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Inorganica Chimica Acta 229 (1995) 365–371

Inorganica Chimica Acta

Reaction of $Rh_2(\mu^2\text{-}O_2CCH_3)_3[\mu^2\text{-}(C_6H_4)PMePh](HO_2CCH_3)_2$ with triphenylphosphine: rearrangement of the metalated $PMePh_2$ ligand and formation of a compound with a diphenylphosphinomethanide group in (P,C) coordination; crystal structure of $[Rh_2(\mu^2\text{-}O_2CCH_3)_2\{\mu^2\text{-}(CH_2)PPh_2\}\text{-}\{\mu^2\text{-}(C_6H_4)PPh_2\}(PPh_3)]\cdot 2CH_2Cl_2$ ☆

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Received 15 July 1994; revised 21 September 1994

Abstract

The reaction of $[Rh_2(\mu^2\text{-}O_2CCH_3)_3\{\mu^2\text{-}(C_6H_4)PMePh\}]$ (**1**) in $CHCl_3$ with one mole of PPh_3 gives the two phosphine mono-adducts, which are in rapid equilibrium above −40 °C. After 6 h at room temperature this mixture gives $[Rh_2(\mu^2\text{-}O_2CCH_3)_2\{\mu^2\text{-}(C_6H_4)PMePh\}\{\mu^2\text{-}(C_6H_4)PPh_2\}](HO_2CCH_3)_2$ (**3**), a doubly metalated compound with a head-to-head configuration. **1** reacts with two moles of PPh_3, forming the bis-adduct **1.P₂**, which at 10 °C gives a mixture of **3**, in the form of its phosphine adduct **3.P**, and $[Rh_2(\mu^2\text{-}O_2CCH_3)_2\{\mu^2\text{-}(CH_2)PPh_2\}\{\mu^2\text{-}(C_6H_4)PPh_2\}(PPh_3)]$ (**2**). It is confirmed that **3.P** is not the kinetic product in the reaction from **1.P₂** to **2**. The structure of $[Rh_2(\mu^2\text{-}O_2CCH_3)_2\{\mu^2\text{-}(CH_2)PPh_2\}\{\mu^2\text{-}(C_6H_4)PPh_2\}(PPh_3)]\cdot 2CH_2Cl_2$ has been determined by X-ray diffraction: $M_r = 1216.55$, monoclinic, space group $P2_1/c$, $a = 19.930(8)$, $b = 15.29(2)$, $c = 16.84(2)$ Å, $\beta = 90.14(9)°$, $V = 5129(9)$ Å^3, $Z = 4$, $D_c = 1.58$ g cm^{-3}, Mo Kα radiation (graphite monochromator, $\lambda = 0.71073$ Å), μ (Mo Kα) = 9.80 cm^{-1}, $F(000) = 2464$, $T = 200$ K. The final conventional R factor was 0.061 for 4749 'observed' reflections. The compound contains an orthometalated triphenylphosphine and a diphenylphosphinomethanide group bridging the two rhodium atoms. The two ligands are in a head-to-head configuration. Two bridging acetate groups and one axial PPh_3 complete the coordination around the rhodium atoms. The Rh–Rh bond distance is 2.532(2) Å.

Keywords: Crystal structures; Rhodium complexes; Carboxylate complexes; Metalated ligand complexes; Binuclear complexes

1. Introduction

The reaction of rhodium tetraacetate and triphenylphosphine, first reported by Cotton and co-workers [1], yielded some novel bimetallic orthometalated compounds. This was an interesting example of intramolecular C–H activation in bimetallic compounds; mechanistic studies are scarce and limited to monometallic species [2]. Further studies indicated that by using this simple synthetic procedure with different triaryl- or alkylarylphosphines and different rhodium tetracarboxylates, compounds with the general formula $Rh_2(\mu^2\text{-}O_2CR_3)_{4-x}[\mu^2\text{-}PC]_x\cdot L_2$ ($x = 1,2$; PC = metalated arylphosphine; R = CH_3, CF_3, CMe_3; L = O, N, P axial donor ligand) could be obtained. Monometalated compounds (Fig. 1(a)) [3–5] and doubly metalated compounds with a head-to-tail (H–T) configuration (Fig. 1(b)) [3,6,7] and a head-to-head (H–H) configuration (Fig. 1(c)) [3,8] have been structurally characterized.

It is already clear that acetic acid acts as a catalyst of these reactions, and the kinetics of a thermal and an acid-catalyzed reaction have been studied [9]. $Rh_2(\mu^2\text{-}O_2CCF_3)_4$ reacts faster with arylphosphines than $Rh_2(\mu^2\text{-}$

☆ Dedicated to Professor F.A. Cotton on his 65th birthday.

