Ligand-Controlled Regioselectivity in the Hydrothiolation of Alkynes by Rhodium N-Heterocyclic Carbene Catalysts

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ABSTRACT: Rh-N-heterocyclic carbene compounds $[Rh(\mu\text{-Cl})(IPr)(\eta^2\text{-olefin})]_2$ and $RhCl(IPr)(py)(\eta^2\text{-olefin})$ (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene, py = pyridine, olefin = cyclooctene or ethylene) are highly active catalysts for alkyne hydrothiolation under mild conditions. A regioselectivity switch from linear to 1-substituted vinyl sulfides was observed when mononuclear $RhCl(IPr)(py)(\eta^2\text{-olefin})$ catalysts were used instead of dinuclear precursors. A complex interplay between electronic and steric effects exerted by IPr, pyridine, and hydride ligands, accounts for the observed regioselectivity. Both IPr and pyridine ligands stabilize the formation of square-pyramidal thiolate-hydride active species, in which the encumbered and powerful electron donor IPr ligand directs the coordination of pyridine *trans* to it, consequently blocking the access of the incoming alkyne in this position. Simultaneously, the higher *trans* director hydride ligand paves the way to a *cis* thiolate-alkyne disposition, favoring the formation of 2,2-disubstituted metal-alkenyl species and subsequently the Markovnikov vinyl sulfides via alkenyl-hydride reductive elimination. DFT calculations support a plausible reaction pathway where the migratory insertion of the alkyne into the rhodium-thiolate bond is the rate-determining step.

INTRODUCTION

Hydrothiolation of carbon-carbon multiple bonds is a direct and atom economical method for the formation of carbon-sulfur bonds present in many biologically active compounds.[1] Among them, vinyl sulfides, in addition to their interesting biological properties,[2] are also useful synthetic intermediates in organic transformations,[3] ranging from enol substitutes,[4] Diels-Alder,[5] thio-Claisen,[6] Michael acceptors,[7] or olefin metathesis,[8] among others.[9] Several metal catalysts including Mo,[10] Pd,[11] Pt,[12] Ni,[13] Ru,[14] Rh,[11c,15,16] Ir,[16] Cu,[17] Au,[18] Co,[19] In,[20] Zr,[21] An (Th, U)[22], and Ln (La, Sm, Lu, Nd, Y)[22b] are effective for hydrothiolation of unsaturated compounds, but the stereo- and regioselectivity control still remains an important challenge.

In general, regioselectivity in the X-H addition across carbon-carbon triple bonds proceeding *via* X-H activation arises from a complex interplay between migratory insertion and reductive elimination steps (Scheme 1).[23,24] Although electronic and steric properties of the alkyne and the catalyst play an important role, the formation of linear metal-alkenyls *via* 1,2-insertion (**a,d**) is generally preferred to that of branched isomers *via* 2,1 insertion (**b,c**).[25,26] Therefore, in a simplified overview, insertion into metal-hydride bond (**a**) gives rise to linear olefins (anti-Markovnikov or β-type products) whereas insertion into metal-heteroatom bond (**d**) generates branched olefins (Markovnikov or α-type products). Particularly for hydrothiolation, insertion into metal-hydride bonds is favored with regard to that into metal-thiolate, thus linear vinyl sulfides are preferably obtained.[11c,27] Preparation of the branched vinyl sulfides, more valuables as synthetic intermediates,[3] could be accomplished in a controlled manner if a method for directing alkyne insertion into metal-thiolate bonds is developed.

Scheme 1. Pathways for the alkyne migratory insertion into M-H or M-X bonds.
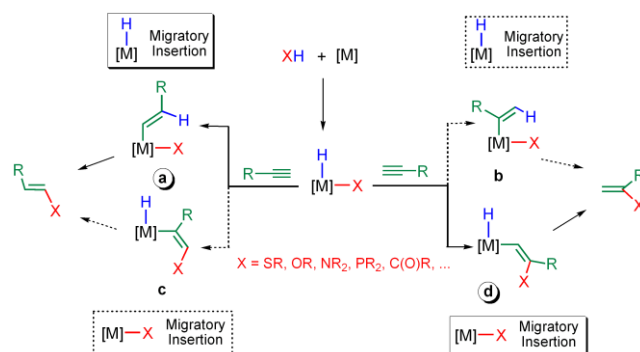
A common strategy for the previously described selective preparation of 1-substituted vinyl sulfides catalyzed by a wide variety of metal complexes is to design active species bearing thiolate ligands and lacking of an hydride moiety (Scheme 2).[11-13,15c,21,22] In these catalytic systems the first step is thiol-promoted protonolysis of an anionic ligand present in the precatalyst, or alternatively the formation of a bisthiolate complex accompanied with the release of molecular hydrogen. However, in these cases it is difficult to inhibit the formation

of byproducts such as disulfide or bis(thio)alkenes. A priori, the formation of these unwanted products should be minimized if a catalytic cycle involving initial S-H oxidative addition to the metal and successive alkyne insertion into metal-thiolate bond, and alkenyl-hydride reductive elimination will be operative. Thus, the following question arises: How to favor alkyne M-S insertion in the presence of a hydride ligand? Perhaps the well-established high *trans*-director capacity of hydrides may be useful. Due to this property, the coordination of the incoming alkyne to the unsaturated hydride-thiolate catalytic intermediate may be channeled at the vacant position *trans* to the hydride ligand and concomitantly *cis* to the thiolate, thus favoring the formation of a 2,2-disubstituted alkenyl ligand and subsequently the branched vinyl sulfide. Particularly, Rh^I complexes are promising precursors to achieve this task as they are efficient catalysts for alkyne hydrothiolation.[11c,15,16] Interestingly, their general tendency to favor linear vinyl sulfides can be reversed by ligand control, as was elegantly shown for Tp*Rh(PPh$_3$)$_2$ (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) by Love's group.[15b,d-f]

Scheme 2. Strategies directed to the preparation of branched vinyl sulfides.
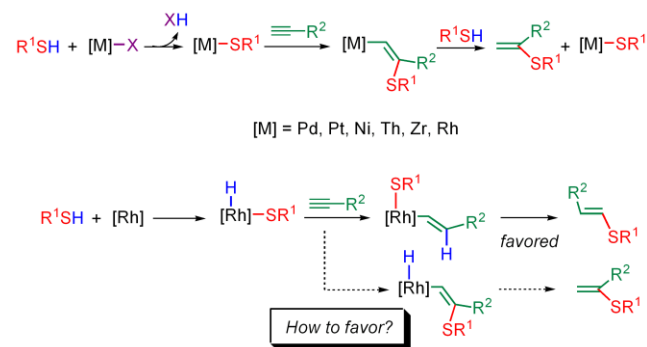

