

HYDROFORMYLATION OF OLEFINIC HYDROCARBONS WITH RHODIUM AND COBALT CATALYSTS: ANALOGIES AND DISSIMILARITIES

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Introduction

Although the possibility of using rhodium as catalyst in the hydroformylation of olefins was recognized almost 25 years ago [1], the first papers on the subject appeared only in the mid 1960's [2], at a time when, due to the work done by Kirch and Orchin [3] and particularly by Heck and Breslow [4], important advances had been made in the understanding of the mechanism of the cobalt-catalyzed hydroformylation.

In view of some common general features (nature of reaction products, order of the reaction with respect to hydrogen, effects of phosphines as additional ligands on regioselectivity in hydroformylation of 1-olefins) it has been accepted without more direct experimental evidence that the mechanisms of hydroformylation of olefins with rhodium and cobalt catalysts are the same [5,6].

In the course of our investigation of the use of mixtures of cobalt and rhodium carbonyls as catalysts for some unusual hydrocarbonylation reactions [7], an attempt was made to identify analogies and differences in the details of the catalytic action of the two metal carbonyls, both by new experiments and by a critical reconsideration of the information already in the literature. In the present paper we review some recent results which show that some details of the catalytic behaviour of the carbonyl complexes of the two metals are, indeed, remarkably different. In particular we discuss the following aspects of the hydroformylation of simple aliphatic olefins, mainly using $\text{Co}_2(\text{CO})_8$ and $\text{Rh}_4(\text{CO})_{12}$ as catalyst precursors: 1. Kinetics; 2. Stereochemistry; 3. Composition of reaction products; 4. Intermolecular hydrogen exchange, and 5. Migration of the metal along the olefinic substrate during hydroformylation.

The differences between the two catalytic systems in their applications for synthetic purposes have already been extensively reviewed [2,8,9] and will not be considered here.

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1. Kinetics

A comparison between the overall kinetics of cobalt and rhodium catalyzed hydroformylation using $\text{Co}_2(\text{CO})_8$ or $\text{Rh}_4(\text{CO})_{12}$ as catalyst precursors shows that the present knowledge in the field is not satisfactory (Table 1).

The order of reaction with respect to the carbon monoxide pressure has positive values at low p_{CO} and negative values at high p_{CO} [5,11,12]. Under the conditions used the rate passes through a maximum, which is around 10 atm p_{CO} using $\text{Co}_2(\text{CO})_8$ at 110°C [10] and 40 atm using $\text{Rh}_4(\text{CO})_{12}$ at 75°C as catalyst precursor [5]. Broadly speaking, catalytic species with different carbon monoxide to metal ratios seem to be present in solution. However, it is not clear whether in both cases species with different CO/metal ratios are catalytically active, as has been postulated for the cobalt catalyst [15]. The alternative is that a single active species with low CO/metal ratio is in equilibrium with non-active species with a higher CO/metal ratio.

Much more difficult to understand are the reasons why with rhodium catalysts the order with respect to the olefin and to the partial pressure of hydrogen depends on the olefin structure [14], while in the case of cobalt, the reaction is always first order with respect to the substrate and to hydrogen [10]. These results show that the relative rates of the steps involving the olefinic substrate and hydrogen with respect to the slowest reaction step are probably different in the two cases. In fact, monitoring of the hydroformylation by IR-spectroscopy in the cobalt catalyzed reaction, has revealed the presence of acyl-cobalt tetracarbonyl with ethylene but not with hindered olefins [16]; in the rhodium catalyzed reaction with ethylene, bands attributable to an ethylrhodium tetracarbonyl have been found [17].

No explanation has been given up to now for the change of order with respect to the concentration of the metal observed on changing the carbon monoxide pressure in the case of the cobalt catalysts. Equally obscure is the reason for the fractional order with respect to the metal observed for the rhodium catalyzed reaction with cyclohexene as substrate.

In conclusion, in keeping with the rather complex multistep mechanism

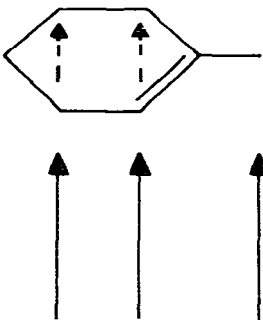
TABLE 1
KINETICS OF HYDROFORMYLATION WITH $\text{Co}_2(\text{CO})_8$ OR $\text{Rh}_4(\text{CO})_{12}$ AS CATALYST PRECURSOR

	Catalyst precursor	
	$\text{Co}_2(\text{CO})_8$	$\text{Rh}_4(\text{CO})_{12}$
Apparent order with respect to olefin concentration	1 [10]	0-1 ^a [14]
Apparent order with respect to hydrogen	1 [10]	0.5-1 ^a [14]
Apparent order with respect to metal concentration (g At of Me/l)	1 ($p_{\text{CO}} = 100$ atm) [10] 0.5 ($p_{\text{CO}} = 10-15$ atm) [10]	0.25-1 ^a [14]
Apparent order with respect to carbon monoxide	>0 ($p_{\text{CO}} < 10$ atm) [11] -1 ($p_{\text{CO}} > 10$ atm) [12]	>0 ^b ($p_{\text{CO}} < 40$ atm) [5] -1 ^b ($p_{\text{CO}} > 40$ atm) [5]
Overall activation energy ^v	27-35 kcal/mol ^{c, d} [13]	27.8 kcal/mol ^{b, e} [5]

^a Dependent on olefin structure. ^b Heptene-1 as the substrate. ^c Cyclohexene as the substrate. ^d 100-122°C
^e 66-90°C.

TABLE 2

PRODUCT COMPOSITION (%) OF RHODIUM- AND COBALT-CATALYZED HYDROFORMYLATION OF 1-METHYLCYCLOHEXENE [18]



Catalyst precursor	Type of stereoisomer						
Rh ₂ O ₃	<i>cis</i>	0	3.5	1.5		Σ <i>cis</i>	5
	<i>trans</i>	0	2.5	85	7.5	Σ <i>trans</i>	87.5
Co ₂ (CO) ₈	<i>cis</i>	1	4	0.5		Σ <i>cis</i>	5.5
	<i>trans</i>	36	10	28	20	Σ <i>trans</i>	74

postulated for the hydroformylation, the overall kinetic results do not give adequate information about the reaction mechanism, but show that even if the reaction steps are substantially the same in the rhodium and cobalt catalyzed hydroformylation, the relative rates of the single steps must be significantly different. Unfortunately, since kinetic investigation of single reaction steps is not easy, no substantial contribution from this type of investigation to understanding of the differences between cobalt and rhodium catalyzed hydroformylations is expected in the near future.

