Anti-Markonikov Reactions, 6[+]

Rhodium-Catalyzed Amination of Vinylpyridines: Hydroamination versus Oxidative Amination

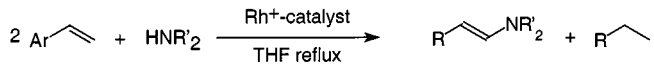
Matthias Beller,*[a,b] Harald Trauthwein,[b] Martin Eichberger,[†] Claudia Breindl,[b] and Thomas E. Müller[b]

Keywords: Coordination chemistry / Rhodium / Aminations / Hydroaminations / Oxidative aminations / Vinylpyridines

Cationic rhodium complexes catalyze the amination of 2- and 4-vinylpyridine with secondary amines. Depending on the substrate and the reaction conditions either oxidative amination to yield the corresponding enamines **1a−8a** or hydroamination to give 2-aminoethylpyridines **1b−8b** occurs. In all cases products with anti-Markovnikov regioselectivity are obtained. For mechanistic studies novel cationic complexes of rhodium(I)-containing cyclooctadiene and vinylpyridine **12** as well as complexes containing cyclooctadiene, vinylpyridine, and morpholine **13** were prepared and characterized by NMR spectroscopy and X-ray diffraction analysis.

Introduction

The construction of carbon−nitrogen bonds by using transition metal catalysts, especially for the synthesis of amines, has become an area of intensive research. Catalytic aminations of olefins[2] to selectively give primary, secondary, or tertiary amines are particularly interesting because of the atom efficiency of the process and the availability of feedstocks. One of the few examples is the newly developed intermolecular oxidative amination of aromatic olefins to give enamines.[3] Interestingly, this reaction yields the anti-Markovnikov products in a highly selective manner (Scheme 1).



Ar = aryl; R' = aryl, alkyl

Scheme 1. Anti-Markovnikov oxidative amination of styrene

This amination process allows the conversion of simple monoamines, such as piperidine and diethylamine, into the corresponding ω-enamines in good yields by employing cationic (phosphane)rhodium complexes as catalysts. An additional equivalent of the aromatic olefin is concurrently reduced to ethylbenzene. For the first time the transition-metal-catalyzed hydroamination of styrene is possible in an anti-Markovnikov manner with amines, such as morpholine, that contain a hemilabile second coordination site.[1]

In connection with mechanistic studies to understand the features that control whether hydroamination or oxidative amination of olefins occurs, we became interested in the reaction of vinylpyridines. Additional interest in these reactions results from the fact that 2-(2′-aminoethyl)pyridines are used as building blocks for pharmaceuticals and fine chemicals for hydrometallurgy.[4]

In contrast to styrene, 2- and 4-vinylpyridine are Michael systems, i.e. the double bond is in conjugation with an electron-withdrawing group. This activation favors the anti-Markovnikov hydroamination of 2- and 4-vinylpyridine. However, in contrast to acrylamide or acrylnitrile, which react quantitatively with amines without a catalyst even under mild conditions, 2- and 4-vinylpyridine react only sluggishly without a catalyst due to the weaker electron-withdrawing effect of the pyridine ring.

The hydroamination of vinylpyridines was first reported in the late 1940s.[5] Typically, the hydroamination of vinylpyridines is catalyzed by either acid or base.[6] For example, Matusko et al. obtained good results with vinylpyridines by employing a mixture of methanol and acetic acid.[7] However, some amines, like pyrrolidine, are not basic enough to react under these conditions. Successful amination of 2-vinylpyridine occurs when the reaction is performed with the addition of catalytic sodium metal in order to generate the more nucleophilic amide.[8] Surprisingly, the use of transition metal catalysts in the amination of vinylpyridines is rare.[9]

In this report we present for the first time various amination reactions of 2- and 4-vinylpyridines using cationic rhodium catalysts. Depending on the reaction conditions, varying amounts of hydroamination and oxidative amination products are obtained. In order to understand the mechanistic background, new cationic rhodium complexes that contain 2-vinylpyridine as a ligand have been isolated and characterized by X-ray crystallography. These complexes are shown to be important intermediates in the catalytic hydroamination of vinylpyridines.

[+] Part 5: Ref.[1]

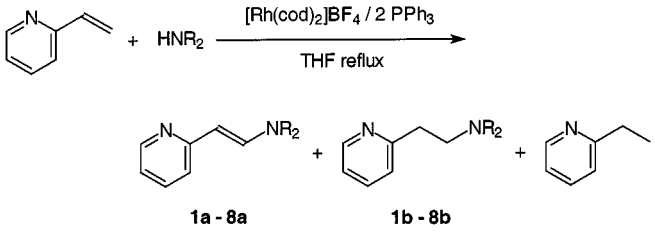
[a] Institut für Organische Katalyseforschung (IfOK) an der Universität Rostock e.V.,
Buchbinderstraße 5−6, D-18055 Rostock, Germany
[b] Anorganisch-chemisches Institut, Technische Universität München,
Lichtenbergstraße 4, D-85747 Garching, Germany
[†] Deceased 1997.

  1434−1948/99/0707−1121 $ 17.50+.50/0

Results and Discussion

Catalytic Amination of 2- and 4-Vinylpyridine

Cationic (phosphane)rhodium complexes such as $[Rh(cod)_2]BF_4/2\ PPh_3$ are the only known class of active transition metal catalysts for the intermolecular anti-Markovnikov amination and hydroamination of styrenes.[2] In order to investigate how these catalysts effect the amination of a more activated olefin the reaction of 2-vinylpyridine with piperidine was chosen for initial studies (Scheme 2). Under the typical reaction conditions of the oxidative amination of styrene (THF reflux, 2.5 mol-% $[Rh(cod)_2]BF_4$/ 2 PPh_3, 20 h) three products are obtained. The major product, *N*-[2-(2′-pyridyl)ethyl]piperidine (**2b**), resulting from a hydroamination reaction, was isolated in 53% yield. Also, for the first time an intermolecular oxidative amination of 2-vinylpyridine was achieved giving *N*-[2-(2′-pyridyl)ethenyl]piperidine (**2a**) in 47% yield. A second equivalent of 2-vinylpyridine is concurrently reduced to 2-ethylpyridine, which was isolated in 42% yield. All yields are based on piperidine.



Scheme 2. Rhodium-catalyzed amination of 2-vinylpyridine

As expected, all amination reactions occur exclusively with anti-Markovnikov regioselectivity. This is explained by the strong polarization of the vinyl group by the pyridine ring. When the reaction is performed under identical conditions without a catalyst the hydroamination product *N*-[2-(2′-pyridyl)ethyl]piperidine is obtained in only 3% yield. Hence, both the hydroamination and the oxidative amination are catalyzed by the cationic rhodium catalyst.

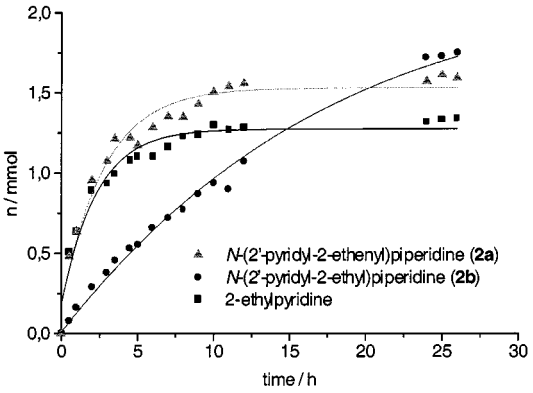


Figure 1. Time/concentration diagram for the reaction of 2-vinylpyridine and piperidine

In a further catalysis experiment the reaction of piperidine with 2-vinylpyridine to form the different amination products was followed with time. As depicted in Figure 1 it is evident that enamine and ethylpyridine are formed mainly during the first hours. After about 10 h, no further enamine formation is observed. In contrast, only a small amount of aminoalkylpyridine is formed at the beginning of the reaction, but the rate of its formation remains nearly constant until all piperidine is consumed. Similar to the oxidative amination of styrene, the enamine formation is probably catalyzed by cationic rhodium species that contain monodentate phosphane ligands. During the course of the reaction the rhodium catalyst is deactivated, either by loss of its cationic character or by the formation of chelate complexes with the products behaving as bidentate ligands. Independent of the oxidative amination process, the formation of the alkylamine proceeds by a different mechanism. In order to gain further insight into the different reaction pathways and to evaluate the critical reaction parameters for both oxidative amination and hydroamination we varied the catalyst system and the reaction conditions (Table 1).

The oxidative amination proceeds best with THF as the solvent (entries 1, 6). The catalyst is also active in toluene, although the formation of alkylamine is increased (entry 2). The dipolar aprotic solvent dimethylacetamide (DMAC) completely inhibits the enamine formation and lowers the yield of alkylamine (entry 3). By reducing the amount of catalyst from 2.5 mol-% to 1 mol-% (entry 1 vs. 4) it is shown that the oxidative amination is more sensitive than the hydroamination to the concentration of the cationic catalyst. This is a good indication that the hydroamination reaction is catalyzed by various rhodium species, while the oxidative amination is catalyzed by a discrete cationic (phosphane)rhodium complex. Further support for this assumption comes from the fact that the presence of phosphane is a prerequisite for enamine formation (entry 5). In the presence of $[Rh(cod)_2]BF_4$ without triphenylphosphane, only hydroamination occurs to give *N*-[2-(2′-pyridyl)ethyl]-piperidine (**2b**) in high yields (97%). By lowering the ratio of vinylpyridine to piperidine to 2:1 the oxidative amination becomes the major reaction pathway and *N*-[2-(2′-pyridyl)ethenyl]piperidine (**2a**) is isolated in 82% yield (entry 6). The different influence of the olefin/amine ratio on the oxidative amination of styrenes and 2-vinylpyridines can be explained by the different coordination ability of styrene and 2-vinylpyridine. 2-Vinylpyridine is able to coordinate to the rhodium center through the pyridine-nitrogen atom, which is not possible for styrene. The coordination of the nitrogen atom of pyridine activates the olefinic bond in 2-vinylpyridine for a nucleophilic attack of the amine, which enhances hydroamination but has no effect on the oxidative amination. In contrast, we assume that the oxidative amination proceeds by an amine-activation mechanism. A lower concentration of 2-vinylpyridine would favor the coordination of the amine to the rhodium center, which facilitates N−H activation.

In order to investigate the influence of pK_a, steric and electronic parameters of the amines on the amination reaction, we tested different aliphatic amines R_2NH, such as piperazines, which have an additional functional group (Table 2).

