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Rhodium(I)-N-Heterocyclic Carbene Catalyst for Selective Coupling of *N*-Vinylpyrazoles with Alkynes via C−H Activation

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Supporting Information

ABSTRACT: The complex $[Rh(\mu\text{-}Cl)(IPr)(\eta^2\text{-}coe)]_2$ {*IPr* = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-carbene, coe = *cis*-cyclooctene} efficiently catalyzes the coupling of alkynes and *N*-vinylpyrazole via C−H activation, leading to Markovnikov-selective butadienylpyrazole derivatives under mild conditions. A straightforward approach to cross-conjugated acyclic trienes is also operative through a one-pot alkyne dimerization-hydrovinylation tandem reaction. The proposed mechanism involves C−H activation of vinylpyrazole directed by nitrogen coordination to the metallic center. Subsequent alkyne coordination, insertion, and reductive elimination steps lead to the coupling products. Several key intermediates participating in the catalytic cycle have been detected and characterized, including a κ-N, η^2-C═C coordinated vinylpyrazole complex and a Rh^{III}-hydride-alkenyl species resulting from the C−H activation of the vinylpyrazole

KEYWORDS: *C−H activation, C−C coupling, pyrazole, N-heterocyclic carbene, rhodium*

INTRODUCTION

Transition-metal-catalyzed C−C bond formation via C−H activation has been revealed as a very powerful, selective, and atom-economical tool of increasing importance in current organic synthesis.[1] This impressive success would have not been possible without an in-depth study of the factors that control the reactivity of catalytic intermediate species, whose understanding is essential to rationally design active and selective catalysts.[2] Particularly, rhodium catalysts play a relevant role in this area because of their functional group tolerance, substrate scope, and high level of activity and selectivity for a wide range of synthetic transformations.[3] In particular, the Murai reaction has allowed for the construction of intricate conjugated structures from the coupling of aromatic or vinylic heteroatom-substituted substrates with carbon−carbon unsaturated partners, such as olefins or alkynes (Figure 1).[1a,4] Although oxygen-containing moieties have been widely used as directing groups, a range of nitrogen-based functional groups, such as amine,[5] imine,[6] pyridine,[7] oxime,[8] oxazoline,[9] nitrile,[10] or others,[11] have also been investigated to reduce the energy barrier for C−H activation. Regarding the nature of the C−H bond, aromatic protons have been commonly involved in this process, but functionalization of vinyl C−H is more problematic because of competitive polymerization or Michael-type addition reactions.[3c] Moreover, electron-rich olefins are much less reactive, and actually, the activation of α-heteroatom alkenes is limited to enamides,[12] ketoenamines,[13] or cyclic

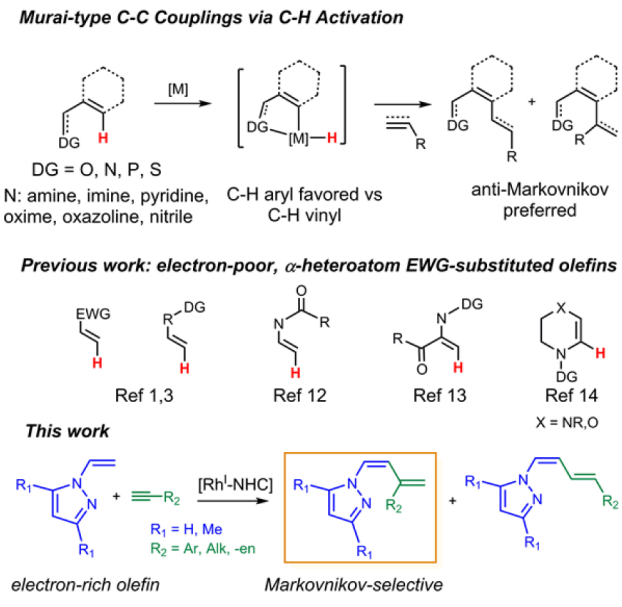

Figure 1. Hydrovinylation of alkynes mediated by Rh-NHC catalysts.

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compounds.[14] It is thus of paramount importance to broaden the applicability of C−H bond activation synthetic strategy to challenging substrates.

Pyrazole-based derivatives have attracted increased interest in recent years owing to their widespread applications in medicine, agriculture, material science or catalysis.[15] Classical synthetic approaches consist of the assembly of the pyrazole core via dicarbonyl-hydrazine cyclocondensations, or dipolar cycloadditions, albeit more recently, cross-coupling substitution into the pyrazole framework has emerged as an alternative procedure.[16] Despite this plethora of preparative methods, the development of new selective and atom-economical processes still remains an important target. In this context, pyrazole coordination directs the functionalization of aromatic or aliphatic C−H bonds,[17] but activation of vinylic protons in the electron-rich *N*-vinyl derivatives has not been yet reported to date. Reactivity studies on vinylpyrazole derivatives are scarce[18] and mainly restricted to Diels−Alder[19] or polymerization reactions.[20]

A practical approach to overcome the challenging C−H activation of *N*-vinylpyrazole is based on catalyst design by using powerful electron-donating ligand, such as an N-heterocyclic carbene (NHC), to facilitate the C−H activation process.[21] Moreover, the steric bulk of these ligands has a significant influence on the selectivity control over the catalytic outcome, which is also an important issue.[22] In this context, we have recently disclosed Rh^{I}−NHC catalysts for alkyne hydrothiolation,[23a,d] hydroalkynylation,[23c,e] or hydrovinylation[23b] with high selectivity to Markonikov-type addition products. Now, we present herein an efficient and unprecedented Markovnikov-regioselective *N*-vinylpyrazol hydrovinylation of terminal or internal alkynes, and 1,3-disubstituted enynes catalyzed by a rhodium-NHC catalyst. The mechanism of this transformation has been investigated by means of stoichiometric low-temperature NMR experiments. In addition, the successful isolation and characterization of key intermediate species has allowed us to propose a plausible catalytic cycle.

RESULTS AND DISCUSSION

Catalytic Hydrovinylation of Alkynes with Vinylpyrazole. Recently, our research group has demonstrated that dinuclear compounds of type $[Rh(\mu\text{-}Cl)(NHC)(\eta^2\text{-olefin})]_2$,[24] {**1a**; NHC = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-carbene (*I*Pr); olefin = *cis*-cyclooctene (coe)} are valuable starting materials for the preparation of mononuclear complexes of type $RhCl(NHC)(\eta^2\text{-olefin})(L)$ by simple bridge cleavage with a nucleophilic ligand.[23] Particularly, treatment of **1a** with 2-vinylpyridine leads to the isolation of $RhCl(IPr)\{\kappa\text{-}N,\eta^2\text{-}CH_2{=}CH(C_5H_4N)\}$, which is an efficient catalyst for the synthesis of 2-butadienylpyridines via C−C coupling with terminal and internal alkynes without apparent dimerization or polymerization.[23b] Moreover, subsequent thermal 6π-electrocyclization of internal-substituted 2-butadienylpyridines gives access to 4*H*-quinolizines. The efficiency demonstrated by these Rh^{I}−NHC complexes in the alkyne hydrovinylation reaction prompted us to apply this methodology to the more challenging C−H activation of the electron-rich olefin of *N*-vinylpyrazole derivatives.

As a preliminary test, 1-vinylpyrazole (vpz, **2a**) and 1-hexyne (**3a**) were chosen as model substrates (Scheme 1, Table 1). After 24 h at 40 °C, the formation of two hydrovinylation products was observed with an overall conversion of 37%. Both products arise from syn addition with a clear preference for the

Scheme 1. Catalyst Precursors for the Coupling Reaction of 1-Vinylpyrazole with 1-Hexyne and Products Formed Thereof

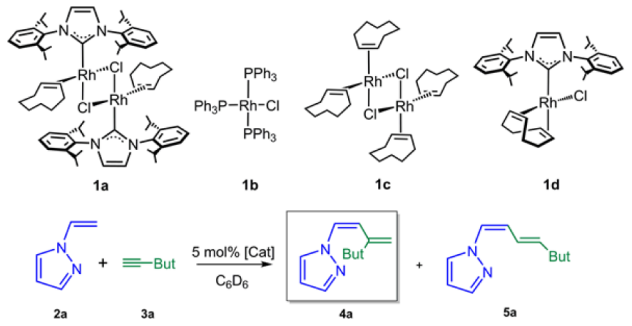

Table 1. Screening of Catalyst and Conditions for the Coupling of 1-Vinylpyrazole with 1-Hexyne[a]

entry	catalyst	T(°C)	t(h)	conversion(%)[b]	4a	5a
1	**1a**	40	24	37	83	17
2	**1a**	70	2	95	84	16
3	**1b**	70	24	11	54	46
4	**1c**	70	24			
5	**1d**	70	24	8	82	18
6	**1a** + py	70	2	70[c]	47[d]	10[d]

[a]Reaction conditions: 0.01 mmol of **1** in C_6D_6 (0.5 mL), 0.2 mmol of 1-vinylpyrazole and 1-hexyne. [b]Formation of *Z*/gem + *Z*/*E* butadienylpyrazole relative to 1-vinylpyrazole. [c]Calculated from 1-hexyne consumption. [d]Formation of 43% of 7-methylene-5-undecyne.

