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ortho-Metallation of $P(m\text{-}MeC_6H_4)_3$ in Dirhodium(II) Tetraacetate. Molecular Structure of $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2\cdot CH_3CO_2H$

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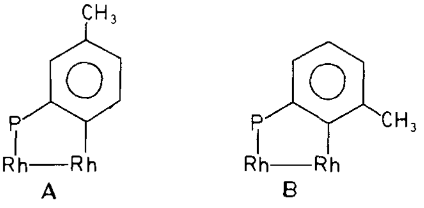
Abstract

The thermal reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$ and $P(m\text{-}MeC_6H_4)_3$ in a 1:2 molar ratio in acetic acid yielded $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2$. Purple monoclinic crystals of this compound and one molecule of acetic acid, space group $P2_1/c$, were obtained by evaporation of a solution of the original reaction product in acetic acid/CH_2Cl_2 mixture. The unit cell parameters are $a = 21.346(3)$, $b = 11.909(2)$, $c = 20.071$ Å, $\beta = 97.98(1)°$ and $Z = 4$. The structure consists of a dinuclear rhodium core bridged by cisoid acetate groups and two *ortho*-metallated phosphine ligands. The *ortho*-metallation occurs at the least sterically hindered carbon atom which is *trans* to the methyl substituent. If the reaction is performed in a 1:1 molar ratio, a monometallated species $Rh_2(O_2CCH_3)_3[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2](HO_2CCH_3)_2$ is obtained in high yield, with the above mentioned doubly metallated compound as a minor reaction product.

Introduction

Relatively few examples of *ortho*-metallation of P-donor ligands at bimetallic centers containing metal–metal bonds have been described to date [1–10]. Several papers have appeared in the literature dealing with the synthesis and reactivity of *ortho*-metallated dirhodium(II) compounds [11–17]. In all the cases the metallation occurred in the phenyl ring of an aryl phosphine. We have recently studied the influence which substitution in the phenyl rings of the phosphine has on the metallation reaction. We found [14] that in the reaction of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)]$ with *para*-substituted phosphines, $P(p\text{-}XC_6H_4)_3$, the rate of the metallation reaction to give doubly metallated compounds $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][\mu\text{-}PC']$, $[\mu\text{-}PC'] = [(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]$, increases in the order $X = Cl < H < CH_3$. Following our investigation on *ortho*-metallation at dirhodium(II) compounds, we have explored the behavior of the phosphine $P(m\text{-}MeC_6H_4)_3$. This phosphine can react in two different ways: with the metallated carbon in *para* position to the methyl group (A), or in *ortho* position to the methyl group (B).



Scheme 1.

We report here the preparation of $Rh_2(O_2CCH_3)_3[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2](HO_2CCH_3)_2$ and $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2$. The crystal structure determination of this last compound confirms that a metallation of type A is selectively produced.

Experimental

Materials

$Rh_2(O_2CCH_3)_4(MeOH)_2$ was prepared according to the literature procedures [18]. Commercially available $P(m\text{-}MeC_6H_4)_3$ (Aldrich) was used as purchased without prior recrystallization. All used solvents were of analytical grade. Chloroform and toluene were dried and degassed before using; acetic acid was only degassed.

Preparation of $Rh_2(O_2CCH_3)_3[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2](HO_2CCH_3)_2$

A green suspension of $Rh_2(O_2CCH_3)_4(MeOH)_2$ (100 mg, 0.198 mmol) in 50 cm^3 of a 3:1 toluene/acetic acid mixture, under an argon atmosphere was taken to reflux until total solution of the green solid.

