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Hydroformylation of 1-octene using rhodium-1,3-R_2-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R = 2-Pr, mesityl)

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Abstract

Four different Rh (I) complexes, i.e. [RhBr(1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)] (**1**), [RhCl(1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)] (**2**), [RhBr(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)] (**3**) and [RhCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)] (**4**), (COD = η^4-1,5-cyclooctadiene, mesityl = 2,4,6-trimethylphenyl), were used in the hydroformylation of 1-octene. All compounds were active in the hydroformylation, showing a time dependant *n*:*iso* ratio, indicative for olefin isomerization. This olefin isomerization was also monitored as a function of time. TOFs for hydroformylation obtained with **1** and **2** were around 500, those achieved with **3** and **4** around 1500 h^{-1}.

Keywords: Homogeneous catalysis; Hydroformylation; *N*-Heterocyclic carbenes; 1-Octene; Rhodium

1. Introduction

Hydroformylation reactions are the most important among industrial processes with a worldwide production of several million tons. Starting from readily available alkenes, (di)hydrogen and carbon monoxide, highly valuable *n*-aldehydes as well as the corresponding regioisomers are available [1]. In the case of classic systems based on phosphanes or related ligands, the mechanisms depend on the ligands employed, yet are well understood. In due consequence, one was able to optimize these reactions to an extent that they may nowadays even be conducted in parallel with other reactions in form of tandem reaction sequences [2]. Numerous transition metals such as Rh, Pt, Co and Ru may be used for these purposes, however, Rh-based catalysts work at lower temperatures and are therefore generally the preferred systems [3,4]. Usually, phosphane-based ligands are used, since they offer access to highly active systems and allow regio-, and in case of chiral phosphanes, even enantioselective reactions [5–14]. During the last two decades, environmental aspects including catalysts and solvent recycling became an issue. Therefore, supported [15–22] or biphasic systems [23,24], as realized in the Rhone–Poulenc process, have been developed [25–28]. Alternatively, the use of ionic liquids [29–32] or supercritical CO_2 has been reported [33]. Despite the numerous favorable properties of phosphanes, some intrinsic properties of these systems are disadvantageous. An excess of ligand is usually applied during catalysis for multiple reasons. First, this class of compounds is easily oxidized by molecular oxygen. Second, chemicals used in industrial processes possess only bulk quality and therefore contain other metal ions, e.g. Fe (III) and Ni (II) at the ppm level. These show often similar or even higher binding constants with phosphanes compared to Rh. Finally, high selectivities in terms of *n*:*iso* ratios need to be accomplished. Since phosphanes and CO show similar

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binding constants for rhodium and high CO pressures are applied during hydroformylation, an excess of phosphane is required in order to generate a sterically demanding environment around the metal center, a prerequisite for high selectivities. With the development of *N*-heterocyclic carbenes (NHCs) [34–39], chemists now have highly potent substitutes for phosphanes in hand since they usually possess higher binding constants for metals and metal ions than phosphanes. This is evidenced by the fact that phosphane ligands are easily replaced by most NHCs [39]. Numerous transition metal complexes of such *N*-heterocyclic carbenes including those of Rh(I) have already been reported [40]. Recently, Schütz and Herrmann reported on purine-based carbenes [41], however, most of the existing Rh–NHC complexes are based on 1,3-R_2-imidazol-2-ylidenes or dihydroimidazolin-2-ylidenes. Recently, we described the synthesis of novel Rh(I) 1,3-R_2-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R = 2-propyl, mesityl) [42,43]. In this contribution, we wish to present a preliminary set of data on their reactivity in the hydroformylation of 1-octene.

2. Experimental

All experiments involving transition metals were performed under a nitrogen atmosphere in an MBraun glove box or by standard Schlenk techniques. Reagent grade tetrahydrofuran (THF), toluene and pentane were distilled from sodium benzophenone ketyl under argon. Dichloromethane and chloroform were distilled from calcium hydride under argon. The synthesis of the rhodium complexes **1**–**4** is described elsewhere [42,43]. All other compounds and reagents were commercially available and used as received.

