Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 690 (2005) 6233–6237
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Rhodium–NHC-complexes as potent catalysts in the hydroformylation of 1-octene

Martin Bortenschlager [a], Jan Schütz [b], Denise von Preysing [b], Oskar Nuyken [a], Wolfgang A. Herrmann [b], Ralf Weberskirch [a,*]

[a] Department Chemie, Lehrstuhl für Makromolekulare Stoffe, TU München, Lichtenbergstrasse 4, D-85747 Garching, Germany
[b] Department Chemie, Lehrstuhl für Anorganische Chemie, TU München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received 25 May 2005; received in revised form 15 September 2005; accepted 15 September 2005
Available online 27 October 2005

Abstract

We present an overview of eight different rhodium-N-heterocyclic carbene (NHC) complexes **1**–**8** and their catalytic activity and selectivity in hydroformylation of 1-octene. It could be shown that activity can be increased by going from electron-rich NHC- to electron-poor NHC-ligands. However, no increase in the selectivity could be achieved by introducing bulky substituents to the NHCs.

Keywords: Hydroformylation; NHC/rhodium catalysts; Steric/electronic effects

1. Introduction

Hydroformylation of olefins is one of the most important homogeneous catalyzed reactions in industry. Formally, it is an addition of CO and H_2 to a C–C-double bond yielding the corresponding *n*- and *iso*-aldehydes [1]. In case of aliphatic olefins of long chain double-bond-isomerization may also occur during the reaction resulting in mostly internal olefins. Due to their superior properties *n*-aldehydes are usually the preferred product for most applications. Therefore, selectivity is very important in hydroformylation and is expressed by the ratio of *n*-aldehyde to *iso*-aldehydes (*n*/*iso*-ratio).

Nowadays most of the hydroformylation catalysts are based on rhodium and phosphines (e.g., Wilkinson-catalyst $Rh(I)Cl(PPh_3)_3$ [2]). The catalytic mechanisms of such systems, depending on the ligands employed, are well understood [3–5]. Therefore, it is possible to optimize both activity and selectivity by adjusting the structure of the phosphine ligands. However, phosphine ligands have some disadvantages in common: in solution they are easily oxidized by molecular oxygen. Furthermore, phosphines and CO show similar binding constants to rhodium. Due to the fact, that CO-pressures applied during hydroformylation are quite high, an excess of phosphine is required to generate a sterically demanding environment around the active rhodium-center, a prerequisite for high *n*/*iso*-ratios.

With the introduction of N-heterocyclic carbenes (NHCs) [6–10] a novel class of ligands have been developed that display similar binding properties than phosphines. They act also as very strong σ-donors and very poor π-acceptors but form at the same time much more stable metal–NHC-bonds in many cases [11]. The resulting complexes are stable towards air and moisture. Recently, it could even be shown that rhodium–NHC-bonds remain stable under hydroformylation conditions (CO/H_2-pressure: up to 50 bar, temperature up to 100 °C) [12,13], meaning that CO is not able to substitute NHC-ligands in rhodium–NHC complexes. Therefore, rhodium–NHC-complexes should be well suitable as catalysts for hydroformylation, even in aqueous systems, as has been repeatedly proven [12–15]. More recently, we demonstrated

* Corresponding author.
E-mail address: Ralf.Weberskirch@ch.tum.de (R. Weberskirch).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.09.038

the first successful aqueous biphasic hydroformylation of 1-octene with a NHC/rhodium catalyst when immobilized to an amphiphilic polymer [16].

In this contribution, we give an overview of different rhodium–NHC-complexes and their catalytic activity and selectivity in hydroformylation of 1-octene. Sterical as well as electronical variations of the NHC-ligand and their influence on the catalytic results are discussed.

2. Experimental part

All experiments were carried out in a 300 mL Parr high pressure reactor. The reactor was evacuated, flushed with nitrogen and filled with Rh-complex (10^{-5} mol), toluene (100 mL), and 1-octene (5.6 g) leading to a substrate:catalyst ratio of 5000. Undecane was added as internal standard. The mixture was pressurized twice to 30 bar synthesis gas ($CO:H_2 = 1:1$) 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 via gas chromatography.

3. Results and discussion

A selection of imidazole- (**5**–**6**), xanthin- (**7**) and tetrazole-based rhodium–NHC-complexes (**8**) (Fig. 1) have been characterized with regard to their catalytic activity and selectivity of the hydroformylation of 1-octene. The results have been compared to that of the recently published tetrahydropyrimidine-based NHC-complexes (**1**–**4**) [13]. The synthesis and structural data of the rhodium–NHC-complexes presented here have already been published elsewhere by Buchmeiser and Herrmann, respectively [17,18].