Z/geminal (gem) isomer 1-{3-methylene-1(*Z*)-heptenyl}-pyrazole (**4a**) versus the *Z*/*E* 1-{1(*Z*),3(*E*)-octadienyl}pyrazole (**5a**) derivative (83:17). Interestingly, the catalytic activity was improved significantly at 70 °C. After 2 h, a 95% conversion was attained while maintaining the selectivity (Table 1, entry 2). Notably, neither dimerization nor cyclotrimerization of the alkyne was observed.[23c,e] This process represents a new straightforward method for butadienylpyrazole derivatives that could find potential applications as building blocks for further functionalization via cyclization, addition, or oxidation reactions among other transformations.[25]

The presence of a NHC ligand seems to be essential for a high efficient catalytic coupling, as is reflected from the low conversion or total inactivity observed when the Wilkinson catalyst $RhCl(PPh_3)_3$ (**1b**) or the dinuclear complex $[Rh(\mu\text{-}Cl)(\eta^2\text{-coe})_2]_2$ (**1c**) were used as catalysts (Table 1, entries 3 and 4). Moreover, mononuclear complex $RhCl(IPr)(\eta^4\text{-cod})$ (**1d**) (cod =1,5-cyclooctadiene) was also much less active than **1a** (Table 1, entry 5). The strong coordination of the diolefin compared with the labile coe ligands may account for the very different catalytic activity.[23a,b] In early works, we discovered that addition of pyridine (py) to catalyst **1a** dramatically improves the regioselectivity to Markonikov-type additions to unsaturated compounds.[23a,c,e] In sharp contrast, the presence of pyridine is detrimental for the hydrovinylation process (Table 1, entry 6), resulting in a decrease in the catalytic activity with concomitant formation of the alkyne dimerization product 7-methylene-5-undecyne (43%).

The scope of catalyst **1a** was evaluated for various aliphatic and aromatic alkynes using **2a** and 3,5-dimethyl-1-vinylpyrazole (vpz_{Me}, **2b**) (Table 2). High conversion was attained under relatively mild conditions (70 °C) and short times (2−8 h) with a clear bias to (*Z*)/*gem*-butadienylpyrazoles **4a**−**i** (see

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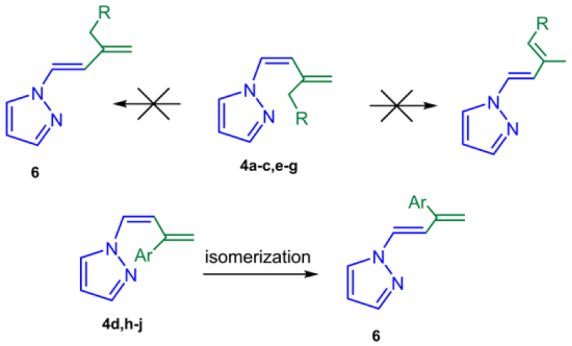
Table 2. Hydrovinylation of Terminal Alkynes with 1-Vinylpyrazoles[a]

entry	2	alkyne	t(h)	conv (%)[b]	4	5	6	yield (%)[c]
1	**2a**		2	95	**84**	16	--	80 (**4a**)
2	**2a**		3	94	**83**	17	--	75 (**4b**)
3	**2a**		3	98	**90**	10	--	67 (**4c**)
4	**2a**		2	98[d]	24[e]	--	13[e]	--
5	**2b**		8	92	**95**	5	--	85 (**4e**)
6	**2b**		8	90	**98**	2	--	81 (**4f**)
7	**2b**		5	96	**98**	2	--	78 (**4g**)
8	**2b**		5	99[d]	56[e]	--	28[e]	53[f] (**6h**)
9	**2b**		4	98[d]	55[e]	--	35[e]	62[f] (**6i**)
10	**2b**		1	98[d]	29[e]	--	14[e]	--

[a]Reaction conditions: 0.01 mmol of **1a** in C_6D_6 (0.5 mL), 0.2 mmol of 1-vinylpyrazole derivative and terminal alkyne at 70 °C. [b]Formation of *Z*/*gem* + *Z*/*E* butadienylpyrazole relative to 1-vinylpyrazole. [c]Isolated yield. [d]Calculated from alkyne consumption. [e]Formation of alkyne dimerization and cyclotrimerization products. [f]*E*/*gem* butadienylpyrazole derivatives were isolated.

Supporting Information (SI)). As a general trend, **2a** reacted faster than **2b**, but in contrast, an outstanding Markonikov selectivity was attained for the substituted vinylpyrazole, reaching up to 98% for benzylacetylene and 1-octyne (Table 2, entries 1−3 vs 5−7). No isomerization was observed for aliphatic alkynes, either for the internal double bond of **4** to form (*E*)/*gem*-butadienylpyrazoles (**6**) or for the exomethylene to give rise to an internal diene (Scheme 2). However, aromatic

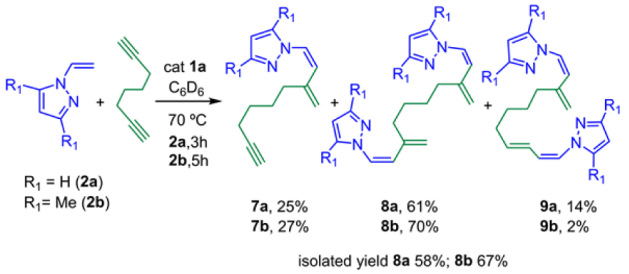
Scheme 2. Isomerization of Butadienylpyrazol Derivatives



alkynes behave differently. The formation of the coupling products of phenylacetylene with **2a** (37%) competed with the dimerization (26%) and cyclotrimerization (39%) of the alkyne. These side reactions were significantly reduced when using the substituted pyrazole **2b** (see Supporting Information). Moreover, the initially formed *Z*/*gem*-butadienylpyrazoles **4d,h−i** isomerized to *E*/*gem* dienes **6** to the point that only **6h−i** could be recovered from the chromatographic column (Table 2, entries 8 and 9) (Scheme 2). The presence of an electron-donating group in the aromatic ring slightly increased the catalytic activity, whereas an electron-withdrawing group results in an increase in alkyne cyclotrimerization byproducts (Table 2, entries 8−10).

Hydrovinylation with 1-vinylpyrazoles is also operative for terminal diynes. Under the optimized reaction conditions, 1,7-octadiyne was completely transformed in 3−5 h. A mixture of monohydrovinylated *Z*/*gem* product, 1-{3-methylene-1(*Z*),8-nonenynyl}pyrazole (**7**) (25−27%), and the doubly coupled derivatives bis-*Z*/*gem*, 1,1′-{3,8-dimethylene-1(*Z*),9(*Z*)-decadiene-1,10-diyl}bis(pyrazole) (**8**) (61−70%), and *Z*/*gem*, *Z*/*E* 1,1′-{3-methylene-1(*Z*),8(*E*),10(*Z*)-undecatriene-1,10-diyl}bis(pyrazole) (**9**) (2−14%), were obtained (Scheme 3). In both

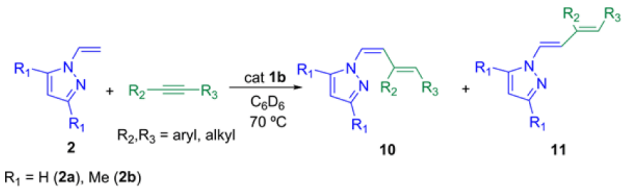
Scheme 3. Coupling Reaction of 1-Vinylpyrazole Derivatives and 1,7-Dioctyne



cases, the major component having two exomethylene substituents, **8a** and **8b**, were isolated in 58 and 67% yield, respectively, after chromatographic purification. It is noteworthy that the selectivity trend to Markonikov addition products is maintained, with the disubstituted pyrazole **2b** being slightly more selective than **2a**.

