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Rhodium(I) complexes with 1′-(diphenylphosphino)ferrocenecarboxylic acid as active and recyclable catalysts for 1-hexene hydroformylation

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Abstract

The rhodium complex *trans*-[Rh(CO)(Hdpf-κ*P*)(dpf-κ^2*O*,*P*)] (**1**), (Hdpf = 1′-(diphenylphosphino)ferrocenecarboxylic acid) was used as an efficient and recyclable catalyst for 1-hexene hydroformylation producing ca. 80% of aldehydes at 10 atm CO/H_2 and 80 °C. After the reaction, unchanged complex **1** was separated from the reaction mixture and used again three times with the same catalytic activity. The effect of modifying ligands, phosphines and phosphites, on the reactivity of **1** was investigated. The active catalytic systems containing **1** or *trans*-[Rh(CO)(L)(dpf-κ^2*O*,*P*)] (**2**) were formed in situ from acetylacetonato rhodium(I) precursors $[Rh(CO)_2(acac)]$ (**3**) or [RhL(CO)(acac)] (**4**) and Hdpf or Medpf (L = phosphine, Medpf = methyl ester of Hdpf).

Keywords: Rhodium; Hydroformylation; Ferrocenyl ligands; Recyclable catalyst

1. Introduction

Ferrocene-based donors and their catalytic properties have attracted considerable attention ever since the discovery of ferrocene in the early 1950s. Until now, numerous ferrocene phosphines have been synthesized and used in various reactions as catalyst components [1].

As far as hydroformylation reactions are concerned, rhodium(I) and platinum(II) complexes involving ferrocene phosphines (**I** and **II**, Scheme 1, Y = $P(OPh)_2$), including chiral ones, have been tested in hydroformylation of styrene, 1-octene, 1-hexene, and cyclohexene [2]. It has been found that regioselectivity of the hydroformylation reactions can be changed by varying the stereoelectronic properties of the substituents at the ferrocene unit (Y in Scheme 1) or the substituents on the phenyl ring [2].

Novelty of the ligand used in the present study, 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf, Scheme 1), results from its bifunctional, "hybrid" nature, which enables it to coordinate to a transition metal either via the phosphorus atom (as a neutral ligand) [3] or via one or more of the oxygen atoms of the carboxylic group (as a carboxylate ligand) [4]. Combined donor mode, bidentate chelating coordination of the 1′-(diphenylphosphino)ferrocenecarboxylate anion (dpf^-) was observed in a rhodium(I) complex featuring two forms of the Hdpf ligand, acid and carboxylate, *trans*-[Rh(CO)(Hdpf-κ*P*)(dpf-κ^2*O*,*P*)] (**1**), and in the related compounds *trans*-[Rh(CO)(L)(dpf-κ^2*O*,*P*)] (**2**), where L is a monodentate phosphine (L = PPh_3 (**a**), PCy_3 (**b**), $FcPPh_2$ (**c**); Cy = cyclohexyl, Fc = ferrocenyl). These complexes are readily accessible by acid-base reactions

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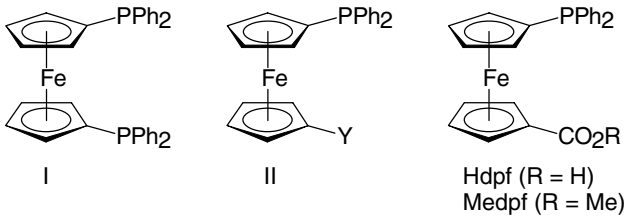


Scheme 1.

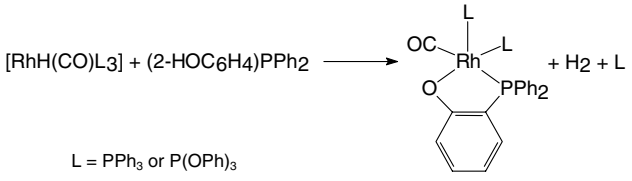
of Hdpf with $[Rh(CO)_2(acac)]$ (**3**) and the respective [RhL(CO)(acac)] (**4**) precursors (Hacac = pentane-2,5-dione, L = phosphine) [5].

