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Evidence for formation and different evolution of tertiary rhodium alkyl intermediates under rhodium-catalyzed deuterio-(hydro)formylation of 1-(*n*-pyridyl)-1-phenylethenes

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Abstract

Deuterioformylation of the vinylidenic substrates 1-(*n*-pyridyl)-1-phenylethenes, in the presence of phosphine modified $Rh_4(CO)_{12}$ as catalyst precursor, was carried out at 100 atm of CO and D_2 (1:1), 80 °C and at partial and complete substrate conversion.

The direct ^2H NMR analysis of the crude reaction mixture led to the conclusion that, under these conditions, the branched alkyl rhodium intermediate is formed almost exclusively. It can: (i) β-eliminate, (ii) undergo migratory insertion on CO or (iii) oxidative addition of deuterium to various extents depending on the position of the nitrogen atom with respect to the olefinic double bond, thus accounting for the observed different chemo- and regioselectivities.

Keywords: Hydroformylation; Deuterioformylation; Tertiary rhodium-alkyl; Catalysis

1. Introduction

The formation of alkyl metal intermediates via metal hydride addition to the olefinic double bond as well as the reverse reaction, i.e., β-hydride elimination are well known processes in organometallic chemistry [1,2]. It is well known that in the case of rhodium alkyls they play a crucial role in determining the different aspects of the selectivity (chemo-, regio- and stereo-) in the rhodium catalyzed hydroformylation of olefins [3]. Direct experimental evidence for the formation of the alkyl rhodium intermediates is, however, unavailable, because these species are very reactive under typical hydroformylation conditions. In the last decade theoretical investigations [4] have contributed significantly, but deuterioformylation experiments remain the best probe to investigate the nature and the fate of the involved intermediates. Primary and secondary rhodium alkyls have been extensively investigated and show a very different behavior in dependence on reaction conditions as well as substrate nature [3]. Very few tertiary alkyl-metal compounds have so far been described [1a,5]. We recently reported the formation and subsequent evolutions of a tertiary alkyl rhodium intermediate in the hydroformylation of vinylidenic olefins bearing two phenyl groups [6]. It does not exhibit migratory insertion to

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CO but only undergoes a β-hydride elimination process followed by isomerization to primary alkyl, accounting for exclusive formation of the corresponding linear aldehyde. Surprisingly, Botteghi and coll [7] reported that in the hydroformylation of the analogous substrates 1-phenyl-1-pyridylethenes **nPyE** (Scheme 1) the chemo- and regioselectivity values are very different with respect to those ones found for 1,1-diphenylethene and they are strongly affected by the relative position of the nitrogen and the carbon atom bearing the double bond.

Whereas with 1-(3-pyridyl)-1-phenylethene **3PyE** and 1-(4-pyridyl)-1-phenylethene **4PyE** the linear aldehydes **3β** and **4β**, respectively, are predominantly obtained, in the case of 1-(2-pyridyl)-1-phenylethene **2PyE** hydroformylation occurs with the exclusive formation of the branched aldehyde **2α** [7]. Hydrogenation product **nH** is present in all cases too. Some hypotheses have been proposed to explain the different behavior of the three olefin isomers: among those the formation of a tertiary alkyl metal intermediate in equilibrium with the linear one is also invoked but experimental evidences are not reported.

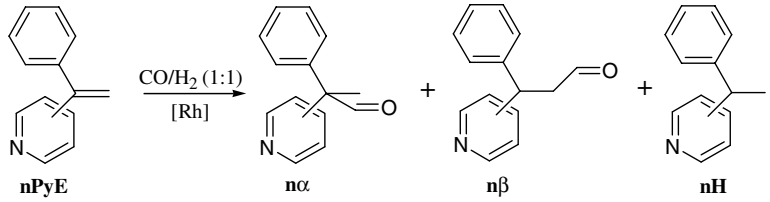
Now we demonstrate that the above results can be completely explained via deuterioformylation experiments: interestingly, we found that the branched alkyl rhodium does still form as the almost exclusive intermediate, but it undergoes different fates depending on the isomeric structure involved.