The scope of the hydrovinylation reaction was extended to a series of internal alkynes (Scheme 4 and Table 3). In all cases,

Scheme 4. Coupling Reaction Between 1-Vinylpyrazoles and Internal Alkynes



1-(*Z*)-butadienylpyrazoles (**10**) were formed as the main products accompanied by a small amount of the 1-(*E*)-

Table 3. Hydrovinylation of Internal Alkynes[a]

entry	2	alkyne	t(h)	conv %	10	11	yield (%)[b]
1	**2a**		14	87	96	4	75 (**10a**)
2	**2a**		1	99	95	5	77 (**10b**)
3	**2a**		1	92	53[c]/47[d]	1	78 (**10c+c'**)[e]
4	**2b**		24[f]	98	92	8	83 (**10d**)
5	**2b**		23	94	81	19	64 (**10e**)
6	**2b**		24	99	82[c]/16[d]	2	76 (**10f**)

[a]Reaction conditions: 0.01 mmol of **1a** in C_6D_6 (0.5 mL), 0.2 mmol of 1-vinylpyrazole derivative, **2a** or **2b**, and internal alkyne at 70 °C. [b]Isolated yield. [c]3-Phenyl-4-methylbutadienylpyrazole. [d]3-Methyl-4-phenylbutadienylpyrazol. [e]Isolated as a mixture of regioisomers. [f]80 °C.

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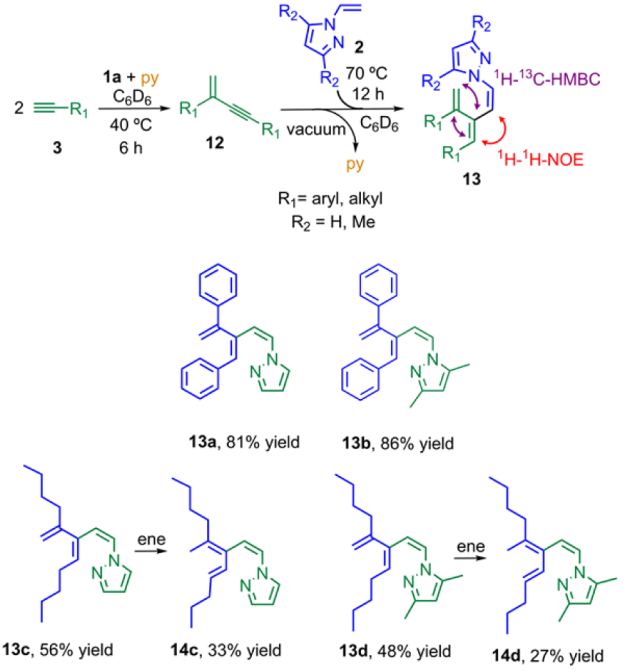
stereoisomer **11**. The increment of isomerized products with regard to terminal alkynes is probably due to prolonged reaction times. Aryl derivatives reacted faster than aliphatic alkynes and, as was observed before, substituted pyrazole **2b** was transformed more slowly than **2a**. Notably, the unsymmetrical 1-phenyl-1-propyne showed different behaviors, depending on the vinylpyrazole derivative. A mixture of regioisomers was isolated from reaction with **2a**, whereas 1,3-dimethyl-1-{3-phenyl,1(*Z*),3(*Z*)-pentadienyl}pyrazole was obtained in 76% isolated yield from the reaction with substituted pyrazole **2b** (Table 3, entries 3 and 6).

Recently, our research group has disclosed that the catalytic system **1a**/py is very efficient for the regioselective Markonikov-type head-to-tail dimerization of terminal alkynes to enynes.[23c,e] Thus, we envisaged the possibility of further transforming these enynes by reaction with vinylpyrazoles in one pot. Gratifyingly, this goal has been achieved (Scheme 5).

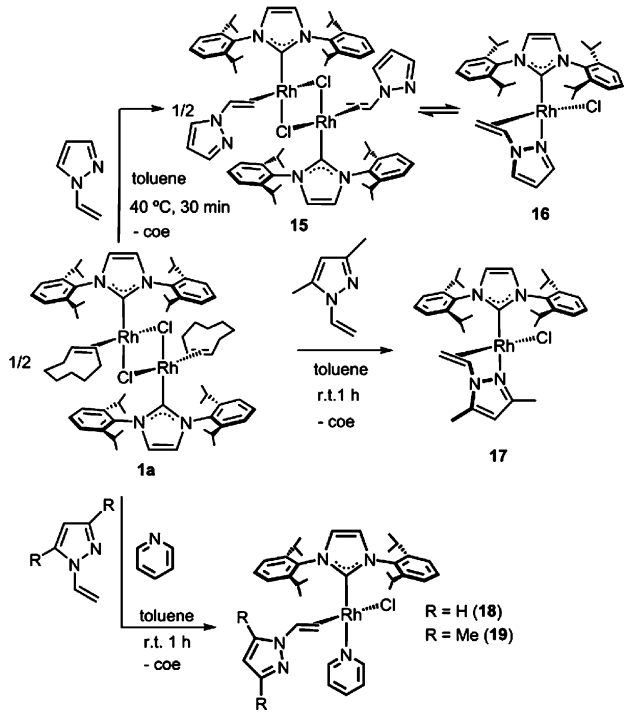
Scheme 5. One-Pot Alkyne Dimerization/Hydrovinylation



Initially, the catalytic system **1a** + 10 equiv py triggered the dimerization of phenylacetylene to 1,3-diphenyl-3,1-butenyne (**12a**) after 6 h at 40 °C. Then, pyridine was removed from the reaction media under vacuum; otherwise, the subsequent hydrovinylation would not proceed efficiently. Refill of the NMR tube with C_6D_6 and the corresponding 1-vinylpyrazole resulting in the selective formation of the cross-conjugated 1-{3-benzylidene-4-phenyl-1(*Z*),4-pentadienyl}pyrazole derivatives, **13a,b**, after heating at 70 °C for 12 h. The identity of this branched acyclic trienes was unambiguously established from ^{1}H−^{13}C HMBC and ^{1}H−^{1}H NOE NMR experiments. This methodology is also applicable for coupling of 1-vinylpyrazoles with the enyne obtained from the dimerization of 1-hexyne. Remarkably for these cases, the triene products, **13c,d**, undergo an intramolecular thermal Alder-ene transformation to give 1-(3-{1(*E*)-pentenyl}-4-methyl-1(*Z*),3(*Z*)-octadienyl)pyrazole derivatives, **14c,d**, that were isolated and fully characterized. These examples demonstrate the potential and versatility of this catalytic transformation.

Isolation of Intermediate Species Relevant for the Catalytic Mechanism. To gain information on the mechanism of this catalytic transformation, we have studied the reactivity of catalytic precursor **1a** with 1-vinylpyrazole derivatives under stoichiometric conditions. Treatment of complex **1a** with **2a** in toluene at 40 °C for 30 min resulted in an equilibrium between the dinuclear species [Rh(μ-Cl)(*I*Pr)(η^2-vpz)]$_2$ (**15**), resulting from olefin exchange, and the mononuclear complex RhCl(*I*Pr)(κ-N,η^2-vpz) (**16**), arising from the cleavage of the chloride bridges in **15** by coordination of the pyrazole moiety, in a 60:40 ratio (Scheme 6). The ^{1}H

Scheme 6. Preparation of Rh^I Vinylpyrazole Complexes



and ^{13}C{^{1}H} NMR spectra showed two sets of signals corresponding to coordinated olefin and carbene in both complexes. In particular, the two doublets observed in the ^{13}C{^{1}H} NMR spectra at $\delta \approx 65$ and 26 ppm (J_{C-Rh} = 17−19 Hz) are diagnostic of the coordination of the olefin moiety of the *N*-vinylpirazole ligands (see the Experimental Section).

In contrast to that observed for vinylpyrazole, treatment of **1a** with 3,5-dimethyl-1-vinylpyrazole in toluene at room temperature led to the isolation of complex RhCl(*I*Pr)(κ-N,η^2-vpz$_{Me}$) (**17**) as a yellow solid in 68% yield. The clean formation of **17** is in agreement with the higher basicity of **2b** compared with **2a**. The chelate coordination of *N*-vinylpyrazole ligands in complexes **16** and **17** is labile, and donor ligands produce N-decoordination. Thus, when the reactions were conducted in the presence of pyridine complexes, RhCl(*I*Pr)-(η^2-vpz)(py) (**18**) and RhCl(*I*Pr)(η^2-vpz$_{Me}$)(py) (**19**) were obtained as result of coordination of the amine with vinylpyrazole ligands bound in an η^2-olefin fashion. At room temperature, complex **19** is in equilibrium with **17**; however, the equilibrium is completely shifted to the opened-vinylpyrazole compound **19** at −40 °C, indicating the higher coordination ability of **2b** with regard to **2a**.

