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Hydroaminomethylation with Novel Rhodium–Carbene complexes: An Efficient Catalytic Approach to Pharmaceuticals

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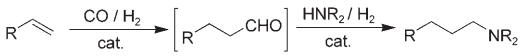
Abstract: Starting from [{Rh(cod)Cl}$_2$] and 1,3-dimesitylimidazole-2-ylidenes the novel [RhCl(cod)(carbene)] complexes **1–5** have been synthesized, characterized, and tested in the hydroaminomethylation of aromatic olefins. The influence of different ligands and reaction parameters on the catalytic activity was investigated in detail applying 1,1-diphenylethylene and piperidine as a model system. The scope and limitations of the novel catalysts is shown in the preparation of 16 biologically active 1-amino-3,3-diarylpropenes. In general, high chemo- and regioselectivity as well as good yields of the desired products were achieved.

Keywords: amines · carbenes · carbonylation · hydroaminomethylation · pharmaceuticals · rhodium

Introduction

Providing amines directly from ubiquitous available alkenes carbonylative aminination (so-called hydroaminomethylation) offers a direct and efficient synthesis of various pharmaceuticals, natural products, agrochemicals, and fine chemicals (Scheme 1).[1] Among other alkenes, especially aromatic olefins (i.e., substituted styrene derivatives) are of significant importance as they provide either 3- and 2-arylpropylamines, which constitute the basic core in many compounds of biological importance.[2]



Scheme 1. Hydroaminomethylation of olefins.

As an example, 3,3-diarylpropylamines (pheniramines) represent a well-known first-generation family of H_1 antihistaminic agents. By varying the amine core the biological activity of 3,3-diarylpropylamines can be tuned from antiallergic to choleretic, antipyretic, coronardilatic, and antispasmodic (Figure 1).[3]

On the other hand, varying substituents at the aromatic groups gives access to novel biologically active compounds. Most known synthetic strategies leading to 3,3-diarylpropylamines make use of nucleophilic substitutions of the corresponding 3,3-diarylpropylhalides.[4] Often the synthesis of these halides requires several steps with low overall yields. In addition, these starting materials do not meet todays criterion for atom economy, as at least one equivalent of halide by-product is produced.

Obviously a synthetic route directly from olefins eliminates the need of alkyl halide intermediates thereby making the procedure more environmentally benign and economic. In this regard the work of Botteghi et al. is noteworthy, who for the first time described the synthesis of 3,3-diphenylpropylamines using a sequential hydroformylation–reductive amination sequence (Scheme 2).[5] The overall yields of the synthesis range between 60 and 70%. Comparably good results have been obtained in the preparation of pheniramines starting from acetals.[6] The more efficient one-pot synthesis of 3,3-diphenylpropylamines via rhodium-catalyzed hydroaminomethylation of 1,1-diarylethenes was developed by Eilbracht and Rische.[7] More recently, we showed that a catalyst system based on rhodium and Xantphos is more active for this class of olefins.[8]

As shown in Scheme 2 all known protocols for the carbonylation of 1,1-diarylethenes suffer from long reaction times, high catalyst loading, and thus low catalyst activity. Here, we report for the first time the use of novel rhodium–

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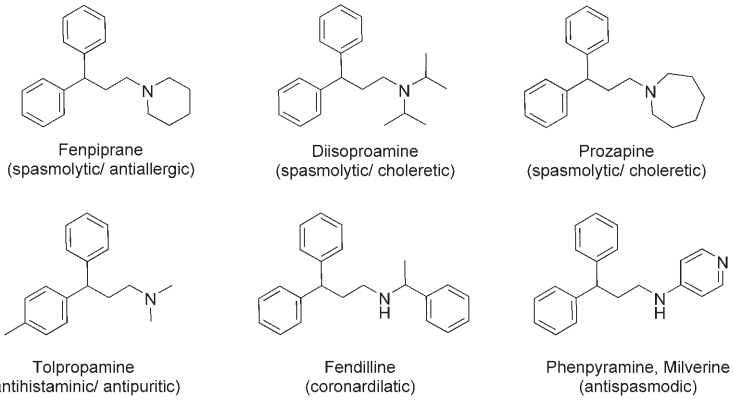
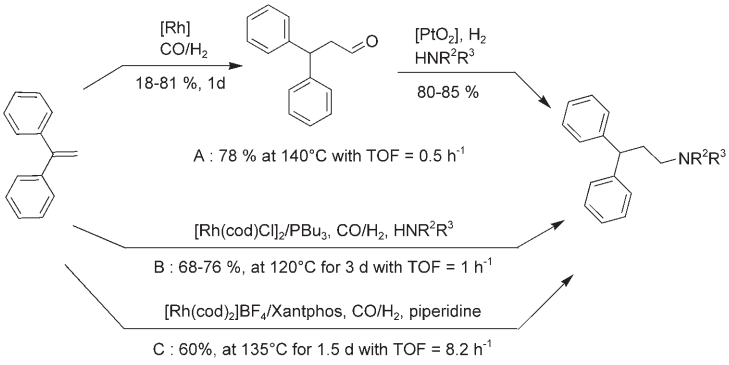


Figure 1. Selected examples of pharmaceutically active 3,3-diarylpropylamines (pheniramines).



Scheme 2. Synthesis of Fenpiprane: A comparison of literature data A,[9] B[7] and C.

