

# Inter- and Intramolecular Protium-Deuterium Exchange in the Rhodium-Catalyzed Deuterioformylation of Styrene

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Rhodium-catalyzed deuterioformylation of styrene has been investigated at various temperatures (25–130 °C) and for different degrees of substrate conversion. The isomeric aldehydes 2-phenylpropanal and 3-phenylpropanal have been analyzed by MS and <sup>1</sup>H NMR spectroscopy, and the distribution of deuterated species and deuterium content at each carbon atom have been determined. At room temperature, only the two aldehydes expected on a stoichiometric basis are formed and neither HD nor labeled styrenes are found in the reaction mixture. At high temperature, variable deuterium incorporation occurs in the reactants and in the products. In particular, an increasing of deuterium content in the aldehydes with increasing of reaction temperature and substrate conversion and a larger amount of deuterium incorporated in the branched aldehyde have been observed. These results have been explained taking into account the different behaviors of the two alkyl metal intermediates toward the β-hydride elimination process: at room temperature this process is not reversible for both isomers, whereas at high temperature it is still irreversible for the linear alkyl but becomes reversible for the branched one.

## Introduction

In the framework of hydroformylation of unsaturated substrates, styrene and para-substituted styrenes receive particular attention, especially because they show an anomalous α regioselectivity, i.e. a large prevalence of the branched isomer (2-phenylpropanal), as compared with that observed for simple alkyl α-olefins.<sup>1-4</sup> It has been also observed that the reaction parameters affect the regioselectivity of the reaction, the amount of α isomer decreasing at high temperature, and low gas pressure.<sup>5,6</sup> An isomerization of the branched alkyl-rhodium intermediate to the linear one under hydroformylation conditions has been hypothesized to explain the results discussed above.<sup>2,6</sup>

In a previous report on the rhodium-catalyzed deuterioformylation of styrene at partial conversion of the substrate, the occurrence of such an isomerization process was pointed out by the analysis of the unconverted styrene.<sup>7</sup>

We report here a detailed investigation on the protium-deuterium exchange occurring in both inter- and intramolecular ways between the olefin, the reagent gas, and the aldehydes. We studied the deuterioformylation of styrene at various temperatures, in the range 25–130 °C, and, for the reaction at 90 °C, at different degrees of conversion of the substrate. The isomeric aldehydes 2-phenylpropanal (α isomer, 2PP) and 3-phenylpropanal (β isomer, 3PP) have been analyzed by MS spectrometry and <sup>1</sup>H NMR spectroscopy with the aim to determine the distribution of deuterated species as well as the deuterium content at each carbon atom. Inter-molecular protium-deuterium exchange between substrate and gas phase has been investigated via MS analysis of residual gas.

## Results

**Deuterioformylation of Styrene.** Deuterioformylation of styrene (Scheme I) has been carried out at different temperatures between 25 and 130 °C under 160 atm of CO and D<sub>2</sub> (1/1) at constant pressure with Rh<sub>4</sub>(C-

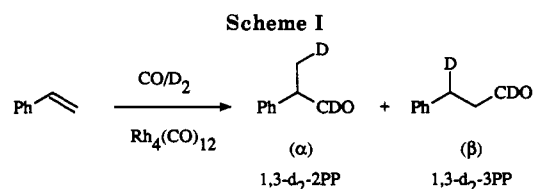


Table I. Degree of Regioselectivity in the Rh-Catalyzed Deuterioformylation of Styrene at Different Reaction Temperatures and Substrate Conversions<sup>a</sup>

reacn temp, °C	reacn time, min	converts to aldehydes, <sup>b</sup> %	α/β ratio <sup>c</sup>
25	3000	100	98/2
60	1200	100	94/6
90	18	25	83/17
90	30	42	83/17
90	85	90	83/17
90	120	100	83/17
110	95	100	76/24
130	45	100	63/37

<sup>a</sup> A 5-mL benzene solution containing 0.02 mol of substrate and 0.1 mg (ratio substrate/Rh 37 000; 10 mg for the 25 °C run, ratio 370) of Rh<sub>4</sub>(CO)<sub>12</sub>; CO/D<sub>2</sub> (1/1), 180 atm (±2 atm); volume of reaction vessel 50 mL. <sup>b</sup> Refers to styrene, determined by GC with toluene as internal standard. <sup>c</sup> Estimated accuracy ±1%.

O)<sub>12</sub> as a catalytic precursor (Table I). The reaction at 90 °C has been carried out for various degrees of substrate conversion. Less than 5% of polymerization of styrene occurs when the reaction is carried out at 25 °C, but no high-boiling compounds are formed in reactions at higher

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**Table II. Deuterium Content of the Branched and Linear Aldehydes Determined via MS Analysis of the Rh-Catalyzed Deuterioformylation of Styrene**

temp, °C	conv, %	isotopic species distribution for the $\alpha$ aldehydes, <sup>a</sup> %							NDM <sup>b</sup>	isotopic species distribution for the $\beta$ aldehyde, <sup>a</sup> %							NDM <sup>b</sup>	
		d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>5</sub>	d <sub>0</sub>		d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>5</sub>				
25	100	0.5	2.4	95.0	1.4	0.7			1.99									
60	100	0.8	8.2	78.9	10.5	1.6	0.1		2.04	0.6	9.9	78.3	9.8	1.3				2.01
90	25	0.6	39.6	50.5	8.1	0.9			1.69	1.8	42.6	48.8	6.1	0.6				1.61
90	42	0.6	30.1	54.2	12.8	2.3	0.1		1.86	1.9	33.9	52.8	10.0	1.4				1.75
90	90	0.5	20.7	46.5	23.6	8.4	0.2		2.19	1.1	23.8	49.9	20.0	5.1	0.1			2.04
90	100	0.9	16.2	46.4	25.0	11.3	0.3		2.31	1.1	19.8	52.2	20.5	6.2	0.3			2.12
110	100	0.8	13.4	31.5	28.6	25.0	0.8		2.66	1.1	18.7	39.8	25.9	13.7	0.9			2.35
130	100	1.0	9.8	21.7	29.4	34.6	3.7		2.98	1.4	15.1	30.7	28.7	19.8	4.3			2.63

