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# Rhodium complexes with dioximes as catalysts of hydroformylation and hydrogenation of 1-hexene

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**Abstract**

Rhodium(II) complexes with dioximes $[Rh(Hdmg)_2(PPh_3)]_2$ [**I**] (Hdmg = monoanion of dimethylglyoxime) and $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ [**II**] catalyse hydroformylation and hydrogenation reactions of 1-hexene at 1 MPa $CO/H_2$ and 0.5 MPa $H_2$ at 353 K, respectively. Hydroformylation with complex [**I**] produces 94% of aldehydes ($n/iso = 2.2$) and 6% 2-hexene whereas the second catalyst [**II**] gives ca. 40% of aldehydes ($n/iso = 2.1$) and 60% of 2-hexene. Corresponding Rh(III) complexes are inactive in hydroformylation except of $RhH(Hdmg)_2(PPh_3)$ [**III**], which shows activity similar to [**I**]. Complexes $[Rh(Hdmg)_2(PPh_3)]_2$ [**I**], $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ [**II**], $RhH(Hdmg)_2(PPh_3)$ [**III**] and $[Rh(Hdmg)_2(PPh_3)_2]ClO_4$ [**V**] catalyse 1-hexene hydrogenation with an average TON ca. 18 cycles/mol [Rh] × min. Complex [**II**] has also been found to catalyse hydrogenation of cyclohexene, 1,3-cyclohexadiene and styrene. © 1998 Elsevier Science B.V.

*Keywords:* Rhodium complexes; Rhodoximes; Hydroformylation; Hydrogenation

## 1. Introduction

Much of the extensive works on the rhodium hydrogenation and hydroformylation reactions have been devoted to the rhodium (I) compounds [1–4]. There are only few examples of the active rhodium catalysts in the oxidation state other than 1+. It was found that the dimeric rhodium(II) acetate, $Rh_2(CH_3CO_2)_4$, acts as homogeneous catalyst for hydrogenation of olefins in a wide variety of solvent media [5,6]. The rhodium(II) complexes with heterocyclic nitrogen ligands, $[Rh_2Cl_2(RCO_2)_2(N\text{-}N)_2]$ (*N-N* = 2, 2,-dipirydine, 1,10-phenanthroline) appeared to be effective and selective catalysts for the hydrogenation of ketones and alkenes [7–9].

Mononuclear Rh(II) species $RhCl_2(Pcy_3)_2$ and $RhCl_2(P(o\text{-tol})_3)_2$ ($Pcy_3$ = cyclohexylphosphine, $P(o\text{-tol})_3$ = *ortho*-tolylphosphine) in the presence of $AlEt_3$ [10], as well as $RhCl_2$(dppe) (dppe = diphenylphosphinoetane) [11] and $RhCl_2$(dppb) dppb = diphenylphosphinobutane) [12], catalyse olefin hydrogenation.

Rhodium complexes with dioximes (rhodoximes) have been studied for many years but

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catalytic properties of these species are known scarcely. It has been demonstrated that $RhH(Hdmg)_2(PPh_3)$ **[III]** is an effective catalyst of hydrogenation of nitrobenzene [13,14] and butadiene [15] at very mild conditions. The dimeric Rh(II) complex $[Rh(Hdmg)(PPh_3)]_2$ **[I]** appeared to be a catalyst precursor for hydrosililation of various unsaturated organic molecules [16]. In addition the reactions of alkyl halides with some rhodoximes are of considerable interest [17–24].

In this paper we present the results of hydrogenation and hydroformylation reactions of 1-hexene with $[Rh(Hdmg)(PPh_3)]_2$ **[I]**, $RhH(Hdmg)_2(PPh_3)$ **[III]** and $[Rh(Hdmg)(ZnCldmg)(PPh_3)]_2$ **[II]** as catalysts precursors, at 0.5–1 MPa and 353 K. The activity of Rh(III) oximato complexes, $Rh(Hdmg)_2(PPh_3)Cl$ **[IV]** and $[Rh(Hdmg)_2(PPh_3)_2]ClO_4$ **[V]** have also been tested.

