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Rhodium(III)-Catalyzed Dimerization of Aldehydes to Esters

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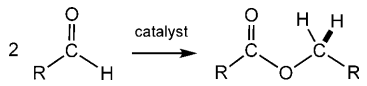
In response to the increasing social demand for clean and environmental friendly procedures, recent years have witnessed a dramatic growth in the search for selective chemical processes with 100% atom economy. Among them, the catalyzed coupling of aldehydes to the corresponding esters (Tishchenko reaction, Scheme 1) is key for the synthesis of



Scheme 1. Dimerization of aldehydes to esters.

these valuable chemicals.[1] This reaction and the related dismutation of aldehydes, known as the Cannizzaro reaction, typically suffer from the formation of side products, but it represents an attractive alternative to traditional ester syntheses that require, in general, the activation of the free acid through conversion to the acyl chloride or anhydride[2] with the subsequent production of wastes. In this context, a new catalytic approach providing esters by dehydrogenation of alcohols has been recently reported by Milstein.[3]

A number of homogenous catalysts have been designed and tested for the Tischenko coupling.[1,2,4] Representative catalysts are alkaline[5] and alkaline earth amides,[6] aluminum alkoxides,[7] and lanthanide[8] and actinide compounds.[9] Special mention requires a lanthanide formamidinate complex reported by Roesky,[10] for being the most active catalyst for the Tishchenko reaction known up to date. Late-transition-metal complexes have been comparatively quite less studied as catalysts for this reaction.[11] Pioneering work in rhodium chemistry showed that low-valent rhodium(I) hydrides such as $[RhH(CO)(PPh_3)_3]$[12] and $[RhH(PPh_3)_4]$[13] catalyze the coupling of aldehydes, while better results were achieved using cationic rhodium(I) compounds.[14] Nonetheless, either warming or long reaction times are required to achieve acceptable results and their activity is not comparable to that reported for the Roesky's catalyst. We have recently found that the rhodium scaffold "$Rh(PhBP_3)$", bearing the tripodal anionic phosphinoborate ligand $[PhB(CH_2PPh_2)_3]^-$ ($PhBP_3$), is able to stabilize unusual peroxo and hydroperoxo compounds,[15] and shows a good catalytic activity in selective hydrogenation of the carbaldehyde group in α,β-unsaturated aldehydes.[16] This led us to study the potential of hydrido complexes containing this platform in reactions with carbonyl compounds seeking to find details in the reduction to above-mentioned alcohols. However, we found instead a disproportionation of aldehydes that traditionally has been promoted by a Lewis acid. Thus, herein we report on the exceptional catalytic activity of a $PhBP_3$–rhodium(III) complex for the selective dimerization of aromatic and aliphatic aldehydes to esters under remarkably mild conditions, which seems to be related to an unusual mechanism for rhodium catalyzed reactions.

To compare results, reactions of rhodium(I) complexes bearing the "$Rh(PhBP_3)$" moiety with benzaldehyde, cynnamaldehyde, and cyclohexylcarbaldehyde in a close to stoichiometric ratio were assayed. All the Rh^I complexes tested produced systematically the decarbonylation of the aldehyde[17] along with the complexes $[(PhBP_3)Rh(CO)_2]$ and $[Rh(PhBP_3)(CO)(H)_2]$. However, reactions of the Rh^{III} hydrido complex $[Rh(PhBP_3)(H)_2(NCMe)]$ (**1**)[16] with benzaldehyde and cyclohexylcarbaldehyde immediately gave the corresponding esters from the dimerization of the aldehyde. Preliminary catalytic experiments at room temperature in C_6D_6 (1 mol% of **1**), with benzaldehyde as model, showed the reaction to be fully selective to benzylbenzoate by NMR spectroscopy and completed within 10 min with a initial TOF of 2830 h^{-1}, being thus even faster than Roesky's catalyst.[10] Analysis of the solution after the catalysis indicated the dihydride **1** (56%) along with $[Rh(PhBP_3)(H)_2(CO)]$[16] (**2**, 12%) and $[Rh(PhBP_3)(H)(O_2CPh)]$ (**3**, 31%) to be the sole rhodium complexes by ^1H and $^{31}P\{^1H\}$ NMR spectrosco-