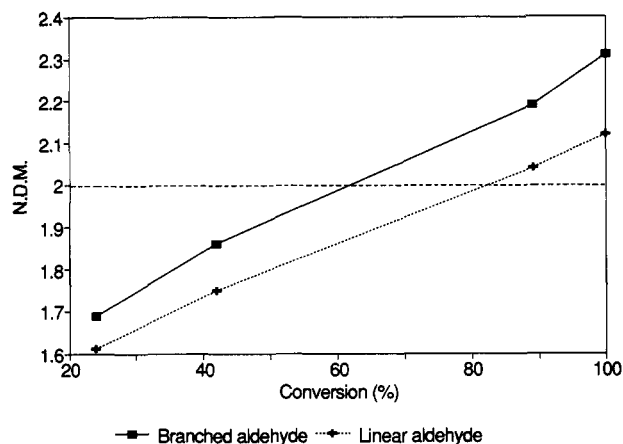
<sup>a</sup> Estimated accuracy  $\pm 1\%$ . <sup>b</sup> Average number of deuterium atoms per molecule.

temperatures. The ratio between 2-phenylpropanal ( $\alpha$  isomer) and 3-phenylpropanal ( $\beta$  isomer) obtained in each experiment was determined by GLC analysis. At 25 °C the  $\alpha$  isomer strongly predominates over the  $\beta$  one ( $\alpha/\beta$ : 98/2); the ratio becomes smaller and smaller by increasing the reaction temperature ( $\alpha/\beta$ : 63/37 at 130 °C). Chemically pure samples of  $\alpha$ - and  $\beta$ -isomeric aldehydes and of unreacted styrene were obtained by fractional distillation at reduced pressure followed by preparative GLC.

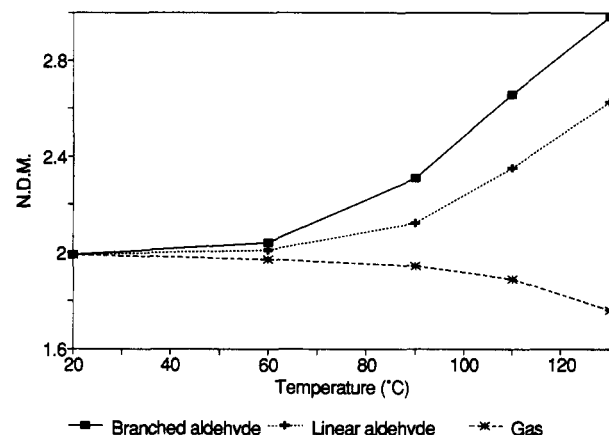
The crude reaction mixture was analyzed by MS spectrometry, as well as the pure samples of isomeric aldehydes, and these last were analyzed also by <sup>1</sup>H NMR spectroscopy in order to determinate the extent of incorporation of deuterium atoms and their position in the molecules.

**Deuterium Content of Isomeric Aldehydes. MS Analysis.** It is known that the mass spectrum of aldehydes at 70 eV shows beside the molecular ion peak the M - 1 peak,<sup>8</sup> this last one being especially significant in the case of the linear  $\beta$  isomer. This fact complicates the analysis of a mixture of deuterated aldehydes, and an accurate evaluation of the relative amounts of the various deuterated components is, under these conditions, practically impossible. We found that the M - 1 peak is completely absent, analogously to that found for the styrene<sup>7</sup> if the spectrum is obtained at lower energy (ca. 10 eV). Thus the distribution of deuterated species in the isomeric aldehydes was very easily determined from the mass spectra at low energy.

Another problem for this determination arises from a partial separation of the various deuterated components in the gas-chromatographic columns, and the retention times of the more deuterated compounds are slightly smaller with respect to the less deuterated ones. This partial separation strongly affects the analysis as the MS spectrum changes depending on the acquisition point onto the chromatographic peak. There are several possibilities to override this problem. We tried some different methods, in particular the GLC-MS analysis in selected ion recording (SIR) mode, the GLC-MS analysis in continuum acquisition mode, and the direct introduction of pure samples into the source. All of them gave comparable results, and we describe here only the first one. The results obtained are shown in Table II. When the reaction is carried out at 25 °C, practically no hydrogen-deuterium exchange takes place, and the only products of the reaction are the isomeric dideuterated (d<sub>2</sub>) aldehydes 1,3-dideuterio-2-phenylpropanal ( $\alpha$  isomer, 1,3-d<sub>2</sub>-2PP) and 1,3-dideuterio-3-phenylpropanal ( $\beta$  isomer, 1,3-d<sub>2</sub>-3PP). The average number of deuterium atoms per molecule (NDM) is the same of the starting deuterium (1.99).



**Figure 1.** Average number of deuterium atom per molecule versus conversion for the isomeric aldehydes obtained from the deuterioformylation of styrene.



