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Preliminary Communication

Selective *ortho*-metallation reaction of the phosphine $P(o\text{-ClC}_6\text{H}_4)\text{Ph}_2$. Synthesis and crystal structure of $[\text{Rh}_2(\mu\text{-O}_2\text{CCH}_3)_3\{\mu\text{-}(\text{ClC}_6\text{H}_3)\text{PPh}_2\}(\text{OH}_2)_2] \cdot \text{CHCl}_3$

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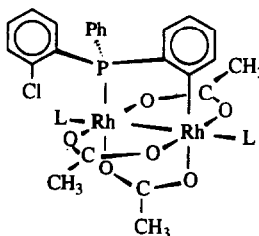
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Abstract

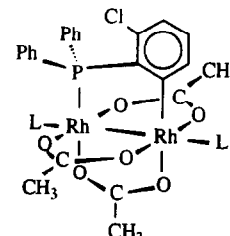
From the reaction of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{MeOH})_2]$ in hot acetic acid with $P(o\text{-ClC}_6\text{H}_4)\text{Ph}_2$, two monometallated compounds $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3\{(\text{C}_6\text{H}_4)\text{P}(o\text{-ClC}_6\text{H}_4)\text{Ph}\}(\text{HO}_2\text{CCH}_3)_2]$ (**1**), already described, and $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3\{(\text{ClC}_6\text{H}_3)\text{PPh}_2\}(\text{OH}_2)_2]$ have been isolated. The new compound has been characterized by an X-ray study. It crystallizes in the triclinic space group $P\bar{1}$. It contains three acetate groups bridging a Rh_2^{4+} unit that has a Rh–Rh bond distance of 2.426(1) Å; the fourth bridging ligand is derived from one $P(o\text{-ClC}_6\text{H}_4)\text{Ph}_2$ metallated in the halogenated ring. The two water molecules occupy the axial coordination sites.

In the course of our investigations of *ortho*-metallation reactions in binuclear dirhodium(II) compounds we have found that the orthohaloarylphosphines, such as $P(o\text{-BrC}_6\text{F}_4)\text{Ph}_2$ [**1**] and $P(o\text{-ClC}_6\text{H}_4)\text{Ph}_2$ [**2**] are considerably less reactive than triphenylphosphine [**3**], allowing the isolation of interesting reaction intermediates. In particular, $P(o\text{-ClC}_6\text{H}_4)\text{Ph}_2$ has two types of *ortho*-carbon–hydrogen bonds where the metallation can occur, the four in the phenyl rings and the one in the substituted ring. Only the compound $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3\{(\text{C}_6\text{H}_4)\text{P}(o\text{-ClC}_6\text{H}_4)\text{Ph}\}(\text{HO}_2\text{CCH}_3)_2]$,

metallated in an unsubstituted phenyl ring, has been prepared and structurally characterized by X-ray methods [**2b**]. This communication reports the preparation and crystal structure of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3\{(\text{ClC}_6\text{H}_3)\text{PPh}_2\}(\text{H}_2\text{O})_2]$ (**2**), showing that *ortho*-metallation in the substituted phenyl ring has occurred.



L = $\text{CH}_3\text{CO}_2\text{H}$ (**1**)



L = H_2O (**3**)

L = $\text{CH}_3\text{CO}_2\text{H}$ (**2**)

The reaction of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2]$ in hot acetic acid with $P(o\text{-ClC}_6\text{H}_4)\text{Ph}_2$ (1 : 1 molar ratio) for 3 h gave a mixture of **1**, already described [**2**], and $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3\{(\text{ClC}_6\text{H}_3)\text{PPh}_2\}(\text{HO}_2\text{CCH}_3)_2]$ (**2**).

The mixture was separated by column chromatography using acetone:hexane (1:2) as eluent; in these conditions the axial molecules of acetic acid are replaced by water and **3** was obtained in 45% yield. Recrystallization from a mixture of dichloromethane–acetic acid–hexane regenerated the acetic acid adduct **2** again. For solubility reasons this compound is more suitable for spectroscopic studies. The ^1H and ^{13}C NMR spectra* of this adduct are more simple than those of compound **1**, consistent with the presence of a symmetry plane along the Rh–Rh bond. The ^{31}P NMR spectrum shows a resonance at 19.19 ppm ($^1J(\text{RhP})$ 147 Hz, $^2J(\text{RhP})$ 6 Hz). These spectroscopic values are similar to those observed for other monometallated compounds [**2,3b**].

* ^1H NMR spectrum (CDCl_3): δ (ppm) 2.30 (CH_3 , s, 3H), 2.19 (CH_3 , s, 6H), 1.31 (CH_3 , s, 6H), 8.7–6.8 (aromatic CH, m, 13H). ^{13}C NMR spectrum (CDCl_3): δ (ppm) 23.8 (CH_3 , s), 23.2 (CH_3 , s), 21.5 (CH_3 , s), 189.7 (OCO, s), 182.7 (OCO, s), 179.0 (OCO, s), 141–124 (aromatic C, m).