Table 1. Rhodium-catalyzed reaction of 2-vinylpyridine and piperidine[a]

Entry	Olefin/Amine	Catalyst (mol-%)	Solvent, reaction time	Amine product (%)	Enamine (%)	Ethylpyridine (%)	Amine product/Enamine
1	4:1	$[Rh(cod)_2]BF_4$/2 PPh_3 (2.5)	THF, reflux, 20 h	53	47	42	1.1
2	4:1	$[Rh(cod)_2]BF_4$/2 PPh_3 (2.5)	Toluene, reflux, 20 h	61	30	24	2.0
3	4:1	$[Rh(cod)_2]BF_4$/2 PPh_3 (2.5)	DMAC, 140 °C, 20 h	44	< 0.1	21	–
4	4:1	$[Rh(cod)_2]BF_4$/2 PPh_3 (1.0)	THF, reflux, 20 h	47	8	7	5.9
5	4:1	$[Rh(cod)_2]BF_4$ (2.5)	THF, reflux, 20 h	97	2	2	48.5
6	2:1	$[Rh(cod)_2]BF_4$/2 PPh_3 (2.5)	THF reflux, 20 h	16	82	46	0.2

[a] The yield was determined by GC with hexadecane as internal standard and is referred to amine.

Table 2. Rhodium-catalyzed amination of 2-vinylpyridine with aliphatic amines[a]

Entry	Amine (pK_a)[23]	Enamine (%)	Amine product[b] (%)	Ethylpyridine (%)	Amine product/Enamine
1	Pyrrolidine (11.27)	54 [**1a**]	21 (3) [**1b**]	56	0.4
2	Piperidine (11.02)	47 [**2a**]	53 (8) [**2b**]	42	1.1
3	Hexahydroazepine	30 [**3a**]	29 (< 1) [**3b**]	25	1.0
4	Morpholine (8.33)	2 [**4a**]	98 (5) [**4b**]	2	49
5	Thiomorpholine	< 1	98 (26) [**5b**]	< 1	> 99
6	Piperazine (9.83)	[c]	[c]	[c]	–
7	*N*-Methylpiperazine	20 [**7a**]	62 (6) [**7b**]	23	3.1
8	*N*-Phenylpiperazine	8 [**8a**]	91 (10) [**8b**]	6	11.4
9a–c	HNR_2, R = Et (10.49), *i*Pr, *n*Bu	< 1	< 1	< 1	–
10	*n*-Butylamine	< 1	< 1	< 1	–

[a] 2-Vinylpyridine/amine = 4:1, 2.5 mol-% $[Rh(cod)_2]BF_4$/2 PPh_3 referred to amine, THF reflux, 20 h. The yield was determined by GC with hexadecane as internal standard and is referred to amine. – [b] The results of the uncatalyzed reaction under the same conditions as the rhodium-catalyzed reaction are shown in parentheses. – [c] The reaction of piperazine is shown in Scheme 3.

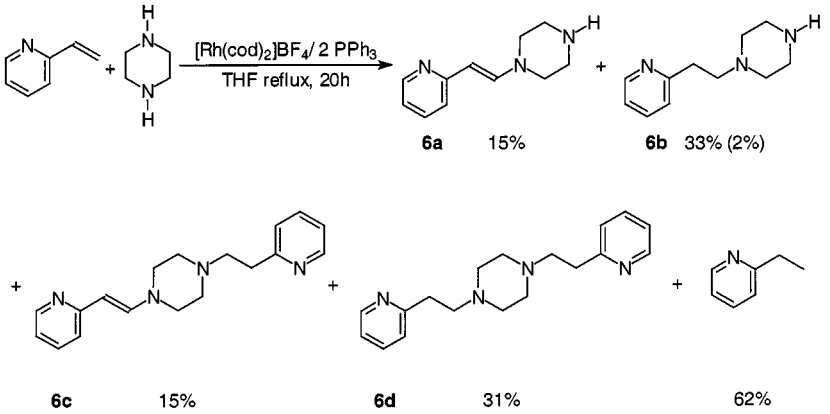
The reactions were performed in refluxing THF for 20 h. In all cases only the 2-(2′-aminoethyl)pyridine derivatives were detected as hydroamination products due to the polarization of the double bond. The yields, which were obtained without a catalyst, are given in brackets. Apart from thiomorpholine the amines reacted only to a slight extent (< 10%) without a catalyst. Also, no oxidative amination was observed, i.e. neither the corresponding enamine nor ethylpyridine was formed. Comparing the ring size of the amine applied (pyrrolidine, piperidine, and hexahydroazepine) it is evident that the yield of the oxidative amination product decreases with increased ring size of the amine, with pyrrolidine providing the highest yield in enamine. Bifunctional amines predominantly led to hydroamination reactions. It is likely that the conformation favored by the chelating effect infers the β-H-elimination step that is required for oxidative amination. Interestingly, enamine formation was observed to some extent with all three piperazine derivatives. This is in contrast to the rhodium-catalyzed amination of styrene and piperazine derivatives. In the latter reaction chelating amines inhibit the reaction, which is caused by the formation of insoluble (piperazine)rhodium complexes.[10] Thus, we assume that the amination of 2-vinylpyridine proceeds by activation of the 2-vinylpyridine.

Piperazine, which has two reactive N–H groups, leads to the formation of five different products (Scheme 3). Apart from 2-ethylpyridine, mono- and dialkylated piperazines **6a–d** were obtained in a ratio of 2.2:1:2.1:1.

The ratio of hydroamination products **6b** and **6d** to enamines **6a** and **6c** is approximately 2:1. Surprisingly, no product with two enamine groups was detected. Hence, it is assumed that the dialkylated products are formed mainly by a consecutive reaction of *N*-[2-(2′-pyridyl)ethyl]piperazine. This might be due to the better coordination ability of *N*-[2-(2′-pyridyl)ethyl]piperazine (**6b**) in comparison to *N*-[2-(2′-pyridyl)ethenyl]piperazine (**6a**).

In addition to aliphatic amines, we tested aromatic amines (aniline, pyrrole) as well as amides (acetamide) in the rhodium-catalyzed amination of 2-vinylpyridines. Unfortunately, these substrates did not react in either a hydroamination or in an oxidative reaction. We explain this behavior as being due to the lower pK_a value of these substrates compared to that of 2-vinylpyridine [pK_a(pyridine) = 5.2]. Due to the lower nucleophilicity, hydroamination does not occur even after activation of vinylpyridine. Oxidative amination is not observed because the formation of (amine)rhodium complexes is unfavorable. Hence, N–H activation by the rhodium center is not possible.

Next, we studied the reaction of 4-vinylpyridine with three amines (Table 3). None of the amines reacted with 4-vinylpyridine in the absence of a rhodium catalyst. In the presence of the catalyst system $[Rh(cod)_2]BF_4$/2 PPh_3 all



Scheme 3. Reaction of 2-vinylpyridine and piperazine; the yields obtained without catalyst are given in parentheses

Table 3. Rhodium-catalyzed amination of 4-vinylpyridine with aliphatic amines[a]

Entry	Amine	Enamine (%)	Pyridylamine (%)	Ethylpyridine (%)
1	Piperidine	< 1	57 [**9**]	< 1
2	Hexahydroazepine	< 1	21 [**10**]	< 1
3	Morpholine	< 1	54 [**11**]	< 1

[a] 4-Vinylpyridine/amine = 4:1, 2.5 mol-% $[Rh(cod)_2]BF_4$/2 PPh_3 referred to amine, THF reflux, 20 h. The yield is referred to amine and was determined by GC with hexadecane as internal standard.

amines employed gave only the terminal hydroamination products **9**, **10**, **11**. Oxidative amination was not observed. It is evident that for oxidative amination to occur both the nitrogen atom of the pyridine ring and the vinyl group have to be in steric proximity to the rhodium center.

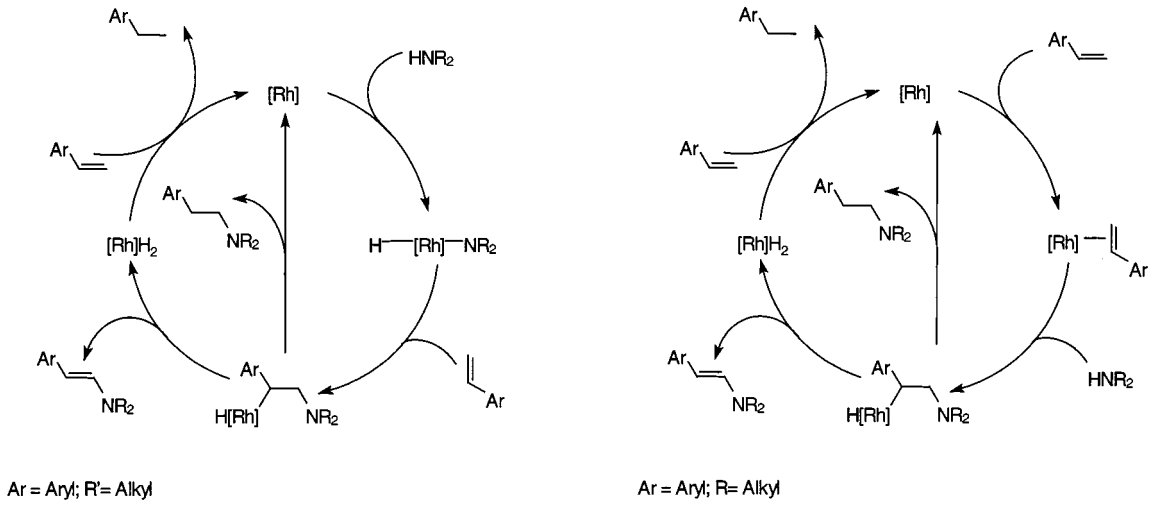
Mechanistic Studies − Cationic Rhodium Complexes with 2-Vinylpyridine as Ligand

Amination of olefins can take place either by activation of the olefin or by activation of the amine N−H bond.[11] In general, non-functionalized olefins become susceptible towards nucleophiles upon complexation to an electrophilic metal center. Addition of a nucleophile to the metal-bound olefin and protolysis yields the corresponding product and the catalyst. Alternatively, β-hydride elimination results in the formation of imines or enamines. It is important to note that catalytic activation of olefins in the presence of amines is difficult to achieve due to the strong binding of amines to electrophilic metal centers. One possible amine activation pathway involves oxidative addition of an amine to an unsaturated metal center in a low oxidation state. The resulting amido hydrido complex may insert an olefin into the metal−nitrogen bond yielding an aminoalkyl hydrido complex. Subsequent reductive elimination of the amine produced regenerates the catalyst. Alternatively, β-hydride elimination can take place to give enamines and dihydridometal complexes.

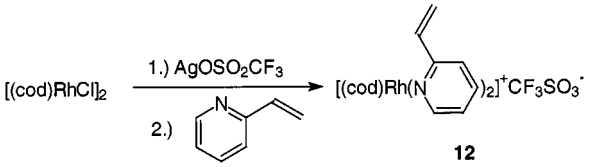
In contrast to other olefins, vinylpyridines can be activated by cationic rhodium complexes either by coordination of the double bond, the heteroaromatic ring or by coordination of the nitrogen atom. As suggested above, the mode of coordination of the vinylpyridine is of fundamental importance for explaining the various results obtained in the amination of 2- and 4-vinylpyridine. Therefore, we investigated the coordination chemistry of cationic rhodium complexes with amines and 2-vinylpyridine as ligands.

