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Well-Defined Regioselective Iminopyridine Rhodium Catalysts for Anti-Markovnikov Addition of Aromatic Primary Amines to 1-Octyne

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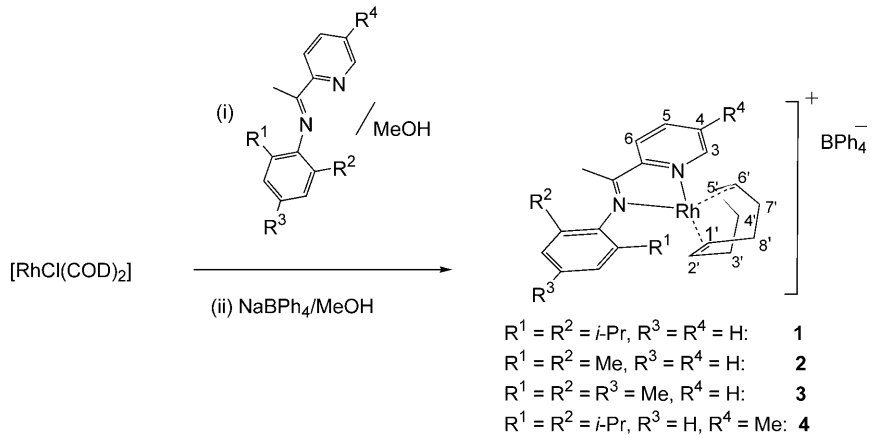
Abstract: A series of cationic rhodium(I) complexes of the type [Rh(N-N)(COD)][BPh_4], containing the following iminopyridine-based bidentate nitrogen donor ligands (N-N): 2,6-diisopropyl-*N*-[1-(pyridin-2-yl)ethylidene]aniline (dipea, **1**), 2,6-dimethyl-*N*-[1-(pyridin-2-yl)ethylidene]aniline (dmpea, **2**), 2,4,6-trimethyl-*N*-[1-(pyridin-2-yl)ethylidene]aniline (tmpea, **3**) and 2,6-diisopropyl-*N*-[1-(4-methylpyridin-2-yl)-ethylidene]aniline] (dipmpea, **4**), were synthesized and fully characterized. The intermolecular hydroamination of a terminal alkyne, such as 1-octyne, with primary aromatic amines in the presence of these cationic rhodium(I) catalysts occurred in an anti-Markovnikov fashion. The rhodium complexes catalyzed the regioselective formation of the *E*-isomer of the corresponding imine, without the formation of the *Z*-isomer or the Markovnikov product. These compounds are also presented as efficient regioselective catalysts for the hydroamination of anilines in the presence of air and/or water.

Keywords: anti-Markovnikov addition; hydroamination reaction; iminopyridine ligands; rhodium compounds

Introduction

C–N bond forming reactions are of considerable interest in both synthetic organic and industrial chemistry due to the importance of amines and their derivatives in almost all areas of chemistry. The catalytic coupling of amines with either alkenes or alkynes by hydroamination is an area that has attracted intense research effort.[1] Hydroamination processes must be regarded as highly desirable transformations in organic chemistry, since the starting materials (alkenes, alkynes and allenes) are inexpensive and readily available and the products are important bulk and fine chemicals, biologically interesting compounds, or versatile synthetic intermediates (amines, imines, enamines). More specifically, imines are commonly employed in C–C bond formations, such as Mannich reactions and aza-Diels–Alder cycloadditions.[2]

An ideal catalytic coupling would combine high TOF (turnover frequency) and broad functional group compatibility. Recent advances have been made using lanthanide and early and late transition metal catalysts; however, a general catalyst for the coupling of alkenes or alkynes to amines is still an unresolved problem. The efficient hydroamination of aliphatic alkenes is not yet possible and remains one of the most important challenges in catalysis research. In contrast, alkynes are generally more reactive in hydroamination reactions.[3] A wide variety of catalysts have successfully been employed in the catalytic cyclization of aminoalkynes, although intermolecular amination reactions with alkynes are much more difficult. Pioneering work was carried out by Barluenga et al., who employed mercury and thallium salts for the Markovnikov hydroamination of alkynes with anilines.[4] In general, a wide variety of metals, including early and late transition metals or lanthanides, have been employed in catalytic intermolecular hydroamination of terminal alkynes to yield Markovnikov products.[5] In contrast, the hydroamination of termi-



Scheme 1. Synthesis of compounds **1–4**.

nal alkynes in an anti-Markovnikov fashion is rare. Eisen et al. reported an anti-Markovnikov hydroamination of terminal alkynes with primary amines using an organouranium complex.[6] Some titanium derivatives have also been applied for anti-Markovnikov alkyne hydroamination, although the use of bulky primary amines was required in these cases.[7] Schafer et al. used bis(amidate)titanium complexes as highly regioselective catalysts for the anti-Markovnikov hydroamination of terminal alkynes with a wide range of primary amines.[8] Recently, Fukumoto et al. described the first catalytic system that allows both primary and secondary amines to react with terminal alkynes to give anti-Markovnikov products.[9]

The work described here concerns our initial approach to develop effective methods for C–N bond formation. The importance of steric protection in late metal-catalyzed chemistry stimulated our interest in the synthesis of bulky iminopyridine-rhodium complexes. We envisaged that the use of these bulky compounds as catalysts for hydroamination reactions might by suitable to achieve better control over the regioselectivity of the reaction. The work described here involved the synthesis and full characterization of novel cationic rhodium complexes of the type [Rh(N-N)(COD)][BPh_4], where (N-N) represents iminopyridine-based ligands with different levels of steric congestion, the regioselective intermolecular hydroamination reaction of aromatic primary amines with 1-octyne and, finally, the influence that the presence of air or water has in such reactions.

Results and Discussion

Iminopyridine ligands were conveniently prepared by condensation of the appropriate amine and ketone.[10] Complexation of the ligand to Rh(I) was achieved by reaction of the ligand with [$RhCl(COD)_2$] in MeOH at room temperature, followed by the addition of $NaBPh_4$ to give the cationic rhodium complexes **1–4** (Scheme 1). All of the complexes are quite air stable in the solid state and in solutions in organic solvents such as acetone, MeOH or CH_2Cl_2.

