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Novel Unsymmetrical Ortho-Metalated Dirhodium (II) Catalysts: *Trans* Influence of the Axial Ligand

Pascual Lahuerta[*a], Julia Pérez-Prieto[*b], Salah-E. Stiriba[a], M. Angeles Ubeda[a]

[a] Departamento de Química Inorgánica, Facultad de Químicas, Universidad de Valencia. [b] Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia[b],Av. Vicent Andrés Estellés, s/n, 46100 Burjasot, Valencia, Spain

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Abstract: *Inductive effects of an X axial group which are transmitted through the Rh-Rh bond influence the reactivity of ortho-metalated dirhodium complexes **3** in the cyclization of 1-diazo-5-penten-2-one (**4**).*

Key words: Catalysts, Complexation, Diazo compounds, Phosphines, Rhodium and compounds

Dirhodium carboxylates are known to catalyse a variety of important diazo transformations, such as cyclopropanation, C-H insertion and aromatic substitution.[1] Quantum chemical calculations for the carbenoid intermediate suggest a polarised structure with participation of the second Rh atom *trans* to the exocyclic carbon (Figure 1).[2] The coordination of an X donor group at the *"distal"* Rh atom appears to influence the electron distribution at the carbenoid carbon, while the bridging carboxylates remain relatively unaffected. Thus, it has been anticipated[2] that additive complexation to the Rh carbenoid should attenuate the catalytic activity of the rhodium complexes.

Ortho-metalated Rh(II) complexes with $[Rh_2(\mu\text{-}OOCR)_{4-x}(\mu\text{-}PC)_x]$ (PC= metalated arylphosphine), [x = 2 (**1**), x = 1 (**2**)][3] structures are efficient catalysts for the transformation of diazo compounds.[4] Isolation and characterisation of Rh (II) complexes with the general formula $[Rh_2(\mu\text{-}OOCR)_2(\eta^2\text{-}OOCR)(\mu\text{-}PC)(\eta^2\text{-}PX)]$, [PX = equatorial phosphine, X = donor group] (**3**) have been achieved in some cases when *ortho*-aryl functionalized phosphines have been used.[5] These compounds contain : a) three bridging ligands, two are carboxylates and one is a metalated triphenylphosphine, b) two chelating ligands, a carboxylate and a phosphine (PX) occupying an equatorial position and, c) the X group of the equatorial phosphine coordinating through an axial Rh centre (Figure 2). This type of rhodium compound has never been used before as a catalysts.

Previously it has been reported that the reactivity and selectivity of Rh dimers for α-diazo compound transformation can be altered by changes made on either of their bridging ligands.[4,6] Interestingly, rhodium compounds **3** could be used to study the *trans* influence of the donor X axial ligand on the Rh(II) complex reactivity. Thus, we present here the synthesis of type **3** compounds and studies of their behaviour in the cyclopropanation of 1-diazo-5-penten-2-one (**4**).[7] Results are compared with those obtained from other Rh(II) compounds.

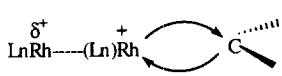

Figure 1

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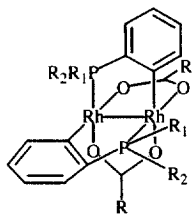
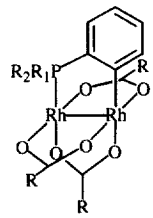
Synthesis of Catalysts. Compounds of the general formula $Rh_2(\mu\text{-}OOCCH_3)_2(\eta^2\text{-}OOCCH_3)(\mu\text{-}PC)(\eta^2\text{-}PX)$, [PC = $(C_6H_4)P(C_6H_5)_2$], PX = [$P(o\text{-}XC_6H_4)(C_6H_5)_2$], X = Cl (**3a$_1$.Cl**),[5] X= OCH_3 (**3a$_1$.OCH$_3$**) and [PC = $(C_6H_4)P(C_6F_5)(C_6H_5)$], X= OCH_3 (**3d$_1$.OCH$_3$**) were best synthesised by photochemical irradiation of the corresponding $Rh_2(\mu\text{-}OOCCH_3)_3(\mu\text{-}PC)(\eta^2\text{-}PX)$ adducts. A good yield of **3a$_2$.Cl**, **3a$_2$.OCH$_3$**, **3d$_2$.OCH$_3$** complexes were obtained by direct exchange of acetates for heptafluorobutyrates in **3a$_1$.Cl**, **3a$_1$.OCH$_3$**, **3d$_1$.OCH$_3$**.



