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New cationic rhodium–amine complexes and their implication in the catalytic anti-Markovnikov oxidative amination of styrenes

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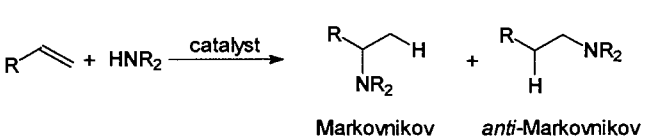
Abstract

The oxidative anti-Markovnikov amination of styrenes catalyzed by cationic rhodium complexes provides a new access to enamines. As catalyst precursors $[Rh(cod)(amine)_2]^+$ complexes have been identified and characterized for the first time by X-ray crystallography and NMR. While piperazine, *N*-methylpiperazine, and thiomorpholine form 1:1 Rh–amine complexes, non-chelating amines such as piperidine and diethylamine form 1:2 Rh–amine complexes. The easier dissociation of the amine ligand explains why monodentate amines give good yields of the corresponding enamines in contrast to bidentate amines.

Keywords: Amines; Amination of olefins; Anti-Markovnikov reaction; Catalysis; Oxidation; Rhodium complexes

1. Introduction

The catalytic construction of carbon–nitrogen bonds to selectively produce amines is of fundamental importance in organic synthesis. Particularly interesting are catalytic aminations of olefins [1] to give primary, secondary or tertiary amines due to the atom efficiency of the process and the availability of starting materials [2]. In regards to the regioselectivity of the process it is interesting to note that Markovnikov as well as anti-Markovnikov products can be produced (Scheme 1).



Scheme 1. Hydroamination of olefins.

In general the linear anti-Markovnikov products are more interesting for industrial applications. Unfortunately, so far no transition metal catalyzed process is known for anti-Markovnikov aminations of neutral terminal olefins [3]. Thus, this type of reaction has been named as one of the ten most important goals for future catalytic processes [4].

Recently, we have developed a new intermolecular oxidative amination of aromatic olefins to give enamines in good yields (Scheme 2) [5]. Thereby simple monoamines like piperidine or diethylamine are converted in the presence of cationic rhodium–phosphine complexes as in situ catalysts to the corresponding ω-enamine in good yields. A further equivalent of the aromatic olefin is concurrently reduced to a substituted ethylbenzene. This reaction is remarkable for several reasons: it is one of the rare examples of a catalytic intermolecular oxidative amination reaction of olefins, [6] and it provides the enamine for the first time with excellent anti-Markovnikov regioselectivity (>99:1).

The mechanism of the reaction can follow two alternative pathways as depicted in Scheme 3. On the one

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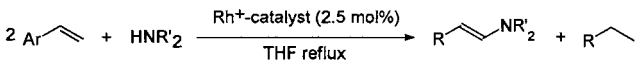


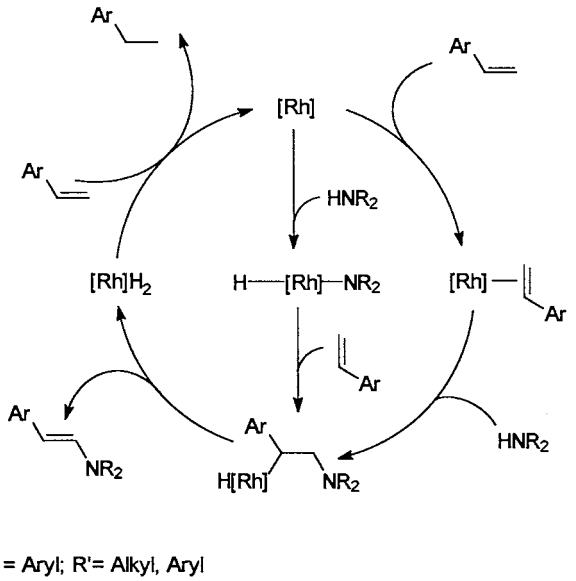
Scheme 2. Anti-Markovnikov oxidative amination of styrene.

hand, an up to now unidentified Rh complex activates the olefin by complexation, thus the olefin is prone to a nucleophilic attack of the amine. The resulting aminoalkylrhodium species eliminates the enamine and the rhodium dihydride complex hydrogenates a second olefin to yield the catalytically active species. On the other hand activation of the amine by an oxidative addition to give an amidohydridorhodium complex [7] may also take place. Insertion of the olefin into the Rh–N bond and subsequent β-hydride elimination leads (similar to the previous cycle) to an enamine and a rhodium dihydride complex.

In order to gain more insight into this new catalytic reaction as well as taking a further step in the development of a general anti-Markovnikov amination methodology, it is necessary to approach the actual catalytically active rhodium species by isolating and characterizing intermediates of the oxidative amination reaction.

Cationic $[Rh(amine)_x(olefin)_y]^+$ $(x+y=4)$ or $[Rh(amine)_x(olefin)_y(phosphine)_z]^+$ $(x+y+z=4)$ complexes are supposed to play an important role in the formation of the active species, which is unknown up to now. Thus we were interested in the preparation of a series of cationic $[Rh(amine)_x(olefin)_y]+$ $(x+y=4)$ complexes and comparing the structural data of these complexes with results from catalysis. Unfortunately, apart from pyridine or nitrile ligands rhodium amine complexes are not very well investigated [8]. Up to now secondary amine groups were only used as one coordination side in chelating ligands with further donor centers, e.g. 2-(aminoalkyl)pyridines, which resulted in the formation of either ion pairs, dimers, tetra- or pentacoordinated complexes [9,10]. Apart from the ammonia complex $[Rh(cod)(NH_3)_2]^+$ [11] there is to the best of our knowledge no structural characterization of cationic diolefin–rhodium complexes with primary or secondary amines as ligands [12].