Since these complexes are analogues of the archetypal hydroformylation catalysts, we decided to test them in hydroformylation reactions and to study the behavior of the Hdpf ligand under the hydroformylation conditions. Our interest in the influence of the carboxyphosphine was prompted by earlier findings that proton donor ligands negatively impact on the rate of hydroformylation reactions [6,7]. The inhibiting effect of carboxylic acids on the catalytic activity of the catalyst precursor $[RhH(CO)(PPh_3)_3]$ (**5**) [8] has been explained by an interaction between a catalytically active rhodium hydrido complex and the proton of carboxylic acid (Eq. (1)), leading to the formation of dihydrogen and deactivation of the catalysts [6].

$$[RhH(CO)(PPh_3)_3] + RCO_2H \rightarrow [Rh(RCO_2)(CO)(PPh_3)_2] + PPh_3 + H_2 \quad (1)$$

A significant retardation of hydroformylation reaction has also been reported for (2-hydroxyphenyl)diphenylphosphine, which coordinates to rhodium(I) as an *O*,*P*-chelating ligand [7]. The catalytic process is hampered by the high stability of the *O*,*P*-chelate ring, which does not permit the formation of an active catalyst from the precursor complex $[Rh(CO)(2\text{-}HOC_6H_4PPh_2\text{-}\kappa P)(2\text{-}OC_6H_4PPh_2\text{-}\kappa^2 O,P)]$. Likewise, the inhibiting effect of (2-hydroxyphenyl)diphenylphosphine in reactions catalyzed with hydridorhodium precursors $[RhH(CO)L_3]$ (L = PPh_3 (**5**) and $P(OPh)_3$) can be most likely attributed to the formation of stable phosphinophenolate complexes (Scheme 2).

In this paper, we report on our studies of the catalytic properties of rhodium(I) complexes with coordinated Hdpf-type ligands (**system A**) in the model hydroformylation reaction of 1-hexene and on the behavior of Hdpf as a co-catalyst with acetylacetonato rhodium(I) complexes (**system B**).



Scheme 2.

System A

1-hexene $\xrightarrow{(\mathbf{1}) \text{ or } (\mathbf{2a}) \text{ or } (\mathbf{2b})}$ (*n* + *iso*)aldehydes

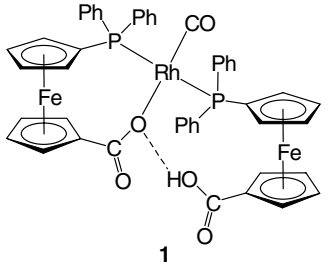
System B

1-hexene $\xrightarrow[+\text{Hdpf or Medpf}]{(\mathbf{3}) \text{ or } (\mathbf{4a}) \text{ or } (\mathbf{4c})}$ (*n* + *iso*)aldehydes

2. Results and discussion

2.1. Catalytic activity of the trans-[Rh(CO)(Hdpf-κP)(dpf-κ²O,P)(CO)] (1) precursor in hydroformylation of 1-hexene (system A)

From the very start, tests showed that rhodium(I) complexes containing the *O*,*P*-chelating anion dpf^-, *trans*-[Rh(CO)(Hdpf-κ*P*)(dpf-κ^2*O*,*P*)(CO)] (**1**), *trans*-[Rh(CO)(PPh_3)(dpf-κ^2*O*,*P*)(CO)] (**2a**), and *trans*-[Rh(CO)(PCy_3)(dpf-κ^2*O*,*P*)(CO)] (**2b**) (Scheme 3), are good hydroformylation catalysts producing 84–91% of (*n* + *iso*) aldehydes even without added modifying ligands (Table 1). The *n*/*iso* ratios are 2.4–2.5 for complexes **1** and **2a**, whereas complex **2b** exhibits a lower *n*/*iso* ratio, 1.6, like other catalytic systems involving PCy_3 [9]. On the other hand, very low catalytic activities were observed for complexes with halogen ligands and *P*-monodentate Hdpf, *trans*-[RhCl(CO)(Hdpf-κ*P*)$_2$(CO)] (**6a**) and *trans*-[RhBr(CO)(Hdpf-κ*P*)$_2$(CO)] (**6b**) (Scheme 3) [5]. These complexes hardly catalyze hydroformylation at all (only ca. 1% aldehydes) and show insignificant activity in hexene isomerization, producing 4–10% of 2-hexene after 5 h.



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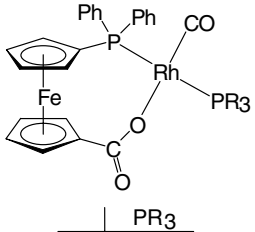
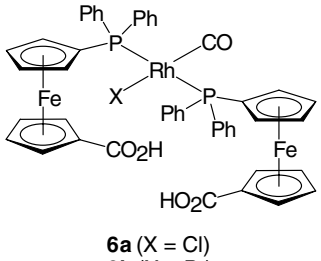


	PR3
2a	PPh_3
2b	PCy_3
2c	Medpf



6a (X = Cl)
6b (X = Br)

Scheme 3.

