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Phosphine ligands in the ruthenium-catalyzed reductive amination without an external hydrogen source

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ABSTRACT

A systematic study of the phosphine additives influence on the activity of a ruthenium catalyst in reductive amination without an external hydrogen source was carried out. $[CymeneRuCl_2]_2$ was used as a reference catalyst, and a broad set of phosphines including Alk_3P, Alk_2ArP, Ar_3P and X_3P was screened. Three complexes of general formula $(Cymene)RuCl_2PR_3$ were isolated in a pure form, and their catalytic activity was compared with the *in situ* generated complexes. Nonhindered triarylphosphines with electron acceptor groups were found to be the most perspective activating agents, increasing the activity of the catalyst approx. six times, Alk_2ArP ligands have less noticeable influence, while trialkylphosphines strongly deactivate the ruthenium catalyst.

1. Introduction

Development of new approaches towards rapid and atom-efficient build-up of molecular complexity is a global aim of the synthetic community. [1–9] As catalytic reactions are highly important to solve the titled fundamental task, understanding of the factors, influencing the activity of the particular catalyst is a key to optimize preparation of desirable compounds. Herein we consider the influence of phosphine ligands on the activity of the ruthenium catalysts in the reductive amination without an external hydrogen source. This reaction allows a direct preparation of secondary and tertiary amines from carbonyl compounds utilizing carbon monoxide as a reducing agent. Amines are a crucial class of organic molecules with a great variety of applications in multiple fields. [10–16] However, synthesis of secondary and tertiary amines still remains challenging. [17–18] One of the highly prospective approaches towards amines is reductive amination: during 2019 and 2020 three huge reviews considering this reaction were published [19–21] However, the correct choice of a reducing agent is not so straightforward as it seems to be. Classical reductants such as hydrogen or different types of borohydrides are not enough selective or efficient for the reductive amination of challenging substrates with high sterical hindrance or reducible functional groups. [22] In this context, development of alternative reducing systems without such disadvantages is highly desirable.

Carbon monoxide was demonstrated to be a very powerful reducing agent in organic transformations. Despite the fact that CO is a toxic gas and one should take necessary safety precautions working with this reagent (first of all, good ventilation is required), it is a highly desirable reagent in organic chemistry. It is widely used for nitro group reductions [23,15,24] or as an indirect reducing agent working via the water-gas shift reaction (WGSR) [25,26,27,28,29]. Hence, carbon monoxide or its synthetic equivalents could be considered as a good alternative to classical reducing agents. Such reducing systems achieve high selectivity towards reducible functional groups [30,31] and high efficiency in preparation of sterically hindered substrates [32,33]. They also allow to solve some special problems like amine methylation [34] or Vasicinone-like alkaloids preparation [35].

One of the most popular ligands, used in catalysis, are phosphines. [36,37] To the best of our knowledge there was no systematic study on the influence of phosphine ligands on the outcome of reductive amination without an external hydrogen source. Only single experiments with phosphines were reported. For example, Kolesnikov et al. demonstrated a strong decrease of the reaction yield after addition of triphenylphosphine to ruthenium chloride-catalyzed reductive amination without an external hydrogen source.[38] Later Makarova et al. demonstrated an increase of the reaction rate with SPhos if $[CymeneRuCl_2]_2$ was used as a pre-catalyst. [39]

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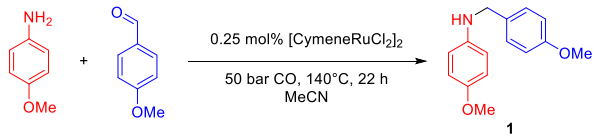
Table 1
Phosphine ligands comparison under the standard conditions.



Phosphine	Yield of 1[a]
No ligand	50%
Alk_3P	
PCy_3 **2a**	40%
$PnBu_3$ **2b**	19%
Alk_2PAr	
RuPhos **3a**	25%
XPhos **3b**	33%
BrettPhos **3c**	42%
DavePhos **3d**	43%
tBuXPhos **3e**	51%
SPhos **3f**	64%
CyJohnPhos **3g**	83%
Ar_3P	
$P(2\text{-}MeOC_6H_4)_3$ **4a**	32%
$P(2,6\text{-}(MeO)_2C_6H_3)_3$ **4b**	43%
$P(oTol)_3$ **4c**	46%
$P(4\text{-}MeOC_6H_4)_3$ **4d**	48%
$PMes_3$ **4e**	66%
JackiePhos **4f**	72%
PPh_3 **4g**	96%
$P(pTol)_3$ **4h**	91%
$P(3\text{-}MeOC_6H_4)_3$ **4i**	96%
$P(4\text{-}FC_6H_4)_3$ **4j**	96%
$P(4\text{-}ClC_6H_4)_3$ **4k**	96%
Bidentate	
XantPhos **5a**	56%
BINAP **5b**	47%
Bis(dicyclohexylphosphinophenyl) ether **5c**	52%
Other ligands	
PCl_3 **5d**	49%
PBr_3 **5e**	71%
$P(OEt)_3$ **5f**	50%

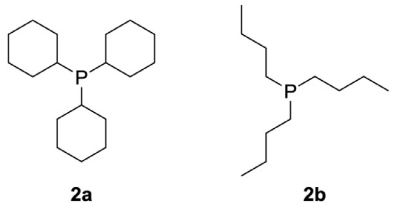
[a] Reaction conditions: 0.33 mmol scale, 2 equiv. *p*-anisidine, 1 equiv. *p*-anisaldehyde, 0.25 mol% $[CymeneRuCl_2]_2$ (0.5 mol% Ru), 0.5 mol% ligand, 300 μL MeCN, 140°C, 50 bar CO, 22 h. Yields were determined by GC using an external calibration. At least two replicate runs for each ligand were carried out.