1



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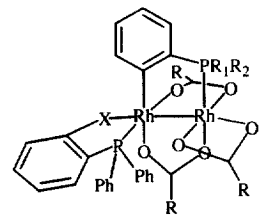


3

Catalysts	R_1	R_2	R	X	Ref	Catalysts	R_1	R_2	R	X	Ref
1a$_1$	C_6H_5	C_6H_5	CH_3	-	[3a]	**3a$_1$.Cl**	C_6H_5	C_6H_5	CH_3	Cl	[3c]
1a$_2$	C_6H_5	C_6H_5	C_3F_7	-	[4b]	**3a$_2$.Cl**[a]	C_6H_5	C_6H_5	C_3F_7	Cl	[b]
2a$_1$	C_6H_5	C_6H_5	CH_3	-	[3d]	**3a$_1$.OCH$_3$**[a]	C_6H_5	C_6H_5	CH_3	OCH_3	[b]
2a$_2$	C_6H_5	C_6H_5	C_3F_7	-	[4c]	**3a$_2$.OCH$_3$**[a]	C_6H_5	C_6H_5	C_3F_7	OCH_3	[b]
2d$_1$	C_6H_5	C_6F_5	CH_3	-	[4c]	**3d$_1$.OCH$_3$**[a]	C_6H_5	C_6F_5	CH_3	OCH_3	[b]
2d$_2$	C_6H_5	C_6F_5	C_3F_7	-	[4c]	**3d$_2$.OCH$_3$**[a]	C_6H_5	C_6F_5	C_3F_7	OCH_3	[b]

[a]Data for new compounds in reference 11. [b]This work.

Figure 2. List of Catalysts

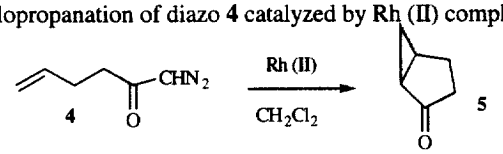
Compounds of structure **3** have backbone chirality as do the doubly metalated compounds **1**.[8] In the case of the **3d** compounds, the substituents joined to the phosphorus of the metalated phosphine are different, and two diastereoisomers can be formed. The photochemical reaction of $Rh_2(OOCCH_3)_3[C_6H_4P(C_6F_5)(C_6H_5)]$ with two PX phosphines proved to be highly diastereoselective and according to the ^{31}P-NMR data the isomers were obtained in a 20:1 ratio. Both isomers could be isolated by chromatography, but only the major isomer was used for catalytic studies. All efforts to grow single crystals of either of the **3d** compounds, suitable for X-ray structure determination, were unsuccessful. Catalysts of type **1** and **2** were prepared according to literature procedures.[3,4]

Catalytic Reactions. These reactions were performed by adding the corresponding rhodium (II) complex (1 mol %) to a dichloromethane solution of the α-diazo ketone **4**. The mixture was refluxed for 1h and monitored by TLC until the consumption of the diazo compound had occurred. The solvent was removed and the crude mixture was analysed by ^{1}H- and ^{13}C-NMR.

$Rh_2(OOCCH_3)_4$ gave rise to 81% of the cyclopropanation product, [3.1.0]bicyclo-2-pentanone (**5**). The more acidic $Rh_2(OOCCF_3)_4$ only produced dimerization products (Table 1). Addition of monometalated **2a$_1$** with acetate and $P(C_6H_5)_3$ as bridging ligands, resulted in 67% of ketone **5**. Changing of the *ortho*-metalated phosphine in the Rh dimer to a less basic one, such as $P(C_6F_5)(C_6H_5)_2$, resulted in catalyst **2d$_1$**, which provided a similar yield of cyclization product (70% of **5**). Catalysts **2a$_2$** and **2d$_2$**, with highly electron-withdrawing carboxylate groups, showed the same behaviour as $Rh_2(OOCCF_3)_4$ and no ketone formation was detected. On

the other hand, in the case of doubly metalated compounds **1**, the exchange of only two carboxylate groups gave good yields of ketone (70% for $\mathbf{1a_2}$ *versus* 62% for $\mathbf{1a_1}$)

Table 1. Cyclopropanation of diazo **4** catalyzed by Rh (II) complexes.