In contrast to the organometallic chemistry of cationic rhodium complexes with secondary amines that has been described recently,[10] rhodium complexes with 2-vinylpyridine as a ligand have not been studied in detail. Denise and Pannetier described the synthesis of $[Rh(cod)(2\text{-vinylpyridine})_2]PF_6$ by treatment of $[Rh(cod)Cl]_2$ with 2-vinylpyridine and $NaPF_6$.[12] However, no detailed characterization by NMR and X-ray studies of this complex has been performed. Therefore, we synthesized $[Rh(cod)(2\text{-vinylpyridine})_2]OSO_2CF_3$ (**12**) by combining $[Rh(cod)Cl]_2$ and $AgOSO_2CF_3$ followed by addition of 2-vinylpyridine.

At room temperature the ^{1}H-NMR spectrum (Figure 2) of **12** shows several broad resonances indicating fluxionality in the molecule. The signals at $\delta = 8.9$ and 8.7 are assigned to 6-H in the pyridine ring and the internal proton of the olefin, respectively. The other signals in the olefinic and aromatic region of the ^{1}H-NMR spectrum are sharper and are ascribed to 4-H ($\delta = 7.66$), 3-H ($\delta = 7.55$), and 5-H ($\delta = 7.32$). The terminal olefinic protons of the vinyl group show resonances at $\delta = 6.05$. Clearly, the protons that are adjacent to the rhodium center have broader signals compared to the protons that are further away from the metal center. The resonances of both the olefinic protons at $\delta = 4.0$ and the two sets of aliphatic protons of the cod ligand at $\delta = 2.7$ and 2.0 are very broad at room temperature, which is most likely caused by free rotation of the 2-vinylpyridine. Upon cooling **12** to −60°C the broad signals in the ^{1}H-NMR spectrum sharpen to give clearly distinguishable signals. It is interesting to note that the resonances of the olefins show a vicinal and geminal coupling of $J = 11$



Scheme 4. Catalytic cycles for the amination of aromatic olefins by (a) amine activation and (b) olefin activation



Scheme 5. Synthesis of the cationic complex [Rh(cod)(2-vinylpyridine)$_2$]CF_3SO_3 (**12**)

and 17 Hz, respectively. The signals of the cod protons, which appear as three sharp pseudo-doublets, can be used as a probe for the conformation of **12**. Due to steric reasons, both vinyl groups should be opposite to each other.

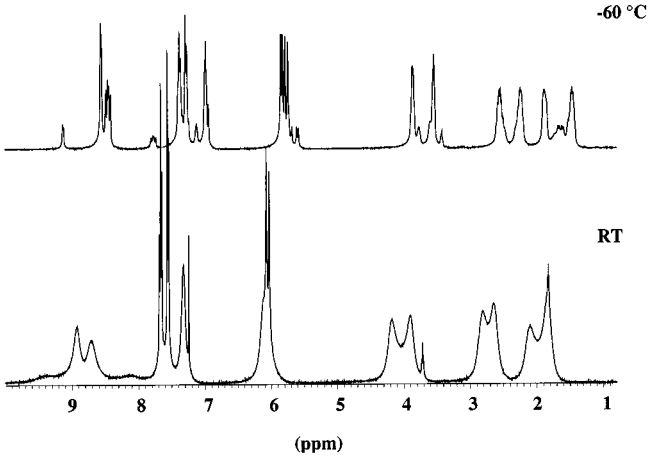


Figure 2. ^{1}H-NMR spectrum of [Rh(cod)(2-vinylpyridine)$_2$]CF_3SO_3 at room temperature and at −60°C in $CDCl_3$

The ^{13}C-NMR spectrum supports this conformational analysis. At room temperature the resonances of the olefinic carbon atoms of the cod ligand are very broad. However, at −60°C two doublets appear, due to the Rh-C coupling ($J_{Rh\text{-}C}$ = 12.6 and 11.7 Hz). This confirms that the olefinic carbon atoms are not identical. Also, there is no interaction between the vinyl group of the 2-vinylpyridine and the rhodium center, as no Rh-C coupling was detected here.

In both the ^{1}H-NMR and the ^{13}C-NMR spectra a second set of patterns (5% intensity) appears upon lowering the temperature. We tentatively ascribe this minor pattern to a rhodium species with pyridine rings, where both vinylic groups are pointing in the same direction.

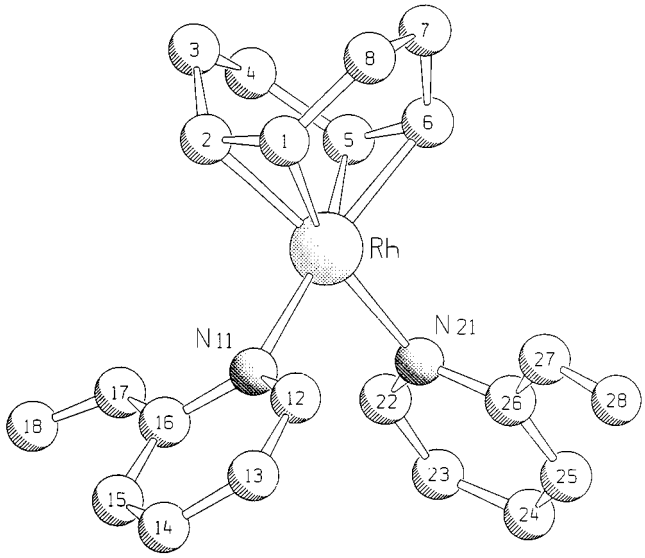


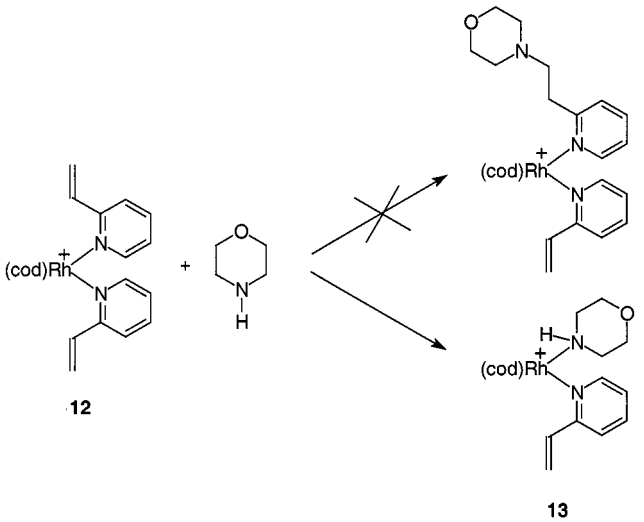
Figure 3. The molecular structure of [Rh(cod)(2-vinylpyridine)$_2$]$^+$

Crystals of **12** were obtained by slowly adding diethyl ether to a dichloromethane solution of **12**. The X-ray analysis (Table 4) is in agreement with the conformation discussed on the basis of the NMR studies. The rhodium center is in an approximately square-planar coordination sphere. The lengths of the rhodium−amine bonds [Rh−N11 = 2.129(2) Å and Rh−N21 = 2.118(3) Å] and the distances from rhodium to the centers X1 and X2 of the cod double bonds C1−C2 and C5−C6 (Rh−X1 = 2.019 Å, Rh−X2 = 2.018 Å) are within the typical range. The angles X1−Rh−X2 (87.6°) and N11−Rh−N21 [89.2(1)°] are close to right angles. The coordination sphere is distorted tetraedric. Associated distances from a mean plane contain-

Table 4. Selected bond lengths [Å] and angles [°] of [Rh(cod)(2-vinylpyridine)$_2$]CF_3SO_3 (**12**)

Rh−N(11)	2.129 (2)	Rh−N(21)	2.118 (3)
Rh−C(1)	2.122 (4)	Rh−C(2)	2.139 (3)
Rh−C(5)	2.121 (3)	Rh−C(6)	2.143 (3)
C(1)−C(2)	1.385 (5)	C(5)−C(6)	1.386 (6)
C(17)−C(18)	1.303 (6)	C(27)−C(28)	1.308 (6)
N(11)−Rh−C(2)	92.42 (11)	N(11)−Rh−C(6)	163.90 (13)
N(21)−Rh−C(1)	157.70 (13)	N(21)−Rh−C(2)	164.34 (13)
N(21)−Rh−C(5)	91.04 (14)	N(21)−Rh−C(6)	92.74 (14)
N(11)−Rh−N(21)	89.23 (10)	N(11)−C(16)−C(17)	117.4 (3
N(21)−C(26)−C(27)	117.2 (3)	C(1)−Rh−C(2)	37.93 (14)
C(1)−Rh−C(5)	97.9 (2)	C(1)−Rh−C(6)	82.2 (2)
C(1)−Rh−N(11)	89.94 (12)	C(2)−Rh−C(5)	81.7 (2)
C(2)−Rh−C(6)	90.0 (2)	C(5)−Rh−C(6)	37.9 (2)
C(5)−Rh−N(11)	158.06 (13)		

ing the rhodium atom are X1 +0.057 Å, X2 −0.061 Å, N21 +0.053 Å and N11 −0.057 Å. The 2-vinylpyridine ligands are arranged perpendicular to the coordination plane (82.1°, 89.2°), so that both ring systems are also perpendicular to each other (88.2°). The vinylic groups are on opposite sides of the coordination plane and are slightly twisted against the parent aromatic ring (5.9° and 13.6° for the vinyl group defined by C16, C17, C18 and C26, C27, C28, respectively). There is no coordinative interaction of the vinylic group in the two 2-vinylpyridine ligands with the rhodium center. This is confirmed by a shorter vinylic double bond [C17−C18 = 1.303(6) Å, C27−C28 = 1.308(6) Å] compared to the double bonds in the cod ligand [C1−C2 = 1.385(5) Å, C5−C6 = 1.386(6) Å].



Scheme 6. Reaction of [Rh(cod)(2-vinylpyridine)$_2$]CF_3SO_3 (**12**) with morpholine

Cationic rhodium complexes containing an amine as well as a 2-vinylpyridine ligand are likely intermediates in the catalytic cycle of the amination of 2-vinylpyridine. In order to gain more insight into this system we studied the stoichiometric reaction of [Rh(cod)(2-vinylpyridine)$_2$]CF_3SO_3 (**12**) with 2 equivalents of morpholine. The reaction led to [Rh(cod)(morpholine)(2-vinylpyridine)]CF_3SO_3 (**13**), which was formed in 84% yield (Scheme 6). This is confirmed by mass spectrometry and elemental analysis as well as by IR spectroscopy, where a strong N−H frequency at 3215 cm^{-1} is observed. Interestingly, there is no indication for an attack of the amine on the activated vinyl group of the 2-vinylpyridine.

The ease of formation of the (morpholine)(2-vinylpyridine)rhodium complexes suggests that these complexes are precursors for the intermediates in the catalytic cycle.