2. Results and discussion

Herein we report a study of the ligand influence on the ruthenium-catalyzed reductive amination, as this metal is comparably cheap and known to form stable phosphine complexes.[40] $[CymeneRuCl_2]_2$ was used as a ruthenium precatalyst. This is a stable well-defined ruthenium source, often used in organometallic chemistry. Ruthenium chloride, known to catalyze the titled reaction [38], is much cheaper, however it does not have any well-defined structure, and an amount of crystalline water might impact the formation of the organometallic complexes. [41]. The goal of this study is identification of ligand parameters influencing the catalytic activity, therefore all other factors interfering the reproducibility and performance of the reaction should be avoided. Hence $[CymeneRuCl_2]_2$ was chosen as the preferable ruthenium source.

The ligand impact was compared using the model reaction of *p*-anisidine and *p*-anisaldehyde (Table 1). Catalyst loading and other reaction conditions (temperature, CO pressure, solvent, reaction time, reagents ratio) were chosen to provide 50% yield of **1** without any phosphine additives. Such yield allows catching both activation and deactivation of the catalytic system.

All available phosphine ligands were divided into few classes according to their structure: trialkylphosphines Alk_3P **2** (nBu_3P, Cy_3P), Dialkylarylphosphines Alk_2PAr **3** (BrettPhos, RuPhos, SPhos, DavePhos, XPhos, tBuXPhos, CyJohnPhos), triarylphosphines Ar_3P **4**, bidentate ligands (XantPhos, BINAP, Bis(dicyclohexylphosphinophenyl) ether), and three additional phosphine and phosphite ligands $P(OEt)_3$, PCl_3, and PBr_3 to achieve a comprehensive study of the sterical and electronical parameters influencing the reaction outcome. Structures of these ligands are provided below (Figs. 1, 2, 3, 4). Initially all ligands were compared under the standard conditions (Table 1).



2a **2b**

Fig. 1. Trialkylphosphines tested.

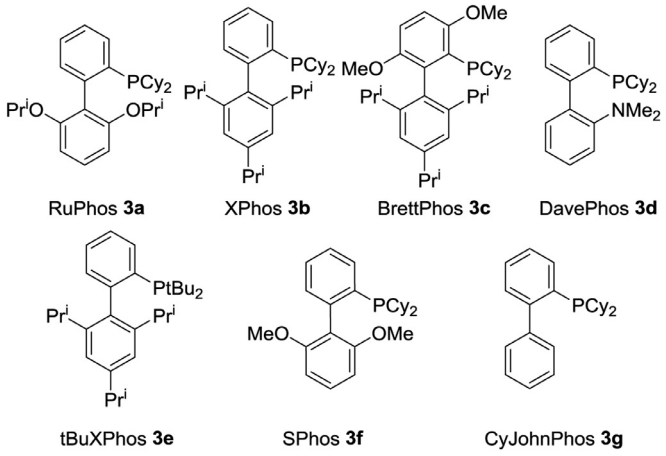


Fig. 2. Dialkylarylphosphines tested.

Here are two factors with a crucial impact on the reaction performance: electronic and sterical properties of the ligand. Electron-rich ligands with low sterical hindrance form very stable complexes that do not catalyze the reaction. Ligands with high sterical hindrance either do not form complexes (in this case, yield of the reaction is the same as without ligand) or form stable complexes and block the coordination with substrates (this is the case of sterically hindered electron-rich ligands). In the intermediate cases, these two factors can compensate each other. These considerations are illustrated below.

Trialkylphosphines (Fig. 1) are very strong ligands, inhibiting the activity of the ruthenium catalyst. However, tricyclohexylphosphine **2a** decreases the reaction yield only by 1.25 times (40% vs 50%), while tributylphosphine **2b** has a stronger influence reducing the reaction rate by 2.5 times (19% vs 50%). Cy_3P is characterized with a bigger Tolman cone angle then nBu_3P (170 vs 132)[42]. As electronic properties of these ligands are almost the same, nBu_3P forms a much more stable ruthenium complex which catalyzes the reaction poorly. Electronic deactivation in the case of Cy_3P is compensated by increased sterical hindrance, so the resulting complex works better than the one with nBu_3P.

