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Pincer Complexes

Cyclometalated Ruthenium Pincer Complexes as Catalysts for the α-Alkylation of Ketones with Alcohols

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Abstract: Ruthenium PNP pincer complexes bearing supplementary cyclometalated C,N-bound ligands have been prepared and fully characterized for the first time. By replacing CO and H^- as ancillary ligands in such complexes, additional electronic and steric modifications of this topical class of catalysts are possible. The advantages of the new catalysts are demonstrated in the general α-alkylation of ketones with alcohols following a hydrogen autotransfer protocol. Herein, various aliphatic and benzylic alcohols were applied as green alkylating agents for ketones bearing aromatic, heteroaromatic or aliphatic substituents as well as cyclic ones. Mechanistic investigations revealed that during catalysis, Ru carboxylate complexes are predominantly formed whereas neither the PNP nor the CN ligand are released from the catalyst in significant amounts.

Introduction

In the past two decades, metal pincer complexes have proven to be exceptionally powerful catalysts for hydrogenation and dehydrogenation reactions.[1–2] Especially ruthenium complexes such as Ru-MACHO ([RuHCl(CO)(HN($CH_2CH_2PPh_2$)$_2$)], **[Ru]-1** in Scheme 1) were introduced for the catalytic hydrogenation of esters,[3] organic carbonates,[4] nitriles,[5] and others as well as for dehydrogenation reactions of compounds like methanol[6] or ethanol.[7] In addition to that, specifically **[Ru]-1** was applied in hydrogen autotransfer reactions producing γ-butyrolactones[8] and chiral N-alkyl sulfinamides.[9] Furthermore, pyridine-based Ru pincer complexes **[Ru]-2** and **[Ru]-3** were developed by Milstein and co-workers and have been applied as efficient catalysts for numerous (de)hydrogenation reactions.[10] Based on that, manifold variations concerning the nature of the pincer ligand have been performed and the thus obtained complexes have shown to be interesting catalysts as well.[1]

Looking at the popular pincer complexes, it is evident that most of them rely on a similar set of ligands. Typically, in addition to the pincer unit, carbon monoxide and hydride ligands are employed herein. Although this arrangement is generally known to be crucial for reactivity and stability,[2d] it obviously does not allow for any further variations. Hence, we had the idea to introduce alternative ligands mimicking the behavior of CO and H^- ligands. More specifically, cyclometallation of N-heterocycles should provide an active metal center due to the strongly σ-donating C-donor (H^- analogue) and the π-back bonding interaction with the heterocycle (CO analogue).

Although neglected for a long time, in the past years cyclometalated ruthenium complexes became of interest as redox catalysts.[11] For example, Ru half-sandwich complexes bearing bidentate ligands with a C and a P,[12] N,[13] or N-heterocyclic carbene (NHC)[14] donor were used for the transfer hydrogenation of ketones. Additionally, ruthenacycles have been applied in the direct hydrogenation of olefins,[15] the dehydrogenation of alcohols,[16] and the α-alkylation of amides by a hydrogen autotransfer protocol.[17] In addition to that, complexes bearing a carbon donor as part of the pincer ligand were applied as catalysts for transfer hydrogenations,[18] direct hydrogenations,[19] and acceptorless dehydrogenations.[20]

In line with this, Baratta and co-workers established highly efficient Ru CNN pincer complexes for the transfer hydrogenation of ketones[21] or aldehydes,[22] the direct hydrogenation of ketones,[23] and the racemization or deuteration of alcohols.[24]

Results and Discussion

Following our concept above, we attempted the synthesis of **[Ru]-5** through cyclometalation of [Ru(*p*-cym)Cl_2]$_2$ with 2-phe-

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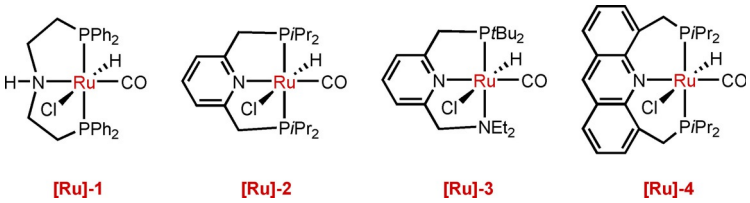


Scheme 1. Frequently used Ru PNP pincer complexes.[1]

nylpyridine.[25] Next, an array of further heterocycles was employed to prepare the corresponding intermediates, which were reacted with aliphatic pincer ligands in 2-butanol. The desired complexes **[Ru]-5**–**[Ru]-12** precipitated during this reaction, giving powdery solids ranging from bright yellow to ruby-red in color (Scheme 2). All complexes were subsequently characterized by NMR, IR, and MS analyses and for representative examples, X-ray structural analyses were performed (see Figure 1 and Supporting Information).