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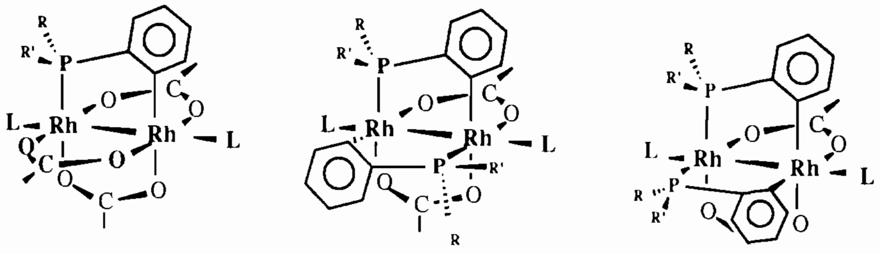
SSDI 0020-1693(94)04267-Y



a) b) c)

Fig. 1. Compounds with the general formula $Rh_2(\mu^2\text{-}O_2CR_3)_{4-x}[\mu^2\text{-}PC]_x\cdot L_2$: (a) monometalated; (b) doubly metalated, head-to-tail configuration; (c) doubly metalated, head-to-head configuration.

$O_2CCH_3)_4$ following the same reaction pathway [10]. Exchange of carboxylate groups with carboxylic acids has been reported for some of these compounds. Reversible Rh–C bond cleavage has been observed for $Rh_2(\mu^2\text{-}O_2CCH_3)_3[\mu^2\text{-}(C_6H_4)PPh_2]\cdot(HO_2CCH_3)_2$ in CD_3CO_2D medium [11].

The reactions of rhodium tetracarboxylates with $PMePh_2$ or PMe_2Ph reported by Morrison and Tocher [7] show that in all of the cases the metalation occurs at the *ortho* aromatic carbon atoms of the phosphines.

In the course of our investigation on the reactivity of monometalated compounds, we have found that when $Rh_2(\mu^2\text{-}O_2CCH_3)_3[\mu^2\text{-}(C_6H_4)PMePh]\cdot(HO_2CCH_3)_2$ (**1**) reacts with an excess of triphenylphosphine, $Rh_2(\mu^2\text{-}O_2CCH_3)_2[\mu^2\text{-}(CH_2)PPh_2][\mu^2\text{-}(C_6H_4)PPh_2]\cdot PPh_3$ (**2**) is formed. The crystal structure of compound **2**, reported in this paper, confirms the presence of a four-atom metallocycle, Rh–Rh–P–C, resulting from the rearrangement of the metalated $PMePh_2$, which is now metalated at the CH_3 group. Some of these results have been published in preliminary communications [12,13].

2. Experimental

2.1. *Materials*

$Rh_2(\mu^2\text{-}O_2CCH_3)_3[\mu^2\text{-}(C_6H_4)PMePh](HO_2CCH_3)_2$ (**1**) [12] was prepared according to a literature method. Commercially available PPh_3, $PMePh_2$ (Strem), CD_3CO_2D and $CDCl_3$ (Euriso-Top) were used as purchased. NMR measurements were recorded on Varian Unity 300 and Unity 400 spectrometers. All solvents were of analytical grade. Chloroform and toluene were dried and degassed before using; acetic acid was only degassed.

2.2. *Synthesis of $Rh_2(\mu^2\text{-}O_2CCH_3)_2[\mu^2\text{-}(CH_2)PPh_2][\mu^2\text{-}(C_6H_4)PPh_2]\cdot PPh_3\cdot 2CH_2Cl_2$ (2)*