Due to this lack of knowledge, we present here our initial studies on stoichiometric reactions of the cationic bis(cyclooctadienyl)rhodium complex with various secondary aliphatic amines. The resulting rhodium species are pre-catalysts forming the catalytic active species in the oxidative anti-Markovnikov amination reaction.



Scheme 3. Possible catalytic cycles of the anti-Markovnikov oxidative amination.

2. Results and discussion

2.1. Variation of the amine in the oxidative amination of styrene

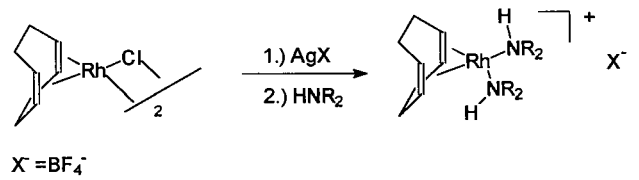
The regioselective oxidative amination of styrenes by secondary amines permits the effective synthesis of valuable enamines. In order to investigate the scope and limitations of the amine compound for the rhodium catalyzed oxidative amination we tested either monoamines, which possess only one functional group as well as amines with two coordinating groups within the molecule, such as piperazine (Table 1).

While monodentate amines like piperidine and diethylamine provide good yields of the corresponding enamine, bidentate amines like piperazine and its derivatives or thiomorpholin react very sluggishly or even not at all under our previously optimized reaction conditions (one equivalent amine, four equivalents styrene, THF reflux, 2.5 mol% $[Rh(cod)_2]BF_4$, 5 mol% PPh_3). As a consequence, the coordination chemistry of

Table 1
Oxidative amination of styrene with various amines[a]

Amine	Enamine (%)	Ethylbenzene (%)
Piperidine	55	57
Diethylamine	40	54
Thiomorpholine	<1	<1
Piperazine	<1	<1
N-Methyl-piperazine	4	5

[a] 2.5 mol% Rh catalyst relative to amine, styrene: amine = 4:1, 20 h reflux in THF.
The yields of enamine and ethylbenzene are referred to amine.



Scheme 4. Preparation of cationic $[Rh(cod)(amine)_2]^+$ complexes with monodentate amines.

these two kinds of amines, monodentate and bidentate, with cationic rhodium centers has to be different.

2.2. Cationic rhodium–amine complexes

2.2.1. Monodentate amine ligands

The starting point of our investigation was the observation that the reaction mixture, the orange colored $[Rh(cod)_2]BF_4$ complex which is insoluble in THF immediately dissolves by adding a surplus of monodentate amine. Spectroscopic studies of the resulting clear yellow solution by means of in situ ^{1}H-NMR spectroscopy reveal that the yellow color is due to the formation of a cationic $[Rh(cod)(NHR_2)_2]^+$ complex which arises due to displacement of one cod ligand by two amines [13].

In isolating the cationic $[Rh(cod)(NHR_2)_2]^+$ complex this route proved to be inconvenient as the replaced cod ligand causes side-reactions and cod is not easily separated from the product. Hence, as an alternative synthesis the reaction of an equimolar mixture of $[RhL_2Cl]_2$ (L = olefin) and AgX (X = BF_4, CF_3SO_3) [14] was tested. Thereby $[Rh(cod)Cl]_2$ was dissolved in THF and treated with $AgBF_4$. After filtration of AgCl 2.2 equivalents of piperidine or diethylamine were added at 0°C to the mixture and a yellow precipitate was obtained in nearly quantitative yield (Scheme 4) (Table 2).

The IR spectra of all compounds, recorded in KBr pellets, showed a characteristic decrease in the amine (N–H) stretching frequency of $\Delta\nu$ ca. 100–150 cm^{-1} compared to the free amine suggesting that coordination of the amine occurs to the rhodium center. The strong absorption bands at ca. 1000 cm^{-1} can be assigned to the BF_4 ion indicating a cationic species. Elemental analysis and mass spectroscopy revealed that in the case of **1** and **2** (diethylamine and piperidine as amine ligands) two amine molecules coordinate to the rhodium center, which is confirmed by ^{1}H-NMR. The proton NMR of **1** shows one signal at 3.85 ppm for the olefinic cod protons and two signals at 2.38 and 1.78 ppm for the aliphatic cod protons. The α-CH_2 group in the ethyl group of the diethylamine ligand gives two different multiplets at 2.75 and 2.56 ppm indicating a chemical inequivalence for the two geminal protons. This can be explained by a hindered rotation of the Rh–N and the N–C bond due to the steric demand of the cod ligand. The N–H proton signal is located at 2.93 ppm and the triplet at 1.50 ppm corresponds to the methyl group of the diethylamine ligand. A quite similar pattern in the ^{1}H-NMR is observed for the piperidine complex **2**.

Suitable crystals for X-ray diffraction were obtained by diffusing pentane in a solution of **2** in THF. The crystals contain discrete molecules, separated by normal van der Waals distances. An ORTEP drawing of the cationic complex $[Rh(cod)(piperidine)_2]^+$ is shown in Fig. 1, and a selection of intraatomic distances are given in Table 3.