In order to succeed with our proposal, a high control over coordination positions and potential isomerizations within the metal catalytic intermediates is essential.[28] An *N*-heterocyclic carbene (NHC) ligand may fulfill the aimed requirements due to its special stereoelectronic properties.[29] The high steric hindrance and powerful electron-donor capacity of bulky NHCs could govern the coordination positions of labile ligands and substrates in the active species, thus determining the selectivity outcome. Indeed, NHC ligands have been revealed as suitable ligands not only for the stabilization of reactive intermediates, but also for the improvement of catalytic activity. In particular, substitution of typical ancillary ligands such as phosphanes by a more electron-donating NHC has extended the scope of many catalytic transformations.[30] Interestingly, these type of ligands has also been applied to the design of Ni,[13c] Cu,[17] and Au[18] alkyne hydrothiolation catalysts. Herein, we present a catalytic system for the selective hydrothiolation of alkynes based on a rhodium N-heterocyclic carbene framework. A complex interplay between electronic and steric effects exerted by NHC, hydride and pyridine-type ligands accounts for the regioselective formation of branched vinyl sulfides.

RESULTS AND DISCUSSION

Synthesis of rhodium-NHC catalysts. Dinuclear rhodium-NHC monolefin complexes of type [Rh(μ-Cl)(NHC)(η^2-

olefin)]$_2$[31] are adequate precursors for a set of catalysts *via* either a controlled substitution of the η^2-olefin or bridge-cleaving reactions by different ligands. Specially, [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (**1**) (coe = cyclooctene; IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene), described by James' group,[31b] has been successfully applied in our laboratories as starting material for a variety of Rh^I and Rh^{III}-NHC complexes.[32] Interestingly, the two coe ligands can be exchanged by bubbling of ethylene through a toluene solution of **1** resulting in the formation of the dimer [Rh(μ-Cl)(IPr)(η^2-CH$_2$=CH$_2$)]$_2$ (**2**) (Scheme 3), which was isolated as a yellow solid in 92% yield. During the preparation of the manuscript an alternative method for the synthesis of **2** has been reported.[33] The structure of **2** has been determined by X-ray analysis on crystals obtained from slow diffusion of *n*-hexane over toluene (see Supporting Information). This structure shows a very different unit cell dimension compared to that reported for **2**·CH$_2$Cl$_2$.[33]

Scheme 3. Synthesis of rhodium-NHC catalysts.

R = H (**3**), 2-Me (**5**), 4-Me (**7**), 2-Et (**9**)

R = H (**4**), 2-Me (**6**), 4-Me (**8**), 2-Et (**10**)
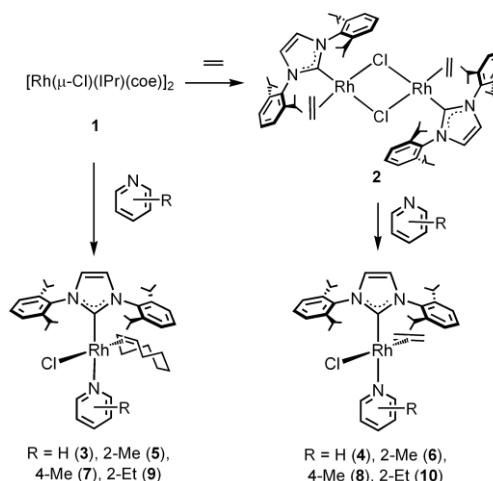
Complex **2** showed a dynamic behavior as it was evidenced in a ^{1}H VT-NMR study. That fact may be ascribed to two rotational processes involving both the η^2-ethylene[32b,34] and the carbene ligands (see Figure 2 for a similar behavior of **4**).[32b,35] In the case of IPr, activation parameters were calculated by simulation of the coalescence of the two signals located at δ 2.93 and 2.60 ppm corresponding to the two types of CH-isopropyl protons (C$_2$ symmetry). The values obtained from the corresponding Eyring analysis were $\Delta H^{\neq}$ = 13.9 ± 0.5 kcal mol^{-1} and $\Delta S^{\neq}$ = −1.3 ± 1.1 cal K^{-1} mol^{-1} for the ethylene rotation and $\Delta H^{\neq}$ = 11.8 ± 0.4 kcal mol^{-1} and $\Delta S^{\neq}$ = −1.5 ± 0.9 cal K^{-1} mol^{-1} for the IPr rotation.

The chloro bridges in **1** and **2** were easily cleaved by nucleophilic pyridine ligands at room temperature, resulting in the formation of the mononuclear complexes RhCl(IPr)(L)(η^2-coe) (L = pyridine (**3**), 2-picoline (**5**), 4-picoline (**7**), 2-ethylpyridine (**9**)) and RhCl(IPr)(L)(η^2-ethylene) (L = pyridine (**4**), 2-picoline (**6**), 4-picoline (**8**), 2-ethylpyridine (**10**)) which were isolated as yellow solids in 77-86% yields.[36] It is noticeable that the alkene ligand was not replaced by pyridine even at 80 ºC in net pyridine overnight.[37] Monocrystals of **3** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane over a saturated solution of **3** in toluene (Figure 1). The complex has distorted square-planar geometry with pyridine and chloro ligands disposed mutually *trans* to IPr and

coe, respectively [N(3)-Rh-C(10) 169.36(15)°; Cl-Rh-Ct 166.02(14)°]. The rhodium-carbon separation [Rh-C(10) 1.986(4) Å] compares well with previously reported rhodium-NHC single bond distances.[29b] The wingtips of IPr, the η^2-olefin and the pyridine adopt an out-of-plane disposition from the square-planar metal environment.[38]
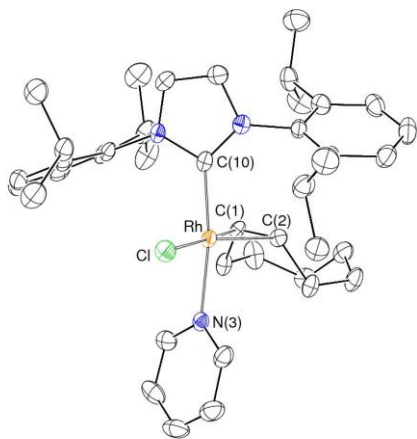

Figure 1. Molecular diagram of **3**. Selected bond lengths (Å) and angles (°): Rh-Cl(1) 2.3886(13), Rh-N(3) 2.115(4), Rh-C(1) 2.149(4), Rh-C(2) 2.113(4), Rh-C(10) 1.986(4); Cl-Rh-N(3) 84.43(10), Cl-Rh-C(10) 86.21(12), Cl-Rh-Ct 166.02(14), N(3)-Rh-C(10) 169.36(15), N(3)-Rh-Ct 94.42(17), C(10)-Rh-Ct 95.89(18).