1 (100 mg, 0.14 mmol) and PPh_3 (74 mg, 0.28 mmol) were dissolved in $CHCl_3$ under argon atmosphere. The resulting brown-red solution was stirred for 2 h and the solvent was removed under reduced pressure. The crude solid was transferred to a column for column chromatography with silica gel. Elution with CH_2Cl_2:hexane:acetone (10:10:2) separated a major yellow band containing $Rh_2(\mu^2\text{-}O_2CCH_3)_2[\mu^2\text{-}(CH_2)PPh_2][\mu^2\text{-}(C_6H_4)PPh_2]\cdot PPh_3\cdot 2CH_2Cl_2$ (**2**) (35% yield). Spectroscopic data of **2**: $^{31}P\{^1H\}$ NMR spectrum: $\delta(P_a)$ 35.8 ppm, $^1J(Rh1\text{–}P_a)$ 154.3 Hz, $^2J(P_a\text{–}P_b)$ 8.6 Hz, $^3J(P_a\text{–}P_c)$ 36.5 Hz; $\delta(P_b)$ 17.4 ppm, $^1J(Rh2\text{–}P_b)$ 143.1 Hz, $^2J(Rh1\text{–}P_b)$ 29.3 Hz, $^3J(P_c\text{–}P_b)$ 19.2 Hz; $\delta(P_c)$ 12.1 ppm, $^1J(Rh1\text{–}P_c)$ 134.3 Hz, $^2J(Rh2\text{–}P_c)$ 17.7 Hz. ^1H NMR spectrum: 1.10 (1H, CH_2, s), 1.14 (3H, CH_3, s), 1.16 (3H, CH_3, s), 1.48 (1H, CH_2, s), 5.24 (2H, CH_2Cl_2), 5.8–8.2 (39H, aromatics, m) ppm. $^{13}C\{^1H\}$ NMR spectrum: −5.2 (CH_2, metalated, m), 22.2 (CH_3, s), 22.9 (CH_3, s), 53.4 (CH_2, CH_2Cl_2, s), 120.5–145.9 (aromatics, m), 162.4 (aromatic, metalated, m), 178.1 (OCO, s), 178.3 (OCO, s) ppm. *Anal.* Calc. for $C_{55}H_{51}Cl_4O_4P_3Rh_2$: C, 54.30; H, 4.22. Found: C, 54.83; H, 4.40%.

2.3. *Synthesis of $Rh_2(\mu^2\text{-}O_2CCH_3)_2[\mu^2\text{-}(C_6H_4)PMePh][\mu^2\text{-}(C_6H_4)PPh_2]\cdot(HO_2CCH_3)_2$ (3)*

1 (100 mg, 0.14 mmol) and PPh_3 (37 mg, 0.14 mmol) were dissolved in $CHCl_3$ under argon atmosphere. The resulting brown-red solution was stirred for 6 h at room temperature and the solvent was removed under reduced pressure. The crude solid was transferred to a column for column chromatography with silica gel. Elution with CH_2Cl_2:hexane:acetone (10:10:2) separated a minor yellow band containing compound **2** (10%). Further elution with CH_2Cl_2:hexane:acetone (10:10:10) produced the separation of a major red band, which was collected. The solvent was removed under vacuum and the crude solid containing **3** was precipitated in a mixture of CH_2Cl_2:hexane:acetic acid (52% yield). Spectroscopic data of **3**: $^{31}P\{^1H\}$ NMR: $\delta(P_a)$ 24.4 ppm, $^1J(Rh1\text{–}P_a)$ 150.0 Hz, $^2J(Rh2\text{–}P_a)$ 6.0 Hz; $\delta(P_b)$ 5.8 ppm, $^1J(Rh1\text{–}P_b)$ 145 Hz, $^2J(Rh2\text{–}P_b)$ 6.4 Hz, $^2J(P_a\text{–}P_b)$ 42 Hz. ^1H NMR: 0.85 (3H, CH_3, s), 1.27 (3H, CH_3, d, $^1J(H\text{–}P)$ 15 Hz), 1.63 (3H, CH_3, s), 2.11 (6H, CH_3, s), 6.2–8.1 (23H, aromatics, m) ppm. $^{13}C\{^1H\}$ NMR: 14.2 (CH_3, s), 22.8

(CH_3, s), 23.4 (CH_3, d, ^1J(P–C) 32 Hz), 29.9 (CH_3, s), 127–145 (aromatics, m), 161.8 (metalated C, m), 163.6 (metalated C, m), 181.7 (OCO, s), 182.6 (OCO, s), 182.8 (OCO, s) ppm. *Anal.* Calc. for $C_{39}H_{40}O_8P_2Rh_2$: C, 51.78; H, 4.45. Found: C, 51.12; H, 4.71%.

2.4. *Study of the evolution of* ***1.P₂***

1 (30 mg, 0.042 mmol) and PPh_3 (22 mg, 0.084 mmol) were introduced in an NMR tube and the mixture was dissolved with 0.6 ml of $CDCl_3$ at −60 °C. The tube was introduced in the NMR probe and ^{31}P NMR spectra were recorded every 10 °C between −60 and 0 °C, the sample being left each time for about 15 min for the temperature to equilibrate. ^{31}P NMR spectra were recorded at 10 °C every ten minutes.

2.5. *H/D exchange in compound 1*

1 (30 mg, 0.042 mmol) was introduced in an NMR tube and dissolved in 0.6 ml of a mixture of $CDCl_3$:CD_3CO_2D (1:2). The NMR tube was equilibrated at 60 °C and the spectra were recorded first every hour and later on every twelve hours. The signal at 2.11 ppm (5 methyl groups resulting from substitution of acetate groups in **1**) was taken as an internal reference to quantify the disappearance of the signals due to the methyl and the *ortho* phenyl protons of the metalated phosphine.