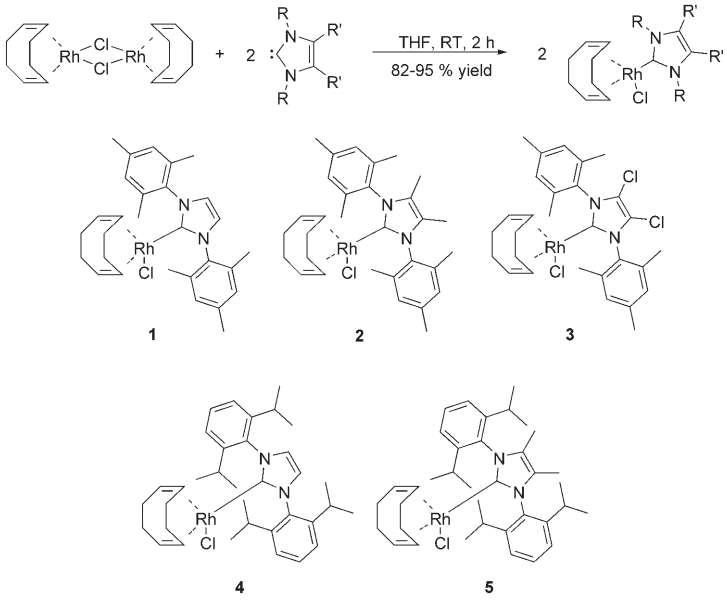
carbene complexes, which allow for a more efficient hydroaminomethylation of 1,1-diarylethenes compared with previously known catalysts.

Since the first report by Öfele in 1968,[10] the metal coordination chemistry of N-heterocyclic carbenes has been extended dramatically. Based on the initial finding of Arduengo N-heterocyclic carbenes are nowadays used as universal ligands in organometallic and inorganic coordination chemistry.[11,12] With respect to hydroaminomethylation the use of N-heterocyclic carbenes as ligands in hydroformylation reactions is noteworthy. The first catalytic hydroformylation in the presence of N-heterocyclic carbenes was disclosed elegantly by Herrmann et al. in the mid 90s.[13] Later on Crudden et al. presented [Rh(IMes)(PPh_3)(CO)Cl] as catalyst for the isoselective hydroformylation of styrene.[14] Latest investigations are dated to 2003. Claver et al. studied the Hydroformylation of olefins in presence of a dirhodium(I)–bisimidazol carbene complex via high-pressure NMR spectroscopy.[15] Moreover very familiar N-heterocyclic carbenes complexes have been synthesized with palladium for oxidation of methane[11] and with ruthenium to catalyze olefine metathesis.[16] Herrmann et al. also determined in his work from 2002[11] that heterocarbenes show more or less the same bonding properties as trialkylphosphanes.

Results and Discussion

Synthesis of novel rhodium–carbene complexes: As a starting point for our investigations we applied the known synthesis for monocarbenepalladium–diolefin complexes[17] for the preparation of [Rh(IMes)(cod)Cl] (IMes = 1,3-dimesitylimidazole-2-ylidene) (**1**). Starting from [{Rh(cod)Cl}$_2$] and five 1,3-dimesitylimidazole-2-ylidenes the corresponding complexes **1–5** were prepared in 82–95% yield (Scheme 3).

In a general procedure, a THF solution (10 mL) of 1,3-dimesitylimidazole-2-ylidene (1.0 mmol) was added slowly to a solution of [{Rh(cod)Cl}$_2$] (0.5 mmol) in THF (20 mL) at room temperature. After stirring for 2 h the solvent was evaporated and the yellow solids obtained were analytically pure. All obtained complexes are highly stable at room temperature and can be easily handled in air. In spite of the potential catalytic performance of Rh–carbene complexes, so far only few X-ray crystal structures of these complexes have been reported.[18] Thus, we were interested in the detailed structural information of some of our complexes. Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane to a dichloromethane solution of the complexes **2** and **4** at room temperature. Crystallographic data of the complexes are given in Table 1 and selected distances and angles are shown in Table 2.



Scheme 3. Synthesis of Rh carbene complexes **1–5**.

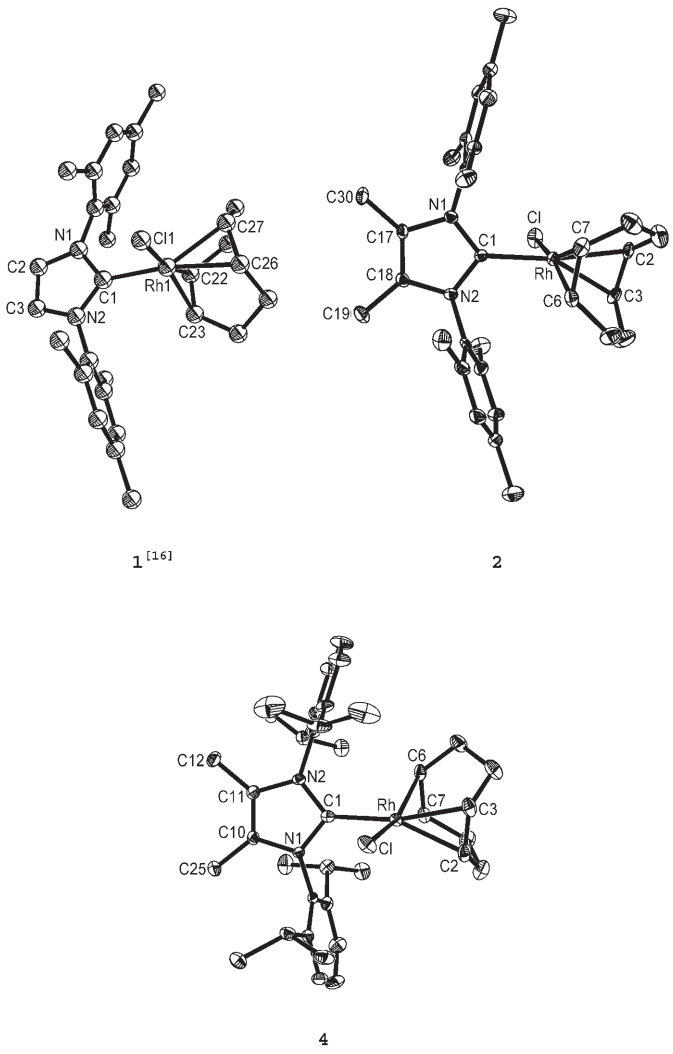


Figure 2. Molecular structure of complexes **1**, **2** and **4**. The thermal ellipsoids correspond to 50% (**1**[19]) or 30% (**2** and **4**) probability.