The catalysts (**1**–**8**) vary in both sterical demand and in electron density around the rhodium-center. Both parameters are determined by the attached NHC-ligand only. The activity and selectivity of catalysts **1**–**4** was recently studied in our group [13]. Catalysts **5**–**8** have been investigated under the same reaction conditions and activities were calculated in all cases from the point of inflection in the slope of aldehyde formation. As has been shown recently neither the cyclooctadiene (COD) nor the halide has any influence on the results of the hydroformylation of 1-octene (Table 1, entries 1–4) [13]. In all cases, the catalytically active species is supposed to be a Rh(NHC)-carbonyl-hydrido-complex which is formed in situ under hydroformylation conditions analogous to the Wilkinson-catalyst [19] (Fig. 2). First the COD-ligand is substituted by CO. Second the rhodium-hydrido-complex, the active species, is formed by an oxidative addition of hydrogen and a consecutive reductive

Table 1
Catalytic hydroformylation activity[a] (TOFs) of complex (**1**–**8**)

Complex	TOF (h^{-1})[c]	Conversion (%)[d]
1[b]	480	8.1
2[b]	520	11.8
3[b]	1340	21.5
4[b]	1480	23.0
5	1785	28.8
6	1150	19.1
7	2410	39.7
8	3540	50.4

[a] Reaction conditions: $T = 100$ °C, $p(H_2/CO) = 50$ bar, $CO:H_2 = 1:1$, substrate:catalyst ratio = 5000, $c(Rh) = 10^{-4}$ mol/L, solvent:toluene.
[b] Published by Buchmeiser et al. [13].
[c] Based on the amount of aldehydes formed, olefin isomerization also occurred.
[d] Determined after 1 h reaction time (induction period is not taken into account).

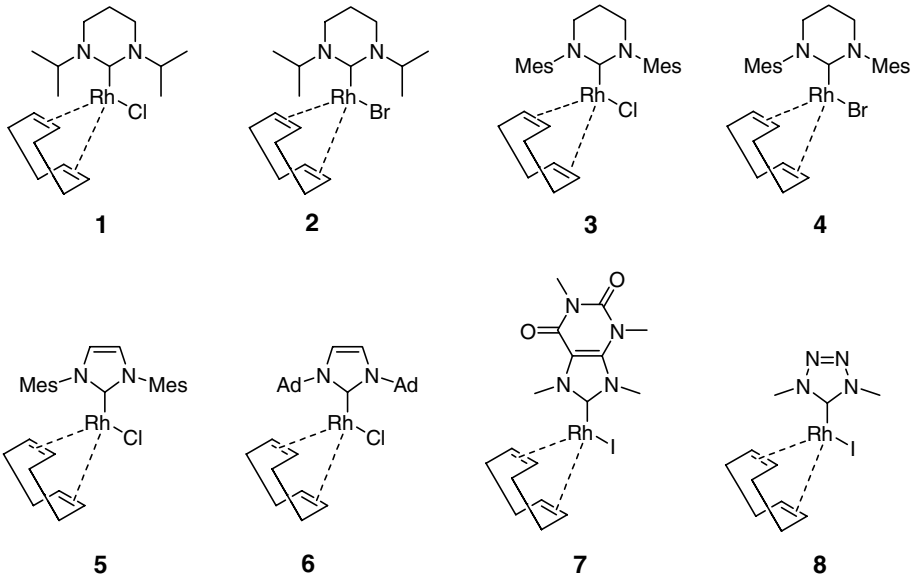

Fig. 1. Rh–NHC-complexes (**1**–**8**) for the hydroformylation of 1-octene.

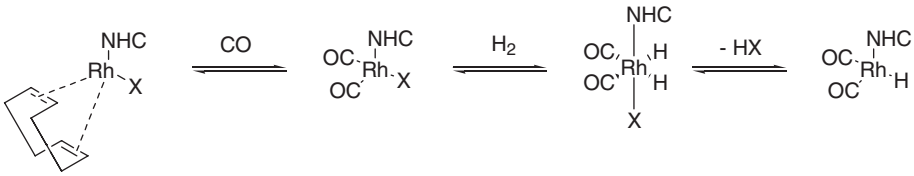

Fig. 2. Proposed mechanism for the formation of the active Rh(NHC)-carbonyl-hydrido-species.

elimination of HX. During the whole process, the rhodium–NHC-bond remains stable as successfully has been shown by several groups [12,13,16]. Complex **7** has been investigated by ^{13}C NMR after 20 h hydroformylation (100 °C, 50 bar CO/H_2). The spectrum shows a signal for the carbon atom of the Rh–NHC complex with a chemical shift of 186.5 ppm and a coupling constant (Rh–C) of $J = 55.2$ Hz. This is in good accordance with the literature values found for compound **7** [18], where a chemical shift of 189.6 ppm and a coupling constant of 52.2 is given considering the fact that compound **7** after 20 h hydroformylation should have lost the iodo as well as the COD ligand (substituted by CO and H) according to the underlying mechanism of hydroformylation.