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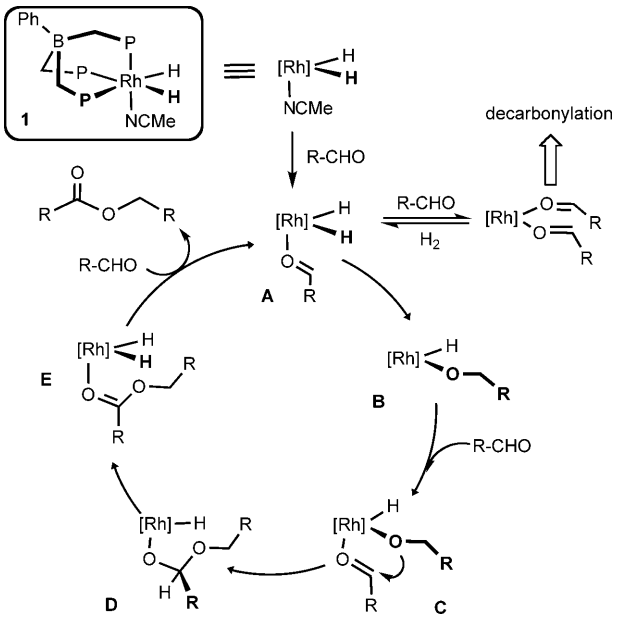
py. The last two complexes, **2** and **3**, were the result of undesirable lateral reactions. They are inactive for the dimerization of benzaldehyde, as verified in separate experiments. Complex **2** results from aldehyde decarbonylation, probably triggered by rhodium(I) species of the type $[Rh(PhBP_3)(PhCHO)_2]$ (Scheme 2) ensuing from hydrogen release (observed by ^{1}H NMR spectroscopy).[18] Complex **3** and hydrogen result from the protonation of **1** with benzoic acid, as shown in a separate experiment. Moreover, water produces **3** and the alcohol $PhCH_2OH$ in equimolar amounts (see below). Since water and acids destroy the catalyst, the optimal conditions for the catalytic assays are workup under anhydrous conditions with freshly distilled aldehydes and saturation of the solution with hydrogen to avoid Rh^I species in the reaction medium.

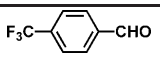
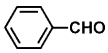
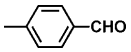
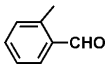
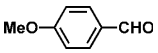
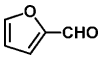
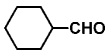
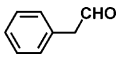


Scheme 2. Proposed mechanism for the dimerization of aldehydes catalyzed by **1**.

The generality and scope of the reaction under these conditions is summarized in Table 1. The reactions were completed in a few minutes, while the fully selective and quantitative conversion to the esters was observed. The reaction runs with substituted benzaldehydes containing electron-withdrawing groups (CF_3, entry 1) and with moderate electron-donating groups (Me, entries 3 and 4) with no appreciable effects due to the *ortho* substitution. The presence of strong electron-donating groups at the *para* position, such as MeO, significantly reduce the conversion rate because of a partial carbonylation of the catalyst, shown for *p*-methoxybenzaldehyde (entry 5) and in to a lesser extent for *p*-methylbenzaldehyde (entry 3).[19]

For comparative purposes we have also tested the activity of **1** for the coupling of furfural (entry 6), a reaction that has been reported to be difficult. Traditionally, aluminium alkoxides or lanthanide compounds as catalysts require long reaction times to produce acceptable yields, while the more active catalyst, calcium oxide in a heterogeneous way, produces quantitatively 2-furylmethyl-2-furancarboxylate after 6 h at 353 K.[20] As shown in Table 1, complex **1** showed an excellent catalytic activity with this difficult substrate. Significantly, complex **1** is also effective for the dimerization of enolizable aldehydes containing one, two, and three α-protons, as verified in the reactions with cyclohexylcarbaldehyde and phenylacetaldehyde (entries 7 and 8). Moreover, acetaldehyde (a chemical highly susceptible for aldol condensation) is also converted into ethyl acetate. No special caution was taken to prevent the undesirable aldolic condensation with these substrates, which was not detected. Further, scaling-up the reaction was undertaken and the esters could be isolated on a gram preparative scale with satisfactory to excellent yields (Table 1) with the loss in the isolated yield depending on the volatility of the ester.