The rhodium atom has a square planar coordination geometry of cod and two amines with the two piperidine molecules being *cis* to each other. Rhodium nitrogen bond lengths (Rh–N11 = 2.159(4), Rh–N21 = 2.186(4) Å) are longer than those in the corresponding ammonia complex $[Rh(cod)(NH_3)_2]PF_6$ (between 2.114(4) and 2.134(4) Å) [11] where the rhodium centre is coordinated by a dibenzo crown ether in a second sphere. Surprisingly, in the neutral complex $RhCl(C_2H_4)(piperidine)_2$ [15] Rh–N bond lengths are even shorter (2.087(3) and 2.111(3) Å, respectively). The angle between the two piperidine nitrogens N11–Rh–N21 in **2** is 90.1(1)° which indicates that there is no steric strain around rhodium. Each of the nitrogens are in a tetrahedral environment with N–H forming hydrogen bonds with the fluorine atoms of the counterion (N11–H11···F1 = 3.08, N21–H21…F3 = 3.29 Å).

2.2.2. Bidentate amine ligands

We synthesized and isolated according to the above mentioned procedure, i.e. treatment of $[Rh(cod)Cl]_2$ with AgX and subsequent addition of bidentate amine, several cationic cod–rhodium complexes with cyclic amine ligands which possess an additional donor atom in the ring. With piperazine as amine complex **3** was obtained, with *N*-methylpiperazine complex **4a** and **4b**, and with thiomorpholine complex **5** was obtained. All prepared complexes **1–5** are air and moisture stable. However, for a prolonged time they are best stored under an argon atmosphere (Scheme 5).

Although bidentate cyclic amines like piperazines are known to act as chelating ligands, especially for transition metals like Cu, Ni, Pt [16] no cationic Rh complex with cyclic chelating diamines has been described to the best of our knowledge.

IR spectroscopic studies show a characteristic decrease in the amine (N–H) stretching frequency of complexes **3–5**. This indicates a coordination of the amine on the rhodium center. However, by the presence of two coordinating sides these bidentate amine molecules react as chelating ligands. This is confirmed by the rhodium–cod–amine ratio of 1:1:1 shown by elementary analysis and mass spectroscopy.

Table 2
Yields, analytical results and N–H vibration frequencies of the cationic rhodium compounds **1**–**5** compared to the free amine in CCl_4

No	Complex	Yield (%)	C calc. C found	H calc. H found	N calc. N found	ν(N–H) complex {free amine} (cm^{-1})
1	$[Rh(cod)(HN(C_2H_5))_2]BF_4$	91	43.0	8.1	6.3	3181
			42.6	7.7	6.1	{3278}
2	$[Rh(cod)(HNC_5H_{10})_2]BF_4$	83	46.1	7.3	6.0	3251, 3186
			46.0	7.3	5.7	{3346}
3	$[Rh(cod)(HNC_4H_8NH)]BF_4$	93	37.5	5.8	7.3	3259
			38.1	5.8	7.3	
4a	$[Rh(cod)(HNC_4H_8NCH_3)]BF_4$	82	37.5	5.8	7.3	3304, 3193
			38.1	5.8	7.3	{3349}
4b	$[Rh(cod)(HNC_4H_8NCH_3)]OTf$	75	35.4	5.3	6.1	
			35.5	5.2	6.2	
5	$[Rh(cod)(HNC_4H_8S)]BF_4$	88	35.9	5.3	3.5	3278
			35.8	5.2	3.4	{3358}

Due to the norbornan-like structure of these chelating hexacyclic amines complexes, whereby the nitrogen atoms act as bridgehead atoms and the rhodium atom as a bridge, [17] a splitting of the CH_2 ring protons of the coordinated amine is observed in the ^{1}H-NMR spectra of **3**, **4**, and **5**. This non-equivalence of the *exo* and *endo* protons of the amine CH_2 groups gives a further indication that the cyclic amine behaves as a bidentate ligand. In regards to **4** and **5** the non-equivalence of the amine CH_2 groups is clearly observed. Interestingly, in case of the *N*-methylpiperazine rhodium complex the methyl group even changes the chemical surrounding of the olefinic cod protons resulting in two different signals (Fig. 2). The exact assignement of Fig. 2 was performed by means of a HMQC experiment.

A comparison of the ^{1}H-NMR spectra of **4a** and **4b** reveals, that the chemical shift of the N–H signal is different (**4a**: 4.34) and (**4b**: 4.96 ppm). We ascribe this effect to the different interactions of the non-coordinating anions BF_4^- (**4a**) and $CF_3SO_3^-$ (**4b**) with the amine proton via the hydrogen bonds.

The ^{13}C-NMR of **4a** and **4b** also show a splitting of signals which is caused by the different substitution of the nitrogen atoms. Hence, two different signals appear for the olefinic and aliphatic carbon atoms of the cod ligand as well as for the carbon atoms in the ethylen bridge of the *N*-methylpiperazine ligand.

The chelating structure of the bidentate amine ligand was corroborated by X-ray diffraction studies of **4b**. Suitable crystals were obtained by diffusing diethylether in a solution (CH_2Cl_2) of **4b**. The molecular structure of the cation [Rh(cod)(*N*-methylpiperazine)]$^+$ **4b** is shown in Fig. 3. The rhodium atom is in a distorted square planar surrounding, ligated by both nitrogen atoms of one *N*-methylpiperazine molecule. The rhodium–nitrogen bonds observed in **4b** (Rh–N11 = 2.091(2), Rh–N21 = 2.133(2) Å) are significantly shorter than those in **2** and comparable to those in $[Rh(cod)(NH_3)_2]PF_6$ and $RhCl(C_2H_4)(piperidine)_2$ (vice supra) (Table 4).