Table 1. Crystallographic data of complexes **1**,[19] **2** and **4**.

	1[19]	**2**	**4**
cryst system	tetragonal	monoclinic	monoclinic
space group	$I4_1/a$	$P2_1/c$	$P2_1/c$
a [Å]	32.464(2)	13.993(3)	17.563(4)
b [Å]	32.464	12.057(2)	11.208(2)
c [Å]	9.9286(7)	17.040(3)	18.774(4)
α [°]	90.00	90.00	90.00
β [°]	90.00	100.48	114.74
γ [°]	90.00	90.00	90.00
V [Å^3]	10463.7(10)	2826.9(9)	3356.4(4)
Z	16	4	4
ρ [g cm^{-3}]	1.399	1.360	1.312
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.774	0.720	0.616
T [K]	113(2)	200(2)	200(2)
no. rflns (measd)	7032	4449	4387
no. rflns (indep)	7677	4450	4387
no. rflns (obsd)	6359	2844	3750
no. params	340	316	370
$R1$ ($I>2\sigma(I)$)	0.0276	0.0430	0.0307
$wR2$ (all data)	0.0635	0.0886	0.0795

As shown in Figure 2 the central rhodium atom is coordinated by the 1,3-cyclooctadiene unit, the chlorine atom and the corresponding carbene ligand in a contorted square planar coordination in **1**, **2** and **4**. The distance between the rhodium and the carbene atom varies between 2.049(16) and 2.067(5) Å, which is equal within the measurements failure. Surprisingly, the substituents on the carbene backbone, the methyl groups in complex **2** or the chloro substitution in complex **4** do not influence significantly the carbene–rhodium bond length or carbon–carbon double bond length within the imidazole ring. The same phenomenon one can see in case of the carbene carbon–nitrogen bond length. An expected fact is the difference between the two double bond lengths in the 1,3-cyclooctadiene ring. The carbene ligand with its bulky substituents takes up significant space in the coordination sphere of the rhodium center, which results in a non-symmetric coordination mode.

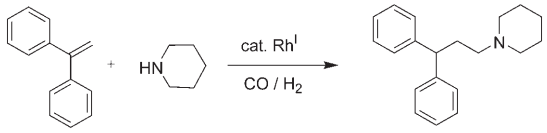
Table 2. Selected bond lengths and angles in complexes **1**, **2** and **4**.

	1[19]	**2**	**4**
Rh–C(carbene)	2.049(16)	2.067(5)	2.060(3)
C=C(carbene)	1.344(3)	1.346(7)	1.347(4)
C=C(olefin)	1.408(3)	1.399(7)	1.396(4)
	1.383(3)	1.372(7)	1.361(5)
C(carbene)–N	1.363(2)	1.363(6)	1.367(4)
	1.364(2)	1.369(6)	1.373(4)
Rh–Cl	2.377(4)	2.368(14)	2.356(11)
N-C(carbene)-N	103.5(14)	104.0(4)	103.6(2)
N-C(carbene)-Rh	132.4(12)	130.1(3)	128.0(2)
	124.1(11)	125.0(3)	126.6(2)

Hydroaminomethylation of 1,1-diphenylethene—optimizing the model system: As a start the rhodium-catalyzed hydroaminomethylation of 1,1-diphenylethene and piperidine to produce 3,3-diphenylpropylpiperidine with **1** as modifying ligand was used to investigate the influence of reaction parameters; that is, reaction time, p_{CO}, p_{H_2}, T, catalyst precursor, and solvent (Table 3). As a reference, our results previously obtained with Xantphos as ligand are also included (Table 3, entries 1–2). It should be noted that the model reaction is not connected with regioselectivity problems. Due to the steric hindrance of the phenyl substituents this type of hydroaminomethylation proceeds with excellent regioselectivity towards the linear amines. On the other hand catalyst activity, productivity, and reaction time are not satisfactory with the known catalyst systems.

According to our previous efforts[20] the hydroaminomethylation in the presence of 0.2 mol% $[Rh(cod)_2]BF_4$ and 0.8 mol% Xantphos gave 76% of the desired amine. In exploratory experiments it was discovered that a slightly increased partial pressure (p_{CO} = 10 bar; p_{H_2} = 50 bar) allowed for lower reaction temperature (125 °C) and a lower catalyst amount (0.1 mol%) (Table 3, entries 3–9). Noteworthy, in the presence of 0.01 mol% catalyst still 49% 3,3-diphenylpiperidine is formed. This corresponds to a catalyst turnover frequency (TOF) of 204 h^{-1}, which is the highest

Table 3. Hydroaminomethylation of 1,1-diphenylethene.[a]



Entry	Rh catalyst (mol %)	Ligand (mol %)	Solvent	p_{CO} [bar]	p_{H_2} [bar]	T [°C]	t [h]	Conv. [%][b]	Sel.	Yield [%][b]	TOF [h^{-1}]
1	$[Rh(cod)_2]BF_4$ (0.2)	Xantphos (0.8)	toluene	5	33	140	30	78	97	76	13
2	$[Rh(cod)_2]BF_4$ (0.2)	Xantphos (0.8)	THF	5	33	140	30	75	52	39	7
3	**1** (0.1)	–	toluene	10	50	125	24	89	90	80	33
4	**1** (0.1)	–	toluene	10	50	125	24	61	80	49	204
5	**1** (0.1)	–	MeOH	10	50	125	24	85	67	57	24
6	**1** (0.1)	–	THF	10	50	125	24	77	99	76	32
7	**1** (0.1)	–	toluene	5	50	125	24	81	93	75	32
8	**1** (0.1)	–	toluene	5	5	125	24	62	84	52	22
9	**1** (0.1)	–	toluene	10	50	105	16	68	99	67	28
10	**2** (0.1)	–	toluene	10	50	125	24	56	95	53	22
11	**3** (0.1)	–	toluene	10	50	125	24	82	94	77	32
12	**4** (0.1)	–	toluene	10	50	125	24	82	88	72	30
13	**4** (0.1)	–	toluene	10	50	125	24	76	91	69	288
14	**5** (0.1)	–	toluene	10	50	125	24	41	41	17	7
15	**5** (0.1)	–	toluene	10	50	125	24	18	11	2	8