The products [Rh(N-N)(COD)][BPh_4] where (N-N) represents 2,6-diisopropyl-*N*-[1-(pyridin-2-yl)ethylidene]aniline (dipea, **1**), 2,6-dimethyl-*N*-[1-(pyridin-2-yl)ethylidene]aniline (dmpea, **2**), 2,4,6-trimethyl-*N*-[1-(pyridin-2-yl)ethylidene]aniline (tmpea, **3**) and 2,6-diisopropyl-*N*-[1-(4-methylpyridin-2-yl)ethylidene]aniline] (dipmpea, **4**) were isolated as purple crystalline solids and were fully characterized by spectroscopy, elemental analysis and, in the cases of **1, 3** and **4**, X-ray crystallographic studies. The NMR characteristics of the complexes are consistent with those reported for related Pd(II) complexes containing these types of ligands.[10] The ^{1}H NMR spectra of compounds **1–4** in acetone-d_6 contained resonances at relatively high frequency and these are assigned to protons of the pyridyl ring. ^{1}H NMR spectroscopy also provided some information about the behaviour of the aryl susbtituents in the iminopyridine ligand.[11] In compounds **1** and **4** the isopropyl groups became magnetically non-equivalent and this change can be attributed to hindered rotation of the aryl rings. Solutions of compounds **1–4** in acetone-d_6 give rise to dynamic ^{1}H and ^{13}C NMR spectra in the temperature range between 310 and 183 K. At 273 K only one broad signal is observed for the olefinic protons of the COD ligand, whereas four signals can be detected below 210 K. Each of these four resonances shows Rh coupling, which indicates that the Rh–carbon bonds remain intact. Dissociation of the Rh–N(imine) bond and subsequent 180° rotation about the intact Rh–N(pyridine) bond may account for this process, although other mechanisms cannot be ruled out.

Complexes **1**·CH_2Cl_2, **3**·2 CH_2Cl_2 and **4**·0.25 $C_4H_{10}O$·CH_2Cl_2 were characterized by single-crystal X-ray diffraction studies. Selected bond

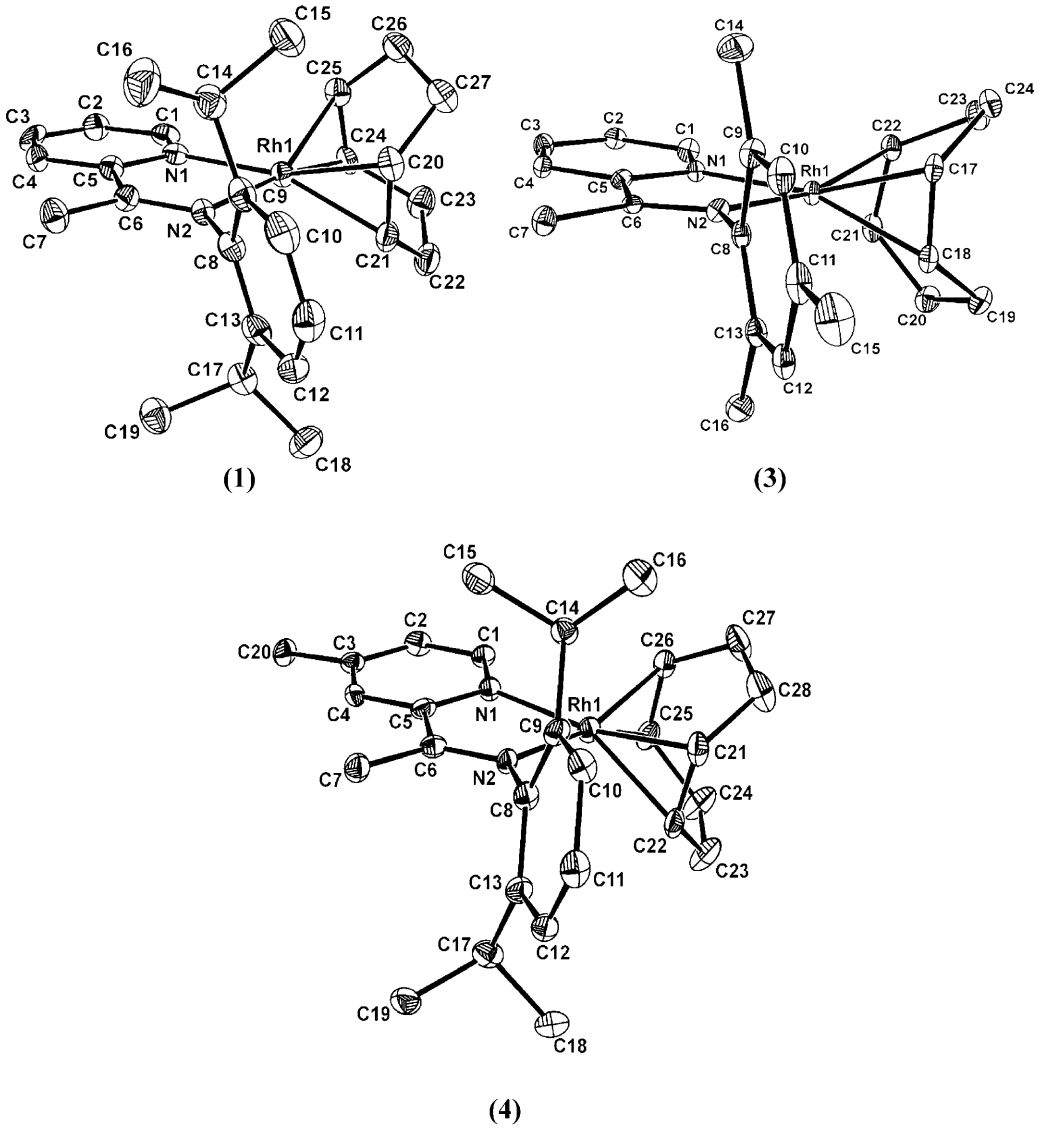


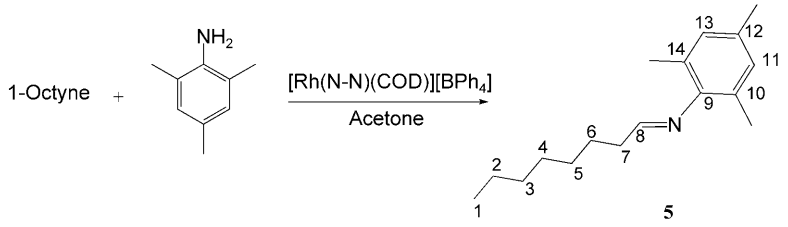
Figure 1. ORTEP plots for the structures of complexes **1**, **3** and **4**. Thermal ellipsoids are given at the 30% probability level.

lengths and angles, and crystallographic details are collected in the Supporting Information.