Table 1. Scope of the coupling of aldehydes to esters catalyzed by complex **1**.[a]

Entry	Substrate	Conversion [%][b]	*t* [min]	Yield [%][c]
1		>99	3	92
2		>91	4	81
3		82 (90)	3 (14)	75
4		>99	3	81
5		40 (55)	3 (15)	n.a.
6		>99	3	91
7		>99	3	88
8		>99	3	85
9	CH_3CHO	>99	3	68

[a] Conditions: substrate/catalyst mol ratio 100/1, 0.5 mL C_6D_6, rt, H_2 atmosphere. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield on a preparative gram-scale in toluene (5 mL).

Reutilization of the catalyst was also investigated using the model reaction with benzaldehyde. After completion of the first catalytic run, and once confirmed the presence of **1**, two consecutive additions of benzaldehyde were loaded. The activity slowly decreased in each new catalytic run (see Supporting Information), which was associated to the partial destruction of the catalyst by water contained by the substrate, reaching a maximum TON of 400 in our hands.

Because few catalysts are effective for both aromatic and aliphatic aldehydes, the catalytic activity of **1** was assayed with aliphatic aldehydes, which were carefully distilled and dried. The reactions were carried out under argon in a NMR tube with initial aldehyde/catalyst loadings of 100:1 mol. No hydrogen atmosphere is needed for the reactions of aliphatic aldehydes. The results collected in Table 2 show an exceptionally high activity of the catalyst with a full conversion and 100% selectivity to the ester in around

Table 2. Scope of the condensation of aliphatic aldehydes to esters catalyzed by complex **1**.[a]

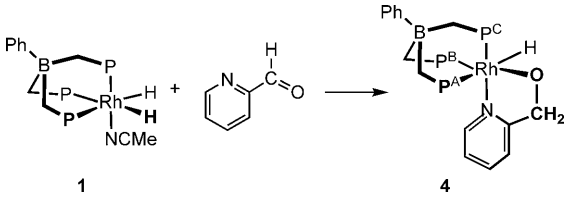
Entry	Substrate	Conversion [%][b]	t [min]
1	propanal	>99	1
2	butanal	>99	1
3	isobutanal	>99	1
4	valeraldehyde	>99	1
5	isovaleraldehyde	>99	1
6	hexanal	>99	1
7	crotonaldehyde	<1	–
8	*trans*-2-hexen-1-al	<1	–

[a] Conditions: substrate/catalyst mol ratio 100/1, 0.5 mL C_6D_6 RT, argon atmosphere. [b] Determined by ^{1}H NMR spectroscopy.

1 min. No other organic compounds such as condensation, decarbonylation, or hydrogenation products were detected by NMR spectroscopy. Again, analysis of the solutions from the catalytic runs indicated the dihydride **1** to be the major rhodium complex along with variable amounts of the carboxylate complex [Rh(PhBP$_3$)H(O$_2$CR)] depending on the amount of acid/water contained by the substrate. Thus, this solution is still active for further catalytic cycles as long as it contains the dihydride complex **1**, which is the resting state of the catalyst. Consequently, the solutions could be reutilized indefinitely in the absence of acid or water. Although the reaction is apparently insensitive to steric effects, as shown for isobutanal and isovaleraldehyde (entries 3 and 5), the presence of functional groups in the substrate, particularly donor groups behaving as ligands, such as double C=C bonds, may prevent the catalysis. Thus, no conversion to the ester is observed with crotonaldehyde and *trans*-2-hexen-1-al.