2.1. Hydroformylations

All experiments were carried out in a 300-mL Parr high-pressure reactor. The reactor was evacuated, flushed with nitrogen and filled with the corresponding Rh-complex (10^{-5} mol), toluene (100 mL), and 1-octene (5.6 g, 0.05 mol) leading to a substrate to catalyst ratio of 5000:1. Undecane was added as internal standard. The mixture was pressurized twice with a 1:1 mixture of CO and H_2 up to a pressure of 30 bar to clean all supplies before the pressure was adjusted to 50 bar with a back-pressure regulator. Then the autoclave was heated to 100 °C and kept at this temperature. Samples were taken every 15–30 min and the products were quantified by gas chromatography.

3. Results and discussion

The rhodium complexes [RhBr(1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)] (**1**), [RhCl(1,3-di-(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)] (**2**), [RhBr(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)] (**3**) and [RhCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)] (**4**), (COD = η^4-1,5-cyclooctadiene, mesityl = 2,4,6-trimethylphenyl) were prepared by reaction of $[Rh(COD)Cl]_2$ with lithium-*tert*-butoxide followed by addition of 1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidinium bromide, 1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate, 1,3-dimesityl-3,4,5,6-tetrahydropyrimidinium bromide, and 1,3-dimesityl-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate, respectively (Scheme 1) [42,43].

Their structural data and properties are summarized elsewhere [42,43]. Complexes **1**–**4** were used in the hydroformylation of 1-octene. Reactions were carried out at $T = 100$ °C at 50 bar (H_2:CO = 1:1) in toluene. The kinetics of the hydroformylation of 1-octene using catalyst **1** up to a conversion of 30% ($s/s_0 = 70\%$) is shown in Fig. 1.

As can be deduced therefrom, hydroformylation starts after an initiation period of approximately 1 h. This initiation period is attributed to the inhibiting effect of the halide, also a well-known phenomenon for Wilkinson's catalyst [44]. In analogy to this catalyst and to other reports [45] the actual active catalyst is believed to be $[Rh(NHC)(CO)_2H]$, formed via reductive elimination of HX from intermediary $[Rh(NHC)(CO)_2XH_2]$ (X = Cl, Br). Evidence for this assumption was provided by reacting a solution of **1** in toluene at 100 °C with CO and H_2 for 4 h ($p = 50$ bar). ^{13}C NMR analysis of the crude reaction mixture showed signals at $\delta = 204.6$ ppm and $\delta = 192.1$ (NCN, $J = 37.6$ Hz), 186.9 (CO, $J = 53.4$ Hz), 183.0 (CO, $J = 78.63$ Hz) and 57.8 ppm (NCH of 2-Pr). These chemical shifts are similar to those reported for $[Rh(NHC)(CO)_2Cl]$ (192.8 ($J = 38$ Hz), 186.4 ($J = 53$ Hz), 183.5 ppm ($J = 77$ Hz) and 58.2 ppm (NCH of 2-Pr) [42,43], respectively, indicating the formation of a similar species. No signals for 1,3-di(2-propyl)tetrahydropyrimidinium bromide (151.5 ppm) or Rh-complexes containing two NHC-ligands as is the case with certain phosphorus amidites [46] were observed. Such a preferred persistence of Rh-mono-NHC complexes even under hydroformylation conditions has also been reported by Peris and co-workers [47]. The ESI-LOOP-MS spectrum shows a mol peak at $m/z = 705.4$ (21%), corresponding to the bridged, dinuclear species $[Rh(NHC)(CO)(\mu\text{-}CO)(\mu\text{-}Br)Rh(NHC)(CO)]$ (NHC = 1,3-