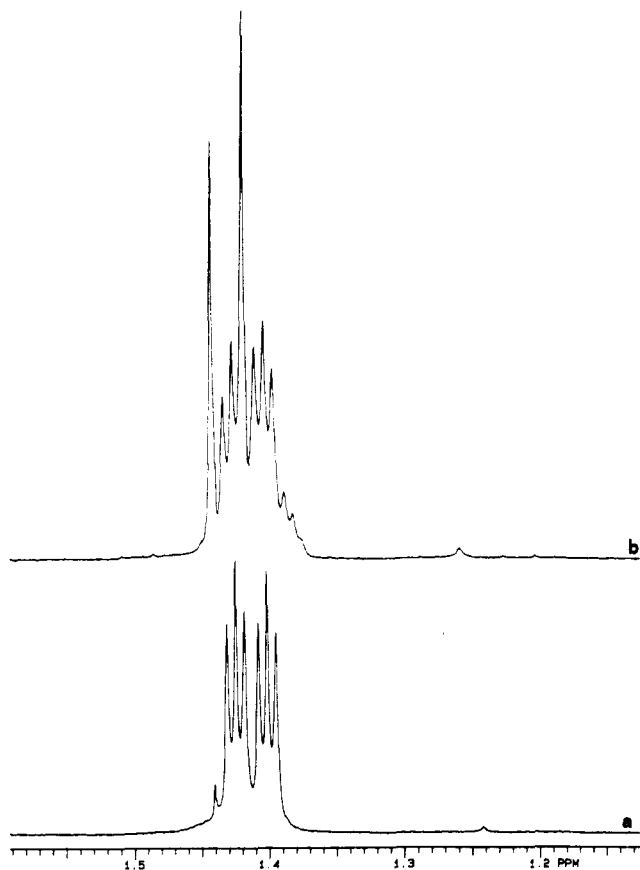
**Figure 2.** Average number of deuterium atoms per molecule versus temperature for the isomeric aldehydes obtained from the deuterioformylation of styrene and for the residual deuterium gas.

In the case of the reaction at 90 °C, at partial and complete conversion of substrate, we can observe an increasing of the NDM with the increasing of the conversion (Figure 1), the NDM being higher for the  $\alpha$  isomer. It is worthy to note that the NDM is less than 2 for low conversions and more than 2 for higher conversions.

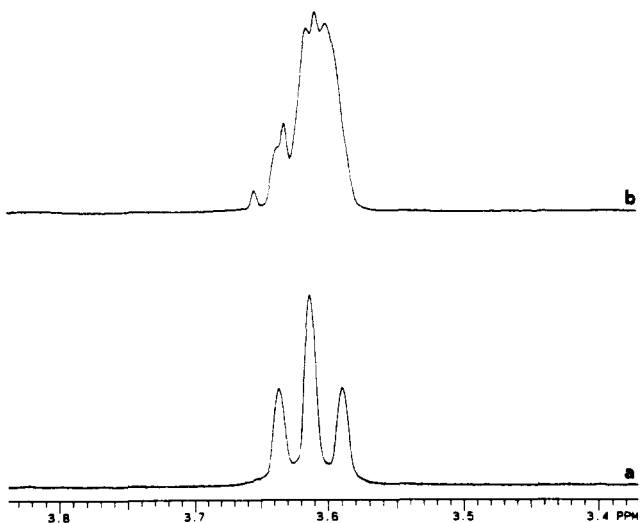
As far as the influence of the temperature is concerned, we can observe an increasing of the NDM with the increasing of the temperature. The effect is remarkably stronger for the  $\alpha$  aldehyde than for the  $\beta$  one (Figure 2).

**NMR Analysis.** Chemically pure samples of aldehydes in CCl<sub>4</sub> solution were analyzed by <sup>1</sup>H NMR spectroscopy at 300 MHz. The proton spectrum of the  $\alpha$  isomer, produced in the reaction at 25 °C, mainly shows signals coming from the 1,3-dideuterio-2-phenylpropanal: a doublet

(8) See for example: Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Mass Spectrometry of Organic Compounds*; Holden-Day: San Francisco, CA, 1967; pp 129-162.



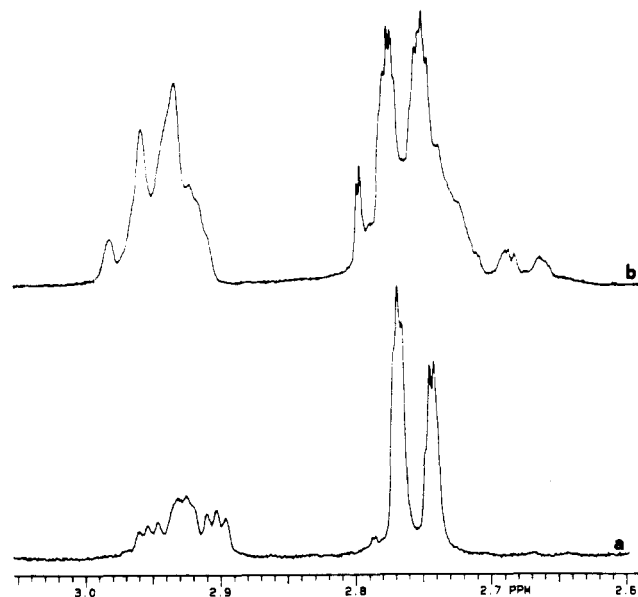
**Figure 3.**  $^1\text{H}$  NMR spectra of the methyl region (300 MHz,  $\text{CCl}_4$ , 25  $^\circ\text{C}$ , TMS as internal standard) of the branched aldehyde obtained from the deuteroformylation of styrene: (a) reaction carried out at 25  $^\circ\text{C}$ ; (b) reaction carried out at 130  $^\circ\text{C}$ .



**Figure 4.**  $^1\text{H}$  NMR spectra of the methine region (300 MHz,  $\text{CCl}_4$ , 25  $^\circ\text{C}$ , TMS as internal standard) of the branched aldehyde obtained from the deuteroformylation of styrene: (a) reaction carried out at 25  $^\circ\text{C}$ ; (b) reaction carried out at 130  $^\circ\text{C}$ .

of triplets centered at 1.414 ppm ( $^3J_{\text{H-H}} = 7.0$  Hz;  $^2J_{\text{H-D}} = 1.9$  Hz) due to the  $\text{CH}_2\text{D}$  group (Figure 3a) and a triplet at 3.612 ppm due to its vicinal methine group (Figure 4a). The minor signal at 1.442 ppm (Figure 3a) is the low-field component of the doublet due to a small amount (<2%) of nondeuterated methyl group.