Having these novel complexes in hand, we were interested to apply them in hydrogen autotransfer—also called hydrogen borrowing—reactions.[26] In these cascade reactions, first, hydrogen gets abstracted from an unreactive substrate, mostly an alcohol, generating a more reactive intermediate like an aldehyde. By this activation step, a variety of transformations is now accessible, for instance forming new C–C or C–N double bonds under elimination of water. Finally, the newly formed double bond is hydrogenated using the hydrogen abstracted in the first step. More specifically, the α-alkylation of ketones with alcohols was of interest.[27]

To compare the reactivity of the novel catalysts with the parent Ru-MACHO system, the reaction of acetophenone with 2-methoxyethanol was investigated in *tert*-amyl alcohol at 130 °C in the presence of catalytic amounts of cesium carbonate as base. Under these conditions, **[Ru]-1** only yielded in 16% of the desired product (see Table 1, entry 1). In contrast, when the newly synthesized catalysts are applied under identical conditions higher yields up to 48% were obtained (Table 1, entries 2–8). Thus, having confirmed that the introduced phenyl heterocycle ligands can be beneficial for catalysis, we started optimizing the reaction conditions using **[Ru]-7**, which bears benzo[h]quinoline as additional ligand. Proceeding with this catalyst, an optimal yield of 68% was obtained (Table 1, entry 19). Notably, performing the reaction without any catalyst or without base yielded in no product formation at all. Interestingly, the application of **[Ru]-12**, in which the NH is replaced by a N-methyl group gave 46% of the desired product. This comparably high yield suggests that the NH proton, while being beneficial to the catalyst performance, is not essential. For the **[Ru]-12**, for which an outer-sphere mechanism cannot be put forward, it can be proposed that the strong *trans* influence of the C–Ru bond very

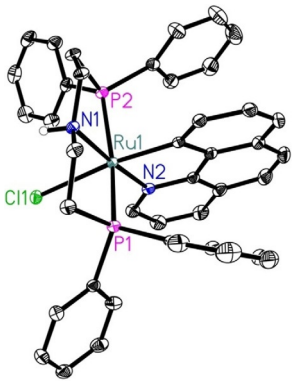
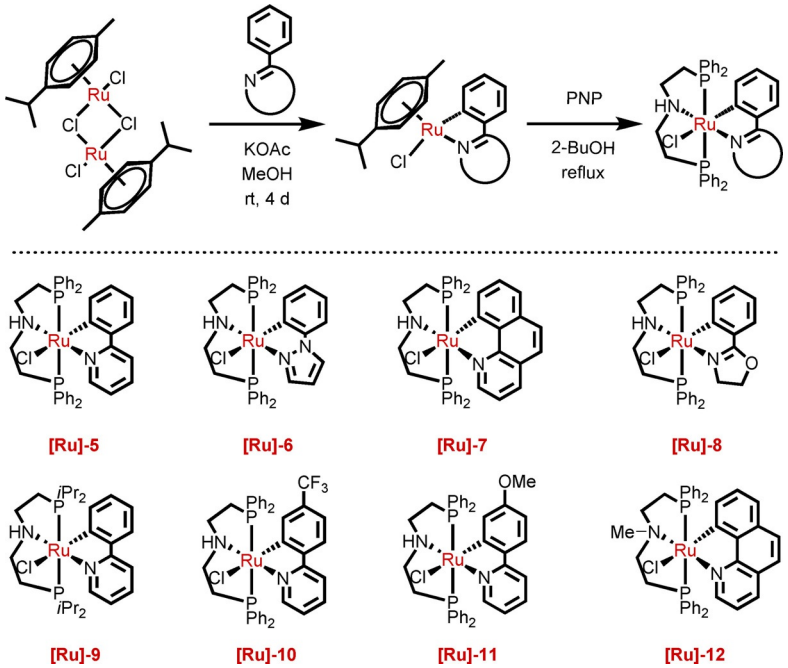
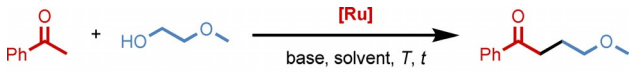