The solid state structures of **17** and **19** were determined by single crystal X-ray diffraction studies (Figures 2 and 3). To the

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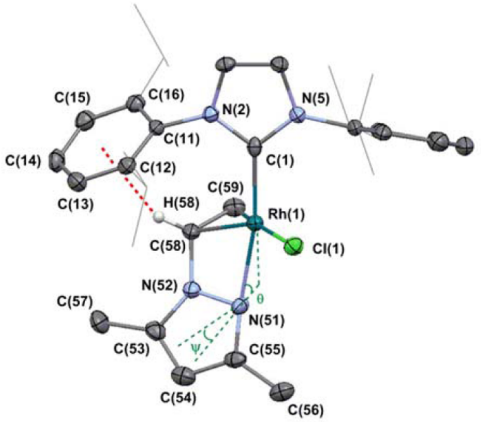


Figure 2. ORTEP view of one of the independent molecules of **17** (ellipsoids at 50% of probability). Wireframe view of isopropyl groups is adopted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−C(1), 1.954(4); Rh(1)−Cl(1), 2.3483(10); Rh(1)−C(58), 2.067(4); Rh(1)−C(59), 2.105(4); C(58)−C(59), 1.399(5); Rh(1)−N(51), 2.186(3); C(1)−Rh(1)−Cl(1), 89.13(10); C(1)−Rh(1)−N(51), 169.98(13).

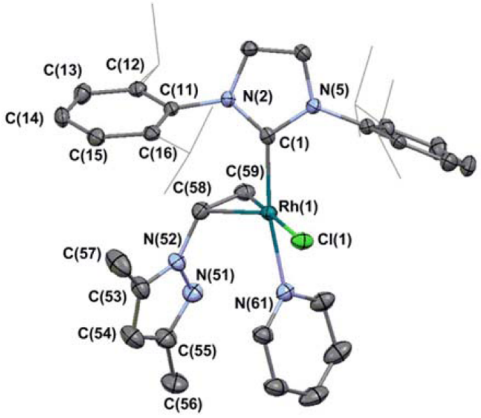


Figure 3. ORTEP view of **19** (ellipsoids at 50% of probability). Wireframe view of isopropyl groups is adopted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−C(1), 1.991(3); Rh(1)−Cl(1), 2.3757(7); Rh(1)−N(61), 2.107(2); Rh(1)−C(58), 2.080(3); Rh(1)−C(59), 2.105(3); C(58)−C(59), 1.402(4); C(1)−Rh(1)−Cl(1), 92.91(8); C(1)−Rh(1)−N(61), 169.96(10).

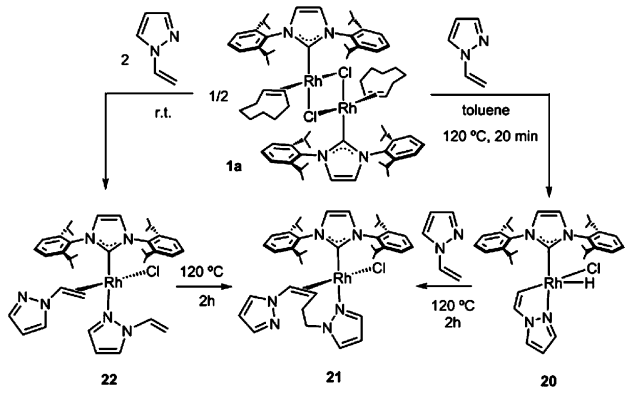
best of our knowledge, they are the first structurally characterized metal complexes containing a κ-N,η^2-C═C, and a η^2-C═C coordinated vinylpyrazole ligand, respectively. The asymmetric unit of **17** contains two crystallographically independent pseudo mirror-image molecules featuring different configuration at the −CH═ vinylic atom. Both molecules display very similar angles and bond distances; therefore, only the molecule with *R* configuration will be discussed herein (Figure 2). The metal center presents a distorted square planar geometry with coordination sites occupied by the chlorido ligand, the carbene carbon atom, and the vinylpyrazole coordinated in a κ-N,η^2-C═C fashion with the nitrogen atom trans to the carbene ligand {C(1)−Rh(1)−N(51), 169.98(13)°}. The Rh(1)−C(1) length {1.954(4) Å} falls within the shortest reported for other rhodium-NHC single bond distances.[21d,23,24] The vinylpyrazole moiety displays a short bite angle (71.9°), which causes a severely distorted arrangement of the pyrazole ring with pitch (θ, 24.4°) and yaw angles (ψ, 38.4°)[26] significantly different from the expected values close to 0° (see Supporting Information for further details). In addition, it is worth mentioning that a CH/π interaction was observed between the vinyl hydrogen H(58) and the C(11)−C(16) phenyl ring of *I*Pr. As a matter of fact, the vinyl hydrogen H(58) stays at 2.47 Å from the centroid of the phenyl ring and at 2.44 Å from the phenyl plane, and consequently, the angle between the vector joining H(58) with the centroid and the perpendicular to the ring is 8.9°. Accordingly, the interatomic distances between H(58) and the carbon atoms of the phenyl ring are in the range 2.67−2.99 Å, shorter than the sum of the van der Waals radii (3.05 Å).[27]

The molecular structure of **19** is shown in Figure 3 along with selected bond distances and angles. The metal center features a slightly distorted square planar coordination containing the chloro atom Cl(1), the carbene carbon atom C(1), and the nitrogen atom N(61) of bonded pyridine in an almost planar arrangement with nitrogen in the trans position with respect to the carbene ligand {C(1)−Rh(1)−N(61), 169.96(10)°}. The coordination sphere is completed by the vinylpyrazole featuring a η^2-C═C coordination mode. The distances around the rhodium atom are similar to those of **17**.

The NMR spectra of **17**−**19** are in agreement with the structure observed in the solid state. The ^{1}H NMR spectra show the expected set of resonances for the η^2-olefin moiety. Noticeable is the shielding of the vinyl ═CH− resonance of **17** (δ 3.55 ppm) compared with that of **18** and **19** (≈5.5 ppm), which suggests that the CH/π interaction observed in the solid state is maintained in solution. More interesting is the ^{15}N−^{1}H HMBC spectra of **17**−**19**. The coordinated nitrogen atom of the *N*-vinylpyrazole moiety in **17** appeared at δ 235.6 ppm, whereas the resonance corresponding to the uncoordinated nitrogen atom was downfield-shifted to δ 304.7 (**18**) and 316.0 ppm (**19**). The pyridine ligand in both complexes was observed upfield-shifted to δ 266.8 (**18**) and 263.7 ppm (**19**) with regard to free pyridine (δ 318.3 ppm).[23c]

The formation of complexes **15**−**17** should take place in the first step of the catalytic process. Coordination on vinylpyrazole by the nitrogen atom may favor the C−H activation of the olefin. Thus, when the reaction of **1a** with vinylpyrazole was carried out at 120 °C for 20 min, the presence of the hydride−alkenyl complex RhClH[κ-N,κ-C{CH═CH(pz)}](*I*Pr) (**20**) was observed (Scheme 7). The ^{1}H NMR spectrum of **20** showed a doublet at δ −30.31 ppm with J_{H-Rh} = 38.2 Hz assigned to the hydride ligand. In addition, the ^{13}C{^{1}H} NMR spectrum displayed a doublet at δ 185.0 ppm (J_{C-Rh} = 38.9 Hz)

Scheme 7. Rhodium-*I*Pr Intermediates of the Catalytic Process



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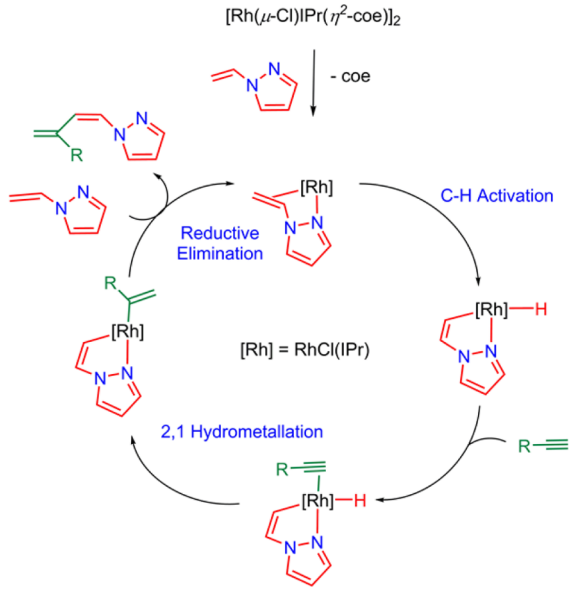
corresponding to the Rh-carbene carbon atom and, more interestingly, another doublet at δ 137.4 ppm (J_{C-Rh} = 12.8 Hz) that can be ascribed to a rhodium-alkenyl moiety. In addition to complex **20**, a small amount of a new complex was observed. Heating the reaction at 120° for 2 h led to the enrichment of that species, which allowed its characterization as RhCl(*I*Pr){κ-N_a,η^2-CH(pz)$_b$=CH(CH$_2$)$_2$(pz)$_a$} (**21**) Interestingly, the (*Z*)-1,1′-(1-butene-1,4-diyl)bis(pyrazole) ligand of **21** results from self-hydrovinylation of the 1-vinylpyrazole.