The spectrum of the same isomer recovered from the run at 130  $^\circ\text{C}$  is more complex because of the presence of several labeled and unlabeled species. As shown in Figure 3b, a complex pattern of signals is observed between 1.370



**Figure 5.**  $^1\text{H}$  NMR spectra (300 MHz,  $\text{CCl}_4$ , 25  $^\circ\text{C}$ , TMS as internal standard) of the linear aldehyde obtained from the deuteroformylation of styrene: (a) reaction carried out at 25  $^\circ\text{C}$ ; (b) reaction carried out at 130  $^\circ\text{C}$ .

and 1.460 ppm. The following absorptions can be easily recognized: a doublet at 1.432 ppm due to the unlabeled methyl group ( $^3J_{\text{H-H}} = 7.0$  Hz), a doublet of triplets centered at 1.414 ppm ( $^3J_{\text{H-H}} = 7.0$  Hz;  $^2J_{\text{H-D}} = 1.9$  Hz) due to the monodeuterated methyl group  $\text{CH}_2\text{D}$ , and a more complex signal between 1.380 and 1.425 ppm, partially covered by the  $\text{CH}_2\text{D}$  absorption, which is originated by the resonance of the dideuterated methyl group  $\text{CHD}_2$  (the high-field component is observed). Correspondingly, in the methine absorption region (Figure 4b), a quartet at 3.623 ppm is found, which is due to the methine proton adjacent to the nondeuterated  $\text{CH}_3$  group. This signal is partially superimposed on the triplet at 3.612 ppm arising from the methine proton vicinal to the  $\text{CH}_2\text{D}$  group. The signals due to the  $\text{CH}$  vicinal to  $\text{CHD}_2$  or  $\text{CD}_3$  are not resolved.

As far as the  $\beta$  isomer is concerned, its absorptions are found between 2.700 and 2.980 ppm (Figure 5). The product obtained by deuteroformylation at 25  $^\circ\text{C}$  originates only signals due to the 1,3-dideuterated species. The resonance centered at 2.928 ppm (Figure 5a) is due to the  $\text{CHD}$  group  $\beta$  to the  $\text{CDO}$  group. This absorption is a triplet of triplets due to vicinal coupling to the adjacent  $\text{CH}_2$  protons ( $^3J_{\text{H-H}} = 7.0$  Hz) and geminal coupling to deuterium ( $^2J_{\text{H-D}} = 2$  Hz). The doublet at 2.755 ppm ( $^3J_{\text{H-H}} = 7.0$  Hz) is due to the nondeuterated methylene protons that are  $\alpha$  to the  $\text{CDO}$  group; their further splitting arises from the long-range coupling to the deuterium of  $\text{CDO}$ .

In the linear product formed at 130  $^\circ\text{C}$  a larger number of labeled species is detected in the proton spectrum (Figure 5b); however, the resolution was not sufficient to get their complete characterization.

The analysis of the proton spectra also revealed that the carbonyl function is fully deuterated in the linear and the branched products obtained from the run at temperatures lower than 90  $^\circ\text{C}$ . The products obtained at 110 and 130  $^\circ\text{C}$  show detectable proton resonances at 9.670 ppm (doublet;  $^2J_{\text{H-H}} = 1.4$  Hz) and 9.820 ppm (triplet;  $^2J_{\text{H-H}} = 1.4$  Hz), which are due to the  $\text{CHO}$  absorptions of the branched and the linear isomers, respectively.

An accurate quantitative determination of the deuterium content was also performed on the basis of the analysis of

**Table III. Deuterium Content of the Branched and Linear Aldehydes Determined via NMR Analysis<sup>a</sup> of the Rh-Catalyzed Deuterioformylation of Styrene<sup>b</sup>**

$$\begin{array}{c}
 3 \quad 1 \\
 \diagdown \quad / \\
 \text{C} \\
 | \\
 \text{Ph} \\
 \alpha
 \end{array}$$

$$\begin{array}{c}
 3 \quad 1 \\
 \diagdown \quad / \\
 \text{C} \\
 | \\
 \beta
 \end{array}$$

temp, °C	conv, %	H content at each C for the $\alpha$ aldehyde			NDM <sup>c</sup>	H content at each C for the $\beta$ aldehyde			NDM <sup>c</sup>
		H(C <sub>1</sub> )	H(C <sub>2</sub> )	H(C <sub>3</sub> )		H(C <sub>1</sub> )	H(C <sub>2</sub> )	H(C <sub>3</sub> )	
25	100	<0.01	1.00	2.01	1.99	<0.01	2.00	1.01	1.99
60	100	0.01	1.00	1.97	2.02	<0.01	1.89	1.07	2.03
90	25	0.00	1.00	2.33	1.67	0.01	1.87	1.50	1.62
90	42	0.02	1.00	2.11	1.87	0.01	1.81	1.45	1.73
90	90	0.02	1.00	1.78	2.21	0.02	1.60	1.33	2.05
90	100	0.03	1.00	1.65	2.32	0.02	1.60	1.28	2.10
110	100	0.06	0.98	1.30	2.64	0.05	1.30	1.28	2.37
130	100	0.12	0.90	1.03	2.95	0.10	1.03	1.27	2.60

<sup>a</sup> Calculated by using the five protons of the phenyl group as an internal standard, estimated accuracy  $\pm 1\%$ . <sup>b</sup> Reaction conditions: 5-mL benzene solution containing 0.02 mol of substrate and 0.1 mg of Rh<sub>4</sub>(CO)<sub>12</sub>; CO/D<sub>2</sub> (1/1), 180 atm ( $\pm 2$  atm); volume of reaction vessel 50 mL. <sup>c</sup> Average number of deuterium atoms per molecule.

the proton spectra. Taking into account that no labeling at the phenyl ring occurred, we assumed the resonances of the aromatic protons as an internal standard. Thus, by comparing their areas to those of the other proton resonances, we calculated the amount of protons and hence of deuterium atoms on each carbon atom of the  $\alpha$  and  $\beta$  aldehydes. The corresponding data are summarized in Table III.

