Rhodium–*N*-Heterocyclic Carbene Catalyzed Hydroalkenylation Reactions with 2-Vinylpyridine and 2-Vinylpyrazine: Preparation of Nitrogen-Bridgehead Heterocycles

Ramón Azpíroz,[†] Andrea Di Giuseppe,[†] Vincenzo Passarelli,^{‡,†} Jesús J. Pérez-Torrente,[†] Luis A. Oro,[†] and Ricardo Castarlenas,^{*,†}

[†]Departamento de Química Inorgánica – Instituto de Síntesis Química y Catálisis Homogénea-ISQCH, Universidad de Zaragoza – CSIC, C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain

[‡] Centro Universitario de la Defensa, Ctra Huesca S/N 50090 Zaragoza, Spain

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ABSTRACT: Dinuclear rhodium–NHC complexes of formula $[\text{Rh}(\mu\text{-Cl})(\text{NHC})(\eta^2\text{-coe})]_2$ react with 2-vinylpyridine to yield the chelate compounds $\text{RhCl}(\text{NHC})(\kappa\text{-N},\eta^2\text{-CH}_2=\text{CHC}_5\text{H}_4\text{N})$ {NHC = IPr, 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-carbene; IMes, 1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-carbene}. The strained metallacycle can be opened by substitution of the pyridine ring by the small electron-rich PEt_3 to give $\text{RhCl}(\text{IPr})\{\eta^2\text{-CH}_2=\text{CH}(\text{C}_5\text{H}_4\text{N})\}(\text{PEt}_3)$, whereas π -ligands such as olefins or alkynes undergo C-C coupling to yield 2-(butenyl)pyridine or 2-(butadienyl)pyridine $\text{RhCl}(\text{NHC})\{\kappa\text{-N},\eta^2\text{-CH(R)}=\text{CH}(\text{C}_5\text{H}_4\text{N})\}$ complexes by formal hydroalkenylation of the unsaturated bond by vinylpyridine. Reaction of the dinuclear precursors with 2-vinylpyrazine in the presence of pyridine affords the η^2 derivative $\text{RhCl}(\text{IPr})\{\eta^2\text{-CH}_2=\text{CH}(\text{C}_4\text{H}_3\text{N}_2)\}(\text{py})$. Compound $\text{RhCl}(\text{IMes})(\kappa\text{-N},\eta^2\text{-CH}_2=\text{CHC}_5\text{H}_4\text{N})$ is an efficient catalyst for the hydroalkenylation of a range of alkenes and alkynes with 2-vinylpyridine and 2-vinylpyrazine. The butadienyl-heterocycle derivatives resulting from coupling of 2-vinylazines with alkynes undergo a thermal 6π -electrocyclization to yield 4*H*-quinolizines or 6*H*-pyrido-[1,2-*a*]pyrazines depending on the nature and position of the substituent of the butadienyl fragment. DFT calculations reveal that fused N-bridgehead heterocycles are more stable than opened butadienylazine derivatives, in spite of the dearomatization of the azine moiety.

INTRODUCTION

Transition metal mediated C-C coupling via C-H activation has become nowadays a selective and atom-economical tool for synthetic chemists.¹ In general, a nucleophilic directing group facilitates the activation process. Pyridine scaffolds constitute a prevalent family of these auxiliaries which have been successfully applied in the activation of aromatic $\text{C}(\text{sp}^2)\text{-H}^2$ or even $\text{C}(\text{sp}^3)\text{-H}$ bonds.³ However, functionalization of olefinic C-H bonds is more problematic owing to the dichotomic behavior of alkenyl-substituted pyridines in C-C coupling transformations (Scheme 1). Alkenylpyridines can be involved in Heck-type processes due to the π -electrons of the double bond⁴ or, alternatively, undergo direct C-H cleavage by the metal center. In the latter case, depending on the coupling partner and the catalyst, two main processes can take place. A non-oxidative base-promoted C-H activation of the alkenylpyridine and subsequent coupling with an electrophile⁵ or a Murai-type hydroalkenylation of unsaturated substrates.⁶

Scheme 1. Functionalization of the Olefinic C-H Bond of Pyridine-Substituted Olefins

Regardless of the coupling mechanism, coordination of 2-vinylpyridine moiety to the metallic center is essential for the catalytic activity. The versatility of vinylpyridine as ligand is reflected in the variety of coordination modes (Scheme 2). The most typical is that both the nitrogen and the double bond coordinate in a chelate fashion (**a**)⁷ or as a bridge between two metals (**b**).^{7a,8} In some cases, depending on the metal and the co-

ligands, monocoordination by the nitrogen atom (**c**)⁹ or the double bond (**d**)¹⁰ have also been observed. Notably, dearomatization of pyridine ring to an alkyl-amido ligand has been described in bis-cyclopentadienyl zirconium complexes (**e**).¹¹ In spite of the chelate coordination of 2-vinylpyridine in species **a**, it does not bind strongly to the metal center, mainly due to the high strain of the metallacycle formed, therefore allowing it to participate in catalytic transformations.

Scheme 2. Coordination Modes of 2-Vinylpyridine

Fused heterocycles containing a bridgehead nitrogen are widespread in natural and synthetic alkaloids.¹² Extensive research has been carried out for the development of efficient synthetic protocols, among which organometallic catalysts have played a prominent role.¹³ Quinolizine-based derivatives belong to this interesting family.¹⁴ However, the usual instability of these species precludes its isolation,¹⁵ and consequently, they have been alternatively obtained as quinolizidines,¹⁶ quinolizinium salts¹⁷ or quinolizinones.¹⁸ Moreover, examples of formation of pyrido[1,2-a]pyrazines are even more scarce.¹⁹ In this context, we have described in a previous report that the quinolizine skeleton can be formed by thermal 6 π -electrocyclic rearrangement within a butadienylpyridine framework.²⁰ However, that synthetic pathway presents an important handicap, the lack of an efficient and straightforward access to butadienylpyridines. With the aim to circumvent this problem, we designed a synthetic approach consisting in the C-C coupling between 2-vinylazines and alkynes promoted by a rhodium-*N*-heterocyclic carbene (NHC) catalyst (Scheme 3). This atom economical reaction proceeds under mild conditions with high chemoselectivity, since neither alkyne dimerization nor polymerization has been observed.²¹ Although, it has been previously described that rhodium-phosphane catalysts efficiently promote the C-C coupling between alkenylpyridines and olefins,⁶ we were the first to describe the coupling with terminal alkynes. Now, herein we report on the isolation and characterization of key organometallic intermediates in these catalytic processes as well as new alkene hydroalkenylation reactions. Notably, we extend the alkyne hydroalkenylations reported in our previous communication to 2-vinylpyrazine, which have led to the preparation of pyrido[1,2-a]pyrazines.

Scheme 3. Synthetic Approach for the Access to 4*H*-Quinolizines

RESULTS AND DISCUSSION

Synthesis and Reactivity of 2-Vinylpyridine and 2-Vinylpyrazine Rh-NHC Complexes. Dinuclear rhodium-NHC complexes of formula $[\text{Rh}(\mu\text{-Cl})(\text{NHC})(\eta^2\text{-coe})_2]$ (**1**) (coe = cyclooctene) {NHC = IPr (**1a**), IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-carbene; IMes (**1b**), IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-carbene} are adequate precursors for the synthesis of mononuclear Rh-NHC species by chlorido-bridge cleavage with nitrogenated ligands.²² Thus, treatment of a toluene solution of **1** with 2-vinylpyridine for 1 h at room temperature afforded the chelate mononuclear derivatives $\text{RhCl}(\text{NHC})(\kappa\text{-N},\eta^2\text{-CH}_2=\text{CHC}_5\text{H}_4\text{N})$ {NHC = IPr (**2a**), IMes (**2b**)} in good yields (Scheme 4).²⁰

Scheme 4. Preparation of $\text{Rh}^{\text{I}}\text{Cl}(\text{NHC})(\kappa\text{-N},\eta^2\text{-Vinylpyridine})$ Complexes

Single crystals of **2a** were grown by slow diffusion of hexane into a saturated toluene solution of the complex. Figure 1 shows a view of the crystal structure of **2a** and Table 1 contains selected bond lengths and angles. A distorted square planar coordination polyhedron was observed at the metal center with a *cis* arrangement of the NHC and the chlorido ligands [$\text{Cl-Rh-C}(1)$ 92.24(5)°]. The remaining coordination sites are occupied by 2-vinylpyridine exhibiting a $\kappa\text{-N},\eta^2\text{-CC'}$ coordination mode. Notably the small bite angle of vinylpyridine [$\text{N}(30)\text{-Rh-ct}$ 73.52(5)°] renders a severely distorted arrangement of this ligand. Accordingly, the pitch (θ_{py} 13.7°) and yaw (ψ_{py} 25.0°) angles of the heterocyclic moiety indicate that it largely deviates from its ideal position with respect to the rhodium-nitrogen bond.²³ Further, the dihedral angle $\text{C}(37)\text{-C}(36)\text{-Rh-N}(30)$ [-110.39(13)°] reveals that the coordinated C=C bond, namely C(36)-C(37), largely deviates from the perpendicular arrangement with respect to the coordination plane, observed in related square planar complexes.^{22,23b,24} As for the NHC ligand, the Rh-C(1) bond length [1.9837(17) Å] nicely fits in with a single metal-carbon bond.^{22,23b,24} Notably, a $\text{CH}\cdots\pi$ interaction²⁵ between the π system C(6)-C(7)-C(8)-C(9)-C(10)-C(11) and the C(36)-H(36) group is observed (Figure 1), along with a concomitant deviation from the ideal arrangement of the imidazole with respect to the Rh-C(1) bond (θ_{im} 8.2°, ψ_{im} 4.2°). For the sake of comparison, the related $\text{RhCl}(\text{IPr})(\kappa\text{-N},\eta^2\text{-vpZMe})$ (vpZMe = 5-dimethyl-1-vinylpyrazole) features a very similar $\text{CH}\cdots\pi$ interaction.^{23b}

Figure 1. View of the crystal structure of **2a**. Most hydrogen atoms are omitted for clarity. Brandl-Weiss parameters of the C(36)-H(36)··· π {C(6)-C(7)-C(8)-C(9)-C(10)-C(11)} interaction are: d_{CX} 3.54 Å; α 137.4°, d_{HpX} 0.75 Å. X, centroid of the π -system; Hp, projection of the interacting hydrogen atom onto the plane containing the π -system.