The ^1H and $^{13}C\{^1H\}$ spectra of compounds **3**-**10** confirm the presence of η^2-olefin, pyridine and IPr ligands. Similarly to **2,** the IPr and ethylene ligands in **4** exhibited restricted rotation (Figure 2). The activation parameters obtained from the rate constants derived from a ^1H VT-NMR study and the corresponding Eyring analysis were $\Delta H^{\neq} = 13.9 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\neq} = -1.7 \pm 1.2$ cal K^{-1} mol^{-1} for the ethylene rotation and $\Delta H^{\neq} = 14.1 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\neq} = -0.7 \pm 1.4$ cal K^{-1} mol^{-1} for the IPr rotation. The values obtained for the rotation of ethylene in **4** are almost identical to that calculated for the dimer **2**. In contrast, the barrier for the rotation of IPr around the Rh-C axis in **4** is 2.3 kcal mol^{-1} higher than in **2**.
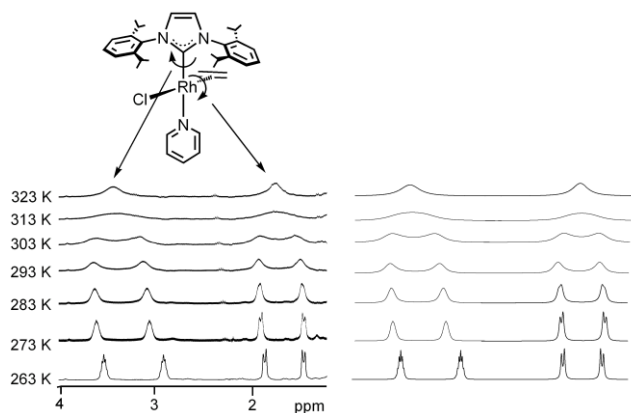

Figure 2. Variable-temperature ^1H-NMR spectra of RhCl(IPr)(pyridine)(η^2-ethylene) (**4**) in CD$_2$Cl$_2$ showing the coalescence of the CH-isopropyl and ethylene resonances: experimental (left) and calculated (right).

The rotation barrier for the IPr ligand is also affected by the nature of the η^2-olefin. Thus, substitution of ethylene by coe slightly hinders the rotational process as it is observed from the parameters calculated for **3** ($\Delta H^{\neq} = 15.1 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\neq} = -0.4 \pm 1.9$ cal K^{-1} mol^{-1}). Similar values for IPr rotation were calculated for complex **6** bearing a 2-picoline ligand ($\Delta H^{\neq} = 15.0 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\neq} = ^-1.6 \pm 1.6$ cal K^{-1} mol^{-1}). However, in this case, four CH-isopropyl signals were observed at low temperature (δ 4.37, 4.09, 3.09, and 2.62 ppm) which coalesced into two at 4.17 and 2.91 ppm. This fact can be explained by hindered rotation of 2-picoline, that breaks the plane of symmetry.

The presence of a substituent in the 2-position of pyridine not only affects the rotation of the ligand but also the coordination to the metallic center. Thus, a temperature-dependent dynamic equilibrium between **6** and **2**, as a result of the decoordination of 2-picoline, was observed between 293 and 353 K (Figure 3). Thermodynamic parameters calculated from the Van't Hoff representations (Ln K$_{eq}$ vs 1/T) were $\Delta H^o = 14.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^o = 32.5 \pm 1.3$ cal K^{-1} mol^{-1}. The process is endothermic whereas the slightly positive ΔS^o agrees well with an increase of internal disorder in the products due to decoordination of 2-picoline. It seems clear that an *ortho*-substituent on pyridine hinders the coordination of the ligand to the metallic center. In accordance to this, the disubstituted 2,6-dimethylpyridine was found unable to cleave the chloro bridges in **1**-**2**.
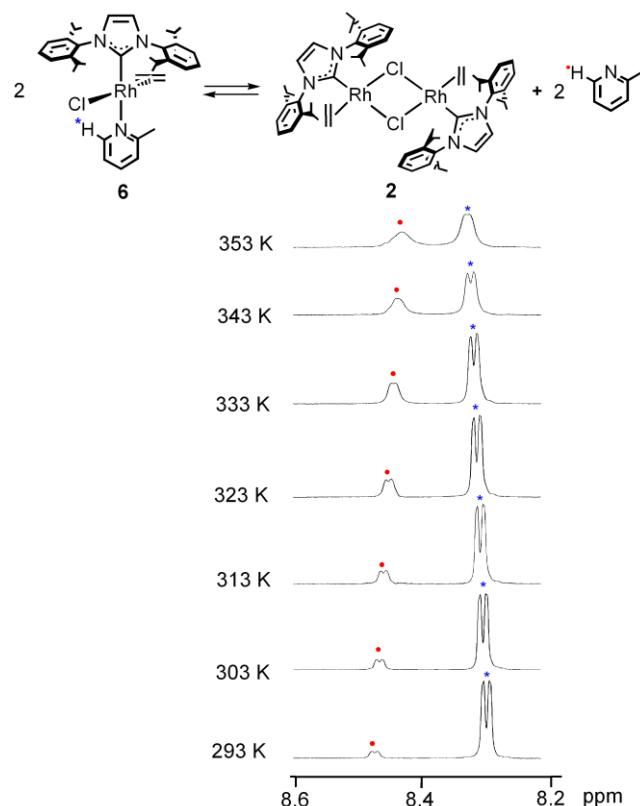

Figure 3. Variable-temperature ^1H-NMR spectra in the *ortho*-piridine proton region for the dynamic equilibrium between **6** and **2**.