Figure 1. Crystal structure of **[Ru]-7**. Displacement ellipsoids correspond to 30% probability. Hydrogen atoms (except the N-bound) and co-crystallized solvent are omitted for clarity.



Scheme 2. Preparation of ruthenium pincer complexes bearing C,N-bound heterocycle ligands.

Table 1. Catalyst comparison and optimization for α-alkylation of acetophenone with 2-methoxyethanol.



1a **2a** **3aa**

Entry	[Ru]	Base	Base loading [mol%]	Solvent	T [°C]	Yield [%]
1	**[Ru]-1**	Cs_2CO_3	10		130	16
2	**[Ru]-5**	Cs_2CO_3	10		130	42
3	**[Ru]-6**	Cs_2CO_3	10		130	44
4	**[Ru]-7**	Cs_2CO_3	10		130	48
5	**[Ru]-8**	Cs_2CO_3	10		130	32
6	**[Ru]-9**	Cs_2CO_3	10		130	22
7	**[Ru]-10**	Cs_2CO_3	10		130	38
8	**[Ru]-11**	Cs_2CO_3	10		130	43
9	**[Ru]-7**	Cs_2CO_3	10		140	58
10	**[Ru]-7**	Cs_2CO_3	10	*t*-amyl alcohol	150	65
11	**[Ru]-7**	KO*t*Bu	10		150	44
12	**[Ru]-7**	NaO*t*Bu	10		150	45
13	**[Ru]-7**	NaOH	10		150	38
14	**[Ru]-7**	K_2CO_3	10		150	36
15	**[Ru]-7**	NEt_3	10		150	-
16	**[Ru]-7**	Cs_2CO_3	20		150	66
17	**[Ru]-7**	Cs_2CO_3	30		150	64
18[a]	**[Ru]-7**	Cs_2CO_3	10		150	57
19[b]	**[Ru]-7**	**Cs_2CO_3**	**10**		**150**	**68**
20[c]	**[Ru]-7**	Cs_2CO_3	10		150	60
21[b]	**[Ru]-7**	Cs_2CO_3	10	heptane	150	41
22[b]	**[Ru]-7**	Cs_2CO_3	10	toluene	150	38
23[b]	**[Ru]-7**	Cs_2CO_3	10	THF	150	53
24[b]	**[Ru]-7**	Cs_2CO_3	10	1,4-dioxane	150	37
25[b]	**[Ru]-7**	Cs_2CO_3	10	water	150	10
26[b]	**[Ru]-7**	–	–		150	–
27	–	Cs_2CO_3	10	*t*-amyl alcohol	150	–
28	**[Ru]-12**	Cs_2CO_3	10		150	46
29	**[Ru]-1**	Cs_2CO_3	10		150	31

Unless otherwise specified, reactions were carried out with **1a** (1.0 mmol), **2a** (1.2 mmol), the catalyst (0.02 mmol), and the base (0.1 mmol) in 1 mL of solvent at the indicated temperature for 22 h; [a] catalyst loading: 0.5 mol%; [b] catalyst loading: 1 mol%; [c] catalyst loading: 3 mol%; yields determined by GC using *n*-hexadecane as internal standard.