Catalyst	Yield (%)	Catalyst	Yield (%)
$Rh_2(OOCCH_3)_4$	81	$\mathbf{2d_2}$	0
$Rh_2(OOCCF_3)_4$	0	$\mathbf{3a_1.Cl}$	53
$\mathbf{1a_1}$	62	$\mathbf{3a_2.Cl}$	74
$\mathbf{1a_2}$	70	$\mathbf{3a_1.OCH_3}$	No reaction
$\mathbf{2a_1}$	70	$\mathbf{3a_2.OCH_3}$	55
$\mathbf{2a_2}$	0	$\mathbf{3d_1.OCH_3}$	95
$\mathbf{2d_1}$	67	$\mathbf{3d_2.OCH_3}$	75

The existence of two different rhodium centres in compounds **3**, raised the question of which was the reactive centre. The $\mathbf{3a_1.Cl}$ molecular structure has been obtained by X-ray methods [5] and has shown that, in its solid state, both axial positions along the rhodium-rhodium axis are occupied by chelating ligands, $OOCCH_3$ and PX. The fact that this and other structurally related compounds are reactive indicates that, in solution, at least one of these axial coordination sites must be available for interaction with the diazo compound. Which is the reactive one, is a matter for discussion. The X-ray structure for $\mathbf{3a_1.Cl}$ shows that the Rh-O axial distance (2.27 Å) is considerably longer than the Rh-O equatorial distance (2.04 Å), which suggests that in solution the axial coordination site might be available. Furthermore, the influence of the basicity of the metalated phosphine on the catalyst reactivity is evidence that the reactive Rh centre in catalysts **3** is that which is joined to the phosphorus atom of the *ortho*-metalated phosphine. Thus, while $\mathbf{3a_1.OCH_3}$ was unreactive towards the diazo compound **4**, $\mathbf{3d_1.OCH_3}$, which only differs by having a less basic metalated phosphine, gave 95% of the cyclopropanation product (Table 1). Similarly, in the case of dimers having perfluorobutyrates, a better yield of ketone **5** was obtained using $\mathbf{3d_2.OCH_3}$ than $\mathbf{3a_2.OCH_3}$ (75% and 55%, respectively).

On the other hand, the influence of the donor ability of group X on the reactivity of dimers **3** was evident when the $\mathbf{3a_1.OCH_3}$ and $\mathbf{3a_1.Cl}$ catalytic results were compared. While the first compound proved incapable of transforming diazo compound **4**, complex $\mathbf{3a_1.Cl}$, with a less basic axial ligand (a chlorine atom) gave rise to 53 % of ketone **5**. Furthermore, a higher yield of cyclopropanation was obtained with $\mathbf{3a_2.Cl}$ (74%) than with $\mathbf{3a_2.OCH_3}$ (55%). These results corroborate that inductive effects from group X, are transmitted through the metal-metal bond,[9] and reduce the catalytic activity of the dirhodium complexes. As Padwa *et al.*[2] have predicted, the second Rh centre seems to be a versatile electron reservoir in the formation of the carbenoid complex. Higher basicity of the coordinating X group reduces the electrophilicity of the carbenoid carbon. This report is, to our knowledge, the first study of Rh dimer catalysis regarding the nature of the axial coordinating group. In future work, it will be interesting to study our ability to influence the selectivity of Rh dimers **3** in competitive α-diazo compound cyclizations by changing the basicity of X.