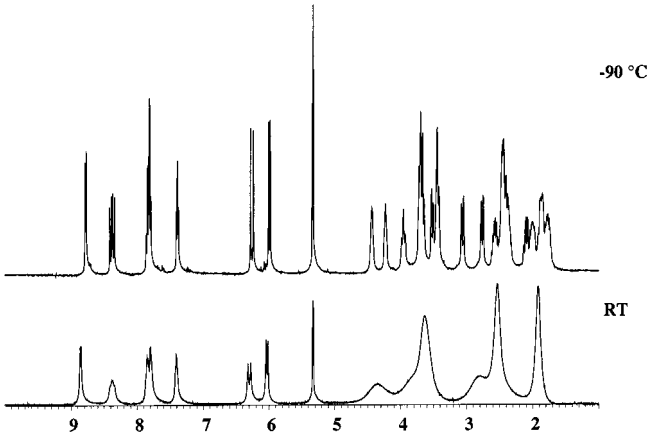


Figure 4. ^{1}H-NMR spectrum of [Rh(cod)(morpholine)(2-vinylpyridine)]CF_3SO_3 (**13**) at room temperature and at −90°C in CD_2Cl_2

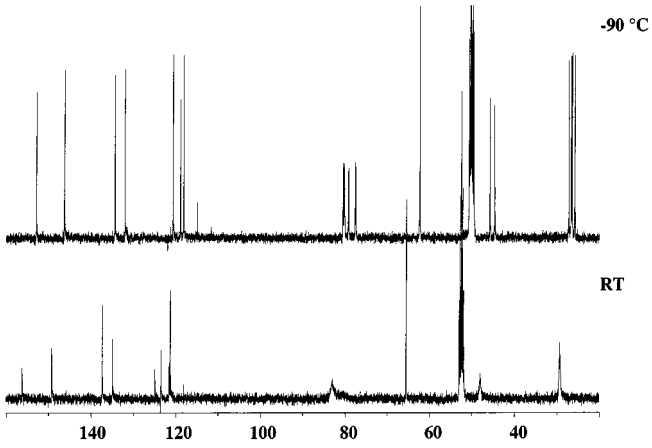


Figure 5. ^{13}C-NMR spectrum of [Rh(cod)(morpholine)(2-vinylpyridine)]CF_3SO_3 (**13**) at room temperature and −90°C in $CDCl_3$

The ^{1}H- and ^{13}C-NMR spectra of [Rh(cod)(morpholine)(2-vinylpyridine)]CF_3SO_3 (**13**) are depicted in Figures 4 and 5, respectively. The signals in the ^{1}H-NMR spectrum at room temperature are broad, especially in the aliphatic region. ^{1}H-NMR analysis at −90°C shows sharper signals, which indicates the existence of a preferential conformation. The splitting of the resonances reveals interesting details about the preferred low-temperature conformation. The multiplets at δ = 3.67 and 3.43 are assigned to the olefinic cod protons as well as the protons of the morpholine protons adjacent to the oxygen atom. There is also a splitting of the resonance of the methylene group of the morpholine ligand adjacent to the nitrogen atom with signals observed at δ = 3.05 and 2.75.

The ^{13}C-NMR spectrum shows similar behavior. The olefinic and the aliphatic cod resonances are very broad at room temperature, but at −90°C the broad olefinic signal at δ = 82.9 is split into four doublets, while the broad aliphatic signal at δ = 29.3 is split into four singlets. Information about the conformation of the morpholine ligand can be obtained from the ^{13}C-NMR spectrum at −90°C. The signal of the methylene group adjacent to the oxygen atom is a singlet, whereas the resonance of the methylene group adjacent to the nitrogen atom is a doublet. The latter methylene groups seem to be influenced by the 2-vinylpyridine ring, whereas the methylene groups adjacent to the oxygen atom in the morpholine ligand are too far away from the pyridine ring for the resonance to be split. Complex **13** was also characterised by X-ray crystallography. The molecular structure of **13** is shown in Figure 6 and selected bond lengths and angles are summarized in Table 5.

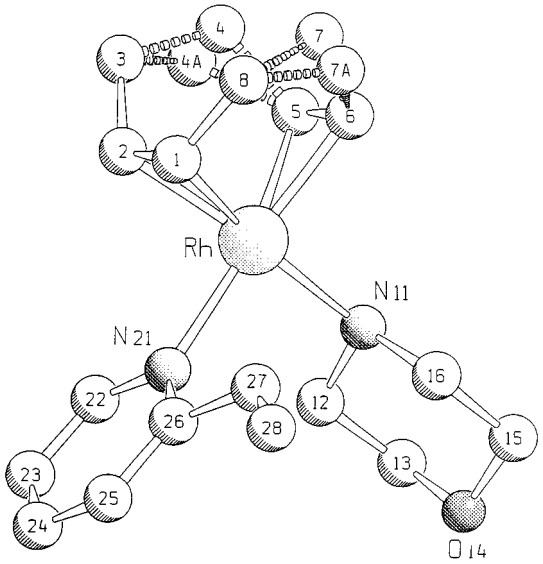


Figure 6. The molecular structure of [Rh(cod)(morpholine)-(2-vinylpyridine)]$^{+}CF_3SO_3^{-}$

Table 5. Selected bond lengths [Å] and angles [°] of [Rh(cod)(morpholine)(2-vinylpyridine)]CF_3SO_3 (**13**)

Rh−C(1)	2.132(3)	Rh−C(2)	2.139(3)
Rh−C(5)	2.123(3)	Rh−C(6)	2.111(3)
Rh−N(11)	2.155(2)	Rh−N(21)	2.129(3)
C(1)−C(2)	1.360(5)	C(5)−C(6)	1.360(6)
C(27)−C(28)	1.310(6)		
C(1)−Rh−C(2)	37.12(14)	C(1)−Rh−C(5)	94.4(2)
C(1)−Rh−C(6)	82.26(14)	C(1)−Rh−N(11)	162.78(13)
C(2)−Rh−C(5)	81.01(13)	C(2)−Rh−C(6)	92.33(14)
C(2)−Rh−N(11)	160.00(12)	C(5)−Rh−C(6)	37.5(2)
C(5)−Rh−N(11)	90.60(12)	C(5)−Rh−N(21)	157.1(2)
C(6)−Rh−N(11)	91.89(12)	C(6)−Rh−N(21)	165.0(2)
C(12)−N(11)−Rh	115.0(2)	C(16)−N(11)−Rh	112.7(2)
C(16)−N(11)−C(12)	109.5(2)	N(21)−Rh−C(1)	90.46(12)
N(21)−Rh−C(2)	89.65(11)	N(21)−Rh−N(11)	91.30(9)
N(21)−C(26)−C(27)	115.3(3)		

The rhodium center is coordinated in a square-planar fashion with the bond lengths Rh−N11 = 2.155(2) Å and Rh−N21 = 2.129(3) Å, as expected for cationic amine−-rhodium bonds.[10] The bond lengths from rhodium to the centers X1 and X2 of the two double bonds C1−C2 and C5−C6 associated with the cod ligand are 2.023 Å and 2.007 Å, respectively. Each ligand around the rhodium center is arranged nearly perpendicular to the two neighbors with X1−Rh−X2 = 87.4°, X2−Rh−N11 = 91.3°, N11−Rh−N21 = 91.3(1)° and N21−Rh−X1 = 89.9°. There is a slight pyramidal distortion, which can be seen by positive distances for each of the coordinating atoms from a plane through the rhodium center (X1 +0.022 Å, X2 +0.075 Å, N11 +0.027 Å and N21 +0.073 Å). The 2-vinylpyridine is arranged nearly perpendicular (87.8°) to the coordination plane. The vinyl group is twisted by 1.7° against the aromatic ring of the 2-vinylpyridine. The double bond of the vinyl group is significantly shorter than the double bonds of the cod ligand [C27−C28 = 1.310(6) Å vs. C1−C2 = 1.360(5) Å, C5−C6 = 1.360(6) Å]. This is in agreement with an elongation of the C1−C2 and C5−C6 bonds caused by their coordination to the rhodium center. There is no coordinative interaction of the rhodium center with the vinyl group in 2-vinylpyridine. The proton of the amine forms a hydrogen bond with the tosylate [H11···O1 = 2.27 Å, N11−H11 = 0.83(2) Å, N11−H11···O1 = 160.3°] and there is a C−H···O hydrogen bond between the aromatic ring and the oxygen atom of the morpholine ligand in a neighboring molecule (H24···O14 = 2.33 Å, C24−H24 = 0.93 Å, C24−H24···O14 = 159.0°).[13]

Table 6. Examples for complexes containing vinylpyridine as ligand; the lengths of the vinylic C−C bond, its distance from the metal center and the twist of the vinyl group against the pyridine ring are given

Complex	*d*(CC) [Å]	*d*(MX) [Å]	α [°]	Ref.
12	1.303(6)	n. b.	5.9	
	1.308(6)	n. b.	13.6	
13	1.310(6)	n. b.	1.7	
$[Cu_2(\mu\text{-vpy})_2(vpy)_2](ClO_4)_2$	1.307(23)	n. b.	10.0	[24a]
	1.368(17)	1.917	2.4	
	1.358(16)	1.903	5.7	
	1.319(23)	n. b.	14.9	
$[Cu(vpy)Cl]_\infty$	1.380(7)	1.940	1.9	[24b]
	1.378(7)	1.984	7.8	
$[Cu(vpy)I]_\infty$	1.29(2)	n. b.	10.0	[24b]
$[Ni(PPh_3)(vpy)]_2$	1.414(5)	1.848	9.9	[24c]
	1.433(5)	1.854	9.6	
$[Os_3(\mu\text{-H})_2(CO)_9(\mu\text{-CH-}\eta^2\text{-vpy})]$	1.43(2)	2.068	17.0	[24d]
$[Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-C-vpy})]$	1.39(2)	n. b.	28.2	[24d]

X = center of the vinylic C−C bond, vpy = 2-vinylpyridine, n. b. = non bonded.