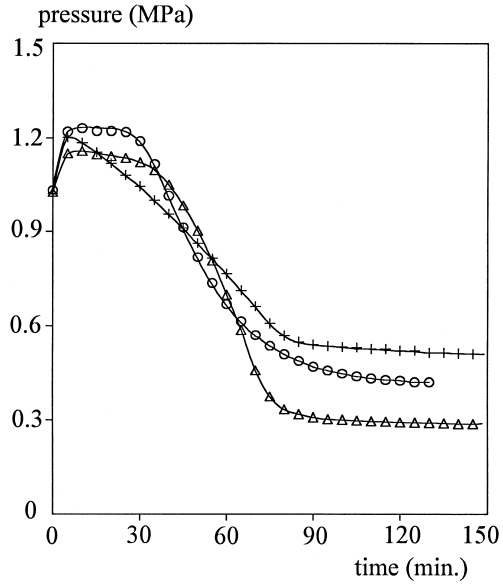


Fig. 1. $CO/H_2$ pressure drop in time during hydroformylation of 1-hexene catalysed by $[Rh(Hdmg)_2(PPh_3)]_2$ **[I]**. +, $[Rh] = 1.16 \times 10^{-5}$ mol; △, $[Rh] = 11.6 \times 10^{-6}$ mol, $[PPh_3] = 4.3 \times 10^{-5}$ mol; ○, $[Rh] = 11.6 \times 10^{-6}$ mol, $[PPh_3] = 1.4 \times 10^{-4}$ mol.

## 2. Results and discussion

### *2.1. Hydroformylation of 1-hexene with $[Rh(Hdmg)_2(PPh_3)]_2$ [I] and $[Rh(Hdmg)_2(PPh_3)]_2/PPh_3$ system*

$[Rh(Hdmg)_2(PPh_3)]_2$ **[I]** catalyses the hydroformylation of 1-hexene without an induction period and the reaction rate is measured as the $CO/H_2$ pressure drop in time (Fig. 1). Since hexane was not found in reaction products it may be suggested that hydroformylation is the only reaction which causes a $CO/H_2$ pressure drop in the autoclave. This allowed us to estimate the maximum reaction rate and pseudo-first order of the reaction in respect to the catalyst concentration (Table 1).

The concentration ratio of 1-hexene to rhodium catalyst effects only the reaction rate but not the product composition. Under the conditions applied (353 K, 1 MPa) the average composition of the products was as follows: 60% heptanal, 27% 2-Me-hexanal and 2% 2-ethylpentanal. The rest was a 2-hexene-isomerization reaction product (Table 1).

The presence of 2-hexene was detected in all the reaction mixtures analysed however its concentration decreased in those reactions which were carried out for a longer time (ca. 4 h) (Table 1, entry 3, 4 and 9). This may be explained by the slower hydroformylation of 2-hexene than that of 1-hexene as the parallel reaction consumes 2-hexene. Elongation of the hydroformylation reaction time resulted in a somewhat higher *n/iso* factor as a result of a higher concentration of heptanal, the main product of 2-hexene hydroformylation.

Introduction of free phosphine to the system drastically changes the reaction kinetic which is first demonstrated by the appearance of the induction period (ca. 40 min) accompanied with constant pressure (Fig. 1) of $CO/H_2$ in autoclave. Secondly, the complete amount of 1-hexene used undergoes hydroformylation within 20 min which is twice as fast as in the reaction without the free phosphine added. The hydroformylation reaction rate does not depend on the