Table 1. Selected bond lengths (Å) and angles (°) of RhCl(IPr)(κ -N, η^2 -CH₂=CHC₅H₄N) (**2a**), RhCl(IPr){ κ -N, η^2 -(Z)-CH(Et)=CH(C₅H₄N)} (**4**) and RhCl(NHC)[κ -N, η^2 -CH(CEt=CHEt)=CH(C₅H₄N)] (**6a**).

	2a	4	6a
Rh–Cl	2.3603(7)	2.3721(5)	2.3486(15)
Rh–C(1)	1.9837(17)	1.9884(18)	1.989(5)
Rh–N(30)	2.0914(16)	2.0771(16)	2.087(4)
Rh–ct	1.9680(5)	1.9729(16)	1.9646(6)
C(36)–C(37)	1.409(3)	1.424(3)	1.429(8)
Rh–C(36)	2.1021(19)	2.0950(19)	2.103(5)
Rh–C(37)	2.078(2)	2.100(2)	2.078(5)
C(1)–Rh–Cl	92.24(5)	91.11(5)	91.28(14)
C(1)–Rh–N(30)	167.79(7)	176.41(7)	170.67(18)
N(30)–Rh–ct	73.52(5)	74.21(4)	73.76(12)
ψ_{py}	25.0	24.5	24.3
θ_{py}	13.7	12.8	12.2
ψ_{im}	4.2	-2.0	2.8
θ_{im}	8.2	11.1	10.8

ct: centroid of C(36) and C(37).

The solid state structure of **2a** is maintained in solution. The ¹H NMR spectra of **2a** and **2b** show three shielded signals around δ 3.4–2.1 ppm which corroborate the coordination of the vinyl

fragment of the 2-vinylpyridine ligand. The *trans* and *cis* proton-proton couplings of around 9.7 and 6.8 Hz, respectively, are significantly smaller than the typical values of a vinyl moiety. Indeed, the *trans*-to-proton terminal hydrogens of **2a** and **2b** features a scalar coupling with the rhodium atom of about 3 Hz. Moreover, the ¹³C{¹H}-APT NMR spectra display two doublets around δ 46 and 45 ppm with J_{C-Rh} about 12–16 Hz, ascribed to the coordinated alkene. The carbene carbon atom was observed at 183.3 (**2a**) and 181.1 (**2b**) ppm as a doublet with J_{C-Rh} around 57 Hz. The long-range ¹H-¹⁵N HMQC NMR spectrum of **2a** displays a cross-peak at δ 249.2 ppm for the nitrogen atom which lies in the range observed for a pyridine fragment coordinated *trans* to a carbene ligand.²¹

In view of the high strain of the 2-vinylpyridine ligand in Rh-NHC complexes, we carried out some experiments in order to assess its lability. After treatment of **2a** at room temperature with σ -donors, such as pyridine or triphenylphosphine, any reactivity was observed. Heating of the samples resulted in a mixture of unidentified compounds. However, reaction of **2a** with the small electron-rich triethylphosphine, in C₆D₆ at -30 °C, led to the *in-situ* formation of the tetraligated species RhCl(IPr){ η^2 -CH₂=CH(C₅H₄N)}(PEt₃) (**3**), as a result of the opening of the chelate ligand by substitution of the heterocyclic moiety of 2-vinylpyridine by the phosphine (Scheme 5). The η^2 -olefin coordination is confirmed by the appearance of shielded signals at δ 4.89, 2.97, and 2.58 ppm in the low temperature ¹H NMR spectrum. In addition, two doublets at δ 53.9 (J_{C-Rh} = 15.2 Hz) and 30.0 (J_{C-Rh} = 14.7 Hz) ppm are observed in the ¹³C{¹H}-APT NMR spectrum. The carbene carbon atom appears at 187.8 ppm as doublet of doublets (J_{C-P} = 136.7 and J_{C-Rh} = 43.9 Hz). The ³¹P{¹H} NMR spectrum of **3** shows a doublet at δ 16.1 ppm with J_{P-Rh} coupling constant of 121.0 Hz. The Rh-P and C-P coupling constants are in agreement with a phosphine-carbene *trans* disposition.^{22c} Indeed, the long-range ¹H-¹⁵N HMQC spectrum is indicative of a η^2 -olefin coordination of the 2-vinylpyridine ligand with uncoordinated pyridine since a cross-peak appears at δ 305.5 ppm for the nitrogen atom, which is deshielded with regard to that found in the κ -N, η^2 ligand in **2a** (249.2 ppm) and lies in the range of the free ligand (311.2 ppm). This fact excludes the possibility for **3** to be a rhodium(I)-pentacoordinated species. The stability of complex **3** is limited. Warming of the toluene solution of **3** to room temperature caused the releasing of 2-vinylpyridine to yield RhCl(IPr)(PEt₃)₂ in addition to traces of RhCl(PEt₃)₃ and other unidentified rhodium species. Moreover, Rh-IMes counterpart **2b** is more reactive. Treatment of **2b** with PEt₃ resulted in the formation of bis-phosphine complexes even at low temperature.

Scheme 5. Reaction of **2a** with PEt₃

In view that a powerful σ -donor can promote the decoordination of the nitrogen atom of the 2-vinylpyridine ligand, we next ex-

explored the possible decoordination of the vinyl fragment by reactivity with π -donor ligands. Thus, a Young-type NMR tube containing a C_6D_6 solution of **2a** was charged with 2 bar of ethylene and heated at 80 °C for 2 h. The expected η^2 -ethylene derivative was not observed but in contrast, the 2-butenylpyridine complex $RhCl(IPr)\{\kappa\text{-}N,\eta^2\text{-}(Z)\text{-CH(Et)=CH(C}_5\text{H}_4\text{N)}\}$ (**4**) was obtained as a result of the formal hydroalkenylation of ethylene with 2-vinylpyridine (Scheme 6). Complex **4** could not be isolated in pure form since it evolves to $[Rh(\mu\text{-Cl})(IPr)(\eta^2\text{-ethylene})_2]^{22a}$ and free 2-{1-(*Z*)-butenyl}pyridine, likely due to ethylene excess. Indeed, the same reaction starting from **2b** gave directly the coupled organic product and $[Rh(\mu\text{-Cl})(IMes)(\eta^2\text{-ethylene})_2]$. On the other hand, reaction of **2a** with the stoichiometric amount of styrene at 80° C for 48 h resulted in the formation of $RhCl(IPr)\{\kappa\text{-}N,\eta^2\text{-}(Z)\text{-CH(CH}_2\text{CH}_2\text{Ph)=CH(C}_5\text{H}_4\text{N)}\}$ (**5**), as a result of C-C coupling of styrene and 2-vinylpyridine, which could be isolated as an orange solid in 58% yield.

Scheme 6. Preparation of $Rh^I Cl(IPr)(\kappa\text{-}N,\eta^2\text{-Butenylpyridine})$ Derivatives by Hydroalkenylation

Single crystals of **4** were grown by slow diffusion of hexane into a saturated C_6D_6 solution of the complex. A view of the crystal structure of **4** is shown in Figure 2, and Table 1 contains selected bond lengths and angles. Similarly to **2a**, the metal center exhibits a distorted square planar coordination polyhedron (Figure 2) with a *cis* arrangement of the NHC and the chlorido ligands [$Cl\text{-Rh-C}(1)$ 91.11(5)°] and a Rh-C(1) bond length [1.9884(18) Å] indicative of a single metal-carbon bond (*vide supra*). The remaining coordination sites are occupied by 1-*Z*-butenylpyridine exhibiting a $\kappa\text{-}N,\eta^2\text{-CC'}$ coordination mode. Notably, the $Rh(\kappa\text{-}N,\eta^2\text{-CC'}$ -alkenylpyridine) moiety of **4** and the related fragment $Rh(\kappa\text{-}N,\eta^2\text{-CC'}$ -vinylpyridine) of **2a** are virtually superimposable (Figure 2). As a confirmation, the pitch (θ_{py} 12.8°) and yaw (ψ_{py} 24.5°) angles of the heterocyclic moiety and the dihedral angle C(37)-C(36)-Rh-N(30) [-111.30(13)°] of **4** are similar to the corresponding angles of **2a** (*vide supra*). At variance of **2a**, a $CH\cdots\pi$ interaction exists between the π system C(18)-C(19)-C(20)-C(21)-C(22)-C(23) and the allylic C(38)-H(38b) group (Figure 2). Accordingly the C(1)-Rh-N(30) angle is wider in **4** [176.41(7)°] than in **2a** [167.79(7)°] and the yaw angle of the imidazole ring of **4** (ψ_{im} -2.0°) is opposite to that of **2a** (ψ_{im} 4.2°) (*cf.* Figure 2-bottom). This observation reflects the flexibility of a NHC ligand in a square-planar environment.

Figure 2. (top) View of the crystal structure of **4**. Most hydrogen atoms are omitted for clarity. Brandl-Weiss parameters (*cf.* Figure 1) of the C(38)-H(38b)··· π {C(18)-C(19)-C(20)-C(21)-C(22)-C(23)} interaction are: d_{CX} 3.76 Å; C-H-X 148.2°, d_{HPX} 0.34 Å. (bottom) Structure overlay of **4** (green) and **2a** (orange).

The NMR spectra of **4** and **5** corroborate the η^2 -olefin coordination, since a set of shielded signals between 3.4-2.7 ppm were observed in the 1H NMR spectra. The olefinic proton proximal to the pyridine fragment (H_7) resonates as a doublet with J_{H-H} = 7.2 Hz, in agreement with a *cis* configuration of the double bond (Figure 3). In contrast, the alkenyl proton H_8 is observed as complex resonance which can be described as a doublet of doublets of doublets. Besides the *cis* CH=CH coupling, a J_{H-H} = 10.4 Hz and a J_{H-Rh} = 3.4 Hz are observed. The former interaction is ascribed to the coupling with only one of the diastereotopic methylene protons whereas the latter reflects the coordination to the metal center. The $^{13}C\{^1H\}$ -APT NMR spectra display two doublets around δ 65 and 44 ppm with J_{C-Rh} about 18 and 12 Hz, respectively.

Figure 3. Comparison of the ^1H NMR resonances of the vinyl moiety for **2a** (top) and **4** (bottom).

The unexpected hydroalkenylation reaction observed in the formation of complexes **4** and **5** led us to explore the reactivity with other π -donors such as alkynes. Thus, treatment of a toluene solution of **2a** or **2b** with 3-hexyne or diphenylacetylene

resulted in the formation of $\text{RhCl}(\text{NHC})(\kappa\text{-}N,\eta^2\text{-CH}\{\text{C}(\text{R})=\text{CH}(\text{R})\}=\text{CH}(\text{C}_5\text{H}_4\text{N}))$ (**6a,b-7a,b**) {NHC = IPr (**6**), IMes (**7**); R = Et (**a**), Ph (**b**)} in good yields (Scheme 7).

