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Research Note

Highly selective organometallic ruthenium catalysts for aldehyde olefination

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Abstract

Complexes of general formula $(\eta^5\text{-L})RuCl(PR_3)_2$ are shown to be active and highly selective catalysts for the olefination of aldehydes in the presence of phosphines and diazoacetate at moderate temperatures. With equal catalyst loadings of $Cp^*RuCl(PR_3)_2$ shows comparable activity and higher selectivity with regard to the most active catalysts known to date for this reaction. Spectroscopic investigations demonstrate that the reaction mechanism includes the quantitative formation of the corresponding phosphorus ylide from the preformed phosphazine.

1. Introduction

The classic approach for constructing carbon–carbon double bonds in organic synthesis involves the Wittig reaction and its numerous variants [1]. Despite being broadly applicable methods, they still have some significant drawbacks such as the requirement of stepwise synthesis of ylide precursors under basic conditions [1]. Accordingly, growing research interest arose in the development of new methods that can directly use easily accessible diazo compounds for in situ generation of the ylides under neutral conditions [2]. Several transition-metal complexes, among them Mo, Re, Rh, Fe, Co, and Cu, have been shown to catalyze the olefination of aldehydes with diazo compounds in the presence of tertiary phosphines [3]. The mechanism of these reactions, however, is still under debate and it seems likely that different pathways are involved [3,4]. Usually the catalysts are employed in ratios between 1 and 5, sometimes even 10 mol% (with respect to diazo compound) in order to avoid unwanted side reactions such as the formation of azines. The preferred product of the olefination reaction is the (E) isomer being formed with E/Z ratios between 90:10 and 99:1 [3]. Unfortunately, the most active catalysts do not have the best E selectivities [3].

2. Experimental

All preparations and manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (THF, n-hexane, and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under nitrogen, and used immediately (THF) or kept over 4 Å molecular sieves. Compounds **1** [5a], **2–4** [6b], **5** [5b], and **6** [5c] were synthesized according to literature procedures or adaptations of these procedures.

2.1. *Catalytic aldehyde olefination*

4-Nitrobenzaldehyde, benzaldehyde, or N,N'-dimethylaminobenzaldehyde (3.31 mmol), PPh_3, PPh_2Cy, $PPh_2(o\text{-tolyl})$, or $P(m\text{-tolyl})_3$ (3.6 mmol), fluorene (0.4 g, internal standard), 0.1–2.5 mol% of compounds **1–6**, and EDA (0.5 mL, 4.6 mmol) were dissolved in 20 mL of dry THF and

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allowed to react at 50 °C. For benzaldehyde, 0.6 mol% of compound **5** has been used as catalyst. Samples were taken after the first 5 min of reaction and then every 30 min for at least 2 h. The conversion of aldehyde (4-nitrobenzaldehyde and benzaldehyde and N,N'-dimethylaminobenzaldehyde) and the formation of ethyl-4-nitrocinnamate, ethyl-4-N,N'-dimetylaminocinnamate and ethylcinnamate were monitored by GC and calculated from calibration curves ($r^2 = 0.999$, internal standard fluorene) recorded prior to the reaction course.

2.2. ^{31}P NMR experiments

PPh_3 (100 mg, 0.38 mmol) and ethyldiazoacetate (EDA) (44 µL, 0.38 mmol) were allowed to react at RT in THF; the complete formation of phosphazine was confirmed by ^{31}P NMR spectroscopy. The temperature was then raised to 50 °C and the catalyst was added (0.038 mmol, 1 mol%) of compound **6**, Fe(TPP)Cl or $ReOCl_3(PPh_3)_2$, respectively. ^{31}P NMR spectra were then measured within regular time intervals. The integration was made taking as unity the peak of a 1 M aqueous (D_2O) solution of H_3PO_4 in a sealed inlet tube.

3. Results and discussion

We set out to develop catalysts with both high activities and selectivities and compared them with the best aldehyde olefination catalysts reported so far. For our examinations we selected organometallic ruthenium compounds of the general formula (η^5-L)$RuCl(PR_3)_2$, since they display rather unique possibilities for easy ligand modifications [6]. However, their catalytic potential has not yet been exploited and to the best of our knowledge only one derivative, namely $CpRuCl(PPh_3)_2$, has been mentioned in the context of catalytic aldehyde olefination [3e,4b].