2. Results and discussion

Deuterioformylation reactions of the vinylidenic olefins 1-(4-pyridyl)-1-phenylethene (**4PyE**), 1-(3-pyridyl)-1-phenylethene (**3PyE**) and1-(2-pyridyl)-1-phenylethene (**2PyE**) were carried out in benzene, in a stainless steel autoclave (25 ml), at 80 °C and 100 atm total pressure (CO/D_2 = 1:1). $Rh_4(CO)_{12}$ modified with triphenylphosphine (Rh/P = 1/4) was used as a catalyst precursor. The analysis of the reaction products was carried out by GC and GC–MS. The chemo- and the regioselectivity values resulted in agreement with hydroformylation data reported by Botteghi [7] and they are depicted in Table 1.

The crude reaction mixtures at partial substrate conversion have been examined by ^2H NMR technique using deuterobenzene as internal standard (7.2 ppm). As far as the region of the vinyl deuterium atoms (6.5–5.0 ppm) is concerned, the signals of deuterated E and Z isomers are sufficiently separated for **2PyE** and **3PyE** while they are superimposed in the case of **4PyE** (Fig. 1). In the case of **4PyE** a signal of medium intensity at 5.20 ppm (Fig. 1(a)) was observed. In contrast, with **3PyE**, a strong resonance partially splitted in two signals at 5.32 and 5.24 ppm, respectively (Fig. 1(b)) was found. Two signals of very low intensity centered at 5.40 and 6.21 ppm were present in the case of **2PyE** (Fig. 1(c)).

The deuterium resonances of both carbonylation and deuteration products as well as of deuterated olefins are



Scheme 1.

Table 1
Distribution of the reaction products in the rhodium catalyzed deuterioformylation of 1-(*n*-pyridyl)-1-phenylethenes **nPyE** at 80 °C, in benzene, at partial substrate conversion[a]

Substrate	Reaction time (h)	Conversion (%)	Composition of reaction products (%)			CS[e] (**D/α + β**)	RS[f] **α/β**
			D[b]	α[c]	**β**[d]		
2PyE	5	34	34	66	–	34/66	>99/1
3PyE	8	42	68	2	30	68/32	6/94
4PyE	4	30	94	–	6	94/6	<1/99

[a] Determined via GLC by using toluene as an internal standard, reaction conditions; 2.75 mmol of vinylidenic olefin, 5 ml of benzene; 0.0106 mmol of $Rh_4(CO)_{12}$, $P(Ph)_3$ (P/Rh = 4), autoclave volume 25 ml, 100 atm total pressure, CO/D_2 (1:1). Similar values of regio- and chemoselectivity were also obtained at total substrate conversion.
[b] Deuteration product.
[c] Branched aldehyde.
[d] Linear aldehyde.
[e] Chemoselectivity.
[f] Regioselectivity.