2. Stereochemistry

The stereochemistry of hydroformylation has been shown (at least in the cases investigated) to be substantially or completely of the *cis* type both with cobalt and rhodium catalysts. This has been shown for the hydroformylation of 1-methylcyclohexene, in which (*E*)-(Z) isomerization is not possible [18] (Table 2).

In the case of rhodium catalysts the same has been shown to be true (Table 3) also for (*E*)- and (*Z*)-3-methyl-2-pentene (RhH(CO)(PPh₃)₃ as the catalyst precursor) [18] and for (*E*)- and (*Z*)-2-phenyl-2-butene (Rh on Al₂O₃ as the catalyst precursor) [19]. With cobalt catalysts the experiments with these substrates (Table 3) do not reveal the type of stereochemistry because of a concurrent intramolecular hydrogen shift and (*E*)-(Z) isomerization [18,19].

In multistep addition reactions, *cis*-stereochemistry can be the result of two steps each occurring with *trans*-stereochemistry [18]. This is not the case, at least in the cobalt catalyzed hydroformylation. Thus in the cobalt catalyzed hydroformylation of 1,2-dimethylcyclohexene, the ratio between *cis*- and *trans*-2-methyl-1-cyclohexaneacetaldehyde was found to be 7.3, indicating that the products are predominantly formed by a *cis* addition followed by a hydrogen shift which occurs with retention of configuration [18] (Scheme 1). The

TABLE 3
 PRODUCT COMPOSITION (%) IN THE HYDROFORMYLATION OF (E)- AND (Z)-3-METHYL-2-PENTENE [18]

Catalyst precursor	Stereoisomer	$\text{CH}_3\text{---CH}_2\text{---}\underset{\substack{ \\ \text{CH}_3 \\ \uparrow}}{\text{C}}\text{=CH---CH}_3$		
RhH(CO)(PPh ₃) ₃	(E)	3	5/81 ^a	11
	(Z)	3	78/7 ^a	12
Co ₂ (CO) ₈	(E)	18	2.5/3.5 ^a	76
	(Z)	17	3/4 ^a	76

^a Erythro/threo.

results described in this section are in keeping with the proposed mechanism [2,5,6] for cobalt and rhodium catalyzed hydroformylations, and probably have a general significance independent of the type of olefinic substrate. The first attack of the catalytic species on the substrates has very similar features in both cases. However, the results do not allow any conclusion to be reached about the structure of the first intermediate of the reaction. Either π -complexation of the substrate to the metal atom(s) of the catalytic complexes followed by insertion into a M—H bond or a direct addition of a M—H group to a double bond through a 4-center transition state would have the same stereochemical consequences.