The received olefin yield with $CpRuCl(PPh_3)_2$ (**1**) as catalyst applied for 4-nitrobenzaldehyde (4-NBA) with ethyldiazoacetate and triphenylphosphine (PPh_3) with a catalyst:4-NBA ratio of 1:50 (2 h reaction time) increases with increasing temperature from ca. 30% at 20 °C to 65% at 70 °C. The E/Z ratio, however, remains nearly unchanged at ca. 9:1, which is (within the measurement error range) identical to the product ratio of the noncatalyzed Wittig reaction. The turnover frequency increases at the same temperature interval from ca. 40 to ca. 130 h^{-1}. Replacing the coordinated PPh_3 ligands with bulkier phosphines PPh_2Cy (Cy = cyclohexyl), PPh_2(o-tolyl), and P(m-tolyl)$_3$ leads to compounds **2**–**4** (Chart 1).

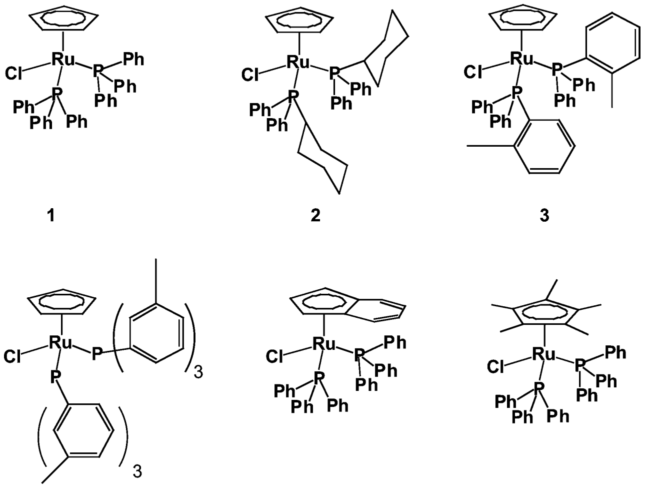


Chart 1. Compounds **1**–**6**.

Table 1
Catalytic results for compounds **1**–**6** in the olefination of 4-NBA

Catalyst	Selectivity (E/Z)	GC yield[a] (%)	Isolated yield[a,b] (%)	TOF[c] (h^{-1})
1	7.3:1	42	38	40
2	15.6:1	46	44	55
3	24:1	92	88	460
4	49:1	63	58	120
5	49:1	100	96	310
6	99:1	100	97	600
6[d]	99:1	100	98	1200
Fe(TPP)Cl[d]	11.5:1	100	97	900
$Cl_3ORe(PPh_3)_2$[d]	49:1	100	95	890
5[e]	24:1	68	65	60
6[e]	24:1	100	96	460
Fe(TPP)Cl[e]	10.1:1	100	96	450
6[f]	19:1	20[g]	16[g]	40

[a] Yield determined after 2 h reaction time at 50 °C, 2 mol% catalyst phosphine ligands and oxygen acceptors are identical.

[b] The spectroscopic data and elemental analysis values are as expected for the received olefins.

[c] TOF determined after 5 min.

[d] Conditions as under footnote a, but 1 mol% catalyst.

[e] Benzaldehyde as substrate, 0.6 mol% catalyst; yield determined after 2 h, after 24 h the yield is quantitative.

[f] 4-Dimethylaminobenzaldehyde as substrate, 1% catalyst.

[g] Yield determined after 24 h.

Compounds **2**–**4** show all higher catalytic activity than complex **1**, particularly when the phosphine applied as oxygen acceptor is identical to the phosphine present in the complex. With complex **3**, bearing the most labile (and bulky, as seen from its Tolman angle) coordinating phosphine among the examined compounds, the yield at 50 °C after 2 h reaction time is 92%, the TOF is 460 h^{-1}, and the E/Z ratio is 24:1 when the same phosphine is used as ligand and as oxygen acceptor (see Table 1).