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$P(m\text{-}CH_3C_6H_4)_3$ (60 mg, 0.198 mmol), dissolved in 5 cm^3 of a 1:3 $CHCl_3$/toluene mixture, was added to the green solution, which turned to brown–orange. The resulting solution was stirred and refluxed for 30 min; the solution changed to deep violet. The solvent was removed under vacuum and the crude product redissolved in a mixture of CH_2Cl_2/hexane (5 cm^3/5 cm^3). The solution was transferred to a chromatography column (30 × 2 cm) packed with silica gel in hexane. Elution with CH_2Cl_2/hexane (1:2) separated one minor yellow band which was discarded. Further elution with hexane/CH_2Cl_2/acetic acid (10:10:1) separated two purple and blue–violet bands. Both solutions were concentrated under reduced pressure to 10 cm^3. Hexane was added to precipitate purple $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2$ (yield 15%; see later) and the blue–violet compound $Rh_2(O_2CCH_3)_3[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2](HO_2CCH_3)_2$ (yield 70%): ^{1}H NMR ($CDCl_3$) spectrum (in ppm): 1.31 (CH_3, 6H, s), 2.24 (CH_3, 3H, s), 2.28 (CH_3, 6H, s), 2.31 (CH_3, 3H, s), 2.38 (CH_3, 6H, s), 6.6–8.5 (aromatics, 11H, m). $^{31}P\{^1H\}$ NMR spectrum (CH_2Cl_2): $\delta_P = 16.4$ ppm, $^1J(Rh\text{–}P) = 143$ Hz, $^2J(Rh\text{–}P) = 6$ Hz. $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum (in ppm): 20.71 (CH_3, s), 21.42 (CH_3, s), 22.45 (CH_3, s), 23.48 (CH_3, s), 23.99 (CH_3, s), 127–142 (aromatics, m), 181.57 (OCO, s), 182.48 (OCO, s), 189.70 (OCO, s). Infrared spectrum (KBr disc): 3400(m), 2910(s), 2605(w), 2520(w), 1690(s), 1570(s), 1425(s), 1346(s), 1285(s), 1174(w), 1136(w), 1110(m), 1086(w), 1043(w), 1028(m), 872(w), 820(w), 785(m), 696(s), 625(w), 564(m), 495(m), 475(m) cm^{-1}.

Preparation of $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2$

(a) Synthesis from $Rh_2(O_2CCH_3)_4(MeOH)_2$

A 1:2 molar ratio mixture of $Rh_2(O_2CCH_3)_4(MeOH)_2$ (100 mg) and $P(m\text{-}CH_3C_6H_4)_3$ (120 mg) was stirred and refluxed in acetic acid for 90 min. The resulting deep purple solution was concentrated under vacuum to dryness. The crude product was dissolved in CH_2Cl_2 (2 ml) and addition of hexane yielded a purple solid. Yield 95%.

(b) Synthesis from $Rh_2(O_2CCH_3)_3[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2](HO_2CCH_3)_2$

A total of 100 mg of $Rh_2(O_2CCH_3)_3[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2](HO_2CCH_3)_2$ was dissolved in acetic acid (20 ml). An equimolar amount of $P(m\text{-}CH_3C_6H_4)_3$ was added. The solution colour changed to brown–red, and was refluxed for 90 min. The product was precipitated as with method (a). Yield 95%.

$Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2$: ^{1}H NMR ($CDCl_3$) spectrum (in ppm): 1.24 (CH_3, 6H, s), 1.93 (CH_3, 6H, s), 2.06 (CH_3, 6H, s), 2.12 (CH_3, 6H, s), 2.36 (CH_3, 6H, s). 6.1–7.6 (aromatics, 22H, m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum: $\delta_P = 18.4$ ppm, $^1J(Rh\text{–}P) = 160$ Hz. $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum (in ppm): 20.61 (CH_3, s), 21.09 (CH_3, s), 21.53 (CH_3, s), 21.80 (CH_3, s), 22.57 (CH_3, s), 126–147 (aromatics, m), 178.20 (OCO, s), 181.38 (OCO, s). Infrared spectrum (KBr disc): 3400(m), 2910(s), 2610(w), 2525(w), 1703(m), 1681(s), 1561(s), 1480(w), 1449(m), 1412(s), 1340(w), 1291(s), 1245(w), 1110(m), 1086(w), 1026(m), 815(m), 780(m), 696(s), 563(m), 487(m), 475(m) cm^{-1}.