2.6. *X-ray crystallography*

A well-formed yellow crystal of compound **2** was used for the structure determination. A Nonius CAD4 single-crystal diffractometer was used ($\lambda = 0.71073$ Å). Unit cell dimensions were determined from the angular settings of 25 reflections within the range 15–25°. The space group $P2_1/c$ was determined from systematic absences and after a careful Laue check on some strong reflections. 9712 reflections were collected in the *hkl* range −23 to 23, 0 to 18 and 0 to 20, theta limits ($0° < \theta < 25°$); ω–2θ scan technique with a variable scan rate and a maximum scan time of 60 s per reflection. The intensity was checked throughout the data collection by monitoring three standard reflections every 60 min. Profile analysis was performed on all reflections [14,15]. Some double measured reflections were averaged, $R_{int} = \Sigma(|I| - <I>)/\Sigma I = 0.054$, 8988 unique reflections and 4749 'observed' with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values. The structure was solved by Patterson using the program SHELX86 [16] and expanded by DIRDIF [17]. Isotropic least-squares refinement using SHELX76 [18,19] converged to $R = 0.061$. Semiempirical and empirical absorption corrections were applied [20]. Positional parameters and anisotropic thermal parameters of the nonhydrogen atoms were refined. All hydrogen atoms were refined isotropically riding on their parent atoms from their idealized geometrical positions, with a common thermal parameter. The final conventional agreement factors were $R = 0.061$ and $R_w = 0.061$ for the 4749 'observed' reflections and 500 variables. The final difference Fourier map showed no peaks higher than 1.8 e Å^{-3} or deeper than −0.9 e Å^{-3}. Atomic scattering factors were taken from the 1974 *International Tables for X-ray Crystallography* [21]. Geometrical calculations were made with PARST [22]. Drawings were made using the Pluto program. All calculations were made on a MicroVax 3400 at the Scientific Computer Center, University of Oviedo. The crystallographic parameters and the remaining experimental details for the structure are collected in Table 1.

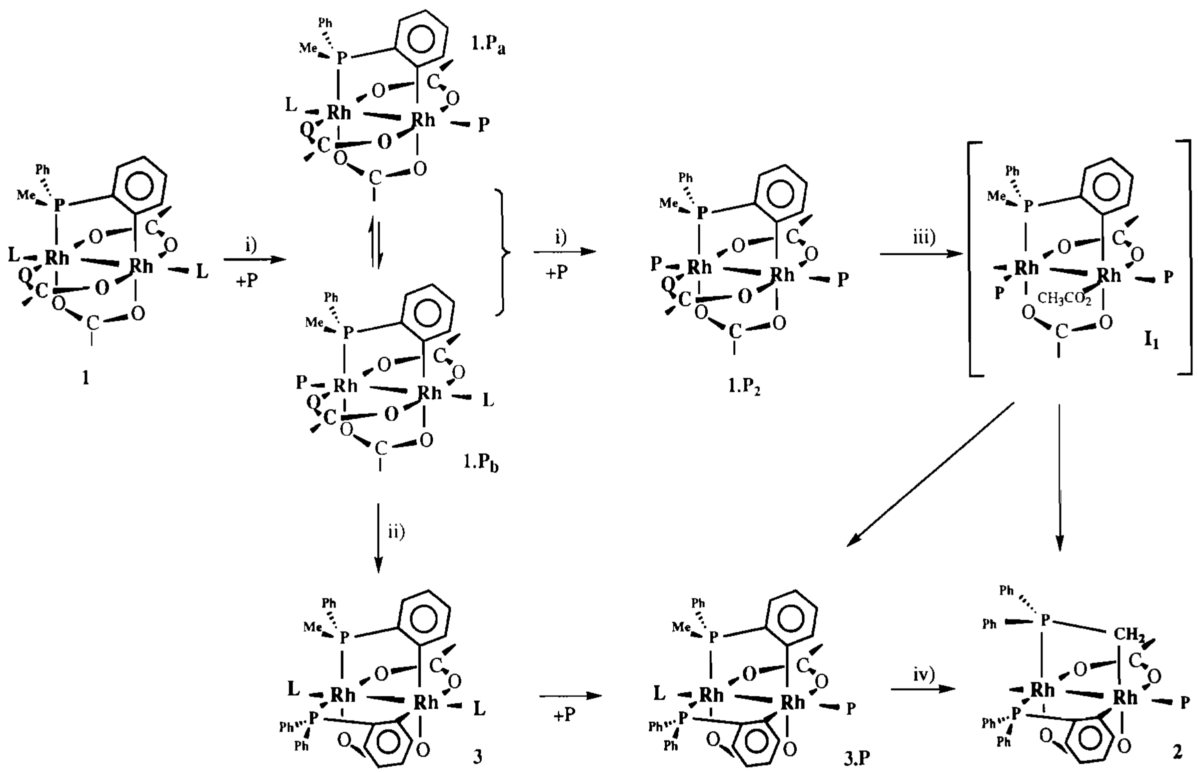
Table 1
Crystallographic data for $[Rh_2(O_2CCH_3)_2\{(CH_2)PPh_2\}\{(C_6H_4)PPh_2\}(PPh_3)] \cdot 2CH_2Cl_2$