Table 1
Composition of 1-hexene hydroformylation products at different concentrations of catalyst precursor $[Rh(Hdmg)_2(PPh_3)]_2$ [**I**]

| Entry | [Rh][a] ($\times 10^{-6}$ mol) | Time (min) | $v$[b] ($mol_{ald}$/min, $\times 10^{-5}$) | Products (% mol) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 2-hexene | 2-ethyl-pentanal | 2-methyl-hexanal | heptanal | *n/iso* |
| 1 | 7.0 | 440 | 2.67 | 4 | 3 | 29 | 65 | 2.0 |
| 2 | 7.8 | 205 | 3.03 | 16 | 3 | 26 | 55 | 1.9 |
| 3 | 7.6 | 250 | | 4 | 1 | 26 | 68 | 2.5 |
| 4 | 11.6 | 250 | 5.45 | 7 | 2 | 27 | 64 | 2.2 |
| 5 | 11.4[c] | 170 | 10.0 | — | — | 23 | 77 | 3.0 |
| 6 | 11.6[d] | 130 | 10.5 | — | — | 25 | 75 | 3.4 |
| 7 | 13.0 | 200 | 6.65 | 6 | 3 | 29 | 63 | 2.0 |
| 8 | 15.0 | 160 | 6.9 | 13 | 5 | 28 | 54 | 1.6 |
| 9 | 15.0 | 255 | | 6 | 2 | 28 | 65 | 2.3 |

[a]As monomeric complex.
[b]$v$: Maximum reaction rate.
[c]Reaction with $4.3 \times 10^{-5}$ mol of $PPh_3$.
[d]Reaction with $1.4 \times 10^{-4}$ mol of $PPh_3$.
Reaction conditions: [1-hexene], $6.5 \times 10^{-3}$ mol; 353 K, 1 MPa $CO/H_2 = 1$, solvent: THF.

free phosphine concentration over the range from $[PPh_3]$: [**I**] = 3.8 to 12.

Other positive effects of free phosphine are the slight increase of *n/iso* (from ca. 2 to 3) and the total inhibition of isomerization (no 2-hexene and 2-ethylpentanal were found in reaction products).

### 2.2. Hydroformylation of 1-hexene with $RhH(Hdmg)_2(PPh_3)$ [III] and $RhH(Hdmg)_2(PPh_3)/PPh_3$ system

According to the present state of knowledge the rhodium–hydride–carbonyl complexes of formula $HRh(CO)_xP_{3-x}$ (P = phosphorus ligand) are responsible for catalytic activity in the hydroformylation reaction [1–4]. Therefore it was reasonable to check the catalytic activity of the rhodium hydride complex $RhH(Hdmg)_2(PPh_3)$ [**III**]. This complex is sparingly soluble in organic solvents and unstable in solution. Nevertheless its catalytic activity was similar to that of $[Rh(Hdmg)_2(PPh_3)]_2$ [**I**] (Table 2) (reaction rate and reaction selectivity are for both complexes almost identical).

The addition of free phosphine accelerates the reaction by almost four times which allows 100% conversion to be achieved within 105 min

Table 2
Composition of 1-hexene hydroformylation products at different concentrations of catalyst precursor $[RhH(Hdmg)_2(PPh_3)]$ [**III**]

| Entry | [Rh] ($\times 10^{-6}$ mol) | Time (min) | $v$[a] ($mol_{ald}$/min, $\times 10^{-5}$) | Products (% mol) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 2-hexene | 2-methyl-hexanal[d] | heptanal | *n/iso* |
| 1 | 4.8 | 280 | | 3 | 27 | 68 | 2.4 |
| 2 | 9.5 | 245 | 5.5 | 6 | 28 | 65 | 2.3 |
| 3 | 5.3[b] | 105 | 20.6 | 5 | 23 | 72 | 3.1 |
| 4 | 8.6[c] | 105 | 18.2 | 7 | 22 | 70 | 3.2 |

[a]Maximum reaction rate.
[b]Reaction with $4.2 \times 10^{-5}$ mol of $PPh_3$.
[c]Reaction with $6.5 \times 10^{-5}$ mol of $PPh_3$.
[d]1–2% of 2-ethylpentanal was also found.
Reaction conditions: [1-hexene], $6.5 \times 10^{-3}$ mol; 353 K, 1 MPa $CO/H_2 = 1$, solvent: THF.