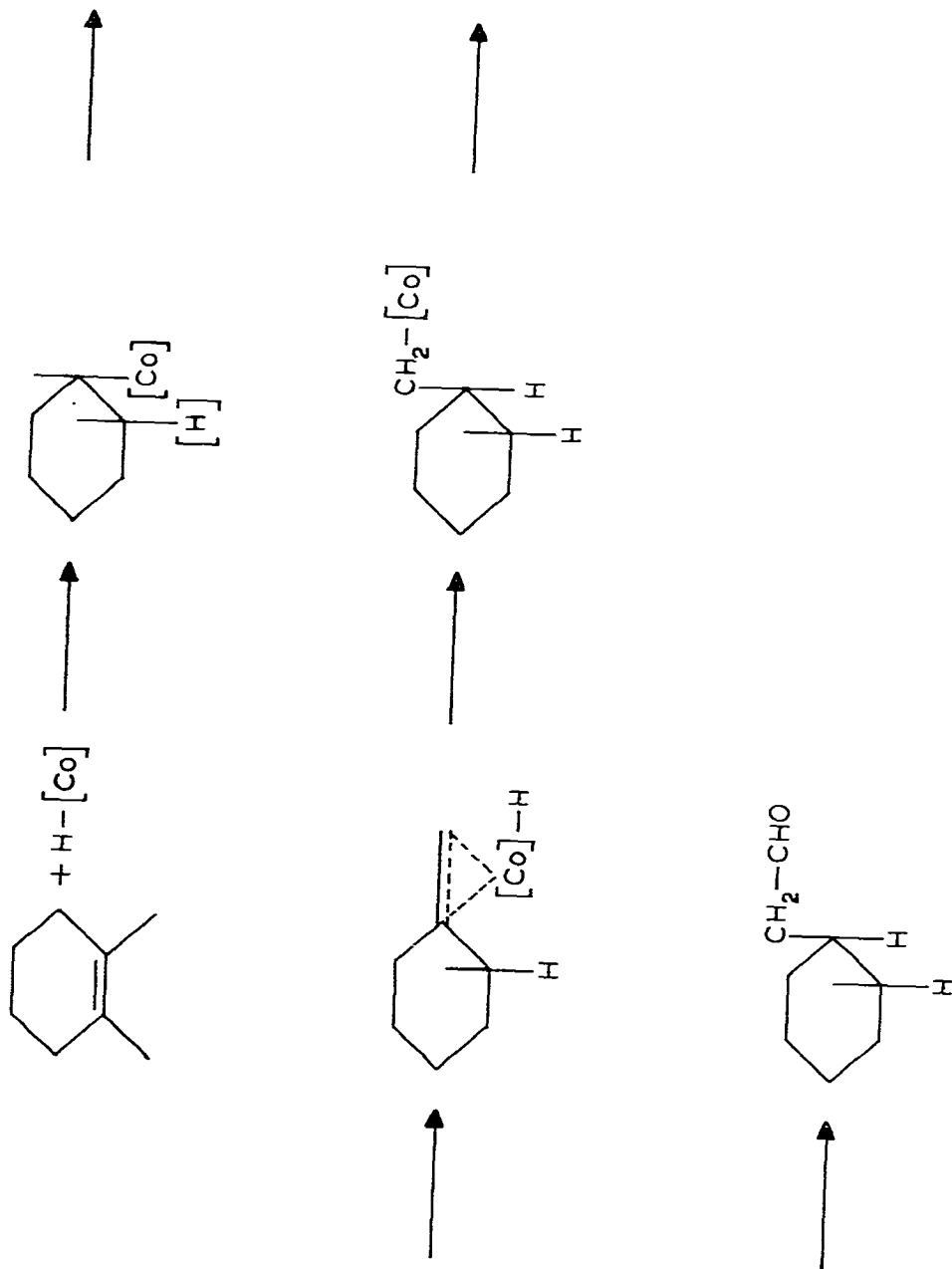
3. Composition of reaction products

It is well known that when a C_s olefin is hydroformylated at least two isomeric aldehydes are formed. Since the practical importance of the two products is usually different [6] a large research effort has been devoted to identifying the factors which control the regioselectivity in hydroformylation. With CO₂(CO)₈, when mono-, di- or trisubstituted saturated carbon atoms are present in the substrate, more than two aldehydes are formed during the reaction [15], as shown in Scheme 2 for the hydroformylation of (S)-3-methyl-1-pentene. In principle, formylation in position 4 and 5 can also take place, but the extent of formylation at position 5 must be very small at high p_{CO} (>50 atm) as the racemization observed in the main reaction product ((S)-3-methylhexanal) is very small (~4%) [20].

The easiest way to explain the above results is to postulate a double bond shift in the substrate occurring through a series of addition and elimination reactions (Scheme 3). However, the relatively small amount of racemization (~30%) observed in the formation of (R)-2-ethylhexanal from (S)-3-methyl-1-hexene [21,22] clearly shows the existence, at least when Co₂(CO)₈ is used as catalyst precursor, of a second and prevailing path in which a hydrogen shift takes place in the catalyst-olefin complex without formation of the isomerized substrate, from which only racemic 3-ethylhexanal can form (Scheme 4).

An equally small proportion of racemization (23–30%) has been observed in hydroformylation of some other chiral olefins in which the formation of alde-

SCHEME 1



$[\text{Co}] = \text{Catalytic Complex Containing Cobalt.}$

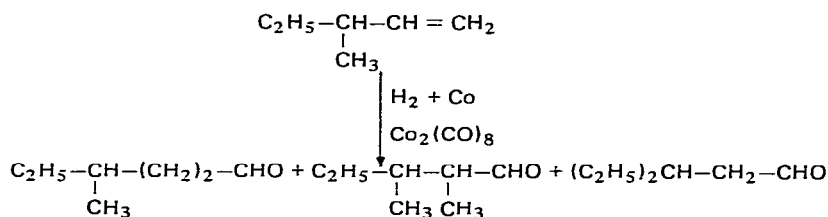
hydrides implies a hydrogen shift involving the hydrogen atom bound to the asymmetric carbon atom [23].

No similar experiments have yet been carried out with rhodium catalysts. However, the identical diastereomeric composition of the 2-methyl-1-cyclohexylacetaldehyde (*trans/cis* = ~4) produced in the hydroformylation of either 1,2-dimethylcyclohexene or 2-methyl-1-methylidenecyclohexane using Rh_2O_3 as the catalyst precursor [18] indicates that with this catalyst the double bond shift in the substrate occurs substantially through a series of addition and elimination reactions, with intermediate formation of isomerized free olefins.

From the above considerations it appears that the relationships between the isomerization of the substrate and the formation of isomeric aldehydes are not obvious, and are different for rhodium and cobalt catalysts under similar reaction conditions.

The hydroformylation of labelled olefins was therefore carried out [24–26] in order to reach a better understanding of the relationship between substrate isomerization and isomeric composition of the reaction products. We shall consider first the results of the hydroformylation of labelled linear olefins, which have yielded the most complete quantitative information about the position of attack of the formyl group to the substrate, and then a few scattered results obtained for substrate isomerization with various catalysts under various reaction

SCHEME 2



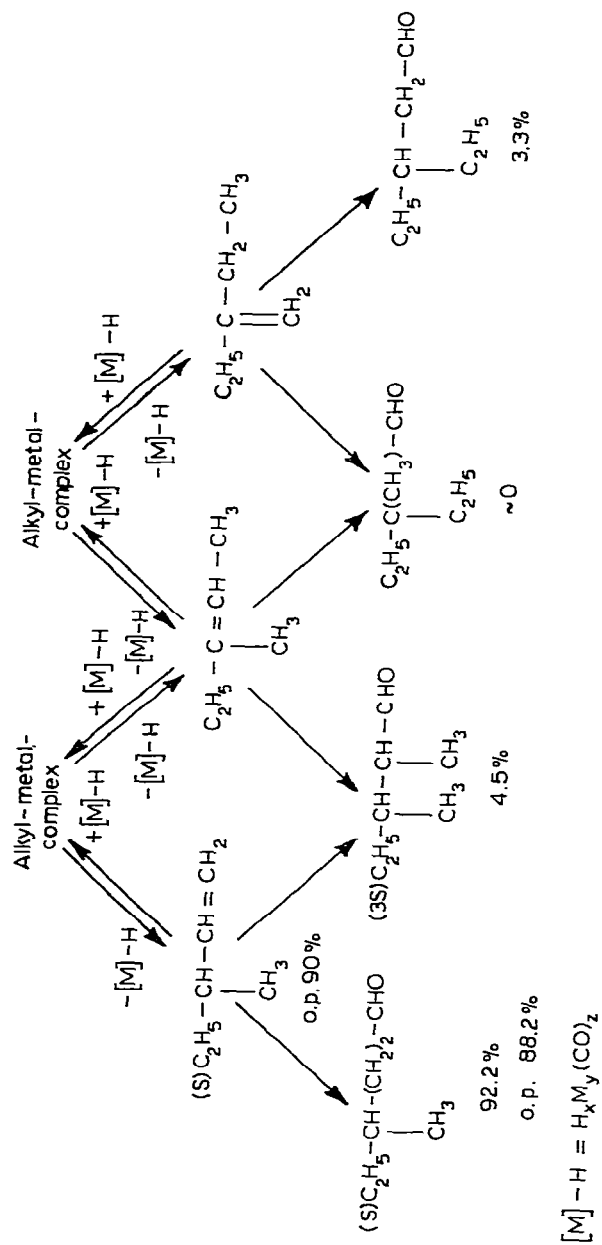
conditions. The results obtained with the rhodium and cobalt catalytic systems will be compared at the end of the two sections.

a) Reaction products composition in the hydroformylation of labelled linear olefins

The results obtained in the hydroformylation of some linear olefins with $\text{Co}_2(\text{CO})_8$ and $\text{Rh}_4(\text{CO})_{12}$ are listed in Table 4. The extent of formylation at each carbon atom was determined from the NMR and mass spectra as described previously [24,25].