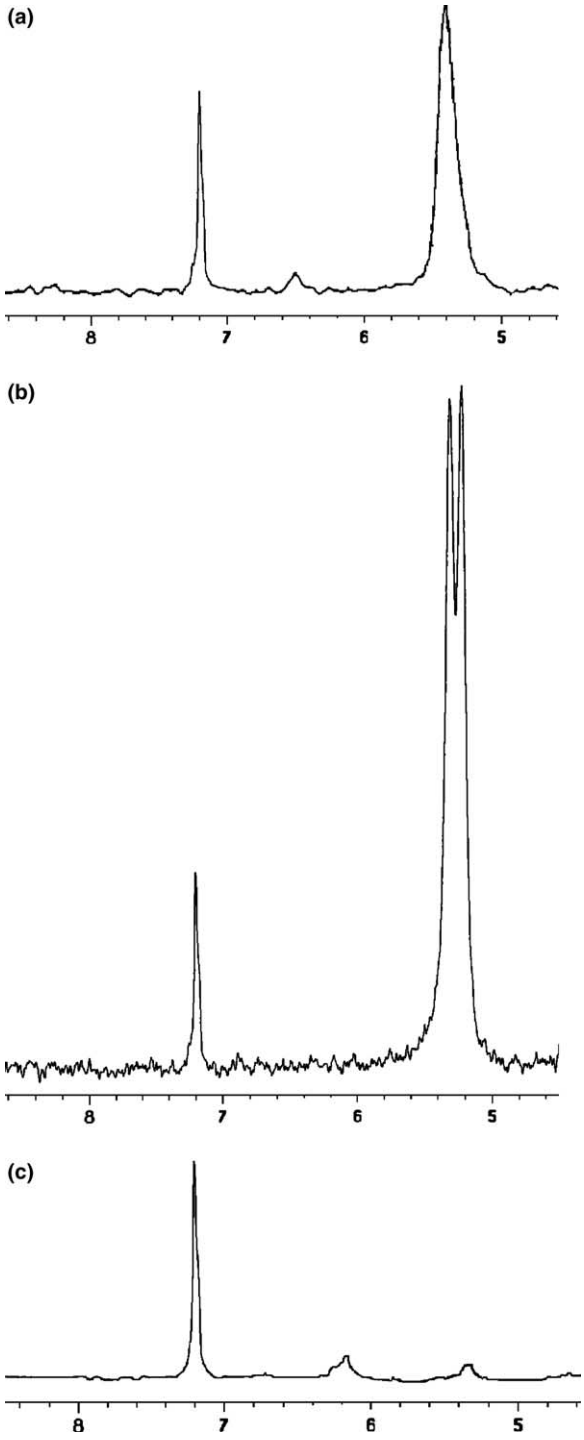


Fig. 1. ^{2}H NMR spectrum (46 MHz) in the range 4.6–8.6 ppm of the crude reaction mixtures recovered from deuterioformylation of: (a) 1-(4-pyridyl)-1-phenylethene; (b) 1-(3-pyridyl)-1-phenylethene; (c) 1-(2-pyridyl)-1-phenylethene at partial substrate conversion, with $Rh_4(CO)_{12}$/$P(Ph)_3$ at 80 °C and 100 atm CO/D_2 (1:1) total pressure, in benzene.

reported in Table 2 and they have been assigned on the basis of the resonances of the corresponding completely undeuterated substrates. Regarding the reduction products, it is to point out that **2D** and **4D** the signals of D^1 and D^2 are of the same intensity while in the case of **3D** the signal of these deuterium atoms are in a 1.0/2.5 ratio. As far as the carbonyl compounds is concerned, an expected 1:1 ratio of the D^1 and D^3 signals was found into the linear aldehyde **4β**. In contrast, an additional resonance of high intensity at 2.46 ppm was present into **3β**.

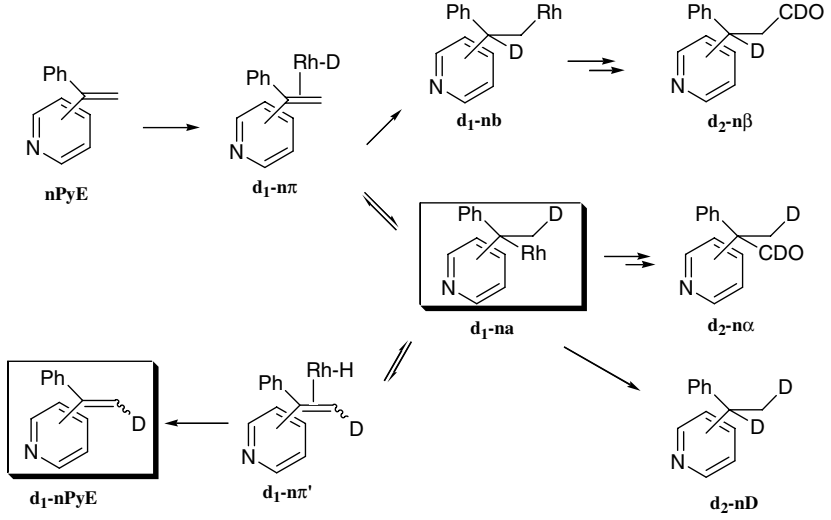
The above results allow us to formulate proper mechanistic rationalizations. The presence of deuterium atoms onto the terminal carbon atom of the olefin indicates that a β-elimination occurs and it necessary involves a tertiary rhodium-alkyl intermediate (Scheme 2).