The X-ray structures of complexes **12** and **13** reveal that in the solid state there is no binding interaction of the rhodium center with the vinyl group in 2-vinylpyridine. The consequence of this are relatively short C−C bond lengths in the vinyl groups, a fact that is in agreement with other late transition metal complexes containing the 2-vinylpyridine ligand (Table 6). The dimeric $[Cu_2(\mu\text{-vpy})_2(vpy)_2](ClO_4)_2$ (vpy = 2-vinylpyridine) incorporates two copper

centers bridged by two vinylpyridine molecules with each of the copper atoms coordinating one further vinylpyridine molecule in a monodentate fashion through the nitrogen atom. The C−C bonds of the two vinyl groups coordinated to the copper center [1.368(17) Å, 1.358(16) Å] are slightly longer compared to non-coordinated vinyl groups [1.307(23) Å, 1.319(23) Å]. Similar vinylic C−C bond lengths are observed in the complexes $[Cu(vpy)Cl]_\infty$ and $[Ni(PPh_3)(vpy)]_2$ [1.380(7) Å, 1.378(7) and 1.414(5) Å, 1.433(5) Å, respectively], which contain the vinylpyridine in a bridging fashion, whereas the vinylpyridine ligand in the complex $[Cu(vpy)I]_\infty$ is bound only through the nitrogen atom that is associated with a shorter vinylic C−C bond [1.29(2) Å]. Other examples are the complexes $[Os_3(\mu\text{-}H)_2(CO)_9(\mu\text{-}CH\text{-}\eta^2\text{-}vpy)]$ and $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C\text{-}vpy)]$. In these complexes the nitrogen atom of the vinylpyridine moiety is bound to a methylidyne and methylidene bridge connecting three or two osmium atoms, respectively. The vinyl group in the former complex is coordinated to the metal center, whereas it is not coordinated in the second complex. This is associated with slightly longer C−C bond lengths in the first complex [1.43(2) Å] compared to the latter complex [1.39(2) Å].

The comparison with these data confirms that in **12** and **13** there is no binding interaction of the rhodium center with the vinyl group in 2-vinylpyridine. Hence, the activation of 2-vinylpyridine in the presence of cationic rhodium complexes towards hydroamination most likely proceeds by a coordination of the rhodium center to the pyridine nitrogen atom, which leads to a decrease in the electron density of the vinyl group. Clearly, oxidative amination that takes place in the presence of additional phosphane ligands must take place by a different mechanism. Unfortunately, all efforts to isolate or characterize an (amine)(phosphane)(vinylpyridine)rhodium complex turned out to be unsuccessful. Further work in this direction is in progress.

Conclusion

For the first time the oxidative amination of 2-vinylpyridine is described. In the presence of cationic (phosphane)rhodium complexes both oxidative amination as well as hydroamination occurs to yield products with anti-Markovnikov regiochemistry. Interestingly, the ratio of enamine to alkylamine is strongly influenced by the solvent, the phosphane and the ratio of olefin to amine. It is assumed that the hydroamination is initiated by an activation of the 2-vinylpyridine through coordination of the pyridine nitrogen atom to the rhodium center. In contrast, oxidative amination proceeds by a different mechanism. While cyclic amines that do not contain additional heteroatoms give good yields of the corresponding enamines, hydroamination dominates in the case of bidentate amines such as morpholine. Hydroamination of 4-vinylpyridine is achieved under surprisingly mild conditions.

A possible intermediate for the catalyst formation, $[Rh(cod)(2\text{-vinylpyridine})_2]CF_3SO_3$ (**12**) was synthesized and completely characterized. **12** reacts selectively with morpholine to give $[Rh(cod)(morpholine)(2\text{-vinylpyridine})]CF_3SO_3$ (**13**), which is a likely intermediate in the catalytic cycle.

Experimental Section

Materials and Methods: All reactions of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk 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 or Aldrich and used as received. $[Rh(cod)Cl]_2$[14] and $[Rh(cod)_2]BF_4$[15] were prepared as described in the appropriate reference.

Physical and Analytical Methods: ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AT 360 and referenced in ppm relative to tetramethylsilane. − Infrared spectra were obtained with a Perkin−Elmer 1600 spectrometer. − Mass-spectrometric analysis was performed with a Finnigan MAT 311A by the Fast Atom Bombardment (FAB) method. − Elemental analyses were performed by the Microanalytical Laboratory of the Technische Universität München. − GC analyses were conducted with a Hewlett−Packard 6890 instrument using an HP-1 capillary column. Yields were determined against hexadecane as an internal standard. GC/MS analyses were conducted with a Hewlett-Packard 5890 with 70-eV electron impact ionization (detector: HP 5970 B).

Reaction of 2-Vinylpyridine with Pyrrolidine: 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol) were mixed in 10 mL of THF. Subsequently, 0.37 mL of pyrrolidine (4.40 mmol) and 1.90 mL of 2-vinylpyridine (17.6 mmol) were added at room temperature. The reaction was heated to reflux for 20 h before being cooled to room temperature. The yield of (*E*)-*N*-[2-(2-pyridyl)ethenyl]pyrrolidine (**1a**) was determined by gas chromatography with hexadecane as an internal standard. − In order to isolate a more stable derivative of (*E*)-*N*-[2-(2-pyridyl)ethenyl]-pyrrolidine (**1a**) , 0.5 g of Pd/C (5%) was added to the crude reaction and the mixture was stirred for 48 h under H_2 at a pressure of 1 atm. After filtration, the solvent was removed by evaporation. The residue was dissolved in 20 mL of dichloromethane and extracted three times with 5% HCl. The combined aqueous phases were neutralized by adding NaOH until pH = 9 was reached and the product was extracted three times with dichloromethane. The combined organic layers were dried with $MgSO_4$ and the solvent was distilled off. *N*-[2-(2-Pyridyl)ethyl]pyrrolidine (**1b**) was obtained after column chromatography (chloroform/methanol, 50:1) in 75% yield.

(*E*)-*N*-[2-(2-Pyridyl)ethenyl]pyrrolidine (1a): GC yield: 54%. − MS; *m/z*: 174 [M^+], 145 [$M^+ - C_2H_3$], 131 [$M^+ - C_3H_7$], 118 [$M^+ - C_3H_7N$], 105 [$C_5H_4N{-}C_2H_5^+$].

***N*-[2-(2-Pyridyl)ethyl]pyrrolidine (1b):** GC yield (before hydrogenation): 54%; GC yield (after hydrogenation): 75%. − MS; *m/z*: 176 [M^+], 106 [$C_5H_4N{-}C_2H_4^+$], 84 [$(C_5H_{10})NCH_2^+$]. − ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.50 [d, ^3J(H,H) = 5.6 Hz, 1 H, 6-H], 7.57 [dt, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 4.8 Hz, 1 H, 4-H], 7.14 [d, ^3J(H,H) = 7.8 Hz, 1 H, 3-H], 7.08 (m, 1 H, 5-H), 3.04 (m, 2 H, Py−CH_2−CH_2−N), 2.87 (m, 2 H, Py−CH_2), 2.61 (m, 4 H, N−CH_2), 1.79 [q, ^3J(H,H) = 3.2 Hz, 4 H, N−CH_2−CH_2]. −^{13}C{^{1}H} NMR (91 MHz, 25°C, $CDCl_3$): δ = 160.2 (C-2), 149.2 (C-6), 136.2 (C-4), 123.1 (C-3), 121.2 (C-5), 56.0 (Py−C−*C*), 54.1

(*C*−N), 35.7 (Py−*C*), 22.5 (N−C−*C*). − MS; *m*/*z*: 176 [M^+], 106 [$C_5H_4N-C_2H_4^+$], 84 [$(C_5H_{10})NCH_2^+$].

Reaction of 2-Vinylpyridine with Piperidine: In a procedure analogous to the synthesis of **1**, 0.44 mL of piperidine (4.40 mmol) and 1.90 mL of 2-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol).

(*E*)-*N*-[2-(2-Pyridyl)ethenyl]piperidine (2a): GC yield: 47%. − MS; *m*/*z*: 188 [M^+], 159 [$M^+ - C_2H_5$], 131 [$M^+ - C_3H_7N$], 118 [$M^+ - C_4H_8N$], 106 [$C_5H_4N-C_2H_5^+$].

***N*-[2-(2-Pyridyl)ethyl]piperidine (2b):** GC yield (before hydrogenation): 53%; GC yield (after hydrogenation): > 99.9%; isolated yield: 86% (718 mg). − ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.47 [d, ^3J(H,H) = 4.8 Hz, 1 H, 6-H], 7.54 [dt, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 4.8 Hz, 1 H, 4-H], 7.14 [d, ^3J(H,H) = 7.9 Hz, 1 H, 3-H], 7.05 (m, 1 H, 5-H), 2.96 (m, 2 H, Py−CH_2−CH_2−N), 2.68 (m, 2 H, Py−CH_2), 2.44 (m, 4 H, CH_2−N), 1.56 (m, 4 H, N−CH_2−CH_2), 1.40 (m, 2 H, N−CH_2−CH_2−CH_2). − $^{13}C\{^1H\}$ NMR (91 MHz, 25°C, $CDCl_3$): δ = 160.6 (C-2), 149.1 (C-6), 136.2 (C-4), 123.1 (C-3), 120.9 (C-5), 59.2 (Py−C−*C*), 54.4 (*C*−N), 35.7 (Py−*C*), 25.9 (N−C−*C*), 24.3 (N−C−C−*C*). − MS; *m*/*z*: 190 [M^+], 106 [$C_5H_4N-C_2H_4^+$], 98 [$(C_5H_{10})NCH_2^+$].

Reaction of 2-Vinylpyridine with Hexahydroazepine: In a procedure analogous to the synthesis of **1**, 0.50 mL of hexahydroazepine (4.40 mmol) and 1.90 mL of 2-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol).

(*E*)-*N*-[2-(2-Pyridyl)ethenyl]hexahydroazepine (3a): GC yield: 30%. − MS; *m*/*z*: 202 [M^+], 187 [$M^+ - CH_3$], 173 [$M^+ - C_2H_5$], 145 [$M^+ - C_4H_9$], 131 [$M^+ - C_5H_{11}$], 117 [$M^+ - C_6H_{13}$], 106 [$M^+ - C_6H_{13}N$].

***N*-[2-(2-Pyridyl)ethyl]hexahydroazepine (3b):** GC yield (before hydrogenation): 30%; GC yield (after hydrogenation): 59%; isolated yield: 36% (323 mg). − ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.37 [d, ^3J(H,H) = 5.6 Hz, 1 H, 6-H], 7.56 [t, ^3J(H,H) = 8.8 Hz, 4-H], 7.16 (m, 1 H, 3-H), 7.07 (m, 1 H, 5-H), 2.94 [t, ^3J(H,H) = 4.7 Hz, 4 H, CH_2−N−Py], 2.75 (m, 4 H, Py−CH_2−CH_2), 1.64 (m, 8 H, CH_2−CH_2−CH_2−N). − $^{13}C\{^1H\}$ NMR (91 MHz, 25°C, $CDCl_3$): δ = 160.4 (C-2), 149.0 (C-6), 136.0 (C-4), 123.0 (C-3), 120.9 (C-5), 58.0 (Py−C−*C*), 54.6 (*C*−N−Et), 35.9 (Py−*C*), 27.6 (C−*C*−C−N), 26.8 (*C*−C−C−N). − MS; *m*/*z*: 204 [M^+], 112 [$C_6H_{12}NCH_2$].

Reaction of 2-Vinylpyridine with Morpholine: In a procedure analogous to the synthesis of **1**, 0.38 mL of morpholine (4.40 mmol) and 1.90 mL of 2-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol).