With both cobalt and rhodium catalysts, formylation at the originally saturated carbon atoms is favoured at lower carbon monoxide pressures. At 4–5 atm p_{CO} , complete intramolecular scrambling of deuterium atoms was observed with cobalt catalysts [25,26,30] but not with rhodium catalysts [24]. Furthermore, a significant difference exists between the two catalysts not only in the extent of formylation at the saturated carbon atoms under similar conditions but also in the type of saturated carbon atom preferentially formylated. Thus in the hydroformylation of 5,5,5-trideutero-2-pentene under 100 atm p_{CO} both the methyl and the methylene groups adjacent to the double bond were

SCHEME 3



SCHEME 4

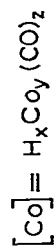
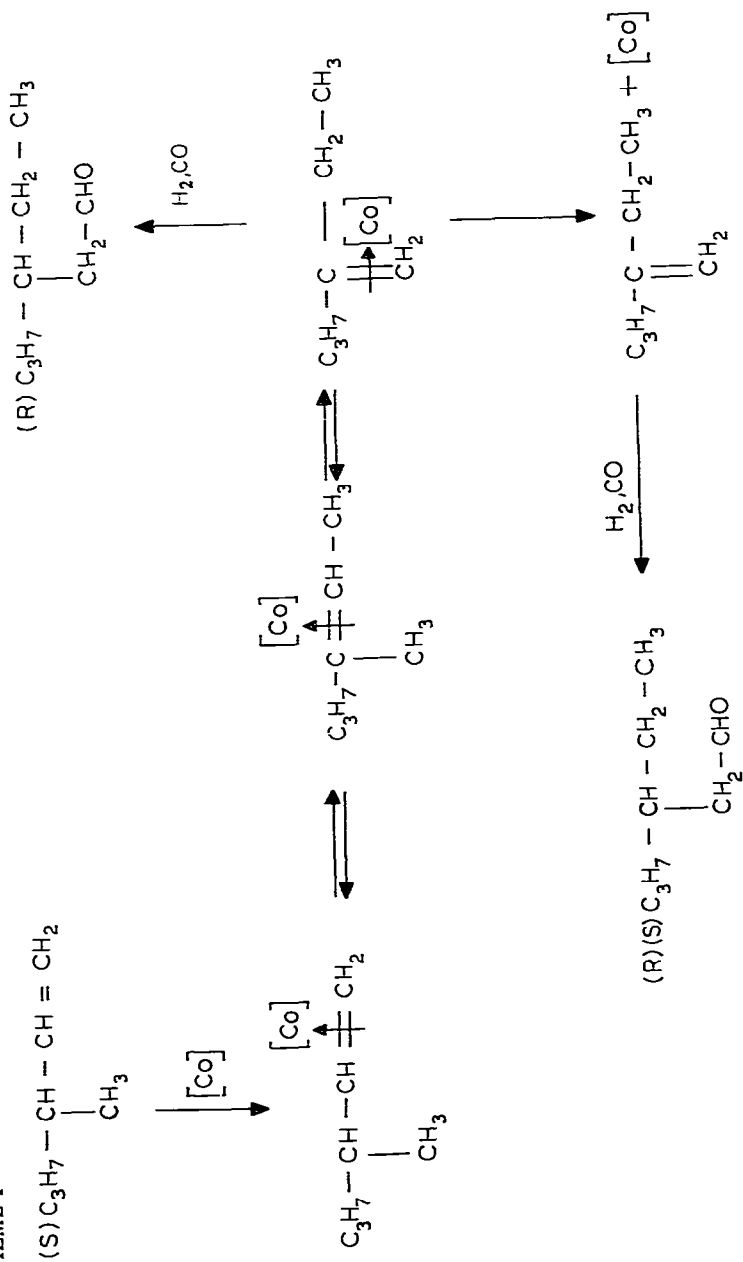


TABLE 4
 SKELETON POSITION OF LABELLED OLEFINS TO WHICH THE FORMYL GROUP IS BOUND ($p_{H_2} = 80-100$ atm; $T = 100^\circ C$)

Catalyst Precursor	PCO	Amount of formylation at each position (%)
$Co_2(CO)_8$	100	$CH_3-CH=^{14}CH_2$ 32 20 28 [27]
		$CD_3-CH_2-CH=CH_2$
$Co_2(CO)_8$	100	9 3 3 12 72 [24]
$Co_2(CO)_8$	80	9 2 3 15 71 [28]
$Rh_4(CO)_{12}$	4-5	8 19 12 25 36 [24]
$Rh_4(CO)_{12}$	100	0 4 6 35 54 [24]
$Co_2(CO)_8$	100	$CH_3-CH=CH-CH_3$ 25 7 7 14 47 [24]
		$CD_3-CH_2-CH=CH-CH_3$
$Co_2(CO)_8$	400	29 19 12 20 39 [24]
$Rh_4(CO)_{12}$	4-5	11 24 14 26 25 [24]
$Rh_4(CO)_{12}$	100	1 16 28 48 7 [24]
$Co_2(CO)_8$	80	$CD_3-CH_2-CH_2-CH_2-CH=CH_2$ 6 3 3 74 [28]
		$CD_3-CH_2-CH_2-CH_2-CH=CH_2$

formylated. However, the methyl group was formylated about 7 times as fast as the methylene group with cobalt, whereas with rhodium the methylene group was formylated 2.3 times as fast as the methyl group. At high p_{CO} the difference is even larger in the case of the perdeuterated methyl group when compared with the same methylene group. In this case the results reflect not only the different tendencies of the two metals to attack the methyl groups, but also the different rates at which metals migrate along the substrate chain, and also the existence in the case of rhodium, but not in the case of cobalt, of an isotope effect in the formylation of a perdeuterated methyl group [29], as discussed below.

The greater tendency for cobalt to formylate methyl groups is also clearly shown by the results obtained in the hydroformylation of labelled 1-butene, 1-pentene, 1-hexene [28], and some branched olefins [18,23], as well as of cyclic methyl-substituted olefins [18].