A plausible catalytic cycle is shown in Scheme 2. The initial step consists on the replacement of the labile acetonitrile ligand in **1** by the aldehyde in excess to give **A**. Insertion of the C=O bond into the Rh–H bond follows to give the coordinatively insaturated hydride-alkoxo intermediate **B**. Coordination of a second molecule of aldehyde would give the octahedral complex **C**, in which a migratory insertion of the carbonyl group into the Rh–alkoxide bond renders the hemiacetal-rhodium(III) intermediate **D**. Insertion of aldehydes into Rh–alkoxo bonds, although rare, has been previously reported.[21] Again, **D** is coordinatively unsaturated allowing a direct β-elimination reaction to produce the dihydride rhodium(III) complex **E**. The cycle is closed with the replacement of the ester by the aldehyde in **E** to regenerate **A**. A similar cycle has been proposed by Roesky[10] and Darses[11a] for lanthanide and ruthenium catalysts, respectively. It is interesting to note that no changes of the oxidation state of the metal [Rh^{I}/Rh^{III}] occur in this catalytic cycle, being all intermediates rhodium(III) compounds.

Support for the first steps of the cycle comes from the reaction of **1** with 2-pyridylcarbaldehyde. Upon mixing, a pale yellow solution of the new alkoxyhydride complex [Rh(PhBP$_3$)H(OCH$_2$Py)] (**4**, Scheme 3) results. Evidence for the aldehyde insertion into one of the Rh–H bonds comes from the new signals at $\delta = 5.86$ ppm for the CH$_2$O–Rh group,

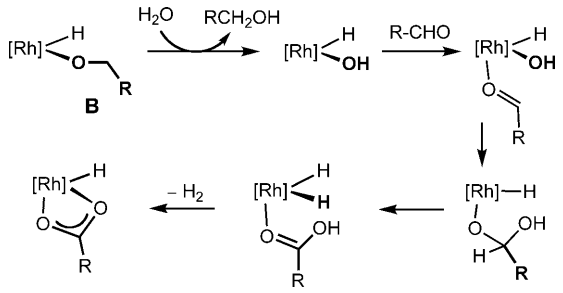


1 4

Scheme 3. Reaction of **1** with pyridylcarbaldehyde.

while the remaining hydride appears at $\delta = -6.29$ ppm in the ^{1}H NMR spectrum of **4**. Consistent with the proposed structure, complex **4** exhibits three inequivalent phosphorus nuclei in the ^{31}P{^{1}H} NMR spectrum.

Complex **4** is inactive for aldehyde dimerization, since it lacks a vacant coordination site for the second molecule of aldehyde. In the same way, donor groups in the substrates or molecules in the reaction medium may become coordinated to the metal in **B** avoiding thus the catalysis to proceed. This would account for the lack of catalysis with unsaturated aldehydes (Table 2, entries 7, 8) and the adverse action of water. Thus, reactions of **1** with benzaldehyde and isobutanal in the presence of added water showed the systematic formation of the alcohol RCH$_2$OH and [Rh(PhBP$_3$)(H)(O$_2$CR)] in equimolar amounts. Almost no catalysis occurred if water/catalyst ratio is 1:1, whereas decreasing the amount of water the catalysis took place, but with variable activity depending on the actual concentration of the catalyst. A reasonable explanation for the action of water is summarized is Scheme 4. Coordination of water in



Scheme 4. Adverse action of water in the dimerization of aldehydes.

B promotes the elimination of the alkoxo group as alcohol. Then, insertion of aldehyde into the Rh–OH bond followed by a β-hydrogen elimination and hydrogen evolution would result in the hydride-carboxylate [Rh(PhBP$_3$)(H)(O$_2$CR)] complexes.

