Pyridine-Enhanced Head-to-Tail Dimerization of Terminal Alkynes by a Rhodium–N-Heterocyclic Carbene Catalyst

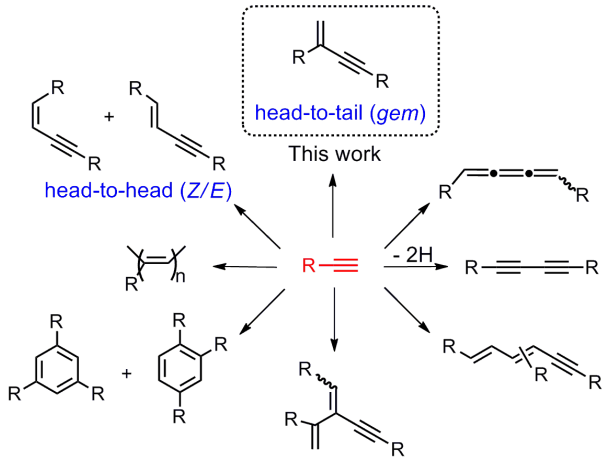
Laura Rubio-Pérez, Ramón Azpíroz, Andrea Di Giuseppe, Victor Polo, Ricardo Castarlenas,* Jesús J. Pérez-Torrente, and Luis A. Oro*[a]

Abstract: A general regioselective rhodium-catalyzed head-to-tail dimerization of terminal alkynes is presented. The presence of a pyridine ligand (py) in a Rh-N-heterocyclic carbene (NHC) catalytic system not only switches dramatically the chemoselectivity from alkyne cyclotrimerization to dimerization but also enhances catalytic activity. Several intermediates in the catalytic process have been detected included π-alkyne coordinated Rh^{I} RhCl(NHC)(η^2-HC≡CCH$_2$Ph)(py) (**3**) and RhCl(NHC){η^2-C(^{t}Bu)≡C(*E*)CH=CH^{t}Bu}(py) (**4**) and the Rh^{III}-hydride-alkynyl RhClH{-C≡CSi(Me)$_3$}(IPr)(py)$_2$ (**5**). Computational DFT studies reveal an operational mechanism consisting in sequential alkyne C-H oxidative addition, alkyne insertion and reductive elimination. A 2,1 hydrometallation of the alkyne is the more favourable pathway in accordance with a head-to-tail selectivity.

Keywords: Alkyne dimerization • N-heterocyclic carbene • rhodium catalysts • C-C coupling

Introduction

Conjugated 1,3- or 1,4-disubstituted enynes are key subunits of a variety of biologically active molecules,[1] polymers,[2] or photoactive derivatives,[3] as well as building blocks for further structural elaborations.[4] A powerful atom-economical synthetic approach consists in the catalytic C-C coupling reaction of two alkynes,[5] although chemo-, regio- and stereoselectivity control still remains a major challenge. Competitively to the formation of head-to-head (*E*/*Z*) and head-to-tail (*gem*) enynes, other products such as butatrienes,[6] diynes,[7] dieneynes,[8] cyclotrimers,[9] oligomers[10] or polymers[11] can also be obtained depending on the catalyst and reaction conditions (Scheme 1). A broad range of catalysts based on Pd,[12] Ru,[13] Rh,[14] Ni,[15] Ir,[16] Fe,[17] Au,[18] Co,[19] Os,[20] Ti,[21] Zr,[22] Re,[23] Y,[24] Sc,[25] Hf,[26] Cr,[27] lanthanides,[28] actinides,[29] and main group elements[30] promote the alkyne dimerization, nonetheless with different grade of success concerning selectivity. In particular, preferential preparation of head-to-tail enynes have been disclosed for aromatic[13i,14e,16b,24a] or aliphatic[12d,14a,c,g,k,22a,24c,26,29b] alkynes, although examples of selective initiators regardless of the substituent of the alkyne are limited to Nakamura (Ti),[21a] Trost (Pd),[12b] Eisen (Al),[30b] and Zhang (Au)[18] catalysts.



Scheme 1. Organic products arising from C-C coupling of terminal alkynes.

In order to control the selectivity of a catalytic transformation an in-depth knowledge of mechanistic issues is essential. Regarding alkyne dimerization the alkyne plays a dual role: the rather acidic terminal C-H proton of an alkyne is activated and subsequently added across the triple bond of a second alkyne molecule. Two main mechanisms for this transition-metal mediated dichotomy behavior have been proposed: *a*) oxidative addition of the terminal C-H bond of one alkyne to generate hydride-alkynyl species followed by migratory insertion of other alkyne into M-H (hydrometalation) or M-C (carbometalation) bonds and subsequent reductive elimination, or *b*) formation of a metal-vinylidene intermediate and successive nucleophilic attack of hydride or alkynyl group to the electrophilic C$_\alpha$ of the cumulene moiety and elimination. The vinylidene pathway produces *E*/*Z*-enynes and is generally proposed for ruthenium catalysts. In contrast, the migratory insertion route generates *E*- or *gem*-enynes depending on the bond the alkyne is inserted into (M-C or M-H) and the orientation of insertion (1,2 or 2,1) (Scheme 2).

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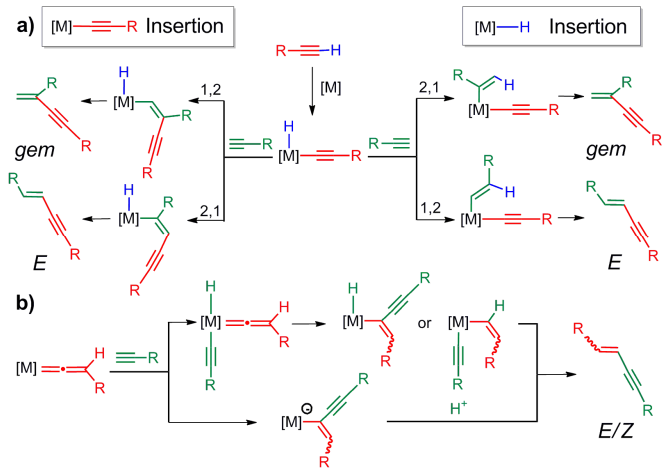


Scheme 2. General overview for the formation of conjugated 1,3- or 1,4-disubstituted enynes.