Measurements

The infrared spectra were recorded on a Perkin-Elmer 1750 spectrophotometer. NMR spectra were measured on a BRUCKER AC-200 FT spectrometer, operating at 300 K. In $^{31}P\{^1H\}$ NMR spectra, chemical shifts are referred to external 85% H_3PO_4 in D_2O. In ^{1}H and $^{13}C\{^1H\}$ NMR spectra, chemical shifts are referred to TMS and $CDCl_3$, respectively. The electrochemical experiments were carried out in a three-electrode cell under an inert atmosphere. The working and auxiliary electrodes were platinum, the reference electrode was a saturated calomel electrode, electrically connected to the non-aqueous solution by a salt bridge containing the non-aqueous solvent (CH_2Cl_2 freshly distilled) and the supporting electrolyte ($[NBu^n_4][PF_6]$, which had been recrystallized from ethanol and dried at 80 °C under vacuum for 48 h). Cyclic voltammograms were obtained with a 305 H.Q. instrument programming function generator which was connected to a 552 Amel potentiostat, and recorded with a Riken-Denshi F35 x-y recorder. The system was calibrated against cobaltocene, $[Co(\eta\text{-}C_5H_5)_2]$.

X-ray Crystallographic Procedures

A well formed purple single crystal of compound $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2$ grown from an acetic acid/CH_2Cl_2 mixture of solvents was used for the structure determination. X-ray intensities were recorded on a Nonius CAD4 diffractometer using monochromatized Mo Kα radiation. Cell constants and orientation matrix for data collection were obtained from least-squares refinement of 25 well centered reflections. From systematic absences the space group was determined to be $P2_1/c$. A total of 9647 reflections was measured, hkl range (−25, 0, 0) to (25, 14, 23), theta limits $(0 < \theta < 25)$ using the $\omega\text{–}2\theta$ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. Intensity was checked by monitoring three standard reflections every 60 min. Final drift corrections were between 0.99 and 1.03. On all reflections profile analysis was performed [19, 20]. Empirical absorption correction was applied using Ψ scans [21] (correction factors were in the range 0.965 to 1.000). Some double-measure reflections were averaged, $R_{int} = \Sigma(I - \langle I \rangle)/\Sigma(I) = 0.011$, resulting in 8822 unique reflections of which only 7259 were 'observed' with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data reduced to $|F_o|$ values.

The structure was solved by Patterson interpretation using the program SHELX86 [22] which led to the location of the two Rh atoms. The remaining non-hydrogen atoms were located from successive Fourier Synthesis. The structure was refined by least-squares using SHELX76 [23]; because of the large number of parameters a block-matrix refinement was used. A final difference Fourier map showed poor peaks for the hydrogen atoms and their positions were calculated on the basis of d(C–H) = 1.08 Å; the hydrogen atoms associated with the OH groups could not be located so their positions were updated as appropriate but were not refined. Final conventional agreements factors were $R = 0.038$ and $R_w = 0.045$. For the 7259 'observed' reflections and 594 variables. Atomic scattering factors and corrections for anomalous dispersion for the Rh atom were taken from the International Tables for X-ray Crystallography [24]. The geometrical calculations were performed with PARST [25] and the molecular illustration was drawn with ORTEP.

Results and Discussion

The thermal reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$ with $P(m\text{-}MeC_6H_4)_3$ (1:2 molar ratio) in refluxing acetic acid gave the doubly metallated compound $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2$ (2) in high yield.

