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Ruthenium(II)–salen complexes-catalyzed olefination of aldehydes with ethyl diazoacetate

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Abstract—Several salen–ruthenium(II) complexes, which are derived from commercial ligands or simply ethylenediamine, can be successfully applied as catalysts for the olefination of a broad variety of aldehydes. Depending on the electron richness of the applied aldehydes, good to very good olefin yields and high *E*:*Z* selectivities are reached at 60 or 80 °C reaction temperature with ethyl diazo acetate being the reaction partner. The reaction rate depends on the electron donor capabilities of the aldehydes. Electron poor aldehydes undergo faster reactions than electron rich aldehydes, but both electron rich and bulky aldehydes can be transformed to corresponding olefins in very good yields and high *E*-selectivity.

1. Introduction

The Wittig reaction occupies an important position in the assembly of organic molecules as it generates a double bond with usually high levels of geometrical control,[1,2] however, it still has several drawbacks.[3] To avoid the basic conditions required for the generation of phosphorane precursors, the catalytic alternative to the classic Wittig reaction for stereoselective synthesis of alkenes has proven to be quite promising.[4,5] Up to now, several efficient catalytic aldehyde-olefination reactions have been reported based on Re,[6–12] Ru,[13–17] Rh,[16,18] Fe,[15,19–22] and Co[23] complexes. In some cases they operate under very mild conditions, with short reaction times, and quantitative olefin yields with high *E*-selectivities. Recently, we demonstrated that a ruthenium(II)–salen complex of formula **1**, derived from cyclohexanediamine, is capable of catalyzing the aldehyde olefination reaction with both high yield and selectivity.[24]

Although the catalytic activity of this ruthenium(II) complex is often good, in order to synthesize this complex an expensive *trans*-cyclohexanediamine has to be applied. Thus, we were interested in alternative, more practical catalyst systems. In this present work, we report on several simple Ru(II)–salen complexes **2**–**4**, which are derived from ethylenediamine.

2. Results and discussion

Salen ligands with more flexible structures, which can be easily introduced by substitution, have been attached to a broad variety of transition metals and the resulting compounds have been successfully applied for a plethora of catalytic reactions.[25–36] Ru(II)(salen)$(PPh_3)_2$ complex **2** can be easily synthesized from commercially available salen ligand and Ru(II)$(PPh_3)_3Cl_2$ according to the literature procedures.[37] Complexes **3** and **4** were prepared according to the literature procedures by reacting $Ru(PPh_3)_2Cl_2$ with H_2 salen in ethanol.[25]

As a control experiment, complexes **2**–**4** were applied as catalysts in the olefination reaction of 4-methylbenzaldehyde, utilizing aldehyde (see Table 1), ethyl diazo acetate (EDA), and triphenylphosphine (PPh_3) as substrates in a 1:1.2:1.2 relationship. All reactions were performed in toluene at 60 or 80 °C. 1 mol % of catalyst was applied. The general catalytic reaction is given as Eq. 1. All the catalysts exhibit high catalytic activity, leading to the desired product in excellent yields. The reaction also can be performed at lower temperatures with high excess of *E*-olefin, however, the reactions need more time.

Keywords: Aldehyde olefination; Homogeneous catalysis; Ruthenium; Salen.

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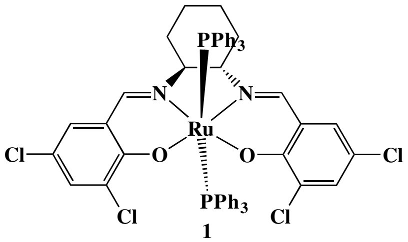
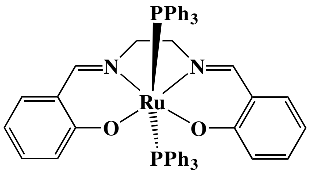