A convenient view of the molecules is shown in Figure 1 along with the numbering systems used in the crystallographic study. Complexes **3**·2 CH_2Cl_2 and **4**·0.25 $C_4H_{10}O$·CH_2Cl_2 crystallize in the triclinic $\bar{P}$ space group and compound **1**·CH_2Cl_2 crystallizes in the monoclinic $P2_1/n$ space group. All complexes have a monomeric structure in the solid state and the compounds have a square planar geometry with the rhodium centre coordinated by a chelating iminopyridine ligand and by the COD group. As in related systems, the plane of the N–aryl group lies approximately perpendicular to the metal coordination plane.[12] In this conformation the two *ortho*-alkyl groups are located in positions that are expected to influence the reactivity in associative processes. As a consequence of this orientation, the free space available at the rhodium in the coordination plane is partly controlled by the imino aryl susbtituents.The geometry around the Rh atom is almost identical in all three compounds. The values of the chelating angles N–Rh–N are comparable in the three compounds and reflect the small bite sizes of the ligands.[11,13]

Following the pioneering work carried out by Barluenga et al. on the Markovnikov hydroamination of alkynes with anilines,[4] intermolecular hydroaminations have been achieved with catalysts of the alkali metals,[14] early transition metals,[15] lanthanides and actinides.[6,16] The applicability and efficiency of these various types of catalysts are still limited due to their sensitivity to air, humidity and functional groups. In 1999 Wakatsuki et al. introduced a $Ru_3(CO)_{12}$/acid catalyst system that predominantly allowed the conversion of anilines with terminal phenylacetylenes to give the corresponding branched imines.[17] However,

Table 1. Rhodium-catalyzed hydroamination of 1-octyne with 2,4,6-trimethylaniline. Reactions performed in an NMR tube at 50 °C with acetone-d_6 as the solvent.



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Entry	Catalyst	1-Octyne/2,4,6-trimethylaniline	Conversion [%]	Time [h]	TOF $Nt_{25\%}$ [h^{-1}]
1	**1** (1.5 mol%)	2	63	16	1.32
2	**2** (1.5 mol%)	2	55	75	0.20
3	**3** (1.5 mol%)	2	70	40	0.53
4	**4** (1.5 mol%)	2	71	43	0.46
5	**1** (1.5 mol%)	2[a]	27	72	0.11
6	**1** (1.5 mol%)	1	63	16	2.64
7	**1** (1.5 mol%)	0.5	63	16	1.32
8	**1** (1.5 mol%)	2[b]	30	97	0.10
9	**1** (2.5 mol%)	2	63	24	0.21
10	**1** (3.5 mol%)	2	63	28	0.13
11	**1** (1.5 mol%)	2[c]	63	16	1.32
12	**1** (1.5 mol%)	2[d]	63	16	1.32

[a] Reaction at room temperature.
[b] 3 mol% PCy_3.
[c] Reaction exposed to the air.
[d] Mixture of acetone-d_6/D_2O 9/1 as solvent.

only one example was given for the hydroamination of the aliphatic compound 1-octyne with aniline, which gave the corresponding product in 63% yield. Alternative methods that employed titanium complexes were developed by Ackermann,[18] Doye,[7c,d] and Odom[19]. It is noteworthy that all of these approaches involved reaction temperatures of about 100 °C and that non-activated aliphatic alkynes have only given low to moderate yields to date. Late transition metal complexes have the advantage of a low oxophility and better functional group tolerance. Rhodium or iridium complexes have previously been reported to catalyze intermolecular hydroaminations.[9,20] Iminopyridines constitute a broad family of chelating dinitrogen ligands whose coordination chemistry has been used in palladium and nickel catalysis, particularly in olefin polymerization.[11,21] The results of these studies motivated us to study complexes **1**–**4** as suitable active catalysts in intermolecular hydroamination reactions. The initial experiments involving the hydroamination of alkynes were performed under previously described standard reactions conditions.[20a] The most stable imine was obtained by hydroamination of the alkyne followed by tautomerization of the resultant enamine.

Complexes **1**–**4** were tested as catalysts in intermolecular hydroamination reactions; 1.5 mol% of the rhodium complex was added to a mixture of 1-octyne and 2,4,5-trimethylaniline (1:0.5) in acetone-d_6 and the reaction mixture was heated at 50 °C. All of the complexes tested catalyzed the intermolecular hydroamination regioselectively to give the *E*-isomer, through anti-Markovnikov addition, with varying degrees of efficiency (Table 1, entries 1–4). After 16–43 h, compounds **1**, **3** and **4** had promoted a maximum conversion of near 70% (Table 1, entries 1, 3 and 4) while compound **2** needed 75 h (Table 1, entry 2). Compound **1** was significantly more effective than the other catalysts. The substituents on the ligand proved to be an important feature for catalyst activity. The presence of a more electron-donating alkyl group in the aryl ring seems to improve the efficiency of the catalyst in the hydroamination reaction. Imine **5** was obtained in moderate to high yields and with excellent selectivity. Two potential mechanisms for the rhodium catalyst in intermolecular hydroamination reaction of 1-octyne with 2,4,6-trimethylaniline are outlined in Figure 2: Path A involves activation of the C-C multiple bond by coordination to a Lewis acidic metal centre, which renders the alkyne susceptible to nucleophilic attack by the lone electron pair of the amine nitrogen atom. Subsequent protolytic cleavage of the metal-carbon bond provides the enamine product, which desorbs from the coordination sphere of the metal. The resulting enamine isomerizes to the corresponding imine. On the other hand, an amine ac-