[a] Reaction conditions: alkene/amine 1:1 (100 mmol), solvent (30 mL). [b] Conversions and yields were determined by GC using bis(methoxyethyl)ether as an internal standard.

activity obtained for this type of reaction. Among the different solvents tested, toluene, which is known to coordinate to the rhodium center, thereby slowing down hydrogenation reactions,[21] gave the best product yield (80%; TOF = 33 h^{-1}). In methanol high conversion is also obtained, however 28% *N*-formylpiperidine is formed via direct carbonylation of piperdine. In THF the reaction proceeded with slightly lower conversion and yield.

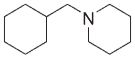
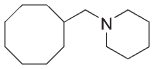
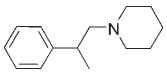
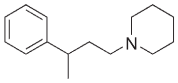
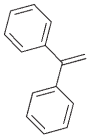
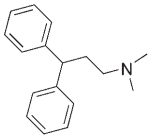
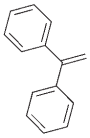
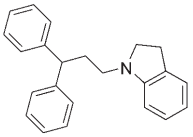
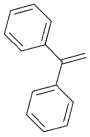
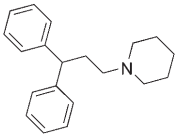
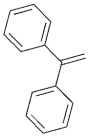
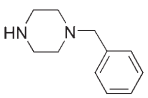
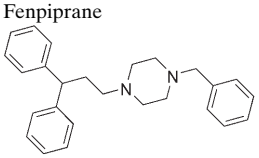
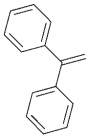
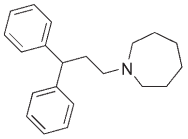
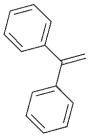
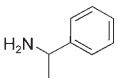
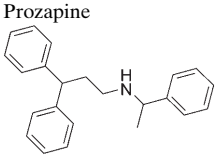
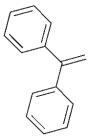
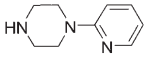
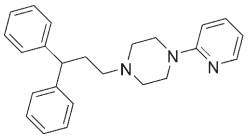
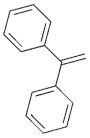
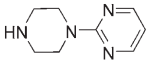
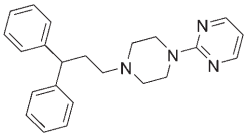
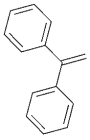
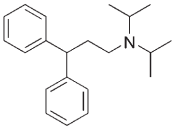
Next, we studied the effect of partial pressures of CO and H_2 (Table 3, entries 8–9). A reduced yield and conversion were obtained, by decreasing the partial pressure of CO up to 5 bar. Decreasing both the partial pressure of CO and H_2 resulted in only 52% yield of 3,3-diphenylpiperidine. In order to compare **1** with other rhodium–carbene catalysts, the reaction of 1,1-diphenylethene was also performed in the presence of complexes **2–5** (Table 3, entries 11–16). While complexes **3** and **5** gave significantly lower product yield, complex **3** showed mediocre activity. The highest catalyst activity (TOF = 287 h^{-1}) is observed in the presence of complex **4**.

Scope and limitations: In the following, our standard catalyst **1** was employed to study the hydroaminomethylation reaction of different aliphatic and aromatic olefins. Apart from styrene, cyclohexene, cyclooctene, α-methylstyrene, and 1,1′-diarylethenes were used as substrates (Table 4). It should be noted that all olefins are significantly less reactive than the typically used terminal aliphatic olefins. With regard to the amine piperidine, dimethylamine and *n*-hexylamine were employed as substrates. Both the reaction of piperidine with cyclohexene and cyclooctene gave excellent yields of the cyclic amines (Table 4, entries 1–2). In agreement with hydroformylations, the hydroaminomethylation of styrene gave preferentially the branched product in good yield (Table 4, entry 3). Due to the increased steric hindrance high linear selectivity (*n*/*iso* = >99:1) is obtained with α-substituted styrenes (Table 4, entries 4–18). In general, the hydroaminomethylation of 1,1-diarylethenes proceeded well with different potentially important amines furnishing in good to excellent yield various currently applied pheniramines, such as Fenpiprane (90%), Prozapine (85%), Fendilline (91%), Diisopromine (88%), and Tolpropamine (86%). Worth mentioning, the reaction of 1-phenylethylamine (primary amine) and 1,1-diphenylethene proceeded smoothly to give the corresponding secondary amine (Fendilline) selectively (Table 4, entry 10).

In addition, novel potentially active compounds are easily accessible in one step in good yield. In this regard the use of *N*-substituted piperazines is interesting because of the well-known biological activity of piperazines. Despite of the potential coordination of chelating 1-(2-pyridyl)piperazine and 1-(2-pyrimidyl)piperazine, the hydroaminomethylated products are produced with good yields and high selectivity of 99% (Table 4, entries 11–12).