1



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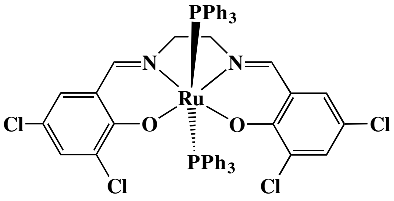

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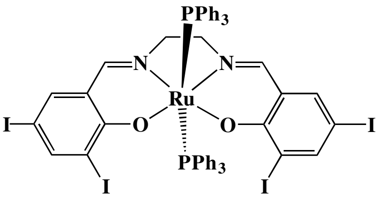

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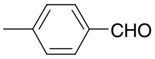
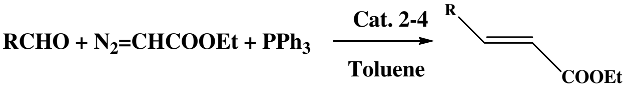
Table 1. Catalytic results obtained with complexes **2**–**4** in toluene as the solvent[a]

Entry	Substrate	Catalyst[a]	Temperature	Time (h)	Yield[b] (%)	*E*/*Z*-Ratio
1	 CHO	**2**	80	1	98	17.6
2		**2**	60	3	96	18.9
3		**3**	80	1	97	11.3
4		**4**	80	1	97	9.45

[a] Reactions were carried out at 60 or 80 °C in 2.5 ml toluene for 1–3 h under N_2 with 0.5 mmol of aldehyde, 0.6 equiv of EDA, 0.6 equiv of Ph_3P, and 1 mol % of salen–Ru(II) catalysts.

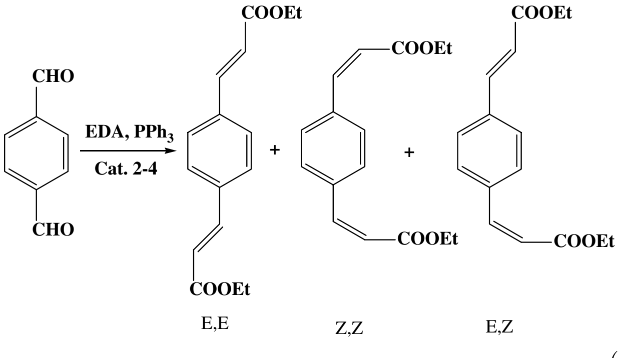
[b] Isolated yield.



(1)

The scope of the olefination reactions by the Ru(II)(salen)$(PPh_3)_2$ complex of formula **2** was further explored for a variety of aldehydes, the results are summarized in Table 2. With all applied aldehydes, regardless whether they are electron neutral (Table 2, entries 1–3) or electron poor (Table 2, entry 7) isolated yields of benzaldehydes >90% (quantitative GC-yields) can be reached at 60 °C within 3 h. Furthermore, also sterically demanding aldehydes lead to quantitative product yields under the same conditions (Table 2, entry 2). The less-reactive electron rich 4-methoxybenzaldehydes can be transformed to the desired olefin in 97% yield and 10.8:1 *E*/*Z*-selectivity with EDA (Table 2, entry 4). The electron rich 4-dimethylaminobenzaldehyde (Table 2, entries 8–9), which can be regarded as an nonactivated aldehyde, was selectively converted to the corresponding olefin in high yield and *E*-selectivity with longer reaction time (24 h) and higher temperature (100 °C). Non-aromatic aldehydes, such as cyclic aldehyde (Table 2, entry 10), were also suitable as substrates for olefination with excellent yields.

In the case of a dialdehyde (Table 2, entries 13–15) both yield and selectivity are comparable to a mono-aldehyde (entry 1), all the catalysts show quantitative yields with high *E*-selectivity within 2 h at 80 °C. The *E*,*E*-product is predominant while the *Z*,*Z*-product is minor (19.9:1). *Z*,*E*-Product is only found in traces (see Eq. 2). The salen–Ru(II) complexes, derived from ethylenediamine, also exhibit much higher *E*-selectivity than complex **1**.[23]