Preliminary kinetic investigations showed that 1/[PhCHO] is linearly related to the reaction time, in accordance with a second-order reaction rate relative to the aldehyde (see Supporting Information). This kinetics would also be compatible with a Rh^{I}/Rh^{III} catalytic cycle generated by active rhodium(I) species resulting from the reductive elimination of the alcohol from **B** or **C**. This alternative cycle would be similar to the proposed for hydroacylations of C=O bonds.[22] How-

ever, this possibility is quite unlikely in our case, since 1) the dihydride **1** is found in the solutions after the catalytic runs even in the absence of hydrogen, 2) isolated rhodium(I) complexes with the "$Rh(PhBP_3)$" scaffold and labile ligands produce systematically the aldehyde decarbonilation reaction, and 3) hydrogenation of the C=O bond requires high pressure of hydrogen.[16]

In summary, we disclose that a dihydridorhodium(III) complex $[(PhBP_3)Rh(H)_2(NCMe)]$ is an extremely efficient catalyst for the dimerization of both, aliphatic and aromatic, enolizable and non-enolizable aldehydes under exceptionally smooth conditions. Its outstanding activity likely results from an operative way in which the insertion of the carbaldehyde group into the Rh–H bond to give an alkoxo group, and insertion of a second aldehyde into the resulting rhodium alkoxide seems to be essential steps for the dismutation of aldehydes. Most probably, the excellent effectiveness of the lanthanide catalyst and complex **1** could be due to common distinctive steps in spite of the divergent nature of the metals.

Experimental Section

NMR-scale experiments: A NMR tube was charged with the catalyst, $[Rh(PhBP_3)(H)_2(NCMe)]$ (**1**; 5.0 mg, 0.006 mmol) and dried C_6D_6 (0.4 mL) under argon. For the aldehydes in Table 1, the argon atmosphere was replaced by hydrogen through 3 freeze–thaw cycles and then, dry and freshly distilled aldehyde was added (in a 100:1 mol ratio vs. catalyst). The tube was introduced into the NMR probe and the mixture was analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy obtaining the proton spectrum in 2–3 min after mixing. For the aliphatic aldehydes of Table 2 no hydrogen was introduced into the NMR tube and the first proton spectrum was obtained in about 1 min after mixing. Clean and quantitative conversions to the Tishchenko esters were observed in all the cases except for *p*-methoxy-benzaldehyde (55%) and for the unsaturated aldehydes of Table 2.

Preparative-scale experiments: Only the preparation and isolation of benzyl benzoate is reported in detail. Procedures for other aldehydes were similar, except for acetyl acetate (see below). A solution of **1** (80.0 mg, 0.096 mmol) in toluene (8 mL) was saturated with hydrogen (1 atm; 3 freeze–thaw cycles) and then benzaldehyde (0.98 mL, 9.6 mmol) was added. After stirring for 10 min the solution was analyzed by GC-MS, observing the quantitative formation of benzylbenzoate. The solution was evaporated under vacuum and the residue extracted with hexane (2×5 mL). The extract was subjected to chromatography on a SiO_2 column affording a colorless solution, which was evaporated up to dryness affording benzyl benzoate as a colorless viscous liquid. Yield 0.83 g (81%); ^1H NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 8.18$ (m, 2H), 7.60 (m, 1H), 7.55–7.38 (m, 7H), 5.45 ppm (s, 2H); $^{13}C\{^1H\}$ NMR (500 MHz $CDCl_3$, 25°C): $\delta = 166.4$ (CO_2), 136.2, 133.1, 129.8, 128.7, 128.5, 128.3, 128.3, 66.75 ppm (CH_2). For ethyl acetate: after finished the catalysis, hexane (10 mL) was added to precipitate the catalyst and the suspension was filtered over a silica gel column affording a colorless solution, which was fractionally distilled to afford acetyl acetate. Yield 0.45 g (68%); ^1H NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 4.02$ (q, $J(H,H) = 6.8$ Hz, 2H), 1.94 (s, 3H), 1.16 ppm (t, $J(H,H) = 6.8$ Hz, 3H). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 170.8$ (CO_2), 60.2 (CH_2), 20.8 (CH_3), 14.0 ppm (CH_3).

