H_4)_2](P(p\text{-}XC_6H_4)_3)$ are formed (X = $CH_3$ (**8**), H (**9**), Cl (**10**)). In both conditions, with or without excess phosphine, the reaction rates increase in the order $Cl < H < CH_3$. The two metalated phosphines bridge the rhodium atoms in a head-to-tail (compounds **5** and **6**) or head-to-head fashion (compounds **7–10**). Two different reaction pathways are proposed in order to account for these structural differences.

## Introduction

In contrast to the well-studied intramolecular metalation reactions in mononuclear compounds,[1] little is known about such reactions in dinuclear compounds containing metal–metal bonds.[2] Cotton and co-workers[3] first reported ortho-metalation of triphenylphosphine in dirhodium(II) tetraacetate characterizing compounds of formula $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2L_2$ (L = $HO_2CCH_3$, Py, DMSO) (I). The compounds contain two triphenylphosphines, each ortho-metalated at one of the phenyl rings. Similar reactions have been noted with $P(CH_3)(C_6H_5)_2$[4a] and $P(m\text{-}CH_3C_6H_4)_3$.[4b]

Another synthetic method of less general application has been also reported for the formation of rhodium(II) compounds containing a bridging metalated phosphine.[5] It involves a 2c–2e oxidative-addition reaction in pyrazolyl-bridged dirhodium(I) compounds with cleavage of the C–Br bond of the phosphine $P(o\text{-}BrC_6F_4)(C_6H_5)_2$.

In order to gain insight into the mechanistic aspects of the metalation reaction in dirhodium(II) compounds, we have initiated studies aimed at fully characterizing potential intermediates in this process, with regard to both structure and reactivity. Although the reaction of dirhodium tetraacetate with the phosphine $P(o\text{-}BrC_6F_4)(C_6H_5)_2$ allowed the isolation of some intermediate compounds,[6] $P(o\text{-}ClC_6H_4)(C_6H_5)_2$ (PCCl) has shown to be a more convenient ligand for these type of studies. We have previously reported[7] the isolation of a dirhodium(II) compound of stoichiometry $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)](PCCl)$ [(**1**)PCCl] by heating $Rh_2(O_2CCH_3)_4(PCCl)_2$ under very mild and controlled reaction conditions. Interestingly, (**1**)PCCl reacts with $P(C_6H_5)_3$ yielding[7] doubly metalated compounds of general type $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2]$ having the two metalated phosphines in either a head-to-tail (H–T) or a head-to-head (H–H) configuration, depending on the amount of $P(C_6H_5)_3$ used (Figure 1). It should be noted that the analogous monometalated compound of triphenylphosphine,[8] under similar reaction conditions, gives only doubly metalated compounds with a head-to-tail configuration. These unexpected results prompted us to extend the studies of reactivity in an attempt to explain the observed differences of chemical behavior.

We report here the crystal structure of the monometalated compound in the form of its adduct with acetic acid [(**1**)$(HO_2CCH_3)_2$]. The reactivity of this compound with para-substituted triarylphosphines is also reported here; two different reaction pathways are proposed in order to rationalize the observed results.

## Experimental Section

**Procedures and Materials.** $Rh_2(O_2CCH_3)_4{\cdot}2MeOH$[9] and PCCl[10] were prepared according to literature procedures. Commercially available $P(C_6H_5)_3$ (Aldrich) was recrystallized from hot ethanol prior to use. $P(p\text{-}CH_3C_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$, $P(CH_3)(C_6H_5)_2$, $P(CH_3)_2(C_6H_5)$, $P(OCH_3)_3$, and $P(OC_6H_5)_3$ (Strem) were used as purchased. All solvents were of analytical grade and were dried and degassed before use.

All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques. $^{31}P\{^1H\}$ NMR spectra were measured on Bruker AC-200 FT spectrometer, operating at 300 K with broad-band decoupling. Chemical shifts are referred to external 85% $H_3PO_4$ in $D_2O$.

The reactions to form doubly metalated compounds were monitored by $^{31}P\{^1H\}$ NMR spectroscopy under controlled-temperature conditions.

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[‡] Universitat de Barcelona.

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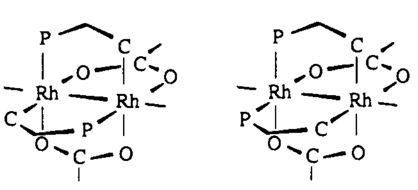

H-T H-H

**Figure 1.** Schematic structures for dirhodium doubly metalated compounds: head-to-tail (H-T) and head-to-head (H-H) configurations.

In each case a concentrated solution of the compound $(1)(HO_2CCH_3)_2$ in $CHCl_3$ or a 3:1 $CHCl_3/HO_2CCH_3$ mixture with the correspondingly amount of phosphine was placed in a 5-mm NMR tube. The samples were kept at constant temperature. The reactions to form compounds **5**, **6**, **7**, and **10** were performed at 326 K, and the rest of the experiments were run at 300 K. $^{31}P\{^1H\}$ NMR spectra were periodically recorded until the total disappearance of the starting compounds. The NMR probe was stabilized at 300 K; at this temperature during the accumulation time (about 15 min) no progress of the reaction was observed in any case.

**Synthesis of Compounds. Compound $(1)(HO_2CCH_3)_2$.** A 200-mg (0.205-mmol) sample of (**1**)PCCl 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 1:10 acetone/hexane mixture, the band of the top changed from brown-red to blue color. Increasing the polarity (acetone/hexane (1:2)) eluted a blue band. After addition of 1 mL of acetic acid, the solution was concentrated under reduced pressure. Addition of hexane gave 131 mg (80% yield) of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)](HO_2CCH_3)_2$ [$(1)(HO_2CCH_3)_2$] as a blue solid. $^1H$ NMR: 8.6–6.5 (13 H), 2.37 (3 H), 2.23 (6 H), 1.69 (3 H), 0.90 ppm (3 H).

**Compounds 2–4.** A 100-mg (0.125-mmol) sample of compound $(1)(HO_2CCH_3)_2$ was dissolved in 5 mL of $CHCl_3$, and 0.125 mmol of the corresponding triarylphosphine dissolved in 5 mL of $CHCl_3$ were added. The resulting solution was concentrated under reduced pressure and hexane was added. The suspension was cooled at −15 °C for 12 h, yielding a brown-red solid. Yields are in the order 90–95%. Anal. Calcd for **3**, $C_{44}H_{41}O_8ClP_2Rh_2$: C, 52.74; H, 3.98. Found: C, 52.56; H, 3.98.