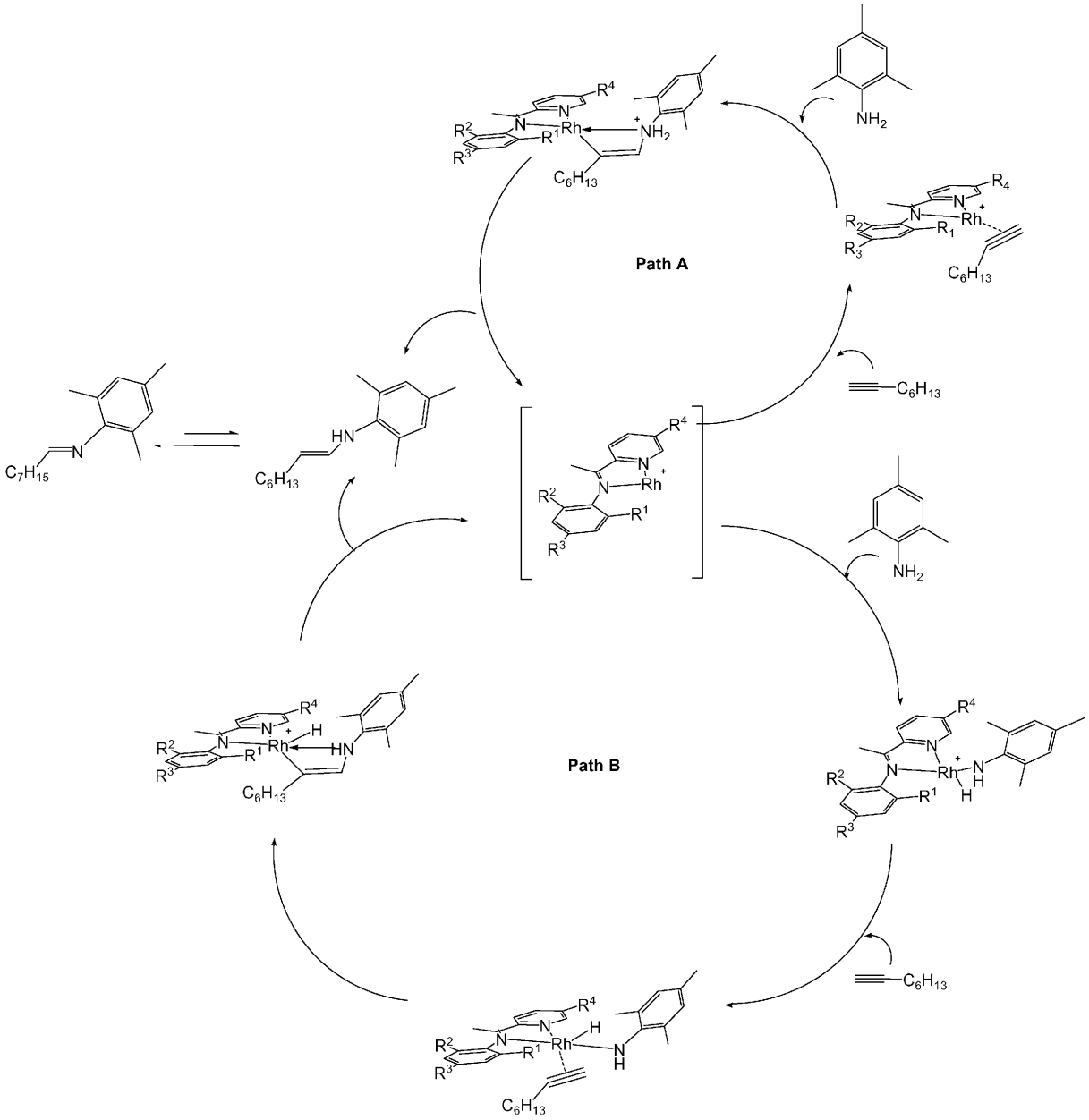


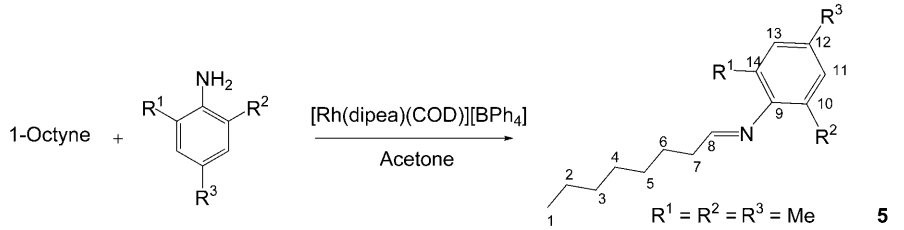
Figure 2. Proposed mechanisms for the hydroamination reaction of 1-octyne with 2,4,6-trimethylaniline in the presence of a cationic rhodium catalyst **1**–**4**.

tivation pathway cannot be excluded (Path B). This pathway might be effective for the couple Rh(I)/Rh(III).[20c,d,22] Oxidative addition of the amine provides a hydrido-amido complex. Subsequently, the alkyne inserts into the M–N bond. Reductive elimination of the product regenerates the active low-valent metal species and generates the enamine product, which tautomerizes to the more stable imine.

Oligomerization of the alkyne was observed as a side reaction. It is important to note that the use of a lower reaction temperature can be a decisive factor in the activity (Table 1, entry 5) but did not appreciably influence in the production of oligomers. With respect to the alkyne/amine ratio, the yields did not increase on using an excess of either amine or alkyne (Table 1, entries 6 and 7).

In 2001 Beller et al.[20a] reported the efficient conversion of aliphatic alkynes with anilines by means of a commercially available rhodium catalyst. However, the addition of a phosphine is a prerequisite for a successful reaction since in the absence of phosphine the product is only formed in very low yields. In order to improve the activities obtained in our experiments, we attempted to achieve the hydroamination reaction of 1-octyne and 2,4,6-trimethylaniline with compound **1** as the catalyst in the presence of PCy_3. Appreciable

Table 2. [Rh(dipea)(COD)][BPh_4] **1** (1.5 mol%) catalyzed hydroamination of 1-octyne with aromatic primary amines.[a]



$R^1 = R^2 = R^3 = Me$ **5**
$R^1 = R^2 = R^3 = H$ **6**
$R^1 = R^2 = i\text{-Pr}, R^3 = H$ **7**
$R^1 = Br, R^2 = R^3 = H$ **8**
$R^3 = Br, R^1 = R^2 = H$ **9**
$R^3 = t\text{-Bu}, R^1 = R^2 = H$ **10**
$R^3 = Me, R^1 = R^2 = H$ **11**
$R^1 = R^2 = t\text{-Bu}, R^3 = H$ **12**
$R^1 = R^2 = Me, R^3 = H$ **13**

Entry	Amine	Conversion [%]	Time [h]	TOF $Nt_{25\%}$ [h^{-1}]
1	2,4,6-trimethylaniline	63	16	1.32
2	aniline	25	4	2.08
3	2,6-diisopropylaniline	50	96	0.17
4	2-bromoaniline	50	2	8.3
5	4-bromoaniline	31	7	1.49
6	4-*tert*-butylaniline	42	2.5	5.6
7	4-methylaniline	42	8	1.73
8	2,6-di-*tert*-butylaniline	70	8	2.98
9	2,6-dimethylaniline	40	50	0.27

[a] Reactions were run in an NMR tube at 50 °C with acetone-d_6 as solvent and a ratio 1-octyne/amine of 2.

improvement in the activity was not observed after the test (Table 1, entry 8). Compounds **1–4** are presented as convenient catalysts for hydroamination reactions without the need to use an external base and these reactions give moderate to good yields.