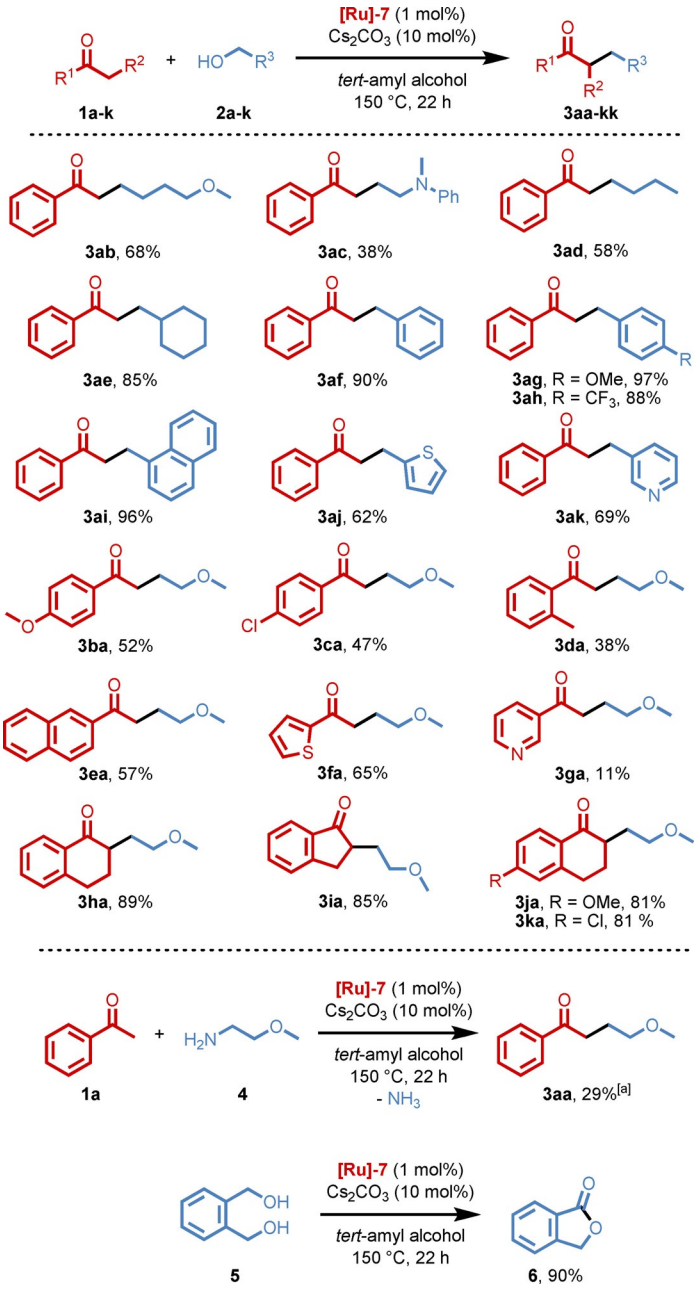
likely promotes labilization of the Ru–Cl bond and its substitution by the alkoxide. Although further mechanistic investigations would be required to confirm the following hypothesis, subsequent β-hydride elimination could generate a Ru-hydride complex with ensuing formation of the aldehyde.

Ultimately, we performed the reaction with **1a** (1.0 mmol), **2a** (1.2 mmol), **[Ru]-7** (0.01 mmol), and Cs_2CO_3 (0.1 mmol) in 1 mL of *t*-amyl alcohol at 150 °C and chose these optimal conditions for testing different substrates (Scheme 3).

Reaction of 4-methoxybutanol (**2b**) gave 68% of the desired product **3ab** and exchanging the ether group for a tertiary amine, the corresponding product **3ac** was obtained in 38% yield. Additionally, starting from simple, aliphatic alcohols like 1-butanol **2d** or cyclohexylmethanol **2e**, acetophenone was alkylated in satisfying yields (58 and 85%, respectively). Pleasingly, when benzyl alcohol **2f** is applied, the yield rises to 90%. Similarly, substituted benzyl alcohols were used to give alkylated ketones **3ag** and **3ah** in 97 and 88% yield, respectively, and moreover, 1-naphthyl methanol **2i** was converted to give the desired product **3ai** in an excellent 96% yield. Finally, 2-thiophenemethanol **2j** and 3-pyridylmethanol **2k** were applied as representatives of heterocycle-bearing alcohols. Here, the corresponding products were obtained in 62 and 69% yield, respectively.