Formula	$C_{53}H_{47}O_4P_3Rh_2 \cdot 2CH_2Cl_2$
Formula weight	1216.55
Space group	$P2_1/c$
a (Å)	19.930 (8)
b (Å)	15.29(2)
c (Å)	16.84(2)
β (°)	90.14(9)
V (Å^3)	5129(9)
Z	4
F(000)	2464
$D_{calc.}$ (mg m^{-3})	1.58
Crystal size (mm)	0.23 × 0.23 × 0.13
μ (Mo Kα) (cm^{-1})	9.80
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temp. (K)	200
No. unique data	8988
Total with $I > 3\sigma(I)$	4749
No. parameters	605
R [a] (for some double measurements)	0.054
R' [b]	0.061
R_w [c]	0.061

[a] $R = \Sigma(I - <I>)/\Sigma I$.
[b] $R' = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[c] $R_w = \Sigma w(|F_o| - |F_c|)/\Sigma w|F_o|$.

3. Results

We have studied the reactivity of **1**, in $CHCl_3$ solution, with triphenylphosphine by ^{31}P NMR spectroscopy. The spectrum of the solution (molar ratio P:Rh_2 = 1) at −40 °C shows the presence of two species in equilibrium, which we label **1.P$_a$** and **1.P$_b$** (Scheme 1). The spectroscopic data for these compounds are given in Table 2. We propose for the species **1.P$_a$** the structure with the phosphine coordinated at the less sterically hindered



Scheme 1. Proposed reaction pathways, $CHCl_3$ solution. (i) −40 °C; (ii) 6 h at r.t.; (iii) 10 °C; (iv) 24 h at r.t. P = PPh_3; L = CH_3CO_2H.

Table 2
Spectroscopic data for the compounds (shifts in ppm, coupling constants in Hz)

Compound	δP	(^1J(Rh–P); ^2J(Rh–P))	δP′	(^1J(Rh–P′); ^2J(Rh–P′))	δP″	(^1J(Rh–P″); ^2J(Rh–P″))	J(P–P′)	J(P–P″)	J(P′–P″)
1.P$_a$	3.9	(140.1; 4.8)	−49.2	(76.5; 51.2)			4.7		
1.P$_b$	16.8	(154.3; −[a])	−14.9	(108.0; 25.3)			9.0		
1.P$_2$	17.9	(149.3; −[a])	−1.5	(95.1; −[a])	−16.5	(66.5; 17.8)	−[a]	−[a]	287.3
2	35.8	(154.3; −[a])	17.4	(143.1; 29.3)	12.1	(134.3; 17.7)	8.6	36.5	19.2
3	24.4	(150.0; 6.0)	5.8	(145.3; 6.4)			42.0		
3.P	31.2	(153.9; −[a])	7.3	(151.2; −[a])	3.7	(81.7; 19.9)	46.5	5.9	5.9

[a] The coupling is not observed.

axial site of the rhodium dimer, while in **1.P$_b$** the axial phosphine is bonded to the other rhodium atom. Other possible assignments for this species have been ruled out based on some labelling experiments [12]. The relative ratio [**1.P$_a$**]/[**1.P$_b$**] reversibly changes from 0.3 to 1.5 in the temperature range −60 to 0 °C.

If one additional mole of triphenylphosphine is added to this mixture (molar ratio P:Rh_2 = 2), the bis-adduct species $Rh_2(\mu^2\text{-}O_2CCH_3)_3[\mu^2\text{-}(C_6H_4)PMePh]\cdot(PPh_3)_2$ (**1.P$_2$**) is quantitatively formed, according to the ^{31}P NMR spectrum recorded at −40 °C. Three separate P signals are observed: a simple doublet at $\delta_1 = 17.9$ ppm and the two axial phosphines forming an *AB* path with the Rh couplings at $\delta_2 = -1.5$ and $\delta_3 = -16.5$ ppm (Table 2). At higher temperature (0 °C) the signals due to the axial phosphines become broad, losing the ^1J(Rh–P) and ^3J(P–P′) coupling, while the resonance due to the metalated $PMePh_2$ remains sharp.