For catalyst (**5**–**8**) time-conversion-rates were measured and the initial activity (turnover frequency, TOF) was derived from the maximum slope at the onset of hydroformylation (Table 1). This method limits the uncertainties coming from (i) different inductions periods for each catalyst and (ii) the time for heating up the reaction vessel to 100 °C/50 bar pressure.

Selectivity was measured as a ratio between formed *n*-aldehyde to formed *iso*-aldehydes. Due to the fact, that olefin-isomerization occurred with all eight catalysts, the *n*/*iso*-ratio dropped with increasing conversion in all cases. Therefore, the selectivity of all catalysts is compared in a *n*/*iso*-conversion-plot (Fig. 3).

The activities of the different catalysts (Table 1) range from 480 h^{-1} for catalyst **1** up to 3500 h^{-1} for catalyst **8**. An exception is catalyst **6**, which decomposes during hydroformylation and precipitates as a brown solid that cannot be further analyzed. With its extremely bulky adamantyl-substituents the NHC-ligand seems no longer be able to form a stable bond towards the rhodium in this case. We assume that the increase in the catalytic activity can be explained by a decrease of the electron-donating strength of the NHC-ligands going from catalysts **1**–**8** as it is with phosphine ligands [20,21]. While the tetrahydropyrimidine-based NHC-complexes are very strong donor-ligands, indicated by very low wavenumbers $\nu(COI)/\nu(COII) = 2063/1982\ cm^{-1}$ for the CO-complex of **1** and $\nu(COI)/\nu(COII) = 2062/1976\ cm^{-1}$ for the CO-complex of **3** [17], the purine- and tetrazole-based NHCs have poor electron-donating properties for this class of ligand showing high wavenumbers $\nu(COI)/\nu(COII) = 2080/2009\ cm^{-1}$ for the CO-complex of **7** [18] and $\nu(COI)/\nu(COII) = 2086/2015\ cm^{-1}$ for the CO-complex of **8** [22]. The increase in activity with a decrease of the electron-donating properties of the NHC-ligand can be explained by the formation of the intermediate rhodium-π-alkene complex (Fig. 4) which leads to the rhodium-alkyl complex, the first step in the catalytic cycle of hydroformylation. Although the low electron density at the rhodium center make the formation of the π-complex more difficult attack of the hydride to the double bond is facilitated by the electron metal center.

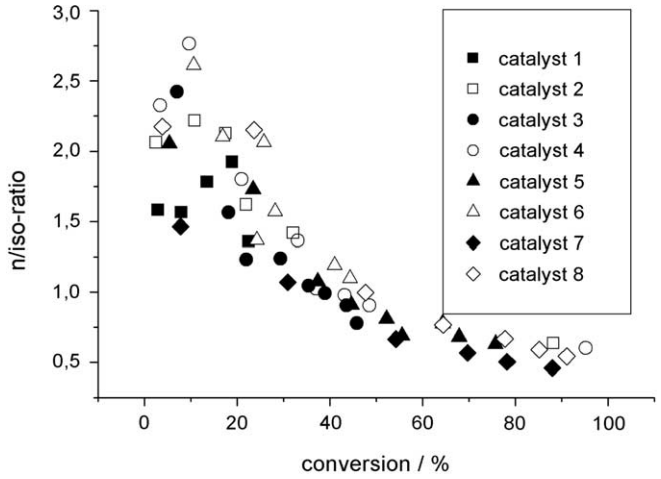

Fig. 3. *n*/*iso*-selectivities for catalysts **1**–**8** as a function of conversion.

Looking at the selectivities (Fig. 3) it becomes clear that all catalysts presented here show similar *n*/*iso*-ratios with increasing conversion. The *n*/*iso*-ratios are quite high at the beginning of the reaction ranging from 1.5 to 2.5 but are rapidly dropping with increasing conversion. In Fig. 5 are the different fractions occurring during hydroformylation depicted showing clearly the strong isomerization behavior of the catalysts **5**–**8** which is the reason for low *n*/*iso* ratio's after complete 1-octene conversion.