**$\alpha$  Isomer.** No deuterium atom are present on the C<sub>2</sub> carbon atom of the branched isomer when the reaction is carried out at temperatures lower than 110 °C (protium content 0.98–1.00), whereas at 130 °C about 10% of the protium atoms are replaced by deuterium atoms. Two protons and hence one deuterium are present on the C<sub>3</sub> carbon atom in the experiment performed at 25 °C, in agreement with the stoichiometry of the reaction. At complete conversion the amount of protium atoms on the C<sub>3</sub> carbon atom decreases by increasing the temperature, ranging from 2 at 25 °C to 1.03 at 130 °C. At partial conversion (experiments at 90 °C) the protium content is more than 2 at low conversion (2.33 after 25%) and less than 2 at higher conversion (1.65 after 100%). As a consequence, the NDM is 2 at 25 °C, lower than 2 at 90 °C for low conversions, and it approximates 3 at 130 °C after complete conversion.

**$\beta$  Isomer.** Stoichiometric amounts of protium and hence of deuterium are present on the C<sub>2</sub> and C<sub>3</sub> atoms at room temperature. The protium amount on the C<sub>2</sub> atom decreases with increasing temperature and conversion and approximates 1 at 130 °C. The protium content on C<sub>3</sub> increases from 1 to 1.27–1.28 with increasing temperature, and it decreases from 1.50 to 1.28 with increasing conversion at 90 °C. The NDM is 2 at room temperature, lower than 2 at 90 °C for low conversion, and more than 2 at higher temperatures after complete conversion. It is noteworthy that the NMR data are in a very good agreement with the MS data.

**Deuterium Content of Unconverted Styrene.** The incorporation of deuterium in the unconverted styrene in the deuterioformylation experiments carried out at 25 and 90 °C has been carefully determined by <sup>1</sup>H NMR and MS techniques as described in a previous paper.<sup>7</sup> The results obtained can be summarized as follows: At 25 °C no deuterium is present in the unconverted styrene, and at 90 °C styrene incorporates deuterium exclusively at the terminal carbon atom; the average number of deuteriums per molecule (NDM) increases from 0.24 to 0.96 with increasing conversion from 24 to 96%. In the experiment

**Table IV. Composition of Deuterium Present in the Residual Gases Recovered from the Rh-Catalyzed Deuterioformylation of Styrene at Different Temperatures**

reacn temp °C	isotopic species distribution for the deuterium, <sup>a</sup> %			NDM <sup>b</sup>
	H <sub>2</sub>	HD	D <sub>2</sub>	
25	0.1	0.7	99.2	1.99
60	0.2	2.2	97.6	1.97
90	0.2	5.6	94.2	1.94
110	0.5	10.3	89.2	1.89
130	2.0	20.4	77.6	1.76

<sup>a</sup> Estimated accuracy  $\pm 1\%$ . <sup>b</sup> Average number of deuterium atoms per molecule.

at 130 °C deuterium is also present on the C<sub>2</sub> carbon atom of the vinyl group but only in a small amount.

**Deuterium Content of Residual Reaction Gas.** The deuterium contents of residual reaction gases have been determined via MS analysis by direct introduction of samples of gas into the source of the spectrometer, using He ( $m/z$  4.0026, coming from the GLC column) as a standard. Under these conditions (resolution around 2000) it is possible to distinguish among the peaks due to H<sub>2</sub> ( $m/z$  2.0156), D ( $m/z$  2.0141), coming from the fragmentation of D<sub>2</sub> and HD, HD ( $m/z$  3.0219), and D<sub>2</sub> ( $m/z$  4.0282). The results are reported in Table IV and shown in Figure 2.

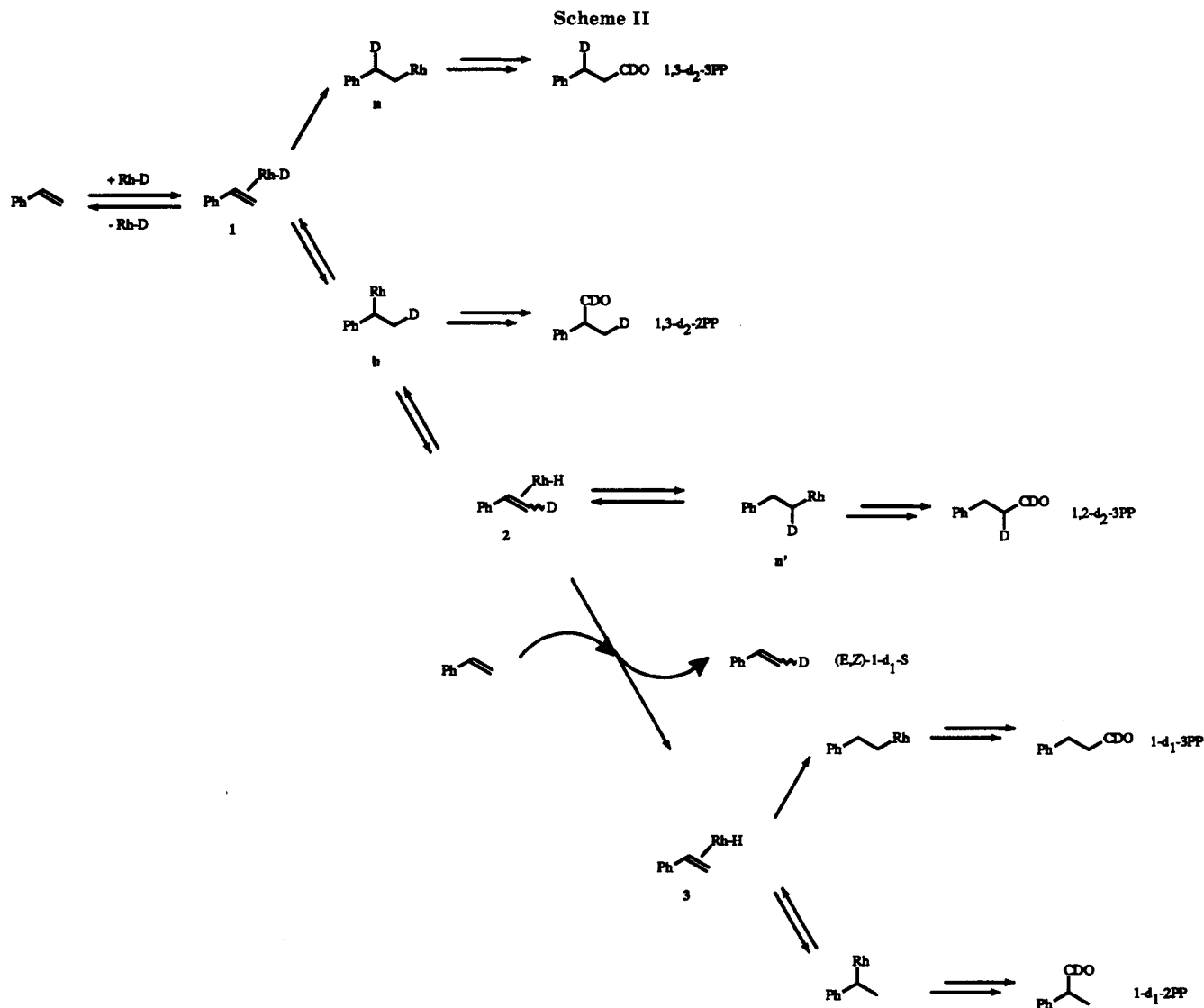
The results found point out that an intermolecular hydrogen–deuterium exchange occurs, besides the intramolecular one, when the reaction is carried out at temperatures higher than 25 °C.

