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Preliminary communication

Fast orthometalation reactions at a binuclear dirhodium(II) complex. Synthesis, crystal structure and reactivity of $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2] \cdot (HO_2CCH_3)_2$

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Abstract

From the reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$, in hot acetic acid with PPh_3 the monometalated intermediate $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)_2$ has been isolated and characterized by an X-ray study. This compound rapidly reacts with an excess of PPh_3 in dichloromethane at room temperature to give $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2(PPh_3)_2$ with a head-to-tail structure. The same procedure at higher temperatures gives a mixture of this compound and another doubly metalated compound with a head-to-head structure.

After the report of the preparation of $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2 \cdot (HO_2CCH_3)_2$ by the thermal reaction of $Rh_2(O_2CCH_3)_4 \cdot (MeOH)_2$ and triphenylphosphine (1/2 molar ratio) in refluxing acetic acid [1], we investigated in detail the mechanistic aspects of this reaction. We isolated several monometalated intermediates as well as doubly metalated compounds in a similar reaction with orthohaloarylphosphines, such as $P(o\text{-}BrC_6F_4)Ph_2$[2] or $P(o\text{-}ClC_6H_4)Ph_2$ [3]. These intermediates provided mechanistic information about the metalation reaction and allowed us to suggest a general reaction scheme (Scheme 1).

A $^{31}P\{^1H\}$ NMR study of the reaction of dirhodium tetraacetate with PPh_3 allowed us to detect a short lived and correspondingly very reactive intermediate. These results prompted us to devise a synthesis of this intermediate to study its reactivity. This communication reports the high yield preparation and crystal structure of $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2] \cdot (HO_2CCH_3)_2$ (**1**) *, as well as some related reactions involving fast aromatic C–H activation in the presence of excess of PPh_3.

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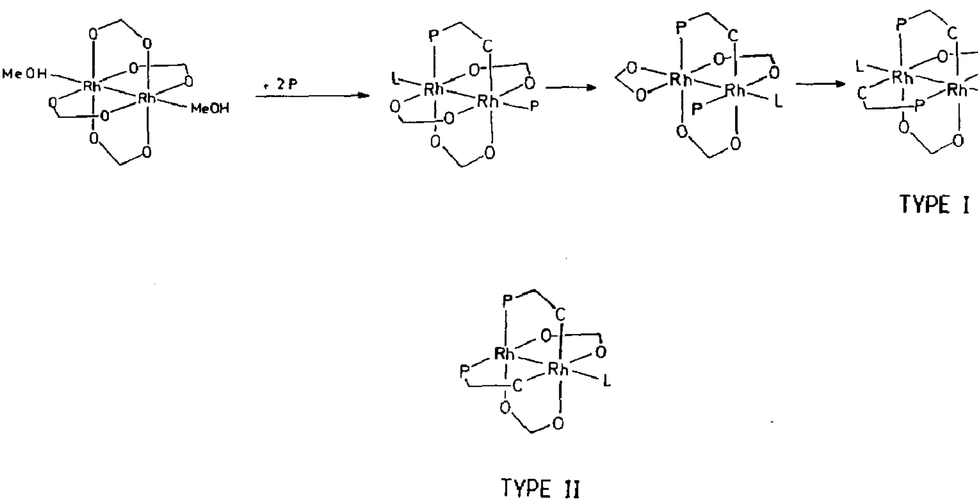

Scheme 1. L = Neutral axial ligand, P = triarylphosphine.

The reaction of $Rh_2(O_2CCH_3)_4 \cdot (MeOH)_2$, in hot acetic acid with PPh_3 (1/1 molar ratio) gave **1** in ca. 70% yield. Small amounts of $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2 \cdot (HO_2CCH_3)_2$ and unchanged dirhodium(II) tetraacetate were also detected in the reaction mixture.

The structure of **1**, represented in Fig. 1, shows it to be a binuclear complex in which the two Rh atoms are bridged by three acetate groups and a triphenylphosphine metalated in one phenyl ring. The Rh–Rh distance is rather short, 2.430(2) Å. Two oxygens of acetic acid occupy the axial coordination sites. The OH groups of these acetic acid molecules are bound to oxygen atoms of bridging acetate ligands through intramolecular hydrogen bonds (O(5)...O(8) 2.705(5) and O(6)...O(10) 2.586(6) Å; O(5)H(8)O(8) 168(8)°, O(6)H(10)O(10) 169(9)°). The bridge involving the metalated PPh_3 is nearly coplanar with an acetate bridge, and almost perpendicular to the other two acetate bridges (dihedral angles 4.9(1), 89.2(1) and 83.5(1)°, respectively). As expected the Rh–O bond *trans* to the carbon atom, 2.218(4) Å, is longer than that *trans* to the P atom, 2.163(3) Å, and both bonds are much longer than the other four involving acetate ligands (in the range 2.025(4)–2.073(4) Å).