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Single crystals suitable for X-ray measurements were obtained for **3** **. The structure represented in Fig. 1 consists of a Rh_2^{4+} unit bridged by three acetate groups and a $P(o\text{-ClC}_6\text{H}_4)_2\text{Ph}_2$ phosphine ortho-metallated in the substituted ring. The Rh–Rh distance is 2.426(1) Å, slightly longer than in **1** (2.410(1) Å). However, in **1** the axial ligands are molecules of acetic acid. As expected, the Rh–O bond *trans* to the carbon atom, is longer (2.216(2) Å), than that *trans* to the P atom (2.155(2) Å), and both are significantly longer than the other four Rh–O bonds involving acetate ligands (in the range 2.037(2)–2.062(2) Å).

The use of acetic acid is required in order to obtain compound **2**. Non protic solvents such as toluene produce compound **1** in moderate yield together with $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3\{\{\eta^2\text{-P}(o\text{-ClC}_6\text{H}_4)_2\text{Ph}_2\}\}(\eta^2\text{-P}(o\text{-ClC}_6\text{H}_4)_2\text{Ph}_2)]$, already described [2], and some unreacted $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$. If the reaction is performed in acetic acid:toluene (1:3) only compound **1** is obtained. In pure boiling acetic acid, **1** slowly isomerizes to give some **2**. It is not yet completely clear if in the experimental conditions used **2** is formed only by isomerization or also by direct metallation.

Further studies of the reactivity of this new metallated species are in progress.

Acknowledgment

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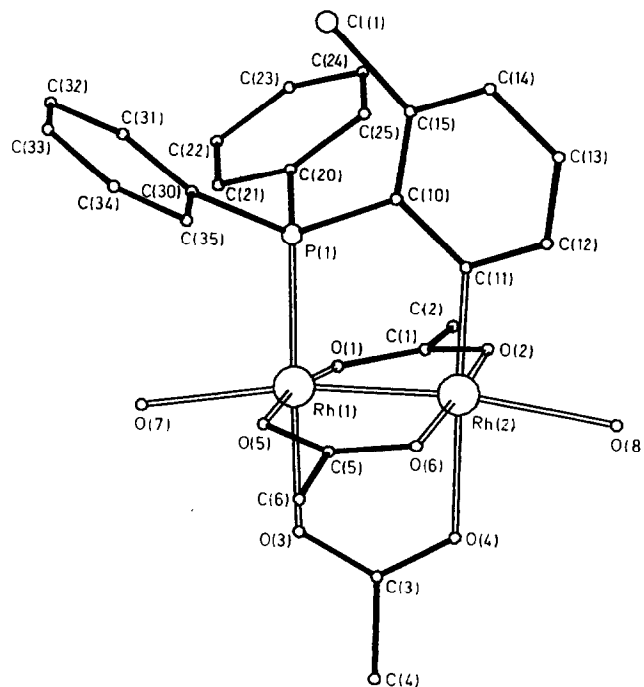


Fig. 1. A PLUTO [4] view of the complex $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3\{\{\text{C}_6\text{H}_4\text{Ph}_2\}(\text{OH}_2)_2\} \cdot \text{CHCl}_3$, **3**, with the atomic numbering scheme. Selected bond distances (Å) and angles ($^\circ$): Rh(1)–Rh(2) 2.426(1), Rh(1)–P(1) 2.214(1), Rh(1)–O(1) 2.039(2), Rh(1)–O(3) 2.155(2), Rh(1)–O(5) 2.061(2), Rh(1)–O(7) 2.325(2), Rh(2)–C(11) 1.979(4), Rh(2)–O(2) 2.032(2), Rh(2)–O(4) 2.216(2), Rh(2)–O(6) 2.062(2), Rh(2)–O(8) 2.318(2), Rh(1)–Rh(2)–O(8) 166.8(1), Rh(2)–Rh(1)–O(7) 169.6(1), O(1)–Rh(1)–O(5) 171.6(1), P(1)–Rh(1)–O(3) 178.3(1), O(4)–Rh(2)–C(11) 176.4(1), O(2)–Rh(2)–O(6) 173.9(1).

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**Crystal data: $\text{C}_{24}\text{H}_{26}\text{ClO}_8\text{PRh}_2 \cdot \text{CHCl}_3$, $M = 834.08$, triclinic, space group $P\bar{1}$, $a = 14.707(6)$, $b = 12.272(8)$, $c = 9.532(5)$ Å, $\alpha = 110.41(5)$, $\beta = 75.06(7)$, $\gamma = 96.52(6)^\circ$, $V = 1557(2)$ Å³, $Z = 2$, $D_c = 1.78$ g cm⁻³; $F(000) = 828$, $\mu(\text{Mo K}\alpha) = 14.83$ cm⁻¹; $T = 293$ K. Red crystal, $0.33 \times 0.20 \times 0.10$ mm size. The intensities of 5442 independent reflections were collected on an Enraf Nonius CAD4 diffractometer with $0^\circ < \theta < 30^\circ$ using Mo K α radiation and ω - 2θ scan technique. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 4574 observed reflections (having $I > 3\sigma(I)$) to the final conventional R value of 0.025.

The atomic coordinates for this work and a complete set of bond lengths and angles have been deposited at Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Any request should be accompanied by the full literature citation.