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# Selective reductive dimerization of phenylacetaldehyde to 2,4-diphenylbutanal catalysed by novel dirhodium complexes

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## Abstract

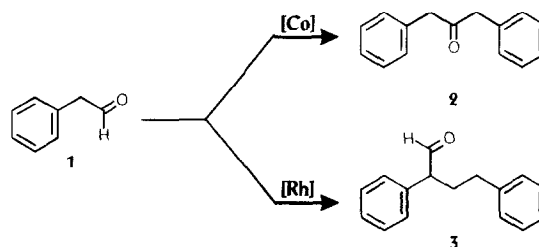
The selective dimerization of phenylacetaldehyde (**1**) into 2,4-diphenylbutanal (**3**) is catalysed by novel *ortho*-metallated dirhodium(II) compounds (**I–III**), in dry pyridine and under a pressure of carbon monoxide and hydrogen. Among the by-products, two other coupling products, 2,4-diphenylbutan-1-ol (**4**) and 2,4-diphenylbut-2-enal (**5**), as well as phenethyl alcohol (**6**) are present but in low amounts. A comparison with systems in which phosphines are added to dirhodium tetraacetate complex has been realised. When triphenylphosphine is used in a blank experiment, only 2,4-diphenylbut-2-enal (**5**) is produced with 38% yield and no aldehyde 2,4-diphenylbutanal (**3**) is formed. We have also checked that aldehyde **3** does not result from the hydrogenation of enal **5**. This report illustrates the first application of *ortho*-metallated dirhodium(II) compounds in organic catalysis.

**Keywords:** Coupling reactions; Dimerization; Dirhodium complexes; Phenylacetaldehyde; Reduction; Rhodium

## 1. Introduction

Some time ago, we reported two straightforward catalytic coupling reactions of aldehydes. The first reaction is catalysed by dicobaltoctacarbonyl and leads to the formation of symmetrical ketones [1]. In a typical reaction, 1,3-diphenyl-2-propanone (**2**) was obtained selectively from phenylacetaldehyde (**1**). The second reaction is catalysed by rhodium complexes, in particular the Wilkinson's catalyst ( $\text{RhCl}(\text{PPh}_3)_3$ ) and, under the same experimental conditions, phenylacetal-

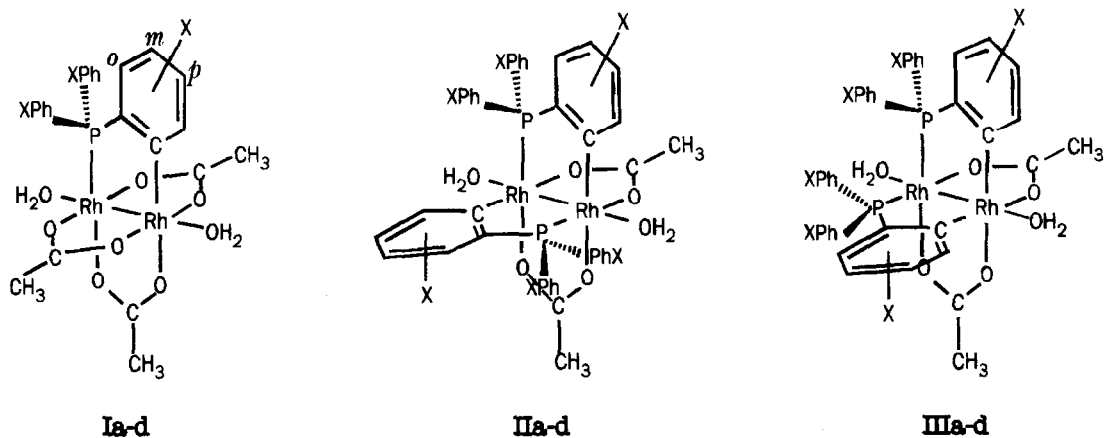
dehyde undergoes an aldol-type reaction yielding selectively a new aldehyde, 2,4-diphenylbutanal (**3**) (Eq. 1) [2].



A number of monometallic rhodium complexes have been tested for the selective reductive dimerization of phenylacetaldehyde to 2,4-diphenylbutanal [2]. The most efficient and selective

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Scheme 1. Structure of the *ortho*-metallated dirhodium(II) complexes.

catalytic systems are those containing at least one triphenylphosphine ligand in the coordination sphere of the catalyst (or catalyst precursor).

It is known that the selectivity of various catalytic reactions (i.e., the hydroformylation reaction [3]) can be controlled to some extent by using homo- (or hetero)bimetallic complexes. In order to modify the selectivity of the title reaction, we tested some *ortho*-metallated dirhodium(II) compounds (I–III) – whose use in organic catalysis has never been reported – bearing two different types of chelating ligands,  $\mu$ -acetato and *o*-metallated phosphines, respectively (Scheme 1). In fact, three main different structures are known for these complexes [4]: first, the monometallated (Ia–Id) in which the dirhodium unit is bridged by three acetate ligands and one phosphine ligand; next, the doubly metallated for which two configurations are possible: the head-to-tail (IIa–IId) and the head-to-head (IIIa–IIId).