The ^{1}H NMR spectrum of **21** showed a doublet of doublets at δ 5.29 ppm and a multiplet at 3.43 ppm, corresponding to the coordinated olefin, in addition to the signals ascribed to four aliphatic protons at δ 3.92, 3.12, 2.45, and 1.79 ppm. The ^{13}C{^{1}H} spectrum was also in agreement with the proposed structure and shows one doublet at δ 183.4 ppm (J_{C-Rh} = 54.4 Hz), corresponding to the Rh-*I*Pr carbon atom, and two doublets at 63.9 (J_{C-Rh} = 18.0 Hz) and 44.7 ppm (J_{C-Rh} = 15.8 Hz) for the η^2-coordinated olefin. The ^{15}N−^{1}H HMBC spectrum also supports the proposed structure for **21**. The coordinated nitrogen atom of a pyrazole moiety is upfield-shifted to δ 250.3 ppm compared with the uncoordinated nitrogen atom of the free heterocyclic fragment that is observed at 306.8 ppm. The nitrogen atoms attached to the connector in both cycles were observed at similar chemical shifts (219.6 and 209.5 ppm). Alternatively, complex **21** could be obtained from the reaction of **1a** with **2a** (molar ratio 1:4), after heating at 120 °C for 2 h through the intermediate complex RhCl(*I*Pr)(κ-N,vpz)(η^2-vpz) (**22**) bearing two 1-vinylpirazole ligands having different coordination modes. The more noticeable NMR features of **22** are the signal corresponding to the free and coordinated olefinic moiety. The −CH= proton of the uncoordinated double bond appears at δ 8.29 ppm in the ^{1}H NMR spectrum, which correlates with a singlet in the ^{13}C{^{1}H} NMR at δ 134.4 ppm, whereas these resonances for the coordinated olefin were observed at 5.43 and 66.5 ppm (J_{C-Rh} = 17.7 Hz).

In view of the detected intermediate species, a plausible mechanism for the alkyne hydrovinylation is depicted in Scheme 8. The first step consists of the substitution of the η^2-coe ligand with 1-vinylpyrazole, which is supported by the identification of compounds **16**−**17**. Subsequent C−H oxidative addition of the olefin affords a Rh^{III}−hydride−alkenyl species **20**. Then, alkyne coordinates and subsequent insertion into the Rh−H bond lead to a bis-alkenyl complex that undergoes reductive elimination to give the coupled organic products. More likely, the origin of Markovnikov selectivity arises from the preferred 2,1-hydrometalation driven by the steric hindrance between the bulky NHC ligand and the alkyne as previously observed for hydrothiolation or hydroalkynylation transformations using a related catalytic system. The distorted chelate coordination arrangement of the vinylpyrazole facilitates the exchange between the coupling organic products and a new molecule of the substrate regenerating the active species of the catalytic cycle. The activation of C$_{sp}$-H proton of the alkyne can compete with the C−H activation of the vinylpyrazole, particularly for the more acidic aromatic alkynes; thus, the dimerization process may be operative under this circumstances (See Table 2, entries 4,8−10). In the absence of the alkyne, the double bond of the vinylpyrazole would insert into the Rh−H moiety, leading to the formation of **21**.

Scheme 8. Proposed Catalytic Cycle for the Hydrovinylation of Alkynes



CONCLUSION

Complex [Rh(μ-Cl)(*I*Pr)(η^2-coe)]$_2$ efficiently catalyzes the hydrovinylation of alkynes via C−H activation of *N*-vinylpyrazoles, leading to Markovnikov-selective butadienylpyrazole derivatives under mild conditions. The presence of the carbene ligand in the rhodium catalyst seems to be essential for the catalytic coupling to afford the challenging C−H activation of the electron-rich nitrogenated olefin. It has been observed that 1-vinylpyrazol reacts faster than 3,5-dimethyl-1-vinylpyrazole but with slightly lower selectivity. Aliphatic terminal alkynes are preferentially hydrovinylated without dimerization, cyclotrimerization, or polymerization of the alkyne. In addition, no isomerization of the exomethylene group leading to an internal diene has been observed. The synthetic utility of the catalytic process is reflected in the preparation of cross-conjugated acyclic trienes through a one-pot alkyne dimerization−hydrovinylation tandem reaction.

The proposed mechanism involves C−H activation of vinylpyrazole directed by nitrogen coordination to the metallic center. Subsequent alkyne coordination, insertion and reductive elimination steps leads to the coupling products. Several intermediates participating in the catalytic cycle have been detected and characterized. The first step consists of the coordination of the vinylpyrazole in a κ-N,η^2-C=C fashion. The assistance of the nitrogen atom facilitates the vinyl C−H activation process, leading to a Rh^{III}-hydride-alkenyl intermediate species that has been detected by NMR. Further work on the application of this catalytic system for the functionalization of pyrazole and other nitrogenated heterocycles is currently being developed in our laboratories.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out with rigorous exclusion of air using Schlenk tube techniques. Alkynes were purchased from commercial sources and were used as received, except for phenylacetylene, which was distilled under argon and stored over molecular sieves. 1,3-Disubstituted enynes[23c] and 1-vinylpyrazole[28] derivatives were synthesized following the procedure described in the literature. Organic

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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 precursor $[Rh(\mu\text{-}Cl)(IPr)(\eta^2\text{-coe})]_2$ (**1a**) was prepared as previously described in the literature.[24] ^1H, $^{13}C\{^1H\}$, and HMBC $^1H-^{15}N$ spectra were recorded on either a Bruker ARX 300 MHz or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or liquid NH_3 (^{15}N). Coupling constants, *J*, are given in Hertz. Spectral assignments were achieved by combination of $^1H-^1H$ COSY, $^{13}C\{^1H\}$-APT and $^1H-^{13}C$ HSQC/HMBC experiments. C, H, and N analyses were carried out in a PerkinElmer 2400 CHNS/O analyzer. GC/MS analyses were recorded 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 × 250 mm with a 0.25 mm film thickness).

Standard Catalytic Conditions. A NMR tube was charged with 0.01 mmol of catalyst, 0.2 mmol of vinylpyrazole and 0.2 mmol of the alkyne in 0.5 mL of C_6D_6 under an argon atmosphere. The solution was heated at 70 °C and monitored in a NMR spectrometer. The conversion was quantified by the integration of the ^1H NMR signals of 1-vinylpyrazole derivative and the products. After reaction completion, the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel using 99:1 hexane/diethyl ether as eluent to give the compounds.