Alk_2PAr are generally less nucleophilic than Alk_3P. It is the reason why in this case (Fig. 2) a balance between electronic and sterical properties should be found. For example, RuPhos **3a** led to a two-fold decrease of the reaction yield while SPhos **3f** increased it 1.3 times. While electronic properties are almost the same, RuPhos has a higher sterical hindrance, which in this case decreases the reaction yield. This trend is opposite to the one detected for tri-

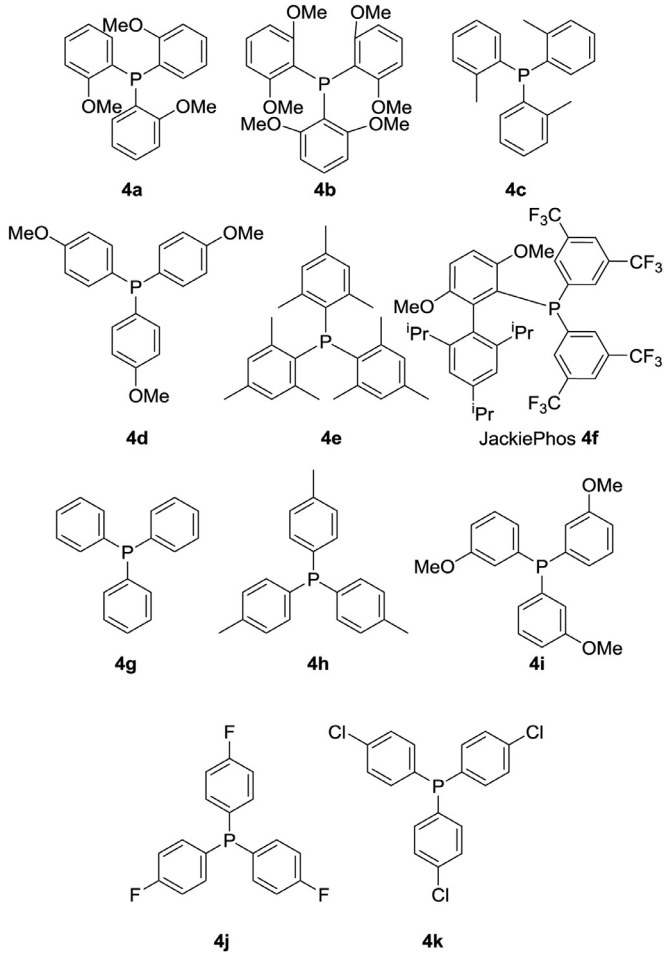


Fig. 3. Triarylphosphines tested.

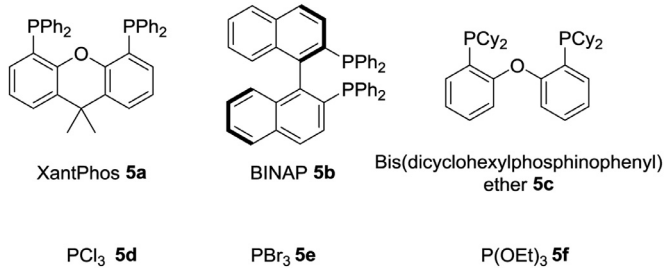


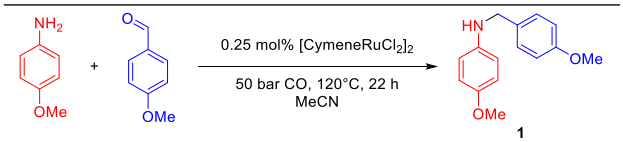
Fig. 4. Bidentate ligands and other ligands.

alkylphosphines. In the case of Alk_3P the coordination was too strong. Sterical factors used to decrease deactivation of the catalyst. For Alk_2PAr coordination is not so strong, and the sterical hindrance interferes the target reaction. tBuXPhos **3e** seems to have very high sterical hindrance so we suppose that it does not form a ruthenium complex and does not influence the catalytic activity. To confirm this an NMR experiment was carried out. tBuXPhos was added to a solution of $[CymeneRuCl_2]_2$ in $CDCl_3$ in NMR tube followed by registration of ^1H, ^{13}C, and ^{31}P NMR spectra after two hours. No phosphine complex formation was noted (Scheme 1).

The most active catalytic system was achieved using CyJohnPhos **3g**. It has low sterical hindrance with moderate donating properties which indicates that the decrease of the sterical factor has a crucial influence on the catalyst activity.

Ortho-substituted triarylphosphines with methoxy groups (**4a, 4b**) (Fig. 3) have very high sterical hindrance in combination with strong donating properties. Strong donation leads to formation of strong coordinating bonds while sterical hindrance blocks the coordination of substrates and inhibits the reaction. Both these ligands more or less deactivate the catalyst. $P(oTol)_3$ **4c** is less electron-donating ligand with less sterical hindrance, and its impact on the reaction yield is negligible. $P(4\text{-}MeOC_6H_4)_3$ **4d** is a strong donating ligand with low sterical hindrance. It also has no influence on the reaction. The last two cases illustrate the compensation of electronic and sterical factors to zero. Combination of electronic and sterical properties of $P(Mes)_3$ **4e** provides slight activation of the catalyst. JackiePhos **4f** has strong acceptor groups in its structure thus activating the catalyst. The most perspective results were achieved using m- and p- substituted triarylphosphines with electron-neutral or electron-withdrawing groups. PPh_3, $P(pTol)_3$, $P(3\text{-}MeOC_6H_4)_3$, $P(4\text{-}FC_6H_4)_3$, $P(4\text{-}ClC_6H_4)_3$ provided almost quantitative yields. To enable accurate comparison of these ligands we set up the reaction at reduced temperature 120°C (Table 2). PPh_3 **4g**, $P(pTol)_3$ **4h**, and $P(3\text{-}MeOC_6H_4)_3$ **4i** increased the yield of the target molecule two times (with reference to experiment without ligand). Halogen-substituted phosphines increased it approx. six times. $P(4\text{-}FC_6H_4)_3$ **4j** provides slightly lower yield of the product as mesomeric effect of fluorine is much higher than of chlorine. So $P(4\text{-}FC_6H_4)_3$ supposed to be a little bit more electron-rich in comparison with $P(4\text{-}ClC_6H_4)_3$ **4k**.