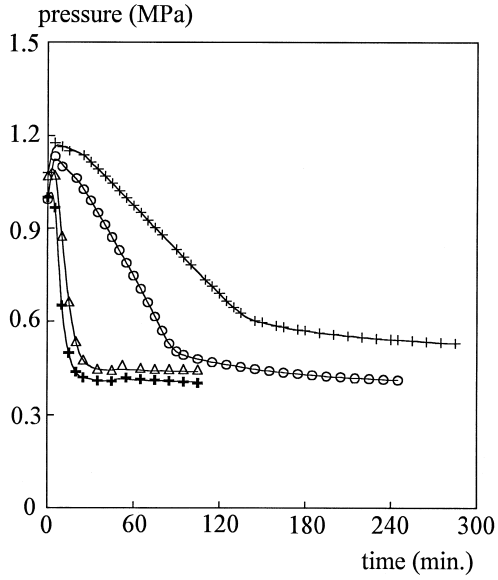


Fig. 2. $CO/H_2$ pressure drop in time during hydroformylation of 1-hexene catalysed by $[RhH(Hdmg)_2(PPh_3)]$ [**III**]. +, $[Rh] = 4.8 \times 10^{-6}$ mol; ○, $[Rh] = 9.5 \times 10^{-6}$ mol; △, $[Rh] = 5.3 \times 10^{-6}$, $[PPh_3] = 4.2 \times 10^{-5}$ mol; +, $[Rh] = 8.6 \times 10^{-6}$ mol, $[PPh_3] = 6.5 \times 10^{-5}$ mol.

(Fig. 2) (*n/iso* increases to ca. 3), but does not cause an induction period which makes this reaction significantly different from that catalysed by the system $[Rh(Hdmg)_2(PPh_3)]_2$ [**I**]$/PPh_3$ (Table 2, entry 3 and 4).

### 2.3. Hydroformylation of 1-hexene with $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ [*II*]

Complex $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ [**II**] is only slightly soluble in organic solvents including THF in which the hydroformylation reaction was conducted. It cannot be excluded that in the hydroformylation reaction condition some amount of complex is dissolved and acts in an homogeneous system, however, in all post-reaction mixtures a solid complex was found. The catalytic activity of such a solid complex separated, washed, dried and used again was identical to that found for the initially used species.

The concentration changes of catalyst [**II**] have no effect on the rate and hydroformylation reaction product composition and the maximum reaction rate determined from the pressure drop was $7 \times 10^{-6}$ $mol_{ald}/min$. In the reaction carried out ca. 300 min, 49% conversion of 1-hexene was found (31% of 2-hexene and 18% of aldehydes (Table 3, entry 2), whereas in a longer reaction (ca. 500 min) conversion was 100% but the yield of aldehydes did not exceed 38% (Table 3, entry 3 and 5). These observations suggest that hydroformylation is a main reaction in the initial stage of the process and

Table 3
Composition of 1-hexene hydroformylation products at different concentrations of catalyst precursor $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ [**II**]

| Entry | [Rh][a] ($\times 10^{-6}$ mol) | Time (min) | Products (% mol) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1-hexene | 2-hexene | 2-methyl-hexanal[e] | heptanal | *n/iso* |
| 1 | 4.6 | 180 | 75 | 19 | 2 | 4 | 2.0 |
| 2 | 4.6 | 305 | 51 | 31 | 5 | 13 | 2.6 |
| 3 | 4.6 | 570 | 3 | 67 | 9 | 21 | 2.1 |
| 4 | 4.6[b] | 530 | 1 | 61 | 11 | 26 | 2.2 |
| 5 | 8.8 | 500 | — | 61 | 12 | 25 | 1.9 |
| 6 | 8.8[c] | 320 | 31 | 28 | 10 | 31 | 3.1 |
| 7 | 11.8[d] | 335 | 35 | 20 | 12 | 33 | 2.8 |

[a]As monomeric complex.
[b]Second time used catalyst.
[c]Reaction with $2.6 \times 10^{-5}$ mol of $PPh_3$.
[d]Reaction with $5.0 \times 10^{-5}$ mol of $PPh_3$.
[e]1% of 2-ethylpentanal was found in some reactions.
Reaction conditions: [1-hexene], $6.5 \times 10^{-3}$ mol; 353 K, 1 MPa $CO/H_2 = 1$, solvent: THF.

hereafter isomerization becomes dominating. In a reaction carried out longer some amounts of 2-ethylpentanal have been found which supports the above assumption. The effect of free phosphine in the reaction catalysed by [**II**] is not clear, however some inhibition of 1-hexene isomerization and an increase in the hydroformylation reaction yield (to ca. 40%) were observed.