In Situ Formation of $[Rh(\mu\text{-}Cl)(IPr)(\eta^2\text{-vpz})]_2$ and $RhCl(IPr)(\kappa\text{-}N,\eta^2\text{-vpz})$ (15, 16). A solution of **1a** (30 mg, 0.023 mmol) in toluene-d_8 (0.5 mL, NMR tube) was treated with 1-vinylpyrazole (5 μL, 0.047 mmol) and heated at 40 °C for 30 min. A 60:40 mixture of **15**:**16** was observed. Data for **15**: ^1H NMR (400 MHz, toluene-d_8, 298 K): δ 7.36 (d, J_{H-H} = 1.6, 2H, $H_{3\text{-}pz}$), 7.3−7.1 (12H, H_{Ph}), 6.59 and 6.56 (both m, 4H, =CHN), 5.71 (m, 2H, C<u>H</u>=CH_2), 5.61 (dd, J_{H-H} = 2.5, 1.6, 2H, $H_{4\text{-}pz}$), 5.45 (d, J_{H-H} = 2.5, 2H, $H_{5\text{-}pz}$), 4.73, 4.18, 3.92, and 2.38 (all br, 8H, C<u>H</u>Me_{IPr}), 2.68 (ddd, J_{H-H} = 10.2, 2.2, J_{H-Rh} = 2.2, 2H, CH=C<u>H_2</u>), 1.97 (d, J_{H-H} = 7.4, 2H, CH=C<u>H_2</u>), 1.38, 1.66, 1.57, 1.50, 1.11, 1.06, 1.04, and 0.93 (all d, J_{H-H} = 6.5, 48H, CH<u>Me_{IPr}</u>). $^{13}C\{^1H\}$-APT NMR (100 MHz, toluene-d_8, 298 K): δ 180.9 (d, J_{C-Rh} = 55.3, Rh−C_{IPr}), 151.6, 150.2, 148.9, and 149.8 (all s, $C_{q\text{-}IPr}$), 138.5 (s, $C_{3\text{-}pz}$), 136.8 and 136.7 (both s, C_qN), 131.4 (s, $C_{5\text{-}pz}$), 129−122 (C_{Ph}), 123.7 and 123.5 (both s, =CHN), 104.5 (s, $C_{4\text{-}pz}$), 68.3 (d, J_{C-Rh} = 19.4, <u>C</u>H=CH_2), 29−22 ($CHMe_{IPr}$), 27.2 (d, J_{C-Rh} = 16.9, CH=<u>C</u>H_2). Data for **16**: ^1H NMR (400 MHz, toluene-d_8, 298 K): δ 7.3−7.1 (br, 6H, H_{Ph}), 6.95 (d, J_{H-H} = 1.0, 1H, $H_{3\text{-}pz}$), 6.63 (s, 4H, =CHN), 6.42 (d, J_{H-H} = 2.1, 1H, $H_{5\text{-}pz}$), 5.75 (dd, J_{H-H} = 2.1, 1.0, 1H, $H_{4\text{-}pz}$), 4.41 (dd, J_{H-H} = 10.2, 8.5, 1H, C<u>H</u>=CH_2), 4.03 (ddd, J_{H-H} = 10.2, 2.2, J_{H-Rh} = 2.2, 1H, CH=C<u>H_2</u>), 2.83 and 2.73 (both sept, J_{H-H} = 6.8, 4H, C<u>H</u>Me_{IPr}), 1.58 (overlapped, CH=C<u>H_2</u>), 1.48, 1.17, 1.16, and 1.12 (all d, J_{H-H} = 6.8, 24H, CH<u>Me_{IPr}</u>). $^{13}C\{^1H\}$-APT NMR (100 MHz, toluene-d_8, 298 K): δ 181.2 (d, J_{C-Rh} = 62.3, Rh−C_{IPr}), 145.9 and 145.5 (both s, $C_{q\text{-}IPr}$), 137.9 (s, C_qN), 137.4 (s, $C_{3\text{-}pz}$), 129−123 (C_{Ph}), 128.0 (s, $C_{5\text{-}pz}$), 122.9 (s, =CHN), 104.6 (s, $C_{4\text{-}pz}$), 63.0 (d, J_{C-Rh} = 17.7, <u>C</u>H=CH_2), 29−22 ($CHMe_{IPr}$), 26.1 (overlapped, CH=<u>C</u>H_2).

Preparation of $RhCl(IPr)(\kappa\text{-}N,\eta^2\text{-}vpz_{Me})$ (17). A yellow solution of **1a** (100 mg, 0.078 mmol) in 10 mL of toluene was treated with 3,5-dimethyl-1-vinylpyrazole (19 μL, 0.157 mmol) and stirred for 1 h at room temperature. 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 × 4 mL) and dried in vacuo. Yield: 70 mg (68%). Anal. Calcd. for $C_{34}H_{46}N_4ClRh$: C, 62.91; H, 7.14; N, 8.63. Found: C, 63.13; H, 7.35; N, 8.41. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.38 (t, J_{H-H} = 7.6, 2H, $H_{p\text{-}Ph}$), 7.31 (dd, J_{H-H} = 7.8, 7.6, 4H, $H_{m\text{-}Ph}$), 6.67 (s, 2H, =CHN), 5.20 (s, 1H, $H_{4\text{-}pz}$), 4.08 and 3.05 (both br, 4H, C<u>H</u>Me_{IPr}), 3.55 (dd, J_{H-H} = 7.5, 7.2, 1H, C<u>H</u>=CH_2), 3.13 (d, J_{H-H} = 7.2, 1H, CH=C<u>H_2</u>), 2.23 (dd, J_{H-H} = 7.5, J_{H-Rh} = 2.2, 1H, CH=C<u>H_2</u>), 2.17 (s, 3H, $Me_{3\text{-}pz}$), 1.72, 1.21, 1.20, and 1.16 (all d, J_{H-H} = 7.0, 24H, CH<u>Me_{IPr}</u>), 1.63 (s, 3H, $Me_{5\text{-}pz}$). $^{13}C\{^1H\}$-APT NMR (75 MHz, C_6D_6, 298 K): δ 181.5 (d, J_{C-Rh} = 61.0, Rh−C_{IPr}), 150.7 (s, $C_{3\text{-}pz}$), 147.2 and 146.2 (both s, $C_{q\text{-}IPr}$), 137.0 (s, C_qN), 136.0 (s, $C_{5\text{-}pz}$), 129.5 (s, $C_{p\text{-}Ph}$), 123.9 and 123.6 (both s, $C_{m\text{-}Ph}$), 123.5 (s, =CHN), 103.8 (s, $C_{4\text{-}pz}$), 60.9 (d, J_{C-Rh} = 14.6, <u>C</u>H=CH_2), 34.7 (d, J_{C-Rh} = 14.5, CH=<u>C</u>H_2), 29.0 and 28.7 (both s, <u>C</u>HMe_{IPr}), 26.6, 25.5, 23.4, and 22.9 (all s, CH<u>Me_{IPr}</u>), 12.5 (s, $Me_{3\text{-}pz}$), 8.4 (s, $Me_{5\text{-}pz}$). ^{15}N-HMBC (40 MHz, C_6D_6, 298 K): δ 235.6 ($N_{2\text{-}pz}$), 231.2 ($N_{1\text{-}pz}$), 191.5 (N_{IPr}).

Preparation of $RhCl(IPr)(\eta^2\text{-vpz})(py)$ (18). A solution of **1a** (30 mg, 0.023 mmol) in 10 mL of toluene was treated with 1-vinylpyrazole (5 μL, 0.047 mmol) and pyridine (18 μL, 0.25 mmol) and stirred for 1 h at room temperature. 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 × 4 mL) and dried in vacuo. Yield: 70 mg (63%). Anal. Calcd. for $C_{37}H_{47}N_5ClRh$: C, 63.47; H, 6.76; N, 10.00. Found: C, 63.23; H, 7.10; N, 9.74. ^1H NMR (400 MHz, toluene-d_8, 243 K): δ 7.96 (d, J_{H-H} = 4.8, 2H, $H_{o\text{-}py}$), 7.5−6.9 (m, 6H, H_{Ph}), 6.95 (d, J_{H-H} = 2.2, 1H, $H_{5\text{-}pz}$), 6.75 and 6.74 (both m, =CHN), 6.60 (d, J_{H-H} = 1.9, 1H, $H_{3\text{-}pz}$), 6.50 (t, J_{H-H} = 7.7, 1H, $H_{p\text{-}py}$), 6.05 (dd, J_{H-H} = 7.7, 4.8, 2H, $H_{m\text{-}py}$), 5.88 (dd, J_{H-H} = 2.2, 1.9, 1H, $H_{4\text{-}pz}$), 5.52 (dd, J_{H-H} = 9.6, 6.4, 1H, C<u>H</u>=CH_2), 4.75, 3.78, 3.06, and 2.31 (all br, 4H, C<u>H</u>Me_{IPr}), 3.06 (d, J_{H-H} = 9.6, 1H, CH=C<u>H_2</u>), 2.51 (dd, J_{H-H} = 6.4, J_{H-Rh} = 2.3, 1H, CH=C<u>H_2</u>), 1.97, 1.67, 1.66, 1.23, 1.14, 1.13, 1.05, and 1.04 (all d, J_{H-H} = 6.6, 24H, CH<u>Me_{IPr}</u>). $^{13}C\{^1H\}$-APT NMR (100 MHz, toluene-d_8, 298 K): δ 182.6 (d, J_{C-Rh} = 53.5, Rh−C_{IPr}), 151.5 (s, $C_{o\text{-}py}$), 146.0, 145.8, 145.6, and 145.5 (all s, $C_{q\text{-}IPr}$), 135.1 and 134.4 (both s, C_qN), 136.6 (s, $C_{3\text{-}pz}$), 133.9 (s, $C_{p\text{-}py}$), 128.7 (s, $C_{5\text{-}pz}$), 124.9, 124.5, 124.4, 123.6, 123.4, and 122.4 (all s, C_{Ph}), 123.4 and 123.1 (both s, =CHN), 122.1 (s, $C_{m\text{-}py}$), 105.5 (s, $C_{4\text{-}pz}$), 66.1 (d, J_{C-Rh} = 18.7, <u>C</u>H=CH_2), 28.3 (d, J_{C-Rh} = 17.2, CH=<u>C</u>H_2), 28.9, 28.8, 28.7, 28.6 (all s, <u>C</u>HMe_{IPr}), 26.8, 26.3, 26.2, 26.0, 25.7, 23.5, 22.4, and 22.3 (all s, CH<u>Me_{IPr}</u>). ^{15}N-HMBC (40 MHz, toluene-d_8, 298 K): δ 304.7 ($N_{2\text{-}pz}$), 266.8 (N_{py}), 223.9 ($N_{1\text{-}pz}$), 191.3 and 193.8 (N_{IPr}).