Table 2
Impact of the most active ligands on the reaction yield at reduced temperature.



Phosphine	Yield[a]
No ligand	10%
PPh_3 **4g**	21%
$P(pTol)_3$ **4h**	24%
$P(3\text{-}MeOC_6H_4)_3$ **4i**	27%
$P(4\text{-}FC_6H_4)_3$ **4j**	56%
$P(4\text{-}ClC_6H_4)_3$ **4k**	63%

[a] Reaction conditions: 0.33 mmol scale, 2 equiv. *p*-anisidine, 1 equiv. *p*-anisaldehyde, 0.25 mol% $[CymeneRuCl_2]_2$ (0.5 mol% Ru), 0.5 mol% ligand, 300 μL MeCN, 120°C, 50 bar CO, 22 h. Yields were determined by GC using an external calibration. At least two replicate runs for each ligand were carried out.

To obtain the whole picture of the phosphine ligands influence, we tested few bidentate ligands (Fig. 4) and other monodentate phosphines PCl_3, PBr_3, and $P(OEt)_3$. The tested bidentate phosphines showed almost no influence on the reaction outcome. This might indicate a balance of opposite sterical and electronic effects in these cases, however to detect any trends more data is required. PCl_3, PBr_3 and $P(OEt)_3$ demonstrate more countable effects. As sterical hindrance for these phosphines is very low, all effects could be assigned to the electronic effects. PBr_3 has a slight activation mode while PCl_3 and $P(OEt)_3$ do not change the reaction yield. This indicates that too strong electron withdrawing groups also deactivate the catalyst.

In addition, to demonstrate the correctness of the assumption that ruthenium phosphine complexes form *in situ*, three well-defined complexes of general formula $CymeneRuCl_2PR_3$ were synthesized and their catalytic activities were compared with activities of the *in situ* generated complexes. $P(4\text{-}ClC_6H_4)_3$ providing highest activation, the most available PPh_3 providing moderate activation, and inactive $P(OEt)_3$ were applied. The latter did not affect the yield of **1**, so an attempt to obtain a well-defined complex with $P(OEt)_3$ allows to distinguish either no complex formation oc-

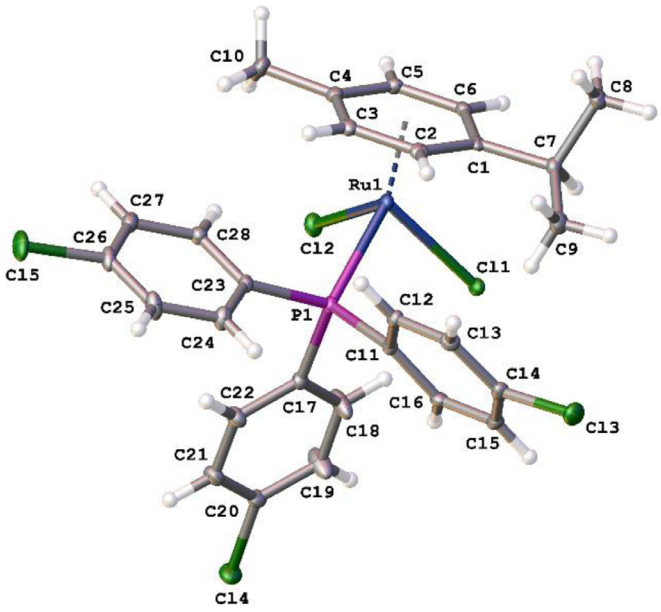
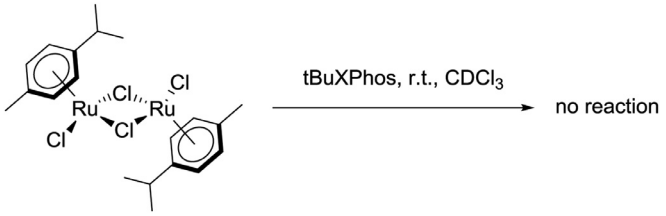
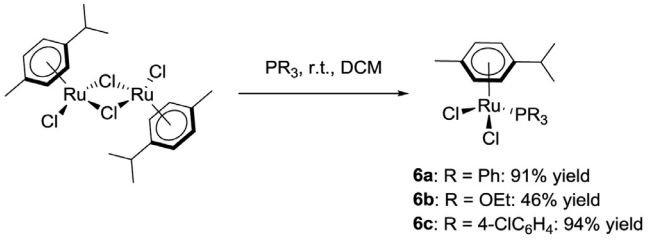


Fig. 5. General view of compound $CymeneRuCl_2P(4\text{-}ClC_6H_4)_3$ (6c) in representation of atoms *via* thermal ellipsoids (p=50%). Selected bond lengths (Å): Ru(1)-Cl(1) 2.4130(8), Ru(1)-Cl(2) 2.4141(8), Ru(1)-P(1) 2.3614(9), Ru(1)-C(1) 2.230(3), Ru(1)-C(2) 2.201(3), Ru(1)-C(3) 2.188(3), Ru(1)-C(4) 2.231(3), Ru(1)-C(5) 2.237(3), Ru(1)-C(6) 2.242(3).