Table 1
Hydroformylation of 1-hexene catalyzed by Rh(I)-Hdpf complexes *trans*-[Rh(CO)(Hdpf-κ*P*)(dpf-κ^2*O*,*P*)] (**1**), *trans*-[Rh(CO)(PPh_3)(dpf-κ^2*O*,*P*)] (**2a**), *trans*-[Rh(CO)(PCy_3)(dpf-κ^2*O*,*P*)] (**2b**), *trans*-[RhCl(CO)(Hdpf-κ*P*)$_2$] (**6a**), and *trans*-[RhBr(CO)(Hdpf-κ*P*)$_2$] (**6b**) (system A)

Catalyst precursor	Co-catalyst	Aldehydes (*n* + *iso*) (%)	2-Hexene (%)	1-Hexene (%)	*n*/*iso*
1[a,c]	None	82	17	–	1.8
1[a,b]	None	76	23	1	1.9
1	None	84	15	1	2.5
1	Hdpf	4	21	75	1.3
1	Medpf	39	2	59	2.6
1	PPh_3	21	32	47	2.4
1	$P(OPh)_3$	81	20	–	4.6
1	$P(OC_6H_4\text{-}3\text{-}CH_3)_3$	88	12	–	4
1	$P(OCH_2CF_3)_3$	79	21	–	3
1	$P(C_6H_4\text{-}4\text{-}OCH_3)_3$	68	6	26	2.6
1	$PPh_2(C_6H_4\text{-}2\text{-}OCH_3)$	63	14	23	2.7
1	PCy_3	88	12	–	2.4
1	$P(NC_4H_4)_3$	77	23	–	2.8
1	$PPh(C_6F_5)_2$	82	18	–	2.4
1	$PPh_2(C_6F_5)$	41	7	52	2.4
2a	None	89	11	–	2.4
2b	None	91	8	1	1.6
2b[a]	None	87	12	1	1.6
6a[a,c]	None	1	11	88	–
6b[a,c]	None	–	4	96	–

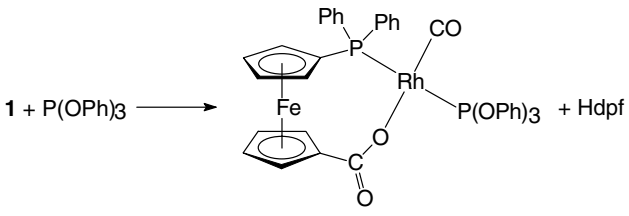
General reaction conditions: [Rh] = 7.5 μmol, [1-hexene] = 0.012 mol in toluene (1.5 ml), 80 °C, 2 h, 10 atm CO/H_2 ($CO:H_2$ = 1).
[a] [Rh] = 15 μmol
[b] Reaction time 3 h.
[c] Reaction time 5 h.

2.2. Testing of various modifying ligands

In most of the catalytic systems applied in hydroformylation, an excess of free phosphorus ligand is used, due to its beneficial effect on both the reaction rate and reaction selectivity [10]. Therefore, for further evaluation of the catalytic properties of catalysts based on complex **1**, we selected several phosphines (PR_3) and phosphites ($P(OR)_3$) with different steric and electronic properties and used them as modifying ligands ([PR_3/$P(OR)_3$]:[Rh] = 1). The results are summarized in Table 1. At first sight, the most attractive ligands for **1** are triphenyl phosphites, which increased the *n*/*iso* hydroformylation selectivity ratio to 4.6 ($P(OPh)_3$) and 4.0 ($P(OC_6H_4CH_3\text{-}4)_3$) at a total yield of aldehydes amounting to 81% and 88%, respectively. A lower increase in the *n*/*iso* ratio, to ca. 3, and similar levels of activity (77–79% yields of aldehydes) were achieved with $P(NC_4H_4)_3$ (NC_4H_4 = 1-pyrrolyl) and $P(OCH_2CF_3)_3$. The obtained results confirmed earlier observations for many catalytic systems that an increase in hydroformylation reaction selectivity towards a higher *n*/*iso* ratio is caused by π-acceptor phosphorus ligands [10].

It is generally assumed that modification of the properties of catalysts with added ligands is usually accomplished by means of their coordination to the metal. This step was confirmed for **1** and $P(OPh)_3$. In reaction of **1** with $P(OPh)_3$ at 60 °C in C_6D_6, the complex [Rh(CO)($P(OPh)_3$)(dpf-κ*P*)] **2d** was identified in the ^{31}P NMR spectra, showing a characteristic pattern of two double doublets at δ_P 14.4 and 110.0 ppm due to Rh-bonded dpf$^-$ and $P(OPh)_3$, respectively. The high value of the $^2J_{PP}$ coupling constant (564 Hz) points to the *trans* arrangement of the *P*-donors (Scheme 4). This is surprising because a more basic ligand, Hdpf, was substituted by a less basic one, $P(OPh)_3$; however, we had already found a similar substitution in our previous studies [7]. The observed effect may be explained not only by electronic but also by steric influence of ligands.