Very commonly, pathway *a* is simplified when only an initiator ligand is present. It is encountered when putative metal-hydride moiety arisen from the alkyne oxidative addition has been removed, or even never formed, by the action of an external[13e,16c] or internal[10b,12b,25] base, resulting in an alkynyl species. In contrast to metal-alkynyl, metal-hydrides are poor initiators for the dimerization process. Therefore, it can be converted to metal-alkynyl species by protonation by the acidic C-H proton of the alkyne with concomitant release of molecular hydrogen, or, alternatively, metal-vinyl intermediates can be formed by insertion of the triple bond into the M-H ligand. Furthermore, metal-vinyl species have been proposed as propagating species for alkyne polymerization.[11a,b] In spite of such potential deactivation processes, catalytic pathways mediated by metal-hydride-alkynyl species have revealed to be operative.[12e,14i,15a,16e] Particularly, the formation of *gem*-enynes may arise from carbometalation via 1,2 insertion pathway,[12b,18,21a,30] or hydrometalation via 2,1 insertion route.[7d,13h,14f] It is worthy to note that, although regioselectivity depends intrinsically on the insertion stage, reductive elimination can be decisive if being the rate-determining step and the migratory insertion is reversible.[31]

The advent of N-heterocyclic carbenes (NHCs) as ligands for transition metal complexes has created a big impact on homogeneous catalysis.[32] Substitution of ubiquitous phosphines in organometallic catalysts by NHCs has enhanced, or sometimes complemented, their catalytic activity and extended the scope of many transition-metal mediated transformations.[33] Alkyne dimerization is not an exception and, in fact, it provides a test ground for NHC-based catalyst.[12d,e,13g,l,16h] On the other hand, our research group has been studying for some time the chemistry of rhodium-NHC complexes for new C-C and C-X bond forming reactions.[34] We have found that the selectivity in alkyne hydrothiolation can be dramatically switch to the formation of branched vinyl sulfides by simple addition of pyridine to dinuclear catalysts of type [Rh(μ-Cl)(η^2-olefin)(NHC)]$_2$.[34e] It has been demonstrated that pyridine coordination *trans* to the NHC in the active species directs the coordination of the incoming alkyne *cis* to the carbene. The higher *trans-influence* of an hydride ligand paves the way to a *cis* thiolate-alkyne disposition thereby favoring thiolate insertion. In view of these results, we became interested in broadening the scope of pyridine-modified Rh-NHC catalysts to other type of addition reactions such as dimerization of terminal alkynes. Herein, we disclose that pyridine-based catalysts not only switch the chemoselectivity from cyclotrimerization to the regioselective formation of 1,3-substituted enynes, but also enhance catalytic activity. The formation of head-to-tail products regardless of the electronic nature of the alkyne substituent have no precedent for rhodium catalysts. We have studied the catalytic process by means of low temperature NMR experiments and DFT theoretical calculations.

Results and Discussion

Catalytic alkyne dimerizations. The catalysts used in this study are the dinuclear monolefin complex [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (**1**) (coe = cyclooctene, IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene) prepared by James' group[35] and the mononuclear derivative RhCl(IPr)(η^2-coe)(py) (**2**) (py = pyridine) synthesized recently in our laboratories by simple chlorido-bridge cleavage of **1** by pyridine.[34e] Chart 1 displays the structure of both catalysts and the products resulting from the catalytic transformations.

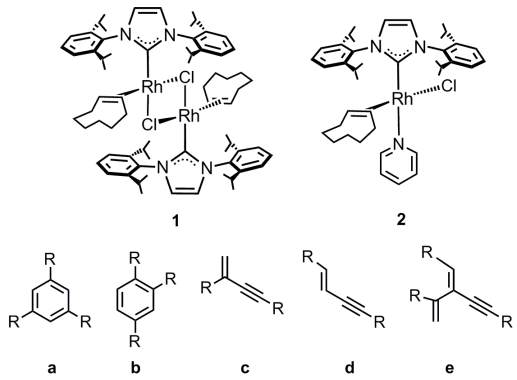
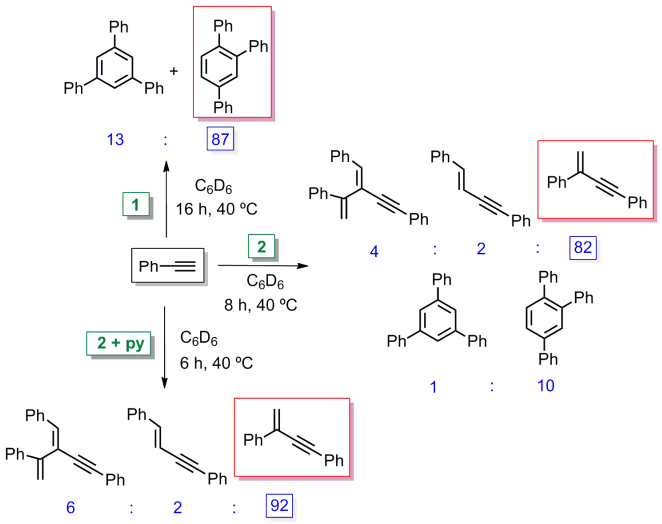


Chart 1. Rh-NHC catalysts and products obtained from catalytic reactions.

A preliminary catalytic test with phenylacetylene using 5 mol % loading of **1** showed that, in contrast to the expected enynes, aromatic products resulting from cyclotrimerization of the alkyne were obtained (Scheme 3, entry 1, Table 1). After one night at 40 ºC 1,3,5-(**a**) and 1,2,4-triphenylbenzene (**b**), were formed in almost quantitative yield in a 13:87 ratio. Interestingly, chemoselectivity was reversed dramatically when catalyst **2** was used. Besides cyclotrimers **a** and **b**, conjugated 1,3- or 1,4-disubstituted enynes, **c** and **d** respectively, and a *gem*-dienyne (**e**) resulting from trimerization, were the significant products detected, with head-to-tail dimer as the mayor isomer. Moreover, addition of 10 equiv of pyridine to **2** increases both catalytic activity and selectivity towards *gem*-dimer up to 92 %, suppressing the formation of cyclotrimers (Scheme 3, entry 4, Table 1). Treatment of catalytic samples of **1** with 10 equiv of NEt_3 did not cause a similar effect (entry 5, Table 1), indicating that the role of pyridine is different from simply acting as a base for the deprotonation of terminal alkyne but rather it is engaged in the coordination to the metallic center.[34e,36] The introduction of an electron-donating group on the nitrogenated aromatic ring does not modify significantly the "pyridine effect" (entry 6, Table 1), whereas 2-ethylpiridine reduce catalytic activity probably by a hindered coordination of the N-donor ligand (entry 7, Table 1).[34e] Addition of 10 equiv of acetonitrile does not favor the formation of head-to-tail dimers but rather slightly modifies the catalytic outcome obtained for dimeric species **1**, with formation of cyclotrimers as the main product.



Scheme 3. Chemoselectivity of Rh-IPr-mediated catalytic coupling of phenylacetylene.

Table 1. Phenylacetylene coupling promoted by Rh-IPr catalysts.[a]

Entry	Catalysts	Aditive[b]	T(ºC)	t(h)	Conversion %	**a**	**b**	**c**	**d**	**e**
1	**1**	-	40	16	99	13	87	-	-	-
2	**2**	-	25	11	99	1	10	78	2	8
3	**2**	-	40	8	99	1	10	82	2	4
4	**2**		40	6	99	-	-	92	2	6
5	**1**	NEt_3	40	16	95	12	88	-	-	-
6	**1**		40	9	98	-	-	94	4	2
7	**1**		40	13	65	-	-	95	3	2
8	**1**	CH_3CN	40	8	95	12	78	9	-	-

[a]0.5 mL of C_6D_6 with 5 mol % of catalyst; [subs] = 0.4 M. [b]10 equiv per mol of metal.