It must be noted that no deuterium incorporation occurs in the solvent: The MS spectrum of the benzene recovered from the reaction shows the normal isotopic cluster expected for unlabeled benzene.

### Discussion and Conclusion

The results of this investigation clearly show that variable deuterium incorporation occurs in the reactants and in the products when deuterioformylation of styrene is carried out at temperatures higher than room temperature.

The deuterated species observed in solution, in addition to HD in the gas phase, are mono- and dideuteriostyrene, labeled at the terminal carbon atom of the vinyl group, and mono-, di-, tri-, and tetra-deuterated isomeric aldehydes ( $\alpha$  and  $\beta$ ) characterized by the presence of one hydrogen atom on the carbon atom in the  $\alpha$  position to the phenyl



ring (HD; PhCH=CHD; PhCH=CD<sub>2</sub>; PhCH(CX<sub>3</sub>)CDO and PhCHXCX<sub>2</sub>CDO, X = H, D). By contrast, when the reaction is carried out at room temperature, only the two aldehydes expected on the basis of the reaction stoichiometry are formed, namely 1,3-dideuterio-3-phenylpropanal and 1,3-dideuterio-2-phenylpropanal. It is also noteworthy that neither HD nor labeled styrenes are found in the reaction mixture under these conditions.

The above results clearly show that, in the outline of the generally accepted mechanism of rhodium-catalyzed hydroformylation,<sup>4a,9-11</sup> the formation of the alkylrhodium intermediates is not reversible at room temperature for both the isomers; at higher temperatures it is still irreversible for the linear isomer, but it becomes reversible for the branched one. Thus, according to Scheme II, the linear rhodium alkyl (n) gives the expected 1,3-dideuterio-3-phenylpropanal (1,3-d<sub>2</sub>-3PP), while the branched isomer (b) gives the branched aldehyde 1,3-dideuterio-2-phenylpropanal (1,3-d<sub>2</sub>-2PP) or undergoes a β-hydride elimination process affording the rhodium hydride π-complex 2, in which 1-deuteriostyrene (1-d<sub>1</sub>-S) is coordinated to a Rh-H. The insertion of the olefin into the Rh-H bond regenerates the starting branched alkyl (b) or produces the isomeric

linear alkyl (n') from which 1,2-dideuterated linear aldehyde (1,2-d<sub>2</sub>-3PP) is formed. The overall process is, therefore, the isomerization of the branched isomer (b) to the linear one (n') in which a deuterium atom is present on the carbon atom bound to the metal. On the other hand the π-complex 2 can undergo an intramolecular exchange process with unlabeled styrene, producing monodeuteriostyrene (1-d<sub>1</sub>-S) and unlabeled π-complex 3. This last can generate the branched or linear unlabeled alkyl and hence the branched and linear monodeuterated aldehydes (1-d<sub>1</sub>-2PP and 1-d<sub>1</sub>-3PP). When the monodeuterated styrene gives a π-complex, 4, with a Rh-D species (Scheme III), dideuterated rhodium alkyls n'' and b'' are formed, which produce trideuterated isomeric aldehydes 1,2,3-d<sub>3</sub>-3PP and 1,3,3-d<sub>3</sub>-2PP. A β-hydride elimination process from the branched rhodium alkyl b'' can originate the π-complex of dideuterated styrene with Rh-H (5) from which 1,2,2-trideuterio-3-phenylpropanal and 1,3,3-trideuterio-2-phenylpropanal are formed. Exchange process with unlabeled styrene gives 1,1-dideuteriostyrene (1,1-d<sub>2</sub>-S). Its coordination to Rh-D gives π-complex 6, i.e. the precursor of tetradeuterated isomeric aldehydes (Scheme IV).