(*E*)-*N*-[2-(2-Pyridyl)ethenyl]morpholine (4a): GC yield: 2%. − MS; *m*/*z*: 190 [M^+], 159 [$M^+ - CH_3O$], 131 [$M^+ - C_3H_7O$], 118 [$M^+ - C_4H_8O$], 105 [$C_5H_4N-C_2H_4^+$].

***N*-[2-(2-Pyridyl)ethyl]morpholine (4b):** GC yield (before hydrogenation): 98%; GC yield (after hydrogenation): > 99.9%; isolated yield: 81% (684 mg). − ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.50 [d, ^3J(H,H) = 4.8 Hz, 1 H, 6-H], 7.55 [dt, ^3J(H,H) = 7.8 Hz, ^3J(H,H) = 4.8 Hz, 1 H, 4-H], 7.19 [d, ^3J(H,H) = 7.8 Hz, 1 H, 3-H], 7.08 (m, 1 H, 5-H), 3.66 [t, ^3J(H,H) = 4.5 Hz, 4 H, CH_2−O], 2.98 (m, 2 H, Py−CH_2−CH_2−N), 2.75 (m, 2 H, Py−CH_2−CH_2−N), 2.50 [t, ^3J(H,H) = 4.5 Hz, 4 H, CH_2−N]. − $^{13}C\{^1H\}$ NMR (91 MHz, 25°C, $CDCl_3$): δ = 159.8 (C-2), 148.8 (C-6), 135.8 (C-4), 122.7 (C-3), 120.7 (C-5), 66.4 (CH_2−O), 58.2 (Py−C−*C*), 53.2 (CH_2−N), 35.1 (Py−*C*). − MS; *m*/*z* = 192 [M − H^+], 132, 106 [$C_5H_4N-C_2H_4^+$], 100 [$CH_2{=}N(CH_2)_4O^+$].

Reaction of 2-Vinylpyridine with Thiomorpholine: In a procedure analogous to the synthesis of **1**, 0.44 mL of thiomorpholine (4.40 mmol) and 1.90 mL of 2-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol). **5** was purified by column chromatography (hexane/ethyl acetate/NEt_3, 1:1:0.01).

***N*-[2-(2-Pyridyl)ethyl]thiomorpholine (5):** GC yield: 98%; isolated yield: 41% (375 mg). − ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.37 [d, ^3J(H,H) = 5.9 Hz, 1 H, 6-H], 7.46 [dt, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.7 Hz, 1 H, 4-H], 7.06 (m, 1 H, 3-H), 6.96 (m, 1 H, 5-H), 2.84 [t, ^3J(H,H) = 4.7 Hz, 4 H, S−CH_2−CH_2−N−Py], 2.75 (m, 4 H, Py−CH_2−CH_2), 2.79 [t, ^3J(H,H) = 4.7 Hz, 4 H, CH_2−S]. − $^{13}C\{^1H\}$ NMR (91 MHz, 25°C, $CDCl_3$): δ = 160.1 (C-2), 149.0 (C-6), 136.1 (C-4), 123.0 (C-3), 121.0 (C-5), 58.8 (Py−C−*C*−N), 54.6 (CH_2−N), 35.2 (Py−CH_2−CH_2−N), 17.8 (CH_2−S). − MS; *m*/*z*: 208 [M^+], 175 [M^+ − SH], 116 [$S(C_4H_8)NCH_2^+$].

Reaction of 2-Vinylpyridine with Piperazine: In a procedure analogous to the synthesis of **1**, 0.38 g of piperazine (4.40 mmol) and 1.90 mL of 2-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol).

***N*-[2-(2-Pyridyl)ethyl]piperazine (6a):** GC yield (before hydrogenation): 33%; GC yield (after hydrogenation): 48%. − ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.26 [d, ^3J(H,H) = 4.0 Hz, 1 H, 6-H], 7.34 [dt, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.8 Hz, 1 H, 4-H], 6.92 [d, ^3J(H,H) = 7.8 Hz, 1 H, 3-H], 6.86 (m, 1 H, 5-H), 2.74 (m, 2 H, Py−CH_2), 2.54 (m, 2 H, Py−CH_2−CH_2), 2.39 (m, 8 H, CH_2−N). − $^{13}C\{^1H\}$ NMR (91 MHz, 25°C, $CDCl_3$): δ = 159.8 (C-2), 149.0 (C-6), 136.1 (C-4), 123.0 (C-3), 121.0 (C-5), 58.1 (Py−C−*C*), 51.6 (*C*−N−C−C−Py), 44.1 (*C*−NH), 35.2 (Py−*C*). − MS; *m*/*z*: 191 [M^+], 149 [$M^+ - C_2H_4N$], 106 [$C_5H_4N-C_2H_4^+$], 99 [$HNC_4H_8NCH_2^+$].

(*E*)-*N*-[2-(2-Pyridyl)ethenyl]piperazine (6b): GC yield: 15%. − MS; *m*/*z*: 189 [M^+], 147 [$M^+ - C_2H_4N$], 133 [$M^+ - C_3H_6N$], 106 [$C_5H_4N-C_2H_4^+$].

Bis{*N*,*N*′-[2-(2-pyridyl)ethyl]}piperazine (6c): GC yield (before hydrogenation): 31%; GC yield (after hydrogenation): 46%. − ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.48 [d, ^3J(H,H) = 5.9 Hz, 2 H, 6-H], 7.56 [dt, ^3J(H,H) = 11.4 Hz, ^4J(H,H) = 1.7 Hz, 2 H, 4-H], 7.15 [d, ^3J(H,H) = 11.4 Hz, 2 H, 3-H], 7.06 (m, 2 H, 5-H), 2.84 [t, ^3J(H,H) = 4.7 Hz, 4 H, Py−CH_2], 2.75 (m, 4 H, Py−CH_2−CH_2), 2.79 [t, ^3J(H,H) = 4.7 Hz, 8 H, CH_2−N]. − $^{13}C\{^1H\}$ NMR (91 MHz, 25°C, $CDCl_3$): δ = 159.9 (C-2), 149.2 (C-6), 136.3 (C-4), 123.2 (C-3), 121.2 (C-5), 58.0 (Py−C−*C*), 57.3 (*C*−N−C−C−Py), 35.4 (Py−*C*).

***(E)*-*N*-[2-(2-Pyridyl)ethenyl]-*N*′-[2-(2-pyridyl)ethyl]piperazine (6d):** GC yield: 15%. − MS; *m*/*z*: 294 [M^+], 279 [$M^+ - CH_3$], 189 [$M^+ - C_5H_4N-C_2H_4$], 161, 133, 106 [$C_5H_4N-C_2H_4^+$].

Reaction of 2-Vinylpyridine with *N*-Methylpiperazine: In a procedure analogous to the synthesis of **1**, 0.49 mL of *N*-methylpiperazine (4.40 mmol) and 1.90 mL of 2-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol).

(*E*)-*N*-[2-(2-Pyridyl)ethenyl]-*N*′-methylpiperazine (7a): GC yield: 20%. − MS; *m*/*z*: 203 [M^+], 188 [$M^+ - CH_3$], 159 [$M^+ - C_2H_6N$], 131 [$M^+ - C_4H_{10}N$], 118, 106 [$C_5H_4N-C_2H_4^+$].

***N*-[2-(2-Pyridyl)ethyl]-*N*′-methylpiperazine (7b):** GC yield (before hydrogenation): 62%; GC yield (after hydrogenation): 82%; isolated

yield: 65% (586 mg). – ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.42 [d, ^3J(H,H) = 5.8 Hz, 1 H, 6-H], 7.50 (m, 1 H, 4-H), 7.08 (m, 1 H, 3-H), 7.00 (m, 1 H, 5-H), 2.94 (m, 2 H, Py−CH_2−CH_2), 2.70 (m, 2 H, Py−CH_2), 2.54 (s, br., 4 H, N−CH_2), 2.48 (s, br., 4 H, N−CH_2), 2.21 (s, 3 H, N−CH_3). – ^{13}C{^{1}H} NMR (91 MHz, 25°C, $CDCl_3$): δ = 160.2 (C-2), 149.1 (C-6), 136.2 (C-4), 123.0 (C-3), 121.0 (C-5), 58.2 (Py−C−*C*), 54.9 (*C*H_2−N), 52.9 (*C*H_2−N), 45.9 (N−*C*H_3), 35.7 (Py−*C*). – MS; *m*/*z*: 205 [M^+], 161 [M^+ − C_2H_6N], 149 [M^+ − C_3H_6N], 135 [M^+ − C_4H_8N], 106 [C_5H_4N−$C_2H_4^+$].

Reaction of 2-Vinylpyridine with *N*′-Phenylpiperazine: In a procedure analogous to the synthesis of **1**, 0.67 mL of *N*-phenylpiperazine (4.40 mmol) and 1.90 mL of 2-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol).

(*E*)-*N*-[2-(2-Pyridyl)ethenyl]-*N*′-phenylpiperazine (8a): GC yield: 8%. – MS; *m*/*z*: 265 [M^+], 207 [M^+ − C_3H_8N], 160 [M^+ − C_5H_4N−C_2H_3], 120 [C_5H_4N−$C_2H_4N^+$], 104 [C_5H_4N−$C_2H_2^+$].

***N*-[2-(2-Pyridyl)ethyl]-*N*′-phenylpiperazine (8b):** GC yield (before hydrogenation): 91%; GC yield (after hydrogenation): 99%; isolated yield: 88% (1033 mg). – ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.52 [d, ^3J(H,H) = 5.9 Hz, 1 H, 6-H], 7.60 [dt, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.7 Hz, 1 H, 4-H], 7.26 (m, 3 H, 3-H, *H*-8), 7.12 (m, 1 H, *H*-10), 6.99 (m, 3 H, 5-H, *H*-9), 3.28 [t, ^3J(H,H) = 4.7 Hz, 4 H, CH_2−N], 3.10 (m, 2 H, Py−CH_2−CH_2), 2.94 (m, 2 H, Py−CH_2), 2.79 [t, ^3J(H,H) = 4.7 Hz, 4 H, CH_2−N]. – ^{13}C{^{1}H} NMR (91 MHz, 25°C, $CDCl_3$): δ = 160.2 (C-2), 151.2 (C-7), 149.1 (C-6), 136.3 (C-4), 129.0 (C-9), 123.2 (C-3), 121.2 (C-5), 119.7 (C-10), 116.0 (C-8), 58.3 (Py−C−*C*), 53.1 (*C*−N), 52.9 (*C*−N), 35.7 (Py−*C*). – MS; *m*/*z*: 267 [M^+], 175 [C_6H_5−N($C_4H_8NCH_2$)$^+$], 161 [C_6H_5−N(C_4H_8N)$^+$], 148 [C_5H_4N−$C_2H_4N(CH_2)_2^+$], 135 [C_5H_4N−$C_2H_4NCH_3^+$], 120 [C_5H_4N−$C_2H_4N^+$], 106 [C_5H_4N−$C_2H_4^+$].