In contrast to phosphites, phosphines, which are stronger σ-donors, inhibited the catalytic activity of complex **1**, decreasing the yield of aldehydes (Table 1). The strongest inhibiting effect was observed for Hdpf (phosphine), which, when used together with **1**, decreased the yield of aldehydes to just 4%. At the same time, the presence of Hdpf not only did not prevent the isomerization of 1-hexene to 2-hexene but even slightly increased its rate compared to **1** alone. The increase in the yield of the isomerization reaction with the concurrent decrease in the yield of aldehydes was



Scheme 4.

also observed with PPh_3. Meanwhile, Medpf showed a different behavior, decreasing the yields of both reactions. Of the phosphines tested, only PCy_3 did not decrease the yield of aldehydes. Instead, a slight promoting effect was observed (88% yield of aldehydes), which is in agreement with the high activity of **2b** (Table 1).

2.3. Catalytic activity of Rh(I) acetylacetonato precursors (3, 4a, 4c) and [RhH(CO)(PPh$_3$)$_3$] (5) modified with Hdpf or Medpf in 1-hexene hydroformylation (system B)

Relatively active catalytic systems were obtained with $[Rh(CO)_2(acac)]$ (**3**) as the catalyst precursor and Hdpf or Medpf (Table 2). The effect of Hdpf is observed already at the ratio [**3**]:[Hdpf] = 1:1, at which 61% yield of aldehydes was obtained, while only 20% yield of aldehydes was obtained with **3** without the added phosphine ligand. The high contribution of the isomerization reactions (39% of 2-hexene) can be accounted for by the presence of unreacted complex **3**, which is known to be a very active isomerization catalyst [11]. This observation is in accordance with the fact that Hdpf reacts with **3** to give **1** regardless of the ratio of the educts [5]. Thus, under the initial reaction conditions, the precatalyst mixture contains equimolar amounts of **1** and **3**. An increase in Hdpf concentration relative to **3** caused an increase in the yield of aldehydes. However, at higher Hdpf concentrations (four equivalents and more), the reaction rate and conversion decreased.

Addition of the ester Medpf, which, unlike the parent acid, cannot displace the acac ligand, to the precursor complex **3** gives a catalytic system producing 82% of aldehydes (*n*/*iso* = 2.1) and 18% of 2-hexene.

The effect of free Hdpf and Medpf is distinctly positive when combined with Rh(I) acetylacetonato complexes, $[Rh(CO)(PPh_3)(acac)]$ (**4a**) or [Rh(CO)(Medpf)(acac)] (**4c**). Addition of Hdpf results in the replacement of the $acac^-$ ligand (*O*,*O*) to give the *O*,*P*-chelated complexes **2a** and *trans*-[Rh(CO)(Medpf-κ*P*)(dpf-κ^2*O*,*P*)] (**2c**) (Scheme 5). As a result, the catalytic activity of the **4a**/Hdpf system is nearly the same as the activity of **2a** alone.

Addition of Hdpf phosphine also has a positive effect on reactions catalyzed with $[RhH(CO)(PPh_3)_3]$ (**5**), leading to a higher yield and selectivity towards the *n*-aldehyde. The reaction between **5** and Hdpf performed separately produced a mixture of rhodium complexes of which none was identified as a rhodium-hydride. Instead, using NMR and MS techniques, two complexes, **1** and **2a**, were identified in the reaction mixture (Eq. (2)).

$$\mathbf{5} + \text{Hdpf} \rightarrow \mathbf{1} + \mathbf{2a} + PPh_3 + \cdots \quad (2)$$

In view of these results, we can attribute the inhibiting effect of free Hdpf as observed in hydroformylation reactions with **1** and **3** as precatalysts (see above) to the decomposition of the rhodium-hydride complex in a way similar to that shown in Eq. (1).

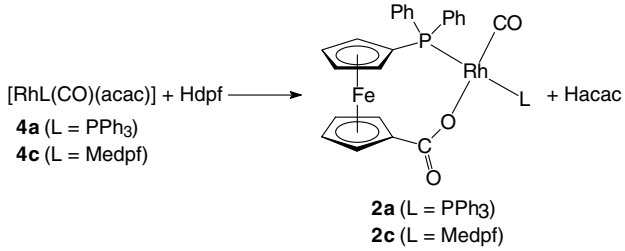
2.4. Spectroscopic identification of catalytically active rhodium complexes

IR analysis of post-reaction mixtures after hydroformylation catalyzed with complex **1** revealed new ν(CO) bands at 2065, 2047, and 1817 cm^{-1}, which could be attributed to a new complexes **7** and **8**, formed under the hydroformylation reaction conditions (Table 3, Scheme 6). The complexity of the IR spectra suggests coexistence of complexes **1**, **7**, and **8**, and the presence of isomers of **7** (trigonal bypiramide and square planar pyramide) cannot be ruled out either. Unfortunately, the concentration of this new species was too low to record its NMR spectra. Only a doublet at δ_P 19.5 ($^1J_{RhP}$ = 135 Hz) characteristic for **1** was observed. Measurements taken after 25 and 50 min of the reaction course showed gradual formation of the new compound.