Alkyne hydrothiolation catalytic studies. Wilkinson's catalyst $RhCl(PPh_3)_3$ has been previously revealed as an active catalyst for alkyne hydrothiolation.[11c,15e] In view that the substitution of phosphanes by a more electron-donating NHC has extended the scope of many catalytic transformations,[30] we have studied that effect in the present transformation (eq. 1). Addition of thiophenol to phenylacetylene was chosen as benchmark reaction (Table 1). Catalytic reactions using a 1:1 thiol:alkyne ratio were monitored in an NMR tube in C_6D_6 at 25 ºC with 2 mol % catalyst loading. A catalytic test with $RhCl(PPh_3)_3$ under our mild standard conditions showed high initial catalytic activity but also catalyst deactivation at about 80 % conversion, displaying a high preference for the β-E isomer (entry 1). In contrast, $RhCl(IPr)(PPh_3)_2$[31b] showed full conversion to clean addition products after 3 h at room temperature with a selectivity switch to 53/47 β-E/α (entry 2). Although Wilkinson´s catalyst is initially more active than $RhCl(IPr)(PPh_3)_2$, the catalyst stability gained by the introduction of a IPr ligand compensates the loss of activity. Then, other phosphane-free Rh-NHC derivatives were tested as catalysts precursors. $RhClIPr(cod)$[39] (cod = 1,5-cyclooctadiene) reacts very slowly (18% after 24 h, entry 3) but the dinuclear η^2-coe compound **1** surpassed the activity observed for $RhCl(IPr)(PPh_3)_2$ while maintaining clean full conversion and the preference for the anti-Markovnikov products (entry 4). The strong coordination of cod ligand in the former compared to the labile coe ligands in **1** may be determinant for the very different catalytic activity.
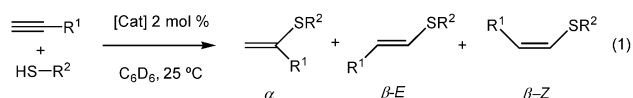

(1)

Table 1. Phenylacetylene Hydrothiolation with thiophenol at 25 ºC.[a]

Entry	Catalyst	t (h)	conv.	β-E/α	$TOF_{1/2}$ (h^{-1})[b]
1	$RhCl(PPh_3)_3$	0.5	80	92/8	300
2	$RhCl(IPr)(PPh_3)_2$	3	99	53/47	55
3	$RhCl(IPr)(cod)$	24	18	68/32	-
4	**1**	1	99	73/27	280
5	**2**	0.4	99	67/33	482
6	**3**	4	99	9/91	38
7	**4**	3	99	11/89	59
8	**6**	2.2	99	58/42	105
9	**8**	4	99	13/87	41
10	**10**	1.6	99	62/38	125
11	**1** + 1 equiv py	4	99	10/90	38
12	**2** + 1 equiv py	3	99	12/88	59
13	**2** + 10 equiv py	7	99	6/94	22
14	**2** + 10 equiv (2-picoline)	6	99	37/63	30
15	none	24	37	8/92[c]/0	--
16	pyridine[d]	24	13	9/91[c]/0	--
17	**1** + 10 equiv NEt_3	7	99	59/41	28
18	**1** + BHT	1	99	72/28	300

[a] 0.5 mL of C_6D_6 with 2 mol % of catalyst. [subs] = 1 M. [b] Determined at 50 % conversion. [c] Yield of β-Z. [d] 20 mol % of pyridine.

The exchange of coe ligands by ethylene in dimer **2** enhanced catalytic rate with similar preference to the linear isomer (entry 5). Surprisingly, catalysts **3** and **4**, bearing a pyridine moiety, showed reverse regioselectivity although also a moderate decrease of catalytic activity (entries 6-7). The *in-situ* addition of 1 equiv of pyridine to **1** and **2** gave similar results to **3** and **4**, respectively (entries 11-12). It was observed that an increase of the amount of pyridine in the reaction media switches the equilibrium to the Markovnikov isomer up to 94 % with the catalytic system **2** + 10 equiv of pyridine (entry 13) (Figure 4). Only traces of disulfide were detected by GC-MS analysis whereas β-Z product was not observed in any of the catalytic runs carried out with **1-4**. A blank test without metal catalysts showed after 24 h the formation of 37 % of linear vinyl sulfides of mainly Z configuration probably via radical process (entry 15).[40] Addition of 2,6-di-tert-butyl-4-methylphenol (BHT) to a sample catalyzed by **1** did not affect either the activity or the selectivity, thus excluding a mechanism via radical species operating with our catalysts (entry 18). Addition of pyridine to the blank test did not increase activity but rather slightly reduced it (entry 16). In order to discard that pyridine acts as a base, NEt_3 was added to a sample catalyzed by **1**. The ratio of the products was only slightly switched to the branched isomers (compare entries 4 *vs* 17). To further assess that the positive role of pyridine is played on coordination to active species, the catalytic activity of complexes **6**, **8**, and **10** having 2-picoline, 4-picoline or 2-ethylpyridine ligands, respectively, was studied (entries 8-10). Complex **8** gave similar results than **4** but catalysts **6** and **10**, bearing 2-substituted pyridines, showed a behavior between **2** and **4** both in terms of activity and selectivity. The hindered coordination of 2-picoline and 2-ethylpyridine, as showed in figure 3, can be the reason for this result. Indeed, displacement of the equilibrium to the coordinated species by addition of 10 equiv of 2-picoline to **2** resulted in an increase of the regioselectivity to the α-isomer (compare entries 8 *vs* 14).
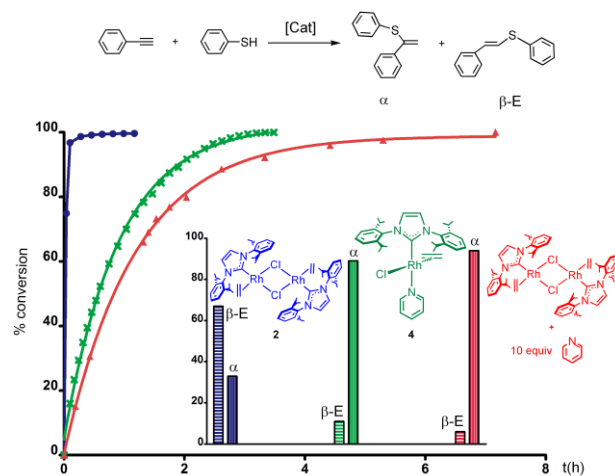
Figure 4. Catalytic activity and regioselectivity outcome in hydrothiolation of phenylacetylene with thiophenol for catalysts **2**(•), **4**(×), **2** + 10 equiv pyridine (Δ).