Other unsymmetrical 1,1-diarylethenes such as 1-(4-methylphenyl)styrene and 1-(2-pyridyl)styrene also react well to give the corresponding pheniramines selectively. Of particular interest is the one-pot synthesis of the linear pheniramine from 1-(2-pyridyl)styrene, as it is known to give the branched aldehyde in the initial hydroformylation step.[22]

Table 4. Synthesis of variety of pheniramines and their derivatives.[a]

Entry	Olefin	Amine	Major product	Conv. [%][b]	Yield [%][c]	*n*:*iso*
1[b]				>99	99	–
2[b]				99	99	–
3[b]				99	93	21:79
4[b]				99	94	>99:1
5				85	75	>99:1
6[d]				90	86	>99:1
7				93	90	>99:1
			Fenpiprane			
8				95	93	>99:1
9				90	85	>99:1
			Prozapine			
10				93	91	>99:1
			Fendilline			
11				90	87	>99:1
12[d]				90	86	>99:1
13				90	88	>99:1
			Diisopromine			

Finally, we were pleased to find that the reaction of 1,1-diphenylethene and 4-aminopyridine gave the desired product (Table 4, entry 18). This represents the first one-step synthesis of phenpyramine (Milverine), an important antispasmodic agent. Previously this was not possible because the reduction of the intermediate aldehyde is promoted by the coupling partner.[23]

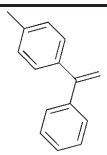
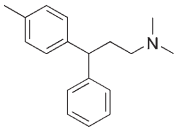
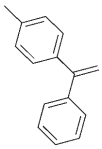
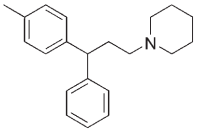
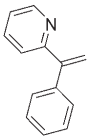
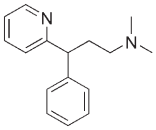
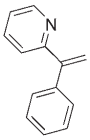
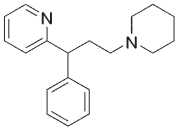
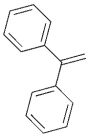
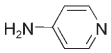
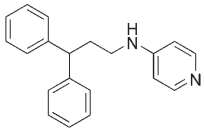
Conclusion

We have demonstrated that novel rhodium–carbene complexes catalyze the synthesis of variety of pheniramines with good activity (TOF up to 288 h^{-1}) compared with any previously reported procedure. In the presence of 0.1 mol% of the catalyst the corresponding arylpropylamines are obtained in high yield and selectivity. This procedure allows for the first time the efficient synthesis of biologically active pheniramines in a single reaction step with high catalyst activity. Thus, the conventional multi-step approach is replaced, thereby, making the procedure more economic and environmentally friendly.

Experimental Section

General methods: Solvents were dried according to the literature.[24] Unless otherwise noted, all reagents were used as received from commercial suppliers. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 with QNP probe head (^1H: 400.1 MHz, ^{13}C 100.6 MHz) at 25 °C. Chemical shifts (δ) are given in ppm and refer to residual solvent ($CDCl_3$) as an internal standard. Coupling constant are reported in Hz. The following abbreviations were used to specify multiplicity, shape, and other properties: s = singlet; d = doublet; t = triplet; q = quartet; quint = quintet; sept = septet; m = multiplet; br = broad; n.o. = not observed. Gas chromatographic analyses

Table 4. (Continued)

Entry	Olefin	Amine	Major product	Conv. [%][b]	Yield [%][c]	*n*:*iso*
14			 Tolpropamine	90	86	>99:1
15				90	86	>99:1
16				90	80	>99:1
17				92	86	>99:1
18			 Phenpyramine	40	35[e]	>99:1

[a] Reaction condition: substrate (10 mmol), [Rh(IMes)(cod)Cl] (0.1 mol%), toluene (30 mL), CO (10 bar), H_2 (50 bar), temperature (125 °C), time (24 h). [b] Conversion were determined by GC analysis using bis(methoxyethyl)ether as an internal standard. [c] Isolated yield based on amines. [d] Reaction time 48 h. [e] 5% of the product with hydrogenated pyridine is obtained as the side product.

were performed on a Hewlett Packard HP 5890 chromatograph with FID detector and a HP5 column (crosslinked 5% phenylmethylsiloxane, l= 30 m, d=250 μm, d_{film}=0.25 μm). Quantitative GC analyses are referenced to bis(methoxyethyl)ether as an internal standard. Mass spectra (GC-MS) experiments were conducted on an Agilent-6890.

In general, the products were isolated from the reaction mixture by solvent evaporation and further purified either by column chromatography on silica gel 60, 0.063–0.2 mm, 70–230 mesh (Merck) or by vacuum distillation wherever necessary. Elemental analyses were determined by C/H/N/S-Analyser 932 (Leco). All yields reported in tables refer to GC yields using bis(methoxyethyl) ether as an internal standard. All isolated yields (varies from <5 to 10% as compared to the GC yield) of compounds estimated to be >98% pure as determined by GC, NMR and elemental analyses. All new compounds were further characterized by HRMS (high resolution mass spectroscopy) and/or elemental analyses. Linear to branched ratio were determined by GC analysis of the crude reaction mixture. Compounds known in the literature were characterized by comparing their ^{1}H NMR, ^{13}C NMR and GC/MS data to the previously reported data. The purity of known compounds were confirmed by GC and have been characterized by comparison (GC) with commercially available samples.

General procedure for the hydroaminomethylation using Rh-carbene catalysts: In a typical experiment, a 100 mL Schlenk flask was charged with [Rh(cod)(carbene)Cl] (0.1 mol%), olefin (10.0 mmol), amine (12.0 mmol), and freshly distilled solvent (30 mL) were added, and the mixture was stirred until it was completely dissolved. The solution was then under argon atmosphere cannula-transferred into a 100 mL stainless steel Parr autoclave. The autoclave was then pressurized with CO (10 bar) and hydrogen (50 bar) and the reaction was carried out at 125 °C for 24 h. After reaction, the autoclave was cooled to about 10 °C and depressurized. The content was transferred to a Schlenk flask under argon atmosphere and analyzed by gas chromatography using bis(methoxyethyl) ether as internal standard.