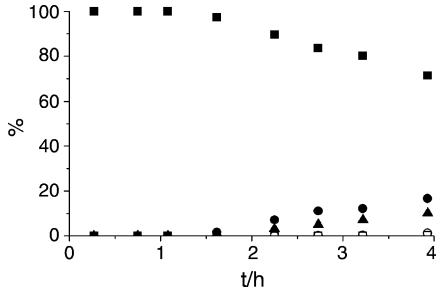
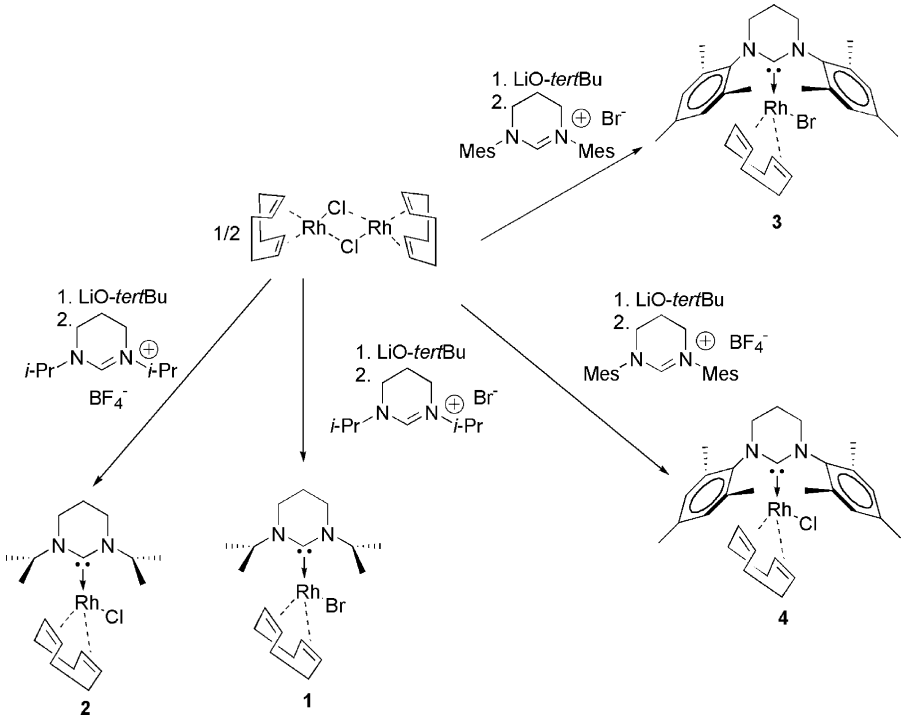


Fig. 1. Conversion of 1-octene and product formation under hydroformylation conditions in the presence of **1**: (■) s/s_0, (●) nonanal, (▲) 2-methyloctanal, (◯) 2-ethylheptanal and (□) 2-propylhexanal.



Scheme 1. Synthesis and structure of catalysts **1**–**4**.

di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene). The IR spectrum shows signals at 2066.6, 1989.0 and 1948.1 cm^{-1}, typical for Rh(NHC)-carbonyl complexes [42]. The initial turn-over frequency TOF_0 (derived from the maximum slope at the onset of hydroformylation) for **1** was 520 h^{-1}, isomerization proceeded in parallel to hydroformylation, nonanal being the major, 2-methyloctanal, 2-ethylheptanal and 2-propylhexanal, the minor products. The *n*:*iso* ratio was reduced from initially 2.1 to 1.4 after 4 h (Fig. 2). Evidently, olefin-isomerization takes place and is fast compared to hydroformylation. Fig. 3 summarizes the fraction (%) of isomeric octenes and aldehydes as a function of time. Changing from the bromo complex **1** to the chloro complex **2** gave similar results (Fig. 4).

The observed TOF_0 (again derived from the maximum slope at the onset of hydroformylation) was 480 h^{-1}, the *n*:*iso* ratio varied from initially 1.6 to 1.4. Fig. 5 summarizes the

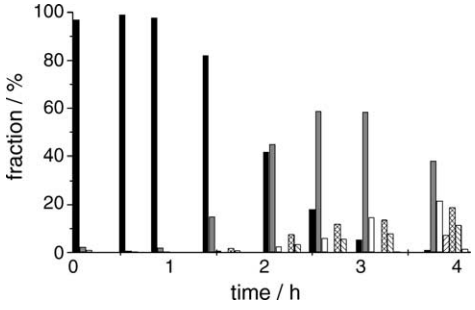


Fig. 3. Product distribution in the hydroformylation of 1-octene as a function of time. Catalyst: **1**, black: 1-octene, grey: 2-octene, white: 3-octene, section-lined up: 4-octene, checkered: nonanal, section-lined down: 2-methyloctanal, section-lined left-to-right: 2-ethylheptanal, section-lined up-to-down: 2-propylhexanal.