The thermal reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$ with $P(m\text{-}MeC_6H_4)_3$ (1:1 molar ratio) in refluxing (3:1) toluene/acetic acid mixture gave, in addition to unreacted dirhodium tetraacetate, two products which were separated by chromatographic methods. The major reaction compound was identified as $Rh_2(O_2CCH_3)_3[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2](HO_2CCH_3)_2$ (1) based on its reactivity and the ^{31}P, ^1H and ^{13}C NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum of the isolated compound shows a signal at 16.4 ppm with the couplings with the two rhodium atoms ^1J(Rh–P) = 143 Hz and ^2J(Rh–P) = 6 Hz. The chemical shift and coupling constant values are very similar to those observed for $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$ which has been recently characterized by X-ray techniques [26].

The minor product isolated from the same reaction was the doubly metallated compound $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2$ (2). This compound showed in the ^{31}P NMR spectrum the characteristic AA'XX' system centered at 18.4 ppm, already found for other doubly metallated compounds [17].

When compound 1 reacts in CH_2Cl_2 with $P(m\text{-}MeC_6H_4)_3$ in a 1:1 molar ratio, one molecule of acetic acid is exchanged by phosphine yielding $Rh_2(O_2CCH_3)_3[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2](HO_2CCH_3)[P(m\text{-}MeC_6H_4)_3]$. The $^{31}P\{^1H\}$ NMR spectrum shows, in addition to the signal due to the metallated phosphine ($\delta_P = 23.4$ ppm, ^1J(Rh–P) = 156 Hz), a high field signal $\delta_P = -10.1$ ppm (^1J(Rh–P) = 111 Hz) which is assigned to the axial phosphine. The rest of the observed spin couplings ^2J(Rh–P) = 28 Hz and ^3J(P–P) = 9 Hz are also very similar to those reported for other related metallated compounds with triphenylphosphine [26, 14]. This compound, after reflux in acetic acid, selectively yields compound 2 in high yield.

These spectroscopic and reactivity results do not allow us to establish in which of the two carbon atoms of the substituted phenyl ring the metallation occurs. In order to determine this structural aspect we solved the crystal structure of 2. Single crystals of compound 2 suitable for X-ray structural analysis were obtained by slow recrystallization from dichloromethane/acetic acid solution.

Figure 1 shows a perspective view of the molecule with the atomic numbering scheme. Table 1 summarizes crystal data. Lists of atomic coordinates for the non-hydrogen atoms are given in Table 2. Selected bond distances and angles are given in Table 3.

The structure consists of a dinuclear Rh_2^{4+} unit with two bridging acetate ligands and two bridging *ortho*-metallated phosphines. The bridging *ortho*-metallated phosphines are in a cisoid arrangement and are coordinated in a head-to-tail fashion (type IV).

The Rh(1)–Rh(2) bond length, 2.502(3) Å, is similar to that found in the related compound with triphenylphosphine [11] (2.508(1) Å). *ortho*-Metallated Rh_2^{4+} compounds always show Rh–Rh distances which are longer than those observed in dirhodium tetraacetate with O-donor molecules in the axial positions.

The two axial sites *trans* to the metal–metal bond are occupied by two molecules of acetic acid which coordinate through the oxygen atom from the C=O group. The packing in the crystal is completed by solvent molecules of acetic acid.

The angles around each rhodium atom range from 83.3(1)° to 101.9(1)° for the *cis* bonds and from 164.5(1)° to 175.5(2)° for the *trans* bonds.

The Rh–O distances ranging from 2.134(3) to 2.412(4) Å, averaging 2.236 Å, are longer than in tetraacetate adducts $Rh_2(O_2CCH_3)_4{\cdot}L_2$; this can be attributed to the *trans* influence of phosphorous and metallated carbon. This *trans* influence is clearly observed in the monometallated compound Rh_2-

TABLE 1. Crystal data for $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2\cdot(CH_3COOH)$