This solution undergoes chemical reaction at room temperature. The spectroscopic data indicate that this reaction is completed in ca. 2 h. The ^{31}P NMR spectrum of this reaction mixture shows three main blocks of signals of equal intensity at 35.8, 17.4 and 12.1 ppm. A yellow crystalline compound, $Rh_2(\mu^2\text{-}O_2CCH_3)_3[\mu^2\text{-}(CH_2)PPh_2][\mu^2\text{-}(C_6H_4)PPh_2]\cdot PPh_3$ (**2**), is isolated in moderate yield from this reaction mixture. Its ^{31}P NMR spectrum has the same three resonances observed in the reaction mixture, indicating that no chemical evolution was produced during the manipulation.

1 also reacts in a similar way with two moles of $P(p\text{-}CH_3C_6H_4)_3$, yielding the compound $Rh_2(\mu^2\text{-}O_2CCH_3)_2[\mu^2\text{-}(CH_2)PPh_2][\mu^2\text{-}(CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2]$-

$[P(p\text{-}CH_3C_6H_4)_3]$, which according to the spectroscopic data must have a molecular structure analogous to that of compound **2**.

When the mixture of **1.P$_a$** and **1.P$_b$** in chloroform is warmed to 25 °C, $Rh_2(\mu^2\text{-}O_2CCH_3)_3[\mu^2\text{-}(C_6H_4)PMePh][\mu^2\text{-}(C_6H_4)PPh_2]\cdot(HO_2CCH_3)_2$ (**3**), a doubly metalated compound with an H–H structure, is formed, together with small amounts of **2**. The reaction is complete after 6 h. Compound **3** could be obtained as a mixture of two isomers (with the methyl group attached to the phosphine in an *endo* or *exo* configuration relative to the dihedral angle formed by the two metalated ligands). The observation of very sharp resonances in the ^{31}P NMR spectra suggests that the reaction is regioselective and only one of the two possible isomers (we propose the less sterically crowded one) is formed. Compound **3** reacts with one additional mole of triphenylphosphine to give the adduct **3.P$_a$**. The ^{31}P NMR spectrum of this adduct shows a doublet of doublets of triplets, diagnostic for an axial phosphine in a doubly metalated compound with the H–H configuration. The structural characterization of a previous compound with a similar structure supports the assignment [8(b)]. In $CHCl_3$ solution at 25 °C compound **3** reacts with PPh_3 in 24 h, giving **2** with important amounts of other unidentified compounds.

3.1. The chemical reaction

We have spectroscopically observed that **1** reacts with triphenylphosphine, yielding in solution the two phosphine mono-adducts **1.P$_a$** and **1.P$_b$**. Up to now, only adducts structurally analogous to **1.P$_a$** had been isolated [5(d)], and the formation of the adduct **1.P$_b$** was considered much less favorable owing to steric reasons. The spectroscopic data reported here confirm that at low temperature (−40 °C) both phosphine adducts are in equilibrium, with **1.P$_b$** being the major product. The **1.P$_a$**/**1.P$_b$** ratio increases with increasing temperature in a reversible and reproducible way. At room temperature the phosphine dissociation is fast and the signals due to the axial phosphines are very broad.

We have found similar equilibria between phosphine adducts for other monometalated dirhodium compounds. However, very bulky phosphines (PCy_3) form only one phosphine mono-adduct in the temperature range −60 to +40 °C.

Some experiments have been performed to support the assignment of the resonance at −50 ppm to the axial phosphine in **1.P$_b$**. Both sets of signals due to **1.P$_a$** and **1.P$_b$** disappear at the same time upon stepwise addition of one mole of triphenylphosphine, with formation of the bis-adduct **1.P$_2$**, which is unambiguously characterized by ^{31}P NMR. Also, an equimolar mixture of **1.P$_2$** and **1** gives the same spectrum as the mixture of isomers **1.P$_a$** and **1.P$_b$**.

Another remarkable result is the formation of the doubly metalated compound with the H–H configuration by reaction of **1** and triphenylphosphine (1:1 molar ratio). Up to now compounds with the H–H configuration had never been obtained using stoichiometric amounts of phosphine, and their preparation required an excess of phosphine ($P{:}Rh_2 \geq 2$). Previous kinetic studies [9] of the metalation reaction in this type of compound confirmed that the reaction occurs by slow migration of the axial phosphine to an equatorial coordination, followed by a fast proton transfer process. In the present case, for $P{:}Rh_2 = 1$, the axial-to-equatorial migration of the phosphine must be favored in the adduct **1.P$_b$**.