Table 2
Hydroformylation of 1-hexene catalyzed with catalyst precursors $[Rh(CO)_2(acac)]$ (**3**), $[Rh(CO)(PPh_3)(acac)]$ (**4a**), [Rh(CO)(Medpf-κ*P*)(acac)] (**4c**) and $[RhH(CO)(PPh_3)_3]$ (**5**) and Hdpf/Medpf modifying ligands (system B)

Catalyst precursor	Added phosphine	Aldehydes (*n* + *iso*) (%)	2-Hexene (%)	1-Hexene (%)	*n*/*iso*
3	1 Hdpf	61	39	–	2.5
3	2 Hdpf	78	20	2	2.3
3	2 Hdpf[a]	83	17	–	2
3	4 Hdpf	69	4	26	2.6
3	6 Hdpf	61	3	36	2.7
3	1 Medpf	55	43	2	2.6
3	2 Medpf	82	18	–	2.1
4a	–	67	33	–	2.4
4a	1 Hdpf	90	10	–	2.5
4c	–	65	9	26	2.3
4c	1 Hdpf	89	11	–	2.2
4c	1 Medpf	89	11	–	2.3
5	–	88	12	–	2.3
5	1 Hdpf	93	7	–	2.8
5	2 Hdpf	97	3	–	3.1

Reaction conditions: [Rh] = 7.5 μmol, [1-hexene] = 0.012 mol, toluene 1.5 ml, 80 °C, 2 h, 10 atm CO/H_2 ($CO:H_2$ = 1).
[a] [Rh] = 15 μmol.



Scheme 5.

Table 3
IR data (in KBr) in the region 2200–1500 cm^{-1} of the post-reaction mixtures involving pre-catalyst **1** (after 2 h of hydroformylation unless noted otherwise)

Catalytic system	IR (ν/cm^{-1})
1[a]	1979vs, 1706s[c], 1562s, 1466s, 1435m
1[b]	2071w, 2042w, 1979vs, 1709w, 1624m, 1564s
1 after 25 min	Solid: 1979vs, 1706m Reaction solution: 2065m, 1982m, 1820vw, 1709vs, 1650m, 1630m, 1570m, 1550m
1 after 50 min	Solid: 2065w, 2042m, 2006m, 1979vs, 1825vw, 1709m, 1564vs Reaction solution: 2065m, 2045m, 2006m, 1989m, 1822s, 1713vs, 1594s, 1570m
1	2065w, 2047w, 1977s, 1817m, 1711s, 1688m, 1589s, 1574s, 1560s
1 + Hdpf	2050m, 1976m, 1825m, 1740vs, 1563m, 1530w
1 + Medpf	2047w, 1979vs, 1816vw, 1720vs, 1589s, 1561s
1 + PPh_3	2049s, 1988s, 1821s, 1732vs, 1598s
1 + $P(OPh)_3$	2054vw, 1991vw, 1821m, 1715vs, 1598w, 1560vw, 1530vw
1 + $P(O\text{-}C_6H_4CH_3)_3$	2070w, 2047w, 1994w, 1964w, 1721w, 1588w
1 + $P(OCH_2CF_3)_3$	2047w, 1979vs, 1706s, 1653m, 1594s, 1556vs
1 + $P(C_6H_4OCH_3)_3$	2054m, 1969vs, 1817w, 1720s, 1680m, 1595vs, 1565s, 1503m
1 + PCy_3	2050m, 2025m, 1969vs, 1825w, 1720vs, 1608s
1 + $P(NC_4H_4)_3$	2047m, 1967m, 1821m, 1721s, 1597vs
1 + $PPh(C_6F_5)_2$	2047w, 1973m, 1818vs, 1718w, 1690w, 1640w, 1597s, 1519m

[a] Before hydroformylation.
[b] After 2 h under 10 atm H_2/CO at 80 °C in toluene *without* added 1-hexene.
[c] Cf. data in Nujol from [5]: 1962s, 1703s, 1551s.