**Compound 5.** A 100-mg (0.103-mmol) sample of compound **2** were dissolved in 10 mL of a $CHCl_3$/acetic acid (3:1) mixture. The solution was refluxed for 5 h yielding a green solution. The solvent was removed under vacuum and the crude oil was dissolved in 5 mL of $CH_2Cl_2$. Hexane (2 mL) was added and the solution was chromatographed on a column (1.5 × 30 cm, silica gel/hexane). After elution with acetone/hexane (1:3), a minor yellow band separated, which was discarded. Increasing polarity (acetone:hexane 1:1) eluted a blue band. The solvent was removed under reduced pressure. Further addition of 0.5 mL of acetic acid and an excess of hexane precipitated 45 mg (45% yield) of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2](HO_2CCH_3)$ (**5**) as a green solid. $^1H$ NMR: 8.0–6.3 (24 H), 2.35 (6 H), 2.30 (3 H), 2.26 (3 H), 1.33 (3 H), 1.24 ppm (3 H).

**Compound 6.** Compound **3** (100 mg, 0.106 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 × 1.5 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. This solution was evaporated to dryness and the product redissolved in 5 mL of $CH_2Cl_2$. After the addition of 0.5 mL of acetic acid, the solution was precipitated with hexane to give a 60 mg (60% yield) of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)$ (**6**) as a blue solid. Anal. Calcd for $C_{42}H_{37}O_6ClP_2Rh_2$: C, 53.32; H, 3.97. Found: C, 53.61; H, 3.97. $^1H$ NMR: 7.8–6.3 (27 H), 2.17 (3 H), 1.31 (3 H), 1.26 ppm (3 H).

**Compound 7.** A 100-mg (0.096-mmol) sample of compound **4** was refluxed for 5 h in a mixture of $CHCl_3$/acetic acid (3:1). After elimination of solvent under vacuum, the crude oil was redissolved in 5 mL of $CH_2Cl_2$ and 2 mL of hexane. The solution was chromatographed in a column (30 × 1.5 cm silica gel/hexane) and was eluted with acetone/hexane/acetic acid (20:20:1). A blue violet band was collected, and the volume was reduced to 2 mL under vacuum. Addition of hexane gave 75 mg (75% yield) of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](HO_2CCH_3)$ (**7**) as a blue solid. $^1H$ NMR: 8.2–6.2 (24 H), 2.25 (3 H), 1.33 (3 H), 1.27 ppm (3 H).

**Compound 8.** A 100-mg (0.125-mmol) sample of compound $(1)(HO_2CCH_3)_2$ was dissolved in 10 mL of $CH_2Cl_2$. After addition of 76 mg (0.250 mmol) of $P(p\text{-}CH_3C_6H_4)_3$, the color changed rapidly to brown-red. The solution was stirred at room temperature for 2 h and yielded a deep red solution. Part of the solvent (ca. 9 mL) was removed under reduced pressure, and hexane was added to precipitate 130 mg (85% yield) of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2]P(p\text{-}CH_3C_6H_4)_3$ (**8**) as a red solid. Anal. Calcd for $C_{64}H_{60}O_4ClP_3Rh_2$: C, 62.32; H, 5.16. Found: C, 62.62; H, 4.94. $^1H$ NMR: 8.6–6.3 (36 H), 2.35 (6 H), 2.32 (9 H), 2.29 (3 H), 1.66 (3 H), 1.33 ppm (3 H).

**Table I.** Crystallographic Data for $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)](HO_2CCH_3)_2$

| | |
|---|---|
| chem formula | $Rh_2ClPC_{28}H_{30}O_{10}$ |
| fw | 798.8 |
| space group | $P\bar{1}$ |
| $a$, Å | 14.324 (3) |
| $b$, Å | 11.627 (3) |
| $c$, Å | 11.105 (3) |
| $\alpha$, deg | 65.25 (2) |
| $\beta$, deg | 112.57 (3) |
| $\gamma$, deg | 100.43 (2) |
| $V$, Å$^3$ | 1551 (1) |
| $Z$ | 2 |
| $T$, °C | 25 |
| $\lambda$, Å | 0.71069 |
| $d_{calc}$, g cm$^{-3}$ | 1.706 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 12.27 |
| $R^a$ | 0.042 |
| $R_w{}^b$ | 0.044 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum w||F_o| - |F_c||/\sum w|F_o|$. $w = (\sigma^2(F_o) + 0.0012|F_o|^2)^{-1}$.

**Compound 9.** Compound $(1)(HO_2CCH_3)_2$ (100 mg, 0.125 mmol) and $PPh_3$ (66 mg, 0.250 mmol) were dissolved in 10 mL of $CH_2Cl_2$. The brown-red solution was stirred for 24 h at room temperature. During this time, the solution changed to deep red. Part of the solvent was removed under reduced pressure and addition of hexane precipitated 129 mg (90% yield) of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2](P(C_6H_5)_3$ (**9**) as a red solid. Anal. Calcd for $C_{58}H_{48}O_4ClP_3Rh_2$: C, 60.91; H, 4.20. Found: C, 60.93; H, 4.24. $^1H$ NMR: 7.9–6.5 (42 H), 1.33 (3 H), 1.18 ppm (3 H).

**Compound 10.** Compound $(1)(HO_2CCH_3)_2$ (100 mg, 0.125 mmol) and $P(p\text{-}ClC_6H_4)_3$ (91 mg, 0.250 mmol) were dissolved in a mixture of $CHCl_3$/acetic acid (3:1), and the solution was heated at 53 °C for 3 h. The resulting red-orange solution was evaporated to dryness, and the residue was dissolved in 2 mL of $CH_2Cl_2$. Slow addition of hexane gave 143 mg (85% yield) of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2](P(p\text{-}ClC_6H_4)_3)$ (**10**) as a red solid.

**Compounds 11–14.** These four adducts were obtained in solution by adding stoichiometric amounts of the P donor ligand to a solution of $(1)(HO_2CCH_3)_2$ in $CH_2Cl_2$. The $^{31}P$ NMR spectra were recorded from the resulting solutions.

**X-ray Crystallography of Compound $(1)(HO_2CCH_3)_2$.** Table I summarizes the pertinent information. A dark blue well-formed single crystal of compound $(1)(HO_2CCH_3)_2$ grown from a $CH_2Cl_2$/*n*-hexane/acetic acid mixture of solvents was used for the structure determination.

A crystal with dimensions of 0.1 × 0.1 × 0.1 mm was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($4° \leq \theta \leq 12°$), and refined by a least-squares method. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz and polarization corrections were applied but no allowance was made for absorption.