Scheme 7. Synthesis of $\text{RhCl}(\text{NHC})(\kappa\text{-}N,\eta^2\text{-Butadienylpyridine})$ Complexes

Slow diffusion of hexane into a saturated toluene solution of **6a** provided single crystals suitable for X-ray diffraction measurements. Two rotamers around the C(37)-C(38) bond were observed in the crystal structure of **6** and they were refined as complementary components of a static positional disorder (Figure 4, A and B). Both rotamers formally contain conjugated double bonds, one *Z* [C(36)-C(37)] and the other *E* [C(38a/b)-C(39a/b)], and differ as for the dihedral angles C(36)-C(37)-C(38a/b)-C(39a/b) [a, 56(1)°; b -135(1)°]. Nevertheless, similar

Figure 4. (A, B) Views of the crystal structure of the two rotamers of **6a**, refined as complementary components of a static positional disorder. Most hydrogen atoms are omitted for clarity. Brandl-Weiss parameters (cf. Figure 1) of the C-H $\cdots\pi$ interactions are: C(42a)-H(42a) $\cdots\pi$ {C(18)-C(19)-C(20)-C(21)-C(22)-C(23)}, d_{CX} 3.63 Å, C-H-X 132.6°, d_{HPX} 0.87 Å; C(39b)-H(39b) $\cdots\pi$ {C(18)-C(19)-C(20)-C(21)-C(22)-C(23)}, d_{CX} 3.44 Å, C-H-X 134.4°, d_{HPX} 0.62 Å. (C) Structure overlay of **6a** (both rotamers, purple) and **2a** (orange).

to **2a**, the rhodium center exhibits a square planar coordination polyhedron with a *cis* arrangement of the NHC and the chlorido ligands (Table 1). Furthermore, the Rh(κ -N, η^2 -CC'-alkenylpyridine) moiety of **6a** is virtually superimposable to that of **2a** (Figure 4-C) exhibiting C(37)-C(36)-Rh-N(30) [$-110.65(34)^\circ$], pitch (ψ_{py} 24.3°) and yaw (θ_{py} 12.2) angles similar to those of **2a** and **4** (*vide supra*). Finally, it is worth mentioning that in each rotamer the π system C(18)-C(19)-C(20)-C(21)-C(22)-C(23) establishes a CH $\cdots\pi$ interaction with either C(42a)-H(42a) or C(39b)-H(39b) (Figure 4, A and B). In this connection, like for **2a** and **4**, the pitch and yaw angles of the imidazole ring (Table 1) reasonably should be a consequence of the CH $\cdots\pi$ interaction.

The NMR spectra of **6-7** are similar to those of the previously described κ -N, η^2 -olefin complexes. Additional 2D ^1H - ^1H -NOESY NMR experiments were recorded in order to confirm the stereochemistry of the double bonds. Coordinated olefin present *Z* configuration in **6-7**, as observed in X-ray structure of **6a**, since a NOE cross-peak is observed between both olefinic protons. Moreover, correlation between the =C(R)H proton of the unbonded olefin and one proton of the coordinated alkene confirms the mutually *cis* disposition of the substituents in the non-coordinated olefin. This configuration arises from a typical *syn*-hydroalkenylation to the triple bond.

The reactivity of **1** with 2-vinylpyrazine is somewhat different to that observed for 2-vinylpyridine. Treatment of **1a** or **1b** with the vinylheterocycle resulted in a mixture of unidentified compounds, including some Rh-hydrides. However, when the reaction was performed in the presence of 2 equiv of pyridine at -30°C , complex RhCl(IPr){ η^2 -CH $_2$ =CH(C $_4$ H $_3$ N $_2$)}(py) (**8**) was formed and characterized by multinuclear low temperature NMR experiments (Scheme 8). Coordination of the olefin moiety of 2-vinylpyrazine in **8** is supported by the appearance of three shielded resonances at δ 4.53, 3.10, and 2.86 ppm and the occurrence of carbon-rhodium scalar coupling around 16 Hz for the corresponding olefinic carbon atoms in the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ -APT NMR spectra, respectively. Moreover, a long-range ^1H - ^{15}N -HMQC NMR experiment corroborates the presence of an uncoordinated pyrazine fragment and the coordination of a pyridine ligand in **8** (Figure 5). Accordingly, the N $_4$ pyrazine atom resonates at δ 331.6 ppm, only slightly shifted from that of the free pyrazine (336.5 ppm). Indeed, the nitrogen atom of the pyridine ligand is observed at 269.5 ppm, shielded

Scheme 8. Preparation of RhCl(IPr)(η^2 -vinylpyrazine)(py) Complex

almost 50 ppm compared to free pyridine (318.6 ppm), reflecting its coordination to the metal center. The structure of a related Rh-NHC complex containing an opened η^2 -vinylpyrazole and pyridine ligands has been previously described by X-ray diffraction analysis.^{23b}

Figure 5. 2D long-range ^1H - ^{15}N -HMOC NMR correlation for **8**, pyridine and vinylpyrazine (inset boxes).

Catalytic Hydroalkenylation. Catalytic addition of an alkenyl fragment to an unsaturated bond is a powerful tool for synthetic chemists.²⁶ These so-called hydroalkenylation reactions can be efficiently promoted by transition metal catalysts using a range of olefins or internal alkynes as acceptor substrates, but the hydroalkenylation of terminal alkynes is more challenging.²⁷ Particularly, C-C coupling between alkenylpyridines and terminal alkynes was unprecedented up to our previous communication.²⁰ In view of the formation of the butenylpyridine complex **4** as a result of stoichiometric hydroalkenylation of ethylene (*vide supra*), we sought to study the catalytic hydroalkenylation of alkenes with 2-vinylazines. Preliminary catalyst optimization showed that complex **2b** displayed slightly better catalytic results than **2a**, thus it was used thereafter. The addition of 2-vinylpyridine (**9a**) or 2-vinylpyrazine (**9b**) to alkenes were monitored in Young-Type NMR tubes containing 0.5 mL of C $_6$ D $_6$ and **2b** as catalyst. A 1:1 ratio was chosen for the substrates or, alternatively, 2 bar of pressure of the olefin was charged in the NMR tube in the case of gaseous substrates, ethylene and propylene, which are involved in this transformation for the first time (Scheme 9, Table 2). At the end of the reaction the organic products were purified by column chromatography. Catalyst **2b** efficiently catalyzed the hydroalkenylation of ethylene with 2-vinylpyridine at 2 mol% loading (entry 1). The main product is the *Z*-butenyl derivative which further undergoes a common metal-mediated olefin isomerization to the compound with *E* configuration.²⁸ Increasing of the catalyst loading to 5 mol% resulted in the selective formation of the thermodynamic product which has been isolated in 92% yield (entry 2). Propylene and 2-vinylpyridine reacted slowly to give the linear (*E*)-1-pentenyl-pyridine product (entry 3). Notably, the branched product resulting from Markonikov-type addition was not detected. However, concomitant to the cross-coupling product, (*E*)-1,4-dipyridyl-1-butene arising from the competing homocoupling

of 2-vinylpyridine, was also formed. 3,3-dimethyl-1-butene afforded lower conversions with similar selectivity, whereas styrene was almost unreactive (entries 4 and 5). Dimerization of 2-vinylpyridine was also slow (entry 6). The reaction of alkenes with 2-vinylpyrazine followed a similar trend (entries 7-10). It is worth mentioning that alkene hydroalkenylation reactions catalyzed by $\text{RhCl}(\text{PPh}_3)_3$, $\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{IMes})(\text{PCy}_3)$, or the catalytic system $[\text{RhCl}(\text{coe})_2]_2 + \text{PR}_3$ required higher catalyst loading (10 mol%) and more elevated temperatures.^{6a-e}

Scheme 9. Catalytic Hydroalkenylation of Olefins

Table 2. Olefin Hydroalkenylation with 2-Vinylazines.^a

Entry	9	[Cat] ^b	alkene	t(h)	Conv (%) ^c	selectivity			Yield (%) ^d
						10	11	12	
1	9a	2		24	95	33	67	--	--
2	9a	5		24	96	99	1	--	92
3	9a	5		72	98	75	--	25	65
4	9a	5		72	88	68	--	32	55
5	9a	5		72	10	--	--	--	-- ^e
6	9a	5		72	21	--	--	84/16 ^f	--
7	9b	5		24	96	99	1	--	90
8	9b	5		72	98	74	1	25	68
9	9b	5		72	88	71	--	29	62
10	9a	5		72	--	--	--	--	--

^aReaction conditions: 0.2 mmol of 2-vinylazine, and 2 bar of pressure or 0.2 mmol of alkene in C_6D_6 (0.5 mL) at 80 °C. ^bCatalyst loading in mol%.

^cNMR conversion determined from 2-vinylazine consumption. ^dIsolated yield. ^e(*E/Z*) styrene/2-vinylpyridine cross coupling and (*E/Z*) 2-vinylpyridine homocoupling products were observed by GC-MS. ^f(*E/Z*)-1,4-dipyril-1-butene selectivity.

As we have described in our previous communication,²⁰ the hydroalkenylation of alkynes promoted by **2b** is more efficient than that of olefins (Scheme 10, Table 3). The catalytic reactions of 2-vinylpyridine with alkynes were performed at 40 °C in C_6D_6 . In addition to several butadienylpyridine isomers (**13-16**), 4*H*-quinolizine derivatives (**17**) was also observed. The formation of these heterocycles can be rationalized by a thermal non-catalyzed 6π-electrocyclization reaction within the butadienyl fragment and a C=N double bond of the pyridine moiety. Similar rearrangements within diene frameworks have been observed from imines²⁹ or oximes³⁰ but dearomatization of pyridine is much more challenging.³¹ Catalyst **2b** is chemoselective for the hydroalkenylation, since competitive dimerization of terminal alkynes to give enyne **18** was not detected. It is noticeable that only the 1*Z*,3*gem* butadienylpyridine isomers **15** rearrange to the corresponding 4*H*-quinolizines. This transformation is very fast for aromatic alkynes, thereby **15** could not be detected. However, the 6π-electrocyclization is slower for aliphatic alkynes, thus 1*Z*,3*gem* butadienyl isomers were ob-

tained in significant amounts. In addition, these compounds displayed the typical kinetic profile for an intermediate species. According to the alkene hydroalkenylation (vide supra), the kinetic products are the 1*Z*-butadienyl derivatives (**13** and **15**), which can be isomerized to 1-*E* products. The absence of 3*Z*-butadienyl isomers accounts for a *syn* addition of C-H alkenyl over the triple bond of the alkyne. 4*H*-quinolizines derivatives could not be isolated by column chromatography^{20,29d,31c} but 3-phenyl-4*H*-quinolizine (**17a**) could be purified by washing with *n*-hexane due to their different solubility with regard to butadienylpyridine isomers.