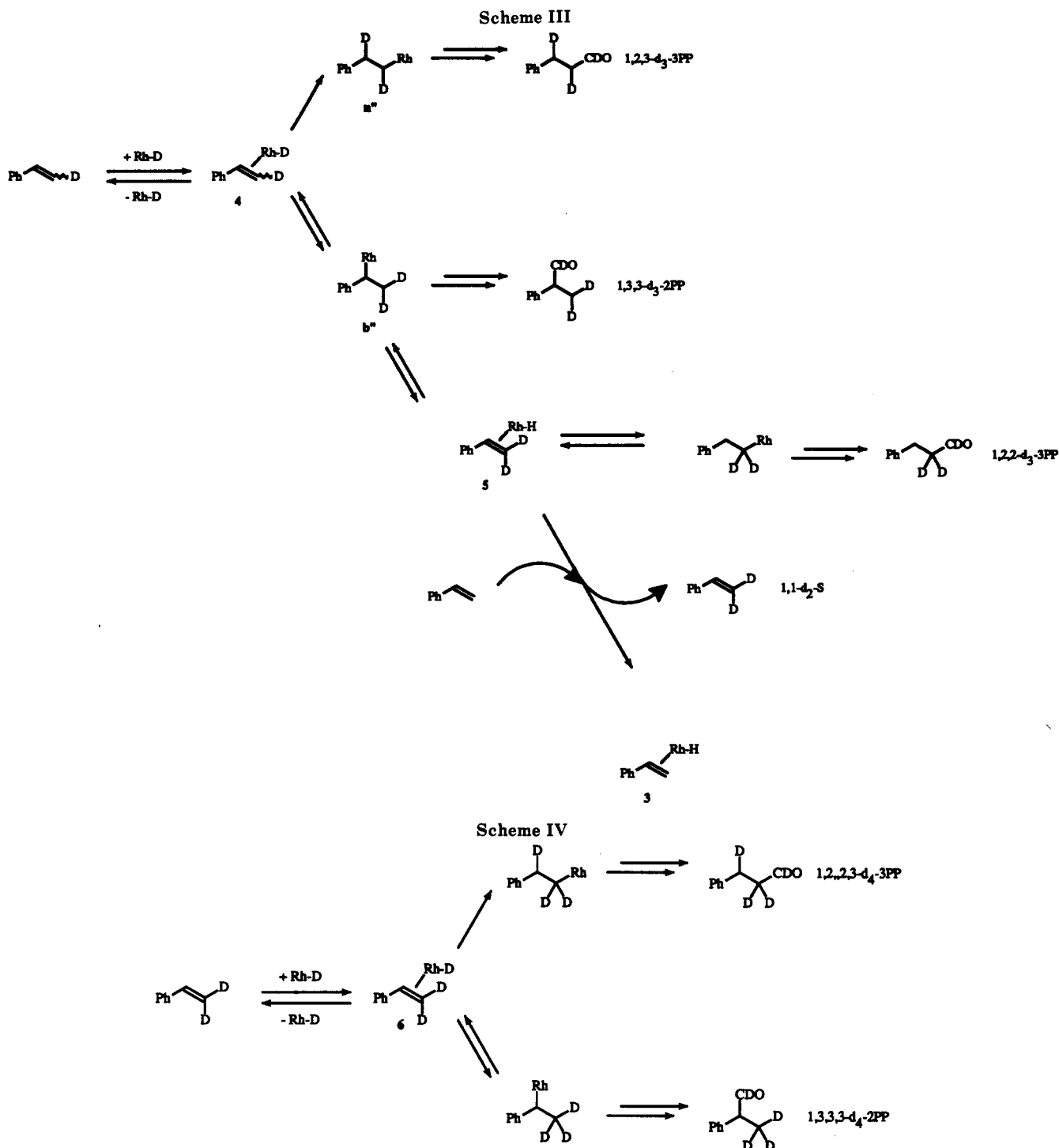
The formation of HD, in agreement with literature reports,<sup>12</sup> can occur via an oxidative addition of a molecule of D<sub>2</sub> to an unsaturated Rh-H, followed by a reductive

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elimination of HD and formation of a Rh-D species.

The reaction schemes discussed above explain the most interesting findings of this research, i.e. the increasing of deuterium content of aldehydes with increasing of substrate conversion and reaction temperature, as well as a larger amount of deuterium incorporated in the branched aldehyde with respect to the linear one. At 90 °C and low conversion the rhodium hydride  $\pi$ -complex 2 preferentially undergoes an exchange process and hence yields unlabeled  $\pi$ -complex 3, from which monodeuterated aldehydes are formed (Scheme II, Table II). At high conversion mono- and dideuteriostyrene, which are present in increasing proportion in the reaction mixture, undergo the deuterioformylation process, producing tri- and tetra-deuterated aldehydes. The increase of reaction temperature strongly favors the  $\beta$ -hydride elimination from the branched al-

kyl-metal intermediates, which gives mono- and dideuteriostyrene, as well as the transfer of protium from the substrate to the gas phase with formation of HD. Therefore, at high temperature and complete substrate conversion, tri- and tetra-deuterated isomeric aldehydes respectively arising from di- and trideuterated alkylmetal intermediates predominate over the monodeuterated species.

The different behaviors of the two alkylmetal intermediates toward the  $\beta$ -hydride elimination process can also explain the larger amount of deuterium found in the branched aldehydes with respect to the linear one, both at low and high conversion. Indeed the linear alkyls, which are formed mainly from the branched isomer via an isomerization process, do not give  $\beta$ -hydride elimination and hence are completely transformed into the linear alde-

hydes. By contrast, the branched alkyls mainly give  $\beta$ -hydride elimination and only in part are transformed into aldehydes. Therefore, the branched aldehydes, to a larger extent than the linear isomers, arise from mono- and di-deuteriostyrene, whose amounts increase with the increasing of substrate conversion and reaction temperature.

### Experimental Section

Benzene was dried over molecular sieves and distilled under nitrogen.  $\text{Rh}_4(\text{CO})_{12}$  was prepared as reported in the literature.<sup>13</sup> GLC analyses were performed on a Dani 6800 gas chromatograph equipped with 2 m  $\times$  0.4 cm columns of 10% SE30 on 60/80 mesh Chromosorb WAW DCMS support or 5% UCON LB 550X on 60/80 mesh Chromosorb WAW DCMS support and a flame-ionization detector, nitrogen was used as the carrier gas. Preparative GLC was carried out on a Perkin-Elmer F21 instrument fitted with 3 m  $\times$  0.95 cm columns of 5% FFAP on 60/80 mesh Chromosorb A-NAW support.