The structure was solved by direct methods using the MULTAN system of computer programs.[11] The structure refinement was carried out by weighted full-matrix least-squares method, first with isotropic and then with anisotropic temperature factors, using the SHELX76 computer program.[12] The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = \sigma^{-2}(F_o)$, $f, f'$, and $f''$ were taken from ref 13. H atoms were not located. The

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**Table II.** Table of Positional Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)](HO_2CCH_3)_2$

| atom | *x/a* | *y/b* | *z/c* | $B_{eq}$,[a] Å$^2$ |
|---|---|---|---|---|
| Rh(1) | 0.15743 (4) | 0.26283 (6) | 0.06268 (9) | 3.43 (4) |
| Rh(2) | 0.30807 (5) | 0.26640 (6) | 0.25780 (9) | 3.69 (4) |
| P | 0.2515 (2) | 0.2323 (2) | −0.0387 (3) | 3.6 (1) |
| Cl | 0.0899 (2) | 0.4051 (2) | −0.3311 (3) | 4.4 (1) |
| C(1) | 0.3659 (6) | 0.1647 (9) | 0.087 (1) | 4.0 (5) |
| C(2) | 0.3960 (7) | 0.1751 (8) | 0.222 (1) | 3.7 (5) |
| C(3) | 0.4854 (7) | 0.1246 (9) | 0.325 (1) | 4.4 (5) |
| C(4) | 0.5464 (8) | 0.060 (1) | 0.309 (1) | 5.7 (6) |
| C(5) | 0.5197 (9) | 0.048 (1) | 0.184 (2) | 6.7 (8) |
| C(6) | 0.4274 (7) | 0.0952 (9) | 0.070 (2) | 5.4 (6) |
| C(7) | 0.2026 (5) | 0.1298 (7) | −0.137 (1) | 2.8 (4) |
| C(8) | 0.2420 (6) | 0.1486 (8) | −0.242 (1) | 4.0 (5) |
| C(9) | 0.2031 (7) | 0.0669 (8) | −0.321 (1) | 3.7 (5) |
| C(10) | 0.1258 (8) | −0.025 (1) | −0.302 (2) | 6.3 (6) |
| C(11) | 0.0940 (9) | −0.035 (1) | −0.181 (1) | 5.1 (6) |
| C(12) | 0.1242 (8) | 0.0388 (9) | −0.110 (2) | 5.9 (7) |
| C(13) | 0.2890 (7) | 0.3786 (8) | −0.164 (1) | 3.7 (4) |
| C(14) | 0.2188 (6) | 0.4512 (8) | −0.285 (1) | 5.1 (5) |
| C(15) | 0.244 (1) | 0.563 (1) | −0.385 (2) | 7.0 (8) |
| C(16) | 0.343 (1) | 0.610 (1) | −0.354 (2) | 7.6 (9) |
| C(17) | 0.4130 (8) | 0.540 (1) | −0.237 (1) | 5.0 (6) |
| C(18) | 0.3878 (7) | 0.4200 (9) | −0.126 (1) | 5.1 (6) |
| O(19) | −0.0107 (5) | 0.2495 (6) | −0.0904 (8) | 4.4 (3) |
| C(20) | −0.0856 (8) | 0.298 (1) | −0.117 (1) | 5.0 (6) |
| O(21) | −0.088 (1) | 0.362 (1) | −0.0412 (2) | 12 (1) |
| C(22) | −0.193 (1) | 0.281 (2) | −0.227 (2) | 5.1 (5) |
| O(23) | 0.4371 (7) | 0.285 (1) | 0.445 (1) | 4.5 (5) |
| C(24) | 0.4356 (6) | 0.320 (1) | 0.531 (2) | 5.4 (6) |
| O(25) | 0.3582 (6) | 0.3630 (9) | 0.540 (1) | 6.1 (4) |
| C(26) | 0.530 (1) | 0.316 (1) | 0.647 (2) | 6 (1) |
| O(27) | 0.0758 (6) | 0.2983 (7) | 0.174 (1) | 5.4 (5) |
| C(28) | 0.1205 (7) | 0.338 (1) | 0.278 (1) | 4.7 (6) |
| O(29) | 0.2112 (6) | 0.3481 (6) | 0.319 (1) | 4.6 (4) |
| C(30) | 0.0571 (7) | 0.362 (1) | 0.344 (2) | 8.0 (8) |
| O(31) | 0.1769 (5) | 0.4548 (5) | −0.0331 (8) | 4.4 (3) |
| C(32) | 0.2622 (5) | 0.5062 (8) | 0.022 (1) | 3.2 (4) |
| O(33) | 0.3323 (5) | 0.4463 (6) | 0.1354 (8) | 4.1 (3) |
| C(34) | 0.2782 (8) | 0.6464 (8) | −0.059 (1) | 4.8 (5) |
| O(35) | 0.1443 (4) | 0.0735 (5) | 0.1791 (7) | 3.2 (3) |
| C(36) | 0.1928 (9) | 0.0368 (9) | 0.314 (1) | 3.1 (5) |
| O(37) | 0.2642 (5) | 0.0931 (8) | 0.3693 (8) | 5.3 (4) |
| C(38) | 0.158 (1) | −0.0926 (9) | 0.396 (1) | 6.4 (8) |

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter $B_{eq} = (8\pi^2/3)\sum_i\sum_j a_i^* a_j^* a_i a_j$.

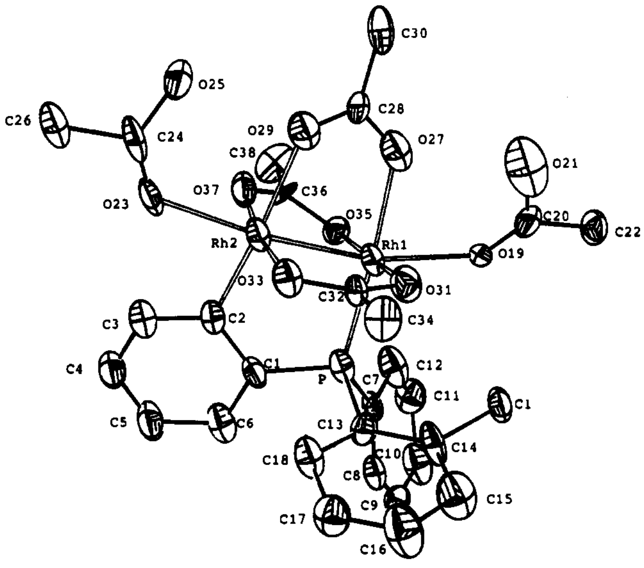


**Figure 2.** ORTEP drawing of compound $(\mathbf{1})(HO_2CCH_3)_2$.

final *R* factor was 0.042 ($R_w$ = 0.044) for all observed reflections.