In order to assess the influence of the catalyst concentration on the outcome of the reaction, different concentrations of catalyst **1** were used, while the concentrations 1-octyne and amine were kept constant (Table 1, entries 1, 9 and 10). A decrease in the turnover frequency was observed on increasing the catalyst concentration. This observation could be indicative of the formation of a less reactive ion aggregate in solution.

The results shown in entry 11 (Table 1) represent a catalyst assay in which purification of solvents and exclusion of air were not performed. It can be seen that catalyst **1** did not lose activity in this assay, showing it to be an efficient catalyst for hydroamination reaction in the presence of air. As special purifications or exclusion of water were not required (Table 1, entry 11), catalyst **1** was evaluated with deuterated water as a co-solvent (Table 1, entry 12). Changes in efficiency were not observed under these conditions.

Encouraged by the performance of complex **1** in the hydroamination of 1-octyne with 2,4,6-trimethylaniline, we decided to expand the scope of the substrate with a series of different substitution patterns in the aniline (Table 2). The results obtained with **1** as a catalyst in the hydroamination reactions of 1-octyne are summarized in Table 2 (entries 1–9). The imines **5–13** were obtained as single products (see isolated yields in the Experimental Section). Electron-donating and electron-withdrawing susbtituents on the aniline ring are tolerated. The conversion levels and the yields in these reactions were found to vary from moderate to high and in all cases the isomer with *E* stereochemistry was obtained as the only product. To make sure that the structure determination of the imine was correct, we synthesized as example the *E*-imine **5** from the corresponding aldehyde and primary amine.[23] The spectral data of (*E*)-2,4,6-trimethyl-*N*-octylideneaniline compare well with those of compound **5**, proving the isolation of the *E*-isomer of the imine products. Unfortunately, the scope of the reaction is strongly limited to aliphatic terminal alkynes and primary amines. In the case of phenylacetylene or 2-octyne, rapid oligomerization occurred and this resulted in very low product yields. Concerning the use of secundary amines, no reaction was observed when *N*-methylaniline, morpholine or piperidine were used as substrates.

Conclusions

In conclusion, a rhodium catalyst stabilized by a chelating iminopyridine ligand has been prepared that had not previously been reported to catalyze the intermolecular hydroamination of alkynes in an anti-Markovnikov fashion to yield the corresponding imine derivatives. Therefore, compounds **1**–**4** were able to catalyze the selective formation of the *E*-isomer. Further studies examining thoroughly the effect of changes to the substituents of the ligand framework on the catalysis behaviour of the complexes are underway.

Experimental Section

General Procedures

All manipulations were performed under nitrogen using standard Schlenk techniques. $[RhCl(COD)]_2$ and MeOH were used as purchased (Aldrich). Liquid amines were distilled from CaH_2. Alkynes were degassed, flushed with nitrogen, and stored over molecular sieves (4 Å). Iminiopyridine ligands were obtained by standard literature methods.[10] Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. Microanalyses were carried out with a Perkin–Elmer 2400 CHN analyzer. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury FT-300 spectrometer and referenced to the residual deuterated solvent. The NOESY-1D, g-HSQC, DEPT, COSY spectra were recorded on a Varian Inova FT-500 spectrometer with the following acquisition parameters: irradiation time 2 s and number of scans 256, using standard Varian-FT software. Two-dimensional NMR spectra were acquired using standard Varian-FT software and processed using an IPC-Sun computer. The imine product structures were confirmed by GC-MS analyses at 'Laboratorio Espectrometría Masas y Cromatografía', University of Córdoba (Spain).

General Procedure for Hydroamination Reactions in NMR Tube Scale

Catalytic reactions were performed on a small scale in an NMR tube fitted with a concentric Teflon valve. Reactions were performed in the NMR spectrometer with 0.5 mmol of aromatic primary amine, 1 mmol of 1-octyne and 1.5 mol% of cationic rhodium complex in approximately 0.6 mL of acetone-d_6 at 50 °C under nitrogen. The conversion of the starting material to product was determined by integration of the product resonances relative to the substrate peaks in the ^1H NMR spectrum. The TOF (turnover frequency) (Nt/h) was calculated as the number of moles of product/mole of catalyst/hour and was calculated at the point of 25% conversion of substrate to product.

X-Ray Crystallographic Structure Determination for Complexes $1{\cdot}CH_2Cl_2$, $3{\cdot}2\,CH_2Cl_2$ and $4{\cdot}0.25\,C_4H_{10}O{\cdot}CH_2Cl_2$

Single crystals were mounted on a glass fibre and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite monochromated Mo-Kα radiation source ($\lambda = 0.71073$ Å). Data were integrated using SAINT[24] and an absorption correction was performed with the program SADABS.[25] The software package SHELXTL version 6.12[26] was used for space group determination, structure solution and refinement by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

CCDC 713863, 713864 and 713865 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Rhodium Complexes

[Rh(dipea)(COD)][BPh$_4$] (1): In a 250-mL Schlenk tube, a solution of dipea [2,6-diisopropyl-*N*-(1-(pyridin-2-yl)ethylidene)aniline] (0.37 g, 1.20 mmol) in CH_3OH (10 mL) was added dropwise by cannula under N_2 to a solution of $[RhCl(COD)]_2$ (0.30 g, 0.60 mmol) in CH_3OH (20 mL). The solution became dark purple and the mixture was stirred for 1 hour. After this time, a solution of $NaBPh_4$ (0.41 g, 1.20 mmol) in CH_3OH (20 mL) was added to the mixture. A dark purple precipitate was observed. The solid was filtered off and recrystallized from CH_2Cl_2/Et_2O (8/2) at −26 °C to give compound **1** as purple crystals suitable for X-ray diffraction; yield: 0.45 g (93%). Anal. calcd. for $C_{51}H_{56}BN_2Rh$: C 75.56, H 6.96, N 3.46; found: C 74.98, H 6.64, N, 3.79; ^1H NMR (300 MHz, acetone-d_6, 297 K): δ = 8.29 (m, 1H, H3-py), 8.26 (m, 1H, H6-py), 8.06 (m, 1H, H5-py), 7.82 (m, 1H, H4-py), 7.41 (m, 2H, *m*-Ar), 6.94 (m, 1H, *p*-Ar), 7.34, 6.77, 6.92 (3 m, 20H, phenyl rings), 4.18 (bs, 4H, H1′,2′,5′,6′-COD), 3.23 [m, 2H, CH(Me)$_2$], 2.48, 2.06 (m, 4H, H3′,4′,7′,8′-COD), 2.05 (s, 3H, (Me)C=N), 1.47, 1.14 [2d, 6H each, $^3J = 7$ Hz, CH(Me)$_2$]; ^{13}C NMR (300 MHz, acetone-d_6, 297 K): δ = 206.3 (C=N), 142.4 (C3-py), 140.1 (C6-py), 131.0 (C5-py), 129.3 (p-Ar), 128.9 (C4-py), 125.3 (*m*-Ar), 122.2, 125.9, 136.9 (phenyl rings), 88.1 (C1′,2′,5′,6′-COD), 30.1, 29.8 (C3′,4′,7′,8′-COD), 29.7 [CH(Me)$_2$], 28.7 [(Me)C=N], 25.2, 23.6 [CH(Me)$_2$].