Formula	$Rh_2P_2O_8C_{50}H_{54}\cdot CH_3CO_2H$
Formula weight	1110.78
Space group	$P2_1/c$
Systematic absences	$h0l\ l = 2n + 1$ $0k0\ k = 2n + 1$
a (Å)	21.346(3)
b (Å)	11.909(2)
c (Å)	20.071(3)
β (°)	97.98(1)
V (Å^3)	5052(1)
Z	4
D_{calc} (g/cm^3)	1.46
Crystal size (mm)	0.5 × 0.3 × 0.2
μ(Mo Kα) (cm^{-1})	7.59
Data collection instrument	Nonius CAD4
Radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
Orientation reflections: no., θ range (°)	25, 20–25
Temperature (°C)	24
Scan method	ω–2θ
Data collection, θ range (°)	0–25
No. unique data with $I > 3\sigma(I)$	7259
No. parameters refined	594
R [a]	0.038
R_w [b]	0.045
Largest shift/e.s.d., final cycle	0.11
Largest peak (e/Å^3)	0.7

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/(\sigma^2(F_o) + 0.0228(F_o)^2)$.

$(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$, recently described [26] where the two Rh–O distances *trans* to the *ortho*-metallated phosphine are considerably longer than the rest.

The bond lengths Rh(2)–C(11), 1.994(4) Å, and Rh(1)–C(41), 1.974(4) Å, are comparable to the values found in other related structures; Rh(II)–C(sp^2) (1.976 [27]–2.09 [28] Å).

The Rh(2), P(2), C(40), C(41), Rh(1) atoms and the Rh(2), C(11), C(10), P(1), Rh(1) atoms deviate significantly from planarity in contrast with the planarity observed when the metallated phosphine closes a four-membered ring. The torsion angles P(1)–Rh(1)–Rh(2)–C(11) and P(2)–Rh(2)–Rh(1)–C(41) are 12.1(1)° and 12.4(1)°, respectively. For the frameworks Rh(1), Rh(2), acetate, the deviation from planarity seems to be also important; in fact, the value of the torsion angle for O(1)–Rh(1)–Rh(2)–O(2) is 15.7(1)° and for O(3)–Rh(1)–Rh(2)–O(4) is 17.1(1)°.

The O(6) and O(8) atoms from the OH groups of the axial acetic acids appear to be orientated towards the O(1) and O(2), respectively from the bridging acetate, making non-bonding distances O(6)....O(1)

TABLE 2. Positional parameters and their e.s.d.s for $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2\cdot(CH_3COOH)$