### *2.4. Hydroformylation of 1-hexene with $Rh(Hdmg)_2(PPh_3)Cl$ [**IV**] and $[Rh(Hdmg)_2(PPh_3)_2]ClO_4$ [**V**]*

In hydroformylation reaction conditions applied in our experiments the complex $Rh(Hdmg)_2(PPh_3)Cl$ [**IV**] does not activate $H_2$ and CO. The hydroformylation experiment realised at 353 K and 1 MPa $CO/H_2$ after 500 min showed no reaction products and the rhodium complex [**IV**] was found unchanged.

$[Rh(Hdmg)_2(PPh_3)_2]ClO_4$ [**V**] was found also inactive in similar experiments, both, with and without free phosphine added.

### *2.5. The studies of complexes in reaction mixture*

A similar course of hydroformylation reactions catalysed with $[Rh(Hdmg)_2(PPh_3)]_2$ [**I**] and $RhH(Hdmg)_2(PPh_3)$ [**III**] suggests that the same species could be catalytically active in both cases. We failed to isolate these intermediate species in pure form, however, spectroscopic analysis of the post-reaction mixture has shown that both complexes ([**I**] and [**III**]) were converted in some extent to similar products. IR measurements have shown the presence of a complex with terminal CO ligands ($\nu_{CO}$ 1995, 2024 and 2061 $cm^{-1}$). The similar IR-spectrum has been obtained also for the product of treatment of $[Rh(Hdmg)_2(PPh_3)]_2$ [**I**] with 0.5 MPa CO at 353 K in 40 min. There was no UV-VIS band at 456 nm characteristic for the dimeric structure of [**I**], although the complex still contained an oxime ligand ($\nu_{NO}$ frequency at 1020 and 1250 $cm^{-1}$) [25]. Additionally some small amounts of $Rh_4(CO)_{12-x}(PPh_3)_x$ ($x = 1$–4) were identified in a post-reaction mixture ($\nu_{CO}$ 1836 and 1983 $cm^{-1}$) [26].

A higher concentration of $Rh_4(CO)_{12-x}(PPh_3)_x$ was obtained when solutions of $[Rh(Hdmg)_2(PPh_3)]_2$ [**I**] or $RhH(Hdmg)_2(PPh_3)$ [**III**] were heated for 1 h at 353 K under 1 MPa $CO/H_2$.

The heating of complexes [**I**] or [**III**] under the same conditions but with the addition of free phosphine lead to the formation of $HRh(CO)(PPh_3)_3$, spectroscopically identified: $^1H$ NMR $\delta$ −9.2 ppm, multiplet, $^{31}P$ NMR $\delta$ 40.8 ppm, J(Rh–P) 155 Hz and IR ($\nu_{CO}$ 1920, $\nu_{Rh-H}$ 2040 $cm^{-1}$) [26,27].

The appearance of an induction period in the reaction catalyzed with [**I**]/$PPh_3$ could be caused by the time required for the splitting of the initial dimeric structure. To check if that splitting can be caused by $PPh_3$ only the $^{31}P$ NMR spectrum of a solution containing [**I**] and a 10-fold excess of phosphine was measured. The spectrum showed an unchanged triplet at $\delta$ −3.2 ppm, J(Rh–P) 100 Hz [25].