The N(11)–Rh–N(21) angle is only 70.56(7)°. Consequently, the angles between the cod double bonds, the rhodium, and the nitrogens are larger than 90°. Because

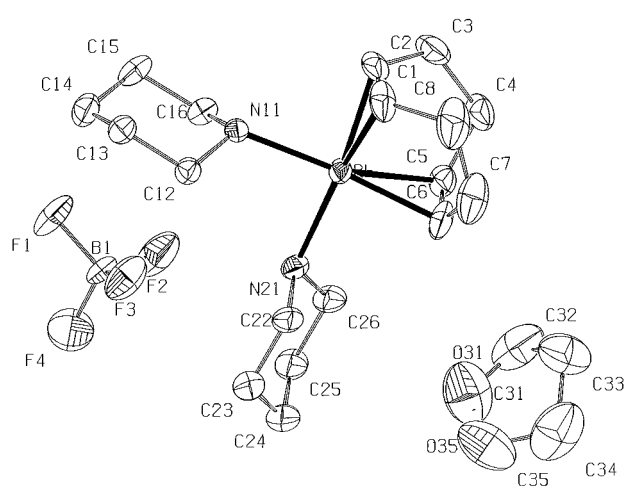
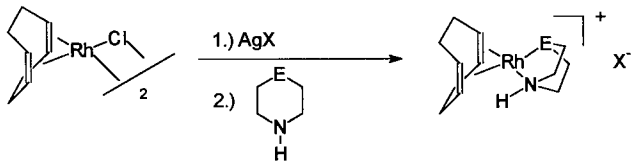


Fig. 1. Molecular structure of **2**. N11–Rh–N21 = 90.08(14)°.

Table 3
Selected bond distances in **2**

Bond length (Å)	
Rh–N11	2.159(4)
Rh–N21	2.186(4)
Rh–C1	2.113(5)
Rh–C2	2.121(6)
Rh–C5	2.161(5)
Rh–C6	2.155(6)
C1–C2	1.38(1)
C5–C6	1.38(1)

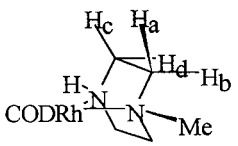


Scheme 5. Preparation of cationic $[Rh(cod)(amine)]^+$ complexes with bidentate amines.

of the larger steric requirement of N–Me the angles N14–Rh–C6 and N14–Rh–C5 (102.0(1) and 101.7(1)°, respectively) are larger than the corresponding angles of N–H (N11–Rh–Cl = 98.4(1), N11–Rh–C2 = 98.1(1)°). Again hydrogen bonds between the N–H group and the counterion (N11–H11···O2 = 3.05 Å) are observed.

2.3. Catalytic activity of cationic rhodium olefin–amine complexes

With regard to mechanistic investigations we were interested in testing the catalytic activity of the new cationic Rh–amine complexes **1–5** in the anti-Markovnikov amination of styrene (Scheme 2). Complexes **3** and **5** are insoluble under the typical reaction conditions, thus no conversion was observed. However, even the use of complex **3** in the presence and absence of triphenylphosphine in DMAc as solvent showed no reactivity. In case of *N*-methylpiperazine complexes



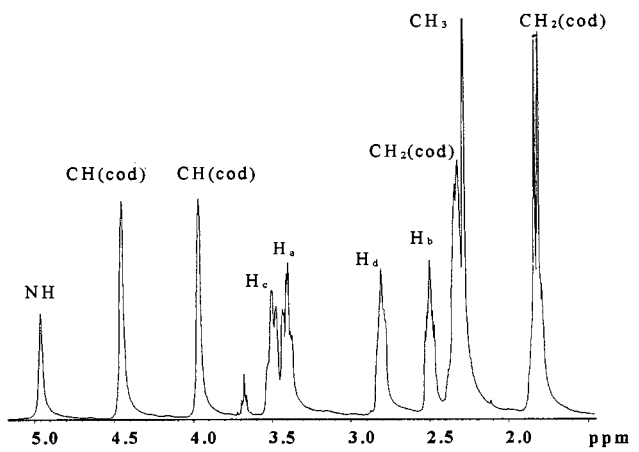


Fig. 2. ^{1}H-NMR of $[Rh(cod)(N\text{-methylpiperazine})]CF_3SO_3$.

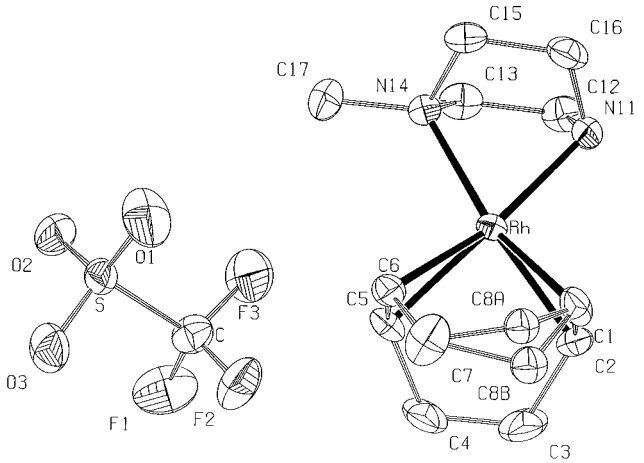


Fig. 3. Molecular structure of **4b**. N11–Rh–N14 = 70.56(7)°.