It is noteworthy that compound **1** in dichloromethane at room-temperature readily reacts with an excess of PPh_3 to give $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2 \cdot (PPh_3)_2$. In stepwise addition of triphenylphosphine to **1** the intermediate $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2](HO_2CCH_3)(PPh_3)$ was first formed, and underwent

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* Crystal data: $C_{28}H_{31}O_{10}PRh_2$, $M = 764.33$, triclinic, space group $P\bar{1}$, $a = 9.807(6)$, $b = 19.822(10)$, $c = 8.476(5)$ Å, $\alpha = 80.10(2)$, $\beta = 111.02$, $\gamma = 93.67(2)°$, $U = 1515(2)$ Å^3, $Z = 2$, $D_c = 1.675$ g cm^{-3}; $F(000) = 768$, $\mu(\text{Mo-}K_\alpha) = 11.75$ cm^{-1}. The intensities of 5364 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3–25°) using the Nb-filtered Mo-K_α radiation and the $\theta/2\theta$ scan technique. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 3374 observed reflections (having $I > 2\sigma(I)$) to the R and R' values of 0.0289 and 0.0388, respectively.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation.

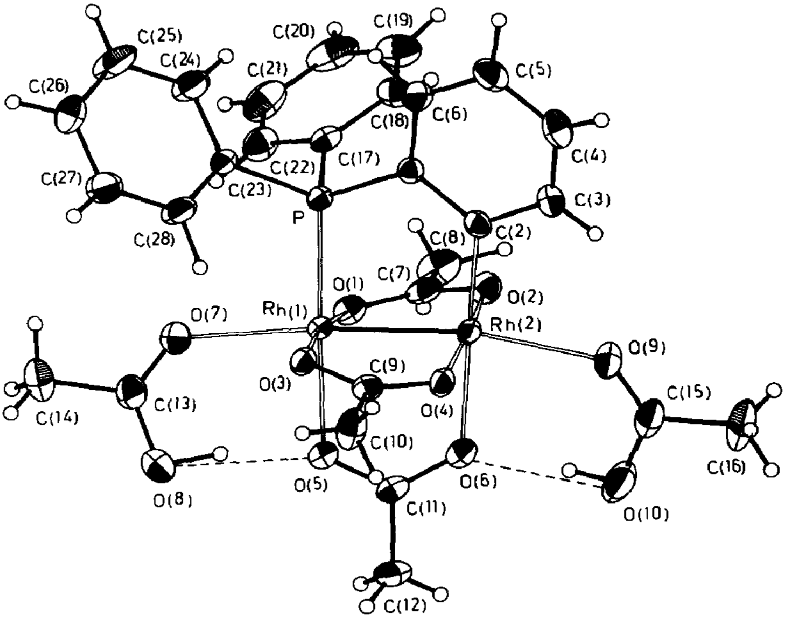

Fig. 1. A view of the complex $Rh_2(O_2CCH_3)_3[(C_6H_4)PPh_2]\cdot(HO_2CCH_3)_2$ (1) with the atomic numbering scheme. Important bond distances (Å) and angles (°): Rh(1)–Rh(2) 2.430(2), Rh(1)–P 2.206(2), Rh(2)–C(2) 1.999(5), Rh(1)–O(1) 2.025(4), Rh(1)–O(3) 2.073(4), Rh(1)–O(5) 2.163(3), Rh(1)–O(7) 2.336(4), Rh(2)–O(2) 2.034(4), Rh(2)–O(4) 2.045(4), Rh(2)–O(6) 2.218(40, Rh(2)–O(9) 2.301(4); P–Rh(1)–O(5) 178.5(2), O(1)–Rh(1)–O(3) 170.9(2), O(7)–Rh(1)–Rh(2) 174.4(1), Rh(1)–Rh(2)–O(9) 169.0(1), O(2)–Rh(2)–O(4) 173.8(2), C(2)–Rh(2)–O(6) 178.5(2).

orthometallation only at higher temperatures (e.g. in refluxing toluene). Addition of a second mol of phosphine results in the activation of the metallation process, which is complete in a few second.

Under both sets of conditions, **1** + one mole of PPh_3 in refluxing toluene or **1** + excess of PPh_3 at room temperature, the resulting $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2\cdot(PPh_3)_x$ has the head-to-tail structure (Type I) previously reported for this compound [1]. However fraction of **1** with an excess of PPh_3 in refluxing chloroform or toluene yielded a mixture of $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2\cdot(PPh_3)_2$, with a Type I structure and the related compound with a head-to-head structure (Type II). We identified this new compound by comparison of its $^{31}P\ \{^1H\}$ NMR data with those for the only reported example [3] of a compound with this type of structure. These two doubly metalated compounds are obtained in various ratios depending on the reaction conditions used, the Type I species always being the major product. All the available data indicate that the formation of the isomer with head-to-head structure is not due to the rearrangement of the one with a head-to-tail structure, but is formed simultaneously in the reaction at higher temperatures.

Further studies of the reactions of the monometallated species are in progress.

References

1 A.R. Chakravarty, F.A. Cotton, D.A. Tocher, J.H. Tocher, Organometallics, 4 (1985) 8.
2 F. Barceló, F.A. Cotton, P. Lahuerta, R. Llusar, M. Sanaú, W. Schwotzer, M.A. Ubeda, Organometallics, 5 (1986) 808.
3 F. Barceló, F.A. Cotton, P. Lahuerta, R. Llusar, J. Payá, M.A. Ubeda, Inorg. Chem., 27 (1988) 1010.