Next, differently substituted acetophenone derivatives were alkylated. Here, reactions preceded smoothly affording 38 to 58% of the corresponding products **3ba** to **3da**. In line with this, 2-acetonaphthone was converted into **3ea** in 57% yield and 2-acetyl heterocycles **1f** and **1g** gave 65 and 11%, respectively. Furthermore, using α-tetralone **1h** or 1-indanone **1i**, the desired products were obtained in good yields of 89 and 85%, respectively. In line with this, when substituted tetralone-derivates **1j** and **1k** are employed, the corresponding products are generated in 81% yield in both cases.

This new class of complexes is not merely limited to the beforehand discussed reactions, but they are as well able to dehydrogenate amines allowing for their application in alkylating ketones. To demonstrate this, 2-methoxyethylamine **4** was used instead of the alcohol **2a**, giving **3aa**. In addition to that, diols like 1,2-benzenedimethanol **5** undergo cyclization to give



Scheme 3. Substrate scope of the Ru-catalyzed α-alkylation of ketones and related reactions. Yields of isolated material; [a] yield determined by GC using hexadecane as internal standard.

the corresponding cyclic lactone **6** under C–O bond formation in a very good yield of 90%.

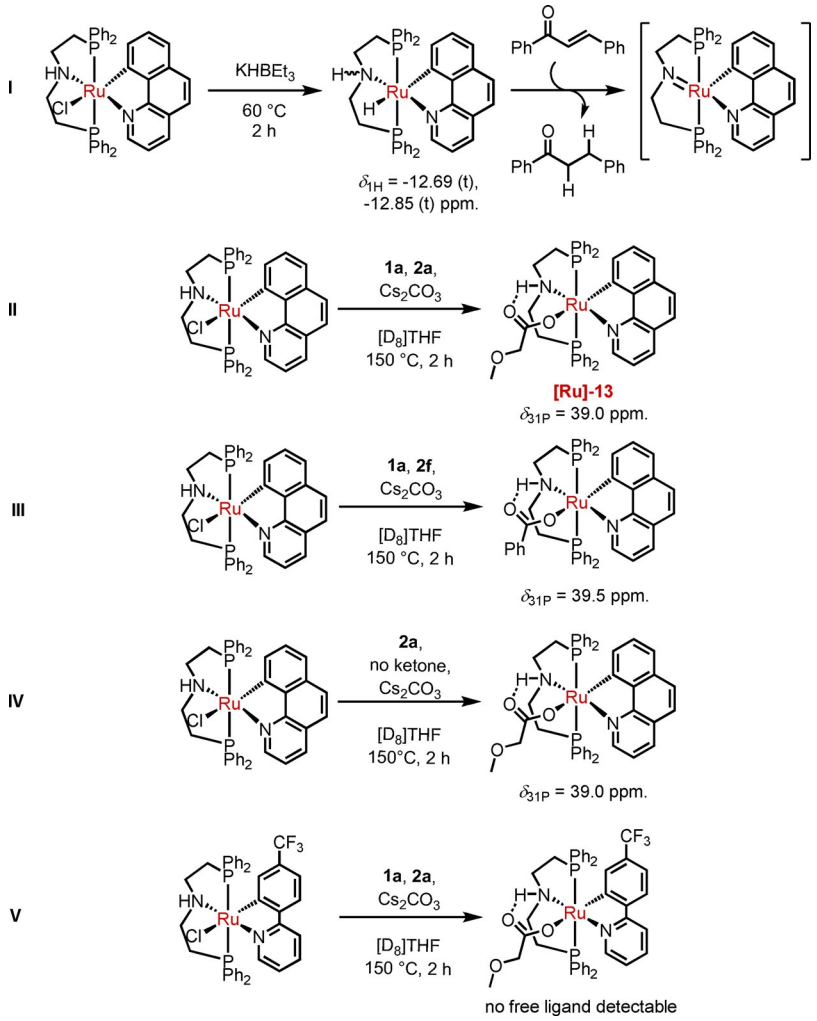
After having established a satisfying substrate scope, investigations concerning the reaction mechanism were carried out. First, we wanted to find out if the applied complex is capable of forming stable ruthenium hydride species. In principle, it would be possible that these species spontaneously release the hydride and the aryl heterocycle ligand through reductive elimination. However, when **[Ru]-7** is treated with $KHBEt_3$, two hydridic species were obtained and detected by ^1H NMR spectroscopy (see Scheme 4, reaction **I** and Supporting Information). In a follow-up experiment, one of these hydride complexes is able to promptly hydrogenate benzylideneacetophenone which corresponds to the last step of the alkylation of ketones with alcohols.