Reaction of 4-Vinylpyridine with Piperidine: In a procedure analogous to the synthesis of **1**, 0.44 mL of piperidine (4.40 mmol) and 1.90 mL of 4-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol).

***N*-[2-(4-Pyridyl)ethyl]piperidine (9):** GC yield: 57%; isolated yield: 36% (301 mg). – ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.34 [d, ^3J(H,H) = 4.9 Hz, 2 H, *H*-2], 7.01 [d, ^3J(H,H) = 4.9 Hz, 2 H, 3-H], 2.65 (m, 2 H, Py−CH_2−CH_2−N), 2.44 (m, 2 H, Py−CH_2−CH_2−N), 2.37 (m, 4 H, N−CH_2), 1.47 (m, 4 H, N−CH_2−CH_2), 1.31 (m, 2 H, N−CH_2−CH_2−CH_2). – ^{13}C{^{1}H} NMR (91 MHz, 25°C, $CDCl_3$): δ = 149.6 (C-2), 149.6 (C-4), 124.1 (C-3), 59.8 (Py−C−*C*−N), 54.4 (*C*−N), 32.9 (Py−*C*), 25.9 (N−C−*C*), 24.3 (N−C−C−*C*). – MS; *m*/*z*: 190 [M − H^+], 105 [C_5H_4N−$C_2H_3^+$], 98 [CH_2=N$(CH_2)_5^+$].

Reaction of 4-Vinylpyridine with Hexahydroazepine: In a procedure analogous to the synthesis of **1**, 0.50 mL of hexahydroazepine (4.40 mmol) and 1.90 mL of 4-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol).

***N*-[2-(4-Pyridyl)ethyl]hexahydroazepine (10):** GC yield: 21%; isolated yield: 13% (116 mg). – ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.40 [d, ^3J(H,H) = 4.9 Hz, 2 H, *H*-2], 7.05 [d, ^3J(H,H) = 4.9 Hz, 2 H, 3-H], 2.71 (m, 8 H, Py−CH_2−CH_2−N−CH_2), 1.17 (m, 8 H, N−CH_2−CH_2−CH_2). – ^{13}C{^{1}H} NMR (91 MHz, 25°C, $CDCl_3$): δ = 149.7 (C-2), 149.6 (C-4), 124.3 (C-3), 58.9 (Py−C−*C*−N), 54.4 (*C*−N), 33.4 (Py−*C*), 27.9 (N−C−*C*), 27.0 (N−C−C−*C*). – MS; *m*/*z*: 203 [M^+], 112 [$C_6H_{12}NCH_2^+$].

Reaction of 4-Vinylpyridine with Morpholine: In a procedure analogous to the synthesis of **1**, 0.38 mL of morpholine (4.40 mmol) and 1.90 mL of 4-vinylpyridine (17.6 mmol) in 10 mL of THF were treated in the presence of 45 mg of $[Rh(cod)_2]BF_4$ (0.11 mmol) and 58 mg of PPh_3 (0.22 mmol).

***N*-[2-(4-Pyridyl)ethyl]morpholine (11):** GC yield: 54%; isolated yield: 44% (37 mg). – ^{1}H NMR (360 MHz, 25°C, $CDCl_3$): δ = 8.28 [d, ^3J(H,H) = 4.5 Hz, 2 H, *H*-2], 7.01 [d, ^3J(H,H) = 4.5 Hz, 2 H, 3-H], 3.60 [t, ^3J(H,H) = 4.4 Hz, 4 H, CH_2−O], 2.67 (m, 2 H, Py−CH_2−CH_2), 2.51 (m, 2 H, Py−CH_2), 2.40 [t, ^3J(H,H) = 4.4 Hz, 4 H, CH_2N]. – ^{13}C{^{1}H} NMR (91 MHz, 25°C, $CDCl_3$): δ = 149.5 (C-2), 149.1 (C-4), 124.0 (C-3), 66.7 (*C*−O), 59.1 (Py−C−*C*), 53.4 (*C*−N), 32.4 (Py−*C*). – MS; *m*/*z*: 192 [M − H^+], 132, 106 [C_5H_4N−$C_2H_4^+$], 100 [CH_2=N$(CH_2)_4O^+$].

[(1,2,5,6-η)-1,5-Cyclooctadiene]bis[*N*-(2-vinylpyridine)]rhodium(I) Tetrafluoroborate (12): 100 mg of $[Rh(cod)Cl]_2$ (0.20 mmol) and 80 mg of $AgBF_4$ (0.41 mmol) were dissolved in 2 mL of THF and the solution was stirred for 10 min. After filtering off the AgCl precipitate, the orange solution was cooled to 0°C and 94 mg of 2-vinylpyridine (0.90 mmol) was added. After stirring the reaction mixture for several minutes, a yellow precipitate was obtained. After filtration, the crude product was washed three times with 1 mL of THF and three times with pentane. Drying in vacuo furnished 154 mg of **12** (76%). – ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 8.92 (s, br., 1 H, 6-H), 8.71 (s, br., 1 H, *H*-7), 7.66 [t, ^3J(H,H) = 7.9 Hz, 1 H, 4-H], 7.55 [d, ^3J(H,H) = 7.9 Hz, 1 H, 3-H], 7.32 (s, 1 H, 5-H), 6.05 [d, br., ^3J(H,H) = 17.6 Hz, 2 H, *H*-8], 4.17 [s, br., 2 H, C*H* (cod)], 3.90 [s, br., 2 H, C*H* (cod)], 2.81 [s, br., 2 H, CH_2 (cod)], 2.64 [s, br., 2 H, CH_2 (cod)], 2.10 [s, br., 2 H, CH_2 (cod)], 1.84 [s, br., 2 H, CH_2 (cod)]. – ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 157.1 (C-2), 151.0 (C-6), 138.2 (C-8), 135.7 (C-4), 124.4 (C-5), 123.0 (C-7), 121.8 (C-3), 85.4 [*C*H (cod)], 83.9 [C*H* (cod)], 31.5 [CH_2 (cod)], 29.6 [CH_2 (cod)]. – At −60°C, in both the ^{1}H-NMR and the ^{13}C-NMR spectra, a second set of weak resonances (w) appears, which has only 1/10 of the intensity of the main one (ss): ^{1}H NMR (400 MHz, $CDCl_3$, −60°C): δ = 9.43 (w, m, 1 H), 8.92 [ss, d, ^3J(H,H) = 4.4 Hz, 1 H, 6-H], 8.74 [ss, dd, ^3J(H,H) = 11.0 Hz, ^3J(H,H) = 17.0 Hz, 1 H, *H*-7], 8.08 [w, dd, ^3J(H,H) = 11.0 Hz, ^3J(H,H) = 17.0 Hz], 7.66 [ss, t, ^3J(H,H) = 7.9 Hz, 1 H, 4-H], 7.55 [ss, d, ^3J(H,H) = 8.0 Hz, 1 H, 3-H], 7.42 (w, m, 1 H), 7.28 (ss, m, 1 H, 5-H), 6.09 [ss, dd, br., ^3J(H,H) = 17.6 Hz, ^3J(H,H) = 11.0 Hz, 2 H, *H*-8], 6.00 (w, m, 1 H), 5.89 [w, d, ^3J(H,H) = 11.0 Hz], 4.16 [ss, m, 2 H, C*H* (cod)], 4.06 (w, s, 1 H), 3.93 (w, s, 1 H), 3.83 [ss, m, 2 H, C*H* (cod)], 2.84 [ss, m, 2 H, CH_2 (cod)], 2.64 [ss, m, br., 2 H, CH_2 (cod)], 2.17 [ss, m, 2 H, CH_2 (cod)], 1.97 (w, m, 1 H), 1.82 (w, m, 1 H), 1.84 [ss, br., 2 H, CH_2 (cod)]. – ^{13}C NMR (100 MHz, $CDCl_3$, −60°C): δ = 157.1 (ss, C-2), 156.0 (w, C-2), 151.1 (ss, C-6), 150.6 (w, C-6), 138.4 (ss, C-8), 138.1 (w, C-8), 136.5 (w, C-4), 135.6 (ss, C-4), 124.7 (w, C-5), 124.5 (ss, C-5), 123.5 (ss, C-7), 122.3 (w, C-7), 122.0 (ss, C-3), 121.6 (w, C-3), 88.2 [w, d, ^1J(C,Rh) = 11.7 Hz, *C*H (cod)], 85.2 [ss, d, ^1J(C,Rh) = 11.7 Hz, *C*H (cod)], 84.9 [ss, d, ^1J(C,Rh) = 11.7 Hz, C*H* (cod)], 81.2 [w, d, ^1J(C,Rh) = 11.7 Hz, C*H* (cod)], 32.1 [ss, CH_2 (cod)], 30.6 [w, CH_2 (cod)], 30.4 [w, CH_2 (cod)], 29.1 [ss, CH_2 (cod)]. – $C_{22}H_{26}BF_4N_2Rh$ (508.17): calcd. C 52.0, H 5.2, N 5.5; found C 51.8, H 5.3, N 5.4.

Crystal Data and Structure Refinement of 12: Crystals were grown by slow diffusion of Et_2O into a solution of [Rh(cod)(2-vinylpyridine)$_2$]CF_3SO_3 in CH_2Cl_2. A yellow crystal of dimensions 0.35 × 0.30 × 0.17 mm was mounted by the Lindeman technique. Cell constants were determined by least-squares refinement of 5000 reflections in the intervall 16.8° < 2Θ < 49.8° with the program

CELL.[16] Crystal data: monoclinic $P2_1/n$; a = 11.3081(7) Å, b = 17.0699(6) Å, c = 12.2946(7) Å, β = 90.911(6)°; V = 2372.9(2) Å^3; formula unit = $C_{23}H_{26}F_3N_2O_3RhS$ with Z = 4; FW = 570.43; F(000) = 1160; μ(Mo-K_α) = 8.59 cm^{-1}; λ(Mo-K_α) = 0.71069 Å; $\rho_{calcd.}$ = 1.597 g cm^{-3}. Preliminary examination and data collection were carried out with an imaging-plate diffraction system (IPDS; STOE & Cie) equipped with a rotating anode (NONIUS FR591; 50 kV; 80 mA) and graphite monochromator. The data were collected at 293(2) K with an exposure time of 5.0 min per image (rotation scan modus from φ = 0.0° to 300° with Δφ = 1°). 24641 reflections were collected (2.05° < Θ < 24.6°). Final full-matrix least-squares refinement (on F^2) based on 3760 unique reflections of which 3753 were used converged with 452 variable parameters and 15 restraints. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined isotropically with U(H) = 1.2 U_{eq}(parent atom). $R1$ = 0.0300, for $F^2 > 2\ \sigma(F^2)$; $wR2$ = 0.0770;[17] Goof(F^2) = 0.953; $\Delta\rho_{max}$ = 0.56, $\Delta\rho_{min}$ = −0.42 e$^-$ Å^{-3}. The data analysis and the drawing were made using the programs STRUX-V,[18] SIR-92,[19] SHELXL-93,[20] and SCHAKAL-97.[21]