### *2.6. Hydrogenation of 1-hexene*

Rhodium oxime complexes ($[Rh(Hdmg)_2(PPh_3)]_2$ [**I**], $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ [**II**] and $RhH(Hdmg)_2(PPh_3)$ [**III**]) were found as catalysts of nearly the same activity in 1-hexene hydrogenation. At 353 K and 0.5 MPa $H_2$, 1830 mol of 1-hexene is totally hydrogenated by 1 mol of catalyst in ca. 100 min. Complexes [**I**] and [**III**] under hydrogenation reaction conditions show a quite constant catalytic activity. This was demonstrated by the experiment in which after 100 and 200 min the autoclave was refilled with substrates (1-hexene and $H_2$) up to 0.5 MPa pressure. The reaction course, monitored by the pressure drop in time (Fig. 3) showed an almost constant activity in both cases which may suggest the existence of the same Rh–hydride species. Un-

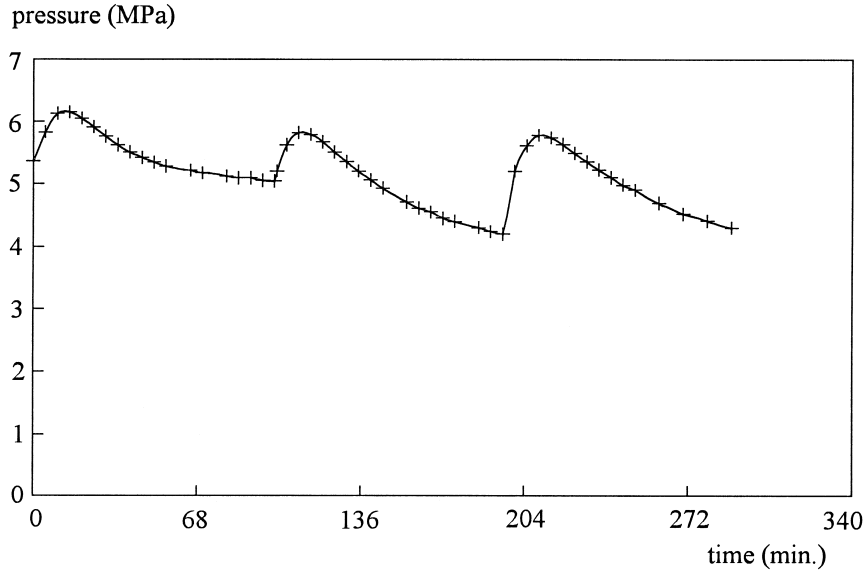


Fig. 3. $H_2$ pressure drop in time during hydrogenation of 1-hexene catalysed by [RhH(Hdmg)$_2$(PPh$_3$)] [**III**] in benzene. [Rh] = $7.3 \times 10^{-6}$ mol; [1-hexene] = $1.3 \times 10^{-2}$; at 100 and 200 min. $1.3 \times 10^{-2}$ mol of 1-hexene were added and the autoclave was filled with $H_2$ up to 0.5 MPa.

fortunately we were unable to find any hydride ligand in compounds isolated from the post reaction mixture.

The reaction catalyzed by [**II**] proceeds a bit slower in toluene or benzene and after 110 min at [1-hexene]: [[**II**]] = 1830 in a reaction mixture 51% of hexane and 35% of 2-hexene were found. This can be explained by the lower solubility of [**II**] in hydrocarbons than in THF, confirmed by UV-Vis measurements of samples taken out from the autoclave during the reaction.

Similarly, as in the case of hydroformylation, complex [**II**] precipitates from the reaction mixture and can be used again with unchanged activity which is the big advantage of this catalytic system. The compound [**II**] has also been found to be an effective catalyst for the hydrogenation of cyclohexene, 1,3-cyclohexadiene and styrene (Table 4).

The rhodium(III) complex [Rh(Hdmg)$_2$(PPh$_3$)Cl] [**IV**], rather inactive in hydroformylation, is also not active in hydrogenation. On the other hand, the similar complex [Rh(Hdmg)$_2$(PPh$_3$)$_2$]ClO$_4$ [**V**] shows some activity in hydrogenation. At the ratio [1-hexene]:[[**V**]] = 1620, after 2 h in reaction products, 78% of hexane and 5% of 2-hexene were found. In the presence of free PPh$_3$ ([PPh$_3$]:[[**V**]] = 8) after 360 min, only 18% of hexane was obtained.