**Table III.** Selected Bond Distances (Å) and Angles (deg) for $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)](HO_2CCH_3)_2$[a]

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Rh(2)–Rh(1) | 2.410 (1) | P–Rh(1) | 2.209 (2) |
| O(19)–Rh(1) | 2.378 (6) | O(27)–Rh(1) | 2.185 (6) |
| O(31)–Rh(1) | 2.051 (4) | O(35)–Rh(1) | 2.051 (4) |
| C(2)–Rh(2) | 2.026 (7) | O(23)–Rh(2) | 2.26 (1) |
| O(29)–Rh(2) | 2.241 (4) | O(33)–Rh(2) | 2.015 (4) |
| O(37)–Rh(2) | 2.009 (5) | | |
| | Bond Angles | | |
| P–Rh(1)–Rh(2) | 89.4 (1) | O(19)–Rh(1)–Rh(2) | 166.3 (1) |
| O(19)–Rh(1)–P | 103.5 (1) | O(27)–Rh(1)–Rh(2) | 86.1 (2) |
| O(27)–Rh(1)–P | 175.3 (2) | O(27)–Rh(1)–O(19) | 81.1 (2) |
| O(31)–Rh(1)–Rh(2) | 88.0 (2) | O(31)–Rh(1)–P | 89.6 (1) |
| O(31)–Rh(1)–O(19) | 96.4 (2) | O(31)–Rh(1)–O(27) | 88.8 (2) |
| O(35)–Rh(1)–Rh(2) | 86.8 (1) | O(35)–Rh(1)–P | 93.9 (1) |
| O(35)–Rh(1)–O(19) | 87.8 (2) | O(35)–Rh(1)–O(27) | 87.3 (2) |
| O(35)–Rh(1)–O(31) | 173.7 (2) | C(2)–Rh(2)–Rh(1) | 96.1 (2) |
| O(23)–Rh(2)–Rh(1) | 172.3 (2) | O(23)–Rh(2)–C(2) | 91.5 (3) |
| O(29)–Rh(2)–Rh(1) | 85.9 (2) | O(29)–Rh(2)–C(2) | 173.7 (2) |
| O(29)–Rh(2)–O(23) | 86.5 (3) | O(33)–Rh(2)–Rh(1) | 87.4 (2) |
| O(33)–Rh(2)–C(2) | 99.7 (2) | O(33)–Rh(2)–O(23) | 90.7 (2) |
| O(33)–Rh(2)–O(29) | 86.3 (2) | O(37)–Rh(2)–Rh(1) | 86.8 (2) |
| O(37)–Rh(2)–C(2) | 86.0 (2) | O(37)–Rh(2)–O(23) | 94.4 (2) |
| O(37)–Rh(2)–O(29) | 88.2 (2) | O(37)–Rh(2)–O(33) | 172.3 (2) |

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

A molecular illustration was drawn with the ORTEP program. Figure 2 shows a perspective drawing of compound $(\mathbf{1})(HO_2CCH_3)_2$. Table II contains the list of positional parameters. Important bond distances and angles are listed in Table III.

## Results

Table IV includes a list and schematic structures of the new compounds mentioned in this paper. The complex $(\mathbf{1})(HO_2CCH_3)_2$ can be readily prepared from the previously described monometalated compound (**1**)(PCCl).[7] It has been characterized by X-ray crystallography.

Compounds of formulation $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)](P(p\text{-}XC_6H_4)_3)$ (X = $CH_3$ (**2**), H (**3**), Cl (**4**)) can be obtained from $(\mathbf{1})(HO_2CCH_3)_2$ by axial ligand exchange and have been characterized by $^{31}P$ NMR spectroscopy. They can be isolated as red-brown solids but analytically pure samples were only obtained for compound **3**. Compounds **2**–**4** undergo a thermal metalation reaction in $CHCl_3/HO_2CCH_3$ (3:1 mixture), according to eq 1, yielding compounds of molecular formula $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2](HO_2CCH_3)$ (X = $CH_3$ (**5**), H (**6**), Cl (**7**)).

$$Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)]P(p\text{-}XC_6H_4)_3 \xrightarrow{\Delta} Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2](HO_2CCH_3) \quad (1)$$

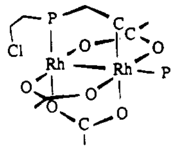
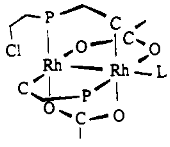
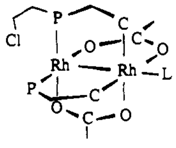
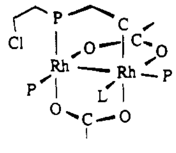
If compounds **2**–**4** are reacted with 1 mol of the corresponding $P(p\text{-}XC_6H_4)_3$ (eq 2), the metalation reaction is considerably faster;

$$Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)](P(p\text{-}XC_6H_4)_3) + P(p\text{-}XC_6H_4)_3 \rightarrow Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]P(p\text{-}XC_6H_4)_3 \quad (2)$$

in chloroform solution it takes place in a few hours at room temperature for compounds **2** and **3** while compound **4** is less reactive and requires higher temperatures to react. Under these conditions, adducts of formula $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]P(p\text{-}XC_6H_4)_3$ (X = $CH_3$ (**8**), H (**9**), Cl (**10**)) are obtained in high yield. The same results are also obtained by direct reaction of $(\mathbf{1})(HO_2CCH_3)_2$ with a 2 mol excess of the corresponding phosphines.

It should be noted that the reactions of $(\mathbf{1})(HO_2CCH_3)_2$ with tri-*p*-tolylphosphine or triphenylphosphine give structurally different products depending on the reaction conditions used. Compounds **5** and **6** have a head-to-tail conformation of the bridging metalated phosphines while in compounds **8** and **9** the

**Table IV.** List and Structure of the Described Compounds

| structure | compd label | P–C ligand $[(XC_6H_3)P(XC_6H_4)_2$ | L | P |
|---|---|---|---|---|
|  | **2** | | | $P(MeC_6H_4)_3$ |
| | **3** | | | $PPh_3$ |
| | **4** | | | $P(ClC_6H_4)_3$ |
| | **11** | | | $PMePh_2$ |
| | **12** | | | $PMe_2Ph$ |
| | **13** | | | $P(OMe)_3$ |
| | **14** | | | $P(OPh)_3$ |
|  | **5** | X = Me | $HO_2CCH_3$ | |
| | **6** | X = H | $HO_2CCH_3$ | |
|  | **7** | X = Cl | $HO_2CCH_3$ | |
| | **8** | X = Me | $P(MeC_6H_4)_3$ | |
| | **9** | X = H | $PPh_3$ | |
| | **10** | X = Cl | $P(ClC_6H_4)_3$ | |
|  | **11′** | | $O_2CCH_3$ | $PMePh_2$ |
| | **12′** | | $O_2CCH_3$ | $PMe_2Ph$ |
| | **13′** | | $O_2CCH_3$ | $P(OMe)_3$ |
| | **14′** | | $O_2CCH_3$ | $P(OPh)_3$ |

bridging phosphines are in a head-to-head conformation. The structural assignment is based on the $^{31}P$ NMR data.

We observe slightly different behavior for the reactions with $P(p\text{-}ClC_6H_4)_3$; the isolated compounds **7** and **10** are structurally equivalent and have a head-to-head configuration. The only structural difference between them is that **7** has acetic acid in the axial sites while **10** has one phosphine bonded to the less sterically hindered axial coordination site of the $Rh_2^{4+}$ unit. (See Spectroscopic Section.) We will refer later to the different behavior observed for the compounds containing $P(p\text{-}ClC_6H_4)_3$.

We have monitored the metalation reactions of compounds **2**–**4** by $^{31}P\{^1H\}$ NMR spectroscopy. Two experimental conditions have been used: (i) $(\mathbf{1})(HO_2CCH_3)_2$ reacting with 2 mol of the corresponding phosphine in $CH_2Cl_2$ at room temperature, and (ii) $(\mathbf{1})(HO_2CCH_3)_2$ reacting with 1 mol of phosphine at 53 °C in a 3:1 $CHCl_3/HO_2CCH_3$ mixture.