[Rh(dmpea)(COD)][BPh$_4$] (2): The synthesis of **2** was carried out in an identical manner to **1**. $[RhCl(COD)]_2$ (0.30 g, 0.60 mmol), dmpea [2,6-dimethyl-*N*-(1-(pyridin-2-yl)ethylidene)aniline] (0.27 g, 1.20 mmol) and $NaBPh_4$ (0.41 g, 1.20 mmol); yield: 0.41 g (91%). Anal. calcd. for $C_{47}H_{48}BN_2Rh$: C 74.81, H 6.41, N 3.71; found: C 75.10, H 6.34, N 3.57; ^1H NMR (300 MHz, acetone-d_6, 297 K): δ = 8.34 (m, 1H, H3-py), 8.29 (m, 1H, H6-py), 8.13 (m, 1H, H5-py), 7.88 (m, 1H, H4-py), 7.24 (m, 2H, *m*-Ar), 7.21 (m, 1H, *p*-Ar), 7.33, 6.77, 6.92 (3 m, 20H, phenyl rings), 4.18 (bs, 4H, H1′,2′,5′,6′-COD), 2.49, 2.08 (2 m, 4H each, H3′,4′,7′,8′-COD), 2.34 (s, 6H, *o*-Me-Ar), 2.05 [s, 3H, (Me)C=N]; ^{13}C NMR (300 MHz, acetone-d_6, 297 K): δ = 206.3 (C=N), 143.8 (C3-py), 143.4 (C6-py), 132.0 (C5-py), 129.8 (*p*-Ar),

129.3 (C4-py), 126.3 (*m*-Ar), 122.2, 125.9, 136.9 (phenyl rings), 88.3 (C1′,2′,5′,6′-COD), 30.4, 30.2 (C3′,4′,7′,8′-COD), 30.3 [(Me)C=N], 19.2 (*o*-Me-Ar).

[Rh(tmpea)(COD)][BPh$_4$] (3): The synthesis of **3** was carried out in an identical manner to **1**. [RhCl(COD)]$_2$ (0.30 g, 0.60 mmol), tmpea [2,4,6-trimethyl-*N*-(1-(pyridin-2-yl)ethylidene)aniline] (0.29 g, 1.20 mmol) and NaBPh$_4$ (0.41 g, 1.20 mmol); yield: 0.42 g (94%); anal. calcd. for $C_{48}H_{50}BN_2Rh$: C 75.00, H 6.56, N 3.64; found: C 75.21, H 6.39, N 3.73; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 8.30 (m, 1H, H3-py), 8.28 (m, 1H, H6-py), 8.10 (m, 1H, H5-py), 7.84 (m, 1H, H4-py), 7.05 (m, 2H, *m*-Ar), 7.34, 6.77, 6.92 (3 m, 20H, phenyl rings), 4.13 (bs, 4H, H1′,2′,5′,6′-COD), 2.48, 2.06 (2 m, 4H each, H3′,4′,7′,8′COD), 2.30 (s, 3H, *p*-Me-Ar), 2.28 (s, 6H, *o*-Me-Ar), 2.05 [s, 3H, (Me)C=N]; ^{13}C NMR (300 MHz, acetone-d_6, 297 K): δ = 206.3 (C=N), 141.8 (C3-py), 139.9 (C6-py), 130.3 (C5-py), 128.7 (C4-py), 125.3 (*m*-Ar), 121.6, 125.4, 136.4 (phenyl rings), 87.5 (C1′,2′,5′,6′-COD), 30.5, 30.1 (C3′,4′,7′,8′-COD), 30.2 [(Me)C=N], 20.2 (*p*-Me-Ar), 17.4 (*o*-Me-Ar).

[Rh(dipmpea)(COD)][BPh$_4$] (4): The synthesis of **4** was carried out in an identical manner to **1**. [RhCl(COD)]$_2$ (0.30 g, 0.60 mmol), dipmpea [2,6-diisopropyl-*N*-(1-(5-methylpyridin-2-yl)ethylidene)aniline] (0.35 g, 1.20 mmol) and NaBPh$_4$ (0.41 g, 1.20 mmol); yield: 0.46 g (94%); anal. calcd. for $C_{52}H_{58}BN_2Rh$: C 75.73, H 7.09, N 3.40; found: C 75.61, H 6.89, N 3.13; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 8.20 (m, 1H, H3-py), 7.94 (m, 1H, H6-py), 7.70 (m, 1H, H5-py), 7.34 (m, 1H, *p*-Ar), 6.90 (m, 2H, *m*-Ar), 7.34, 6.77, 6.92 (3 m, 20H, phenyl rings), 4.13 (bs, 4H, H1′,2′,5′,6-COD), 2.47, 2.07 (2 m, 4H each, H3′,4′,7′,8′-COD), 3.23 [m, 2H, CH(Me)$_2$], 2.60 (s, 3H, Me-Ar), 1.48, 1.14 [2d, 6H each, ^3J = 7 Hz, CH(Me)$_2$], 2.05 [s, 3H, (Me)C=N], ^{13}C NMR (300 MHz, acetone-d_6, 297 K): δ = 206.3 (C=N), 149.4 (C3-py), 139.5 (C6-py), 130.6 (C5-py), 129.5 (*p*-Ar), 128.8 (C4-py), 125.4 (*m*-Ar), 121.6, 124.8, 136.5 (phenyl rings), 87.8 (C1′,2′,5′,6′-COD), 30.3, 29.9 (C3′,4′,7′,8′-COD), 29.4 [CH(Me)$_2$], 28.7 [(Me)C=N], 24.6, 23.0 [CH(Me)$_2$], 20.9 (Me-py).