Scheme 10. Catalytic Hydroalkenylation of Alkynes and Formation of N-Bridgehead Heterocycles

Table 3. Alkyne Hydroalkenylation with 2-vinylpyridine.^a

Entry	Alkyne	t(h)	Conv (%) ^b	Selectivity				
				13	14	15	16	17
1		4	97	3	47	--	--	50
2		1	93	2	52	--	--	46
3		6	92	17	34	9	--	40
4		2	99	37	--	46	10	7
5		5	97	40	--	39	12	9
6		9	98	76	2	15	--	7
7		20	63	74	--	--	--	26
8		14	99	36	12	--	--	52
9		14	98	70	6 ^c	--	--	24
10		12	94	27 ^d	24 ^d	--	--	49 ^e

^aReaction conditions: 0.2 mmol of 2-vinylpyridine, 0.2 mmol of alkyne and 0.01 mmol of **2b** in C_6D_6 (0.5 mL) at 40 °C. ^bNMR conversion determined from 2-vinylpyridine consumption. ^c1*E*,3*Z* isomer. ^d4-Phenyl. ^e4-Methyl.

Compound **2b** also catalyzed the alkyne hydroalkenylation reaction with 2-vinylpyrazine (Table 4). The reactions were slower, thus a higher temperature (60 °C) was required to achieve acceptable conversions. Formation of the N-bridgehead heterocycles 6*H*-pyrido-[1,2-*a*]pyrazines was unambiguously determined by NMR, particularly the 2D long-range ¹H-¹⁵N-HMQC experiment (Figure 6). As a drawback, gem-enynes (**18**) were obtained as byproducts, as a result of the homodimerization of the terminal alkyne, particularly for phenylacetylene (entry 1). For aliphatic alkynes such as 1-hexyne or cyclopropylacetylene dimerization was considerably reduced and formation of the fused heterocycle reached around 30% selectivity (entries 2 and 3). The bulky tert-butyl- and trimethylsilylacetylene reacted slowly. In these cases the *E*-enyne was mainly obtained as by-product as described previously with related Rh-NHC catalysts.²¹ Formation of the N-bridgehead heterocycles 6*H*-pyrido-[1,2-*a*]pyrazine was favored for internal alkynes

reaching up to 85% selectivity for 3-hexyne (entry 6), which can be purified by precipitation with n-hexane. Diphenylacetylene displayed almost half selectivity between the butadienyl- and the N-bridgehead heterocycle (entry 7). Both regioisomeric fused heterocycles were obtained for 1-phenylpropyne in a 74:9 ratio with 6*H*-6-methyl-7-phenylpyrido[1,2-*a*]pyrazine as the major isomer (entry 8).

Table 4. Alkyne Hydroalkenylation with 2-vinylpyrazine.^a

Entry	Alkyne	t(h)	Conv (%) ^b	Selectivity					
				13	14	15	16	17	18
1		2	97 ^c	15	--	--	--	30	55
2		2	93 ^c	27	--	11	15	35	12
3		2	92 ^c	28	8	6	18	23	17
4		11	99 ^c	26	44	2	5	12	2/9 ^d
5		12	94 ^c	22	4	--	--	63	11 ^d
6		3	99	6	9	--	--	85	--
7		3	98	42 ^e	12 ^e	--	--	46	--
8		5	99	--	25	--	--	70/5 ^g	--

^aReaction conditions: 0.2 mmol of 2-vinylpyrazine, 0.2 mmol of alkyne and 0.01 mmol of **2b** in C₆D₆ (0.5 mL) at 60 °C. ^bNMR conversion determined from 2-vinylpyrazine consumption. ^cCalculated from alkyne consumption. ^d(*E*)-enyne. ^e3-*Z* isomer. ^f6*H*-6-methyl-7-phenylpyrido[1,2-*a*]pyrazine. ^g6*H*-6-phenyl-7-methylpyrido[1,2-*a*]pyrazine.

Figure 6. 2D long-range ¹H-¹⁵N-HMOC NMR correlation for 6,7-diethyl-6*H*-pyrido-[1,2-*a*]pyrazine.

The formation of N-bridgehead heterocycles entails the intriguing dearomatization of pyridine within a butadienylpyridine fragment. It would be expected that conjugation of two double bonds with an aromatic heterocyclic fragment provided stability to the butadienyl-heterocyclic derivatives. DFT calculations on ground state minimum energy confirmed the experimental results (Figure 7, see the Supporting Information for pyrazine-based derivatives). The fused heterocycles are 0.8 (py, **17j**) and 2.2 (pz, **17g**) kcal mol⁻¹ more stable than the opened compounds **13**. Likely, a substituent on position 3 of the butadienyl backbone hinders the coplanarity of the pyridinic ring with the two double bonds, thus enforcing a helical disposition and hampering conjugation. Moreover, N-bridge heterocycles **17** are not very stable either. Heating a toluene solution of **17** for 12 h yielded 2-(3-ethyl-2,4-hexadienyl)heterocycle {pyridine (**19**),

pyrazine (**20**)} as a mixture of (2*Z*,4*E*):(2*E*,4*E*) isomers (71:29 for **19**, 74:26 for **20**) as a result of a formal isomerization of two double bonds within **13**.^{6c,28} Although pyridine and the new pentadienyl fragment are not mutually conjugated in **19-20**, re-aromatization of pyridine and conjugation of two double bonds likely resulted in net stabilization of **19** with regard to **17**. Theoretical calculations confirm this point, since the 2,4-pentadienyl derivatives lie 3.2 (py, **19a**) and 1.3 (pz, **20a**) kcal mol⁻¹ below **17**.

Figure 7. Isomerization of butadienyl- to 2,4-pentadienyl-heterocycles via a N-bridgehead heterocyclic intermediate. Optimized structures and relative energies for pyridine-based derivatives (ΔG , 353 K, toluene).

A mechanistic proposal for the formation of N-bridgehead heterocycles is presented in Scheme 11. The first step consists in the C(sp²)-H activation of the vinylazine directed by the coordination of the nitrogen atom to form a hydride-alkenyl-Rh^{III} intermediate. Although we fail to unambiguously detect such species in Rh-NHC systems, we have recently reported the structural characterization of a related phosphine-based Rh-hydride-alkenyl derivative.³² Subsequent insertion of the alkyne can occur into the Rh-H or the Rh-alkenyl bond with 1,2 or 2,1 regioselectivity. Migratory insertion in the Rh-H bond is more likely although alkyne insertion into Rh-alkenylpyridine bond has also been described.³³ Then, reductive elimination within the coordination sphere of the metal will result in butadienyl heterocycle derivatives which can then undergo, depending on the substitution pattern, a thermal metal-free 6- π electrocyclization process to yield the N-bridgehead heterocycles. Substitution on 3-position of the butadienyl fragment as well as a cisoidal configuration seem to be a prerequisite for efficient cyclization, thus 4-substituted derivatives or 1-*E*,3gem isomerized products do not rearrange.

CONCLUSION

An efficient Rh-NHC catalyst for alkene and alkyne hydroalkenylation with vinylazines is presented. Key organometallic intermediates have been characterized. 2-vinylpyridine coordinates to a Rh^I-NHC fragment in a typical chelate fashion. However, the high strain of the metallacycle, reflected by the short bite angle as well as the observed pitch and yaw angles, allows for its opening by substitution of the pyridine ring with PEt₃. In addition, reaction with π -donor ligands such as olefins or alkynes gave κ -*N*, η^2 -2-(butenyl)pyridine or 2-(butadienyl)pyridine rhodium complexes as a result of the stoichiometric C-C coupling by formal hydroalkenylation of both type of substrates with 2-vinylpyridine. CH $\cdots\pi$ interactions involving one aromatic ring of the wingtip of the NHC ligand provide additional

Scheme 11. Mechanistic Proposal for the formation of N-Bridgehead Heterocycles

stability to the complexes. Notably an olefinic and an allylic proton participate in the $\text{CH}\cdots\pi$ interaction in the vinylpyridine and the butenylpyridine complexes, respectively. This bonding scheme results in an opposite tilting of the NHC reflecting its flexibility as a ligand.

The NHC ligand plays an essential role in the catalytic activity, since catalyst loading (5 mol%) and temperature reaction (80 °C) for olefin hydroalkenylations are reduced with regard to previous Rh-phosphino catalysts. Notably, gaseous alkenes and 2-vinylpyrazine participate in this catalytic transformation for the first time. Alkynes react faster than olefins to form butadienyl-heterocycle derivatives. The 1Z,3gem isomers undergo a thermal non-catalyzed 6 π -electrocyclization to yield 4*H*-quinolizines or 6*H*-pyrido-[1,2-*a*]pyrazines. As revealed by DFT calculations, fused heterocycles are more stable than the butadienyl derivatives, in spite of the dearomatization of the nitrogenated ring. The steric demand of the substituent in position 3 of the butadienyl fragment hampers the coplanarity of the pyridinic ring and the two double bonds, thus accounting for the lack of conjugation. Moreover, if an alkyl substituent is located in position 3, the N-bridgehead heterocycle can be reopened yielding 2,4-pentadienyl-heterocycle derivatives in which re-aromatization of nitrogenated ring and unconnected conjugation of two double bonds account for their higher stability.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. The reagents were purchased from commercial sources and were used as received, except for phenylacetylene and 2-vinylpyridine that were distilled and stored over molecular sieves. Organic solvents were dried by standard procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). The organometallic precursors $[\text{Rh}(\mu\text{-Cl})(\text{NHC})(\eta^2\text{-coe})]_2$ (**1a,b**)³⁴ were prepared as previously described in the literature. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H , $^{13}\text{C}\{^1\text{H}\}$) or external H_3PO_4 (^{31}P) and liquid NH_3 (^{15}N). Coupling constants, J , are given in Hz. Spectral assignments were achieved by combination of ^1H - ^1H COSY, $^{13}\text{C}\{^1\text{H}\}$ -APT and ^1H - ^{13}C HSQC/HMBC experiments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra (HRMS) were acquired using a MicroTOF-Q hybrid quadrupole

time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). GC-MS analysis were recorder on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system, using a HP-5MS 5% phenyl methyl siloxane column (30 m x 250 mm with a 0.25 mm film thickness).