Atom	x/a	y/b	z/c	B_{eq} (Å^2)[a]
Rh(1)	0.1975(1)	0.1829(1)	0.1366(1)	2.22(1)
Rh(2)	0.237(1)	0.2810(1)	0.2445(1)	2.23(1)
P(1)	0.1449(1)	0.0676(1)	0.1958(1)	2.42(2)
P(2)	0.3284(1)	0.1942(1)	0.2446(1)	2.38(2)
O(1)	0.1232(1)	0.3126(2)	0.1277(1)	3.27(7)
O(2)	0.1445(1)	0.3616(2)	0.2350(1)	3.19(7)
O(3)	0.2510(1)	0.3021(2)	0.0886(1)	3.27(8)
O(4)	0.02596(1)	0.4149(2)	0.1787(1)	3.09(7)
O(5)	0.1519(1)	0.1394(3)	0.0228(2)	3.91(9)
O(6)	0.0822(2)	0.2775(3)	0.0026(2)	5.2(1)
O(7)	0.2657(1)	0.4081(2)	0.3308(2)	3.49(8)
O(8)	0.1803(2)	0.5196(3)	0.3186(2)	5.3(1)
C(1)	0.1106(2)	0.3671(3)	0.1771(2)	3.1(1)
C(2)	0.0535(2)	0.4401(4)	0.1693(3)	4.7(1)
C(3)	0.2681(2)	0.3920(4)	0.1193(2)	3.2(1)
C(4)	0.3009(2)	0.4786(4)	0.0817(3)	4.5(1)
C(5)	0.1129(2)	0.1905(4)	−0.0159(2)	4.0(1)
C(6)	0.0952(3)	0.1597(6)	−0.0884(3)	5.4(2)
C(7)	0.2396(2)	0.4907(4)	0.3466(2)	3.9(1)
C(8)	0.2658(3)	0.5707(5)	0.4020(3)	6.0(2)
C(10)	0.1695(2)	0.0787(3)	0.2848(2)	2.70(8)
C(11)	0.2097(2)	0.1666(3)	0.3070(2)	2.6(1)
C(12)	0.2276(2)	0.1766(4)	0.3779(2)	3.1(1)
C(13)	0.2030(2)	0.1047(4)	0.4219(2)	3.7(1)
C(14)	0.1624(2)	0.0183(4)	0.3994(2)	3.8(1)
C(15)	0.1454(2)	0.0042(4)	0.3309(2)	3.5(1)
C(16)	0.1354(3)	−0.0594(5)	0.4486(3)	6.5(2)
C(20)	0.0606(2)	0.1034(3)	0.1829(2)	2.8(1)
C(21)	0.0314(2)	0.1459(4)	0.2354(2)	3.8(1)
C(22)	−0.0315(2)	0.1830(5)	0.2221(3)	4.6(1)
C(23)	−0.0639(2)	0.1787(4)	0.1574(3)	4.5(1)
C(24)	−0.0342(2)	0.1380(4)	0.1041(2)	3.9(1)
C(25)	0.0284(2)	0.1000(4)	0.1179(2)	3.1(1)
C(26)	−0.0683(3)	0.1360(6)	0.0333(3)	5.9(2)
C(30)	0.1495(2)	−0.0843(3)	0.1805(2)	2.9(1)
C(31)	0.2050(2)	−0.1382(4)	0.2076(2)	3.4(1)
C(32)	0.2148(2)	−0.2501(4)	0.1955(2)	3.8(1)
C(33)	0.1688(2)	−0.3119(4)	0.1556(2)	4.0(1)
C(34)	0.1120(3)	−0.2587(4)	0.1291(2)	4.3(1)
C(35)	0.1024(2)	−0.1448(4)	0.1404(2)	3.8(1)
C(36)	0.2784(3)	−0.3042(5)	0.2252(4)	5.8(2)
C(40)	0.3231(2)	0.0806(3)	0.1848(2)	2.73(9)
C(41)	0.2673(2)	0.0735(3)	0.1394(2)	2.6(1)
C(42)	0.2632(2)	−0.0163(4)	0.0921(2)	3.2(1)
C(43)	0.3132(2)	−0.0904(4)	0.0905(2)	3.4(1)
C(44)	0.3690(2)	−0.0813(4)	0.1352(2)	3.6(1)
C(45)	0.3737(2)	0.0036(4)	0.1835(2)	3.3(1)
C(46)	0.4228(3)	−0.1622(5)	0.1317(3)	5.3(2)
C(50)	0.3877(2)	0.2920(3)	0.2217(2)	2.88(9)
C(51)	0.4242(2)	0.2685(4)	0.1712(2)	3.8(1)
C(52)	0.4673(2)	0.3486(5)	0.1541(3)	4.8(1)
C(53)	0.4739(2)	0.4503(5)	0.1892(3)	5.1(2)
C(54)	0.4375(2)	0.4737(4)	0.2403(3)	4.0(1)
C(55)	0.3942(2)	0.3949(4)	0.2551(2)	3.4(1)

(continued)

TABLE 2. *(continued)*

Atom	x/a	y/b	z/c	B_{eq} (Å^2)^a
C(56)	0.4430(3)	0.5860(5)	0.2775(3)	5.7(2)
C(60)	0.3676(2)	0.1315(3)	0.3228(2)	2.68(9)
C(61)	0.4174(2)	0.1823(4)	0.3643(2)	3.4(1)
C(62)	0.4431(2)	0.1307(4)	0.4235(2)	4.0(1)
C(63)	0.4210(2)	0.0297(4)	0.4425(2)	4.0(1)
C(64)	0.3708(2)	−0.0242(4)	0.4023(2)	3.9(1)
C(65)	0.3450(2)	0.0275(4)	0.3429(2)	3.3(1)
C(66)	0.3453(3)	−0.1366(5)	0.4220(3)	6.3(2)
C(70)	0.4254(3)	0.4102(5)	0.4998(3)	5.2(2)
C(71)	0.3652(2)	0.3410(5)	0.4997(3)	5.3(1)
O(70)	0.4741(2)	0.3791(4)	0.5356(2)	6.8(2)
O(71)	0.4244(2)	0.4961(5)	0.4617(2)	7.6(2)