An even more pronounced increase in the catalytic activity in comparison to **1** is achieved by replacing the Cp ligand by Ind or particularly by Cp*, leading to compounds **5** and **6**. For compound **5** a 100% yield is reached within 1 h with an E/Z ratio of 49:1 and a TOF > 300 h^{-1} (at 50 °C). Compound **6** shows an even higher activity, the reaction being completed (100% yield) after 5 min at 50 °C with an E/Z ratio of 99:1 and a TOF of 600 h^{-1}. A reduction

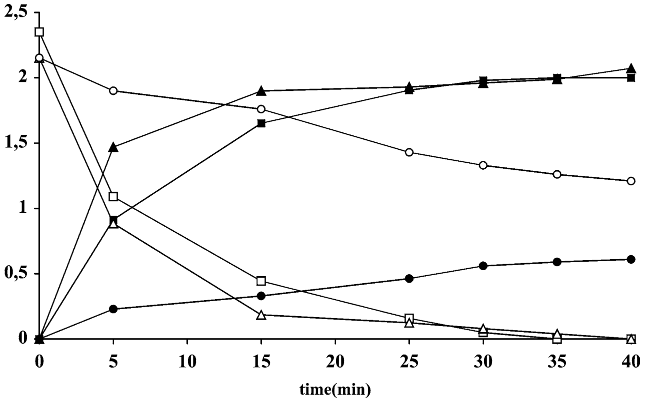
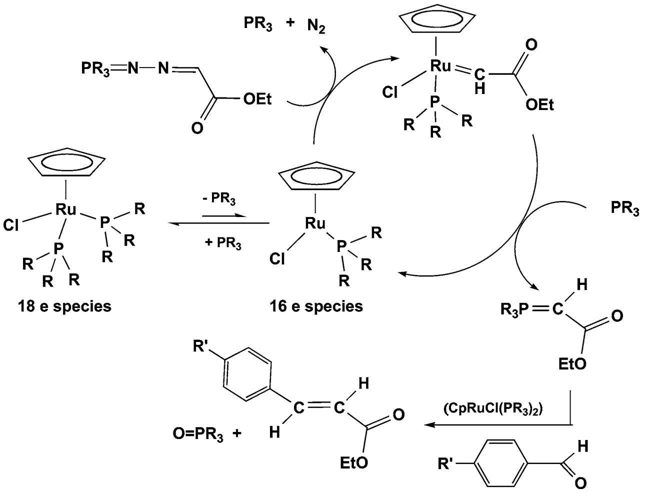


Fig. 1. Areas of phosphazine (open symbols) and phosphorus ylide (closed symbols) from ^{31}P NMR spectra (in relation to a H_3PO_4 standard) of a mixture of $Ph_3P{=}N–N{=}CHCOOCH_2CH_3$ and Fe(TPP)Cl (triangles), $Cl_3ORe(PPh_3)_2$ (circles), and **6** (squares).



Scheme 1.