Preparation of $\text{RhCl}(\text{IPr})(\kappa\text{-N},\eta^2\text{-CH}_2=\text{CH-C}_5\text{H}_4\text{N})$ (2a**).** A yellow solution of **1a** (300 mg, 0.235 mmol) in 10 mL of toluene was treated with 2-vinylpyridine (50 μL , 0.470 mmol) and was stirred at room temperature for 1 h. After filtration through Celite, the solvent was evaporated to dryness. Addition of hexane caused precipitation of a yellow solid, which was washed with hexane (3 x 4 mL) and dried in vacuo. Yield: 250 mg (84%). Anal. Calcd. for $\text{C}_{34}\text{H}_{43}\text{N}_3\text{ClRh}$: C, 64.61; H, 6.86; N, 6.65. Found: C, 64.92; H, 6.89; N, 6.62. ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.09 (d, $J_{\text{H-H}} = 5.3$, 1H, $\text{H}_{6\text{-py}}$), 7.27 (t, $J_{\text{H-H}} = 7.6$, 2H, $\text{H}_{\text{p-Ph-IPr}}$), 7.2 (m, 4H, $\text{H}_{\text{m-Ph-IPr}}$), 6.55 (s, 2H, $=\text{CHN}$), 6.49 (dd, $J_{\text{H-H}} = 7.8$, 7.4, 1H, $\text{H}_{4\text{-py}}$), 6.09 (d, $J_{\text{H-H}} = 7.8$, 1H, $\text{H}_{3\text{-py}}$), 5.94 (dd, $J_{\text{H-H}} = 7.4$, 5.3, 1H, $\text{H}_{5\text{-py}}$), 4.02 and 2.96 (both br, 4H, CHMeIPr), 3.28 (dd, $J_{\text{H-H}} = 9.8$, $J_{\text{H-Rh}} = 2.9$, 1H, $\text{CH}=\text{CH}_2$), 2.73 (d, $J_{\text{H-H}} = 6.7$, 1H, $\text{CH}=\text{CH}_2$), 2.12 (dd, $J_{\text{H-H}} = 9.8$, 6.7, 1H, $\text{CH}=\text{CH}_2$), 1.11 and 1.06 (both d, $J_{\text{H-H}} = 7.12$, 24H, CHMeIPr). $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (100.4 MHz, C_6D_6 , 298 K): δ 183.3 (d, $J_{\text{C-Rh}} = 57.4$, Rh-ClIPr), 168.2 (d, $J_{\text{C-Rh}} = 4.7$, $\text{C}_{2\text{-py}}$), 147.8 (s, $\text{C}_{6\text{-py}}$), 147.3 and 146.5 (both s, $\text{C}_{\text{q-IPr}}$), 137.3 (s, C_{qN}), 134.4 (s, $\text{C}_{4\text{-py}}$), 129.6 (s, $\text{C}_{\text{p-Ph-IPr}}$), 124.1 and 124.0 (both s, $\text{C}_{\text{m-Ph}}$), 123.9 (s, $=\text{CHN}$), 119.4 (s, $\text{C}_{5\text{-py}}$), 116.3 (s, $\text{C}_{3\text{-py}}$), 46.4 (d, $J_{\text{C-Rh}} = 12.3$, $\text{CH}_2=\text{CH}$), 45.3 (d, $J_{\text{C-Rh}} = 16.0$, $\text{CH}_2=\text{CH}$), 29.2 and 29.0 (both s, CHMeIPr), 26.8, 25.8, 23.7, and 23.2 (all s, CHMeIPr). ^1H - ^{15}N HMQC NMR (40.5 MHz, toluene- d_8 , 243 K): δ 249.2 (N_{py}), 191.0 (N_{IPr}).

Preparation of $\text{RhCl}(\text{IMes})(\kappa\text{-N},\eta^2\text{-CH}_2=\text{CH-C}_5\text{H}_4\text{N})$ (2b**).** The complex was prepared as described for **2a** starting from **1b** (300 mg, 0.271 mmol) and 2-vinylpyridine (58 μL , 0.542 mmol). Yield: 260 mg (87%). Anal. Calcd. for $\text{C}_{28}\text{H}_{31}\text{N}_3\text{ClRh}$: C, 61.38; H, 5.70; N, 7.67. Found: C, 61.05; H, 5.80; N, 7.46. ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.16 (d, $J_{\text{H-H}} = 5.3$, 1H, $\text{H}_{6\text{-py}}$), 6.94 and 6.87 (both s, 4H, $\text{H}_{\text{m-Ph}}$), 6.56 (dd, $J_{\text{H-H}} = 7.7$, 7.7, 1H, $\text{H}_{4\text{-py}}$), 6.30 (s, 2H, $=\text{CHN}$), 6.22 (d, $J_{\text{H-H}} = 7.7$, 1H, $\text{H}_{3\text{-py}}$), 6.01 (ddd, $J_{\text{H-H}} = 7.7$, 5.3, 1H, $\text{H}_{5\text{-py}}$), 3.39 (dd, $J_{\text{H-H}} = 9.6$, $J_{\text{H-Rh}} = 3.2$, 1H, $\text{CH}=\text{CH}_2$), 2.90 (d, $J_{\text{H-H}} = 6.9$, 1H, $\text{CH}=\text{CH}_2$), 2.72 and 2.24 (both s, 18H, MeIMes), 2.13 (dd, $J_{\text{H-H}} = 9.6$, 6.9, 1H, $\text{CH}=\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (100.4 MHz, C_6D_6 , 298 K): δ 181.1 (d, $J_{\text{C-Rh}} = 57.1$, Rh-ClIMes), 168.1 (d, $J_{\text{C-Rh}} = 4.4$, $\text{C}_{2\text{-py}}$), 147.3 (s, $\text{C}_{6\text{-py}}$), 137.9 and 137.1 (both s, $\text{C}_{\text{q-IMes}}$), 136.2 (s, C_{qN}), 134.6 (s, $\text{C}_{4\text{-py}}$), 129.3 and 128.7 (both s, $\text{C}_{\text{m-Ph}}$), 122.4 (s, $=\text{CHN}$), 119.4 (s, $\text{C}_{5\text{-py}}$), 116.5 (s, $\text{C}_{3\text{-py}}$), 46.0 (d, $J_{\text{C-Rh}} =$

15.3, $\text{CH}_2=\text{CH}$), 45.8 (d, $J_{\text{C-Rh}} = 12.4$, $\text{CH}_2=\text{CH}$), 20.8 and 19.4 (both s, MeImes).

In situ formation of $\text{RhCl}(\text{IPr})\{\eta^2\text{-CH}_2=\text{CH}(\text{C}_5\text{H}_4\text{N})\}(\text{PEt}_3)$ (3). A solution of **2a** (30 mg, 0.023 mmol) in toluene- d_8 (0.5 mL, NMR tube) at 243 K was treated with triethylphosphine (4 μL 0.060 mmol). The spectra were recorded immediately at low temperature. ^1H NMR (300 MHz, toluene- d_8 , 243 K): δ 8.07 (d, $J_{\text{H-H}} = 4.4$, 1H, $\text{H}_{6\text{-py}}$), 7.42 and 7.33 (both t, $J_{\text{H-H}} = 7.6$, 2H, $\text{H}_{\text{p-IPr}}$), 7.08 and 7.0 (both d, $J_{\text{H-H}} = 7.6$, 4H, $\text{H}_{\text{m-IPr}}$), 6.96 (dd, $J_{\text{H-H}} = 7.6$, 6.0, 1H, $\text{H}_{4\text{-py}}$), 6.60 and 6.54 (both s, 2H, $=\text{CHN}$), 6.49 (dd, $J_{\text{H-H}} = 6.0$, 4.4, 1H, $\text{H}_{5\text{-py}}$), 6.14 (d, $J_{\text{H-H}} = 7.6$, 1H, $\text{H}_{3\text{-py}}$), 4.89 (dd, $J_{\text{H-H}} = 8.9$, 7.7, 1H, $\text{CH}=\text{CH}_2$), 4.65, 3.74, 2.99, and 2.40 (all sept, $J_{\text{H-H}} = 6.6$, 4H, CHMeIPr), 2.97 (d, $J_{\text{H-H}} = 8.9$, 1H, $\text{CH}=\text{CH}_2$), 2.58 (d, $J_{\text{H-H}} = 7.7$, 1H, $\text{CH}=\text{CH}_2$), 1.78, 1.66, 1.56, 1.21, 1.16, 1.11, 1.04, and 0.96 (all d, $J_{\text{H-H}} = 6.6$, 24H, CHMeIPr), 1.40 (dq, $J_{\text{H-P}} = 7.8$, $J_{\text{H-H}} = 7.6$, 6H, PCH_2CH_3), 0.65 (dt, $J_{\text{H-P}} = 14.2$, $J_{\text{H-H}} = 7.6$, 9H, PCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (75 MHz, toluene- d_8 , 243 K): δ 187.8 (dd, $J_{\text{C-P}} = 136.7$, $J_{\text{C-Rh}} = 43.9$, Rh-ClIPr), 165.7 (s, $\text{C}_{2\text{-py}}$), 148.6, 147.8, 146.1, and 145.6 (all s, $\text{C}_{\text{q-IPr}}$), 148.1 (s, $\text{C}_{6\text{-py}}$), 137.4 and 137.0 (both s, C_{qN}), 134.7 (s, $\text{C}_{4\text{-py}}$), 129.8 and 129.5 (both s, $\text{C}_{\text{p-IPr}}$), 125.3, 124.6, 123.8, and 122.6 (all s, $\text{C}_{\text{m-IPr}}$), 125.2 (s, $\text{C}_{3\text{-py}}$), 124.6 and 123.7 (both s, $=\text{CHN}$), 119.3 (s, $\text{C}_{5\text{-py}}$), 53.9 (d, $J_{\text{C-Rh}} = 15.2$, $\text{CH}=\text{CH}_2$), 30.0 (d, $J_{\text{C-Rh}} = 14.7$, $\text{CH}=\text{CH}_2$), 29.3, 28.9, 28.8, and 28.4 (all s, CHMeIPr), 27.2, 26.7, 26.6, 26.2, 23.8, 23.3, 23.2, and 23.1 (all s, CHMeIPr), 13.7 (d, $J_{\text{C-P}} = 22.0$, PCH_2CH_3), 7.86 (s, PCH_2CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, toluene- d_8 , 243 K): 16.1 (d, $J_{\text{P-Rh}} = 121.0$). ^1H - ^{15}N HMQC NMR (40.5 MHz, toluene- d_8 , 243 K): δ 305.5 (N_{py}), 193.1 and 190.2 (N_{IPr}).