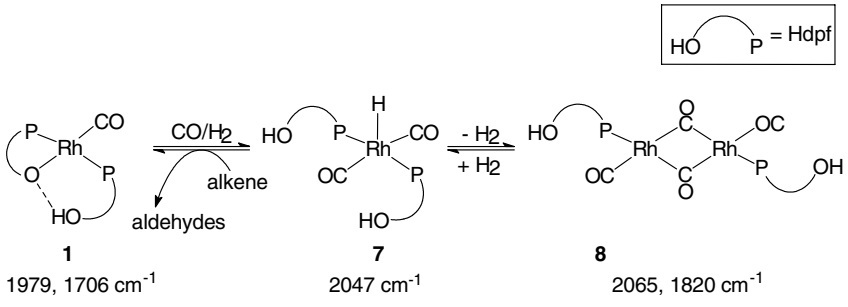
After 25 min of the reaction, the reaction solution was pale yellow and some amount of **1** remained undissolved as confirmed by its IR and UV–Vis spectra. The IR spectrum of the solution showed two new bands at 2065 and 1820 cm^{-1} from **8**. After 50 min, the color of the solution turned to deep red, and several new IR bands appeared in the region 2100–1800 cm^{-1}, suggesting the formation of at least two new compounds.

The color changes of the reaction solution correlate well with the reaction course. Within 50 min a significant CO + H_2 pressure drop in the autoclave occurred, and the real hydroformylation reaction started – most likely because a new compound, probably a rhodium-hydrido-carbonyl complex such as **7**, was formed. The presence of a ν(CO) band at ca. 1800 cm^{-1} in most of the measured spectra, indicative of bridging CO ligands, made it possible to propose an equilibrium between the rhodium(I) hydrido-carbonyl complex and the rhodium(0) carbonyl one, **8** (Scheme 6). Complex **8** was present already in the reaction mixture or, more likely, was formed during evaporation of the solvent in the process of the preparation of samples for IR measurements.

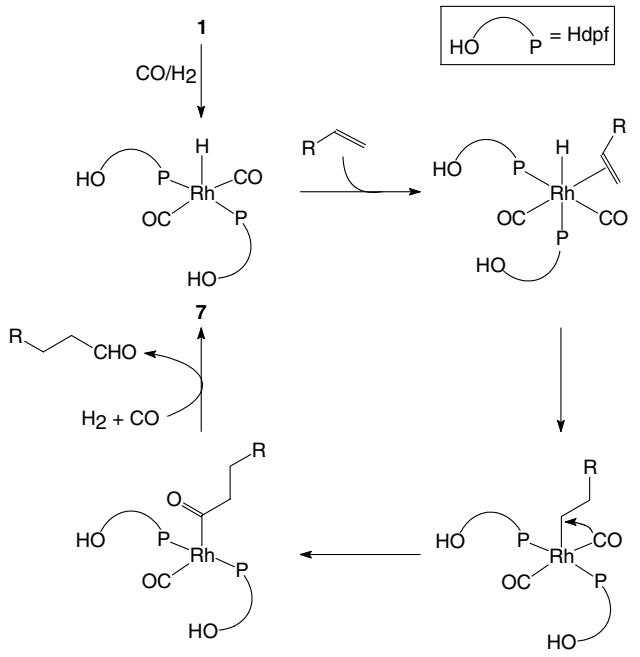
IR studies of the post-reaction mixtures involving **1** as the catalyst precursor (Table 3) and different modifying ligands allowed us to observe both the formed hydrido-carbonyl rhodium complex **7** and unchanged **1**. The IR data (Table 3) indicate the presence of a protonated carboxylic group [5] with vibration at ca. 1700 cm^{-1} in the spectra of all post-reaction mixtures. The bands observed in the region 1600–1400 cm^{-1} are characteristic of a chelating carboxylic group. The carbonyl ν(CO) frequency for **1** was observed at 1979 cm^{-1}. We may conclude that **1** is transformed under hydroformylation reaction conditions into the Rh(I) hydrido-carbonyl complex **7**, playing the role of catalyst, and then converted back into **1** (Table 3). Such transformation may proceed *via* Rh-O bond breaking during activation of the H_2 molecule and reproduction of that bonding after reductive elimination of aldehyde (Scheme 7). The stability of complex **1** under hydroformylation reaction conditions (note that **1** is quite stable when heated to 80 °C for 2 h under 10 atm of H_2/CO) and its high catalytic activity make it a very attractive catalyst precursor and prompted us to test its repeated use.

2.5. Repetitive hydroformylation of 1-hexene with *1*

Results obtained for repetitive hydroformylation of 1-hexene catalyzed with **1** as the catalyst precursor are presented in Table 4. After each reaction cycle (2 h), the reaction mixture was separated using the vacuum-transfer procedure. The organic products were analyzed and the solid residue was used as catalyst for the next



Scheme 6.



Scheme 7.