Compounds **1**-**4** are versatile catalyst precursors. They promote the addition of thiophenol to different alkylic and aromatic alkynes (Table 2). The reaction rates for the alkylic ones were lower than those observed for phenylacetylene and thus the reactions were performed at 50 ºC. Strikingly, the "pyridine effect" on the regioselectivity was maintained. The amount of the Markovnikov thioether product in the hydrothiolation of 1-hexyne was increased from 39/61 (**2**) to 22/78 by using the pyridine complex **4** as catalyst (entries 1-2). Moreover, up to 96 % of branched isomer was obtained using **2** + 10 equiv py as catalytic system with no significant isomerization to internal vinyl thioether. In the case of the enyne 1-ethynyl-1-cyclohexene a similar behavior was observed but it is noteworthy the complete chemoselectivity with the exclusive addition of PhSH to the triple bond. More interestingly, the internal alkyne 3-hexyne gave exclusively the *E*-isomer (entry 7, eq 2) resulting from a *syn* addition of the thiol which, in addition to the absence of the *β-Z* isomer thorough the different catalytic tests, point to a migratory insertion mechanism for the alkyne hydrothiolation with these systems. The effect of modifying the electron density on the aromatic ring of phenylacetylene has been also studied. The introduction of an electron-donating group at the *para* position decreased both activity and selectivity (compare entry 8, table 2 *vs* entry 11, table 1*)* whereas the presence of an electron-withdrawing substituent resulted in higher TOF and regioselectivity (entry 9). A propargyl ether was also effective with similar isomeric distribution (entry 10).

Table 2. Alkyne Hydrothiolation with thiophenol.[a]

Entry	Alkyne	Cat	T(ºC)	t (h)	conv.	β-E/α	TOF$_{1/2}$(h^{-1})
1		**2**	50	7	99	39/61	25
2		**4**	50	9.4	99	22/78	19
3		**2 +** 10 equiv py	50	24	95	4/96	1
4		**2**	50	3.5	99	62/38	47
5		**4**	50	5.5	99	49/51	30
6		**2 +** 10 equiv py	50	13	92	34/66	16
7		**2**	50	20	95	--[b]	1
8	MeO—	**2 +** 10 equiv py	25	18	99	10/90	7
9	F₃C—	**2 +** 10 equiv py	25	4	99	3/97	45
10		**2 +** 10 equiv py	50	18	99	10/90	7

[a] 0.5 mL of C$_6$D$_6$ with 2 mol % of catalyst. [subs] = 1 M.[b] exclusive formation of (*E*)-3-phenylsulfanyl-3-hexene.
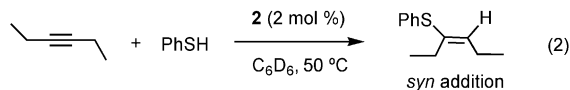
The scope of the catalysts was investigated by using different thiols (Table 3). Again, the regioselectivity can be tuned by pyridine addition. Benzyl hydrosulfide, PhCH$_2$SH, reacted much faster than PhSH (entries 1-4). In fact, full conversion was attained with **2** after the first recorded ^{1}H NMR spectrum (≈3 min) with our standard conditions. A reduction of the amount of catalyst **2** to 0.5 mol % gave the same result, with a calculated TOF of 4000 h^{-1}. As it was previously shown for PhSH, catalyst **4** and the catalytic system **2** + 10 equiv py were less active but much more selective to the α-isomer. A doubly protected N-tert-butoxycarbonyl (Boc) and methylester cysteine was also transformed into the vinyl thioether with high activity under mild conditions (TOF$_{1/2}$ of 250-580 h^{-1}) (entries 5-7). Thus, our catalysts are compatible with other functional groups giving good selectivities to the α vinyl sulfide isomer. Indeed, functionalization of cysteine is an important goal for the synthesis of biologically active derivatives. Interestingly, 1,6-hexanedithiol undergoes a double addition process with good selectivity to the α,α product (88%, entry 8, eq 3).

Table 3. Hydrothiolation of phenylacetylene with different thiols at 25 ºC.[a]

Entry	Thiol	Catalyst	t (h)	conv.	β-E/α	TOF$_{1/2}$ (h^{-1})
1	SH	**2**	0.05	99	33/67	--
2	SH	**2**[c]	0.05	99	31/69	4000[b]
3	SH	**4**	0.08	99	26/74	625[b]
4	SH	**2 +** 10 equiv py	0.4	99	7/93	510
5	HN-Boc ...SH	**2**	0.25	99	37/63	580
6	HN-Boc ...SH	**4**	0.5	99	23/77	420
7	HN-Boc ...SH	**2 +** 10 equiv py	1.2	99	10/90	250
8	HS⌇₆SH	**2 +** 10 equiv py	0.7	99	11/88[d]	..390

[a] 0.5 mL of C$_6$D$_6$ with 2 mol % of catalyst. [subs] = 1 M. [b] Measured at full conversion.[c] 0.5 mol % of **2**.[d] ratio between β-E,α and α,α.
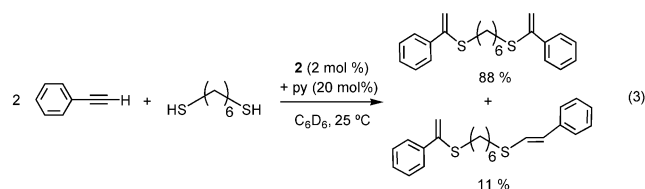
Mechanistic proposal. A number of possible mechanisms for alkyne hydrothiolation have been postulated. The *trans*-addition product, *β-Z* vinyl sulfides, are mainly formed in the

absence of catalyst via a radical pathway.[40] In our catalytic system the inversion of regioselectivity promoted by pyridine addition do not proceed by radical intermediates as the addition of a radical trap (BHT) did not influence either the activity or the selectivity. On the other hand, the external attack of the thiol on a coordinated alkyne is unlikely as the exclusive formation of the *syn*-addition *β-E* vinyl sulfide product was observed in the hydrothiolation of internal alkynes. In fact, we fail to detect any well-defined compound from the addition of a stoichimetric amount of phenylacetylene to **1** or **3**. Thus, the above results suggest a classical S-H oxidative addition and successive alkyne insertion and reductive elimination processes as the plausible mechanism operating with our catalysts (Scheme 1).

In order to shed light on the effect of pyridine coordination on the regioselectivity outcome, several stoichiometric NMR experiments were carried out. Treatment of **1** with thiophenol gave rise to an unidentified mixture of rhodium-hydrides, probably originated from oxidative addition of PhSH.[41] In fact, the formation of several mononuclear or dinuclear thiolate- or chloro-bridged complexes can be envisaged.[42] However, when the pyridine complex **3** was treated with PhSH, a doublet at −26.55 ppm with a J_{Rh-H} = 48.5 Hz appeared as the main hydride species, along with the presence of free coe. The upfield shift and the high coupling constant of this resonance suggest a square-pyramidal structure with the hydride occupying the apical position.[32a,43] Unfortunately, complex RhClH(SPh)(IPr)(py) (**11**) could not be isolated. Addition of 1 equiv of phenylacetylene at −20 ℃ to an NMR sample of **11** generated *in-situ* led to smoothly formation of the organic product phenyl(1-phenylvinyl)sulfane, resulting from the Markovnikov addition of PhSH to the alkyne, and a mixture of unidentified rhodium species with concomitant disappearance of the hydride signal. The fact that alkenyl intermediates could not be detected points to the migratory insertion as the rate-determining step. In accordance to this, alkyl thiols react faster than thiophenol. Although the more acidic thiophenol facilitates the oxidative addition step, the more basic sulfur atom of alkyl thiolate ligands should favor the migratory insertion. Indeed, the observation that an electron-withdrawing group at *para* position of the aromatic ring of phenylacetylene increases the activity is in accordance with this proposal. The insertion of alkyne into the Rh-S bond should be facilitated by a decrease in the electronic density on the C-C triple bond.