In situ formation of $\text{RhCl}(\text{IPr})\{\kappa\text{-N},\eta^2\text{-(Z)-CH}(\text{Et})\text{-CH}(\text{C}_5\text{H}_4\text{N})\}$ (4). A solution of **2a** (30 mg, 0.023 mmol) in C_6D_6 (0.5 mL, NMR tube) was treated with ethylene (2 bars) and was heated at 353 K for 2 h. ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.14 (d, $J_{\text{H-H}} = 5.4$, 1H, $\text{H}_{6\text{-py}}$), 7.3-7.1 (m, 6H, $\text{H}_{\text{p-IPr}}$), 6.63 (s, 2H, $=\text{CHN}$), 6.60 (dd, $J_{\text{H-H}} = 7.7$, 7.4, 1H, $\text{H}_{4\text{-py}}$), 6.21 (d, $J_{\text{H-H}} = 7.7$, 1H, $\text{H}_{3\text{-py}}$), 5.94 (dd, $J_{\text{H-H}} = 7.4$, 5.4, 1H, $\text{H}_{5\text{-py}}$), 3.53 and 3.42 (both br, 4H, CHMeIPr), 3.33 {ddd, $J_{\text{H-H}} = 10.4$, 7.2, $J_{\text{H-Rh}} = 3.4$, 1H, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 2.51 {d, $J_{\text{H-H}} = 7.2$, 1H, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 1.95 and 1.22 (both m, 2H, CH_2CH_3), 1.59, 1.54, 1.09, and 1.07 (all d, $J_{\text{H-H}} = 6.8$, 24H, CHMeIPr), 0.75 (t, $J_{\text{H-H}} = 7.2$, 3H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (125.6 MHz, C_6D_6 , 298 K): δ 184.5 (d, $J_{\text{C-Rh}} = 57.0$, Rh-ClIPr), 165.0 (br, $\text{C}_{2\text{-py}}$), 146.1 (s, $\text{C}_{6\text{-py}}$), 146.9 and 146.1 (both s, $\text{C}_{\text{q-IPr}}$), 137.7 (s, C_{qN}), 134.5 (s, $\text{C}_{4\text{-py}}$), 129.5 (s, $\text{C}_{\text{p-IPr}}$), 124.2 (s, $=\text{CHN}$), 123.9 and 123.8 (both s, $\text{C}_{\text{m-IPr}}$), 119.0 (s, $\text{C}_{3\text{-py}}$), 117.2 (s, $\text{C}_{5\text{-py}}$), 66.6 {d, $J_{\text{C-Rh}} = 18.5$, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 43.9 {d, $J_{\text{C-Rh}} = 12.3$, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 28.9 and 28.7 (both s, CHMeIPr), 26.2, 26.0, 23.2 and 23.0 (all s, CHMeIPr), 26.5 (s, CH_2CH_3), 16.1 (s, CH_2CH_3).

Preparation of $\text{RhCl}(\text{IPr})\{\kappa\text{-N},\eta^2\text{-(Z)-CH}(\text{CH}_2\text{CH}_2\text{Ph})\text{-CH}(\text{C}_5\text{H}_4\text{N})\}$ (5). A solution of **2a** (100 mg, 0.16 mmol) in 10 mL of toluene was treated with styrene (20 μL , 0.17 mmol) and heated at 353 K for 48 h. After filtration through Celite, the solvent was evaporated to dryness. Addition of hexane induced the precipitation of an orange solid, which was washed with hexane (3 x 4 mL) and dried in vacuo. Yield: 68 mg (58%). Satisfactory elemental analysis could not be obtained. HRMS (ESI) m/z Calcd for $\text{C}_{42}\text{H}_{51}\text{N}_3\text{Rh}$ ($\text{M} - \text{Cl}^-$): 700.3138. Found: 700.3133. ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.21 (d, $J_{\text{H-H}} = 4.7$, 1H, $\text{H}_{6\text{-py}}$), 7.33 (t, $J_{\text{H-H}} = 7.2$, 2H, $\text{H}_{\text{p-IPr}}$), 7.28 (d, $J_{\text{H-H}} = 7.2$, 4H, $\text{H}_{\text{m-IPr}}$), 7.16 (dd, $J_{\text{H-H}} = 8.4$, 7.7, 2H, $\text{H}_{\text{m-Ph}}$), 7.09 (t, $J_{\text{H-H}} = 7.7$, 1H, $\text{H}_{\text{p-Ph}}$), 6.99 (d, $J_{\text{H-H}} = 8.4$, 2H, $\text{H}_{\text{o-Ph}}$), 6.71 (s, 2H, $=\text{CHN}$), 6.61 (dd, $J_{\text{H-H}} = 8.1$, 6.8, 1H, $\text{H}_{4\text{-py}}$), 6.09 (d, $J_{\text{H-H}} = 8.1$, 1H, $\text{H}_{3\text{-py}}$), 5.98 (dd, $J_{\text{H-H}} = 6.1$, 4.7, 1H, $\text{H}_{5\text{-py}}$), 3.60 and 3.55 (both sept, $J_{\text{H-H}} = 6.7$, 4H, CHMeIPr), 3.43 {ddd, $J_{\text{H-H}} = 10.4$, 7.2, $J_{\text{H-Rh}} = 3.4$, 1H, $\text{CH}_2\text{CH}=\text{CH}(\text{py})$ }, 2.70 {d, $J_{\text{H-H}} = 7.2$, 1H, $\text{CH}_2\text{CH}=\text{CH}(\text{py})$ }, 2.68 and 2.35 (both m, 2H, CH_2Ph), 2.34 and 1.57 (both m, 2H

$\text{CH}_2\text{CH}=\text{CH}$), 1.71, 1.66, 1.21, and 1.17 (all d, $J_{\text{H-H}} = 6.7$, 24H, CHMeIPr). $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (125.6 MHz, C_6D_6 , 298 K): δ 184.6 (d, $J_{\text{C-Rh}} = 59.0$, Rh-ClIPr), 165.4 (d, $J_{\text{C-Rh}} = 4.5$, $\text{C}_{2\text{-py}}$), 146.9 and 146.7 (both br, $\text{C}_{\text{q-IPr}}$), 146.1 (s, $\text{C}_{6\text{-py}}$), 142.5 (s, $\text{C}_{\text{q-Ph}}$), 137.9 (s, C_{qN}), 134.6 (s, $\text{C}_{4\text{-py}}$), 129.8 (s, $\text{C}_{\text{p-IPr}}$), 128.8 (s, $\text{C}_{\text{o-Ph}}$), 128.3 (s, $\text{C}_{\text{m-Ph}}$), 125.7 (s, $\text{C}_{\text{p-Ph}}$), 124.5 (s, $=\text{CHN}$), 124.2 and 124.0 (both s, $\text{C}_{\text{m-IPr}}$), 119.2 (s, $\text{C}_{5\text{-py}}$), 117.5 (s, $\text{C}_{3\text{-py}}$), 64.1 {d, $J_{\text{C-Rh}} = 18.4$, $\text{CH}_2\text{CH}=\text{CH}(\text{py})$ }, 44.6 {d, $J_{\text{C-Rh}} = 12.4$, $\text{CH}_2\text{CH}=\text{CH}(\text{py})$ }, 38.4 (s, CH_2Ph), 35.5 (s, $\text{CH}_2\text{CH}=\text{CH}$), 29.1 and 29.1 (both s, CHMeIPr), 26.6, 26.2, 23.3, and 23.2 (all s, CHMeIPr).

Preparation of $\text{RhCl}(\text{IPr})[\kappa\text{-N},\eta^2\text{-(Z)-CH}\{(\text{E})\text{-C}(\text{Et})=\text{CH}(\text{Et})\}=\text{CH}(\text{C}_5\text{H}_4\text{N})]$ (6a). A solution of **2a** (100 mg, 0.16 mmol) in 10 mL of toluene was treated with 3-hexyne (20 μL , 0.18 mmol) and stirred at 333 K for 12 h. After filtration through Celite the solvent was evaporated to dryness. Addition of hexane induced the precipitation of an orange solid, which was washed with hexane (3 x 4 mL) and dried in vacuo. Yield: 105 mg (92%). Anal. Calcd. for $\text{C}_{40}\text{H}_{53}\text{N}_3\text{ClRh}$: C, 67.27; H, 7.48; N, 5.88. Found: C, 67.22; H, 7.25; N, 5.71. ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.24 (d, $J_{\text{H-H}} = 5.1$, 1H, $\text{H}_{6\text{-py}}$), 7.40 (t, $J_{\text{H-H}} = 7.6$, 2H, $\text{H}_{\text{p-IPr}}$), 7.30 (d, $J_{\text{H-H}} = 7.6$, 4H, $\text{H}_{\text{m-IPr}}$), 6.75 (s, 2H, $=\text{CHN}$), 6.70 (dd, $J_{\text{H-H}} = 7.4$, 7.3, 1H, $\text{H}_{4\text{-py}}$), 6.27 (d, $J_{\text{H-H}} = 7.3$, 1H, $\text{H}_{3\text{-py}}$), 6.13 (dd, $J_{\text{H-H}} = 7.4$, 5.1, 1H, $\text{H}_{5\text{-py}}$), 5.82 (t, $J_{\text{H-H}} = 6.4$, 1H, $\text{CH}_2\text{CH}=\text{CH}$), 4.06 {d, $J_{\text{H-H}} = 6.0$, 1H, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 3.75 and 3.37 (both sept, $J_{\text{H-H}} = 6.6$, 4H, CHMeIPr), 2.51 {d, $J_{\text{H-H}} = 6.0$, 1H, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 2.07 and 1.86 (both m, 2H, CH_2C_q), 1.77 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}$), 1.66, 1.58, 1.18, and 1.15 (all d, $J_{\text{H-H}} = 6.6$, 24H, CHMeIPr), 1.09 (overlapped, 3H, $\text{CH}_3\text{CH}_2\text{C}_q$), 0.62 (t, $J_{\text{H-H}} = 6.7$, 3H, $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (100.4 MHz, C_6D_6 , 298 K): δ 184.2 (d, $J_{\text{C-Rh}} = 57.9$, Rh-ClIPr), 166.1 (s, $\text{C}_{2\text{-py}}$), 147.0 and 146.7 (both s, $\text{C}_{\text{q-IPr}}$), 145.6 (s, $\text{C}_{6\text{-py}}$), 139.9 {s, $(\text{Et})\text{C}_q$ }, 137.5 (s, C_{qN}), 134.2 (s, $\text{C}_{4\text{-py}}$), 131.9 (s, $(\text{Et})\text{CH}=\text{CH}$), 129.6 (s, $\text{C}_{\text{p-IPr}}$), 124.4 and 123.7 (both s, $\text{C}_{\text{m-IPr}}$), 123.9 (s, $=\text{CHN}$), 118.5 (s, $\text{C}_{5\text{-py}}$), 117.2 (s, $\text{C}_{3\text{-py}}$), 64.8 (d, $J_{\text{C-Rh}} = 21.0$, $\text{CH}(\text{Et})=\text{CH}(\text{py})$), 43.0 (d, $J_{\text{C-Rh}} = 11.3$, $\text{CH}(\text{Et})=\text{CH}(\text{py})$), 29.0 and 28.7 (both s, CHMeIPr), 26.4, 26.2, 23.0, and 22.8 (all s, CHMeIPr), 24.9 (s, $\text{CH}_3\text{CH}_2\text{C}_q$), 21.6 (s, $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$), 14.6 (s, $\text{CH}_3\text{CH}_2\text{C}_q$), 13.8 (s, $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$).