^{a}Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $B_{eq} = \frac{1}{3}\Sigma\Sigma B_{ij}a^*_i a^*_j a_i a_j$.

and O(8)....O(2) of 2.576(4) and 2.566(4) Å, respectively. These values suggest some kind of hydrogen bond between the OH groups and one bridging acetate as was found in the triphenylphosphine monometallated compound $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$. A similar interaction but involving two oxygen groups from two different bridging acetate groups was also reported [11] for $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$. Unfortunately in the present case the hydrogen atoms from the OH groups were not found in the refinement of the structure. No unexpected features were found for intermolecular contacts.

The key information, provided by this crystal structure determination, corresponds to the identification of the metallated carbon atom, which in both phosphines is in the *para* position with respect to the methyl substituent (metallation of type A). No disorder was detected for the position of the methyl groups in the metallated rings. This result and the spectroscopic purity of the bulk solid isolated from the reaction indicates that the metallation selectivity occurs at the less sterically hindered carbon atom.

We have investigated the redox behavior of compounds 1 and 2 by cyclic voltammetry in CH_2Cl_2 using 0.2 M NBu_4PF_6 as supporting electrolyte. Both compounds show a quasi-reversible oxidation peak at

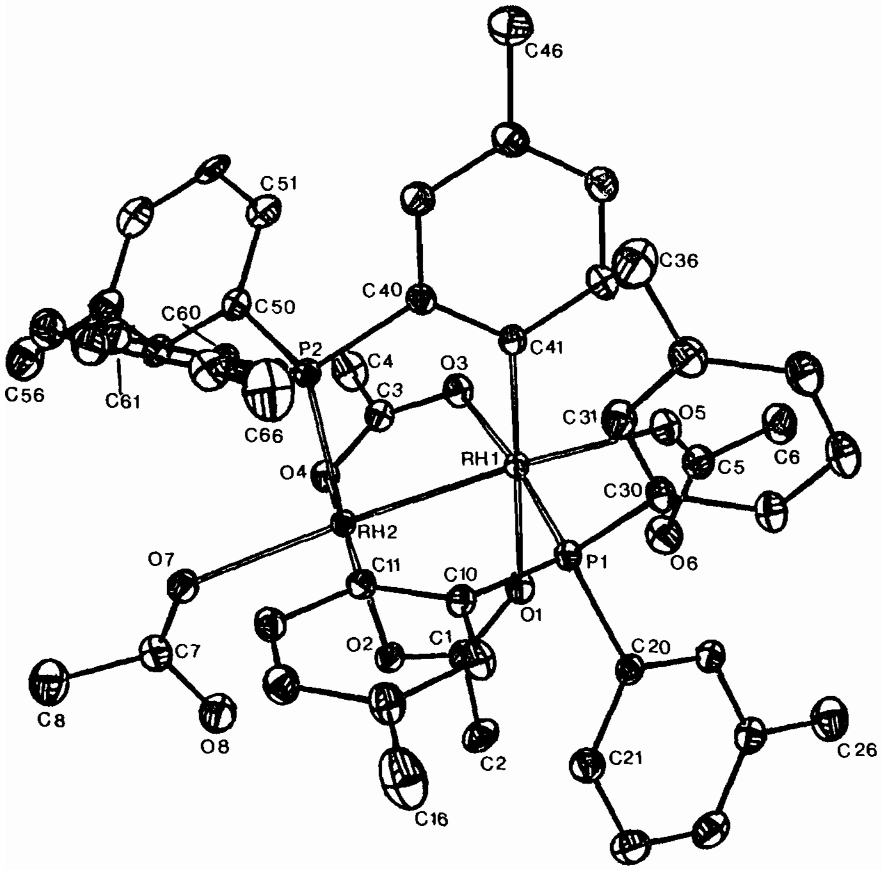

Fig. 1. Perspective view and atomic numbering scheme for $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2 \cdot (CH_3COOH)$.