4a,b are still soluble in the reaction mixture (solvent THF), however the formation of a stable chelating ligand system blocks vacant coordination sites on the rhodium center, slowing down dramatically the rate of the reaction (Table 5).

We compared the catalytic activity of **2** with our previously used in situ catalyst mixture ($[Rh(cod)_2BF_4$/2 PPh_3). While the $[Rh(cod)(piperidine)_2]^+$ complex (**2**) itself is only marginally active (yield enamine = 8%; TON = 3), in the presence of triphenylphosphine the complex is as active as the in situ catalyst mixture (yield = 45%; TON = 18 vs yield = 55%; TON = 22). In order to understand the influence of added triphenylphosphine we performed in situ NMR studies of **2** in the presence of triphenylphosphine in $CDCl_3$. We varied the ratio of triphenylphosphine to **2** using 0.5, 1, 2, and 4. Surprisingly the ^{1}H- and ^{13}C-NMR spectra reveal that both the cod and piperidine ligands are displaced by adding 0.5 equivalents of triphenylphosphine. The ^{31}P-NMR spectrum of this reaction mixture shows at least three doublets, indicating the presence of several species of different Rh–phosphine complexes. One of the doublets can be associated with the $[Rh(cod)(PPh_3)_2]BF_4$ complex [18].

Table 4
Selected bond distances in **4b**

Bond length (Å)	
Rh–N11	2.091(2)
Rh–N14	2.133(2)
Rh–C1	2.111(2)
Rh–C2	2.110(2)
Rh–C5	2.125(2)
Rh–C6	2.124(2)
C1–C2	1.375(4)
C5–C6	1.375(4)

Table 5
Regioselective oxidative amination of styrene[a]

Amine	Catalyst	Solvent	Enamine	Ethylbenzene
Piperidine	$[Rh(cod)_2]BF_4$/2 PPh_3	DMAc	23	40
Piperazine	$[Rh(cod)_2]BF_4$/2 PPh_3	DMAc	<1	<1
Piperazine	**3**/2 PPh_3	DMAc	<1	<1
Di-*n*-ethylamine	**1**	THF	<1	<1
Diethylamine	**1**/2 PPh_3	THF	31	28
Piperidine	**2**	THF	8	8
Piperidine	**2**/2 PPh_3	THF	45	49

[a] 2.5 mol% Rh catalyst relative to amine, styrene: amine = 4:1, 20 h reflux in THF.
The yields of enamine and ethylbenzene are referred to amine.

By increasing the amount of triphenylphosphine in the reaction mixture the concentration of free cod and amine is increased, as well as the number of peaks in ^{31}P-NMR spectra. The presence of more than two equivalents of triphenylphosphine as well as free phosphine was observed in the ^{31}P-NMR spectra. So far no complex has been isolated from this mixture. These observations provide significant evidence that at least three coordination sites on the metal center must be easily accessible in order to observe significant catalysis, otherwise no oxidative amination takes place. Furthermore it is clear that various rhodium-olefin-amine-phosphine complexes are present in solution, thus it has not been possible until now to identify a single active catalyst species.

3. Conclusion

In conclusion we were able to isolate and to synthesize a series of cationic rhodium complexes with olefin and secondary amine ligands for the first time. A systematic structural investigation by NMR and X-ray reveals that the bidentate *N*-methylpiperazine in **4b** is bound more tightly to rhodium than the two piperidine molecules in **2**. This gives an explanation for the lower catalytic activity of **4b**. Cationic $[Rh(cod)(amine)]^+$ complexes prepared by reaction of $[Rh(cod)_2]^+$ with amines play an important role as pre-catalysts in the formation of the catalytic active species in the rhodium catalyzed anti-Markovnikov amination of styrene. In the presence of triphenylphosphine these complexes show similar catalytic activity compared to in situ catalyst mixtures. In case of piperazine, 4-thiomorpholine, and *N*-methylpiperazine inhibition of the catalysis is observed due to blocking of vacant coordination sites on the metal center.

4. Experimental details

4.1. General procedures

All reactions involving organometallic compounds were carried out with the use of vacuum line, Schlenk and syringe techniques. All solvents were dried and distilled prior to use, according to standard procedures. Amines were distilled from CaH_2, silver salts and other chemicals were purchased from Fluka and Aldrich and used as received. Samples of $[Rh(cod)Cl]_2$ [19], and $[Rh(cod)_2]BF_4$ [18] were prepared as described in the appropriate reference.

^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded on a Jeol-GX 400 spectrometer. ^{1}H- and ^{13}C- chemical shifts are reported in ppm relative to TMS. ^{31}P- spectra were referenced to 85% H_3PO_4. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Mass spectroscopic analysis was performed on a Finnigan MAT 311A by using the Fast Atom Bombardment or Field Desorption method. The elemental analyses were carried out by the Microanalytical Laboratory of the Technische Universität München.

GC spectra for analysis of catalytic reactions were recorded with a HP 6890 gas chromatograph using a HP-1 capillary column. Yields were determined by using hexadecane as internal standard.