Preparation of $\text{RhCl}(\text{IMes})[\kappa\text{-N},\eta^2\text{-(Z)-CH}\{(\text{E})\text{-C}(\text{Et})=\text{CH}(\text{Et})\}=\text{CH}(\text{C}_5\text{H}_4\text{N})]$ (6b). A solution of **2b** (100 mg, 0.18 mmol) in 10 mL of toluene was treated with 3-hexyne (23 μL , 0.20 mmol) and stirred at 313 K for 12 h. After filtration through Celite the solvent was evaporated to dryness. Addition of hexane induced the precipitation of a yellow solid, which was washed with hexane (3 x 4 mL) and dried in vacuo. Yield: 100 mg (88%). Anal. Calcd. for $\text{C}_{34}\text{H}_{41}\text{N}_3\text{ClRh}$: C, 64.81; H, 6.56; N, 6.67. Found: C, 65.03; H, 6.43; N, 6.51. ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.27 (d, $J_{\text{H-H}} = 5.4$, 1H, $\text{H}_{6\text{-py}}$), 6.96 and 6.89 (both s, 4H, $\text{H}_{\text{m-IMes}}$), 6.62 (dd, $J_{\text{H-H}} = 7.9$, 7.1, 1H, $\text{H}_{4\text{-py}}$), 6.27 (s, 2H, $=\text{CHN}$), 6.24 (d, $J_{\text{H-H}} = 7.9$, 1H, $\text{H}_{3\text{-py}}$), 6.15 (t, $J_{\text{H-H}} = 7.0$, 1H, $\text{CH}_2\text{CH}=\text{CH}$), 6.04 (dd, $J_{\text{H-H}} = 7.1$, 5.4, 1H, $\text{H}_{5\text{-py}}$), 3.98 {d, $J_{\text{H-H}} = 6.7$, 1H, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 2.84 {d, $J_{\text{H-H}} = 6.7$, 1H, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 2.60, 2.43, and 2.25 (all s, 18H, MeImes), 2.03 (m, 2H, $\text{CH}_3\text{CH}_2\text{C}_q$), 1.85 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$), 1.17 (t, $J_{\text{H-H}} = 7.0$, 3H, $\text{CH}_3\text{CH}_2\text{C}_q$), 0.75 (t, $J_{\text{H-H}} = 7.6$, 3H, $\text{CH}_3\text{CH}_2\text{C}_q$). $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (100.4 MHz, C_6D_6 , 298 K): δ 182.2 (d, $J_{\text{C-Rh}} = 60.4$, Rh-ClIMes), 166.3 (s, $\text{C}_{2\text{-py}}$), 145.6 (s, $\text{C}_{6\text{-py}}$), 139.8 {s, $(\text{Et})\text{C}_q$ }, 138.1 (s, $\text{C}_{\text{q-IMes}}$), 137.6 (s, C_{qN}), 134.4 (s, $\text{C}_{4\text{-py}}$), 132.9 {s, $(\text{Et})\text{CH}=\text{CH}$ }, 129.4 and 129.0 (both s, $\text{C}_{\text{m-IMes}}$), 122.9 (s, $=\text{CHN}$), 119.5 (s, $\text{C}_{5\text{-py}}$), 117.6 (s, $\text{C}_{3\text{-py}}$), 65.8 {d, $J_{\text{C-Rh}} = 18.3$, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 43.1 {d, $J_{\text{C-Rh}} = 13.2$, $\text{CH}(\text{Et})=\text{CH}(\text{py})$ }, 25.4 (s, $\text{CH}_3\text{CH}_2\text{C}_q$), 21.8 (s, $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$), 21.1, 19.3, and 19.1 (all s, MeImes), 14.7 (s, $\text{CH}_3\text{CH}_2\text{C}_q$), 14.3 (s, $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$).

Preparation of $\text{RhCl}(\text{IPr})[\kappa\text{-N},\eta^2\text{-(Z)-CH}\{(\text{Z})\text{-C}(\text{Ph})=\text{CH}(\text{Ph})\}=\text{CH}(\text{C}_5\text{H}_4\text{N})]$ (7a). The complex was prepared as described for **6a** starting from **2a** (100 mg, 0.16 mmol) and diphenylacetylene (32 mg, 0.18 mmol). Yield: 91 mg (70%). Anal.

Calcd. for $C_{48}H_{53}N_3ClRh$: C, 71.15; H, 6.59; N, 5.19. Found: C, 71.30; H, 6.88; N, 5.07. 1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.08 (d, $J_{H-H} = 4.8$, 1H, H_{6-py}), 7.65 (s, 1H, $=CHPh$), 7.23 (t, $J_{H-H} = 8.0$, 2H, H_{p-IPr}), 7.20 and 7.14 (both d, $J_{H-H} = 8.0$, 4H, H_{m-IPr}), 6.97 and 6.89 (both d, $J_{H-H} = 8.2$, 4H, H_{o-Ph}), 6.87 (dd, $J_{H-H} = 8.2$, 7.7, 4H, H_{m-Ph}), 6.86 and 6.81 (both t, $J_{H-H} = 7.7$, 2H, H_{p-Ph}), 6.62 (s, 2H, $=CHN$), 6.36 (dd, $J_{H-H} = 7.9$, 7.2, 1H, H_{4-py}), 5.92 (d, $J_{H-H} = 7.9$, 1H, H_{3-py}), 5.81 (dd, $J_{H-H} = 7.2$, 4.8, 1H, H_{5-py}), 4.39 {dd, $J_{H-H} = 7.5$, $J_{H-Rh} = 1.3$, 1H, $CH(CPh)=CH(py)$ }, 3.75 and 3.30 (both d, $J_{H-H} = 6.7$, 4H, $CHMeIPr$), 2.43 {d, $J_{H-H} = 7.5$, 1H, $CH(CPh)=CH(py)$ }, 1.59, 1.50, 1.08, and 1.05 (all d, $J_{H-H} = 6.7$, 24H, $CHMeIPr$). $^{13}C\{^1H\}$ -APT NMR (100.4 MHz, C_6D_6 , 298 K): δ 183.5 (d, $J_{C-Rh} = 57.5$, Rh- C_{IPr}), 165.7 (d, $J_{C-Rh} = 4.6$, C_{2-py}), 147.1 and 146.9 (both s, C_{q-IPr}), 146.0 (s, C_{6-py}), 143.7 and 138.7 (both s, C_{q-Ph}), 142.7 (s, PhC_q), 137.7 (s, C_qN), 134.9 (s, $PhCH=$), 134.5 (s, C_{4-py}), 129.9 (s, C_{p-IPr}), 129.4 and 129.4 (both s, C_{o-Ph}), 128.1 and 128.0 (both s, C_{m-Ph}), 126.2 and 126.1 (both s, C_{p-IPr}), 124.6 (s, $=CHN$), 124.2 and 124.1 (both s, C_{m-IPr}), 119.5 (s, C_{5-py}), 117.5 (s, C_{3-py}), 65.8 {d, $J_{C-Rh} = 18.3$, $CH(CPh)=CH(py)$ }, 42.6 {d, $J_{C-Rh} = 11.8$, $CH(CPh)=CH(py)$ }, 29.3 and 29.1 (both s, $CHMeIPr$), 26.6, 26.4, 23.4, and 23.1 (all s, $CHMeIPr$).

Preparation of $RhCl(IMes)[\kappa-N,\eta^2-(Z)CH\{(Z)C(Ph)=CH(Ph)\}=CH(C_5H_4N)]$ (7b). The complex was prepared as described for **6b** starting from **2b** (100 mg, 0.18 mmol) and diphenylacetylene (36 mg, 0.20 mmol). Yield: 82 mg (63%). Anal. Calcd. for $C_{42}H_{41}N_3ClRh$: C, 69.47; H, 5.69; N, 5.79. Found: C, 69.75; H, 5.93; N, 5.54. 1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.06 (d, $J_{H-H} = 4.3$, 1H, H_{6-py}), 7.85 (s, 1H, $=CHPh$), 7.05 and 6.88 (both d, $J_{H-H} = 8.1$, 4H, H_{o-Ph}), 6.95 and 6.89 (both dd, $J_{H-H} = 8.1$, 7.6, 4H, H_{m-Ph}), 6.93 and 6.84 (both t, $J_{H-H} = 7.6$, 2H, H_{p-Ph}), 6.84 and 6.74 (both s, 4H, H_{m-IMes}), 6.36 (dd, $J_{H-H} = 7.9$, 7.6, 1H, H_{4-py}), 6.22 (s, 2H, $=CHN$), 5.99 (d, $J_{H-H} = 7.9$, 1H, H_{3-py}), 5.78 (dd, $J_{H-H} = 7.6$, 4.9, 1H, H_{5-py}), 4.26 {dd, $J_{H-H} = 7.6$, $J_{H-Rh} = 1.7$, 1H, $CH(CPh)=CH(py)$ }, 2.85 {d, $J_{H-H} = 7.6$, $J_{H-Rh} = 1.2$, 1H, $CH(CPh)=CH(py)$ }, 2.51, 2.32, and 2.08 (all s, 18H, $MeIMes$). $^{13}C\{^1H\}$ -APT NMR (100.4 MHz, C_6D_6 , 298 K): δ 181.4 (d, $J_{C-Rh} = 55.7$, Rh- C_{IMes}), 165.2 (d, $J_{C-Rh} = 4.8$, C_{2-py}), 145.3 (s, C_{6-py}), 142.6 (s, PhC_q), 138.3 and 138.0 (both s, C_{q-Ph}), 137.9 (s, C_{q-IMes}), 137.0 (s, C_qN), 134.9 (s, $PhCH=$), 134.2 (s, C_{4-py}), 129.3 and 128.8 (both s, C_{m-IMes}), 129.2 and 128.9 (both s, C_{o-Ph}), 127.9 and 127.6 (both s, C_{m-Ph}), 126.0 and 125.7 (both s, C_{p-Ph}), 122.7 (s, $=CHN$), 119.4 (s, C_{5-py}), 117.4 (s, C_{3-py}), 66.8 {d, $J_{C-Rh} = 18.3$, $CH(CPh)=CH(py)$ }, 42.0 {d, $J_{C-Rh} = 12.3$, $CH(CPh)=CH(py)$ }, 20.7, 18.9, and 18.8 (all s, $MeIMes$).