of the catalyst loading to 1% does not lead to a reduction of the olefin yield or to significant azine formation. While the yield (100%) and the E/Z ratio remain constant, the TOF increases to 1200 h^{-1} for compound **6** at 50 °C. A further reduction of the catalyst amount to 0.5 mol% increases the activity of **6** only slightly to ca. 1300 h^{-1}. The good performance of compound **6** tempted us to compare its activity and selectivity with the best known aldehyde olefination catalysts in the literature, namely $Cl_3(O)Re(PPh_3)_2$ [3c] and Fe(TPP)Cl [3n] (TPP = tetra(p-tolyl)porphyrin) under defined reaction conditions. In the case of the latter catalyst both TOF and TON have previously been determined in a single 30-min experiment with a medium active substrate (benzaldehyde) under quite rigorous conditions (resealable, carefully dried Schlenk tube with a Teflon screw cap) at 80 °C [3n]. In contrast to that, for catalyst $Cl_3(O)Re(PPh_3)_2$ the performance had been reported to be optimized for easy application conditions (i.e., not predried, commercial grade solvents, cheap oxygen acceptor) [7]. At a catalyst:4-NBA ratio of 1:100 (50 °C, 2 h reaction time), all three catalysts quickly reach quantitative olefin yields with E/Z ratios of 11.5:1 (Fe(TPP)Cl), 49:1 ($Cl_3(O)Re(PPh_3)_2$), and 99:1 (**6**), the TOFs (after 5 min) being all in the same order of magnitude, namely 900, 890, and 1200 h^{-1}, respectively. With a cat.:4-NBA ratio of 1:1000 (ca. 0.1 mol%) all three complexes do not reach quantitative yield within 2 h at 50 °C. The E/Z ratios are (approximately) the same as with a 1:100 ratio; the TOFs (after 5 min) are 3680, 1230, and 1600 h^{-1}, respectively. While $Cl_3ORe(PPh_3)_2$ gets inactive first (after little more than 5 min), Fe(TPP)Cl shows a significantly higher initial activity than both other compounds. However, Fe(TPP)Cl gets inactive within ca. 30 min. Compound **6** survives about 90 min under the conditions applied. The reasons for the more pronounced differences in the (initial) activity at low catalyst concentrations lay in the (likely) reaction mechanisms of the three catalysts. All of them form ylide intermediates (shown by ^{31}P NMR experiments performed in the absence of aldehydes, see Fig. 1 and Section 2), and phosphazine formation (from phosphine and EDA) is always observed prior to the reaction with the catalyst. The importance of the phosphazine formation preceding the reaction with the catalyst for catalytic aldehyde olefinations has been discussed elsewhere [3i]. However, while the catalytic activity of **6** (and probably also $Cl_3ORe(PPh_3)_2$ is hampered by the presence of a huge excess of phosphine, due to shifting the initial equilibrium toward the 18-electron species (see Scheme 1), Fe(TPP)Cl does not suffer from that disadvantage, having no phosphine ligands coordinated to the metal.

For complexes **1**–**6** a 16-electron species (η^5-L)RuCl-(PR_3) [6a,6b] is formed from the 18-electron starting materials in an equilibrium reaction. When a large excess of PPh_3 is present, the equilibrium is strongly shifted to the side of the 18-electron species. The comparison of the catalytic activity of complexes **1**–**4** and of PPh_3 with PPh_2(m-tolyl) indicates that bulky substituents R on the phosphine increase the reaction rate by shifting the initial equilibrium toward the 16-electron species. The increase in the activity cannot be ascribed to the formation of more reactive phosphorus ylides. It is known for uncatalyzed Wittig reactions that, e.g., the ylide formed with PPh_2(m-tolyl) leads to lower activities than the one derived from triphenylphosphine, although being associated with higher E/Z selectivities [8]. Cp* being both a considerably better electron donor than Cp and also being more bulky shifts the initial equilibrium quite efficiently on the side of the 16-electron species [9]. Accordingly, compound **6** is the best catalyst among the examined Ru catalysts, but nevertheless sensitive to high phosphine excess. Quite interesting, however, is its high E selectivity in comparison to both Fe(TPP)Cl and $Cl_3ORe(PPh_3)_2$.

It is important to note that all three catalysts (as well as compounds **1**–**5**) do not catalyze the aldehyde olefination when diazomalonate is applied instead of diazoacetate. ^{31}P NMR experiments show that the reaction is forming the respective ylide catalytically, but is unable to proceed further. This observation is due to the fact that $Ph_3P{=}C(C(O)Et)_2$ and the other corresponding ylides (from the phosphines of compounds **2**–**4**) are not reactive toward 4-NBA (and other aldehydes) and proves that all examined complexes catalyze the formation of ylides from diazo compounds. The fact that all examined catalysts lead to different olefin E/Z ratios indicates that there should be a certain influence of the catalyst on the second reaction step, as assumed previously for Fe(TPP)Cl [3h].

4. Conclusion

In summary it has been shown that complexes of the type $(\eta^5\text{-L})\text{RuCl}(\text{PR}_3)_2$ can be turned from moderate [3e] to good catalysts, with proper modifications on their ligands. Under the usually applied concentrations (1:50–1:200 cat.:substrate) and under comparatively mild reaction conditions (50 °C) $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ rivals the most active aldehyde catalysts in activity, displaying a superior selectivity toward E olefins. Furthermore, the organometallic Ru systems allow an easy ligand modification, which may lead to further improvements of their catalytic performance.

Superior selectivity combined with a high activity and easily possible synthetic modifications are the advantages of the ruthenium catalysts described here in comparison to previously described aldehyde olefination catalysts.

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