The results obtained show important differences of reactivity for these phosphines. With tri-*p*-tolylphosphine the reaction is complete in about 2 h at room temperature but it takes at least 12 h when triphenylphosphine is used. With $P(p\text{-}ClC_6H_4)_3$ the reaction does not show any progress at room temperature after 48 h and requires about 3 h at 53 °C for completion.

In the absence of free phosphine (eq 1) the metalation of compounds **2**–**4** requires more severe reaction conditions. The experiments were performed at 53 °C in $CHCl_3$/acetic acid (3:1); higher reaction temperatures increased the relative amount of side products. As was previously observed,[6] the presence of acetic acid accelerates the metalation reaction. Under these conditions compound **2** metalates faster than compound **3**, and the reactions are completed after 2–3 h.

We have also studied the reactivity of $(\mathbf{1})(HO_2CCH_3)_2$ with alkylarylphosphines and some phosphites, finding additional information that can be important in order to understand the mechanism of this particular metalation reaction. Adducts of molecular formula $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)]P$ [P = $P(CH_3)(C_6H_5)_2$ (**11**), $P(CH_3)_2(C_6H_5)$ (**12**), $P(OMe)_3$ (**13**), $P(OPh)_3$ (**14**)] have been prepared by stoichiometric addition of the corresponding ligand to a solution of $(\mathbf{1})(HO_2CCH_3)_2$ in $CH_2Cl_2$. They do not react at room temperature unless an excess of ligand is added. Compound **11** in the presence of excess of $P(CH_3)(C_6H_5)_2$ metalates at room temperature, yielding $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(C_6H_4)P(CH_3)(C_6H_5)](P(CH_3)(C_6H_5)_2$ (**15**) that according to the spectroscopic data available has a head-to-head structure. This behavior parallels that of the triarylphosphines but the relevant point now is that we are able to detect one intermediate of the reaction **11** → **15** not observed in the homologous reactions with triarylphosphines. This intermediate **11′** is immediately formed when **11** is reacted with an excess of $P(CH_3)(C_6H_5)_2$; it shows three $^{31}P\{^1H\}$ NMR resonances, and it slowly evolves at room temperature to give **15**.

Adducts **12**–**14** react with an additional amount of the corresponding P donor ligand similar to **11** to give compounds **12′**–**14′** that according to the spectroscopic data (Table V) are structurally analogous to **11′**. These transformations are fast except the reaction with $P(OPh)_3$, which takes about 6 h to complete. No metalation reaction is observed for these compounds in solution; **12′** slowly decomposes, and **13′** and **14′** do not react at all.

**The Chemical Reaction.** The above described results show that the amount of phosphine has a great influence on the reaction rate and also on the structure of the doubly metalated compound. These experimental results can be explained by assuming that the second metalation can occur in compound $(\mathbf{1})(HO_2CCH_3)_2$ by two different reaction pathways, A and B (Scheme I.)

For compounds **2** and **3** prepared in the absence of any additional phosphine, the metalation proceeds by a reaction pathway A which involves two reaction steps: (i) partial displacement of one acetate group by a phosphine that shifts from axial to equatorial coordination yielding **A1** followed by (ii) a proton-transfer process to give a doubly metalated compound with a head-to-tail structure. Compounds of type **A1** have been only isolated when (*o*-haloaryl)phosphines are used.[6a,7] The stabilization of the phosphine in the equatorial position was attributed to the internal formation of an axial Rh–halogen bond. When triphenylphosphine or para-substituted arylphosphines are used the intermediates of type **A1** are not so stable and cannot be obtained in high yield under the reaction conditions. Very recent experiments have confirmed that compounds **2** and **3** in chloroform solution at room temperature undergo slow chemical evolution. The $^{31}P$ NMR spectra of these solutions exhibit new resonances centered at ca. 50 and 16 ppm (compound **2**) and 52 and 17 ppm (compound **3**), which can be assigned to the corresponding intermediates of type **A1**. That can explain the difficulty in isolating **2** and **3** in an analytically pure state.

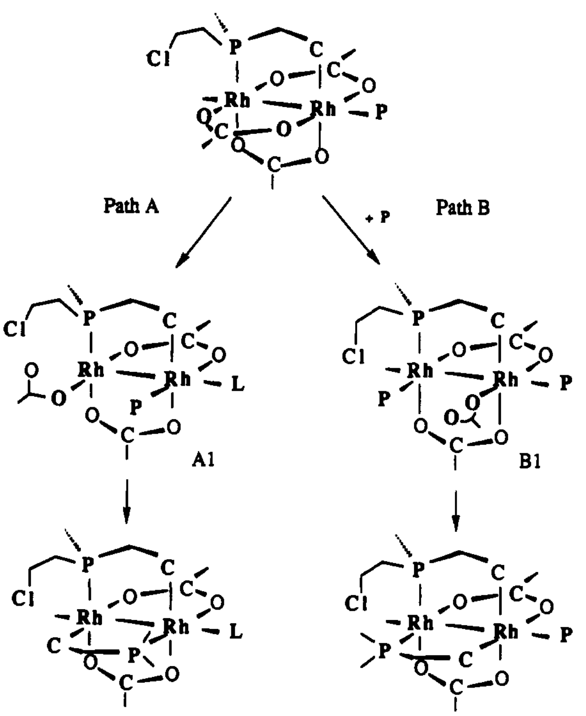
An analogous reaction pathway involving an axial coordination of the phosphine to $Rh_1$, followed by migration to an equatorial