The addition of pyridine has a strong impact not only on selectivity but also on catalytic activity. Figure 1 shows the monitoring of alkyne dimerization promoted by **2** and **2** + 10 equiv pyridine for phenylacetylene, 3-phenyl-1-propyne and 1-hexyne. In all cases, the reaction rate was increased when pyridine was added, more markedly in case of aliphatic alkynes. After one night at 40 ºC, pyridine-added catalytic systems showed more than 80 % of *gem* enynes whereas only 42 and 10 % where attained with 1-hexyne and 3-phenyl-1-propyne respectively, when the reaction was catalyzed by **2** in the absence of added pyridine.

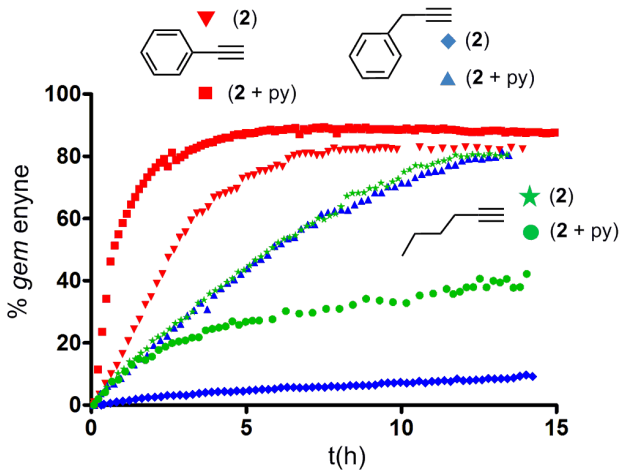
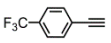
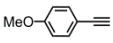
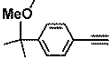


Figure 1. Monitoring of the dimerization of alkynes at 40 ºC in C_6D_6.

The scope of the catalytic system was evaluated for various terminal alkynes under the optimized reaction conditions of **2** + 10 equiv of pyridine at 40 ºC (Table 2). As a general trend, aromatic alkynes reacted faster than aliphatic ones. High selectivity for *gem* enynes was observed regardless of the electronic nature of the substituent on the alkyne except for bulky substituents such as tert-butyl or trimethylsilyl where the (*E*)-1,4-disubstituted enyne is the main product. Phenylacetylene was almost completely transformed after 6 h at 40 ºC, with a TOF at 50% conversion ($TOF_{1/2}$) of 12.5 h^{-1} (entry 1, Table 2). The introduction of an electron-withdrawing group at *para* position of the aromatic ring resulted in a rate increase, while it was diminished when an electron-donating group was incorporated (entries 2-3, Table 2). In contrast, the *meta*-substituted ethynylanisol displays the highest $TOF_{1/2}$ (18.5 h^{-1}) of the alkynes studied with complete selectivity (entry 4, Table 2). The catalytic outcome did not change significantly for the more hindered 4-*tert*-butylphenylacetylene (entry 5, Table 2). Aliphatic alkynes needed one night at 40 ºC for attaining good conversion and selectivity towards head-to-tail dimers (entries 6-8, Table 2). No isomerization of the double bond of the enynes from terminal to internal position was detected in any case. Cyclopropylacetylene was converted selectively to the head-to-tail enyne for the first time that we are aware of. The presence of an heteroatom in the alkyne substituent do not hamper catalytic activity. Thus, 1-dimethylamine-2-propyne was dimerized in 8 h with 89 % selectivity to *gem*-enyne (entry 9, Table 2). However, propargyl methyl ether reacted very slowly at 40 ºC but it was smoothly transformed after 2 days at 60 ºC although with significant formation of the trimeric dienyne species up to 14% (entry 10, Table 2). Highly encumbered alkynes such as *tert*-butylacetylene and trimethylsilylacetylene reacted even slower. After one night at 60 ºC acceptable conversions were obtained but with a preference for the *trans* head-to-head enynes (entries 11-12, Table 2). Finally, enynes such as 2-methyl-1-buten-3-yne and 1-cyclohexenylacetylene were efficiently dimerized to furnish *gem* trienynes selectively (entries 13-14, Table 2). Interestingly, the dimerization reaction can be carried out on a preparative scale (1 mmol). The dimerization of phenylacetylene, 1-hexyne and cyclopropylacetylene was performed in toluene using the catalytic system 5 mol % of **2** + 10 equiv py. The corresponding *gem* enynes were isolated as colourless oils in 85, 73, 61 % yields, respectively, after purification by column chromatography (Silica-gel 70-230 mesh) using *n*-hexane as eluent.

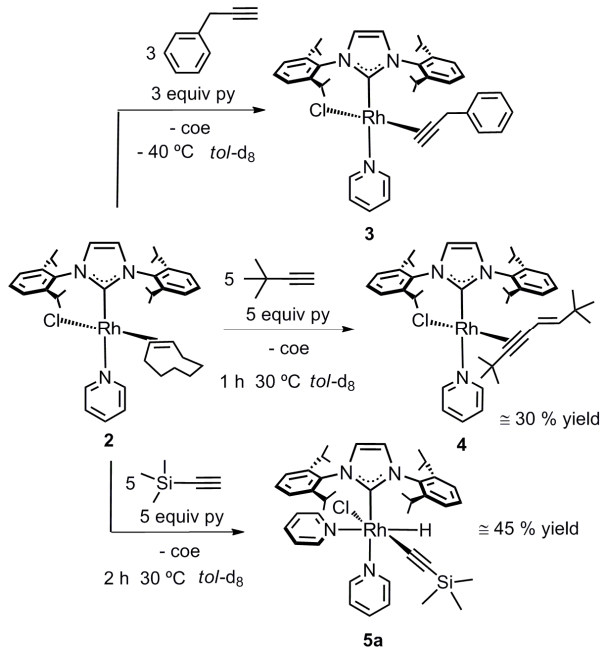
Table 2. Dimerization of terminal alkynes catalyzed by **2** + 10 equiv py.[a]

Entry	Substrate	t(h)	Conversion %	gem	*E*-enyne	trimer	$TOF_{1/2}(h^{-1})$
1		6	99	92	2	6	12.5
2		4	92	98	-	2	14.3
3		13	88	92	2	5	5.5
4		3	96	99	-	1	18.5
5		5	99	96	-	4	14.8
6		13	90	84	13	3	3.9
7		13	87	94	4	2	1.7
8		13	93	92[b]	-	-	1.9
9		8	90	89	11	-	5.0
10		48[c]	98	77	9	14	-
11		13[c]	89	42	53	5	-
12		13[c]	75	14	51/19[d]	15	-
13		13	98	93	7	-	5.4
14		13[c]	98	91	9	-	5.0

[a]0.5 mL of C_6D_6, 0.01 mmol of **2** + 0.1 mmol of pyridine, and [substrate] = 0.4 M at 40 ºC. [b]Plus unidentified products. [c]Performed at 60 ºC. [d]*cis* isomer.