$[(PhBP_3)Rh(H)(O_2CPh)]$ (3): Solid $PhCO_2H$ (12.2 mg, 0.10 mmol) was added to a solution of **1** (83.1 mg, 0.10 mmol) in toluene (5 mL). After stirring for 15 min, the solution was evaporated to ca. 3 mL, layered with hexane (15 mL), and left to stand for two days. The white-off solid that precipitated was washed with hexane and vacuum-dried. Yield: 73.7 mg (81%); ^1H NMR (500 MHz, C_6D_6, 25°C): $\delta = 8.33$ (d, $^3J(H,H) = 7.2$, 2H; H^o) and 7.12 (m, 3H; H^{m+p}) (PhCOO), 8.07 (d, $^3J(H,H) = 7.1$ Hz, 2H; H^o-PhB), 7.88 (m, 4H; H^o-Ph_2P^A), 7.69 (m, 6H; H^o-Ph_2P^A, H^m-PhB), 7.45 (t, $^3J(H,H) = 7.2$ Hz, 1H; H^p-PhB), 7.34 (t, $^3J(H,H) = {}^3J(H,P) = 8.7$ Hz, 4H; H^o-Ph_2P^B), 6.95 (br, 6H; H^{m+p}-Ph_2P^A), 6.82 (t, $^3J(H,H) = 7.3$ Hz, 2H; H^p-Ph_2P^B), 6.70 (t, $^3J(H,H) = 7.1$ Hz , 6H; H^m-Ph_2P^B, H^p-Ph_2P^A), 6.64 (t, $^3J(H,H) = 7.3$ Hz, 4H; H^m-Ph_2P^A), 1.79 (d, $^2J(H,P) = 11.2$ Hz, 2H; CH_2-P^B), 1.72 (m, 4H; CH_2-P^A), −4.92 ppm (ddd, $^2J(H,P^B) = 197.9$, $J(H,Rh) = 18.4$ Hz, $^2J(H,P^A) = 8.2$ Hz, 1H; Rh-H); $^{31}P\{^1H\}$ NMR (500 MHz, C_6D_6, 25°C): $\delta = 52.5$ (dd, $J(P,Rh) = 123$, $J(P,P) = 20$ Hz, 2P; P^A), 7.46 ppm (dt, $J(P,Rh) = 74$, $J(P,P) = 20$ Hz, 1P; P^B); $^{13}C\{^1H\}$ NMR (500 MHz, C_6D_6, 25°C): $\delta = 179.8$ (CO_2), 128.9 (C^o), 131.7 (C^m) and 128.0 ppm (C^p) ($PhCO_2$); elemental analysis calcd (%) for $C_{52}H_{47}BO_2P_3Rh$: C 68.59, H 5.20; found: C 68.49, H 5.38.