Subsequently, we wanted to find out which catalyst species are actually present under reaction conditions. For this, the reaction was carried out in a pressure-resistant NMR tube (reaction conditions were adjusted to this by using $[D_8]$THF as solvent, shortened reaction times and higher catalyst loadings). Here, besides starting complex **[Ru]-7**, one major species was detected in ^{31}P NMR (Scheme 4, reaction **II**). To verify the nature of this species, the NMR-scale reaction was carried out using benzyl alcohol instead of 2-methoxyethanol (reaction **III**). This resulted in a slightly shifted ^{31}P NMR signal suggesting that a different complex is formed herein, when a different alcohol is deployed. Additionally, the experiment was repeated without addition of the ketone (reaction **IV**). Here, a similar species was detected by ^{31}P NMR, whereas it was not observed in a comparison experiment without alcohol or ketone (see the Supporting Information). The species formed in this reaction was further characterized by NMR spectroscopy as well as X-ray structural analysis. By this, it was revealed that the complex predominantly present during catalysis is ruthenium carboxylate complex **[Ru]-13** (see Figure 2). Under reaction conditions, this species is probably generated by hydration of the in situ formed aldehyde followed by catalytic dehydrogenation of the so-formed *gem*-diol.[6c,28] The required water for this likely stems from the aldol condensation occurring during catalysis or from moisture present in the alcohols because these have not been dried prior to use. Attempts to synthesize **[Ru]-13** independently in the best case yielded in a mixture of 78% of it and the starting complex **[Ru]-7** (see the Supporting Information for details). However, when this mixture was applied in the standard reaction, the product was obtained in similar 68%. Due to this, **[Ru]-13** likely depicts a catalyst reservoir and can be activated by base probably through deprotonation of the NH group and formation of a further N–Ru bond with displacement of the carboxylate group, the same way chloride is displaced from **[Ru]-7**.

Finally, experiments were performed concerning the stability of the phenyl heterocycle ligand during catalysis. For this, the NMR reaction was carried out under use of **[Ru]-10** as catalyst to investigate species involving this ligand by ^{19}F NMR. Here again, a species fitting to the corresponding carboxylate complex and the starting material were observed. Besides this, only small traces of other fluorine-containing species were detected, indicating that the applied cyclometalated ligands in fact remain bound to the complex during catalysis.

Conclusions

Summing up, cyclometalated aryl heterocycles can be used as a tunable mimic of carbonyl and hydride ligands in popular



Scheme 4. Experiments to investigate the catalyst species involved in the reaction.

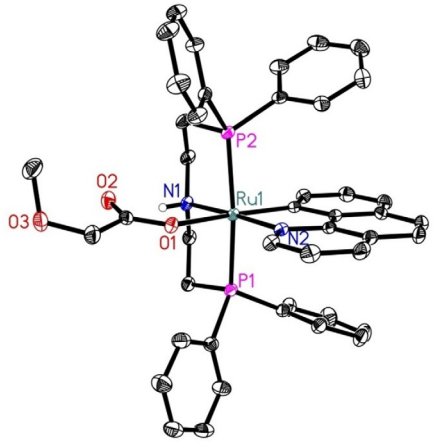


Figure 2. Crystal structure of **[Ru]-13**. Displacement ellipsoids correspond to 30% probability. Only one molecule of the asymmetric unit is shown. Hydrogen atoms (except the N-bound) and co-crystallized solvent are omitted for clarity.

ruthenium pincer complexes. Following this concept, a series of novel potent catalysts for (de)hydrogenations have been obtained. The general advantage of such catalysts compared to the parent complex is demonstrated for the green α-alkylation of ketones with alcohols. Plausible reaction intermediates were investigated for this, all still involving the intact phenyl heterocycle and the pincer ligand. We believe this catalyst design can be used as a guideline for the creation of a variety of other pincer complexes, too; thus, opening the door for more effective catalysis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–C bond formation · hydrogen autotransfer · metallacycles · pincer complexes · ruthenium

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