The dimerization of terminal alkynes by the catalytic system **2** + 10 equiv pyridine also gave variable amounts of *gem*-dienyne trimers which were identified by NMR and MS. These species were mainly formed at the end of the catalytic reaction when the amount of head-to-tail isomers surpasses 80 %. Interestingly, we have been able to characterize the *gem*-dienyne derived from methyl propargyl ether as the (*Z*)-(2-alkynyl)(1,3-disubstituted)1,3-butadiene derivative (See Supporting Information for further details). The structure of this isomer was unambiguously determined by ^1H,^{13}C - APT, ^1H-^{13}C HSQC and HMBC, and ^1H-^1H NOE NMR experiments, thus a similar structure was assumed for the other dienynes.

Mechanistic studies. In order to clarify the mechanism operating in our catalytic system, a series of stoichiometric low temperature reactions of precursors **1** and **2** with alkynes have been performed (Scheme 4). Treatment of complex **1** with benzylacetylene, *tert*-butylacetylene or trimetylsilylacetylene in the absence of pyridine gave rise to a mixture of unidentified products. In contrast, addition of benzylacetylene to a toluene-d_8 solution of **2** at -40 ºC leaded immediately to the formation of RhCl(IPr)(η^2-HC≡CCH$_2$Ph)(py) (**3**) via exchange reaction between coe and the alkyne. The ^1H NMR spectrum of **3** displayed the typical signals for coordinated pyridine, in addition to a broad signal at δ 3.52 ppm (≡CH) and two doublets at 2.45 and 2.04 ppm (CH_2) corresponding to the η^2-alkyne.[37] The $^{13}C\{^1H\}$-APT NMR experiment at low temperature corroborates the assigned structure for **3**. The carbene carbon atom appeared as a doublet at δ 182.8 ppm with $J_{C\text{-}Rh}$ of 53.4 Hz, whereas the C_{sp} carbon atoms were observed at 90.2 and 66.4 ppm, as doublets with $J_{C\text{-}Rh}$ of 16.4 and 15.8 Hz, respectively.



Scheme 4. Detected intermediates relevant to the mechanism of alkyne dimerization.

Formation of **3** is in accordance with a plausible first step consisting in coordination of the triple bond to the metallic center (*vide infra*). Then, the alkyne must undergo C-H oxidative addition to generate hydride-alkynyl species or rearrange to form a metal-vinylidene moiety. Warming an NMR sample of **3** to room temperature gave rise to a small doublet in the hydride region (δ -17.36 ppm, $J_{H\text{-}H}$ = 25.3 Hz) with the concomitant rapid formation of free *gem*-enyne and a mixture of unidentified metal complexes. Unfortunately, it could not be possible to unequivocally ascribe the hydride signal to a rhodium-hydride-alkynyl complex. Vinylidene species were not detected.

In view that putative hydride intermediates derived from benzylacetylene react very fast, we envisage that a less reactive alkyne such as *tert*-butylacetylene or trimetylsilylacetylene could be more informative. Thus, treatment of **2** with 5 equiv of both *tert*-butylacetylene and pyridine at -40 ºC did not lead to the formation of the expected π-alkyne complex, most probably because of the bulky *tert*-butyl substituent that should reduce the stability of this species. However, heating of the sample at 30 ºC for 1 h gave rise to the observation of small hydride species (δ -16.93 ppm, $J_{H\text{-}H}$ = 21.5 Hz) and the formation of a new complex in around 30 % yield. Characterization by NMR spectroscopy at low temperature revealed the nature of the new derivative as RhCl(IPr){η^2-C(^{t}Bu)≡C(*E*)CH=CH^{t}Bu}(py) (**4**) resulting from η^2-triple bond coordination of the *trans* head-to-head enyne formed predominantly from catalytic dimerization of *tert*-butylacetylene (entry 11, Table 2).[14h,i,38] The ^1H NMR spectrum of **4** showed a coupling of 15.9 Hz for the olefinic protons indicating an *E*-conformation of the double bond of the 1,4-disubstituted enyne. The η^2-alkyne coordination of the enyne to rhodium is reflected in the $^{13}C\{^1H\}$ NMR spectrum that showed two doublets for the Rh-C_{sp} carbon atoms at 98.6 ($J_{C\text{-}Rh}$ = 17.8 Hz) and 74.2 ppm ($J_{C\text{-}Rh}$ = 16.8 Hz). The IPr ligand appeared as a doublet at 181.8 ppm with $J_{C\text{-}Rh}$ of 56.7 Hz. After extracting NMR data, heating of the mixture containing **2**, **4** and *tert*-butylacetylene at 60 ºC showed the smooth appearance of the signals corresponding to *free trans* head-to-head and head-to-tail coupled dimers.

It is rather surprising the different behavior of benzylacetylene and *tert*-butylacetylene towards **2**. A complex bearing a η^2-alkyne ligand was observed for benzylacetylene while a similar species was not detected for *tert*-butylacetylene, for which the coordination of the enyne resulting from alkyne dimerization was observed. Taking into account the presence of a high encumbered IPr ligand, the steric properties of the precursor and the enyne formed might play an important role in coordination to metal center. Thus, benzylacetylene is bound tighter than the more bulky *tert*-butylacetylene whereas the head-to-head enyne has less steric demand than the *gem*-dimer arising from benzylacetylene dimerization. In addition, the strong coordination of the enyne to the metal center, also explains the higher temperature required for the catalytic dimerization of *tert*-butylacetylene.