$[(PhBP_3)Rh(H)(OCH_2Py)]$ (4): Neat PyCHO (6.8 μL, 0.072 mmol) was added to a suspension of $[(PhBP_3)Rh(H)_2(NCMe)]$ (**1**) (60 mg, 0.072 mmol) in toluene (3 mL) to immediately give a yellow solution. This was carefully layered with pentane (12 mL) to produce pale-yellow microcrystals in two days. The mother liquor was decanted and the solid was washed with 2×2 mL of pentane and vacuum-dried. Yield: 50 mg (77%); ^1H NMR (300 MHz, C_6D_6, 25°C): $\delta = 8.44$ (m, 2H; H^o-PhP^C), 8.25 (d, $^3J(H,H) = 7.0$ Hz, 2H; H^o-PhB), 8.15 (m, 4H; H^o-PhP^C, H^o-PhP^A), 8.00 (dd, $^3J(H,P) = 11.2$ Hz, $^3J(H,H) = 7.4$ Hz, 2H; H^o-PhP^B), 7.73 (t, $^3J(H,H) = 7.5$ Hz, 2H; H^m-PhB), 7.47 (t, $^3J(H,H) = 7.5$ Hz, 1H; H^p-PhB), 7.29 (dd, $^3J(H,P) = 8.4$ Hz, $^3J(H,H) = 7.2$ Hz, 2H; H^o-PhP^A), 7.03 (m, 6H; PhP), 6.55–6.93 (m, 16H; PhP, H^3 and H^4 Py), 5.86 (br d, $^3J(H,P) = 5.9$ Hz, 2H Rh-OCH_2), 5.69 (td, $^3J(H,H) = 5.9$ Hz, $^4J(H,H) = 2.0$ Hz, 1H; H^5 Py), 5.60 (m, 1H; H^6 Py), 2.38 (δ_A, t, $^2J(H,P) = 15.7$ Hz, 1H), 1.75 (δ_B, m, $J(A,B) = 15.1$ Hz, 1H; CH_2-P^A), 2.19 (m, 2H; CH_2-P^B), 1.96 (δ_A, m, 1H), 1.31 (δ_B, m, $J(A,B) = 15.1$ Hz, 1H; CH_2-P^C), −6.29 ppm (m, $^2J(H,P^A) = 195.0$ Hz, $^2J(H,P^B) = 24.2$ Hz, $^2J(H,P^C) = 9.3$ Hz, $J(H,Rh) = 15.2$ Hz, 1H; H-Rh); $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25°C): $\delta = 45.2$ (ddd, $J(P,Rh) = 108$ Hz, $J(P,P) = 42$, 15 Hz, P^B), 30.7 (ddd, $J(P,Rh) = 115$ Hz, $J(P,P) = 42$, 33 Hz, P^C), −2.1 ppm (ddd, $J(P,Rh) = 70$ Hz, $J(P,P) = 33$ and15 Hz, P^A); $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25°C): $\delta = 172.2$ (C^2-Py), 152.5 (C^6-Py), 135.5 C^4-Py, 119.8 (C^5-Py), 117.0 (C^3-Py), 80.9 ppm (OCH_2-Py); elemental analysis calcd (%) for $C_{51}H_{48}BNOP_3Rh$: C 68.25, H 5.39, N 1.56; found: C 68.15, H 5.59, N 1.53.

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Keywords: aldehydes · esters · homogeneous catalysis · hydrido ligands · rhodium · Tishchenko reaction

[1] T. Seki, T. Nakajo, M. Onaka, *Chem. Lett.* **2006**, *35*, 824–829.
[2] K. Ekoue-Kovi, C. Wolf, *Chem. Eur. J.* **2008**, *14*, 6302–6315.
[3] a) D. Milstein, *Top. Catal.* **2010**, *53*, 915–923, and references therein; b) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841.
[4] M. Haniti, S. A. Hamid, P. A. Slatford, J. M. J Williams, *Adv. Synth. Catal.* **2007**, *349*, 1555–1575.
[5] M. M. Mojtahedi, E. Akbarzadeh, R. Sharifi, M. S. Abaee, *Org. Lett.* **2007**, *9*, 2791–2793.
[6] M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. A. Procopiou, *Org. Lett.* **2007**, *9*, 331–333.
[7] a) Y.-S. Hon, Y.-C. Wong, C.-P. Chang, C.-H. Hsieh, *Tetrahedron* **2007**, *63*, 11325–11340; b) T. Ooi, K. Ohmatsu, K. Sasaki, T. Miura,

K. Maruoka, *Tetrahedron Lett.* **2003**, *44*, 3191–3193; c) T. Ooi, T. Miura, K. Takaya, K. Maruoka, *Tetrahedron Lett.* **1999**, *40*, 7695–7698.

[8] a) R. M. Gauvin, T. Chenal, R. A. Hassan, A. Addad, A. Mortreux, *J. Mol. Catal. A* **2006**, *257*, 31–40; b) M. R. Bürgstein, H. Berberich, P. W. Roesky, *Chem. Eur. J.* **2001**, *7*, 3078–3085; c) H. Berberich, P. W. Roesky, *Angew. Chem.* **1998**, *110*, 1618–1620; *Angew. Chem. Int. Ed.* **1998**, *37*, 1569–1571; d) S. Onozawa, T. Sakakura, M. Tanaka, M. Shiro, *Tetrahedron* **1996**, *52*, 4291–4302.

[9] T. Andrea, E. Barnea, M. S. Eisen, *J. Am. Chem. Soc.* **2008**, *130*, 2454–2455.