Scheme 1. NMR experiment demonstrating that tBuXPhos does not form any complex with ruthenium.



Scheme 2. Synthesis of $CymeneRuPR_3Cl_2$ complexes. Isolated yields.

curs is this case or the catalytic activity of $CymeneRuCl_2(POEt)_3$ is equivalent to that of $[CymeneRuCl_2]_2$.

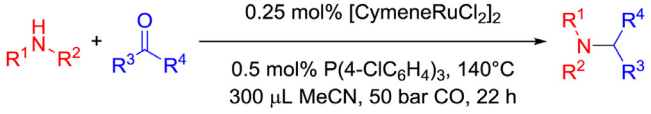
Titled complexes were prepared according to the literature protocols (Scheme 2) [43,44,45]. All the complexes were characterized using NMR, and the structure of $CymeneRuCl_2P(4\text{-}ClC_6H_4)_3$ (**6c**) was confirmed using X-ray analysis for the first time (Fig. 5). The results of the catalytic activity comparison are provided in the Table 3. One can see that in all cases the activity is the same, so the comparison provided above is representative.

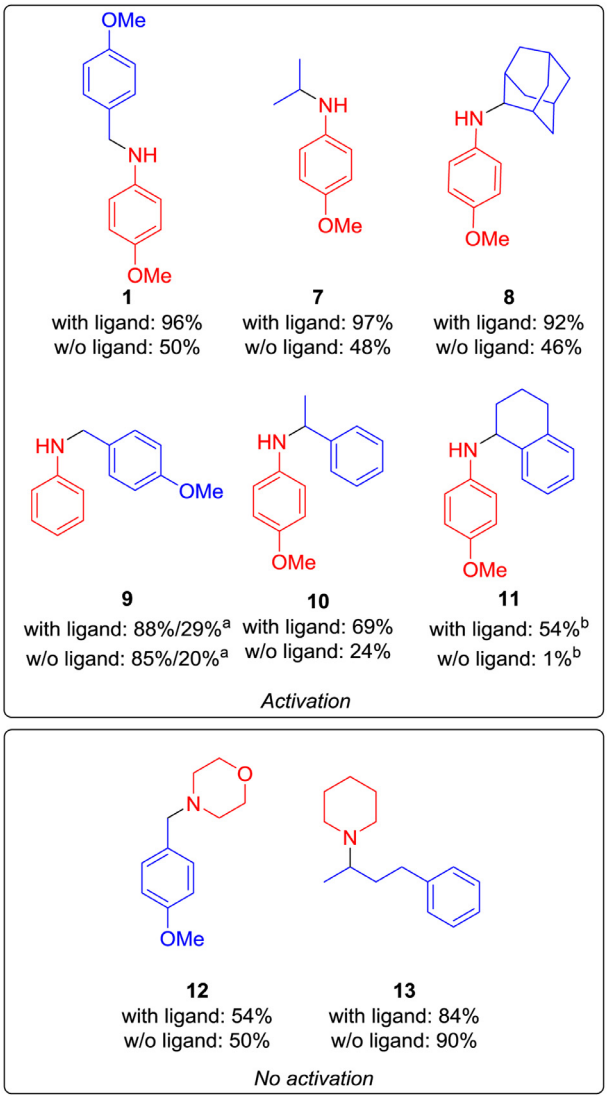
Afterwards, the catalyst activation was checked on substrates of different types (Scheme 3). Aromatic amines demonstrate at least two-fold activation in reactions with an aromatic aldehyde (**1**), aliphatic (**7, 8**) and aromatic ketones (**10, 11**). In case of acetophenone (**10**), activation with phosphine reached 2.9 times, and with tetralone (**11**) only traces of the product were obtained without

Table 3
Comparison of the well-defined complexes vs *in situ* generated.

Catalyst	Yield[a]
PPh_3 + $[CymeneRuCl_2]_2$	96%
$CymeneRuCl_2PPh_3$ **6a**	94%
$P(OEt)_3$ + $[CymeneRuCl_2]_2$	50%
$CymeneRuCl_2P(OEt)_3$ **6b**	49%
$P(4\text{-}ClC_6H_4)_3$+ $[CymeneRuCl_2]_2$	96%
$CymeneRuCl_2P(4\text{-}ClC_6H_4)_3$ **6c**	96%

[a] Reaction conditions: 0.33 mmol scale, 2 equiv. *p*-anisidine, 1 equiv. *p*-anisaldehyde, 0.25 mol% $[CymeneRuCl_2]_2$ or 0.5 mol% ruthenium complex, 0.5 mol% ligand (if required), 300 μL MeCN, 140°C, 50 bar CO, 22 h. Yields were determined by GC using an external calibration. At least two replicate runs for each ligand were carried out.