## 2. Experimental

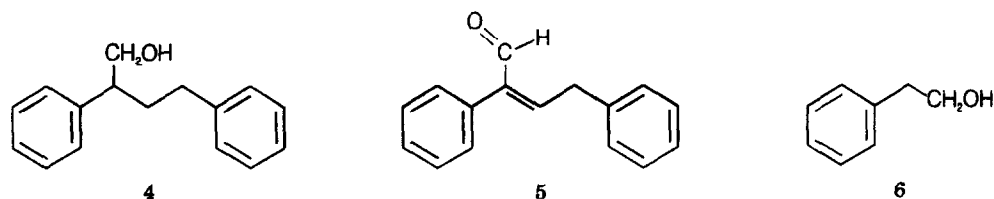
The phenylacetaldehyde was distilled before use and kept under nitrogen. Pyridine was distilled from and kept over KOH pellets under nitrogen. A typical procedure is illustrated hereafter for the synthesis of 2,4-diphenylbutanal (**3**) from phenylacetaldehyde (**1**): 0.065 mmol of a dirhodium complex and 20 mmol of **1** were dissolved in 10

ml of dry pyridine and this homogeneous solution was heated in a Pyrex jacketed stainless-steel autoclave for 12 h under 11 MPa of synthesis gas (CO:H<sub>2</sub> = 9:2). The reaction products were determined by comparison of their retention time on at least two different GC fused silica capillary columns (FID with nitrogen as carrier gas): a 30 m × 0.53 mm WCOT, CP-Sil8-CB, Chrompack and a 30 m × 0.32 mm WCOT, FFAP-CB (RSL).

**3** was identified as the main product. Some by-products were also obtained in varying amounts (Scheme 2); 2,4-diphenylbutan-1-ol (**4**) and phenethyl alcohol (**6**) are the hydrogenation products of **3** and **1**, respectively; 2,4-diphenylbut-2-enal (**5**) is the classical aldol condensation product. Unidentified heavier products resulting from multiple condensation account for the balance of the reaction. Some of our results are summarised in the Table 1.

## 3. Results and discussion

The behaviour of monometallated (Ia–Id) and doubly metallated dirhodium(II) complexes with a head-to-tail structure (IIa–IId) was very close. Indeed, 2,4-diphenylbutanal (**3**) was generally obtained with good yields (between 50 and 60%) and selectivities. In all cases, the two other coupling products (**4** and **5**) as well as phenethyl alcohol (**6**) were present in low amounts (Table



Scheme 2. By-products of the coupling reaction.

1 ( $\pm 3\%$ )). The most efficient catalysts (**Ic** and **IIc**) were those containing the *p*-methylphenylphosphine ligand. The results obtained with the monometallated *p*-chlorophenylphosphine complex (**Id**) were similar to those obtained with the *p*-methyl system (**Ic**) but the doubly metallated *p*-chlorophenylphosphine complex (**IIId**) was much less efficient than its analogues. It also appeared that the third class of *ortho*-metallated dirhodium(II) compounds i.e. those with a head-to-head configuration (**IIIa--IIIId**), was not so

efficient but, again, the best results were obtained with complex (**IIIc**) bearing two *p*-methylphenylphosphine ligands.

Blank experiments showed that, when the reaction was run in the presence of phenylacetaldehyde (**1**) and pyridine under syngas, aldehyde **3** was not formed; enal (**5**) was present in small amount (2%) and the conversion was very low (8%). The specificity of basic solvents, and more particularly of pyridine, has also been demonstrated [2,5]. Moreover, when triphenylphos-

Table 1  
Reductive coupling of phenylacetaldehyde (**1**) catalysed by dirhodium(II) complexes<sup>a</sup>

Catalyst	X	Conversion (%)	Yield (%) <sup>b</sup>			
			1	3	4	5
no catalyst		8	0	0	2	4
Ia	H	91	51	3	2	6
Ib	<i>m</i> -CH <sub>3</sub>	99	55	3.5	<1	4
Ic	<i>p</i> -CH <sub>3</sub>	90	58	<1	22	
Id	<i>p</i> -Cl	79	53.5	–	7	1
IIa	H	97	54	5	7	1
IIb	<i>m</i> -CH <sub>3</sub>	98	56	<1	2.5	3
IIc	<i>p</i> -CH <sub>3</sub>	>99	59	2	1.5	1
IIId	<i>p</i> -Cl	88	30	1.5	11	4
IIIa	H	97	24	5	6	–
IIIb	<i>m</i> -CH <sub>3</sub>	>99	26	1.5	7.5	4
IIIc	<i>p</i> -CH <sub>3</sub>	>99	46	<1	1.5	1.5
IIIId	<i>p</i> -Cl	99	26	15	2	8.5
Rh <sub>2</sub> (OAc) <sub>4</sub>		>99	<1	14	1	15
10 PPh <sub>3</sub>		81	3	<1	38	1.5
Rh <sub>2</sub> (OAc) <sub>4</sub> + 2 PPh <sub>3</sub>		92	57	<1	1	1
Rh <sub>2</sub> (OAc) <sub>4</sub> + 10 PPh <sub>3</sub>		93	47	–	–	4.5
Rh <sub>2</sub> (OAc) <sub>4</sub> + 20 PPh <sub>3</sub>		93	39	–	–	1.5
Rh <sub>2</sub> (OAc) <sub>4</sub> + 2 P( <i>m</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>		98	21	1.5	<1	2
Rh <sub>2</sub> (OAc) <sub>4</sub> + 2 P( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>		98	31	2.5	1	3
Rh <sub>2</sub> (OAc) <sub>4</sub> + 2 P( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>		70	47	4.5	9	1
Rh <sub>2</sub> (OOCCH <sub>3</sub> ) <sub>4</sub>		>99	<1	6	<1	28