Reaction of **2** with trimethylsilyacetylene followed a different route. In accordance with their steric demand, and similarly to *tert*-butylacetylene, formation of π-alkyne was not observed. Heating a mixture of **2**, py and trimethylsilyacetylene (1:5:5) at 30 ºC resulted in the slow formation of rhodium-hydride species that reach ~45 % yield after 2 h. Then, low temperature ^{1}H, ^{13}C{^{1}H} and ^{15}N NMR data evidenced the formation of the hydride-alkynyl complex RhClH{-C≡CSi(Me)$_3$}(IPr)(py)$_2$ (**5**), arising from alkyne C-H oxidative addition[39] and stabilized by coordination of two molecules of pyridine. The ^{1}H NMR spectrum at -50 ºC of **5** displayed a doublet at δ -16.47 ppm (J_{H-Rh} = 21.6 Hz) corresponding to the hydride ligand. The coordination of two molecules of pyridine in **5** at low temperature is reflected in the deshielded *ortho*-pyridine region. Two doublets appeared at 9.35 and 9.29 ppm, integrating each 1:1 with respect to the hydride signal, corresponding to the pyridine located *cis* to IPr that present hindered rotation whereas a doublet at 8.76 ppm integrating by two, was ascribed to the pyridine *trans* to IPr that freely rotates. At 25 ºC the *cis*-IPr pyridine decoordinates from the complex. (See Figure in Supporting Information). Analogous behaviour has been previously described for the related Rh-thiolate complex RhClH(SPh)(IPr)(py)$_2$.[34e] The correlation ^{15}N-^{1}H NMR spectrum confirmed the hindered rotation for the *cis* pyridine ligand in **5**, hence, the two *ortho*-pyridine signals correlate with the same nitrogen atom at δ 278.5 ppm (Figure 2). The resonances at 256.5 ppm and 273.2 ppm correspond to the *trans* pyridine and the pyridine of the starting complex **2**, respectively. Free pyridine was observed at 318.3 ppm (out of the figure). Finally, the ^{13}C{^{1}H} NMR spectrum confirmed the presence of both alkynyl (d, 139.3, J_{C-Rh} = 51.3 Hz) and IPr (d, 174.9, J_{C-Rh} = 51.5 Hz) ligands. Treatment of **2** with trimethylsilyacetylene in the absence of pyridine resulted in decomposition products

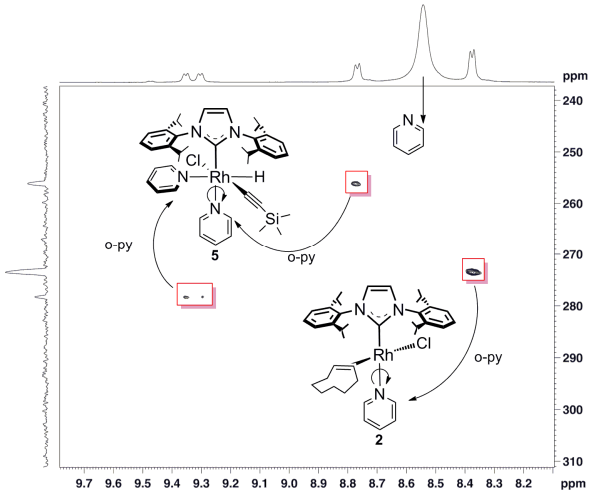


Figure 2. ^{1}H-^{15}N NMR correlation spectrum in the *ortho*-pyridine region for **2** and **5** at -50 ºC.

DFT calculations on the stability of different possible stereoisomers with hydride (**5a**), alkynyl (**5b**) or chloride (**5c**) *trans* to pyridine have been performed (Figure 3). In accordance with the greater *trans-influence* of the hydride ligand, the isomer **5a** is 9.3 and 31.3 kcal mol^{-1} more stable than **5b** and **5c**, respectively.

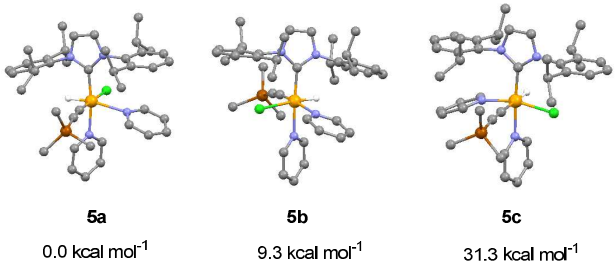
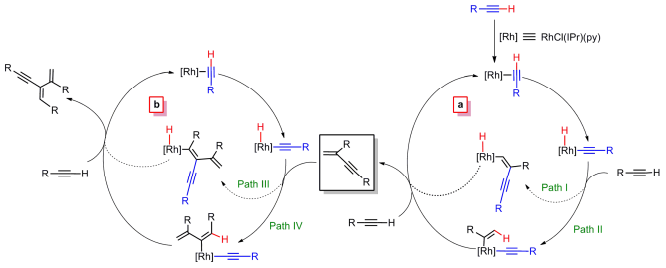


Figure 3. DFT-computed energies for possible stereoisomers of **5**.

Complex **5a** is the catalytic intermediate resulting from C-H oxidative addition and before insertion of the alkyne. The fact that this species could be only detected for the trimethylsilyacetylene should be ascribed to slightly greater acidity of the alkyne with regard the aliphatic ones,[40] and to its high steric demand that hinders coordination to metal center and subsequently the insertion step, which is in agreement with the low reactivity of this alkyne (entry 12, Table 2).

In view of the stoichiometric data, a plausible mechanism for the formation of head-to-tail enynes dimerization products is depicted in Scheme 5. The first step consists in the substitution of coe ligand by the alkyne as reflected by the formation of **3**. Then, C-H oxidative addition of the alkyne affords a Rh^{III} hydride-alkynyl species similar to **5**. At this point two alternative pathways for the formation of head-to-tail enynes are possible, carbometalation via 1,2 insertion (pathway I),[12b,18,21a,30] or hydrometalation via 2,1 insertion (pathway II).[7d,13h,14f] Finally, reductive elimination gives rise to the enyne and regenerates Rh^I-alkyne active species. The role of the pyridine ligands may be played in the stabilization of the hydride-alkynyl intermediate species, thereby increasing catalytic activity, and at the same time preventing cyclotrimerization by blocking vacant sites.



Scheme 5. Mechanistic proposal for the formation of head-to-tail enynes (a) and *gem*-dienynes (b).

A mechanistic proposal for the formation of the minor *gem*-dienynes products is also shown in Scheme 5. The appearance of this product at the end of the catalytic reaction strongly suggests that the enyne product competes with the alkyne to enter into the same catalytic cycle and later evolve similarly. Thus, insertion of the alkyne moiety of the *gem*-dienyne into the alkynyl or hydride ligands (Pathways III and IV, respectively) followed by reductive elimination fully accounts for the formation of the observed (*Z*)-(2-alkynyl)(1,3-disubstituted)1,3-butadiene compound. On the other hand, the alkyne insertion into vinyl moiety of the Rh-alkynyl-vinyl intermediate is less likely as it has been proposed as the propagating step in alkyne polymerizations which was not observed in our case.[11]

DFT calculations on the alkyne dimerization mechanism. In order to support the mechanistic picture proposed in Scheme 5, a detailed computational study using DFT calculations (B3LYP approach) has been carried out. Due to the role of steric hindrance into the reaction regioselectivity, full IPr and pyridine ligands have been considered explicitly in the calculations. This mechanistic study starts at complex **3** (structure **A**) and includes both pathways I and II, corresponding to carbometallation and hydrometallation, respectively, and the formation of head-to-head and head-to-tail enynes for each path. The energetic profiles for these four reactions are presented in Figures 4 (pathway I) and 5 (pathway II). In both cases, the initial step is the C-H bond oxidative addition of the π-coordinated alkyne, with an energetic barrier (**B-TS**) of 16.1 kcal mol^{-1} leading to hydride-alkynyl intermediate **C**, which is only 1.5 kcal mol^{-1} less stable than **A**. Coordination of a second molecule of pyridine in the vacant site of **C**, resembling **5**, stabilizes the complex by 8.1 kcal mol^{-1}. This value indicates that the resting state is stabilized, although substitution of pyridine by alkyne is energetically allowed and the catalytic cycle may be continued.