From the data on the labelled olefins we can obtain a ratio between the quantities of products in which the originally unsaturated and originally saturated carbon atoms of the substrates bear formyl groups (Table 5). On the assumption that, because of concurrent rapid formation of aldehyde, double bond migration can be considered substantially irreversible under the conditions used, these values give an indication of the relative values of the isomerization rate with respect to the formylation rate for the unsaturated carbon atoms. It is interesting to note that in the cobalt catalyzed hydroformylation the attack at position 1 in α -olefins is increased by increasing the bulk of the group bound to the olefinic double bond (Table 6). The extent of the attack at position 1 seems to be lower when $\text{Rh}_4(\text{CO})_{12}$ is used as catalyst precursor. Lewis bases, particularly phosphines, have a large influence on the relative extents of formylation at positions 1 and 2 in the α -olefins, their presence favouring the less hindered terminal position, thus confirming the influence of steric factors with both cobalt and rhodium catalysts.

In contrast, when internal double bonds are hydroformylated, monophos-

TABLE 5

RATIO, R, BETWEEN THE % OF FORMYLATION AT UNSATURATED CARBON ATOMS AND THE % OF FORMYLATION AT THE SATURATED CARBON ATOMS FOR VARIOUS OLEFINS

	p_{CO}	R	
		$\text{Co}_2(\text{CO})_8$	$\text{Rh}_4(\text{CO})_{12}$
Propylene	100	2.15	n.d.
1-Butene	80	4.88	n.d.
1-Pentene	4-5	n.e. ^b	1.56
1-Pentene	80	6.14	n.d.
1-Pentene	100	5.67	8.09
1-Hexene	80	~10	n.d.
2-Butene	100	0.41	8.09
2-Butene	400	0.66	n.d.
2-Pentene	4-5	n.e.	0.67 ^a
2-Pentene	100	0.27	3.17 ^a
2-Pentene	400	0.47	n.d.

^a Affected by isotopic effect. ^b n.e. = not evaluable, n.d. = not determined.

TABLE 6
EXTENT OF FORMYLATION AT THE UNSATURATED CARBON ATOMS

Substrate	p_{CO} atm	$Co_2(CO)_8$			$Rh_4(CO)_{12}$		
		Pos. 1 (%)	Pos. 2 (%)	Σ (%)	Pos. 1 (%)	Pos. 2 (%)	Σ (%)
Propylene	100	48	20	68	<48	52	<100
1-Butene	80	69	14	83			
1-Pentene	100	72	12	84	54	35	89
1-Hexene	80	74	<16.5	<90.5			
4-Methyl-1-pentene	120	85	13	98			
3-Methyl-1-hexene	100	93	3.4	96.4			
		Pos. 2 (%)	Pos. 3 (%)	Σ (%)	Pos. 2 (%)	Pos. 3 (%)	Σ (%)
2-Butene	100	15	15	30	44	44	88
2-Pentene	100	14	7	21	48	28	76

phines influence the regioselectivity in a completely different way for cobalt than for rhodium catalysts (Table 7). In the presence of trialkylphosphine with cobalt, the extent of formation of straight chain aldehydes is increased, i.e., migration of the metal atom along the chain and formylation at a saturated terminal atoms is favoured [31]. With rhodium, phosphines completely prevent formylation at the saturated carbon atoms, showing that elimination of hydride complexes is hindered by the presence of this type of ligand.

With cobalt the effect of phosphines is remarkably dependent on the ligand structure; thus in the hydroformylation of 6-dodecene the presence of 1,2-bis(diphenylphosphino)ethane strongly depresses the formation of the linear products [33], as in the case of rhodium catalyst [32]. However, the presence of 1,4-bis(diphenylphosphino)butane, favours formation of the straight chain product [33].

b) Substrate isomerization during hydroformylation

Unfortunately, only scattered data are available on the double bond shifts and the (*E*)-(Z) isomerizations accompanying hydroformylation. In the case of 3-methyl-2-pentene deuterioformylation using $RhH(CO)(PPh_3)_3$ as the catalyst precursor, the isomerized olefin contained one atom of deuterium and the aldehyde arising from isomerized substrate contained two deuterium atoms in the backbone, as shown by the mass spectra of the corresponding esters. This shows that isomerization occurs through addition of a rhodium deuteride to the substrate, followed by elimination with generation of $[Rh]-H$ [34]. A double bond shift involving a similar mechanism is believed to be responsible for the low *trans/cis* ratio (0.96) in 3- and 4-methylcyclohexanecarboxaldehyde arising from hydroformylation with cobalt catalyst of 1-methylcyclohexene under 5 atm p_{CO} . This ratio is about 12 for the same products when hydroformylation is carried out under 100 atm p_{CO} [18].

For hydroformylation of 1- and 2-pentene with rhodium and cobalt catalysts the ratios between non-isomerized olefin and isomerized olefin at relatively

TABLE 7

INFLUENCE OF THE PRESENCE OF PHOSPHINES ON THE COMPOSITION OF THE ISOMERIC PRODUCTS FROM HYDROFORMYLATION OF LINEAR OLEFINS [31]

Substrate	Ligand	Ligand/metal molar ratio	Temp. (°C)	Isomeric products composition (%)			
				n-Nonanal	2-Methyl-octanal	2-Ethyl-heptanal	2-Propyl-hexanal
1-octene	—	—	150	65	22	7	6
1-octene	P(<i>c</i> -C ₆ H ₁₁) ₃	5	150	80	12	4	4
<i>trans</i> -4-octene	Co ₂ (CO) ₈	—	150	55	22	11	12
<i>trans</i> -4-octene		P(<i>c</i> -C ₆ H ₁₁) ₃	5	150	78	10	6
1-octene	—	—	100	52	40	5	3
1-octene	P(<i>c</i> -C ₆ H ₁₁) ₃	50	140	59	40	1	—
<i>trans</i> -4-octene	Rh ₂ O ₃	—	100	4	23	28	45
<i>trans</i> -4-octene		P(<i>n</i> -C ₄ H ₉) ₃	60	140	—	<0.5	1