In Situ Formation of $RhCl(IPr)(\eta^2\text{-}vpz_{Me})(py)$ (19). A solution of **1a** (30 mg, 0.023 mmol) in toluene-d_8 (0.5 mL, NMR tube) at room temperature was treated with 3,5-dimethyl-1-vinylpyrazole (5 μL, 0.041 mmol) and pyridine (18 μL, 0.25 mmol). After 10 min, NMR spectra were recorded at low temperature. ^1H NMR (400 MHz, toluene-d_8, 243 K): δ 8.03 (d, J_{H-H} = 4.8, 2H, $H_{o\text{-}py}$), 7.3−7.1 (m, 6H, H_{Ph}), 6.70 and 6.40 (both s, =CHN), 6.42 (t, J_{H-H} = 7.0, 1H, $H_{p\text{-}py}$), 6.05 (dd, J_{H-H} = 7.0, 4.8, 2H, $H_{m\text{-}py}$), 5.58 (dd, J_{H-H} = 9.7, 5.6, 1H, C<u>H</u>=CH_2), 5.29 (s, 1H, $H_{4\text{-}pz}$), 4.60, 3.42, 3.28, and 2.45 (all br, 4H, C<u>H</u>Me_{IPr}), 3.20 (d, J_{H-H} = 9.7, 1H, CH=C<u>H_2</u>), 2.15 (d, J_{H-H} = 5.6, 1H, CH=C<u>H_2</u>), 1.88 (s, 3H, $Me_{3\text{-}pz}$), 1.80, 1.73, 1.62, 1.18, 1.15, 1.13, 1.12, and 0.92 (d, J_{H-H} = 6.2, 24H, CH<u>Me_{IPr}</u>), 1.42 (s, 3H, $Me_{5\text{-}pz}$). $^{13}C\{^1H\}$-APT NMR (100 MHz, toluene-

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d_8, 243 K): δ 181.9 (d, J_{C-Rh} = 53.4, Rh−C_{IPr}), 151.5 (s, $C_{o\text{-}py}$), 148.4, 148.0, 146.1, and 145.5 (all s, $C_{q\text{-}IPr}$), 144.5 (s, $C_{3\text{-}pz}$), 138.9 (s, $C_{5\text{-}pz}$), 137.3 and 136.9 (both s, C_qN), 133.8 (s, $C_{p\text{-}py}$), 124.3, 123.7, 122.9, and 121.9 (all s, C_{Ph}), 123.5 and 123.3 (both s, =CHN), 121.9 (s, $C_{m\text{-}py}$), 106.6 (s, $C_{4\text{-}pz}$), 65.6 (d, J_{C-Rh} = 18.5, $\underline{C}H{=}CH_2$), 28.1 (d, J_{C-Rh} = 15.6, $CH{=}\underline{C}H_2$), 28.9, 28.8, 28.7, and 28.5 (all s, $\underline{C}HMe_{IPr}$), 29.4, 29.2, 27.1, 26.5, 26.4, 25.7, 23.3, and 23.1 (all s, $CH\underline{Me}_{IPr}$), 13.2 (s, $Me_{3\text{-}pz}$), 11.0 (s, $Me_{5\text{-}pz}$). ^{15}N-HMBC (40 MHz, toluene-d_8, 243 K): δ 316.0 ($N_{2\text{-}pz}$), 263.7 (N_{py}), 213.9 ($N_{1\text{-}pz}$), 193.1 and 188.0 (N_{IPr}).

In Situ Formation of RhClH[κ-N,κ-C{CH=CH(pz)}](*I*Pr) (20). A solution of **1a** (30 mg, 0.023 mmol) in toluene-d_8 (0.5 mL, NMR tube) was treated with 1-vinylpyrazole (5 μL, 0.047 mmol) and was heated at 120 °C for 20 min. ^{1}H NMR (400 MHz, toluene-d_8, 298 K): δ 7.48 (d, J_{H-H} = 2.0, 1H, $H_{3\text{-}pz}$), 7.3−7.1 (br, 6H, H_{Ph}), 7.03 (m, 1H, RhC$\underline{H}$=CH), 6.85 (J_{H-H} = 7.8, 1H, RhCH=C$\underline{H}$), 6.55 (s, 2H, =CHN), 6.45 (d, J_{H-H} = 2.2, 1H, $H_{5\text{-}pz}$), 5.44 (dd, J_{H-H} = 2.2, 2.0, 1H, $H_{4\text{-}pz}$), 3.29 and 3.08 (both br, 4H, $C\underline{H}Me_{IPr}$), 1.15, 1.11, 1.03, and 1.02 (all br, 24H, $CH\underline{Me}_{IPr}$), −30.31 (d, J_{H-Rh} = 38.2, 1H, Rh−H). ^{13}C{^{1}H}-APT NMR (100 MHz, toluene-d_8, 298 K): δ 185.0 (d, J_{C-Rh} = 38.9, Rh−C_{IPr}), 146.7 and 146.3 (both s, $C_{q\text{-}IPr}$), 141.7 (s, $C_{3\text{-}pz}$), 137.4 (d, J_{C-Rh} = 12.8, Rh$\underline{C}$H=CH), 135.9 (s, C_qN), 129−122 (C_{Ph}), 124.7 (s, $C_{5\text{-}pz}$), 122.5 (s, =CHN), 118.5 (d, J_{H-H} = 3.0, RhCH=$\underline{C}$H), 105.3 (s, $C_{4\text{-}pz}$), 28.2 and 27.8 (both s, $\underline{C}HMe_{IPr}$), 26.2, 25.9, 22.8, and 22.7 (all s, $CH\underline{Me}_{IPr}$).