Table 4
Repeated hydroformylation of 1-hexene catalyzed by *trans*-[Rh(CO)(Hdpf-κ*P*)(dpf-κ^2*O*,*P*)] (**1**)

Catalytic run[a]	Aldehydes (*n* + *iso*) (%)	2-Hexene (%)	1-Hexene (%)	*n*/*iso*
1	84	16	–	2.4
2	89	11	–	2.1
3	83	17	–	2.3
4	69	29	2	2.5
5	48	38	14	2.7
6	13	34	53	2.4

[a] [Rh] = 7.1 μmol, [1-hexene] = 0.012 mol (in each catalytic cycle), toluene 1.5 ml, 80 °C, 10 atm H_2/CO (CO:H_2 = 1). After each reaction the mixture was separated by vacuum transfer, 1-hexene (1.5 ml, 0.012 mol) and toluene (1.5 ml) were added to the catalyst residue, and the mixture was transferred to the autoclave. The reaction time was 2 h for each catalytic run.

hydroformylation reaction with a new portion of 1-hexene. It is worth noting that the first reaction cycle started after an induction period (ca. 50 min), which represents the time necessary for the formation of complex **7**. However, the second cycle started immediately after the insertion of the reactants into the autoclave. In such a way the reaction was carried out three times with the total yield of aldehydes of more than 80% (TON ca. 4500). In the fourth reaction cycle, catalyst activity decreased (see 1-hexene conversion in Table 4) while the concentration of aldehyde condensation products (e.g. 2-pentyl-2-nonenal) increased. Accumulation of that side-product can cause a decrease in the catalytic activity of **1** in subsequent reactions.

3. Conclusions

Complex **1** is an efficient catalyst precursor for hydroformylation reaction. It can be applied even without co-catalysts and/or modifying ligands and used repeatedly without a loss of activity and selectivity during the first three cycles. The selectivity of the catalytic system based on **1** as the precursor can be tuned by adding phosphorus modifying ligands, of which aromatic phosphites showed the highest selectivity (*n*/*iso* ratio) without any loss of catalyst activity.

The spectral data of the reaction mixture indicate that **1** is not the true hydroformylation catalyst, as it requires prior activation. Under the hydroformylation conditions, it is most likely converted to the hydridocarbonyl complex **7**, the real catalyst, with *P*-monodentate Hdpf ligands.

4. Experimental

4.1. Materials and methods

Syntheses of the complexes were performed under an argon atmosphere. NMR grade C_6D_6 was used without purification. Compounds [Rh(acac)$(CO)_2$] [12], **1**, **2a**, **2b**, **6a**, **6b** [5], **4a** [12], **5** [8], and the ligands Hdpf and Medpf [13] were synthesized by the literature procedures.

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer at 25 °C (^{1}H, 399.95; ^{31}P, 161.90 MHz) and on a Bruker 300 spectrometer (^{1}H, 300.0; ^{31}P, 121.5 MHz). Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C) or to external 85% aqueous H_3PO_4 (^{31}P). Electrospray mass spectra (ESI MS) were obtained on a Bruker Esquire 3000 spectrometer operating in positive ion mode. The samples were dissolved in a *small amount* of chloroform and diluted with a large excess of acetonitrile. GC–MS was performed on a Hewlett–Packard 8452A instrument.

IR spectra were recorded on an FT-IR Nicolet Impact spectrometer. Small samples of the reaction mixture were condensed in vacuo and used for measurements as films on KBr pellets.

4.2. Hydroformylation reactions

Hydroformylation reactions have been performed in a steel autoclave (50 ml) with magnetic stirring at 80 °C and 10 atm H_2/CO (1:1). A suitable amount of pre-catalyst in a small Teflon vessel, toluene (1.5 ml) and 1-hexene (1.5 ml, 0.012 mol) were introduced into the autoclave under N_2 atmosphere. Then, the autoclave was closed, filled with H_2 (5 atm) and with CO up to 10 atm. After the reaction, the autoclave was cooled down and the liquid sample was analyzed by GC–MS.

4.3. Micro-scale preparation of trans-[Rh(CO)(Medpf-κP)(acac)] (**4c**) and trans-[Rh(CO)(Medpf-κ P)-(dpf-κ^{2}O,P)] (**2c**)

A solution of Medpf (8.6 mg, 20 μmol) in C_6D_6 (0.7 ml, containing 0.1% $SiMe_4$) was added to solid complex **3** (5.2 mg, 20 μmol). The solid quickly dissolved with effervescence (CO evolution) to give a clear orange solution, which was allowed to stand at room temperature for 90 min and then analyzed with NMR and MS spectroscopy. Evaporation of the reaction solution gave pure **4c** as an orange glassy solid, which was used directly in the next step.

Complex **4c** (11.4 mg, 17 μmol) and Hdpf (7.1 mg, 17 μmol) were dissolved in C_6D_6 (1.0 ml, containing 0.1% $SiMe_4$). The clear mixture was stirred for 90 min at room temperature and evaporated under reduced pressure to give **2c** in quantitative yield. The compound was analyzed as above.