***N*-(3,3-Diphenylpropyl)piperidine**: Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.13 (m, 10H), 4.05–3.91 (m, 1H), 2.92–2.75 (m, 4H), 2.56–2.43 (m, 2H), 2.36–2.19 (m, 2H), 1.85 (quint, J=5.5 Hz, 4H), 1.73–1.59 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 128.9, 128.4, 126.6, 58.3, 55.2, 49.9, 33.4, 26.7, 25.2 ppm; MS (EI, 70 eV): m/z: 279 [M^+], 263, 220, 193, 165, 115, 98, 91, 77, 70, 55, 41; HRMS: m/z: calcd for $C_{20}H_{25}N$: 279.1967; found: 279.1987 [M^+].

***N*-(3-Phenylbutyl)piperidine**:[25] Yield: 88% (GC); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.38 (m, 5H), 3.29–2.96 (m, 1H), 2.61–2.53 (m, 4H), 2.42–2.35 (m, 2H), 2.33–2.15 (m, 2H), 1.81 (quint, J=5.6 Hz, 4H), 1.69–1.62 (m, 2H), 1.50 ppm (d, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 128.7, 127.4, 126.3, 58.3, 55.1, 38.9, 35.8, 26.5, 24.9, 23.2 ppm: GC-MS (EI, 70 eV): m/z: 217 [M^+], 200, 174, 160, 139, 98, 91, 77, 70, 55, 41, 29; HRMS: m/z: calcd for $C_{15}H_{23}N$: 217.1815; found: 217.1830 [M^+].

***N*-(3,3-Diphenylpropyl)piperidine**: Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.13 (m, 10H), 4.05–3.91 (m, 1H), 2.92–2.75 (m, 4H), 2.56–2.43 (m, 2H), 2.36–2.19 (m, 2H), 1.85 (quint, J=5.5 Hz, 4H), 1.73–1.59 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 128.9, 128.4, 126.6, 58.3, 55.2, 49.9, 33.4, 26.7, 25.2 ppm; GC-MS (EI, 70 eV): m/z: 279 [M^+], 263, 220, 193, 165, 115, 98, 91, 77, 70, 55, 41; HRMS: m/z: calcd for $C_{20}H_{25}N$: 279.1967; found: 279.1987 [M^+].

***N*-(3,3-Diphenylpropyl)azepane**: Yield: 85%; ^{1}H NMR ((400 MHz, $CDCl_3$): δ = 7.23–7.13 (m, 10H), 4.08 (t, J=7.7 Hz, 1H), 2.75–2.56 (m, 4H), 2.56–2.43 (m, 2H), 2.21 (quint, J=7.7 Hz, 2H), 1.59–1.39 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 128.2, 127.7, 125.6, 56.3, 55.3, 49.0, 33.4, 28.1, 26.3 ppm; GC-MS (EI, 70 eV): m/z: 293 [M^+], 264, 236, 214, 193, 165, 112, 91, 70, 58, 42; HRMS: m/z: calcd for $C_{21}H_{27}N$: 293.2169; found: 293.2178 [M^+].

***N*-(3-Phenyl-3-*p*-tolyl-propyl)piperidine**: Yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.33 (m, 9H), 4.18–4.18 (m, 1H), 2.60 (s, 3H), 2.61–2.55 (m, 4H), 2.41–2.33 (m, 2H), 2.33–2.25 (m, 2H), 1.84 (quint, J=5.6 Hz, 4H), 1.68–1.67 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.8, 142.5, 136.0, 129.6, 128.9, 128.3, 128.2, 126.5, 58.4, 55.2, 49.5, 33.4, 26.7, 25.0, 21.5 ppm; GC-MS (EI, 70 eV): m/z: 293 [M^+], 236, 165, 98, 70, 55, 42; HRMS: m/z: calcd for $C_{21}H_{27}N$: 293.4565; found: 293.4574 [M^+].

***N*-(3,3-Diphenylpropyl)-*N*-(1-phenylethyl)amine**: Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.21 (m, 15H), 3.96 (t, J=7.8 Hz, 1H), 3.66 (q, J=6.6 Hz, 1H), 2.44 (m, 2H), 2.21–2.18 (m, 2H), 1.28 ppm (d, J= 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 144.6, 128.3, 128.2, 127.7, 126.6, 126.4, 126.0, 58.2, 48.9, 46.0, 35.6, 24.3 ppm; GC-MS (EI, 70 eV): m/z: 315 [M^+], 300, 238, 210, 194, 181, 165, 152, 134, 120, 105,

91, 77, 58, 42; HRMS: *m/z*: calcd for $C_{23}H_{25}N$: 315.1987; found: 315.1968 [M^+].

***N*-(3,3-Diphenylpropyl)-2,3-dihydro-1*H*-indole**: Yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–6.89 (m, 10H), 6.56–6.19 (m, 4H), 4.01 (t, J=7.7 Hz, 1H), 3.23 (t, J=8.3 Hz, 2H), 2.93–2.89 (m, 2H), 2.84 (t, J=8.3 Hz, 2H), 2.26 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3, 144.5, 129.9, 128.4, 127.8, 127.2, 126.2, 124.3, 117.5, 107.1, 53.1, 48.4, 47.7, 32.9, 28.6 ppm; GC-MS (EI, 70 eV): *m/z*: 313 [M^+], 234, 165, 132, 91, 77, 51, 27; elemental analysis calcd (%) for $C_{23}H_{23}N$: C 88.13, H 7.40, N 4.47; found: C 88.15, H 6.94, N 4.42.