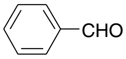
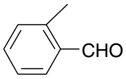
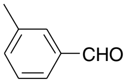
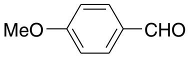
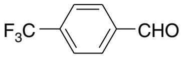
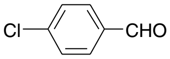
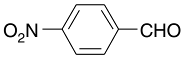
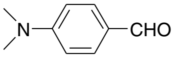
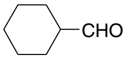
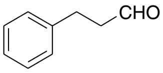
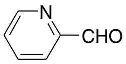
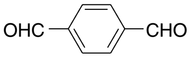


(2)

3. Conclusions

Several ruthenium–salen complexes derived from simple ethylenediamine can be successfully applied as catalysts with low catalyst loadings for the olefination of a broad variety of aldehydes, reaching good *E*/*Z* selectivities and quantitative isolated olefin yields. Even sterically demanding and electron rich olefins, presenting difficulties for several other catalysts can be quantitatively transformed to the desired olefins. Work to further

Table 2. Catalytic results obtained with complexes **2** in toluene as the solvent[a]

Entry	Substrate	Temperature	Time (h)	Yield[b] (%)	*E*/*Z*-Ratio
1		60	3	97	11.4
2		60	3	96	10.1
3		60	3	98	11.1
4		80	2	97	10.8
5		60	3	95	20.2
6		60	3	99	9.2
7		60	3	99	16.2
8		80	30	91	20.0
9		100	24	95	47.7
10		80	2	92	13.9
11		80	2	90	8.7
12		80	2	91	4.3
13		80	2	95	19.9
14		80[c]	1.5	94	19.1
15		80[d]	1.5	94	17.7

[a] Reactions were carried out at 60 or 80 °C in 2.5 ml toluene for 1–3 h under N_2 with 0.5 mmol of aldehyde, 0.6 equiv of EDA, 0.6 equiv of Ph_3P, and 1 mol % of salen–Ru(II) catalyst **2**.

[b] Isolated yield.

[c] 1 mol % complex **3**.

[d] 1 mol % complex **4**.

expand the scope of these metal–salen complexes to apply them to carbonyl substrates and tandem catalytic reactions is currently underway in our laboratory.

4. Experimental

4.1. General remarks

Only freshly distilled, dry, and oxygen-free solvents were used. ^1H and ^{13}C NMR spectra were recorded with a 400 MHz Bruker Avance DPX-400 spectrometer. IR spectra were recorded on a Perkin–Elmer 1650 spectrometer (KBr). Elemental analyses were performed in the Mikroanalytisches Labor of the Technische Universität München (M. Barth). Catalytic runs were monitored by GC–MS on a Hewlett–Packard instrument HP 6890/5973 GC–MS equipped with an Optima-1 column (Column No. 2965/12; SCT-Seitz GmbH). The *E*/*Z*-ratios of products were determined by GC/MS prior to purification of the products. All organic and inorganic starting materials were purchased from Aldrich or Acros and used without further purification. Compounds **2–4** were prepared as described in Refs. 25 and 37.

4.2. General procedure for aldehyde olefination in toluene

In an oven dried Schlenk tube 1 mol % of catalyst, PPh_3 (157.4 mg, 0.6 mmol) and 1 ml of toluene were placed. Aldehyde (0.5 mmol), and EDA (0.6 mmol) dissolved in 1.5 ml of toluene was added and heated to 60 or

80 °C in an oil bath. At that temperature the reaction mixture was kept for the times given in Table 1. The solution was then cooled to room temperature and concentrated. The residue was chromatographed over a silica gel column with *n*-hexane/ethyl acetate (20:1–8:1) affording the olefins.