[10] A. Zuyls, P. M. Roesky, G. B. Deacon, K. Konstas, P. C. Junk, *Eur. J. Inorg. Chem.* **2008**, 693–697.

[11] Ruthenium: a) M.-O. Simon, S. Darses, *Adv. Synth. Catal.* **2010**, *352*, 305–308; b) S. Omura, T. Fukuyama, Y. Murakami, H. Okamoto, I. Ryu, *Chem. Commun.* **2009**, 6741–6743; c) S.-I. Murahashi, T. Naota, K. Ito, Y. Maeda, H. Taki, *J. Org. Chem.* **1987**, *52*, 4319–4327; d) T. Ito, H. Horino, Y. Koshiro, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 504–512; e) H. Horino, T. Ito, A. Yamamoto, *Chem. Lett.* **1978**, 17–20; osmium: f) P. Barrio, M. A. Esteruelas, E. Oñate, *Organometallics* **2004**, *23*, 1340–1348; iridium: g) T. Suzuki, T. Yamada, T. Matsuo, K. Watanabe, T. Katoh, *Synlett* **2005**, 1450–1452; h) K. A. Bernard, J. D. Atwood, *Organometallics* **1988**, *7*, 235–236; nickel: i) S. Ogoshi, Y. Hoshimoto, M. Ohashi, *Chem. Commun.* **2010**, *46*, 3354–3356.

[12] R. Grigg, T. R. B. Mitchell, S. Sutthaivaiyakit, *Tetrahedron* **1981**, *37*, 4313–4319.

[13] M. Massoui, D. Beaupère, L. Nadjo, R. Uzan, *J. Organomet. Chem.* **1983**, *259*, 345–353.

[14] a) D. H. T. Phan, B. Kim, V. M. Dong, *J. Am. Chem. Soc.* **2009**, *131*, 15608–15609, and references therein; b) Z. Shen, H. A. Khan, V. M. Dong, *J. Am. Chem. Soc.* **2008**, *130*, 2916–2917; c) S. H. Bergens, D. P. Fairlie, B. Bosnich, *Organometallics* **1990**, *9*, 566–571.

[15] C. Tejel, M. A. Ciriano, S. Jiménez, V. Passarelli, J. A. López, *Angew. Chem.* **2008**, *120*, 2123–2126; *Angew. Chem. Int. Ed.* **2008**, *47*, 2093–2096.

[16] S. Jiménez, J. A. López, M. A. Ciriano, C. Tejel, A. Martínez, R. A. Sánchez-Delgado, *Organometallics* **2009**, *28*, 3192–3202.

[17] S. Jiménez, PhD Thesis, University of Zaragoza (Spain), **2008**.

[18] Hydrogen was detected by a signal at $\delta = 4.45$ ppm in the ^{1}H NMR spectrum in C_6D_6. In the same line, reaction of *p*-methoxybenzaldehyde with **1** in a 4:1 molar ratio at RT showed the initial evolution of hydrogen, followed by the formation of *p*-methoxybenzene and complex **2** in a 1:1 molar ratio as the sole products from aldehyde decarbonylation.

[19] In these cases, the catalysis was accompanied with the formation of $[(PhBP_3)Rh(H)_2(CO)]$ (**2**) and *p*-methoxybenzene/toluene as products coming from the decarbonylation process commented above.

[20] T. Seki, K. Akutsu, H. Hattori, H. *Chem. Commun.* **2001**, 1000–1001.

[21] a) C. Krug, J. F. Hartwig, *Organometallics* **2004**, *23*, 4594–4607; b) C. Krug, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 1674–1679.

[22] a) M. C. Willis, *Angew. Chem.* **2010**, *122*, 6162–6164; *Angew. Chem. Int. Ed.* **2010**, *49*, 6026–6027, and references therein; b) Z. Shen, P. K. Dornan, H. A. Khan, T. K. Woo, V. M. Dong, *J. Am. Chem. Soc.* **2009**, *131*, 1077–1091; c) M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem.* **2004**, *116*, 3448–3479; *Angew. Chem. Int. Ed.* **2004**, *43*, 3368–3398.

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