It seems likely that the oxidative addition of the thiophenol to **3** generates an unsaturated pentacoordinated complex **11**, *via* decoordination of the olefin on the electron-poor Rh[III] intermediate, with the pyridine occupying the less congested *trans* position regarding to the high sterically demanding IPr. Indeed, DFT calculations on the stability of different unsaturated square-pyramidal isomers with pyridine (**11a**), chloride (**11b**), and thiolate (**11c**) located trans to IPr, showed that **11a** is 13.5 and 14.3 kcal mol⁻¹ more stable than **11b** and **11c**, respectively (Figure 5). The trigonal bypiramidal structure for these species was not found as minima in any case. In addition, the bulky IPr ligand makes difficult the coordination of the amine ligands in the equatorial position. In fact, several studies on saturated complexes having two pyridine ligands have shown that the pyridine ligand *cis* to IPr is more labile or even decoordinates on increasing the steric demand on the NHC ligand.[44]
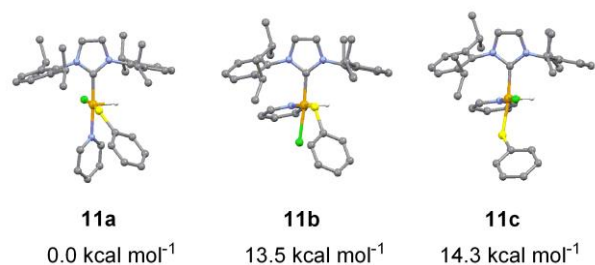

Figure 5. DFT computed energies for the pentacoordinated square-pyramidal structures of **11**.

In contrast to the behavior observed for **3**, the treatment of **1** with 1 equiv of PhSH and 3 equiv of pyridine per metal atom in tol-d_8 gave rise to a mixture of two hydride species in dynamic equilibrium: the unsaturated complex **11** and the saturated RhClH(SPh)(IPr)(py)$_2$ (**11-py**), which exhibited a doublet at δ −16.95 ppm with J_{Rh-H} = 15.6 Hz, in 1:2.5 ratio at 20 ℃. The new saturated octahedral **11-py** results from the coordination of pyridine ligand in **11**. Similar downfield shift and reduction of the J_{Rh-H} coupling constant has been previously observed in related rhodium complexes by coordination of pyridine to the vacant site of the square-pyramidal hydride precursors.[45]

A ¹H VT-NMR study confirmed the dynamic equilibrium between **11** and **11-py** (Figure 6). As can be seen in the right part of the figure, that shows the hydride region of the spectra, on lowering the temperature from 303 to 243 K the intensity of the hydride signal corresponding to **11** diminishes and shifts to lower field approaching to that of **11-py** which slightly broadens. More informative is the left part of the figure. The *ortho*-protons of the pyridine ligand of **11** (●) integrates by 2 related to the hydride located at upfield shift, which suggests the free rotation of the pyridine ligand that makes both *ortho*-protons equivalents. This resonance does not change much with temperature. In contrast, the ¹H NMR spectrum at 243 K of **11-py** displays three signals for the four *ortho*-pyridine protons. The resonance at 9.06 ppm integrates 2:1 with respect to the hydride signal at −16.27 ppm and it is assigned to the both *ortho*-pyridine protons of the ligand *trans* to IPr (‡). In contrast, the signals corresponding to the pyridine ligand *cis* to IPr in **11-py** (□) split into two resonances at 9.58 and 9.31 ppm, probably by hindered rotation of the pyridine due the proximity of bulky IPr. At higher temperature these resonances coalesce to a single resonance over 263 K and exchange with that corresponding to free pyridine (#). Interestingly, the hydride signal for **11** shifts to lowfield at low temperature but remains unchanged over 303 K. This observation suggests that **11** is likely involved in another equilibrium, probably a dimerization process, resulting in the saturation of the vacant site.[42]

Coordination of pyridine *cis* to IPr is not exclusively determined by the steric pressure of the carbene ligand. Treatment of **1** with 1 equiv of benzylthiol and 3 equiv of pyridine per metal atom resulted in the exclusive formation of a pyridine-saturated hydride complex RhClH(SCH$_2$Ph)(IPr)(py)$_2$ (**12-py**) (Figure 7). The ¹H VT-NMR spectra of **12-py** are very similar to that of **11-py**. In particular, the hydride ligand was observed as a doublet at δ −17.31 ppm with J_{Rh-H} = 15.0 Hz at 25 ℃. In