Mass spectra were measured with a VG 70/70E spectrometer at an electron energy such that the  $M - 1$  peak was undetectable (around 10 eV); the accelerating voltage was 6 kV and the emission current was 100  $\mu\text{A}$ . GC-MS analyses of the deuterioformylation mixtures in selected ion monitoring mode were performed by the use of the same spectrometer coupled with a Dani 3800 gas chromatograph equipped with a SE30 silica capillary column (50 m  $\times$  0.53 mm).

<sup>1</sup>H NMR spectra were recorded in  $\text{CCl}_4$  solutions on a Varian VXR 300 spectrometer, operating at 300 MHz for <sup>1</sup>H. TMS was used as an internal standard.

**Deuterioformylation of Styrene: General Procedure.** Deuterioformylation of styrene, at partial and total substrate conversion, was carried out by following a general procedure previously described.<sup>7</sup> In a 50-mL evacuated stainless steel autoclave, a solution of styrene (2.01 g, 20 mmol) and  $\text{Rh}_4(\text{CO})_{12}$  (0.1 mg,  $5.4 \times 10^{-4}$  mmol) in benzene (5 mL) was introduced by

suction. Carbon monoxide was introduced by the desired pressure; the autoclave was then rocked and heated to the reaction temperature, and deuterium was rapidly introduced to the desired total pressure. When the reaction started, drop in pressure was restored by injection of a carbon monoxide-deuterium mixture (1/1) from a high-pressure reservoir. Progress in the reaction was monitored by the pressure drop in the high-pressure container. When the gas absorption reached the value corresponding to the desired conversion to aldehydes, the autoclave was rapidly cooled, the reaction mixture was siphoned out, and GLC was used to determine the isomeric composition. The degree of styrene conversion was measured by GLC, using toluene as an internal standard. The reaction mixture was distilled first at atmospheric pressure and later at reduced pressure (0.4 mmHg), and the isomeric aldehydes were separated from styrene and solvent. Pure samples of unconverted styrene and  $\alpha$  and  $\beta$  aldehydes were isolated by preparative GLC.

**Deuterium Content of Residual Reaction Gas.** The residual reaction gases were collected in evacuated Schlenk tubes closed with a rubber septum. A sample of the gas was taken through the septum by using a gastight syringe and directly introduced into the source of the mass spectrometer. The elium coming from the GLC column ( $m/z$  4.0026) was used as a standard. The resolving power of the instrument was adjusted to about 2000: Under these conditions it was possible to distinguish among the peaks due to  $\text{H}_2$  ( $m/z$  2.0156), D ( $m/z$  2.0141), coming from the fragmentation of  $\text{D}_2$  and HD, HD ( $m/z$  3.0219), and  $\text{D}_2$  ( $m/z$  4.0282). The MS spectra were recorded on UV paper, and the compositions of the gases were obtained by measuring the peak areas.

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**Registry No.**  $\text{PhCH}=\text{CH}_2$ , 100-42-5;  $\text{PhCD}(\text{CHD}_2)\text{CHO}$ , 136391-76-9;  $\text{PhCD}(\text{CH}_2\text{D})\text{CHO}$ , 136391-77-0;  $\text{Ph}(\text{CHD})_2\text{CHO}$ , 136391-78-1;  $\text{PhCHD}_2\text{CHO}$ , 136391-79-2;  $\text{Rh}_4(\text{CO})_{12}$ , 19584-30-6;  $\text{PhCD}(\text{CD}_3)\text{CHO}$ , 136391-80-5;  $\text{PhCH}=\text{CHD}$ , 22139-13-5;  $\text{D}_2$ , 7782-39-0.

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## Polyazolyl Chelate Chemistry. 3.<sup>1</sup> ( $\sigma$ -Organyl)(tris(pyrazol-1-yl)borato)ruthenium Complexes

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The reactions of  $\text{K}[\text{HB}(\text{pz})_3]$  (pz = pyrazol-1-yl) with the coordinatively unsaturated  $\sigma$ -vinyl complexes  $[\text{Ru}(\text{CR}=\text{CHR})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$  (R = H, Me,  $\text{C}_6\text{H}_5$ ) proceed with loss of a chloride and a phosphine ligand to provide the compounds  $[\text{Ru}(\text{CR}=\text{CHR})(\text{CO})(\text{PPh}_3)\{\text{HB}(\text{pz})_3\}]$  in high yield. Similar treatment of the complex  $[\text{Ru}(\text{C}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$  leads to the related  $\sigma$ -aryl derivative  $[\text{Ru}(\text{C}_6\text{H}_4\text{Me-4})(\text{CO})(\text{PPh}_3)\{\text{HB}(\text{pz})_3\}]$ . The  $\alpha$ -(phenylethynyl)-*trans*- $\beta$ -styryl complex  $[\text{Ru}\{\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh}\}(\text{CO})(\text{PPh}_3)\{\text{HB}(\text{pz})_3\}]$  is obtained in high yield via the successive treatment of  $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$  with 1,4-diphenyl-1,3-butadiyne and  $\text{K}[\text{HB}(\text{pz})_3]$ . The molecular structure of  $[\text{Ru}\{\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh}\}(\text{CO})(\text{PPh}_3)\{\text{HB}(\text{pz})_3\}]$ , determined by X-ray diffraction, can be described as pseudooctahedral with two enantiomeric forms in the asymmetric unit. The vinyl ligand is almost coplanar with the carbonyl ligand aligned in such a way as to maximize  $\pi$ -retrodonative interactions.

### Introduction

Research into the coordination chemistry of poly(pyrazol-1-yl)borates has focused on the first-row transition metals and group 6.<sup>2</sup> The chemistry of tris(pyrazol-1-

yl)borato complexes of the second- and third-transition series and in particular that of group 8<sup>3-7</sup> remains less

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