TABLE 3. Selected bond distances (Å) and angles (°) and their e.s.d.s for $Rh_2(O_2CCH_3)_2[(m\text{-}MeC_6H_3)P(m\text{-}MeC_6H_4)_2]_2(HO_2CCH_3)_2\cdot(CH_3COOH)$

Bond distances			
Rh(1)–Rh(2)	2.502(3)	Rh(1)–P(1)	2.220(3)
Rh(1)–O(1)	2.203(3)	Rh(1)–O(3)	2.134(3)
Rh(1)–O(5)	2.412(5)	Rh(1)–C(41)	1.974(4)
Rh(2)–P(2)	2.206(3)	Rh(2)–O(2)	2.182(3)
Rh(2)–O(4)	2.167(3)	Rh(2)–O(7)	2.317(4)
Rh(2)–C(11)	1.994(4)	P(1)–C(10)	1.795(4)
P(1)–C(20)	1.832(5)	P(1)–C(30)	1.840(4)
P(2)–C(40)	1.802(4)	P(2)–C(50)	1.825(4)
P(2)–C(60)	1.832(4)	O(1)–C(1)	1.245(5)
O(2)–C(1)	1.283(4)	O(3)–C(3)	1.264(5)
O(4)–C(3)	1.261(5)	C(10)–C(11)	1.387(5)
C(40)–C(41)	1.398(5)		
Bond angles			
Rh(2)–Rh(1)–C(41)	96.9(1)	Rh(2)–Rh(1)–O(5)	164.5(1)
Rh(2)–Rh(1)–O(3)	86.70(9)	Rh(2)–Rh(1)–O(1)	84.02(9)
Rh(2)–Rh(1)–P(1)	87.75(9)	Rh(1)–Rh(2)–C(11)	97.6(1)
Rh(1)–Rh(2)–O(7)	166.9(1)	Rh(1)–Rh(2)–O(4)	83.85(8)
Rh(1)–Rh(2)–P(2)	88.53(8)	Rh(1)–Rh(2)–O(2)	86.37(9)
Rh(1)–P(1)–C(10)	112.8(1)	Rh(2)–P(2)–C(40)	112.2(2)
Rh(1)–O(1)–C(1)	122.2(2)	Rh(2)–O(2)–C(1)	119.5(2)
Rh(1)–O(3)–C(3)	118.7(2)	Rh(2)–O(4)–C(3)	119.4(3)
Rh(1)–O(5)–C(5)	130.3(3)	Rh(2)–O(7)–C(7)	130.7(3)
O(1)–C(1)–O(2)	122.5(3)	O(3)–C(3)–O(4)	125.1(4)
P(1)–C(10)–C(11)	117.2(3)	Rh(2)–C(11)–C(10)	122.4(3)
P(2)–C(40)–C(41)	116.7(3)	Rh(1)–C(41)–C(40)	123.4(3)

potential values of $E_{p,a}$ 1.00 and 0.90 V, respectively ($\Delta E_p = E_{p,a} - E_{p,o} = 100$ mV). The potential value measured for the single oxidation process in $Rh_2(O_2CCH_3)_4(CH_3COOH)_2$ is $E_{p,a} = 1.30$ V ($\Delta E_p = 80$ mV) indicating that the substitution of acetate groups by *ortho*-metallated phosphines makes the oxidation process more favorable.

Supplementary Material

Positional parameters of the hydrogen atoms are available from the authors on request.

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