The formation of **2** by reaction of **1** with two moles of phosphine involves an unusual rearrangement of the metalated phosphine $PMePh_2$. We have monitored this reaction by ^{31}P NMR. Below 0 °C the observed spectrum was consistent with the presence of only **1.P$_2$** in solution. No evolution was observed for 30 min. After 30 min at 10 °C the signals of the **1.P$_2$** adduct had disappeared and three major sets of signals of equal intensity, centered at 39.5, 7.6 and 0.3 ppm, appeared in the spectrum, together with resonances due to compounds **2** and **3.P**. At higher temperature this intermediate species rapidly evolves to **2** and **3.P**, which can be separated. The fact that **3.P** generates **2** in low yield only after long standing in solution at room temperature (ca. 24 h) confirms that **3.P** is not the kinetic product in the formation of **2** starting from **1.P$_2$**.

These results are best rationalized assuming the formation of an intermediate **I$_1$** (Scheme 1) generated by axial-to-equatorial migration of one phosphine in the bis-adduct **1.P$_2$**. The proposed structure for this intermediate is consistent with the ^{31}P NMR data and also with the formation of **3.P** from this intermediate. A more complex process has to occur for the formation of compound **2**, involving not only metalation of the equatorial PPh_3 but also the rearrangement of the metalated $PMePh_2$ ligand. Such rearrangement requires cleavage of the rhodium–aromatic carbon bond and further metalation at the CH_3 group of the phosphine.

There are some experimental data supporting the feasibility of this rearrangement. Selective H/D exchange at the *ortho* aromatic positions occurs when compounds with metalated triphenylphosphine are dissolved in CD_3CO_2D or CF_3CO_2D under relatively mild conditions [5(c),11]. This exchange has been explained by accepting that demetalation and metalation processes occur in a reversible way. In order to confirm whether aliphatic C–H bonds in $PMePh_2$ can also be activated, we performed additional exchange experiments. Compound **1** was dissolved in a 1:2 mixture of $CDCl_3{:}CD_3CO_2D$ and was kept at 45 °C for three weeks under argon. The occurrence of H/D exchange was confirmed by ^1H NMR spectroscopy, both at the CH_3 protons and at the *ortho* protons of the aromatic rings of the phosphine to a similar extent (ca. 35%).

This result confirms that the rearrangement of the metalated $PMePh_2$ is not a difficult process, and supports the reaction pathway proposed to explain the metalation at the CH_3 group.

3.2. Crystal structure of $Rh_2(\mu^2\text{-}O_2CCH_3)_2[\mu^2\text{-}(CH_2)PPh_2][\mu^2\text{-}(C_6H_4)PMePh]\cdot(HO_2CCH_3)_2$

A view of the molecular structure of compound **2** is shown in Fig 2. Important bond distances and angles are given in Table 3. The structure consists of discrete dinuclear rhodium units, with a single bond linking the two metal centers (Rh–Rh bond distance 2.532(2) Å), and four bridging groups: two acetate ligands, one metalated triphenylphosphine and one metalated methyldiphenylphosphine. Both phosphines are in a head-to-head configuration. Another molecule of PPh_3 coordinates at the less sterically hindered axial position.

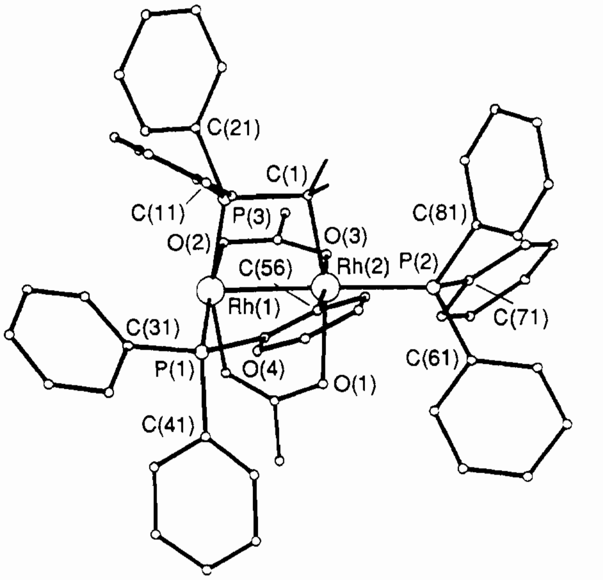


Fig. 2. Molecular structure of compound **2**, with atomic numbering.