4.2. [(1,2,5,6-η)-1,5-Cyclooctadien]bis(diethylamine)rhodium(I) tetrafluoroborate (1)

A total of 100 mg (0.20 mmol) $[Rh(cod)Cl]_2$ and 80 mg (0.41 mmol) $AgBF_4$ were dissolved under nitrogen in 2 ml THF and stirred for 10 min. The clear orange solution was filtered off the white AgCl and cooled to 0°C. Then 66 mg (0.90 mmol) diethylamine was added under stirring and after 5 min a yellow precipitate was obtained, which was washed twice with THF and three times with pentane. After drying in vacuo **1** was obtained in a 91% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, 20°C): $\delta = 3.86$ [s, 4H, C*H*(cod)], 2.92 [t, $^3J_{H-H} = 6.7$ Hz, 2H, N*H*], 2.75 [sext, $^3J_{H-H} = 6.7$ Hz, 4H, N–CH_2], 2.55 [septd, 4H, $^3J_{H-H} = 6.7$ Hz, N–CH_2], 2.40 [d, $^3J_{H-H} = 11.1$ Hz, 4H, CH_2(cod)], 1.78 [d, $^3J_{H-H} = 8.5$ Hz, 4H, CH_2(cod), 1.50 [t, $^3J_{H-H} = 7.1$ Hz, 12H, CH_3]. ^{13}C-NMR (100 MHz, $CDCl_3$, 20°C): $\delta = 81.1$ [d, $^3J_{Rh-C} = 12.9$ Hz, *C*H(cod)], 47.0 [CH_2–N], 30.1 [CH_2(cod)], 14.9 [CH_3–N]. IR(KBr): $\nu(cm^{-1}) = 3181$ s, 2960 s, 2929 s, 2867 m, 2829 m, 1654 w, 1374 m 1145 s, 1066 ss, 1040 ss, 821 m. MS (FAB) m/z (%): 284.3 $[Rh(cod)(HNEt_2)]^+$.

4.3. [(1,2,5,6-η)-1,5-Cyclooctadien]bis(piperidine) rhodium(I) tetrafluoroborate (**2**)

A total of 100 mg (0.20 mmol) $[Rh(cod)Cl]_2$ and 80 mg (0.41 mmol) $AgBF_4$ were dissolved under nitrogen in 2 ml THF and stirred for 10 min. The clear orange solution was filtered off the white AgCl and cooled to 0°C. Then 78 mg (0.90 mmol) were added under stirring and after 5 min a yellow precipitate was obtained, which was washed twice with THF and three times with pentane. After drying in vacuo, **2** was obtained in a 83% yield. ^{1}H-NMR (400 MHz, CD_2Cl_2, 20°C): $\delta =$ 3.95 [s, 4H, *C*H(cod)], 3.10 [s, 4H, N–CH_2], 2.70 [s, N*H*], 2.52 [s, 4H, N–CH_2], 2.40 [d, $^3J_{H-H} = 11.1$ Hz, 4H, CH_2(cod)], 1.78 [d, $^3J_{H-H} = 8.5$ Hz, 4H, CH_2(cod), 1.76 [s, 4H, *meta*-CH_2], 1.64 [m, 6H, *meta*-CH_2, *para*-C*H*2], 1.42 [s, 2H, *para*-C*H*2]. ^{13}C-NMR (100 MHz, CD_2Cl_2, 20°C): $\delta = 81.5$ [d, $^1J_{Rh-C} = 12.5$ Hz, *C*H(cod)], 49.4 [CH_2–N], 29.8 [CH_2(cod)], 25.8 [*meta*-CH_2], 23.4 [*para*-CH_2]. IR (KBr): $\nu(cm^{-1}) = 3251$ m, 3186 s, 2941 s, 2923 s, 2859 m, 2824 m, 1654 m, 1457 m 1095 ss, 1090 ss, 1054 ss, 1040 ss, 871 s. MS (FD, CH_2Cl_2), *m*/*z* (%): 381.6 $[Rh(cod)(piperidine)_2]^+$.

4.4. [(1,2,5,6-η)-1,5-Cyclooctadien]-(N,N′-η)-piperazinerhodium(I) tetrafluoroborate (**3**)

A total of 100 mg (0.20 mmol) $[Rh(cod)Cl]_2$ and 80 mg (0.41 mmol) $AgBF_4$ were dissolved under nitrogen in 2 ml THF and stirred for 10 min. The clear orange solution was filtered off the white AgCl and cooled to 0°C. Then 39 mg (0.45 mmol) piperazine was added under stirring and after 5 min a yellow precipitate was obtained, which was washed twice with THF and three times with pentane. After drying in vacuo, complex **3** was obtained in a 93% yield.

^{1}H-NMR (400 MHz, CD_3NO_2, 20°C): $\delta = 4.40$ [s, 4H, C*H*(cod)], 3.63 [d, 4H, $^3J_{H-H} = 6.0$ Hz, N–CH_2], 2.90 [d, $^3J_{H-H} = 6.5$ Hz, 4H, N–CH_2], 2.38 [s, 4H, CH_2(cod)], 1.78 [d, $^3J_{H-H} = 8.0$ Hz, 4H, CH_2(cod)]. ^{13}C-NMR (100 MHz, CD_3NO_2, 20°C): $\delta = 81.8$ [d, $^1J_{Rh-C} = 12.3$ Hz, *C*H(cod)], 46.7 [CH_2–N], 31.6 [CH_2(cod)]. IR (KBr): $\nu(cm^{-1}) = 3279$ s, 3259 s, 2945 s, 2880 m, 2834 m, 1125 s, 1084 ss, 878 s. MS (FD, CH_2Cl_2), *m*/*z* (%): 297 $[Rh(cod)(piperazine)]^+$.