Table 4
Hydrogenation of cyclohexene, 1,3-cyclohexadiene and styrene with catalyst precursor [Rh(Hdmg)(ClZndmg)(PPh$_3$)]$_2$ [**II**]

| Entry | Substrate | [substrate]:[Rh] | Products (% mol) | |
|---|---|---|---|---|
| 1 | cyclohexene | 1100 | cyclohexane (46) | |
| 2 | 1,3-cyclohexadiene | 1200 | cyclohexene (68) | cyclohexane (32) |
| 3 | styrene | 1000 | ethylbenzene (54) | |

Reaction conditions: [Rh] = $1.74 \times 10^{-5}$ mol calculated per monomer, 353 K, 0.5 MPa $H_2$; time: 2 h.

### 2.7. Conclusions

- The dimeric Rh(II) complex, $[Rh(Hdmg)_2(PPh_3)]_2$ [**I**] and the hydride complex of Rh(III), $RhH(Hdmg)_2(PPh_3)$ [**III**] demonstrate a similar catalytic activity in the hydroformylation and hydrogenation of 1-hexene.
- The lack of catalytic activity of the Rh(III) complex $[RhCl(Hdmg)_2(PPh_3)]$ [**IV**] and the quite significant activity of its hydride analogue, $RhH(Hdmg)_2(PPh_3)$ [**III**] demonstrate an interesting effect of slight structure modification on reactivity. However another Rh(III) complex $[Rh(Hdmg)_2(PPh_3)_2]ClO_4$ [**V**] catalyses hydrogenation but not hydroformylation.
- Most probably, during the hydroformylation reaction both complexes [**I**] and [**III**] are partially reduced to Rh(I) species, however, the catalytic activity of rhodium(II) and (III) oxime complexes can not be excluded. This is supported by the activity of $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ [**II**], whose structure is not changed during the reaction. This compound, because of high stability and quite high activity may find application in organic synthesis.

## 3. Experimental

The following rhodium complexes have been prepared according to the literature: $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ [25], $Rh(Hdmg)_2(PPh_3)Cl$ [28], $[Rh(Hdmg)_2(PPh_3)]_2$ [14], $[Rh(Hdmg)_2(PPh_3)_2]ClO_4$ [29] and $RhH(Hdmg)_2(PPh_3)$ [30].

The *hydroformylation reaction* was carried out in a thermostated steel autoclave (40 $cm^3$) with a magnetic stirrer. Samples of the rhodium complex were introduced to the autoclave in a nitrogen atmosphere in small teflon vessels. Next THF (1.5 $cm^3$) and 1-hexene (0.8 $cm^3$) were added. Finally the autoclave was filled up with a $H_2/CO = 1$ mixture at 1 MPa and heated to 353 K. The products were separated from the catalyst by vacuum transfer and analyzed by GC-MS using xylene as an internal standard.

The *hydrogenation reaction* was carried out in a thermostated steel autoclave (150 $cm^3$) with a magnetic stirrer. Samples of the rhodium complex were introduced to the autoclave in a nitrogen atmosphere in small teflon vessels. Next THF or toluene or benzene (1.5 $cm^3$) and 1-hexene (1.6 $cm^3$) were added. Finally the autoclave was filled up with $H_2$ at 0.5 MPa and heated to 353 K. The products were separated from the catalyst by vacuum transfer and analyzed by GC-MS using xylene as an internal standard.

The hydrogenation of cyclohexene, 1,3-cyclohexadiene and styrene with $[Rh(Hdmg)–(ClZndmg)(PPh_3)]_2$ was performed in a 150 $cm^3$ steel autoclave using 2 $cm^3$ of substrate and 0.01 g of rhodium complex.

The UV-VIS spectra were monitored on a Hewlett-Packard 8452A rapid scan diode-array spectrometer. The IR spectra were measured as KBr disks or nujol mulls on a FT IR Nicolet Impact 400 spectrometer. NMR spectra were recorded on a Bruker 300 spectrometer ($^1H$ 300 MHz, $^{31}P$ 121.5 MHz) with solvent used as an internal standard for $^1H$ NMR and 85% $H_3PO_4$ used as an external standard for $^{31}P$ NMR. Chromatographic analyses were done at GC-MS Hewlett-Packard using xylene as an internal standard.