TABLE 8

SUBSTRATE ISOMERIZATION DURING HYDROFORMYLATION

Substrate	PCO	Co ₂ (CO) ₈	Rh ₄ (CO) ₁₂		
			Conversion to aldehydes (%)	Double bond shift	(<i>E</i>)-(<i>Z</i>) ^a Isomerization
1-pentene	5	78	65	0.95	0.95
1-pentene	100	72	65	0.49	0.49
(<i>E</i>)-2-pentene	5	57	82	0	0.18
(<i>E</i>)-2-pentene	100	67	75	0	0.18
(<i>E</i>)-2-pentene	400	31	—	—	—
(<i>Z</i>)-2-pentene	100	68	52	0	0.12
(<i>E</i>)-2-butene	100	—	21	0	0.20
(<i>Z</i>)-2-butene	100	—	—	—	0.20

^a Molar fraction of the isomerized olefin in the recovered substrate.

high conversion to aldehyde are as shown in Table 8. The values obtained give only qualitative indications of the minimum extent of substrate isomerization, since the composition of the recovered olefinic mixture is markedly affected by the differences in the rates of hydroformylation of the various isomers and stereoisomers (terminal $>(Z)->(E)$ -olefins) [2]. Significant $(E)-(Z)$ isomerization occurs during hydroformylation when $\text{Co}_2(\text{CO})_8$ or $\text{Rh}_4(\text{CO})_{12}$ is used as a catalyst precursor [24]; it may occur through an addition-elimination mechanism, but could involve other mechanisms [35], and is certainly worthy of further investigation.

c) Comparison between rhodium and cobalt catalytic systems

When the results obtained with $\text{Co}_2(\text{CO})_8$ or $\text{Rh}_4(\text{CO})_{12}$ as catalysts precursors under the same conditions are compared it is apparent that with cobalt catalysts, despite the lower substrate isomerization as shown by the analysis of the non-hydroformylated olefin (Table 8), the proportion of aldehydes arising from the formylation of originally saturated carbon atoms is larger than with rhodium catalysts (Table 5). These results are in keeping with the observations [18] that, at least with cobalt catalysts, the hydrogen shift can occur without regenerating free olefinic substrate, and that the ratio between the rates of substrate dissociation and formation of aldehydes is higher in the rhodium than in the cobalt catalyzed hydroformylation. However, other results seem to indicate that there are more profound differences between the mechanisms of hydroformylation and/or the nature of the intermediate complexes in the rhodium and cobalt catalysts.

The differences in the behaviour of the cobalt and rhodium containing catalytic species are better evidenced in the case of 2-pentenes than in the case of 1-pentene, and are also very clear when comparing 2-pentenes with 2-butenes. Rhodium shows a greater tendency to migrate to a >CH_2 than to a CH_3 group, whereas the opposite is true for cobalt (Table 9). In Table 9 the extent of formylation at the saturated carbon atoms has been assumed to provide an indication of the extent of migration of the metal. The values reported are minimum values, the migration being assumed to be irreversible.

Steric effects alone could explain the results if we assume that steric requirements are more stringent for the cobalt than for the rhodium catalytic complexes. However, these differences might also be connected, at least in part, to

TABLE 9
METAL MIGRATION IN 2-PENTENE AND 2-BUTENE HYDROFORMYLATION ^a

Substrate	Catalyst Precursor	Migration to $-\text{CH}_3$	Migration to CH_2	Total Migration
2-Pentene	$\text{Co}_2(\text{CO})_8$	47 ^b	32 ^d	79
2-Pentene	$\text{Rh}_4(\text{CO})_{12}$	7 ^b	17 ^d	24
2-Butene	$\text{Co}_2(\text{CO})_8$	60 ^c	—	60
2-Butene	$\text{Rh}_4(\text{CO})_{12}$	12 ^c	—	12

^a Estimated from the extent of formylation at originally saturated carbon atoms; under 100 atm p_{CO} .

^b Expressed as % of formylation at position 1. ^c Expressed as % of formylation at position 1 and 4.

^d Expressed as % of formylation at position 4 and 5.

the nature of the hydrogen atoms involved in the migration; rhodium shows a preference for the elimination of a >CH_2 hydrogen, having a higher hydridic character, while cobalt migration preferentially involves a —CH_3 hydrogen having a lower hydridic character.

As regards the primary attack at the double bond by the two catalytic systems, significant differences exist in the case of terminal but not in the case of the internal double bonds. In the case of rhodium it has been proposed [36] that regioselectivity is determined, before, or during the formation of the intermediate rhodium alkyl complexes, and an explanation based on minimization of steric repulsion in the postulated π -complex intermediates is in agreement with most of the experimental data [36]. For cobalt the step controlling the regioselectivity has still not been experimentally demonstrated; however, the effect of the increase of p_{CO} on the regioselectivity has been tentatively explained mainly on the basis of steric effects [15], and the results reported in Table 5 seem to confirm this view. On the basis of the above assumptions, the results obtained in the 1-pentene hydroformylation seem to indicate that the rhodium catalytic complexes are less sterically crowded than the corresponding cobalt complexes, at least at p_{CO} of 100 atm and higher. A similar indication of the importance of steric effects in determining regioselectivity comes also from the hydroformylation of 1-olefins carried out in the presence of phosphines.

Both with cobalt and rhodium catalysts, lowering the carbon monoxide partial pressure largely increases the relative amount of formylation at originally saturated carbon atoms; however, again there is a large difference in the behaviour of rhodium and cobalt catalysts. With rhodium, but not with cobalt, the increase in formylation at the originally saturated carbon atom is accompanied by a lowering of the hydroformylation rate; the observed facts can be explained by assuming that lowering the p_{CO} lowers the rate of hydroformylation [5] while the rate of double bond migration in the substrate is much less affected. With cobalt, on the contrary, both the hydroformylation rate and formylation at the saturated carbon atoms increase markedly in the p_{CO} range investigated; the results can be interpreted on the assumption that the rate of migration is increased more than the rate of formylation. This difference points again to a difference in the nature of the intermediates involved in the migration of rhodium and cobalt on the organic substrate.