Following path I, a second alkyne can be coordinated into the vacant position *cis* to the alkyne ligand with two possible orientations. These two complexes, **I-D** and **I-D'**, will lead to the final head-to-tail and head-to-head enynes, respectively. Due to the high *trans-influence* of the hydride ligand, the alkyne coordination is very weak. Insertion of the alkyne into the Rh-C bond is a very exothermic step and it takes place through the transition states **I-E-TS** and **I-E'-TS** with activation barriers respect to the resting state of 42.2 and 37.3 kcal mol^{-1}, respectively. Thus, the formation of the head-to-tail coupling product is more favourable due to the lower energy barrier. The formation of the enynes is completed by C-H reductive elimination through Y-shape transition states, **I-G-TS** and **I-G'-TS**. The energetic barriers are considerably smaller than in the previous step and the overall reaction is highly exothermic.

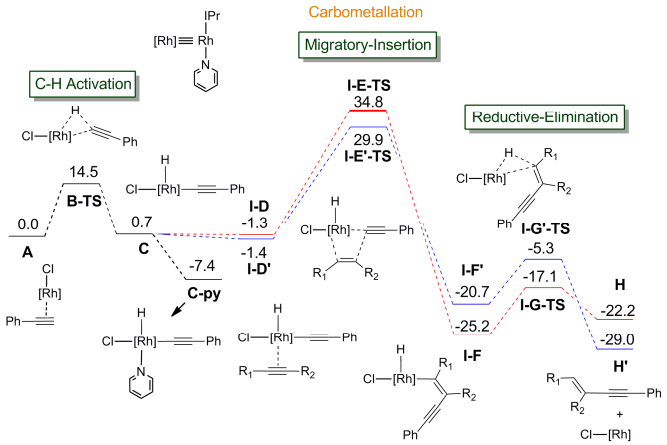


Figure 4. DFT calculated ΔE (in kcal mol^{-1}) along the energy surface of formation of enynes through path I. Structures **I-D** to **I-H** correspond to head-to-tail enynes (R_1 = H, R_2 = Ph) and structures **I-D'** to **I-H'** lead to head-to-head enynes (R_1 = Ph, R_2 = H).

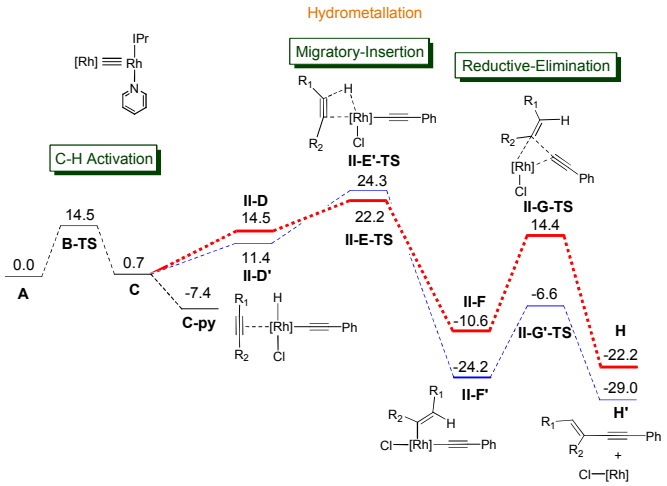


Figure 5. DFT calculated ΔE (in kcal mol^{-1}) along the energy surface of formation of enynes through path II. Structures **II-D** to **II-H** correspond to head-to-tail enynes (R_1 = H, R_2 = Ph) and structures **II-D'** to **II-H'** lead to head-to-head enynes (R_1 = Ph, R_2 = H).

In the hydrometallation pathway the hydride ligand must be located *cis* to the vacant site exerting a considerable *trans-influence* to the chlorine ligand. This situation is energetically more unfavourable than in pathway I and therefore, the relative energies of **II-D** and **II-D'** are higher, 14.5 and 11.4 kcal mol^{-1}, respectively. The alkyne insertion into the Rh-H bond occurs though **II-E-TS** and **II-E'-TS** transition states being the calculated activation barriers with respect to the resting state of 29.6 and 31.7 kcal mol^{-1}, respectively. These energies are much more affordable than the alkyne insertion into the Rh-C bond leading to intermediates **I-F** and **I-F'**. The transition state structures for the C-C reduction elimination also present a Y-shape, typical for en-yne reductive elimination,[41] being the activation energies 25.0 and 17.6 kcal mol^{-1} for **II-G-TS** and **II-G'-TS** respectively.

In all cases, the migratory insertion step is higher in energy than the corresponding reductive elimination step. Therefore, the overall picture shows that regioselectivity and the reaction rate is controlled by the alkyne insertion into the Rh-H bond, being the barrier for the head-to-tail arrangement 2.1 kcal mol^{-1} smaller than that for head-to-head. The molecular geometry of the intermediates and transition states structures along this pathway are shown in Figure 6. It can be

observed that in structures **II-D** and **II-E-TS** the phenyl group of coordinated alkyne is parallel to the bulky isopropyl substituents of the NHC. In fact steric hindrance affects more markedly **II-E'-TS** than **II-E-TS**. Indeed, in structure **II-F** there are steric interactions between the phenyl group of the vinyl and the isopropyl groups, which become more important for **II-G-TS** due to the geometric requirements for the formation of the new C-C bond. In this case, the vinyl ligand must place the phenyl group just in between both isopropyl substituents. Therefore, for alkynes with bulky substituents, the C-C reductive elimination step should be very unfavourable. This finding is consistent with the lack of selectivity found for bulky alkynes, as shown in entries 11 and 12 of Table 2.

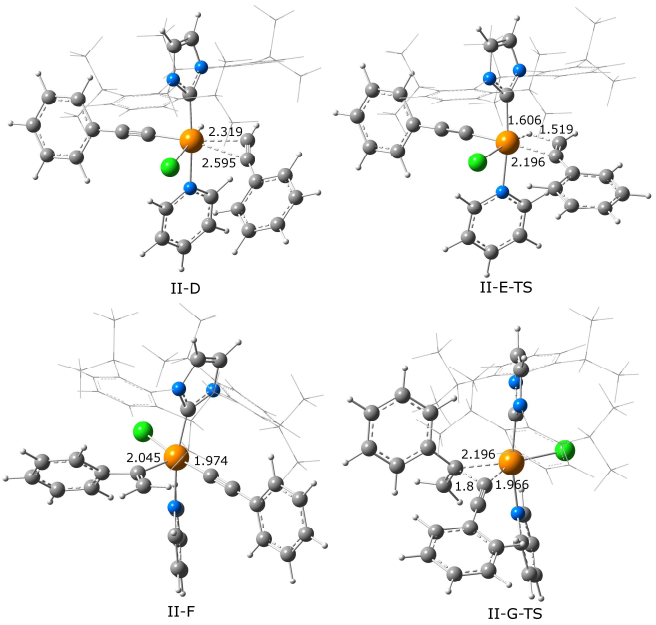


Figure 6. DFT optimized structures and distances (in Å) for intermediates and transition states for alkyne dimerization following pathway II.