Scheme 3. Substrate scope for the reductive amination. NMR yields with DMF as an internal standard. [a] Second yield value corresponds to the reaction at 120°C [b]160°C.

phosphine. Reaction of aniline with *p*-methoxybenzaldehyde (**9**) led to the good yields both with and without phosphine at 140°C, however decreasing the temperature to 120°C allowed to catch the activation effect. In the case of reaction between piperidine and benzylacetone (**13**) the yield was almost the same. Even slight decrease of the yield was noted (84% vs 90%). Similarly no activation was detected in the case of morpholine (**12**). This trend could be explained by the fact that aliphatic amines are much more nucleophilic then aromatic ones. So, piperidine and morpholine could dramatically change the catalyst structure decreasing the activation extent.

3. Conclusions

Finally, the first systematic study of the phosphine additives influence on the catalytic activity of cymene ruthenium chloride in the reductive amination without an external hydrogen source was provided. Different phosphines including Alk_3P, Alk_2PAr, and Ar_3P were compared. Generally the most prominent activation is provided by triarylphoshines with low sterical hindrance and electron-withdrawing groups in aromatic rings structure. This activation was studied on different amines. In the case of aromatic amines yield increased at least twice, while in the case of aliphatic amines the activation was not so powerful. This might be related to the high nucleophilicity of aliphatic amines.

4. Experimental section

4.1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. CH_2Cl_2 and CH_3CN were distilled over calcium hydride.

^1H, ^{13}C and ^{31}P spectra were recorded in $CDCl_3$ on Bruker Avance 300, Bruker Avance 400 and Varian Inova-400 spectrometers. Chemical shifts are reported in parts per million relative to $CHCl_3$ (7.26 and 77.16 ppm for ^1H and ^{13}C respectively). Chemical shifts δ are reported in ppm relative to the solvents resonance signal as an internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, dq = doublet of quartets, m = multiplet, br s= broad singlet; coupling constants are given in Hertz (Hz).

Analytical gas chromatography (GC) was performed using a Chromatec Crystal 5000.2 Gas Chromatograph fitted with a flame ionization detector. GC yields were calculated using external calibration, NMR yields were calculated using DMF as an internal standard. More details are provided in SI.

4.2. Synthesis of ruthenium complexes

4.2.1. [(p-cymene)$RuCl_2$]$_2$

To a solution of $RuCl_3 \bullet 4H_2O$ (1.65 g, 100 mol%, 5.9 mmol) in EtOH (50 mL) in a 250 mL round-bottom Schlenk flask, α-phellandrene (5.67 mL, 600 mol%, 35.2 mmol) was added. The reaction mixture was refluxed for 24 h and then cooled to 0°C. The resulting red precipitate was filtered, washed with Et_2O and dried in vacuo to yield a red solid (1.12 g, 62% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 5.45 (d, J = 5.7 Hz, 2H), 5.31 (d, J = 5.7 Hz, 2H), 2.88 (sept, J = 6.9 Hz, 1H), 2.13 (s, 3H), 1.25 (d, J = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 101.2, 96.7, 81.3, 80.5, 30.6, 22.2, 19.0.

NMR spectra are in agreement with the literature data.[46]

4.2.2. [(p-cymene)Ru(PPh_3)Cl_2] (6a)

A solution of [(p-cymene)$RuCl_2$]$_2$ (100 mg, 100 mol%, 0.16 mmol) and PPh_3 (90 mg, 210 mol%, 0.34 mmol) in CH_2Cl_2 (6 ml) was stirred at room temperature in Schlenk tube under argon atmosphere for 17 h. After this time the solution was reduced in vacuum to ~1,5 ml. Hexanes (~8 ml) were added to yield an orange precipitate. Then it was filtered through a funnel with fritted disc. The solid was washed with hexanes (3 ml 3 times) and dried in vacuum to yield a red-brown solid (169.6 mg, 91.3% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.73 (m, 6H), 7.42 – 7.28 (m, 9H), 5.18 (d, J = 5.9 Hz, 2H), 4.98 (d, J = 5.9 Hz, 2H), 2.84 (sept, J = 6.9 Hz, 1H), 1.85 (s, 3H), 1.08 (d, J = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4 (d, J = 9.3 Hz), 133.9 (d, J = 45.6 Hz), 130.3 (d, J = 2.4 Hz), 128.0 (d, J = 10.0 Hz), 111.2, 96.0, 89.1 (d, J = 3.2 Hz), 87.2 (d, J = 5.5 Hz), 30.3, 21.9, 17.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 24.2.