References and notes

1. Hoffmann, R. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 1411.
2. Lawrence, N. J. In *Preparation of Alkenes: A Practical Approach*; Williams, J. M. J., Ed.; Oxford University Press: Oxford, 1995.
3. Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.
4. Herrmann, W. A. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002; Vol. 3, pp 1078–1086.
5. Kühn, F. E.; Santos, A. M. *Mini-Rev. Org. Chem.* **2004**, *1*, 55.
6. Herrmann, W. A.; Wang, M. *Angew. Chem. Int., Ed. Engl.* **1991**, *30*, 1641.
7. Herrmann, W. A.; Roesky, P. W.; Wang, M.; Scherer, W. *Organometallics* **1994**, *13*, 4531.
8. Ledford, B. E.; Carreira, E. M. *Tetrahedron Lett.* **1997**, *38*, 8125.
9. Santos, A. M.; Romão, C. C.; Kühn, F. E. *J. Am. Chem. Soc.* **2003**, *125*, 2414.
10. Zhang, X.; Chen, P. *Chem. Eur. J.* **2003**, *9*, 1852.
11. Santos, A. M.; Pedro, F. M.; Jogalekar, A. A.; Lucas, I. S.; Romão, C. C.; Kühn, F. E. *Chem. Eur. J.* **2004**, *10*, 6313.
12. Pedro, F. M.; Hirner, S.; Kühn, F. E. *Tetrahedron Lett.* **2005**, *46*, 7777.
13. Fujimura, O.; Honma, T. *Tetrahedron Lett.* **1998**, *39*, 625.
14. Kühn, F. E.; Santos, A. M.; Yogalekar, A. A.; Pedro, F. M.; Rigo, P.; Baratta, W. *J. Catal.* **2004**, *227*, 253.
15. (a) Chen, Y.; Huang, L.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 5925; (b) Chen, Y.; Huang, L.; Ranade, M. A.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 3714.
16. Lebel, H.; Paquet, V.; Proulx, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2887.
17. Lebel, H.; Paquet, V. *Organometallics* **2004**, *23*, 1187.
18. Grasa, G. A.; Moore, Z.; Martin, K. L.; Stevens, E. D.; Nolan, S. P.; Paquet, V.; Lebel, H. *J. Organomet. Chem.* **2002**, *658*, 126.
19. Mirafzal, G. A.; Cheng, G.; Woo, L. K. *J. Am. Chem. Soc.* **2002**, *124*, 176.
20. Cheng, G.; Mirafzal, G. A.; Woo, L. K. *Organometallics* **2003**, *22*, 1468.
21. Chen, Y.; Huang, L.; Zhang, X. P. *Org. Lett.* **2003**, *5*, 2493.
22. Sun, W.; Kühn, F. E. *Tetrahedron Lett.* **2004**, *45*, 7415.
23. Lee, M. Y.; Chen, Y.; Zhang, X. P. *Organometallics* **2003**, *22*, 4905.
24. Sun, W.; Kühn, F. E. *Appl. Catal. A: General* **2005**, *285*, 163.
25. Liang, J. L.; Yu, X. Q.; Che, C. M. *Chem. Commun.* **2002**, 124.
26. Jacobsen, E. N.; Zhang, W.; Güler, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703.
27. Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063.
28. Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326.
29. Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189.
30. Katsuki, T. *J. Mol. Catal. A* **1996**, *113*, 87.
31. Herrmann, W. A.; Rauch, M. U.; Artus, G. R. J. *Inorg. Chem.* **1996**, *35*, 1988.
32. Kohmura, Y.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 3339.
33. Sun, W.; Wang, H. W.; Xia, C. G.; Li, J. W.; Zhao, P. Q. *Angew. Chem., Int. Ed.* **2003**, *42*, 1042.
34. Zhou, X.; Zhao, J.; Santos, A. M.; Kühn, F. E. *Z. Naturforsch.* **2004**, *59b*, 1223.
35. Sun, W.; Herdtweck, E.; Kühn, F. E. *New J. Chem.* **2005**, *29*, 1577.
36. McGarrigle, E. M.; Murphy, D. M.; Gilheany, D. G. *Tetrahedron: Asymmetry* **2004**, *15*, 1343.
37. Murray, K. S.; van den Bergen, A. M.; West, B. O. *Aust. J. Chem.* **1978**, *31*, 203.