**Table V.** $^{31}P\{^1H\}$ NMR Data[a]

| compd | $\delta(P_1)$[b] | $^1J(Rh-P_1)$ | $^2J(Rh-P_1)$ | $\delta(P_2)$[c] | $^1J(Rh-P_2)$ | $^2J(Rh-P_2)$ | $^2J(P_1-P_2)$ | $\delta(P_3)$[d] | $^1J(Rh-P_3)$ | $^2J(Rh-P_3)$ | $^3J(P_1-P_2)$ | $^3J(P_2-P_3)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Monometalated Compounds | | | | | | | |
| (**1**)(AcOH)$_2$ | 17.6 | 150 | | | | | | | | | | |
| **2** | 24.1 | 164 | | | | | | −11.9 | 111 | 25 | 9 | |
| **3** | 23.8 | 161 | | | | | | −9.8 | 113 | 29 | 10 | |
| **4** | 22.9 | 162 | | | | | | −16.2 | 113 | 29 | 10 | |
| **11** | 23.9 | 161 | | | | | | −21.5 | 116 | 28 | 10 | |
| **12** | 24.7 | 162 | | | | | | −26.5 | 120 | 25 | 8 | |
| **13** | 23.3 | 161 | | | | | | 60.1 | 176 | 42 | 13 | |
| **14** | 21.2 | 158 | | | | | | 38.0 | 200 | *e* | *e* | |
| | | | | | Doubly Metalated Compounds | | | | | | | |
| **5** | 18.6 | 170 | 7 | 14.5 | 157 | 10 | | | | | | |
| **6** | 23.4 | 167 | 7 | 15.4 | 161 | 10 | | | | | | |
| **7** | 19.9 | 146 | 7 | 16.9 | 153 | 7 | 41 | | | | | |
| **8** | 24.9 | 153 | 3 | 22.4 | 152 | 3 | 39 | 5.5 | 131 | 27 | 7 | 7 |
| **9** | 24.8 | 152 | 3 | 23.6 | 152 | 3 | 39 | 5.4 | 129 | 27 | 8 | 8 |
| **10** | 24.0 | 155 | 3 | 22.6 | 148 | 3 | 39 | 3.7 | 126 | 29 | 8 | 8 |
| **15** | 28.9 | 153 | 2 | 10.7 | 151 | 3 | 42 | −4.7 | 130 | 27 | 5 | 7 |
| | | | | | Intermediates, B1 Structure | | | | | | | |
| **11′** | 23.2 | 152 | | 32.0 | 169 | | 43 | −7.7 | 124 | 25 | 5 | 11 |
| **12′** | 20.6 | 168 | | 26.4 | 158 | | 46 | −9.3 | 126 | 25 | 9 | 5 |
| **13′** | 25.1 | 152 | | 126.8 | 169 | | 64 | 65.0 | 203 | 32 | | |
| **14′** | 19.9 | 171 | | 113.9 | 293 | | 63 | 43.1 | 209 | 41 | 6 | 7 |

[a] Chemical shifts in ppm; coupling constants in Hz. [b] Metalated PCCl. [c] Second metalated phosphine (or equatorial phosphine in compound **11′**–**14′**). [d] Axial phosphine. [e] Broad signals; coupling not resolved.

**Scheme I**

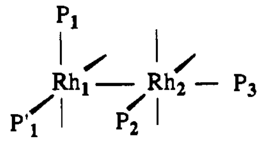


position should lead to the doubly metalated compounds with head-to-head structure (pathway B). That is supported by the observation in solution of the intermediates **11′**–**14′**, which, based on the $^{31}P\{^1H\}$ NMR spectra (Table V), have the structure proposed for the intermediate **B1**. The formation of **B1** involves simultaneous rearrangement of the metalated phosphine from $\eta^2$ to $\eta^3$ coordination modes. This fact could explain why pathway B is faster than pathway A and consequently why there is such an increase of the reaction rate when compound (**1**)($HO_2CCH_3$)$_2$ is in the presence of an excess of phosphine. The first mole of phosphine coordinates $Rh_2$, and only an additional amount of ligand can coordinate $Rh_1$ using the alternative and faster reaction pathway B. Both steric and electronic effects[15] can be responsible for the observed increase of reactivity in excess of phosphine.

The different chemical behavior shown by compound **4** can be due to the lower coordinating capacity of the $P(p\text{-}ClC_6H_4)_3$. The observation of a broad signal at −16.2 ppm in the $^{31}P$ NMR spectrum of compound **4** indicates that the $Rh-P_{axial}$ bond undergoes fast dissociation at room temperature, leaving in solution a certain amount of free phosphine which can undergo metalation by following pathway B.

**Spectroscopic Section.** $^{31}P\{^1H\}$ NMR spectroscopy is especially suitable to monitor the course of the reaction without prior workup. The $^{31}P$ NMR characteristics of doubly metalated compounds of H–T or H–H type as well as intermediates of type **A1** have been reported previously allowing the NMR spectroscopic parameters to assume diagnostic value. It is known[4b,6-8] that $^{31}P$ signals from cyclometalated rhodium dimers appear at ca. $\delta$ 20 ppm, $^{31}P$ signals from axial phosphines appear in the range −20 to +10 ppm and signals from equatorial phosphines appear at ca. $\delta$ 50 ppm.

In addition to these $^{31}P$ chemical shift data, the values of $^1J(Rh-P)$ and in particular $^2J(Rh-P)$ are important in that the latter confirm the binuclear nature of the complex, e.g. coupling from P(1) to Rh(2) and from P(2) to Rh(1).



Moreover, $^2J[Rh(1)-P(3)] \gg {}^2J[Rh(2)-P(1)]$ because the former is a trans coupling. In addition to that, the values of the $J$(P–P) coupling constants show the following trend, $^2J[P(1)-P(1')] \gg {}^3J[P(1)-P(3)] \gg {}^3J[P(1)-P(2)]$, with the last one usually not observed. All these spectroscopic data allow an unambiguous structural assignment of the studied compounds. Spectroscopic data for all compounds are listed in Table V.

**Monometalated Compounds.** The chemical shift values for the orthometalated phosphine PCCl in compounds of the type $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)]L$ are sensitive to the nature of the axial ligand L, the highest values (21.2–24.7 ppm) being observed when L is a P donor ligand. A high-field resonance in the range −9.8 to −26.5 ppm is observed in all the compounds containing an axial phosphine.

Characteristic values of coupling constants are observed for each type of resonance. The direct couplings to rhodium are considerably larger for metalated triarylphosphine (145–170 Hz) than

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(15) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982; Chapter 7, p 314.