Due to olefin-isomerization, which is taking place as a side reaction with all eight catalyst systems, *iso*-aldehydes can be formed from the resulting internal olefins. This leads to a decrease of the *n*/*iso*-ratio down to 0.5 for all catalysts (except for **6**, which decomposes during the reaction). Olefin-isomerization usually can be suppressed by providing a high sterical demand around the rhodium-center of the catalyst. Regarding phosphine-ligands this is achieved by either using an

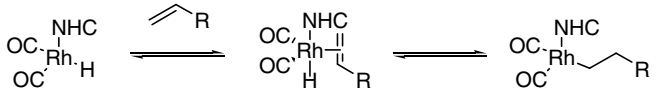

Fig. 4. Formation of the rhodium-alkyl complex via an intermediate π-complex.

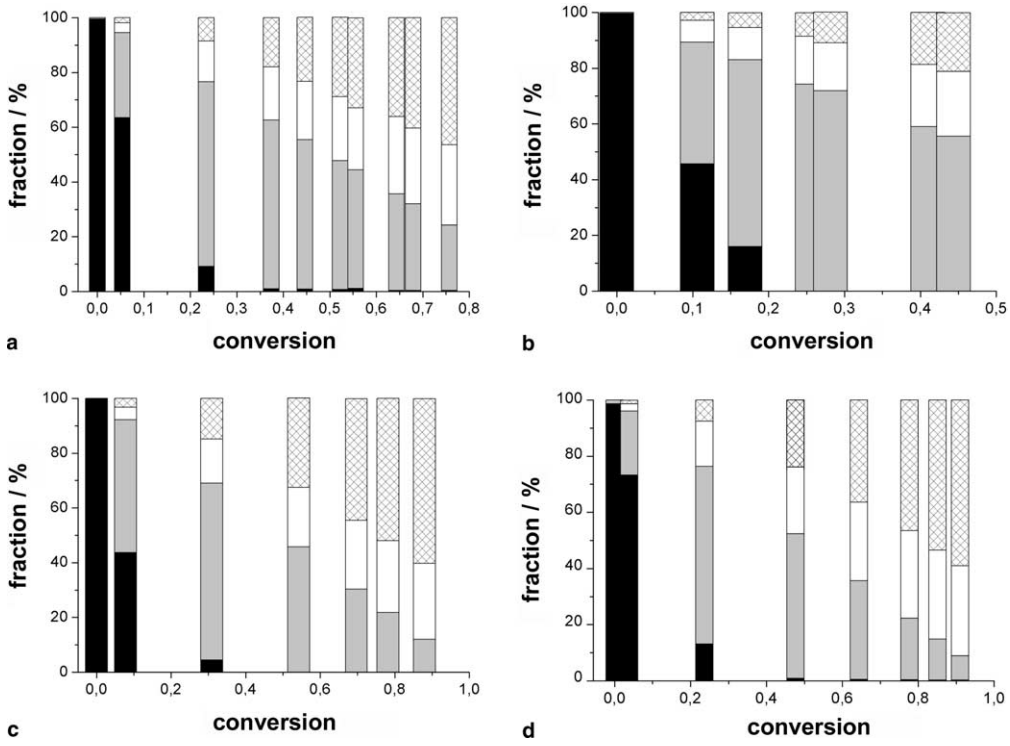

Fig. 5. Fraction of different compounds during the hydroformylation process of 1-octene in the presence of **5** (a), **6** (b), **7** (c) and **8** (d) as a function of conversion (black = 1-octene, gray = internal octenes, white = *n*-aldehyde, crossed = *iso*-aldehydes).

excess of phosphine or by using bidentate phosphines [23–26]. This way it is assured that at least two of the rhodium-coordination centers are occupied by phosphine ligands. In case of rhodium–mono-NHC-complexes the only way for a high sterical demand around the metal center is by using bulky carbene-ligands. The bulky character of carbene ligands is mostly determined by the substituents at the nitrogen atoms of the NHC. Going from methyl- (**7**, **8**) over *iso*-propyl- (**1**, **2**) to mesityl-substituents (**3**, **4**, **5**) obviously has no influence on the *n*/*iso*-ratio. The attempt to further enlarge the substituent by introducing adamantyl-substituents to the NHC-ligand failed due to instability of the resulting complex (**6**) towards hydroformylation conditions. It becomes clear that a suppression of olefin-isomerization and therefore an improvement of the *n*/*iso*-ratio cannot be achieved by a single bulky NHC-ligand.