Conclusions

The catalytic system RhCl(IPr)(η^2-coe)(py) (**2**)/py efficiently catalyzed the head-to-tail dimerization of terminal alkynes. For the first time for a rhodium catalyst, a varied range of terminal alkynes with substituents of different electronic character has been converted into the corresponding 1,3-disubstituted enynes under mild conditions with selectivities higher than 90% in most cases. Dimerization of alkynes with bulky substituents was unselective and gave the *E*-1,3-disubstituted enynes as the major products. The presence of pyridine in the catalytic system not only switches the chemioselectivity from alkyne cyclotrimerization to dimerization but also enhances catalytic activity. Pyridine coordination to the metallic center prevents cyclotrimerization and stabilizes intermediate species of the catalytic cycle.

The proposed dimerization mechanism involves C-H alkyne oxidative addition, alkyne insertion and reductive elimination steps. Several intermediates participating in the catalytic cycle have been detected, which included Rh^{I}–π-alkyne and π-enyne derivatives, and the Rh^{III}-hydride-alkynyl species. Coordination of two molecules of pyridine aid to the stabilization of hydride-alkynyl intermediates and exhibits an interesting fluxional behaviour involving the dissociation of a pyridine ligand that has been studied by low temperature ^{1}H, ^{13}C{^{1}H} and ^{15}N NMR spectra.

Computational DFT studies support the proposed mechanism with 2,1 hydrometallation of the alkyne as determinant for the selectivity and the rate-determining step. The higher *trans-influence* of hydride related to alkynyl ligand suggest that carbometalation could be kinetically favoured as the alkyne coordinates preferentially *cis* to alkynyl moiety,[34e] however, the C-C bond formation step following this pathway represent a upper hurdle than the formation of a C-H bond in the hydrometallation route via a less stable mutually *cis* hydride-π-alkyne intermediate.

Further work on the application of this catalytic system to cross dimerization reactions and the study of the "pyridine effect" in related Rh-NHC-promoted addition reactions is currently being developed in our laboratories.

Experimental Section

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 that was distilled under argon 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 catalysts [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (**1**)[35] and RhCl(IPr)(η^2-coe)(py) (**2**)[34e] were prepared as previously described in the literature. ^{1}H, ^{13}C{^{1}H} and HSQC ^{1}H-^{15}N spectra were recorded either on a Varian Gemini 2000 300 MHz, a Bruker ARX 300 MHz, or Bruker Avance 400 MHz, instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}), or external liquid NH_3 (^{15}N). Coupling constants, *J*, are given in Hz. Spectral assignments were achieved by combination of ^{1}H-^{1}H COSY, ^{13}C{^{1}H}-APT and ^{1}H-^{13}C HSQC/HMBC experiments. 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).

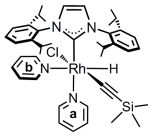
Catalytic alkyne dimerization reactions. A NMR tube containing a solution of 0.01 mmol of catalyst in 0.5 mL of C_6D_6 was treated with 0.20 mmol of alkyne and 0.1 mmol of pyridine and heated at 40 ºC. The reaction course was monitored by ^{1}H NMR and the conversion determined by integration of the corresponding resonances of the alkyne and the products.

***In situ* preparation of RhCl(IPr)(η^2-HC≡CCH$_2$Ph)(py) (3).** A solution of **2** (40 mg, 0.064 mmol) in toluene-d_8 (0.5 mL, NMR tube) was treated with pyridine (15 µL, 0.188 mmol) and 3-phenyl-1-propyne (23 µL, 0.188 mmol) at 233 K. ^{1}H NMR was immediately recorded at low temperature. ^{1}H NMR (400 MHz, toluene-d_8, 233 K): δ 8.40 (d, $J_{H\text{-}H}$ = 4.6, 2H, $H_{o\text{-}py}$), 7.2-6.9 (11H, H_{Ph}), 6.64 and 6.48 (both d, $J_{H\text{-}H}$ = 1.6, 2H, =CHN), 6.56 (t, $J_{H\text{-}H}$ = 6.5, 1H, $H_{p\text{-}py}$), 6.14 (dd, $J_{H\text{-}H}$ = 6.5, 4.6, 2H, $H_{m\text{-}py}$), 4.60, 3.59, 3.58, and 2.17 (all sept, $J_{H\text{-}H}$ = 6.7, C<u>H</u>Me$_{IPr}$), 3.52 (br, 1H, HC≡C), 2.45 and 2.04 (both d, $J_{H\text{-}H}$ = 18.2, 2H, ≡CCH$_2$), 2.12, 1.71, 1.28, 1.20, 1.17, 1.16, 1.06, and 1.03 (all d, $J_{H\text{-}H}$ = 6.7, CH<u>Me</u>$_{IPr}$). ^{13}C{^{1}H}-APT NMR (100.5 MHz, toluene-d_8, 233 K): δ 182.8 (d, $J_{C\text{-}Rh}$ = 53.4, Rh-C$_{IPr}$), 151.5 (s, $C_{o\text{-}py}$), 148.0, 147.7, 145.8, and 145.5 (all s, $C_{q\text{-}IPr}$), 138.7 (s, $C_{q\text{-}Ph}$), 137.6 and 136.0 (both s, C_qN), 135.2 (s, $C_{p\text{-}py}$), 130-122 (CH_{Ph}), 123.3 and 122.7 (both s, =CHN), 122.4 (s, $C_{m\text{-}py}$), 90.2 (d, $J_{C\text{-}Rh}$ = 16.4, HC≡<u>C</u>), 66.4 (d, $J_{C\text{-}Rh}$ = 15.8, H<u>C</u>≡C), 31.2 (s, ≡C<u>C</u>H$_2$), 29.2, 28.7, 28.6, and 28.5 (all s, <u>C</u>HMe$_{IPr}$), 27.0, 25.6, 25.5, 24.5, 24.3, 23.7, 22.9, and 22.7 (all s, CH<u>Me</u>$_{IPr}$).