***N*-(3,3-Diphenylpropyl)-4-pyridin-2-yl-piperazine**: Yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44–6.82 (br m, 4H), 7.70–7.41 (m, 10H), 4.28 (t, J=6.9 Hz, 1H), 3.78 (t, J=4.9 Hz, 4H), 2.75 (t, J=4.9 Hz, 4H), 2.62–2.55 (m, 2H), 2.39–2.32 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 148.4, 145.2, 137.8, 128.9, 128.3, 126.6, 113.7, 107.5, 57.9, 53.6, 49.6, 45.7, 33.2 ppm; GC-MS (EI, 70 eV): *m/z*: 357 [M^+], 263, 238, 190, 165, 107, 71, 56, 42, 28; elemental analysis calcd (%) for $C_{24}H_{27}N_3$: C 80.67, H 7.56, N 11.76; found: C 80.62, H 8.05, N 11.63.

***N*-(3,3-Diphenylpropyl)-4-pyrimid-2-yl-piperazine**: Yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.38–6.35 (m, 1H), 8.21–8.19 (m, 2H), 7.22–7.06 (m, 10H), 3.93 (t, J=7.2 Hz, 1H), 3.74 (t, J=4.9 Hz, 4H), 2.39 (t, J=4.9 Hz, 4H), 2.26–2.21 (m, 2H), 2.08–1.98 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 158.1, 145.1, 128.9, 128.2, 126.6, 110.2, 57.4, 53.6, 49.5, 44.1, 33.1 ppm; GC-MS (EI, 70 eV): *m/z*: 358 [M^+], 250, 177, 148, 122, 70, 41; elemental analysis calcd (%) for $C_{23}H_{26}N_4$: C 77.09, H 7.26, N 15.61; found: C 77.12, H 7.22, N 15.40.

***N*-(3,3-Diphenylpropyl)-pyridin-4-yl-amine**: Yield: 35%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J=6.1 Hz, 2H), 7.23–7.09 (m, 10H), 6.36 (d, J=6.1 Hz, 2H), 3.96 (t, J=7.8 Hz, 1H), 3.10–3.04 (m, 2H), 2.34–2.28 (m, 2H), 1.18 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 145.7, 144.2, 129.1, 128.3, 126.1, 107.8, 49.1, 35.0, 31.0 ppm; GC-MS (EI, 70 eV): *m/z*: 288 [M^+], 260, 209, 193, 179, 165, 152, 116, 107, 95, 78, 65, 51, 39; HRMS: *m/z*: calcd for $C_{20}H_{20}N_2$: 288.3957; found: 288.3968 [M^+].

***N*-(3,3-Diphenylpropyl)diisopropylamine**: Yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.13 (m, 10H), 3.95 (t, J=7.5 Hz, 1H), 3.02–2.90 (m, 2H), 2.37–2.30 (m, 2H), 2.23–2.11 (m, 2H), 0.98 ppm (d, J=6.6 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 129.3, 128.4, 126.3, 49.4, 45.6, 40.1, 38.3, 22.0 ppm; GC-MS (EI, 70 eV): *m/z*: 295 [M^+], 300, 238, 210, 194, 181, 165, 152, 134, 120, 105, 91, 77, 58, 42.

Synthesis of Rh–carbene catalysts: A THF solution (10 mL) of substituted imidazole-2-ylidene (1.0 mmol) at room temperature was added slowly to a solution of [{Rh(cod)Cl}$_2$] (0.5 mmol) in THF (20 mL). The clear solution was stirred for 2 h and the solvent was evaporated. The residue was triturated with pentane. The yellow solid obtained was analytically pure. It can be recrystallized from CH_2Cl_2/pentane.

[Chloro]-[(1,2,5,6-η)-1,5-cyclooctadiene]-[1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene]-rhodium(I) (1): Yield = 82%; ^{1}H NMR (400 MHz, 297 K, $CDCl_3$): δ = 7.03 (s, 4H), 6.96 (s, 2H), 4.40 (s, 2H), 3.30 (s, 2H), 2.38 (s, 6H), 2.34 (s, 6H), 2.10 (s, 6H), 1.83 (m, 4H), 1.54 ppm (m, 4H); ^{13}C NMR (100 MHz, 297 K, $CDCl_3$): δ = 183.5 (d, $^1J_{Rh,C}$=52.5 Hz), 139.2, 137.9, 137.0, 135.1, 129.8, 128.8, 124.3, 96.3 (d $^1J_{Rh,C}$=7.6 Hz), 68.7 (d, $^1J_{Rh,C}$=14.3 Hz), 33.2, 28.9, 21.4, 20.0, 18.5 ppm; MS (EI, 70 eV): *m/z*: 550 (13) [M^+], 404 (21), 303 (100); elemental analysis calcd (%) for $C_{29}H_{36}ClN_2Rh$ (550.98): C 63.22, H 6.58, N 5.08; found: C 63.08, H 6.34, N 5.05.

[Chloro]-[(1,2,5,6-η)-1,5-cyclooctadiene]-[1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl-2*H*-imidazol-2-ylidene]-rhodium(I) (2): Yield: 90%; ^{1}H NMR (400 MHz, 297 K, [D$_8$]THF): δ = 7.04–7.03 (m, 4H), 4.40 (m, 2H), 3.31 (m, 2H), 2.37 (s, 12H), 1.99 (s, 6H), 1.80 (s, 6H), 1.75–1.70 (m, 4H), 1.63–1.34 ppm (m, 4H); ^{13}C NMR (75 MHz, 297 K, [D$_8$]THF): δ = 182.8 (d, $J_{Rh,C}$=52 Hz), 139.3, 139.2, 136.0, 130.6, 129.0, 127.4, 95.4 (d, $J_{Rh,C}$=7.7 Hz), 67.3 (d, $J_{Rh,C}$=14.1 Hz), 33.7, 29.3, 21.4, 20.5, 18.6, 9.2 ppm; MS (EI, 70 eV): *m/z*: 578 (39) [M^+], 542 (7), 434 (40), 333 (100); HRMS: *m/z*: calcd for $C_{31}H_{40}N_2ClRh$: 578.1930; found 578.1920 [M^+].