4. Intermolecular hydrogen exchange reactions during hydroformylation

As we previously mentioned [24], the methods used for the determination of the position on the substrate at which formylation occurs give reasonable results only if no substantial intermolecular hydrogen exchange takes place. Therefore we have carried out a preliminary investigation of the intermolecular hydrogen exchange with either rhodium or cobalt catalysts. Exchange of hydrogen between substrate molecules and exchange between substrate and gaseous hydrogen can occur, even if only to a limited extent, and will be briefly discussed separately.

a) *H/D exchange between substrate molecules*

In the hydroformylation of both trideuterated 1- and 2-pentene, intermo-

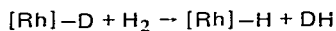
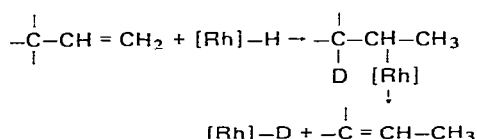
lecular exchange of the label between substrate molecules is revealed by the appearance of molecules containing more than three deuterium atoms [24]. In the case of cobalt this is further accompanied by retention of the average number of the deuterium atoms per molecule and by an increase of the number of molecules containing less than three deuterium atoms.

The extent of this exchange is rather low in each case and therefore subject to substantial experimental error. Both for cobalt and rhodium, 5–6% of the molecules of n-hexanal formed under low p_{CO} are d_4 or d_5 labelled. Under 100 atm p_{CO} practically no exchange takes place, but, surprisingly, an equally small exchange was also found for cobalt under 400 atm p_{CO} ($d_4 + d_5 \approx 5\%$). We believe that with both cobalt and rhodium, the exchange occurs through a sequence of addition and elimination reactions involving $[\text{M}]-\text{H}$ or $[\text{M}]-\text{D}$ and the olefin. We expected a larger exchange with rhodium than with cobalt catalysts; however, as we shall show, in the case of rhodium only part of the deuterium extracted as $[\text{Rh}]-\text{D}$ from the substrate catalyst complex is transferred to another molecule, a larger part being exchanged with gaseous hydrogen. Furthermore, because of the preference of rhodium to interact with >CH_2 rather than $-\text{CH}_3$ groups, which at the start are the only deuterated groups, and because of isotopic effects in the elimination reactions (see section 5a), the formation of metal carbonyldeuterides is less favoured for rhodium than for cobalt catalysts. Similar results have been obtained in the deuterioformylation of 2-butene and will be discussed later.

b) H/D exchange between substrate and gaseous hydrogen

As already mentioned, formylation at a deuterated methyl group is accompanied by a loss of the label with rhodium but not with cobalt catalysts [24,29]. Correspondingly the presence of HD in the gas phase has been qualitatively demonstrated but the amount was not determined (Scheme 5). This difference between the action of rhodium and cobalt in this type of exchange

SCHEME 5



reaction are at first sight surprising in view of some published comments on the exchange between $\text{DCo}(\text{CO})_4$ and H_2 [28]. On the other hand, the exact nature of the hydrides present during the reaction with rhodium or cobalt is still not known. Therefore the difference in behaviour of $[\text{Co}]-\text{H}$ and $[\text{Rh}]-\text{H}$ can be explained by assuming that, depending on the nature of the metal, not only can the exchange rate between hydrides and gaseous hydrogen differ considerably, but the concentrations of the free hydrides during the reaction can also vary greatly. This latter factor will depend on the different tendencies of the substrate-catalyst complexes to dissociate and on the positions of the various equilibria between the metal carbonyl complexes present in the solution.

5. Further investigation of cobalt and rhodium migration along the olefinic substrate during hydroformylation

The differences in behaviour between cobalt and rhodium catalytic systems shown by investigation of the hydroformylation of the olefinic substrates has prompted us to study further the mechanism by which the metal atoms migrate along the substrate. In particular, the possible existence of isotopic effects in the formylation of CD₃ groups and the distribution of deuterium atoms in the hydroformylation of deuterated substrates or in the deuterioformylation of non-deuterated substrates have been investigated.

a) Isotopic effects in the hydroformylation of ω -trideutero-2-butene and -2-pentene

As shown in Table 10, the isomeric composition is the same when deuterated or non-deuterated olefins are hydroformylated in the presence of cobalt, but different for hydroformylation in the presence of rhodium, the differences being in some cases very small but greater than the experimental error. Furthermore, the ratio between the aldehydes having a =CH₂- or a deuterated group (=CHD or =CD₂) in the α -position is 3 : 1 for the rhodium catalyzed butene-2 hydroformylation but 1 : 1 for the cobalt catalyzed process (Table 11).

The data obtained for the rhodium catalyst are consistent with the usually accepted mechanism involving a double bond shift with elimination of a [Rh]-D group. Isotopic effects in corresponding elimination reactions are described in the literature [37,38]. The absence of an isotopic effect with cobalt emphasizes the previously mentioned differences between the two metals in catalysis of the hydrogen shift in the substrate. Explanations have been offered for this phenomenon [29], but no clear indications of the mechanism by which the hydrogen shift occurs are available.

b) Position of deuterium atoms in the products arising from the hydroformylation at deuterated terminal methyl groups

All the aldehydes having at least one deuterium atom in the α -position should arise from the formylation at the CD₃ group. It appears (Table 11) that

TABLE 10

AMOUNT OF THE LINEAR PRODUCT IN THE HYDROFORMYLATION OF SOME LABELLED AND UNLABELLED OLEFINS ^a

Substrate	Amount of linear aldehyde (%)			
	Co ₂ (CO) ₈		Rh ₃ (CO) ₁₂	
CH ₃ -CH=CH-CH ₃	60 (400)		13 (100)	
CH ₃ -CH=CH-CD ₃	61 (400)		8.4 (100)	
CH ₃ -CH ₂ -CH=CH-CH ₃	59 (400)	72 (100)	10 (100)	40 (5)
CH ₃ -CH ₂ -CH=CH-CD ₃	59 (400)	72 (100)	8 (100)	36 (5)
CH ₂ =CH-CH ₂ -CH ₂ -CH ₃		81 (100)		49 (5)
CH ₂ =CH-CH ₂ -CH ₂ -CD ₃		81 (100)		44 (5)

^a In brackets the carbon monoxide partial pressure in atm.

TABLE 11

PROPORTION (%) OF MOLECULES OF NORMAL ALDEHYDES CONTAINING THE GROUP CXY (X, Y = H OR D) IN THE α -POSITION TO THE CARBONYL GROUP

Substrate	p_{CO}	$Co_2(CO)_8$			$Rh_4(CO)_{12}$		
		CH_2	CHD	CD_2	CH_2	CHD	CD_2
$CH_3-CH=CH-CD_3$	100				75	2	23
	400	52	25	23			
$CD_3-CH_2-CH=CH-CH_3$	4-5				73	8	19
	100	67	18	15	90	0	10
	400	68	17	15			
$CD_3-CH_2-CH_2-CH=CH_2$	4-5				81	4	15
	100	89	4	7			

in the case of rhodium at high p_{CO} essentially only CD_2 groups are present in the α -position; with cobalt the deuterated groups in the α -position to the formyl group are largely CDH (about 50% in most cases). Furthermore, in the case of rhodium very little deuterium is transferred to the β -position, while with cobalt the amount of deuterium in the β -position is larger than that expected for a single 1-2 hydrogen shift [24,29].