Table 3
Selected bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses for compound **2**

Rh(1)–Rh(2)	2.532(2)	Rh(1)–P(1)	2.211(4)
Rh(1)–P(3)	2.240(4)	Rh(1)–O(4)	2.117(9)
Rh(1)–O(2)	2.111(9)	Rh(2)–P(2)	2.297(4)
Rh(2)–O(1)	2.228(9)	Rh(2)–O(3)	2.169(9)
Rh(2)–C(1)	2.06(1)	Rh(2)–C(56)	2.05(1)
P(1)–Rh(1)–Rh(2)	87.7(1)	P(3)–Rh(1)–Rh(2)	76.1(1)
P(3)–Rh(1)–P(1)	97.6(1)	O(4)–Rh(1)–Rh(2)	88.1(3)
O(4)–Rh(1)–P(1)	89.7(3)	O(4)–Rh(1)–P(3)	162.2(3)
O(2)–Rh(1)–Rh(2)	90.4(3)	O(2)–Rh(1)–P(1)	172.8(3)
O(2)–Rh(1)–P(3)	88.7(3)	O(2)–Rh(1)–O(4)	83.3(4)
P(2)–Rh(2)–Rh(1)	169.5(1)	O(1)–Rh(2)–Rh(1)	83.1(3)
O(1)–Rh(2)–P(2)	91.1(3)	O(3)–Rh(2)–Rh(1)	81.5(3)
O(3)–Rh(2)–P(2)	89.2(3)	O(3)–Rh(2)–O(1)	84.2(3)
C(1)–Rh(2)–Rh(1)	84.3(3)	C(1)–Rh(2)–P(2)	100.5(3)
C(1)–Rh(2)–O(1)	166.4(4)	C(1)–Rh(2)–O(3)	88.9(5)
C(56)–Rh(2)–Rh(1)	94.6(4)	C(56)–Rh(2)–P(2)	95.2(4)
C(56)–Rh(2)–O(1)	100.9(4)	C(56)–Rh(2)–O(3)	173.2(4)
C(56)–Rh(2)–C(1)	85.2(5)		

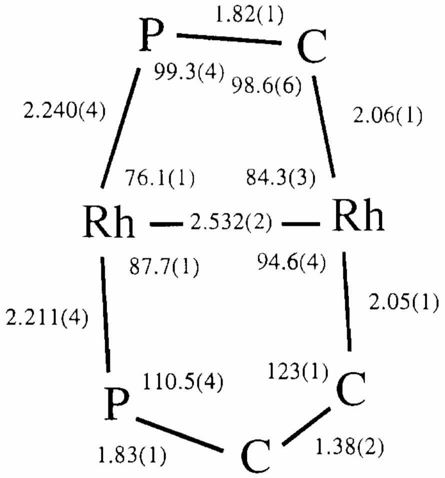


Fig. 3. Schematic representation of some bond angles and distances in metallocycles of compound **2**.

The Rh–P bond distances for the two metalated phosphines (2.211(4) and 2.240(4) Å) are shorter than the observed values (2.493(1) and 2.511(1) Å) for other doubly metalated compounds with a head-to-head configuration [4]. The axial Rh–P bond distance is remarkably short (2.297(4) Å) if we compare it with values reported for other triphenylphosphine bis-adducts of rhodium(II) compounds (2.4771(5) Å [23], 2.560(2) Å [6(b)]). A longer axial Rh–P bond distance (2.455(1) Å) has also been observed for the mono-adducts $Rh_2(\mu^2\text{-}O_2CCH_3)_3[P(o\text{-}CH_3C_6H_4)Ph_2]$ [24]. This short Rh–P distance observed in **2** is in good agreement with the low lability observed for the axial ligand in this compound. The Rh–O bond distances are within the range of values observed for other doubly metalated dirhodium compounds with the same configuration [4].

The most relevant feature in this structure is the fact that the $PMePh_2$ ligand is metalated at the Me group, forming a four-membered Rh–P–C–Rh metallocycle. Fig. 3 gives the bond distances and angles for the four- and five-membered metallocycles in compound **2**, showing the important distortion associated with the four-membered ring.

Several monophosphino-methanide metal complexes showing different coordination modes have been reported in the literature [25]. Diiron complexes with $RR'PCH_2$ ligands bridging the two metal atoms have been reported [26]. In this case the $RR'PCH_2$ group was generated by thermal phosphorus–carbon bond cleavage in diphosphine bridged diiron derivatives rather than by C–H activation.

4. Supplementary material

Additional material is available from the Cambridge Crystallographic Data Centre and includes H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

Acknowledgements

We thank the DGICYT for financial support.

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