NMR spectra are in agreement with the literature data.[47,48]

4.2.3. [(p-cymene)Ru($P(OEt)_3$)Cl_2] (6b)

A solution of [(p-cymene)$RuCl_2$]$_2$ (50 mg, 100 mol%, 0.08 mmol) and $POEt_3$ (70 µL, 500 mol%, 0.41 mmol) in CH_2Cl_2 (5.5 mL) was stirred at room temperature in a Schlenk tube under argon atmosphere overnight. Then the solvent was evaporated in vacuum to yield an oil. Hexanes (~10 ml) were added and the mixture was triturated to yield a red precipitate. Then it was filtered through a funnel with fritted disc. The precipitate was washed with hexanes (10 ml 3 times) and dried in vacuum to yield an orange-brown solid (35 mg, 45.5% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 5.49 (d, J = 6.0 Hz, 2H), 5.35 (d, J = 6.0 Hz, 2H), 4.13 (dq (appears as a quint), J = 6.8 Hz, 6H), 2.89 (sept, J = 6.9 Hz, 1H), 2.13 (s, 3H), 1.25 (t, J = 6.8 Hz, 9H), 1.21 (d, J = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 109.0, 100.6, 89.3 (d, J = 6.1 Hz), 88.8 (d, J = 6.1 Hz), 63.1 (d, J = 6.4 Hz), 30.4, 22.1, 18.4, 16.3 (d, J = 6.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 112.3.

NMR spectra are in agreement with the literature data.[44]

4.2.4. [(p-cymene)Ru($P(p\text{-}ClPh)_3$)Cl_2] (6c)

A solution of [(p-cymene)$RuCl_2$]$_2$ (33 mg, 100 mol%, 0.053 mmol) and P(p-ClPh)$_3$ (50 mg, 256 mol%, 0.137 mmol) in CH_2Cl_2 (8 ml) was stirred at room temperature in Schlenk tube under argon atmosphere for 14 h. Then the solvent was evaporated in vacuum to yield an oil. Hexanes (~5 ml) were added and the mixture was triturated to yield a white-red precipitate. The precipitate was filtered through a funnel with fritted disc. The solid was washed with hexanes (10 mL 3 times) and dried in vacuum to yield a dark-orange solid (68 mg, 94% yield). Crystals were prepared by diffusion crystallization in $CHCl_3$ – hexane system.

^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, J = 9.1 Hz, 6H), 7.35 (d, J = 8.1 Hz, 6H), 5.24 (d, J = 6.0 Hz, 2H), 4.97 (d, J = 6.0 Hz, 2H), 2.88 (sept, J = 7.0 Hz, 1H), 1.86 (s, 3H), 1.14 (d, J = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4 (d, J = 3.2 Hz), 135.6 (d, J = 10.3 Hz), 131.7 (d, J = 46.3 Hz), 128.7 (d, J = 10.4 Hz), 112.2 (d, J = 3.6 Hz), 96.5, 88.9 (d, J = 3.0 Hz), 87.7 (d, J = 5.7 Hz), 30.5, 22.0, 18.1.

^{31}P NMR (121 MHz, $CDCl_3$) δ 23.82.

NMR spectra are in agreement with the literature data.[45]

4.3. General procedure for reductive amination

Caution: carbon monoxide used as a reagent in this protocol is a toxic gas. Corresponding safety precautions should be taken.

A glass vial in a 10 mL stainless steel autoclave was charged with 0.5 mol% [(p-cymene)$RuCl_2$]$_2$, 0.5 mol% of the indicated ligand, and CH_3CN. Then, 2 equivalents of amine and 1 equivalent of

carbonyl compound were added. The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 50 bar of CO. The reactor was placed into a preheated to 140°C oil bath. After 22 h of heating, the reactor was cooled to room temperature and depressurized. Its content was analyzed using NMR or GC, and the product was isolated using chromatography (column chromatography on silica gel or using flash chromatograph InterChim PuriFlash).

4.4. Characterization of the products of the reductive amination

*4-methoxy-N-(4-methoxybenzyl)aniline (**1**)*

Synthesized according to the general procedure. 96% yield by GC. The residue was purified using preparative flash chromatograph InterChim PuriFlash in hexane – ethyl acetate binary system (gradient 3% to 15% ethyl acetate in hexane for 30 min, R_f=0.30 in 10:1 hexane:ethyl acetate) to afford 68 mg (86%) of the product as a white solid. Melting point 89-91°C is in agreement with the literature data[38] (89-90°C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 4.22 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 152.3, 142.6, 131.8, 128.9, 115.0, 114.2, 114.1, 55.9, 55.4, 48.8.

NMR spectra are in agreement with the literature data.[38]

*N-isopropyl-4-methoxyaniline (**7**)*

Synthesized according to the general procedure. 97% yield by NMR with DMF as an internal standard. The residue was purified by column chromatography (eluent: hexane:ethyl acetate 10:1 R_f =0.37) to afford 48 mg (90%) of the product as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 3.55 (sept, J = 6.1 Hz, 1H), 3.16-3.10 (br s, 1H), 1.19 (d, J = 6.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 141.9, 115.0 (2C), 55.9, 45.3, 23.2.

NMR spectra are in agreement with the literature data.[49]

*N-(4-methoxyphenyl)adamantan-2-amine (**8**)*

Synthesized according to the general procedure. 92% yield by NMR with DMF as an internal standard. The residue was purified by column chromatography (eluent: hexane:ethyl acetate 6:1 R_f =0.44) to afford 73 mg (87%) of the product as a grey solid. Melting point 102-103°C is in agreement with the literature data (100-102°C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 3.48 (s, 1H), 2.14 – 1.69 (m, 13H), 1.59 (d, J = 12.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 141.8, 115.1, 114.7, 57.8, 56.0, 37.9, 37.6, 31.8, 31.7, 27.7, 27.5.