In situ formation of $RhCl(IPr)\{\eta^2-CH_2=CH(C_4H_3N_2)\}(py)$ (8). A solution of **2a** (30 mg, 0.023 mmol) in toluene- d_8 (0.5 mL, NMR tube) was treated with 2-vinylpyrazine (5 μ L 0.049 mmol) and pyridine (6 μ L 0.070 mmol) at 253 K. The spectra were recorded immediately at low temperature. 1H NMR (500 MHz, toluene- d_8 , 253 K): 7.86 (d, $J_{H-H} = 5.6$, 2H, H_{2-py}), 7.71 (s, 1H, H_{3-pz}), 7.62 (d, $J_{H-H} = 2.2$, 1H, H_{6-pz}), 7.4–7.1 (6H, H_{Ph}), 7.00 (d, $J_{H-H} = 2.2$, 1H, H_{5-pz}), 6.68 and 6.60 (both br, 2H, $=CHN$), 6.36 (t, $J_{H-H} = 7.1$, 1H, H_{4-py}), 5.88 (dd, $J_{H-H} = 7.1$, 5.6, 2H, H_{3-py}), 4.63, 3.71, 3.05, and 2.40 (all sept, $J_{H-H} = 6.6$, 4H, $CHMeIPr$), 4.53 (dd, $J_{H-H} = 10.2$, 7.2, 1H, $CH=CH_2$), 3.10 (d, $J_{H-H} = 10.2$, 1H, $CH=CH_2$), 2.86 (d, $J_{H-H} = 7.2$, 1H, $CH=CH_2$), 1.88, 1.70, 1.67, 1.25, 1.19, 1.14, 1.08, and 1.06 (all d, $J_{H-H} = 6.6$, 24H, $CHMeIPr$). $^{13}C\{^1H\}$ NMR (100.4 MHz, toluene- d_8 , 253 K): δ 181.3 (d, $J_{C-Rh} = 52.6$, Rh- C_{IPr}), 161.3 (s, C_{2-pz}), 151.8 (s, C_{2-py}), 148.6, 148.5, 145.8, and 145.7 (all s, C_{q-IPr}), 146.2 (s, C_{3-pz}), 142.8 (s, C_{5-pz}), 138.3 (s, C_{6-pz}), 134.1 (s, C_{4-py}), 130.4 and 130.0 (both s, C_{p-IPr}), 125.1, 124.6, 123.6, and 122.5 (all s, C_{m-IPr}), 124.7 and 123.8 (both s, $=CHN$), 122.7 (s, C_{3-py}), 50.4 (d, $J_{C-Rh} = 15.7$, $CH=CH_2$), 35.0 (d, $J_{C-Rh} = 16.5$, $CH=CH_2$), 29.2, 29.1, 28.8, and 28.7 (all s, $CHMeIPr$), 27.0, 26.6, 26.5, 26.0, 23.8, 23.7, 22.6, and 22.4 (all s, $CHMeIPr$). 1H - ^{15}N HMQC NMR (40.5 MHz,

toluene- d_8 , 233 K): δ 331.6 (N_{4-pz}), 319.4 (N_{1-pz}), 269.5 (N_{py}), 193.2 and 192.7 (N_{IPr}).

Standard catalytic reactions: A NMR tube containing a solution of 0.01 mmol of catalyst in 0.5 mL of C_6D_6 under argon atmosphere was treated with 0.20 mmol of heteroarene and 0.20 mmol of substrate or pressurized to 2 bar of gas (ethylene and propene). Then, the NMR tube was sealed under argon atmosphere and heated at the corresponding temperature for the determined time. The reaction course was monitored by 1H NMR and the conversion and selectivities determined by integration of the corresponding resonances of the 2-vinylazine and the reaction products.

6,7-diethyl-6H-pyrido[1,2-a]pyrazine. 1H NMR (500 MHz, C_6D_6 , 298 K): δ 7.61 (s, 1H, H_{11}), 6.46 (d, $J_{H-H} = 4.9$, 1H, H_3), 5.67 (d, $J_{H-H} = 6.1$, 1H, H_8), 5.50 (d, $J_{H-H} = 4.9$, 1H, H_4), 4.77 (d, $J_{H-H} = 6.1$, 1H, H_9), 3.53 (dd, $J_{H-H} = 8.1$, 3.8, 1H, H_6), 1.73 (m, 2H, H_{12}), 1.55 and 1.09 (both m, 2H, H_{10}), 0.90 (t, $J_{H-H} = 7.2$, 3H, H_{13}), 0.70 (t, $J_{H-H} = 7.3$, 3H, H_{11}). $^{13}C\{^1H\}$ -APT NMR (125.6 MHz, C_6D_6 , 298 K): δ 151.3 (s, C_1), 133.3 (s, C_{9a}), 127.2 (s, C_4), 123.9 (s, C_7), 121.9 (s, C_3), 117.7 (s, C_8), 93.3 (s, C_9), 64.8 (s, C_6), 27.0 (s, C_{12}), 24.5 (s, C_{10}), 12.4 (s, C_{13}), 10.5 (s, C_{11}). ^{15}N - 1H HMBC (40 MHz, C_6D_6 , 298 K): δ 307.3 (s, N_2), 109.8 (s, N_5). HRMS (ESI) m/z Calcd for $C_{12}H_{17}N_2$ ($M + H^+$): 189.1386. Found: 189.1384.

Crystal Structure Determinations. X-ray diffraction, data were collected on APEX SMART (4) or APEX-DUO SMART (**2a**, **6a**) Bruker diffractometers with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) using narrow ω rotations (0.3–0.6°). Intensities were integrated and corrected for absorption effects with SAINT-PLUS,³⁵ and SADABS³⁶ programs, both included in APEX2 package. The structures were solved by the Patterson method with SHELXS-2013³⁷ and refined by full matrix least-squares on F^2 with SHELXL-2014³⁸ under WinGX.³⁹

Crystal data for 2a. $C_{34}H_{43}ClN_3Rh$; $M = 632.07$ g mol $^{-1}$; $T = 100(2)$ K; monoclinic, $P2_1/n$, $a = 15.998(4)$ Å, $b = 11.453(3)$ Å, $c = 18.434(5)$ Å, $\beta = 107.862(3)^\circ$, $V = 3214.8(14)$ Å 3 ; $Z = 4$; $D_{calc} = 1.306$ Mg m $^{-3}$; $\mu = 0.640$ mm $^{-1}$; red prism, $0.263 \times 0.225 \times 0.120$ mm 3 ; $\theta_{min}/\theta_{max} = 2.022/26.372^\circ$; reflections collected/unique 49810/6578 [$R(int) = 0.0457$]; data/restraints/parameters 6578/0/360, $GoF = 1.065$; $R_1 = 0.0245$ [$I > 2\sigma(I)$], $wR_2 = 0.0649$ (all data); largest diff. peak/hole $0.372/-0.251$ e Å $^{-3}$.

Crystal data for 4. $C_{36}H_{47}ClN_3Rh$, $M = 660.12$ g mol $^{-1}$; $T = 100(2)$ K; monoclinic; $P2_1/n$, $a = 10.3033(5)$ Å, $b = 29.2535(14)$ Å, $c = 11.0594(5)$ Å, $\beta = 96.2640(10)^\circ$, $V = 3313.5(3)$ Å 3 ; $Z = 4$; $D_{calc} = 1.323$ Mg m $^{-3}$; $\mu = 0.624$ mm $^{-1}$; red prism, $0.190 \times 0.120 \times 0.090$ mm 3 ; $\theta_{min}/\theta_{max} = 1.392/26.371^\circ$; reflections collected/unique 71588/6769 [$R(int) = 0.0436$]; data/restraints/parameters 6769/0/379; $GoF = 1.064$; $R_1 = 0.0267$ [$I > 2\sigma(I)$], $wR_2 = 0.0631$ (all data); Largest diff. peak/hole $0.438/-0.355$ e Å $^{-3}$.

Crystal data for 6a. $C_{40}H_{53}ClN_3Rh$, $M = 714.21$ g mol $^{-1}$; $T = 170(2)$ K, monoclinic, $C2/c$, $a = 39.994(14)$ Å, $b = 10.187(4)$ Å, $c = 18.141(6)$ Å, $\beta = 93.078(5)^\circ$, $V = 7380(4)$ Å 3 ; $Z = 8$; $D_{calc} = 1.286$ Mg m $^{-3}$; $\mu = 0.566$ mm $^{-1}$; red prism, $0.190 \times 0.080 \times 0.035$ mm 3 ; $\theta_{min}/\theta_{max} = 2.040/25.350^\circ$; reflections collected/unique 29939/6748 [$R(int) = 0.0608$]; data/restraints/parameters 6748/12/422; $GoF = 1.054$; $R_1 = 0.0556$ [$I > 2\sigma(I)$], $wR_2 = 0.1603$ (all data); largest diff. peak/hole $2.882/-1.020$ e Å $^{-3}$.

Computational details All calculations were performed with the Gaussian09 package⁴⁰ at the M06-2X level⁴¹ and the Dunning-type basis sets cc-pVTZ.⁴² Full optimizations of geometry without any constraint were performed, followed by analytical computation of the Hessian matrix to confirm the nature of the stationary points as minima on the potential energy surface. Gibbs free energies at 353

K were calculated on the basis of the rigid rotor-harmonic oscillator approximation. The solvent effects (toluene) were calculated by the SMD method.⁴³

ASSOCIATED CONTENT

Supporting Information Available. Supporting Information is available free of charge on the ACS Publications website at DOI: <http://pubs.acs.org>.

NMR data for organometallic and organic products (PDF)

Optimized coordinates for the computed compounds (XYZ).

Accession Codes

CCDC 1825029 (**2a**), 1825032 (**4**), 1825033 (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. X-ray crystallographic information files containing full details of the structural analysis of complexes **2a**, **4**, and **6a** (CIF format). NMR data for organic products and NMR spectra for compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>

AUTHOR INFORMATION

Corresponding Author

* E-mail: rcastar@unizar.es.

Notes

The authors declare no competing financial interest

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