4.5. [(1,2,5,6-η)-1,5-Cyclooctadien]-(N,N′-η)-N-methylpiperazinerhodium(I) tetrafluoroborate (**4a**)

A total of 100 mg (0.20 mmol) $[Rh(cod)Cl]_2$ and 80 mg (0.41 mmol) $AgBF_4$ was dissolved under nitrogen in 2 ml THF and stirred for 10 min. The clear orange solution was filtered off the white AgCl and cooled to 0°C. Then 45 mg (0.45 mmol) *N*-methylpiperazine was added under stirring, after 5 min a yellow precipitate was obtained, which was washed twice with THF and three times with pentane. After drying in vacuo, **4a** was obtained in an 82% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, 20°C): $\delta = 4.46$ [d, $^3J_{H-H} = 2.5$ Hz, 2H, C*H*(cod)], 4.34 [s, 1H, N*H*], 4.01 [d, $^3J_{H-H} = 2.5$ Hz, 2H, CH(cod)], 3.55–3.52 [m, 2H, C*H*H–NH], 3.48–3.42 [m, 2H, C*H*H–N–CH_3], 2.92–2.88 [m, 2H, CH*H*–NH], 2.60–2.54 [m, 2H, CH*H*–NCH_3], 2.41 [m, 4H, CH_2(cod)], 2.33 [s, 3H, CH_3], 1.86 [d, $^3J_{H-H} = 9.0$ Hz, 4H, CH_2(cod)]. ^{13}C-NMR (100 MHz, $CDCl_3$, 20°C): $\delta =$ 82.8 [d, $^1J_{Rh-C} = 12.5$ Hz, *C*H(cod)], 81.1 [d, $^1J_{Rh-C} =$ 112.4 Hz, CH(cod)], 55.0 [CH_2–N–CH_3], 45.5 [CH_3–N], 45.3 [CH_2–NH] 30.5 [CH_2(cod)], 30.4 [CH_2(cod)]. IR (KBr): $\nu(cm^{-1}) = 3304$ s, 3193 s, 3011 w, 2935 s, 2878 s, 2838 m, 2789 m, 1468 m, 1453 m, 1432 m, 1146 ss, 1060 ss, 1000 ss, 959 s, 833 m. MS (FD, CH_2Cl_2), *m*/*z* (%): 311 [Rh(cod)(*N*-methylpiperazine)]$^+$.

4.6. [(1,2,5,6-η)-1,5-Cyclooctadien]-(N,N′-η)-N-methylpiperazinerhodium(I) triflate (**4b**)

A total of 100 mg (0.20 mmol) $[Rh(cod)Cl]_2$ and 105 mg (0.41 mmol) $AgOSO_2CF_3$ was dissolved under nitrogen in 2 ml THF and stirred for 10 min. The clear orange solution was filtered off the white AgCl and cooled to 0°C. Then 45 mg (0.45 mmol) *N*-methylpiperazine was added under stirring, after 5 min a yellow precipitate was obtained, which was washed twice with THF and three times with pentane. After drying in vacuo, **4b** was obtained in a 75% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, 20°C): $\delta = 4.96$ [s, 1H, N*H*], 4.45 [s, 2H, C*H*(cod)], 4.01 [s, 2H, C*H*(cod)], 3.52–3.47 [m, 2H, C*H*H–NH], 3.43–3.37 [m, 2H, C*H*H–NCH_3], 2.82–2.78 [m, 2H, CH*H*–NH], 2.60–2.54 [m, 2H, CH*H*–NCH_3], 2.46–2.32 [m, 4H, CH_2(cod)], 2.33 [s, 3H, CH_3], 1.83 [d, $^3J_{H-H} = 9.0$ Hz, 4H, CH_2(cod)]. ^{13}C-NMR (100 MHz, $CDCl_3$, 20°C): $\delta = 82.8$ [d, $^1J_{Rh-C} =$ 12.5 Hz, *C*H(cod)], 81.1 [d, $^1J_{Rh-C} = 112.4$ Hz, *C*H(cod)], 55.0 [CH_2–N–CH_3], 45.5 [CH_3–N], 45.3 [CH_2–NH] 30.5 [CH_2(cod)], 30.4 [CH_2(cod)].

4.7. [(1,2,5,6-η)-1,5-Cyclooctadien]-(N,S-η)-thiomorpholinerhodium(I) tetrafluoroborate (**5**)

A total of 100 mg (0.20 mmol) $[Rh(cod)Cl]_2$ and 80 mg (0.41 mmol) $AgBF_4$ was dissolved under nitrogen in 2 ml THF and stirred for 10 min. The clear orange solution was filtered off the white AgCl and cooled to 0°C. Then 48 mg (0.45 mmol) 4-thiomorpholine was added under stirring, after 5 min a yellow precipitate was obtained, which was washed twice with THF and three times with pentane. After drying in vacuo, **5** was obtained in an 88% yield.