NMR spectra are in agreement with the literature data.[38]

*N-(4-methoxybenzyl)aniline (**9**)*

Synthesized according to the general procedure except for addition of phosphine. 85% yield by NMR with DMF as an internal standard. The residue was purified using preparative flash chromatograph InterChim PuriFlash in hexane – ethyl acetate binary system (gradient 5% to 20% ethyl acetate in hexane for 20 min, Rf=0.33 in 10:1 hexane:ethyl acetate) to afford 56 mg (80%) of the product as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 2H), 7.22-7.19 (m, 2H), 6.92-6.90 (m, 2H), 6.76-6.73 (m, 1H), 6.67-6.65 (m, 2H), 4.27 (s, 2H), 3.97 (br s, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 148.3, 131.5, 129.4, 128.9, 117.6, 114.1, 112.9, 55.4, 47.9.

NMR spectra are in agreement with the literature data. [50]

*4-methoxy-N-(1-phenylethyl)aniline (**10**)*

Synthesized according to the general procedure. 69% yield by NMR with DMF as an internal standard. The residue was purified using preparative flash chromatograph InterChim PuriFlash in hexane – ethyl acetate binary system (gradient 5% to 10% ethyl acetate in hexane for 12 min, R_f=0.25 in 10:1 hexane:ethyl acetate) to afford 51 mg (69 %) of the product as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.17 (m, 5H), 6.71 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 8.8 Hz, 2H), 4.43 (q, J = 6.6 Hz, 1H), 3.71 (s, 3H), 1.52 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 145.6, 141.8, 128.7, 126.9, 126.0, 114.9, 114.7, 55.9, 54.4, 25.3.

NMR spectra are in agreement with the literature data.[51]

*N-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-amine (**11**)*

Synthesized according to the general procedure. 56% yield by NMR with DMF as an internal standard. The residue was purified using preparative flash chromatograph InterChim PuriFlash in dichloromethane – hexane – ethyl acetate ternary system (gradient 30% to 100% dichloromethane in hexane for 8 min then to 50% ethylacetate in dichloromethane for 8 min, R_f=0.52 in dichloromethane) to afford 42 mg (51 %) of the product as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 1H), 7.30 – 7.18 (m, 3H), 6.90 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 4.64 (m, 1H), 3.85 (s, 3H), 3.66 (brs, 1H), 3.00 – 2.70 (m, 2H), 2.13 – 1.79 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 141.8, 138.5, 137.6, 129.3, 129.0, 127.1, 126.1, 115.1, 114.3, 55.9, 52.0, 29.4, 28.7, 19.4.

NMR spectra are in agreement with the literature data.[52]

*4-(4-methoxybenzyl)morpholine (**12**)*

Synthesized according to the general procedure except for addition of phosphine. 50% yield by NMR with DMF as an internal standard. The residue was purified by column chromatography (eluent: hexane:ethyl acetate:triethylamine 4:1:0.05 Rf =0.17) to afford 33 mg (48%) of the product as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 3.86 (s, 3H), 3.76 (t, J = 4.6 Hz, 4H), 3.49 (s, 2H), 2.48 (t, J = 4.6 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 130.4, 129.7, 113.6, 67.0, 62.9, 55.3, 53.5.

NMR spectra are in agreement with the literature data. [53]

*1-(4-phenylbutan-2-yl)piperidine (**13**)*

Synthesized according to the general procedure except for addition of phosphine. 90% yield by NMR with DMF as an internal standard. The residue was purified by column chromatography (eluent: hexane:ethyl acetate:triethylamine 15:1:0.1 R_f =0.31) to afford 52 mg (73%) of the product as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 5H), 2.73-2.60 (m, 2H), 2.61 – 2.48 (m, 3H), 2.45 – 2.35 (m, 2H), 1.93-1.84 (m, 1H), 1.67 – 1.53 (m, 5H), 1.50 – 1.38 (m, 2H), 1.01 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 128.6, 128.3, 125.6, 59.0, 49.4, 35.7, 33.4, 26.7, 25.2, 13.9.

NMR spectra are in agreement with the literature data.[22]

Crystallographic data: Crystals of **6c** ($C_{28}H_{26}Cl_5PRu$, M = 671.78) are monoclinic, space group $P2_1/n$, at 120 K: a = 9.7252(6), b = 16.3057(10), c = 17.8645(11) Å, β = 91.7160(10)°, V = 2831.6(3) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.576 gcm^{-3}, μ(MoKα) = 10.99 cm^{-1}, F(000) = 1352. Intensities of 32307 reflections were measured with a Bruker APEX2 DUO CCD diffractometer [λ(MoKα) = 0.71073 Å, ω-scans, 2θ<56°], and 6836 independent reflections [R_{int} = 0.0656] were used in further refinement. Using Olex2 [54], the structure was solved with the ShelXT structure solution program [55] using Intrinsic Phasing and refined with the XL refinement package [56] using Least Squares minimisation. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. The refinement converged to wR2 = 0.0896 and GOF = 1.022 for all the independent reflections (R1 = 0.0364 was calculated against F for 5169 observed reflections with I>2σ(I)).

CCDC 2070318 contains the supplementary crystallographic information for **6c**. mmc1.zip

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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