the *ortho*-pyridine region a doublet at 9.28 ppm ($J_{H\text{-}H}$ = 5.2 Hz) corresponds to the pyridine ligand *trans* to IPr whereas the *cis* pyridine ligand splits into two signals at 9.45 and 9.19 ppm at 243 K. However, there is no equilibrium between **12-py** and the potential unsaturated compound **12**. Benzylthiolate is more flexible than phenylthiolate and thus complex **12-py** can accommodate a second pyridine ligand more easily than **11-py**. The steric influence of the ancillary ligands also affects the potential coordination of a N-donor ligand *trans* to the hydride ligand, as observed in the *in-situ* formation of the 2-ethylpyridine complex RhClH(SCH$_2$Ph)(IPr)(Et-py) (**13**). The increase of the steric bulk exerted by the 2-ethylpyridine prevents the formation of the saturated complex **13-py** and thus, the clean formation of square-pyramidal **13** was observed (δ–26.93 ppm, $J_{Rh\text{-}H}$ = 47.0 Hz).
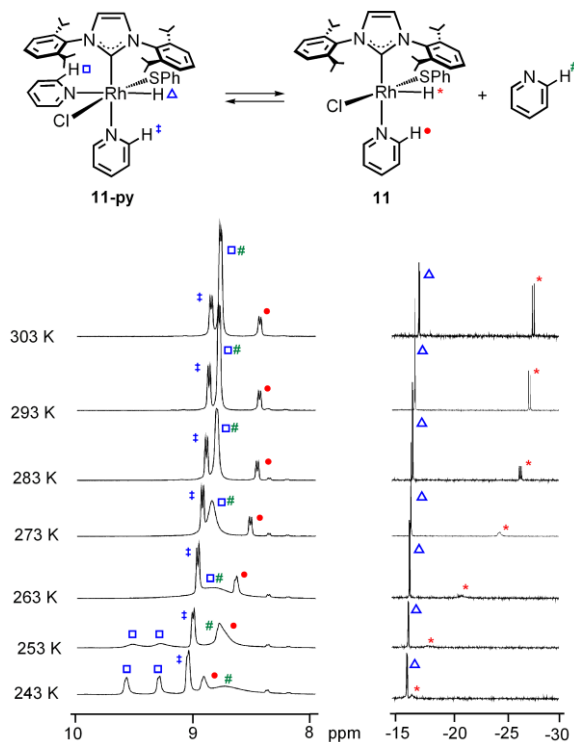
Figure 6. Stacked plot of variable-temperature ^{1}H NMR spectra in tol-d_8 in the *ortho*-pyridine (left) and hydride (right) regions of the equilibrium between **11** and **11-Py**
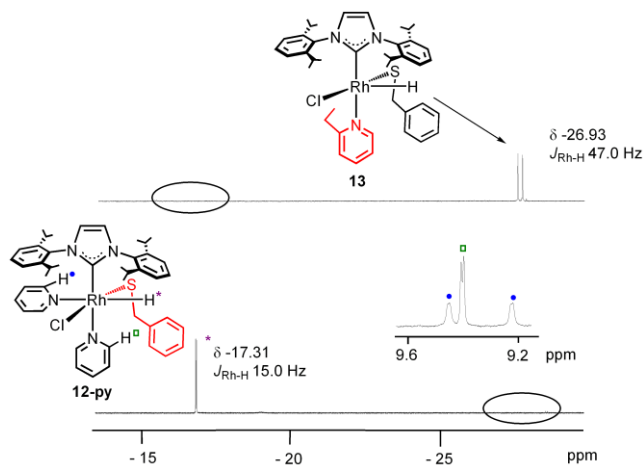

Figure 7. ^{1}H NMR spectra in tol-d_8 at 223 K for **12-py** (octahedral) and **13** (square-pyramidal).

The unsaturated square-pyramidal species **a** similar to **11**, is the key for the explanation of the observed regioselectivity outcome (Scheme 4). The high *trans* influence of the hydride ligand determines the stereochemistry of the complex and directs the coordination of the incoming ligand (alkyne or pyridine) *trans* to it (**b**). Therefore the alkyne is now located in *cis* disposition regarding to the thiolate ligand thus favorig migratory insertion between both groups to generate a 2,2-disubstituted alkenyl ligand (**c**).[46] Reductive elimination within **c** generates a branched vinyl sulfide. The influence of the pyridine excess on the activity and regioselectivity should be related with an increase of the concentration of **a** in the reaction media. Although the formation of the species such as **11-py** may retard the alkyne coordination, resulting in an inferior catalytic activity as it was observed for the catalytic system **2** + 10 equiv pyridine, it could also help to prevent both the decoordination of pyridine and the isomerization of **a** thus increasing the selectivity. In fact, decoordination of pyridine give rise to an hypothetical square–pyramidal pentacoordinated species **d** with the alkyne *trans* to IPr and *cis* to both hydride and thiolate ligands where insertion into Rh-H or Rh-S bonds is now possible therefore accounting for an unselective catalytic outcome. Catalytic pathway *via* **d** is probably operating with the dinuclear catalyst precursors **1** and **2**, or the phosphane catalyst RhCl(IPr)(PPh$_3$)$_2$, which exhibit good activity but moderate regioselectivity. In the case of 2-subtituted pyridine complexes **5**, **6**, **9**, and **10** the steric repulsion between the substituent and the incoming alkyne reduces the ability for these catalyst to generate **b**-type intermediates and also favors pyridine decoordination, as shown in figure 3, driven the catalytic reaction through type **d** intermediates.

Scheme 4. Proposed catalytic cycle for the regioselective alkyne hydrothiolation leading to branched vinyl sulfides.
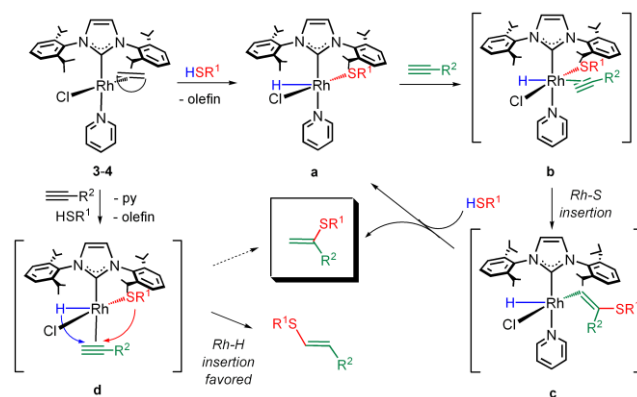
Consequently, a complex interplay between stereoelectronic properties of IPr, pyridine and hydride ligands accounts for the good-to-excellent regioselectivity achieved with these catalytic systems. It is likely that IPr and hydride direct pyridine coordination to the more favorable coordination site, that located *trans* to IPr. Alkyne is now forced to coordinate *trans* to hydride and so *cis* to thiolate favoring Markovnikov selectivity. The absence of pyridine allows the alkyne to coordinate in the preferred site *trans* to IPr position, and thus subsequent unselective migratory insertion takes place. This

catalytic system is an example where pyridine plays an important role as additive in a transition-metal mediated catalytic transformation.[47] The "pyridine effect" in this system has been rationalized with a molecular basis and it is further supported by theoretical calculations.