[Chloro]-[(1,2,5,6-η)-1,5-cyclooctadiene]-[1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-4,5-dichloro-2*H*-imidazol-2-ylidene]-rhodium(I) (3): Yield: 91%; ^{1}H NMR (400 MHz, 233 K, [D$_8$]THF): δ = 7.16–7.11 (m, 4H), 4.44 (m, 2H), 3.35 (m, 2H), 2.43–2.38 (m, 12H), 2.06 (s, 6H), 1.78–1.70 ppm (m, 8H); ^{13}C NMR (100 MHz, 233 K, [D$_8$]THF): δ = 187.9 (d, $J_{Rh,C}$= 53.8 Hz), 140.5, 139.1, 136.1, 134.1, 130.6, 129.1, 96.5 (d, $J_{Rh,C}$=7.4 Hz), 68.4 (d, $J_{Rh,C}$=14.0 Hz), 33.4, 29.1, 21.3, 20.1, 18.5 ppm; MS (EI, 70 eV): *m/z*: 618 (32) [M^+], 580 (27), 474 (9), 434 (40), 400 (40), 373 (100), 333 (40), 299 (10); HRMS: *m/z*: calcd for $C_{29}H_{34}N_2Cl_3Rh$: 618.0837; found 618.083 [M^+].

[Chloro]-[(1,2,5,6-η)-1,5-cyclooctadiene]-[1,3-dihydro-1,3-bis(2,4-diisopropylphenyl)-2*H*-imidazol-2-ylidene]-rhodium(I) (4): Yield: 90%; ^{1}H NMR (400 MHz, 233 K, [D$_8$]THF): δ = 7.54–7.48 (m, 4H), 7.46–7.42 (m, 2H), 7.36–7.33 (m, 2H), 4.46 (s, 2H), 3.72 (quint, J=6.6 Hz, 2H), 3.25 (s, 2H), 2.43 (quint, J=6.7 Hz, 2H), 1.82–1.74 (m, 2H), 1.72–1.61 (m, 2H), 1.54–1.43 (m, 4H), 1.42 (d, J=6.5 Hz, 6H), 1.30 (d, J=6.7 Hz, 6H), 1.08 ppm (d, J=7.0 Hz, 12H); ^{13}C NMR (100 MHz, 233 K, [D$_8$]THF): δ = 186.4 (d, $J_{Rh,C}$=51.9 Hz), 148.5, 146.4, 137.5, 130.4, 126.2, 125.2, 95.4 (d, $J_{Rh,C}$=7.4 Hz), 67.9 (d, $J_{Rh,C}$=25.8 Hz), 33.5, 29.9, 29.4, 29.1, 28.6, 23.9, 22.6 ppm; MS (EI, 70 eV): *m/z*: 634 (39) [M^+], 490 (26), 429 (8), 389 (100), 355 (8), 281 (6), 186 (13), 149 (16). HRMS: *m/z*: calcd for $C_{35}H_{48}N_2ClRh$: 634.2556; found 634.254 [M^+].

[Chloro]-[(1,2,5,6-η)-1,5-cyclooctadiene]-[1,3-dihydro-1,3-bis(2,4-diisopropylphenyl)-4,5-dimethyl-2*H*-imidazol-2-ylidene]-rhodium(I) (5): Yield: 95%; ^{1}H NMR (400 MHz, 232 K, [D$_8$]THF): δ = 7.60–7.45 (m, 4H), 7.40–7.30 (m, 2H), 4.45 (m, 2H), 3.78 (septet, J=6.6 Hz, 2H), 3.25 (m, 2H), 2.24 (m, 2H), 1.95 (s, 6H), 1.73 (m, 2H), 1.57 (m, 2H), 1.46 (m, 4H), 1.45 (d, J=6.3 Hz, 6H), 1.23 (d, J=6.6 Hz, 6H), 1.15 (d, J=6.8 Hz, 6H), 1.01 ppm (d, J=6.6 Hz, 6H); ^{13}C NMR (100 MHz, 232 K, [D$_8$]THF): δ = 186.6 (d, $J_{Rh,C}$=50.4 Hz), 149.5, 147.0, 135.6, 130.7), 129.1, 126.4, 124.4, 94.8 (d, $J_{Rh,C}$=8.0 Hz), 68.0 (d, $J_{Rh,C}$=20.0 Hz), 33.7, 29.5, 29.3, 29.2, 27.1, 26.5, 25.6, 24.2, 10.9 ppm; MS (EI, 70 eV): *m/z*: 662 (45) [M^+], 518 (100), 417 (84), 343 (9), 265 (20), 218 (26), 149 (20); HRMS: *m/z*: calcd for $C_{37}H_{52}N_2ClRh$: 627.3180; found 627.3173.

X-ray crystallographic study of compound 2 and 4: Data were collected with a STOE-IPDS-diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. The structure was solved by direct methods (SHELXS-86)[26] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[27] XP (Bruker AXS) was used for structure representation.

Compound 2: Space group $P2_1/c$, monoclinic, a=13.993(3), b=12.057(2), c=17.040(3) Å, β=100.48(3)°, V=2826.9(9) Å^3, Z=4, ρ_{calcd}= 1.360 g cm^{-3}, 8329 reflections measured, 4450 were independent of symmetry and 2844 were observed ($I > 2\sigma(I)$), $R1$=0.043, wR^2 (all data)= 0.098, 316 parameters.

Compound 4: Space group $P2_1/c$, monoclinic, a=17.563(4), b=11.208(2), c=18.774(4) Å, β=114.74(3)°, V=3356.4(12) Å^3, Z=4, ρ_{calcd}= 1.312 g cm^{-3}, 8073 reflections measured, 4387 were independent of symmetry and 3750 were observed ($I > 2\sigma(I)$), $R1$=0.031, wR^2 (all data)= 0.081, 370 parameters.

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