Taking into account the intensity of the signal corresponding to the deuterium atom in position 1 of the reduction products **d_2-nD** as a standard signal and comparing the intensity of this signal with that one due to the linear aldehydes **d_2-nβ** as well as the deuterated olefin **d_1-nPyE**, we can establish the incidence of the β-elimination on the hydroformylation of the three isomers (Table 2). In the case of **4PyE**, for 1 mol of reduction product **d_2-4D**, 0.44 mol of deuterated olefin **d_1-4PyE** occur (β-elimination) and only 0.09 mol of dideuterated linear aldehyde **d_2-4β** does form. In the case of **2PyE**, for 1 mol of reduction product **d_2-2D**, 0.03 mol of **d_1-2PyE** via β-elimination only is formed, together with 1.9 mol of dideuterated branched aldehyde **d_2-2α**. More complicate is the case of **3PyE** because a β-hydride elimination process occurs both for undeuterated and monodeuterated **3PyE**. For 1 mol of reduction product, 1.14 mol of deuterium on the olefinic double bond is present. Thus a mixture of monodeuterated **d_1-3PE** and dideuterated **d_2-3PyE** is formed. Indeed a portion of **d_1**- and **d_2**-deuterated olefins has been transformed into **d_3**- and **d_4**-reduction product (2.5 deuterium atoms onto the methyl group instead of 1) and into the linear aldehyde (0.46 deuterium atoms in position α to the formyl group). Taking into account all contributions (Table 2, 1.14 mol from **3PyE**, 0.46 mol from **4β** and 1.5 mol from **3D**), we can conclude that, in the case of **3PyE**, the process occurs giving for 1 mol of reduction product 3 mol of β-elimination products. In conclusion the overall β-elimination process is very remarkable for **3PyE**, significant for **4PyE** but negligible for **2PyE**. Thus in all cases a tertiary rhodium alkyl is the almost exclusive intermediate, as previously observed with 1,1-diphenylethene. A possible rationalization of different behavior of three substrates could be done taking into account the different position of the annular nitrogen atom with respect to the vinyl group as well as the different polarization of the carbon–rhodium bond in the three isomers. It is to be noted that the electron poor pyridine ring possesses a positive charge on positions 2 and 4 and no charge on position 3 [8]. With **2PyE** isomer, as previously observed by Botteghi et al. [7b], the rhodium-acyl intermediate is strongly established thanks to an intramolecular coordination of the annular nitrogen to the rhodium atom with formation of a five-membered ring: this

Table 2
Distribution of deuterium atoms in the reaction products in the rhodium catalyzed deuterio formylation of 1-(*n*-pyridyl)-1-phenylethenes[a,b,c]

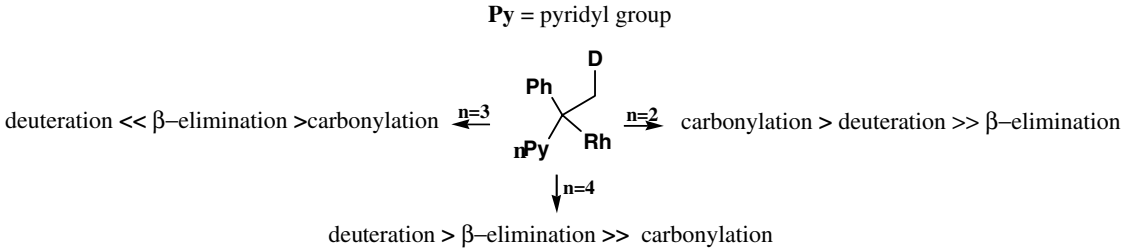
Products	**2PyE**			**3PyE**			**4PyE**		
	D^1	D^2	D^3	D^1	D^2	D^3	D^1	D^2	D^3
D	1.0 (4.17)	1.0 (1.71)	– –	1.0 (3.69)	2.5 (1.30)	– –	1.0 (3.69)	1.0 (1.21)	– –
α	– –	1.86 (1.71)	1.86 (10.21)	– –	0.01 (1.48)	0.01 (9.57)	– –	– –	– –
β	– –	– –	– –	0.25 (4.19)	0.46 (2.46)	0.25 (9.17)	0.09 (4.20)	– –	0.09 (9.21)
PyE	– –	0.03 (5.40) (6.21)	– –	– –	1.14 (5.32)	– –	– –	0.44 (5.20)	– –