[(1,2,5,6-η)-1,5-Cyclooctadiene](*N*-morpholine)[*N*-(2-vinylpyridine)]-rhodium(I) Trifluoromethylsulfonate (13): 100 mg of [Rh(cod)(2-vinylpyridine)$_2$]CF_3SO_3 (0.18 mmol) was dissolved in 1 mL of THF. 16 mg of morpholine was added to the yellow solution. Immediately a yellow precipitate was obtained, which was filtered off and washed three times with 1 mL of THF and 1 mL of pentane. After drying in vacuo, 83 mg (84%) of **13** was obtained. − ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 8.85 (s, 1 H, 6-H), 8.38 (s, br., 1 H, *H*-7), 7.48 [d, ^3J(H,H) = 6.5 Hz, 1 H, 4-H], 7.80 (s, 1 H, 3-H), 7.41 (s, 1 H, 5-H), 6.29 [d, ^3J(H,H) = 17.0 Hz, 1 H, *H*-8 (*trans*)], 6.03 [d, ^3J(H,H) = 11.0 Hz, 1 H, *H*-8 (*cis*)], 4.34 [s, br., 2 H, C*H* (cod)], 3.63 [s, br., 7 H, C*H* (cod), N−*H*, CH_2−O], 2.79 (s, br., 2 H, N−CH_2), 2.53 [s, br., 6 H, CH_2 (cod), N−CH_2], 1.9 [s, br., 4 H, CH_2 (cod)]. − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 156.2 (C-2), 149.2 (C-6), 137.3 (C-8), 134.9 (C-4), 124.9 (C-5), 123.5 (C-7), 121.3 (C-3), 82.9 [C*H* (cod)], 65.5 (*C*−O), 48.0 (*C*−N), 29.3 [CH_2 (cod)]. − IR (KBr): $\tilde{\nu}$ = 3215 cm^{-1} s, 2941 m, 2987 m, 1601 m, 1480 s, 1444 m, 1272 ss, 1263 ss, 1249 ss, 1153 ss, 1029 ss, 880 s. − MS; (FAB) *m/z*: 316 [M$^+$ − morpholine]. − $C_{19}H_{28}BF_4N_2ORh$ (552.41): calcd. C 44.9, H 5.2, N 4.8; found C 44.9, H 4.7, N 5.2.

Crystal Data and Structure Refinement of 13: Crystals were grown by slow diffusion of Et_2O into a solution of [Rh(cod)(morpholine)(2-vinylpyridine)]CF_3SO_3 in CH_2Cl_2. A yellow crystal of dimensions 0.25 × 0.27 × 0.1 mm was mounted by the Lindeman technique. Cell constants were determined by least-squares refinement of 1998 reflections in the intervall 27.3° < 2Θ < 51.7° with the program CELL. Crystal data: triclinic $P-1$; a = 9.7085(2), b = 10.7786(2), c = 12.6294(2) Å, α = 76.3538(14)°, β = 72.1748(14)°, γ = 65.7518(11)°; V = 1137.86(4) Å^3; empirical formula $C_{20}H_{28}F_3N_2O_4RhS$, Z = 2; FW = 552.41; F(000) = 564; μ(Mo-K_α) = 8.95 cm^{-1}; λ(Mo-K_α) = 0.71073 Å; $\rho_{calcd.}$ = 1.612 g cm^{-3}. Preliminary examination and data collection were carried out with a Kappa-CCD equipped with a rotating anode (NONIUS FR591; 50 kV; 80 mA) and graphite monochromator. The data were collected at 293(2) K with an exposure time of 20 s per image (detector−image 30 mm, rotation-scan modus from φ = 0.0° to 360° with Δφ = 1°). 15058 reflections were collected (4.60° < Θ < 26.35°). Final full-matrix least-squares refinement (on F^2) based on 3917 unique reflections converged with 367 variable parameters and 28 restraints. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined isotropically with U(H) = 1.2 U_{eq}(parent atom) using a riding model. The R factor is slightly increased due to disorder in the cod ligand (C4 and C7), the 2-vinylpyridine and the tosylate. $R1$ = 0.0281, for $F^2 > 2\ \sigma(F^2)$; $wR2$ = 0.0701;[17] Goof(F^2) = 1.035; $\Delta\rho_{max}$ = 0.40, $\Delta\rho_{min}$ = −0.50 e$^-$ Å^{-3}. The data analysis and the drawing were made using the programs STRUX-V,[18] SIR-92,[19] SHELXL-93,[20] and SCHAKAL-97.[21]

Acknowledgments

We thank Dr. E. Herdtweck and Dr. W. Scherer (TU München) for performing the X-ray analyses. Prof. B. Hanson (Virginia Tech) is thanked for helpful comments on this manuscript. H. T. thanks the Fonds der Chemischen Industrie for a fellowship and T. E. M. for a Liebig-Stipendium. Financial support (Be 1931−3/1) from the Deutsche Forschungsgemeinschaft (DFG) and loans of precious metals by the Degussa AG and the Hoechst AG are gratefully acknowledged.

[1] M. Beller, H. Trauthwein, M. Eichberger, C. Breindl, T. E. Müller, O. Thiel, J. Herwig, *Chem. Eur. J.* **1999**, *5*, 1306.
[2] For a recent review see: T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675. − [2a] D. R. Coulson (Du Pont), US 3.758.586, **1973**; *Chem. Abstr.* **1973**, *79*, 125808g. − [2b] D. R. Coulson, *Tetrahedron Lett.* **1971**, 429. − [2c] L. S. Hegedus, *Angew. Chem.* **1988**, *100*, 1147; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1113. − [2d] A. L. Casalnuovo, J. L. Calabrese, D. Milstein, *J. Am. Chem. Soc.* **1988**, *110*, 6738. − [2e] D. Steinborn, B. Thies, I. Wagner, R. Taube, *Z. Chem.* **1989**, *29*, 333. − [2f] M. R. Gagné, T. J. Marks, *J. Am. Chem. Soc.* **1989**, *111*, 4108. − [2g] D. Selent, D. Scharfenberg-Pfeiffer, G. Reck, R. Taube, *J. Organomet. Chem.* **1991**, *415*, 417. − [2h] M. R. Gagné, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 275. − [2i] J.-J. Brunet, D. Neibecker, K. Philippot, *Tetrahedron Lett.* **1993**, *34*, 3877. − [2j] R. C. Larock, T. R. Hightower, L. A. Hasvold, K. P. Peterson, *J. Org. Chem.* **1996**, *61*, 3584. − [2k] Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 707. − [2l] Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 9295. − [2m] Y. W. Li, T. J. Marks, *Organometallics* **1996**, *15*, 10212. − [2n] C. Hahn, J. Sieler, R. Taube, *Chem. Ber.* **1997**, *130*, 939. − [2o] R. Dorta, P. Egli, F. Zürchner, A. Togni, *J. Am. Chem. Soc.* **1997**, *119*, 10857. − [2p] C. Hahn, A. Vitagliano, F. Giordano, R. Taube, *Organometallics* **1998**, *17*, 2060.
[3] [3a] M. Beller, M. Eichberger, H. Trauthwein, *Angew. Chem.* **1997**, *109*, 2306; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2225. − [3b] M. Beller, M. Eichberger, H. Trauthwein, *Catalysis of Organic Reactions* (Ed.: F. Herkes), Marcel Dekker, **1998**.
[4] [4a] G. Roscher, F. Hofmann, K. A. Adey, W. Jeblick, H.-J. Klimisch in *Ullmann's Enzyclopädie der Technischen Chemie*, vol. 23, 4th ed. (Ed.: W. Gerhartz), VCH, Weinheim, **1983**, p. 612. − [4b] P. C. Jain, V. Kapoor, N. Anand, A. Ahmad, G. Patnaik, *J. Med. Chem.* **1967**, *10*, 812.
[5] W. Doering, R. A. N. Weil, *J. Am. Chem. Soc.* **1947**, *69*, 2461.
[6] [6a] E. Profft, *J. Prakt. Chem.* **1956**, *4*, 19. − [6b] A. P. Phillips, *J. Am. Chem. Soc.* **1956**, *78*, 4441. − [6c] G. Magnus, R. Levine, *J. Am. Chem. Soc.* **1956**, *78*, 4127.
[7] A. J. Matusko, A. Taurins, *Can. J. Chem.* **1954**, *32*, 538.
[8] H. E. Reich, R. Levine, *J. Am. Chem. Soc.* **1955**, *77*, 4913.
[9] M. I. Druzin, A. K. Valkova, A. B. Pashkov, I. V. Zaitseva, N. V. Bogdanova, L. D. Pertsov, S. F. Kalinkin, B. M. Kuindzhi, U.S.S.R. 215,997, **1968**; *Chem. Abstr.* **1968**, *69*, P52016d.
[10] M. Beller, H. Trauthwein, M. Eichberger, C. Breindl, T. E. Müller, A. Zapf, *J. Organomet. Chem.* **1998**, *566*, 277.
[11] [11a] M. S. Driver, J. F. Hartwig, *J. Am. Chem. Soc.* **1996**, *118*, 4206. − [11b] P. Diversi, L. Ermini, G. Ingrosso, A. Lucherini, C. Pinzino, L. Saramora, *J. Organomet. Chem.* **1995**, *494*, C1. − [11c] M. Schulz, D. Milstein, *J. Chem. Soc., Chem. Commun.* **1993**, 318. − [11d] A. L. Seligson, R. L. Cowan, W. C. Trogler, *Inorg. Chem.* **1991**, *30*, 3371. − [11e] M. D. Fryzuk, C. D. Montgomery, *Coord. Chem. Rev.* **1989**, *95*, 1.
[12] B. Denise, G. Pannetier, *J. Organomet. Chem.* **1978**, *161*, 171.
[13] H. S. Rzepa, M. H. Smith, M. L. Webb, *J. Chem. Soc., Perkin Trans. 2* **1994**, 703; P. N. Jagg, P. F. Kelly, H. S. Rzepa, D. J. Williams, J. D. Woolins, W. Wylie, *J. Chem. Soc., Chem. Commun.* **1991**, 942.
[14] G. Giordano, R. H. Crabtree, *Inorg. Synth.* **1979**, *19*, 218.

[15] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 3089.
[16] *IPDS Operating System*, Version 2.7, STOE & Cie. GmbH, Darmstadt, Deutschland, **1996**.
[17] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$); $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[18] G. Artus, W. Scherer, T. Priermeier, E. Herdtweck, *STRUX-V, A Program System to Handle X-ray Data*, TU München, Germany, **1994**.
[19] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *SIR-92*, University of Bari, Italy, **1992**.
[20] G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures* (Ed.: G. M. Sheldrick), University of Göttingen, Germany, **1993**.
[21] E. Keller, *SCHAKAL-97*, Albert-Ludwigs-Universität Freiburg, Germany, **1997**.

Received November 10, 1998
[I98386]