The data with rhodium are substantially in agreement with our expectation based on a $[Rh]-X$ ($X = H$ or D) addition elimination mechanism for exchange of the $[Rh]-X$ group with gaseous hydrogen. In the case of cobalt it appears that the deuterium shift is much more rapid than aldehyde formation, and the species catalyzing the hydrogen shift do not give rise to an exchange of deuterium atoms with gaseous hydrogen at a sufficient rate to be detectable from the deuterium content of the reaction products.

c) Deuteroformylation of *trans*-2-butene

In these experiments [39] also, interesting differences exist between the rhodium and the cobalt catalyzed reaction. Thus the *n*-pentanoic acid anilide obtained from the linear aldehyde contains about two deuterium atoms (~ 2.2) with rhodium catalysts, as expected, but only slightly more than one (~ 1.1) with cobalt. The intermolecular hydrogen-deuterium exchange observed with cobalt is more evident than in the previous experiments with labelled olefins, the ratio between unlabelled anilides and monolabelled anilides for linear and branched isomer being about 0.17. If hydrogen-deuterium exchange in the free hydride is negligible, this value indicates that the rate of hydroformylation of the complexed substrate is more than twice as large as the rate of substrate dissociation, isotopic effects in hydride elimination being ignored.

This result can be taken as an indication that the dissociation of the substrate-catalyst complex in the case of cobalt catalyst plays a secondary role; however, if the hydrogen-deuterium exchange in the hydride is slow, a large extent of the dissociation of a $[Co]-H$ from the substrate cannot be excluded on this basis.

When rhodium is used as the catalyst, a small excess of deuterium is also present in the branched aldehyde, the average number of deuterium atoms in the corresponding anilide being about 1.3. This shows that part of this aldehyde is

formed after a dissociation of a $[\text{Rh}]\text{-H}$ molecule from the substrate and after the $[\text{Rh}]\text{-H}$ has reacted with gaseous deuterium to regenerate $[\text{Rh}]\text{-D}$.

Concluding remarks

The experimental data discussed in the present review do not bring new direct evidence on the nature of the true catalytic intermediates in the rhodium and in the cobalt catalyzed hydroformylation, which are, in general, assumed to involve similar mechanisms. Although most of the results and particularly the stereochemistry of the reaction, fit into the frame of the accepted mechanism, the following items of experimental evidence point to the existence of rather profound dissimilarities in the catalytic action of the two metals:

i) The overall kinetics are significantly different but, because of the complexity of the multistep catalytic process, no suitable interpretation of all the experimental facts is possible.

ii) There is a greater tendency for formylation at the originally saturated carbon atoms for cobalt than for rhodium catalysts, although the extent of substrate isomerization accompanying hydroformylation is larger in the second case.

iii) For linear internal olefins there is preference for formylation at $-\text{CH}_3$ groups in the case of cobalt and at $-\text{CH}_2$ groups in the case of rhodium catalysts. For labelled olefins, formylation at CD_3 groups is accompanied by an isotope effect in the case of rhodium but not in the case of cobalt.

iv) Steric effects in the hydroformylation are larger for cobalt than for rhodium catalysts, at least in the absence of ligands other than olefins, CO and H.

v) Less exchange of the label between substrate molecules or substrate molecules and gaseous hydrogen has been observed with cobalt than with rhodium. Exchanges are favoured by lower carbon monoxide partial pressure in both cases, but probably for different reasons.

Comparison of the effects of rhodium and cobalt catalysts at different p_{CO} in the absence of added ligands reveals that the catalytic action of rhodium is affected to only a small extent on varying p_{CO} , while much larger effects are evident in the case of cobalt. Furthermore, the catalysis by cobalt at low p_{CO} is similar to that by rhodium. Taking account of the fact that $[\text{Rh}(\text{CO})_3]_4$ species are stable towards fragmentation under high p_{CO} [40] while $[\text{Co}(\text{CO})_3]_4$ rapidly undergoes CO addition with formation of $\text{Co}_2(\text{CO})_8$ under high p_{CO} and at the usual hydroformylation temperature [41], the results seem to be consistent with the existence of catalytic species with CO/metal ratio of about 3 or less for rhodium at low and higher p_{CO} and for cobalt at low p_{CO} . At high p_{CO} , species with CO/metal ratio higher than 3 are probably present in the case of cobalt [10]; these species are probably responsible for the striking differences between the effects of the cobalt and rhodium catalysts at high p_{CO} . The predominant formylation at position 1 found with cobalt for both 1-olefins and 2-olefins has been attributed to steric effects and to the greater tendency of cobalt to occupy the less hindered terminal position of the substrate. Until further experimental evidence in favour of this hypothesis is available, and in view of some indications of the tendency of cobalt to occupy the most substi-

tuted position in the first attack on the olefins, it is not possible to discard the hypothesis that the steric hindrance mainly operates in the CO insertion.

Most of the differences found in the catalytic action are connected with the nature of the olefin-catalyst complexes which are postulated to be the first intermediates of the catalytic cycles. The experiments indicate that in the case of the cobalt catalysts a rapid 1—2 hydrogen shift is possible in the catalyst-substrate complex without dissociation of the isomerized olefin and without any apparent isotope effect, a methyl hydrogen adjacent to the double bond being more easily involved in this reaction than a methylene hydrogen atom in the same position. Concerning the nature of the intermediate(s) involved in this shift, only speculation is possible at present; as well as classical π -olefin complexes, non-canonical intermediates [2] or metallacyclopropanes in which the hydrogen atoms possess unusual mobility could be taken as possible models for the planning of further experiments. We have found no other examples of reactions of this type in cobalt coordination chemistry, the closest analogue being the enhanced mobility of a methylene hydrogen atom adjacent to a π -allyl group bound to a cobalt atom [42], which is believed to be an important factor in butadiene dimerization catalyzed by cobalt.

Acknowledgement

We thank the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung for financial support.

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