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11. Spectral data for compounds **3**: (**3a$_2$.Cl**): ^{1}H NMR ($CDCl_3$): δ 2.60 (H_2O), 6.40-7.80 (m, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 12.3 (d, $^1J_{Rh\text{-}P}$= 140 Hz), 48.3 (d, $^1J_{Rh\text{-}P}$= 183 Hz). ^{19}F NMR ($CDCl_3$): δ -125.6-127.4 (m, 6F), -115.9-(-118) (m, 6F), -81.2 -80.87 (m, 9F). $C_{48}H_{30}ClF_{21}O_7P_2Rh_2$ (1419.89): calcd. C 40.57, H 2.13; found C 40.96, H, 1.73. (**3a$_1$.OCH$_3$**): ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 6H), 1.80 (s, 3H), 4.50 (s, 3H), 6.60-8.90 (m, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.2 (dd, $^1J_{Rh\text{-}P}$= 146 Hz, $^2J_{Rh\text{-}P}$= 8 Hz), 46.7 (dd, $^1J_{Rh\text{-}P}$= 180 Hz, $^2J_{Rh\text{-}P}$= 5 Hz). $^{13}C\{^1H\}$: 21.8 (s), 23.2 (s), 24.0 (s), 58.2 (s), 112.4-161.8 (aromatics), 183.6 (s), 184.0 (s), 185.9 (s). $C_{43}H_{40}O_7P_2Rh_2$ (936.03): calcd. C 55.13, H 4.30; found C 55.66, H, 4.75. (**3d$_1$.OCH$_3$**): ^{1}H NMR ($CDCl_3$): δ 1.19 (s, 3H), 1.21 (s, 3H), 1.22 (s, 3H), 4.20 (s, 3H), 6.90-8.00 (m, 23H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.6 (dd, $^1J_{Rh\text{-}P}$= 158, $^2J_{Rh\text{-}P}$ = 6 Hz), 44.4 (dd, $^1J_{Rh\text{-}P}$= 184, $^2J_{Rh\text{-}P}$= 3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.9 (s), 22.7 (s), 23.5 (s), 58.3 (s), 112.7-158.5 (aromatics), 184.2 (s), 184.8 (s), 185.0 (s). ^{19}F NMR ($CDCl_3$): δ -162.0 (m, 2F), -150.6 (br, 1F), -121.6 (br, 2F). $C_{43}H_{35}F_5O_7P_2Rh_2$ (1026.50): calcd. C 50.29, H 3.44; found C 49.82, H, 3.84. (**3a$_2$.OCH$_3$**): ^{1}H NMR ($CDCl_3$) δ: 2.20 (br, H_2O), 4.20 (s, 3H), 6.20-7.80 (m, 28H). $^{31}P\{^1H\}$ NMR($CDCl_3$) δ: 17.3 (d, $^1J_{Rh\text{-}P}$= 142 Hz, $^2J_{Rh\text{-}P}$= 7 Hz), 46.4 (d, $^1J_{Rh\text{-}P}$= 177 Hz, $^2J_{Rh\text{-}P}$= 4 Hz). $^{13}C\{^1H\}$ NMR($CDCl_3$) δ: 59.2 (s), 113.3-165.0 (aromatics), 182.0 (s), 184.0 (s), 184.8 (s). ^{19}F NMR ($CDCl_3$) δ: -127.3 (m, 6F), -118.0 (m, 6F), -81.1 (m, 9F). $C_{49}H_{33}F_{21}O_8P_2Rh_2$ (1416.52): calcd. C 41.55, H 2.35; found C 41.9, H, 1.95. (**3d$_2$.OCH$_3$**): ^{1}H NMR ($CDCl_3$) δ: 2.20 (br, H_2O), 4.25 (s, 3H), 6.60-7.80 (m, 23H). $^{31}P\{^1H\}$ NMR($CDCl_3$) δ: 13.1 (d, $^1J_{Rh\text{-}P}$= 148 Hz), 38.5 (d, $^1J_{Rh\text{-}P}$= 185 Hz). $^{13}C\{^1H\}$ NMR($CDCl_3$) δ: 58.3 (s), 112.3-167.0 (aromatics), 185.2 (s), 185.8 (s), 188.0 (s). ^{19}F NMR($CDCl_3$) δ: -158.9 (t, 2F), -146.3 (s, 1F), -127.4-(-125.6) (m, 7F), -117.9-(-115.9) (m, 9F), -81.3-(-80.8) (m, 7F). $C_{49}H_{28}F_{26}O_8P_2Rh_2$ (1506.47): calcd. C 39.07, H 1.87; found C 38.69, H, 2.07.