Analytical data for **4c**: ^{1}H NMR (C_6D_6): δ 1.58 and 1.95 (2 × s, 3H, Me of acac); 3.45 (s, 3H, OMe), 4.20 (d of apparent t, 2H), 4.45 (apparent q, 2H), 4.55 (apparent t, 2H), and 4.96 (apparent t, 2H) (4 × CH of fc); 5.32 (s, 1H, CH of acac), 6.98–7.77 (m, 10H, PPh_2). ^{31}P{^{1}H} NMR (C_6D_6): δ 41.6 (d, $^1J_{RhP}$ = 178 Hz). ESI MS: *m/z* 681 ([M + Na]$^+$), 630 ([M − CO]$^+$), 559 ([Rh(Medpf)(CO)]$^+$).

Analytical data for **2c**: ^{1}H NMR (C_6D_6): δ 3.76 (s, 3H, OMe), 4.12 (apparent t, 2H), 4.30 (apparent q, 2H), 4.46 (m, 4H), 4.51 (apparent q, 2H), 4.82 (apparent t, 2H), and 4.89 (br s, 4H) (8 × CH of fc); 7.35–7.81 (m, 10H, PPh_2). ^{31}P{^{1}H} NMR (C_6D_6): δ 18.7 (dd, $^1J_{RhP}$ = 132 Hz, $^2J_{PP}$ = 355 Hz) and 22.9 (dd, $^1J_{RhP}$ = 133 Hz, $^2J_{PP}$ = 355 Hz). ESI MS: *m/z* 995 ([M + Na]$^+$), 973 ([M + H]$^+$).

4.4. NMR study of the reaction between **1** and $P(OPh_3)_3$

A solution of 1 (0.019 g, 19.8 μmol) and $P(OPh)_3$ (0.006 g, 18.7 μmol) in 1 ml of $CDCl_3$ was refluxed for 1 h. After that time a solution was cooled down and ^{31}P{^{1}H} NMR spectrum was recorded. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 14.4 (dd, $^1J_{RhP}$ = 122 Hz, $^2J_{PP}$ = 564 Hz, dpf) and 110.0 (dd, $^1J_{RhP}$ = 220 Hz, $^2J_{PP}$ = 564 Hz, $P(OPh)_3$).

4.5. NMR study of the reaction between **5** and Hdpf

Complex **5** (46 mg, 50 μmol) and Hdpf (21 mg, 51 μmol) were suspended in C_6D_6 (3 ml) and the mixture was heated in an oil bath kept at 50 °C. The solids quickly dissolve with effervescence to a clear orange solution containing some colourless precipitate. After heating overnight, the mixture was filtered, evaporated and analyzed with ESI MS and ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

^{1}H NMR spectra reproducibly showed a broad multiplet due to phenyl groups (δ_H 7.27–8.82, PPh_3 and 'Hdpf'), two sets of signals typical for 1,1′-disubstituted ferrocene unit ('Hpdf'), but no rhodium-hydride signal (cf. **5** gives a broad singlet at δ_H −9.71 in C_6D_6). The ferrocene signals at δ_H 4.13, 4.35, 4.46 and 4.82 (same integral intensity) corresponded nicely to the shifts observed for **2a** [5]. The other, more abundant set had δ_H 3.27 and 3.89 (2 × apparent q), 3.91 and 4.00 (2 × apparent t) (equal intensities). In ^{31}P NMR spectra, the mixture showed a broad band at δ_P −4.78 attributable to liberated PPh_3, a doublet originated from **1** [δ_P 19.5 (d, $^1J_{RhP}$ = 131 Hz)] and pair of double doublets due to **2a** [δ_P 18.73 (dd, $^1J_{RhP}$ = 130, $^2J_{PP} \approx$ 350 Hz) and 28.10 (dd, $^1J_{RhP}$ = 134, $^2J_{PP} \approx$ 350 Hz)]. Signals due to free Hdpf or the corresponding phosphine oxide [13] were not detected.

ESI mass spectra (in $CHCl_3$ + MeOH) clearly showed the peaks due to {[Rh(dpf)(Hdpf)] + H}$^+$ (*m/z* 960), {[Rh(CO)(PPh_3)(dpf)] + H}$^+$ (*m/z* 808), {[Rh(PPh_3)(dpf)] + H}$^+$ (*m/z* 779) and peaks {Rh(PPh_3)$_2$}$^+$ at *m/z* 627.

In the analogous reaction performed at room temperature (3 h) only **1** was detected by means of ^{31}P {^{1}H} NMR spectrum together with unreacted **5** [δ_P 41.0 (d, $^1J_{RhP}$ = 154.3 Hz)].

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