[a] Deuterium atom in the position 1 of the deuteration product **D** (D^1 atom) was taken as a standard (value 1) for evaluating deuterium atom in the different position of the reaction products **D**, **α**, **β** and unconverted olefin **PyE**.
[b] In parenthesis ^2H NMR chemical shifts referred to C_6D_6 as external standard, benzene as solvent, 46 MHz.
[c] The conversion values are the same as reported in Table 1.



Scheme 2.

explain the absence of β-elimination as well as of isomerization of the branched alkyl to the linear one.As far as **4PyE** is concerned, the weak polarization of the C–Rh bond in the branched alkyl could favor the oxidative addition of deuterium with respect to the β-elimination and the migratory insertion. In the case of **3PyE** the polarization of the C–Rh bond in the branched alkyl is probably similar to that one of the branched alkyl derived from 1,1-diphenylethene [9], accounting for the similar behavior of the two substrates. Then, as occurs for 1,1-diphenylethene, the presence of two very polarized groups, on the carbon atom in position 1 of the olefin, favors formation of the tertiary alkyl. However, due to steric hindrance, the migratory insertion onto CO is disfavored, hence this intermediate can either β-eliminate or undergo D_2 addition. A comparison of the



Scheme 3.

results obtained in the hydroformylation of vinylidenic olefins with those previously reported [8] for the corresponding vinyl olefins 2-vinylpyridine, 3-vinylpyridine and 4-vinylpyridine provides evidence for the different behavior of the branched alkyl rhodium intermediates of secondary and/or tertiary type. With the same rhodium–phosphine catalyst system the vinyl olefins give complete selectivity into aldehydes with a large or complete prevalence of the branched aldehyde. Therefore, the secondary rhodium-alkyls give almost exclusive migratory insertion on CO and then branched aldehyde [8c–10]. Neither β-elimination nor isomerization to primary alkyl occurs. In contrast in the case of vinylidenic olefins, in consequence of the high steric hindrance, the migratory insertion of the alkyl on CO is very unfavored for **3PyE** and **4PyE**, in comparison with reduction and β-elimination processes (Scheme 3).

3. Experimental

Benzene was dried over molecular sieves and distilled under nitrogen. $Rh_4(CO)_{12}$ was prepared according to a well-known procedure [11]. 1-(*n*-pyridyl)-1-phenylethenes **nPyE** were prepared as described in the literature [7,12,13]. GC analyses of the reaction mixtures were performed on a Perkin–Elmer 8700 chromatograph equipped with a 12 m × 0.22 mm BP5 capillary column, by using nitrogen as carrier gas. ^2H NMR spectra of the crude reaction mixture in benzene were recorded on a Varian VXR 300 spectrometer operating at 46 MHz for ^2H. Chemical shifts were referred to C_6D_6 as external standard.

3.1. Hydroformylation and deuterioformylation experiments: general procedure

A solution of **nPyE** (2.75 mmol) and $Rh_4(CO)_{12}$ (0.0106 mmol), triphenylphosphine (corresponding to the desired P/Rh = 4/1 molar ratio) in benzene (5 ml) was introduced by suction into an evacuated 25 ml stainless-steel autoclave. Carbon monoxide was introduced, the autoclave was then rocked and heated to 80 °C, and hydrogen or deuterium was rapidly introduced to 100 atm total pressure. When the gas absorption reached the value corresponding to the desired conversion, the reaction mixture was siphoned out and GC was used to determine the reaction composition and the degree of conversion, by using toluene as internal standard.

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