Preparation of RhCl(*I*Pr){κ-N_a,η^2-CH(pz)$_b$=CH-(CH$_2$)$_2$(pz)$_a$} (21). A solution of **1a** (30 mg, 0.023 mmol) in C_6D_6 (0.5 mL, NMR tube) was treated with 1-vinylpyrazole (10 μL, 0.094 mmol) and was heated at 120 °C for 2 h. ^{1}H NMR (300 MHz, toluene-d_8, 298 K): δ 7.55 (d, J_{H-H} = 1.8, 1H, $H_{3\text{-}pza}$), 7.5−7.2 (m, 6H, Ph), 7.24 (d, J_{H-H} = 2.2, 1H, $H_{5\text{-}pzb}$), 7.21 (d, J_{H-H} = 2.2, 1H, $H_{3\text{-}pzb}$), 6.75 (m, 2H, =CHN), 6.25 (d, J_{H-H} = 2.1, 1H, $H_{5\text{-}pza}$), 5.92 (dd, J_{H-H} = 2.2, 2.2, 1H, $H_{4\text{-}pzb}$), 5.53 (dd, J_{H-H} = 2.1, 1.8, 1H, $H_{4\text{-}pza}$), 5.29 (dd, J_{H-H} = 6.7, J_{H-Rh} = 3.3, 1H, NC$\underline{H}$=CH), 4.59, 4.32, 2.59, and 2.58 (all br, 4H, $C\underline{H}Me_{IPr}$), 3.92 (dd J_{H-H} = 12.8, 12.8, 1H, CH_2N), 3.43 (m, 1H, CH=C$\underline{H}CH_2$), 3.12 (d, J_{H-H} = 12.8, 1H, CH_2N), 2.45 and 1.79 (both m, 2H, CH=CHC$\underline{H}_2$), 1.99, 1.71, 1.51, 1.26, 1.24, 1.20, 1.09, and 1.00, (all d, J_{H-H} = 6.4, 24H, $CH\underline{Me}_{IPr}$). ^{13}C{^{1}H}-APT NMR (75 MHz, toluene-d_8, 298 K): δ 183.4 (d, J_{C-Rh} = 54.4, Rh−C_{IPr}), 148.8, 148.7, 145.8, and 145.7 (all s, $C_{q\text{-}IPr}$), 141.9 (s, $C_{3\text{-}pza}$), 137.7 (s, $C_{3\text{-}pzb}$), 137.1 and 137.0 (both s, C_qN), 132.2 (s, $C_{5\text{-}pzb}$), 130.0 and 129.6 (both s, $C_{p\text{-}Ph}$), 128.5 (s, $C_{5\text{-}pza}$), 125.0 and 124.0 (both s, =CHN), 124.5, 124.3, 123.2, and 122.6 (all s, $C_{m\text{-}Ph}$), 104.8 (s, $C_{4\text{-}pza}$), 103.2 (s, $C_{4\text{-}pzb}$), 63.9 (d, J_{C-Rh} = 18.0, NC$\underline{H}$=CHCH$_2$), 49.8 (d, J_{C-Rh} = 2.7, CH_2N), 44.7 (d, J_{C-Rh} = 15.8, NCH=$\underline{C}$HCH$_2$), 25.5 (s, CH=CH$\underline{C}$H$_2$), 29.2, 28.8, 28.7, and 28.6 (all s, $\underline{C}HMe_{IPr}$), 26.8, 26.7, 26.6, 26.2, 23.4, 23.2, 22.3, and 21.6 (all s, $CH\underline{Me}_{IPr}$). ^{15}N-HMBC (40 MHz, toluene-d_8, 298 K): 306.8 ($N_{2b\text{-}pz}$), 250.3 ($N_{2a\text{-}pz}$), 219.6 ($N_{1b\text{-}pz}$), 209.5 ($N_{1a\text{-}pz}$), 193.8 and 189.0 (N_{IPr}).

In Situ Formation of RhCl(*I*Pr)(κ-N,vpz)(η^2-vpz) (22). A solution of **1a** (30 mg, 0.023 mmol) in toluene-d_8 (0.5 mL, NMR tube) was treated with 1-vinylpyrazole (10 μL, 0.094 mmol) at room temperature. The complex was formed immediately. ^{1}H NMR (400 MHz, toluene-d_8, 298 K): δ 8.29 (dd, J_{H-H} = 15.6, 9.0, 1H, C$\underline{H}$=CH$_{2\text{-}a}$), 7.42 and 7.35 (both t, J_{H-H} = 7.8, 2H, $H_{p\text{-}Ph}$), 7.21 and 7.06 (both d, J_{H-H} = 7.8, 2H, $H_{m\text{-}Ph}$), 7.02 (br, 1H, $H_{5\text{-}pza}$), 6.86 (br, 1H, $H_{5\text{-}pzb}$), 6.68 (br, 1H, $H_{3\text{-}pza}$), 6.59 (br, 2H, =CHN), 6.07 (br, 1H, $H_{4\text{-}pza}$), 5.73 (br, 1H, $H_{3\text{-}pzb}$), 5.44 (br, 1H, $H_{4\text{-}pzb}$), 5.43 (br, 1H, C$\underline{H}$=CH$_{2\text{-}b}$), 4.72 (d, J_{H-H} = 15.6, 1H, CH=C$\underline{H}_{2\text{-}a}$), 4.60, 3.81, 2.70, and 2.14 (all sept J_{H-H} = 6.5, 4H, $C\underline{H}Me_{IPr}$), 4.40 (d, J_{H-H} = 9.0, 1H, CH=C$\underline{H}_{2\text{-}a}$), 2.82 (d, J_{H-H} = 10.0, 1H, CH=C$\underline{H}_{2\text{-}b}$), 2.26 (d, J_{H-H} = 3.8, 1H, CH=C$\underline{H}_{2\text{-}b}$), 1.87, 1.56, 1.44, 1.18, 1.09, 1.07, 0.99, and 0.95 (all d, J_{H-H} = 6.5, 24H, $CH\underline{Me}_{IPr}$). ^{13}C{^{1}H}-APT NMR (100 MHz, toluene-d_8, 298 K): δ 182.7 (d, J_{C-Rh} = 54.8, Rh−C_{IPr}), 148.8, 148.6, 145.9, and 145.8 (all s, $C_{q\text{-}IPr}$), 140.9 (s, $C_{3\text{-}pzb}$), 136.8 and 136.7 (both s, C_qN), 134.4 (s, $\underline{C}H{=}CH_{2\text{-}a}$), 133.0 (s, $C_{3\text{-}pzb}$), 130.1, 129.6, 125.2, 124.6, 122.6, and 122.4 (all s, C_{Ph}), 126.2 (s, $C_{5\text{-}pzb}$), 124.0 (s, $C_{5\text{-}pzb}$), 123.6 and 123.5 (both s, =CHN), 107.0 (s, $C_{4\text{-}pzb}$), 106.4 (s, $C_{4\text{-}pza}$), 98.1 (s, CH=$\underline{C}H_{2\text{-}a}$), 65.8 (d, J_{C-Rh} = 17.7, $\underline{C}H{=}CH_{2\text{-}b}$), 28.8, 28.7, 28.4, and 28.3 (all s, $\underline{C}HMe_{IPr}$), 27.2 (d, J_{C-Rh} = 17.2, CH=$\underline{C}H_{2\text{-}b}$), 27.2, 26.5, 26.8, 24.1, 22.9, 22.3, 22.2, and 22.1 (all s, $CH\underline{Me}_{IPr}$).

Molecular Structure Determination for Complexes 17 and 19. Single crystals for the X-ray diffraction study of **17** and **19** were grown by slow diffusion of hexane into a concentrated solution of **17** in toluene and **19** in THF. Intensity data were collected at 100 K (15) and 110 K (21) on a Bruker SMART CCD area detector diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using narrow frames (0.3° in ω). Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied using the SADABS program.[29] The structures were solved by the Patterson method using SHELXS-97[30] included in the APEX2 package and completed by successive difference Fourier syntheses. Refinements were carried out by full-matrix least-squares on F^2 with SHELXL-2013 running under WinGX,[31] including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. The methyl hydrogen atoms were included in calculated positions and refined as riding atoms while the rest of the hydrogen atoms were obtained from difference Fourier maps and refined as free isotropic atoms.

Crystal Data for ***17****.* $C_{34}H_{46}ClN_4Rh$, M = 649.11, monoclinic, space group $P21/c$, yellow, 0.190 × 0.180 × 0.140 mm, a = 24.481(4), b = 13.201(2), c = 20.184(3) Å, β = 93.847(2)°, V = 6508.0(2) Å^3, Z = 8, μ(Mo Kα) = 0.635 mm^{-1}, D_{calc} = 1.325 g cm^{-3}, T_{min} = 0.786; T_{max} = 0.915; 50774 reflections measured (2.44 ≤ θ ≤ 28.326°), 13323 independent reflections (R_{int} = 0.0577); number of data/restrains/parameters 13323/0/869. R_1 = 0.0468 ($I > 2\sigma(I)$); 0.0719 (all data); $wR(F^2)$ = 0.0802 ($I > 2\sigma(I)$); 0.0892 (all data); S = 1.094 (all data). CCDC deposit number: 1012069.

Crystal Data for ***19****.* $C_{39}H_{51}ClN_5Rh$, M = 728.20, monoclinic, space group $P21/n$, yellow, 0.220 × 0.180 × 0.070 mm, a = 15.5790(11), b = 13.8030(10), c = 18.6728(13) Å, β = 112.173(1)°, V = 3718.4(5) Å^3, Z = 4, μ(Mo Kα) = 0.564 mm^{-1}, D_{calc} = 1.301 g cm^{-3}, T_{min} = 0.812; T_{max} = 0.961; 38427 reflections measured (1.888 ≤ θ ≤ 26.021°), 7310 independent reflections (R_{int} = 0.0584); number of data/restrains/parameters 7310/0/509. R_1 = 0.0387 ($I > 2\sigma(I)$); 0.0499 (all data); $wR(F^2)$ = 0.0700 ($I > 2\sigma(I)$); 0.0748 (all data); S = 1.077 (all data). CCDC deposit number: 1012070

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral data and scanned NMR spectra for all organic compounds; determination of pitch and yaw angles of **17** and ratio of cyclotrimerization and

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dimerization for aromatic alkynes (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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