4. Conclusion

In summary, we have investigated the hydroformylation activity and selectivity of four novel Rh–NHC-complexes and compared the results to those Rh–NHC-complexes recently published [13]. We could show that electron-poor NHC-ligands lead to a higher hydroformylation activity with TOFs up to 3500 h^{-1}. However selectivity is still low with all presented catalysts. Applying bulky substituents to the NHC-ligand has no influence on the selectivity at all. Introducing a second NHC-ligand to the rhodium-complexes could be a promising solution to that. Further investigations on rhodium–bis carbene-complexes and their catalytic activity in hydroformylation have yet to be made.

Acknowledgment

Financial support provided by Freistaat Bayern was gratefully acknowledged.

References

[1] K. Weissermel, H.J. Arpe, Industrial Organic Chemistry, VHC, New York, 1993.
[2] D. Evans, J.A. Osborn, G.J. Wilkinson, J. Chem. Soc. A (1968) 3133.
[3] J.D. Unruh, J.R. Christenson, J. Mol. Cat. 14 (1) (1982) 19.
[4] J.J. Carbo, F. Maseras, C. Bo, P.W.N.M. van Leeuwen, J. Am. Chem. Soc. 123 (31) (2001) 7630.
[5] L.A. van der Veen, P.C.J. Kamer, P.W.N.M. van Leeuwen, CATTECH 6 (3) (2002) 116.
[6] H.-W. Wanzlick, E. Schikora, Chem. Ber. 94 (1961) 2389.
[7] H.J. Schönherr, H.W. Wanzlick, Liebigs Ann. Chem. 731 (1970) 176.
[8] H.W. Wanzlick, H.J. Schönherr, Angew. Chem. 80 (1968) 154.
[9] W.A. Herrmann, C. Köcher, Angew. Chem. 109 (1997) 2256.
[10] W.A. Herrmann, Angew. Chem. 114 (2002) 1342.
[11] (a) For example, see: H. Schumann, J. Gottfriedsen, M. Glanz, S. Dechert, J. Demtschuk, J. Organomet. Chem. 617–618 (2001) 588;
(b) K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, T. Priermeier, P. Kiprof, J. Organomet. Chem. 498 (1995) 1;
(c) M.H. Voges, C. Rommig, M. Tilset, Organometallics 18 (1999) 529;
M.V. Baker, B.W. Skelton, A.H. White, C.C. Williams, J. Chem. Soc., Dalton Trans. (2001) 111;
(d) A.A.D. Tulloch, A.A. Danopoulos, S. Kleinhenz, M.E. Light, M.B. Hursthouse, G. Eastham, Organometallics 20 (2001) 2027;

(e) J. Pytkowicz, S. Roland, P. Mangeney, J. Organomet. Chem. 631 (2001) 157.
[12] M. Poyatos, P. Uriz, J.A. Mata, C. Claver, E. Fernandez, E. Peris, Organometallics 22 (2003) 440.
[13] M. Bortenschlager, M. Mayr, O. Nuyken, M.R. Buchmeiser, J. Mol. Catal. A: Chem. 233 (2005) 67.
[14] W.A. Herrmann, M. Elison, J. Fischer, C. Kocher, U.S. Patent 5,663,451, 1997.
[15] A.C. Chen, L. Ren, A. Decken, C.M. Crudden, Organometallics 19 (2000) 3459.
[16] M.T. Zarka, M. Bortenschlager, K. Wurst, O. Nuyken, R. Weberskirch, Organometallics 23 (2004) 4817.
[17] M. Mayr, K. Wurst, K.-H. Ongania, M.R. Buchmeiser, Chem. Eur. J. 10 (2004) 1256.
[18] J. Schütz, W.A. Herrmann, J. Organomet. Chem. 689 (2004) 2995.
[19] D. Cauzzi, M. Costa, L. Gonsalvi, M.A. Pellinghelli, G. Predieri, A. Tiripicchio, R. Zanoni, J. Organomet. Chem. 541 (1997) 377.
[20] X. Wang, H.Y. Fu, X. Li, H. Chen, Catal. Commun. 5 (2004) 739.
[21] H. Klein, R. Jackstell, K.-D. Wiese, C. Borgmann, M. Beller, Angew. Chem., Int. Ed. 48 (2001) 3408.
[22] J. Schütz, Ph.D. Thesis, Technische Universität München, 2005.
[23] L.A. van der Veen, P.C.J. Kramer, P.W.N.M. van Leeuwen, Angew. Chem. 111 (1999) 349.
[24] M. Matsumoto, M. Tamura, J. Mol. Catal. 16 (1982) 209.
[25] J.D. Unruh, J.R. Christenson, O.R. Richard, D.A. Young, Chem. Ind. (Dekker) (1981) 309.
[26] B. Breit, W. Seiche, J. Am. Chem. Soc. 125 (2003) 6608.