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## References

[1] J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer Verlag, 1980.
[2] I. Tkatchenko, in: G. Wilkinson (Ed.), Comprehensive

Organometal. Chem., vol. 8, Pergamon Press, Oxford, 1982, p. 101.
[3] H. Pignolet (Ed.), Homogeneous Catalysis with Metal Phosphine Complexes, Plenum Press, New York, London, 1983.
[4] F. Ungváry, Coord. Chem. Rev. 147 (1996) 547.
[5] B.C.Y. Hui, G.L. Rempel, J. Chem. Soc. Chem. Commun. (1970) 1195.
[6] B.C.Y. Hui, W.K. Teo, G.L. Rempel, Inorg. Chem. 12 (1973) 757.
[7] F.P. Pruchnik, Pure Appl. Chem. 61 (1989) 795.
[8] H. Pasternak, F.P. Pruchnik, K. Wajda-Hermanowicz, M. Zuber, Pol. J. Chem. 63 (1989) 619.
[9] H. Pasternak, E. Lancman, F. Pruchnik, J. Mol. Catal. 29 (1985) 13.
[10] J.P. Howe, K. Lung, T.A. Nile, J. Organomet. Chem. 208 (1981) 401.
[11] F. Pruchnik, Inorg. Nucl. Chem. Lett. 10 (1974) 661.
[12] K. Kaneda, M. Terasawa, T. Imanaka, S. Teranishi, Chem. Lett. (1976) 995.
[13] E.N. Sal'nikova, M.L. Khidekel, Izv. Akad. Nauk SSSR Ser. Khim. (1967) 223.
[14] S.A. Shchepinov, E.N. Sal'nikova, M.L. Khidekel, Izv. Akad. Nauk SSSR Ser. Khim. (1967) 2128.
[15] B.G. Rogachev, M.L. Khidekel, Izv. Akad. Nauk SSSR Ser. Khim. (1969) 141.
[16] W.B. Panov, M.L. Khidekel, S.A. Shchepinov, Izv. Akad. Nauk SSSR Ser. Khim. (1968) 2397.
[17] T. Ramasami, J.H. Espenson, Inorg. Chem. 19 (1980) 1846.
[18] J.H. Espenson, U. Tinner, J. Organomet. Chem. C 43 (1981) 212.
[19] K.R. Hows, A. Bakac, J.H. Espenson, Inorg. Chem. 27 (1988) 3147.
[20] B. Giese, J. Hartung, C. Kesselheim, H.J. Lindner, I. Svoboda, Chem. Ber. 126 (1993) 1193.
[21] D. Steinborn, M. Ludwig, J. Organomet. Chem. 463 (1993) 65.
[22] L. Randaccio, S. Geremia, R. Dreos-Garlatti, G. Tauzher, F. Asara, G. Pellizer, Inorg. Chim. Acta 194 (1992) 1.
[23] D. Steinborn, U. Sedlak, M. Dergatz, J. Organomet. Chem. 415 (1991) 407.
[24] N. Bresciani Pahor, R. Dreos-Garlatti, S. Geremia, L. Randaccio, G. Tauzher, E. Zangrado, Inorg. Chem. 29 (1990) 3437.
[25] M. Kubiak, T. Głowiak, M. Moszner, J.J. Ziółkowski, F. Asaro, G. Costa, G. Pellizer, C. Tavagnacco, Inorg. Chim. Acta 236 (1995) 141.
[26] A.M. Trzeciak, J.J. Ziółkowski, J. Organomet. Chem. 429 (1992) 239.
[27] D. Evans, G. Yagupsky, G. Wilkinson, J. Chem. Soc. A (1968) 2660.
[28] P. Powell, J. Chem. Soc. A (1969) 2418.
[29] M. Moszner, F. Asaro, S. Geremia, G. Pellizer, C. Tavagancco, Inorg. Chim. Acta 261 (1997) 161.
[30] V.B. Ponov, M.L. Khidekel, S.A. Shchepinov, Bull. Acad. Sci. USSR Div. Chem. Sci. (1968) 2272 (English translation).