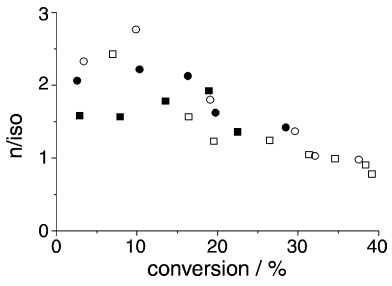


Fig. 2. *n*:*iso* selectivities for catalysts **1**–**4** as a function of conversion. Catalysts **1** (●), **2** (■), **3** (◯), and **4** (□).

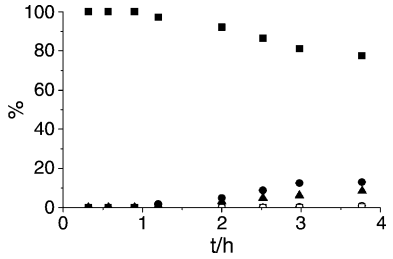


Fig. 4. Conversion of 1-octene and product formation under hydroformylation conditions in the presence of **2**: (■) s/s_0, (●) nonanal, (▲) 2-methyloctanal, (◯) 2-ethylheptanal and (□) 2-propylhexanal.

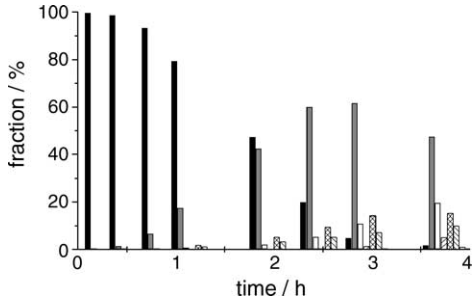


Fig. 5. Product distribution in the hydroformylation of 1-octene as a function of time. Catalyst: **2**, black: 1-octene, grey: 2-octene, white: 3-octene, section-lined up: 4-octene, checkered: nonanal, section-lined down: 2-methyloctanal, section-lined left-to-right: 2-ethylheptanal, section-lined up-to-down: 2-propylhexanal.

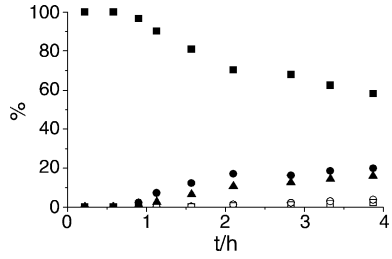


Fig. 6. Conversion of 1-octene and product formation under hydroformylation conditions in the presence of **3**: (■) s/s_0, (●) nonanal, (▲) 2-methyloctanal, (◯) 2-ethylheptanal and (□) 2-propylhexanal.

product distribution as a function of time, which almost identical to the one observed for **1**. This was not surprising at all, since the halogen is replaced by a hydride ligand to form the active catalyst.

However, a significant difference in reactivity was observed when changing from the 1,3-bis(2-propyl) to the 1,3-dimesityl-substituted Rh(I) *N*-heterocyclic carbenes **3** and **4** (Figs. 6 and 7). Thus, the induction period was reduced to approximately 0.5 h. This is a significant improvement compared to Rh (I)-NHC-based systems reported recently [48], showing initiation periods of up to 4 h. Using **3**, the initial TOF_0 increased to 1480 h^{-1}. Not unexpected, isomerization was faster, too, however, the relative ratios of the isomers, i.e. nonanal:2-methyloctanal:2-ethylheptanal:2-propylhexanal, remained virtually unchanged (Fig. 8). The *n*:*iso* ratio dropped from initially 2.3 to 0.90 within 4 h

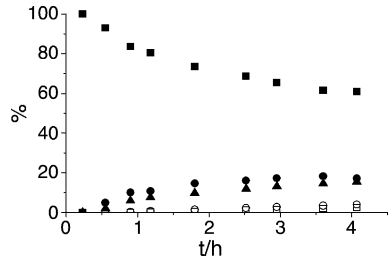


Fig. 7. Conversion of 1-octene and product formation under hydroformylation conditions in the presence of **4**: (■) s/s_0, (●) nonanal, (▲) 2-methyloctanal, (◯) 2-ethylheptanal and (□) 2-propylhexanal.