***In situ* preparation of RhCl(IPr){η^2-C(^tBu)≡C-(*E*)CH=CH^tBu}(py) (4).** A solution of **2** (30 mg, 0.048 mmol) in toluene-d_8 (0.5 mL, NMR tube) was treated with pyridine (19 µL, 0.235 mmol) and *tert*-butylacetylene (29 µL, 0.235 mmol) and heated at 303 K for 2 h (~30 % yield). ^{1}H NMR (300 MHz, toluene-d_8, 273 K): δ 8.50 (d, $J_{H\text{-}H}$ = 5.2, 2H, $H_{o\text{-}py}$), 7.4-6.3(Ph, py), 6.53 and 6.49 (both d, $J_{H\text{-}H}$ = 2.0, 2H, =CHN), 5.91 (d, $J_{H\text{-}H}$ = 15.9, 1H, =CH^tBu), 5.24 (dd, $J_{H\text{-}H}$ = 15.9, $J_{H\text{-}Rh}$ = 1.2, 1H, ≡CCH=), 4.08, 3.81, 3.49, and 3.37 (all sept, $J_{H\text{-}H}$ = 6.5, 4H, C<u>H</u>Me$_{IPr}$), 1.82, 1.81, 1.56, 1.54, 1.19, 1.16, 1.12, and 1.05 (all d, $J_{H\text{-}H}$ = 6.5, 24H, CH<u>Me</u>$_{IPr}$), 1.09 (s, 9H, =CHC<u>Me</u>$_3$), 0.92 (s, 9H, ≡CC<u>Me</u>$_3$). ^{13}C{^{1}H}-APT NMR (75.0 MHz, toluene-d_8, 273 K): δ 181.8 (d, $J_{C\text{-}Rh}$ = 56.7, Rh-C$_{IPr}$), 152.4 (s,

$C_{o\text{-}py}$), 148.0, 146.4, 144.3, and 143.9 (all s, $C_{q\text{-}IPr}$), 143.3 (d, $J_{C\text{-}Rh}$ = 1.5, =$\underline{C}H^tBu$), 138.8 and 138.4 (both s, C_qN), 135-122 (Ph, py), 124.5 and 124. 3 (both s, =CHN), 113.8 (d, $J_{C\text{-}Rh}$ = 1.5, =$\underline{C}HCMe_3$), 98.6 (d, $J_{C\text{-}Rh}$ = 17.8, Rh-η^2-$\underline{C}(^tBu)\equiv CCH$=), 74.2 (d, $J_{C\text{-}Rh}$ = 16.8, Rh-η^2-C(^{t}Bu)≡$\underline{C}$CH=), 33.5 (s, =CH$\underline{C}Me_3$), 30.3 (s, ≡CC$\underline{Me}_3$), 29.9 (d, $J_{C\text{-}Rh}$ = 1.8, ≡C$\underline{C}Me_3$), 28.7 (s, =CHC$\underline{Me}_3$), 28.7, 28.6, 28.4, and 28.3 (all s, $\underline{C}HMe_{IPr}$), 26-22 ($CH\underline{Me}_{IPr}$).

***In situ* preparation of RhClH{-C≡CSi(Me)$_3$}(IPr)(py)$_2$ (5)**. A solution of **2** (30 mg, 0.048 mmol) in toluene-d_8 (0.5 mL, NMR tube) was treated with pyridine (19 µL, 0.235 mmol) and trimethylsilylacetylene (33 µL, 0.235 mmol) and heated at 303 K for 2 h (~45 % yield). ^{1}H NMR (400 MHz, toluene-d_8, 223 K): δ 9.35 and 9.29 (both d, $J_{H\text{-}H}$ = 5.2, 2H, $H_{o\text{-}pyb}$), 8.76 (d, $J_{H\text{-}H}$ = 5.4, 2H, $H_{o\text{-}pya}$), 7.41 (m, 2H, $H_{p\text{-}Ph}$), 7.20 (d, $J_{H\text{-}H}$ = 7.2, 4H, $H_{m\text{-}Ph}$), 6.90 and 6.67 (both d, $J_{H\text{-}H}$ = 1.7, 2H, =CHN), 6.72 (overlapped, $H_{p\text{-}pyb}$), 6.43 (t, $J_{H\text{-}H}$ = 6.5, 2H, $H_{p\text{-}pya}$), 6.41 and 6.27 (both dd, $J_{H\text{-}H}$ = 6.3, 5.2, 2H, $H_{m\text{-}pyb}$), 6.08 (dd, $J_{H\text{-}H}$ = 6.5, 5.4, 2H, $H_{m\text{-}pya}$), 3.93, 3.89, 3.84, and 3.65 (all sept, $J_{H\text{-}H}$ = 6.5, 4H, $C\underline{H}Me_{IPr}$), 1.78, 1.76, 1.56, 1.53, 1.23, 1.19, 1.10, and 1.08 (all d, $J_{H\text{-}H}$ = 6.5, 24H, $CH\underline{Me}_{IPr}$), 0.43 (s, 9H, $H_{Si\text{-}Me}$), -16.47 (d, $J_{Rh\text{-}H}$ = 21.6, 1H, Rh-H). ^{13}C{^{1}H}-APT NMR (100.5 MHz, toluene-d_8, 223 K): δ 174.9 (d, $J_{C\text{-}Rh}$ = 51.5, Rh-C_{IPr}), 153.1 (s, $C_{o\text{-}pya}$), 151.3 and 151.0 (both s, $C_{o\text{-}pyb}$), 147.5, 146.6, 146.2, and 145.8 (all s, $C_{q\text{-}IPr}$), 139.3 (d, $J_{Rh\text{-}C}$ = 51.3, Rh-$\underline{C}$≡C), 139.6 and 137.5 (both s, C_qN), 135.2 (s, $C_{p\text{-}pya}$), 134.7 (s, $C_{p\text{-}pyb}$), 129.5, 127.9, 124.8, and 122.3 (all s, C_{Ph}), 124.4 and 123.5 (both s, =CHN), 122.6, 122.5, and 122.4 (all s, $C_{m\text{-}py}$), 104.0 (d, $J_{Rh\text{-}C}$ = 9.7, Rh-C≡$\underline{C}$), 28.8, 28.6, 28.4, and 28.1 (all s, $\underline{C}HMe_{IPr}$), 26.7, 26.2, 26.1, 25.7, 24.2, 23.4, 23.1, and 22.9 (all s, $CH\underline{Me}_{IPr}$), 2.21 (s, $C_{Si\text{-}Me}$). ^{15}N-^{1}H HMQC (53 MHz, Toluene-d_8, 223 K): δ 318.3 (free py), 278.5 (N_{pyb}), 273.2 (py, **2**), 256.5 (N_{pya}), 196.1 and 191.2 (IPr), 192.5 (IPr, **2**).



Computational details. The geometry of all structures has been optimized with the G09 program package[42] at the DFT level using the B3LYP approximation[43] combined with the 6-31G(d,p) basis set for H, C, N, Cl, and Si atoms[44] and the SDD pseudo-potential[45] for Rh. The nature of the stationary points has been confirmed by frequency analysis and intrinsic reaction paths have been traced connecting the transition structures with the respective minima.

Acknowledgements

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