^{1}H-NMR (400 MHz, CD_3NO_2, 20°C): $\delta = 4.87$ [s, 2H, C*H*(cod)], 4.67 [s, 2H, C*H*(cod)], 3.59 [m, 2H, C*H*H–NH], 3.38 [m, 2H, CH*H*–S], 3.05–2.93 [m, 4H, CH*H*NH, CH*H*S], 2.42 [d, $^3J_{H-H} = 9.9$ Hz, 4H, CH_2(cod)], 2.07 [d, $^3J_{H-H} = 10.2$ Hz, 4H, CH_2(cod)]. ^{13}C-NMR (100 MHz, CD_3NO_2, 20°C): $\delta = 81.7$ [d, $^1J_{Rh-C} = 12.3$ Hz, *C*H(cod)], 48.0 [CH_2–N], 30.5 [CH_2(cod)], 28.8 [CH_2–S]. IR (KBr): ν(cm^{-1}) = 3278 s, 2939 m, 2924 m, 2882 s, 2834 m, 1311 m, 1434 s, 1056 ss, 1019 ss, 872 s. MS (FD, CH_2Cl_2), *m*/*z* (%): 314 [Rh(cod)(thiomorpholine)]$^+$.

4.8. General procedure for the oxidative amination of styrene

Catalytic reactions: 0.11 mmol of catalyst and 0.22 mmol of PPh_3 were suspended under argon in 10 ml THF or DMAc. Subsequently, 4.40 mmol of amine and 17.6 mmol of styrene were added at room temperature (r.t.). The mixture was heated to reflux for 20 h and analyzed by GCMS. The yield was determined by gas chromatography using hexadecane as internal standard. Isolation of amine products was performed according to [5].

4.9. X-ray crystallographic analysis of **2**

Details are given in Table 6. Suitable single crystals were obtained by slow diffusion of pentane in a THF solution of **2** at r.t. A systematic search in reciprocal space using an Enraf Nonius CAD4 diffractometer showed that crystals of **2** belong to the orthorhombic system. The resulting data set was transferred to a DEC 3000 AXP computer, and for all subsequent calculations the STRUX-V package was used [20]. No correction of intensity or absorption was applied. The structure was solved by direct and Fourier methods. The refinements were carried out by full matrix least-squares with isotropic and then with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms. All hydrogen atoms were found and positions were refined with the following restraints: C–H distances at C12, C14, C16, C22, and C26 were fixed (0.99 Å). All hydrogen atoms in THF were put in their geometrically calculated positions and refined 'riding' on the corresponding carbon atoms.

4.10. X-ray crystallographic analysis of **4b**

Details are given in Table 7. Suitable single crystals were obtained by slow diffusion of diethylether in a methylene chloride of **4b** solution at r.t. A systematic search in reciprocal space using an STOE&CIE IPDS diffractometer showed that crystals of **4b** belong to the monoclinic system. The resulting data set was transferred to a DEC 3000 AXP and a Micro-VAX 3100 computer, and for all subsequent calculations the STRUX-V package was used [20]. No correction of intensity or absorption was applied. The structure was solved by direct and Fourier methods. The refinements were carried out by full matrix least-squares with isotropic and then with anisotropic thermal parameters

Table 6
Crystal data and data collection for **2**

Empirical formula	$C_{22}H_{42}BF_4N_2ORh$
Habit	Colorless rectangular parallelepiped
Unit cell dimensions	$a = 11.0228(4)$ Å, $\alpha = 90°$
	$b = 11.8312(5)$ Å, $\beta = 90°$
	$c = 18.9404(6)$ Å, $\gamma = 90°$
V (Å^3)	2457.0(2)
Z	4
Wavelength (Å)	1.54184, Cu–K_α, Graphite monochromator
Temperature (K)	193(2)
Space group	$P2_12_12_1$, Orthorhombic
Crystal size (mm^3)	$0.23 \times 0.23 \times 0.20$
Absorption correction	None, $\mu = 60.2$ cm^{-1}
Diffractometer	CAD4 (Enraf Nonius)
Measurement method	$\theta/2\theta$-scan
θ_{min}	4.41
θ_{max}	67.92
h	$-13 < h < 0$
k	$-14 < k < 14$
l	$0 < l < 22$
Reflections collected	4628
Independent reflections	4287
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0384$, $wR_2 = 0.0940$
R indices (all data)	$R_1 = 0.0428$, $wR_2 = 0.1012$

Table 7
Crystal data and data collection for **4b**

Empirical formula	$C_{14}H_{24}F_3N_2O_3RhS$
Habit	Yellow square plates
Unit cell dimensions	$a = 13.5985(7)$ Å, $\alpha = 90°$
	$b = 9.1768(3)$ Å, $\beta = 103.729(5)°$
	$c = 14.4497(7)$ Å, $\gamma = 90°$
V (Å^3)	1751.67(14)
Z	4
Wavelength (Å)	0.71073, Mo–K_α, Graphite monochromator
Temperature (K)	193(2)
Space group	$P2_1/n$, Monoclinic
Crystal size (mm^3)	$0.25 \times 0.25 \times 0.10$
Absorption correction	None, $\mu = 11.4$ (cm^{-1})
Diffractometer	IPDS (STOE&CIE)
Measurement method	$\theta/2\theta$)-scan
θ_{min}	2.65
θ_{max}	27.72
h	$-17 < h < 16$
k	$-8 < k < 11$
l	$-18 < l < 18$
Reflections collected	8584
Independent reflections	3695
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0247$, $wR_2 = 0.0582$
R indices (all data)	$R_1 = 0.0332$, $wR_2 = 0.0611$

in the last cycles for all non-hydrogen atoms. Hydrogen atoms at C3, C4, C7, and C8 were put in their geometrically calculated positions and refined 'riding' on the corresponding carbon atoms.

5. Summary

Cationic diolefin-rhodium-amine complexes have been identified and characterized by X-ray for the first time. They play an important role in the catalytic regioselective anti-Markovnikov oxidative amination of styrenes.

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