Synthesis of Imine Compounds

(*E*)-2,4,6-Trimethyl-*N*-octylideneaniline (5): 1-Octyne (0.55 g, 5.0 mmol) was added dropwise to a solution of the [Rh(dipea)(COD)][BPh$_4$] **1** (1.5 mol%) and 2,4,6-trimethylaniline (0.34 g, 2.5 mmol) in acetone (30 mL) at room temperature, and the mixture was refluxed for 24 h. Isolation of the product was done by fractional distillation under vacuum; yield: 55%; bp 71–72 °C/0.1–0.2 mbar; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 7.40 (m, 1H, H8), 6.81 (s, 2H, H11,13), 2.27 (m, 2H, H7), 2.23 (s, 3H, Me12), 2.17 (m, 2H, H6), 2.06 (m, 2H, H5), 1.93 (s, 6H, Me10,14), 1.29–1.62 (m, 6H, H2,3,4), 0.92 (m, 3H, H1; ^{13}C NMR (75 MHz, acetone-d_6, 297 K): δ = 163.4 (C8), 146.9 (C9), 136.4 (C11,13), 131.2 (C10,14), 128.7 (C12), 31.5 (C5), 28.9 (C4), 28.7 (C6), 22.7 (C7), 18.3 (C3), 18.1 (C2), 22.6 (Me12), 17.3 (Me10,14), 13.8 (C1); MS: *m*/*z* (%) = 245 (M$^+$, 38), 119 (81), 189 (100).

(*E*)-*N*-Octylideneaniline (6): The synthesis of **6** was carried out in an identical manner to **5**. 1-Octyne (0.55 g, 5.0 mmol), [Rh(dipea)(COD)][BPh$_4$] **1** (1.5 mol%) and aniline (0.51 g, 2.5 mmol). Fractional distillation afforded **6** as a colourless oil; yield: 20%; bp 65–66 °C/0.1–0.2 mbar; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 7.40 (m, 1H, H8), 7.21 (m, 2H, H11,13), 6.69 (m, 1H, H12), 6.51 (m, 2H, H10,14), 2.20–2.06 (m, 6H, H5,6,7), 1.62–1.29 (m, 6H, H2,3,4), 0.92 (m, 3H, H1); ^{13}C NMR (75 MHz, acetone-d_6, 50 °C): δ = 163.4 (C8), 145.1 (C9), 133.4 (C11,13), 125.6 (C12), 117.0 (C10,14), 28.1 (C5), 26.4 (C4), 25.3 (C6), 19.3 (C7), 14.8 (C2,3), 10.4 (C1); MS: *m*/*z* (%) = 203 (M$^+$, 31), 77 (78), 132 (100).

(*E*)-2,6-Diisopropyl-*N*-octylideneaniline (7): The synthesis of **7** was carried out in an identical manner to **5**. 1-Octyne (0.55 g, 5.0 mmol), [Rh(dipea)(COD)][BPh$_4$] **1** (1.5 mol%) and 2,6-diisopropylaniline (0.72 g, 2.5 mmol). Fractional distillation afforded **6** as a colourless oil; yield: 48%; bp 86–87 °C/0.1–0.2 mbar; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 7.40 (m, 1H, H8), 7.08 (t, 1H, $^3J_{H,H}$ = 7.6 Hz, H12), 6.99 (m, 2H, $^3J_{H,H}$ = 7.6 Hz, H11,13), 2.69 [m, 2H, CH(CH$_3$)$_2$], 2.25 (m, 2H, H7), 2.17 (m, 2H, H6), 2.06 (m, 2H, H5), 1.13 [d, 12H, $^3J_{H,H}$ = 6.6 Hz, CH(CH$_3$)$_2$], 1.53–1.10 (m, 6H, H2,3,4), 0.92 (m, 3H, H1); ^{13}C NMR (75 MHz, acetone-d_6, 297 K): δ = 163.4 (C8), 147.1 (C9), 122.8 (C11,13), 119.9 (C12), 31.6 (C5), 29.3 (C4), 27.9 (C6), 26.4 [CH(CH$_3$)$_2$], 22.7 (C7), 22.3 [CH(CH$_3$)$_2$], 18.6 (C3), 18.3 (C2), 14.8 (C1); MS: *m*/*z* (%) = 287 (M$^+$, 28), 216 (100), 161 (70).

(*E*)-2-Bromo-*N*-octylideneaniline (8): The synthesis of **8** was carried out in an identical manner to **5**. 1-Octyne (0.55 g, 5.0 mmol), [Rh(dipea)(COD)][BPh$_4$] **1** (1.5 mol%) and 2-Bromoaniline (0.71 g, 2.5 mmol). Fractional distillation afforded **6** as a colourless oil; yield: 49%; bp 86–87 °C/0.1–0.2 mbar; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 7.42 (m, 1H, H8), 7.33, 7.29, 6.93, 6.84 (4 m, 1H each, H11–14), 2.81 (m, 2H, H7), 2.20–2.06 (m, 4H, H6,5), 1.50–1.00 (m, 6H, H4,3,2), 0.92 (m, 3H, H1); ^{13}C NMR (75 MHz, acetone-d_6, 297 K): δ = 162.2 (C8), 145.9 (C9), 142.1 (C13), 136.2 (C12), 129.3 (C11), 119.1 (C10), 31.9 (C4), 28.5 (C5), 28.3 (C6), 22.5 (C7), 19.9 (C2,3), 17.1 (C1); MS: *m*/*z* (%) = 281 (M$^+$, 21), 209 (100), 154 (44).