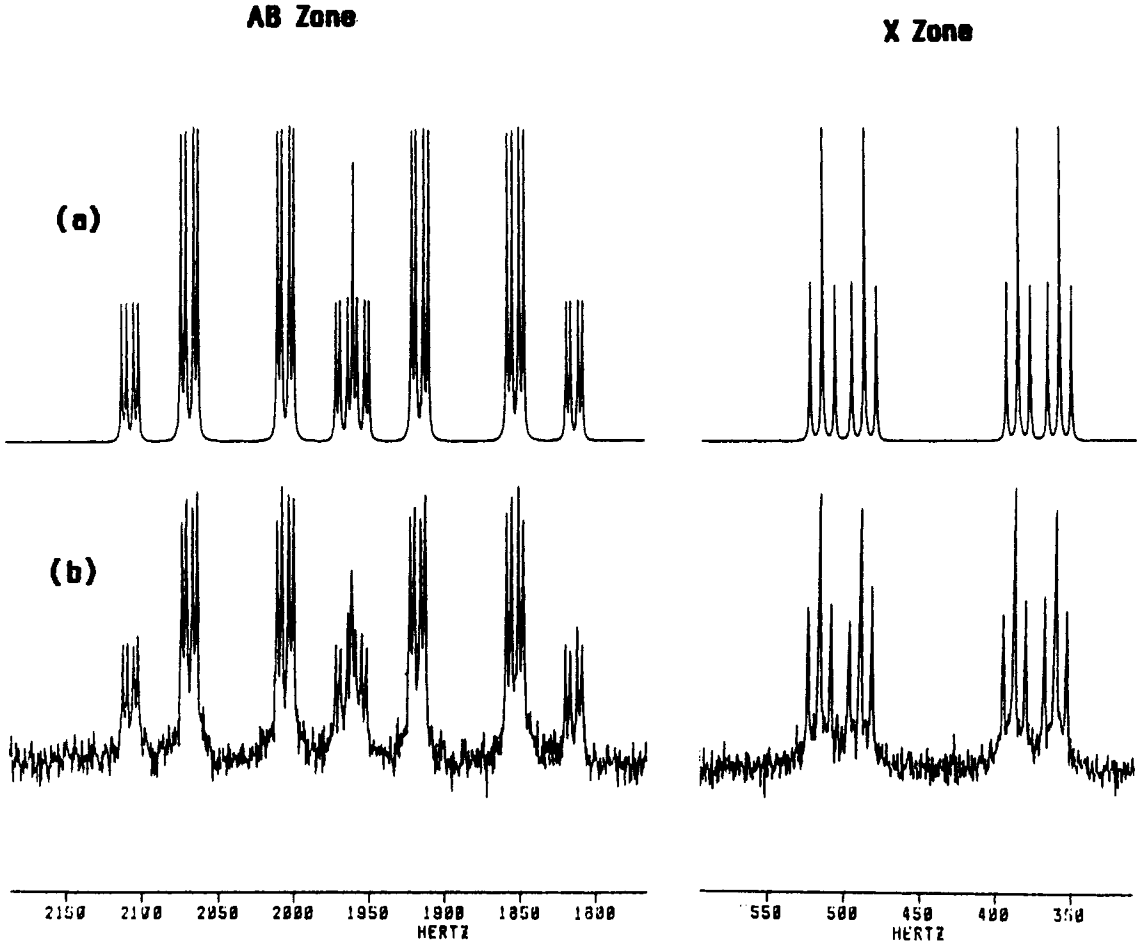

**Figure 3.** Calculated (a) and experimental (b) spectra for compound **9**.

for the axial phosphines (110–130 Hz) reflecting the relative weakness of the axial Rh–P bond. However, $^2J$(Rh–P) coupling constants are only observed for axial phosphines (25–35 Hz).

The signals corresponding to the axial ligand are much broader in **4**, which contains P($p$-ClC$_6$H$_4$)$_3$, than in compounds **2** or **3**, where P($p$-CH$_3$C$_6$H$_4$)$_3$ or P(C$_6$H$_5$)$_3$ is present. This indicates that a dissociation process with cleavage of the axial Rh–P bond occurs in solution for compound **4**, reflecting the lower coordination capacity of the P($p$-ClC$_6$H$_4$)$_3$ ligand. The phosphite adducts **13** and **14** show, as expected, low-field resonances with larger coupling to rhodium than the phosphine adducts.

**Doubly Metalated Compounds.** The $^{31}$P NMR spectra for compounds with the H–T structure (**5**, **6**) are very simple, showing two different resonances with chemical shift and $^1J$(Rh–P) and $^2J$(Rh–P) coupling constant values characteristic of ortho-metalated phosphines. The unobserved coupling between the two P nuclei is indicative of a H–T structure.

Very illustrative spectra are found for compounds with the H–H structure as phosphine adducts (compounds **8–10**, and **15**). In this case all the possible couplings between the five magnetically active nuclei contained in the molecule (two Rh and three P nuclei) are observed. In particular, the resonance corresponding to the axial ligand appears as four triplets (X zone) due to the coupling to the two rhodium and to the two equatorial P nuclei that accidentally show similar $^3J$(P–P) coupling constant values. This resonance with a very well resolved set of signals appears in the range of chemical shift values 6.3–3.7 ppm for compounds with triarylphosphines and can be used as a diagnostic for a H–H configuration.

The resonances due to the two different metalated phosphines appear as an AB system (AB zone) with further splitting of the signals due to the additional coupling to the two rhodium atoms and the axial phosphine. Data for these compounds were obtained by the first-order analysis and by iterative computer analysis (PANIC 80 program[16]). Figure 3 shows the experimental and calculated spectra for compound **9** (AB and X zones). The $^2J$(P–P) coupling constants in the AB zone are in all cases about 40 Hz, supporting a cisoid configuration of the two ortho-metalated ligands.

**Intermediate Compounds.** Compounds **11′** and **12′** are detected in solution as intermediate products of the metalation process. As a representative example **11′** shows two $^{31}$P NMR resonances in addition to the corresponding to the metalated P($o$-ClC$_6$H$_4$)(C$_6$H$_5$)$_2$ ligand; they appear at $\delta$ +32.0 and −7.7 ppm and are assigned to two P(CH$_3$)(C$_6$H$_5$)$_2$ phosphines in equatorial and axial coordinations, respectively. Low-field chemical shift values have been already reported for equatorial phosphines in dinuclear rhodium(II) compounds.[6a,14] The values for the phosphorus–phosphorus coupling constants observed for the intermediate **11′** can be accounted for very consistently assuming for this species the structure assigned to the intermediate **B1**. The analogous phosphite compounds **13′** and **14′** show low field signals for equatorial phosphites 126.8 and 113.9 ppm, respectively, and resonances for axial phosphites at 65.0 and 43.1 ppm, respectively. Similarly, structure **B1** can be assigned to **13′** and **14′**.

**Crystal Structure of Compound (1)(HO$_2$CCH$_3$)$_2$.** The molecule is illustrated in Figure 2, together with the atomic numbering scheme. Positional parameters are reported in Table II. Selected bond distances (Å) and angles (deg) are listed in Table III.

The molecular structure of (**1**)(HO$_2$CCH$_3$)$_2$ shows a binuclear dirhodium unit Rh$_2^{4+}$ with a Rh–Rh bond distance of 2.410 (1) Å. The two metal atoms have different environments, RhO$_4$P for Rh(1) and RhO$_4$C for Rh(2). There are four bridging ligands: three acetate groups and one ortho-metalated phosphine. The roughly octahedral coordination of each rhodium atom is completed by axial coordination of two acetic acid molecules, which are coordinated to the rhodium atoms through carbonylic oxygens.

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(16) Brucker Aspect 2000 NMR Software Manual, Aug. 1979.

The Rh–Rh distance, 2.410 (1) Å, is the shortest found in dirhodium(II) compounds containing acetates and ortho-metalated phosphines acting as bridging ligands.[3-8] The Rh–$O_{eq}$ distances are in the normal range found in bridging acetates. The Rh–$O_{eq}$ distance for oxygens trans to the P atom (2.185 (6) Å) and trans to the C(2) atom (2.241 (4) Å) are significantly longer than the other Rh–$O_{eq}$ distances, which are in the range 2.009 (5)–2.051 (4) Å. This trans influence can be observed in $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$,[3] as well as in other reported ortho-metalated compounds[4a] but the longest Rh–$O_{eq}$ distances are found in (**1**)$(HO_2CCH_3)_2$. The Rh–$O_{eq}$ distance trans to C atom is longer than trans to P atom in agreement with the relative trans influence of P and C observed in other mononuclear metalated compounds.[17] The Rh–$O_{ax}$ distances in compound (**1**)$(HO_2CCH_3)_2$ are different: Rh(1)–O(19) = 2.378 (6) Å, and Rh(2)–O(23) = 2.255 (11) Å. This can be attributed to two factors: (i) steric effects in axial positions of Rh(1) (presence of the chlorine atom and the aromatic rings), and (ii) different acidities of the metal centers, because of the existence of an unsymmetrical P,C ortho-metalated ligand.