<sup>a</sup> Reaction conditions:  $6.5 \times 10^{-2}$  mmol catalyst; 20 mmol phenylacetaldehyde; 10 ml dry pyridine;  $P_{\text{CO}}=9$  MPa,  $P_{\text{H}_2}=2$  MPa;  $T=140^\circ\text{C}$ ; heating time 12 h.

<sup>b</sup> The yields were determined by GLC analysis.

phine was used instead of rhodium complexes, 2,4-diphenylbutanal was not formed but the corresponding unsaturated product, 2,4-diphenylbut-2-enal (**5**), with 38% yield. These blank experiments demonstrate therefore the specificity of our Rh-based catalytic system. We have also checked that, under our experimental conditions, enal **5** was not significantly hydrogenated into aldehyde **3**, indicating unambiguously that *this aldehyde coupling reaction is not an aldolisation followed by an hydrogenation reaction.*

*ortho*-Metallated compounds are usually synthesized via a thermal reaction between dirhodium tetraacetate ( $\text{Rh}_2(\text{OAc})_4$ ) and the phosphine in acetic acid at the reflux temperature. So far – and to the best of our knowledge – they have never been synthesized nor studied in pyridine [6]. In order to check the specificity of these *ortho*-metallated complexes for the selective reductive dimerization of phenylacetaldehyde to 2,4-diphenylbutanal, we have also tested the dirhodium tetraacetate in the absence as well as in the presence of phosphines. In the absence of phosphines, practically no dimerization occurred whereas, in the presence of two equivalents of  $\text{PPh}_3$ , the yields and selectivities were similar to those obtained with the related *ortho*-metallated rhodium complexes. However, in the presence of a higher amount of  $\text{PPh}_3$  or in the presence of two equivalents of  $\text{P}(m\text{-CH}_3\text{C}_6\text{H}_4)_3$  and  $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$ , the production of dimer **3** decreased significantly, an observation which is indicative that the catalytic species formed from the *ortho*-metallated dirhodium core are likely different from those generated in situ from rhodium acetate and a phosphine.

#### 4. Conclusions

These results provide the first application of *ortho*-metallated dirhodium(II) complexes in

organic catalysis. The yields and selectivities are quite good but their synthetic interest is however mitigated by the observation that similar performances are observed simply by mixing rhodium acetate and triphenylphosphine. Currents efforts are directed towards studying the fate of both *ortho*-metallated dirhodium(II) complexes and rhodium(II) acetate dimer–phosphine mixtures in pyridine as well as under our reaction conditions.

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#### References

- [1] M. Fontaine, A.F. Noels, A. Demonceau and A.J. Hubert, *Tetrahedron Lett.*, 31 (1990) 3117.
- [2] A.F. Noels, R. Messere, M. Fontaine and A. Demonceau, *J. Catal.*, 147 (1994) 107.
- [3] (a) P. Kalck, M. Siani, J. Jenck, B. Peyrille and Y. Peres, *J. Mol. Catal.*, 67 (1991) 19; (b) C. Carmen, P. Kalck, L.A. Oro, M.T. Pinillos and C. Tejel, *J. Mol. Catal.*, 43 (1987) 1; (c) F. Senocq, C. Randrianalimanana, A. Thorez, P. Kalck, R. Choukroun, D. Gervais, *J. Chem. Soc., Chem. Commun.*, (1984) 1376.
- [4] (a) P. Lahuerta, J. Payá, E. Peris, M. Pellinghelli and A. Tiripicchio, *J. Organomet. Chem.*, 373 (1989) C5; (b) P. Lahuerta, R. Martínez-Mañez, J. Payá, E. Peris and W. Diaz, *Inorg. Chim. Acta*, 173 (1990) 99; (c) P. Lahuerta, J. Payá, E. Peris, A. Aguirre, S. Garcia-Grailola and F. Gómez-Beltrán, *Inorg. Chim. Acta*, 192 (1992) 43; (d) A.R. Chakravarty, F.A. Cotton, D.A. Tocher and J.H. Tocher, *Organometallics*, 4 (1985) 8.
- [5] T.A. Nielson and W.J. Houlihan, *Org. React.*, 16 (1968) 1.
- [6] The reactions of rhodium trifluoroacetate with triphenylphosphine and pyridine were reported recently; see P. Lahuerta, M.A. Ubeda, J. Payá, S. Garcia-Granda, F. Gómez-Beltrán and A. Anillo, *Inorg. Chim. Acta*, 205 (1993) 91 and references cited therein.