(*E*)-4-Bromo-*N*-octylideneaniline (9): The synthesis of **9** was carried out in an identical manner to **5**. 1-Octyne (0.55 g, 5.0 mmol), [Rh(dipea)(COD)][BPh$_4$] **1** (1.5 mol%) and 4-Bromoaniline (0.65 g, 2.5 mmol). Fractional distillation afforded **9** as a colourless oil; yield: 28%; bp 85–86 °C/0.1–0.2 mbar; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 7.45 (m, 1H, H8), 7.35 (d, 2H, $^3J_{H,H}$ = 8.4 Hz, H13,11), 6.54 (d, 2H, $^3J_{H,H}$ = 8.4 Hz, H14,10), 2.24 (m, 2H, H7), 2.20–2.06 (m, 4H, H6,5), 1.50–1.00 (m, 6H, H4,3,2), 0.92 (m, 3H, H1); ^{13}C NMR (75 MHz, acetone-d_6, 297 K): δ = 160.2 (C8), 148.9 (C9), 132.4 (C11,13), 122.2 (C10,14), 31.2 (C5), 29.1 (C4), 27.9 (C6), 21.1 (C7), 18.6 (C3), 18.3 (C2), 13.9 (C1). MS: *m*/*z* (%) = 281 (M$^+$, 21), 224 (100), 154 (44).

(*E*)-4-*tert*-butyl-*N*-octylideneaniline (10): The synthesis of **10** was carried out in an identical manner to **5**. 1-Octyne (0.55 g, 5.0 mmol), [Rh(dipea)(COD)][BPh$_4$] **1** (1.5 mol%) and 4-*tert*-butylaniline (0.64 g, 2.5 mmol). Fractional distillation afforded **10** as a colourless oil; yield: 40%; bp 87–88 °C/0.1–0.2 mbar; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 7.41 (m, 1H, H8), 7.36 (d, 2H, $^3J_{H,H}$ = 8.1 Hz, H13,11), 6.61 (d, 2H, $^3J_{H,H}$ = 8.1 Hz, H14,10), 2.27 (m, 2H, H7), 2.20–2.06 (m, 4H, H6,5), 1.21 (s, 9H, *t*-Bu12), 1.50–1.00 (m, 6H, H4,3,2), 0.92 (m, 3H, H1); ^{13}C NMR (75 MHz, acetone-d_6, 297 K): δ = 161.6 (C8), 150.1 (C9), 138.6 (C11,13), 120.9 (C10,14), 31.3 (C5), 31.6 (*t*-Bu12), 29.3 (C4), 27.9 (C6), 22.5

(C7), 18.5 (C3), 18.3 (C2), 13.8 (C1); MS: *m/z* (%) = 259 (M^+, 34), 202 (100), 133 (66).

(*E*)-4-Methyl-*N*-octylideneaniline (11): The synthesis of **11** was carried out in an identical manner to **5**. 1-Octyne (0.55 g, 5.0 mmol), [Rh(dipea)(COD)][BPh_4] **1** (1.5 mol%) and 4-methylaniline (0.54 g, 2.5 mmol). Fractional distillation afforded **11** as a colourless oil; yield: 40%; bp 68–69 °C/0.1–0.2 mbar; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 7.44 (m, 1H, H8), 7.10 (d, 2H, $^3J_{H,H}$ = 8.1 Hz, H13,11), 6.59 (d, 2H, $^3J_{H,H}$ = 8.1 Hz, H14,10), 2.27 (m, 2H, H7), 2.20–2.06 (m, 4H, H6,5), 2.23 (s, 3H, Me12), 1.50–1.00 (m, 6H, H4,3,2), 0.92 (m, 3H, H1); ^{13}C NMR (75 MHz, acetone-d_6, 297 K): δ = 161.7 (C8), 152.1 (C9), 135.5 (C11,13), 123.8 (C10,14), 31.6 (C5), 29.3 (C4), 26.6 (Me12), 26.6 (C6), 22.8 (C7), 17.9 (C3), 17.7 (C2), 14.1 (C1); MS: *m/z* (%) = 217 (M^+, 13), 160 (100), 91 (63).

(*E*)-2,6-Di-*tert*-butyl -*N*-octylideneaniline (12): The synthesis of **12** was carried out in an identical manner to **5**. 1-Octyne (0.55 g, 5.0 mmol), [Rh(dipea)(COD)][BPh_4] **1** (1.5 mol%) and 2,6-di-*tert*-butylaniline (0.79 g, 2.5 mmol). Fractional distillation afforded **12** as a colourless oil; yield: 66%; bp 100–102 °C/0.1–0.2 mbar; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 7.41 (m, 1H, H8), 7.14 (t, 1H, $^3J_{H,H}$ = 7.6 Hz, H12), 6.53 (m, 2H, $^3J_{H,H}$ = 7.6 Hz, H11,13), 2.21 (m, 2H, H7), 2.17 (m, 2H, H6), 2.06 (m, 2H, H5), 1.27 (s, 18H, *t*-Bu14,10), 1.50–1.10 (m, 6H, H2,3,4), 0.92 (m, 3H, H1); ^{13}C NMR (75 MHz, acetone-d_6, 297 K): δ = 163.4 (C8), 151.2 (C9), 121.1 (C12), 116.6 (C11,13), 36.0 [$C(CH_3)_3$], 31.6 (C5), 31.4 [$C(CH_3)_3$], 29.3 (C4), 27.8 (C6), 22.7 (C7), 18.8 (C3), 18.5 (C2), 14.18 (C1); MS *m/z* (%) = 315 (M^+, 19), 272 (100), 189 (55).

(*E*)-2,6-Dimethyl-*N*-octylideneaniline (13): The synthesis of **13** was carried out in an identical manner to **5**. 1-Octyne (0.55 g, 5.0 mmol), [Rh(dipea)(COD)][BPh_4] **1** (1.5 mol%) and 2,6-dimethylaniline (0.58 g, 2.5 mmol). Fractional distillation afforded **13** as a colourless oil; yield: 37%; bp 69–70 °C/0.1–0.2 mbar; ^{1}H NMR (300 MHz, acetone-d_6, 297 K): δ = 7.40 (m, 1H, H8), 6.98 (d, 2H, $^3J_{H,H}$ = 7.1 Hz, H11,13), 6.82 (m, 1H, H12), 2.24 (m, 2H, H7), 2.17 (m, 2H, H6), 2.06 (m, 2H, H5), 1.97 (s, 6H, Me14,10), 1.53–1.10 (m, 6H, H2,3,4), 0.92 (m, 3H, H1); ^{13}C NMR (75 MHz, acetone-d_6, 297 K): δ = 160.4 (C8), 149.8 (C9), 127.6 (C12), 116.9 (C11,13), 31.6 (C5), 29.3 (C4), 27.9 (C6), 22.7 (C7), 18.7 (C3), 18.5 (Me14,10), 18.3 (C2), 13.8 (C1); MS: *m/z* (%) = 231 (M^+, 12), 188 (100), 105 (60).

Supporting Information

Full crystallographic data for **1**, **3** and **4** are available in the Supporting Information.

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