Unlike those in most simple adducts of the tetracarboxylates, the angle Rh–Rh–axial ligands deviate significantly from linearity. In (**1**)$(HO_2CCH_3)_2$, the angle O(19)–Rh(1)–Rh(2) is 166.3 (1)° and O(23)–Rh(2)–Rh(1) is 172.3 (2)°. Similar deviations from linearity were observed for the ortho-metalated rhodium compounds[3a] and osmium compounds.[3b] The axial acetic acid molecules are hydrogen bonded to oxygen atoms of the bridging acetates (O(21)–O(27) = 2.57 (1) Å; O(25)–O(29) = 2.60 (1) Å). This fact also appears[3] in $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$ ($d(O \cdots O)$ = 2.527 Å), but in that case each acetic acid interacts with a different carboxylate group.

The distortions from octahedral geometry may be due to significant torsion angles around the metal–metal bond. The four torsion angles are large: P–Rh(1)–Rh(2)–C(2) = 20.3 (3)°, O(27)–Rh(1)–Rh(2)–O(29) = 12.9 (4)°, O(31)–Rh(1)–Rh(2)–O(33) = 10.5 (3)° and O(35)–Rh(1)–Rh(2)–O(37) = 12.0 (3)°. Similar deviations were observed for all the doubly metalated compounds already reported.[3,6b,7]

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**Registry No.** (**1**)$(HO_2CCH_3)_2$, 138093-51-3; (**1**)PCCl, 112841-24-4; **2**, 138093-52-4; **3**, 112841-26-6; **4**, 138093-53-5; **5**, 138093-54-6; **6**, 112841-29-9; **7**, 138093-55-7; **8**, 138093-56-8; **9**, 112841-25-5; **10**, 138093-57-9; **11**, 138093-58-0; **11′**, 138128-60-6; **12**, 138093-59-1; **12′**, 138093-62-6; **13**, 138093-60-4; **13′**, 138093-63-7; **14**, 138093-61-5; **14′**, 138093-64-8; **15**, 138128-59-3; $P(p\text{-}CH_3C_6H_4)_3$, 1038-95-5; $P(p\text{-}ClC_6H_4)_3$, 1159-54-2.

**Supplementary Material Available:** Complete tables of bond distances and angles and anisotropic displacement parameters (3 pages); a table of structure factors (12 pages). Ordering information is given on any current masthead page.

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Contribution from the Centro CNR, Dipartimento di Chimica Inorganica e Metallorganica, Università di Milano,
Via Venezian 21, 20133 Milano, Italy, Dipartimento di Chimica, Università di Sassari,
Via Vienna 2, 07100 Sassari, Italy, and Dipartimento di Chimica Generale,
Università di Pavia, Viale Taramelli 12, 27100 Pavia, Italy

# Mono- and Dinuclear Complexes of Platinum(II) with Chiral Diphosphines: $Pt(P\text{-}P')Cl_2$ and $[Pt(P\text{-}P')(\mu\text{-}OH)]_2[BF_4]_2$ (P-P′ = prolophos, *N*-(Diphenylphosphino)-2-((diphenylphosphinoxy)methyl)pyrrolidine, and butaphos, 1-(Diphenylphosphinoxy)-2-(*N*-ethyl-*N*-(diphenylphosphino)amino)butane). Crystal and Molecular Structure of Pt{*S*-prolophos-*P*,*P*′}$Cl_2$

Anna Laura Bandini,*[,†] Guido Banditelli,[†] Edoardo Cesarotti,[†] Giovanni Minghetti,[‡] and Bruna Bovio*[,§]

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The mononuclear complexes $Pt(P\text{-}P')Cl_2$, **1** and **2**, where P-P′ are the chiral ligands (*S*)-*N*-(diphenylphoshino)-2-((diphenylphosphinoxy)methyl)pyrrolidine, *S*-prolophos, and (*R*)-1-(diphenylphosphinoxy)-2-(*N*-ethyl-*N*-(diphenylphosphino)amino)butane, *R*-butaphos, respectively, were prepared and characterized in solution by $^1H$, $^{13}C$, $^{31}P$, $^{195}Pt$, and two-dimensional correlation spectra. Only one conformer is observed in solution at room temperature. The structure of complex **1**, Pt{*S*-prolophos}$Cl_2$, was solved by X-ray diffraction: $C_{29}H_{29}Cl_2NOP_2Pt$, orthorhombic, space group $P2_12_12_1$, $a$ = 16.557 (6) Å, $b$ = 15.697 (6) Å, $c$ = 10.948 (5) Å, $Z$ = 4, and $V$ = 2845 (2) Å$^3$. The structure was refined to a conventional $R$ factor of 0.040 ($R_w$ = 0.049) for 2700 observed reflections with $I > 3\sigma(I)$. The ligand P-P′ is coordinated in an endobidentate fashion to the platinum atom, which exhibits a slightly distorted square-planar geometry. The seven-membered ring adopts a twist-boat conformation. Treatment of complexes **1** and **2** with silver tetrafluoroborate in methanol solution afforded the dinuclear species $[(P\text{-}P')Pt(\mu\text{-}OH)_2Pt(P\text{-}P')][BF_4]_2$ (**3**, P-P′ = prolophos, and **4**, P-P′ = butaphos). The dinuclear unit is maintained even in the gas phase, as shown by the MS–FAB spectrum of complex **4**. Complex **1**, in the presence of tin(II) chloride, was found to catalyze the hydroformylation of styrene to (*R*)-(−)-2-phenylpropanal with 37% optical purity.

## Introduction

Among the many chiral diphosphines which have been prepared and tested as ligands in asymmetric catalytic processes,[1] two aminophosphine–phosphinite ligands (P-P′), viz. *N*-(diphenylphosphino)-2-((diphenylphosphinoxy)methyl)pyrrolidine, prolophos, and 1-(diphenylphosphinoxy)-2-(*N*-ethyl-*N*-(diphenylphosphino)amino)butane, butaphos, were described several years ago by some members of our group.[2] The cationic rhodium(I) complexes, $[Rh(COD)(P\text{-}P')]^+$, were shown to be efficient homogeneous hydrogenation catalysts toward several prochiral substrates under mild conditions.[2] In ruthenium chemistry, the use of the *S*-prolophos ligand has allowed the high-yield isolation

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[†] Università di Milano.
[‡] Università di Sassari.
[§] Università di Pavia.

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