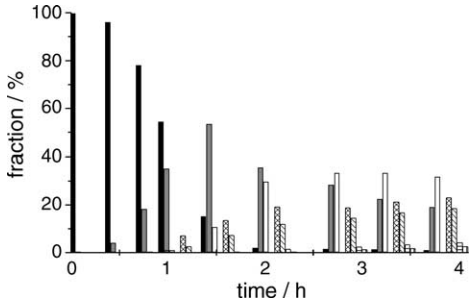


Fig. 8. Product distribution in the hydroformylation of 1-octene as a function of time. Catalyst: **3**, black: 1-octene, grey: 2-octene, white: 3-octene, section-lined up: 4-octene, checkered: nonanal, section-lined down: 2-methyloctanal, section-lined left-to-right: 2-ethylheptanal, section-lined up-to-down: 2-propylhexanal.

(Fig. 2). Again, no change in reactivity or selectivity was observed when replacing the bromine in **3** by chlorine to give **4**. The observed TOF_0 was 1340 h^{-1}, the *n*:*iso* ratio changed from initially 2.4 to 0.8 (Figs. 2 and 9).

In terms of active species, similar results as observed for **1** were obtained. Thus, reacting a solution of **4** in toluene at 100 °C with CO and H_2 for 4 h ($p = 50$ bar) resulted in a compound that showed signals in the ^{13}C NMR at $\delta = 202.6, 185.6$ (NCN, $J = 52.8$ Hz), 181.2 (CO, $J = 72.2$ Hz). These chemical shifts are similar to those reported for [Rh(NHC)$(CO)_2$Cl] (202.3 ($J = 41$ Hz), 185.5 ($J = 52$ Hz) and 183.6 ppm ($J = 76$ Hz), respectively [42,43], again indicating the formation of a Rh(NHC)-carbonyl species. The ESI-LOOP-MS spectrum shows peaks at $m/z = 423.2$ (2%), 451.1 (17%), 479.0 (5%) and 491.9 (56%) corresponding to $[Rh(NHC)]^+$, $[Rh(NHC)(CO)]^+$, $[Rh(NHC)(CO)_2]^+$ and $[Rh(NHC)(CO)(OH)Na]^+$ fragments, respectively (NHC = 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene). The IR spectrum shows signals at 2060.2 and 1987.0 cm^{-1}, typical for Rh(NHC)-carbonyl complex [42,43]. Finally, it is worth mentioning that yields after 19 h were >80% with all four catalysts. No significant catalyst decomposition was observed, allowing in principle their multiple uses.

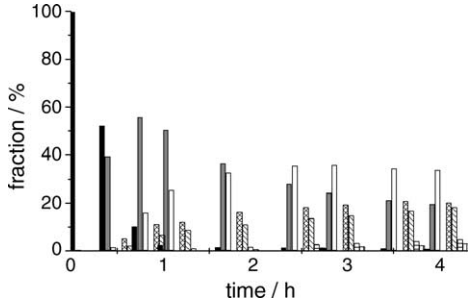


Fig. 9. Product distribution in the hydroformylation of 1-octene as a function of time. Catalyst: **4**, black: 1-octene, grey: 2-octene, white: 3-octene, section-lined up: 4-octene, checkered: nonanal, section-lined down: 2-methyloctanal, section-lined left-to-right: 2-ethylheptanal, section-lined up-to-down: 2-propylhexanal.

4. Conclusion

In summary, we have investigated the hydroformylation activity of four novel Rh(I) complexes based on 1,3-R_2-3,4,5,6-tetrahydropyrimidin-2-ylidenes of the general formula [Rh(X)(NHC)(COD)] (NHC = 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene, 1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene, COD = η^4-1,5-cyclooctadiene, X = Cl, Br) for 1-octene. Not unexpected, the use of different halogens did not reveal any significant changes in reactivity. However, the use of 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene instead of 1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene resulted in a dramatic increase in reactivity, allowing TOFs up to 1500 h^{-1}.

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