Theoretical calculations on the reaction mechanism. To gain more insight about the feasibility of our proposed mechanism, theoretical calculations on the catalytic cycle were performed for phenylacetylene and thiophenol (DFT, B3LYP, kcal mol^{-1}, Figure 8). As far as we know, theoretical studies dealing with alkyne hydrothiolation or insertion of an alkyne into metal-thiolate bonds are scarce.[13d,48] Calculations of the involved organometallic intermediates were performed without any simplifying approximation in order to increase accuracy of the results. The starting point is the square-pyramidal thiolate-hydride species **11a** (Figure 5) and phenylacetylene. In **11a** only migratory insertion of the alkyne into rhodium-thiolate is possible but discrimination between migration into α or β carbon atoms of the alkyne determines the configuration of the final product. Thus, both pathways for the insertion of thiol were calculated. The red line shows the 1,2-insertion or Markovnikov addition pathway (a) whereas the blue line corresponds to the 2,1-insertion or anti-Markovnikov route (b) (Figure 8). Complete energy profile shows that the reaction is kinetically determined by the migratory insertion step as the highest hurdle. In accordance with the experimental results, the formation of branched vinyl sulfides obtained via Markovnikov pathway is favored. The possibility of migratory insertion of the alkyne into the rhodium-hydride bond has been also calculated. In agreement with our mechanistic proposal the transition states for both insertion types are higher in energy than TSIa (25.9 and 27.7 kcal mol^{-1}, see Supporting Information for details).
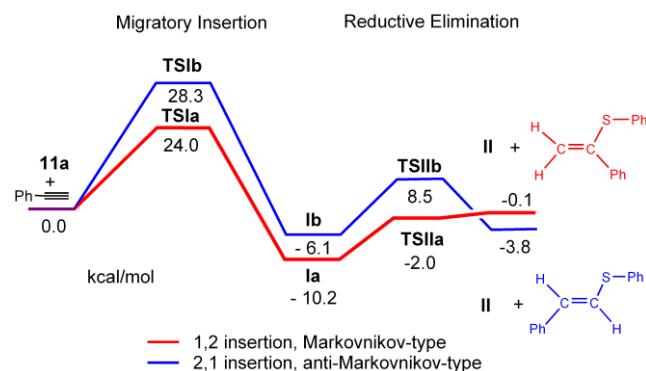
Figure 8. Computed potential-energy profile for the alkyne migratory insertion and reductive elimination for the formation of vinyl sulfid**e**.

It has been determined that the coordination of the alkyne to **11a** is hindered by sterical means, thus a stationary point for the saturated species similar to **b** (Scheme 4) was not found for either alkyne orientation. However, we were able to locate the transition states corresponding to C-S and Rh-C coupling for both pathways (**TSIa** and **TSIb**). An affordable value of 24.0 kcal mol^{-1} was computed for 1,2 insertion **TSIa** which is 4.3 kcal mol^{-1} lower in energy than **TSIb**. Either transition state displays a roughly metalacyclobutene structure including the metal, sulfur and the two carbon atoms of the former alkyne (Figure 9). Rhodium-thiolate and C-C bonds slightly elongate from 2.355 Å in **11a** and 1.210 Å in phenylacetylene to 2.414 Å (Rh-S) and 1.276 Å (C-C) in **TSIa** and 2.399 Å (Rh-S) and 1.260 Å (C-C) in **TSIb**.

Intermediates **Ia** and **Ib** bearing a thioalkenyl ligand, similar to proposed species **c**, were found to be –10.2 and –6.1 kcal mol^{-1} more stable than the starting point. The new Rh-C bond formed agrees with typical simple bond distances, 2.007 Å in **Ia** and 2.010 Å in **Ib**. In the reductive elimination step, two new transition states were located at 8.5 kcal mol^{-1} (**TSIIb**) and –2.0 kcal mol^{-1} (**TSIIa**) being again the anti-Markovnikov pathway unfavorable. The final point corresponding to the unsaturated species RhCl(IPr) **II** and the respective coupled organic products is slightly more favorable for the formation of linear vinyl sulfides (–3.8 vs –0.1 kcal mol^{-1}) although both pathways are thermodynamically less energetic that the starting point.
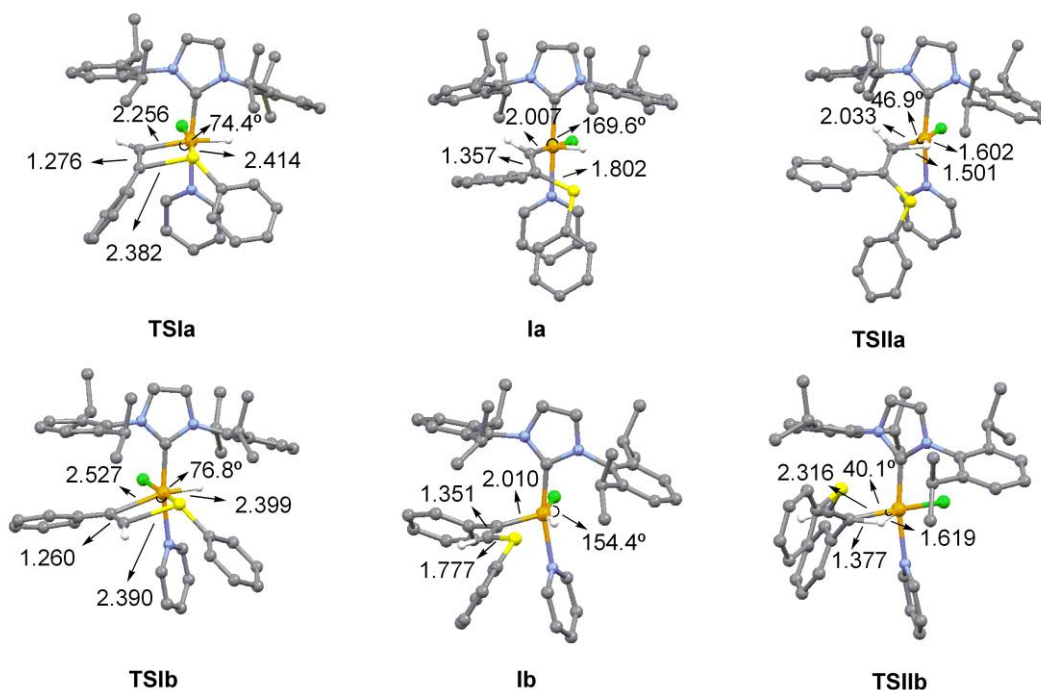
Figure 9. Optimized structures for the intermediates and transition states for migratory insertion and reductive elimination steps including selected distances (Å) and angles (deg).

CONCLUSION

Herein we have presented highly active Rh-NHC catalysts for alkyne hydrothiolation under mild conditions. Pyridine-type ligands easily cleave the chloro-bridges in dinuclear derivatives [Rh(μ-Cl)(IPr)(η^2-olefin)]$_2$ to afford stable mono-nuclear complexes RhCl(IPr)(L)(η^2-coe). The presence of a powerful electron-donor bulky IPr ligand prevents deactivation of active species thus increasing catalytic activity compared to RhCl(PPh$_3$)$_3$. It has been found that dinuclear complexes are more active than their related pyridine mononuclear complexes. However, a reversion in the regioselectivity from β-E to α was observed with mononuclear catalysts compared to dinuclear precursors.

It has been also determined that the mechanism proceeds *via* oxidative-addition of the S-H bond to Rh^I intermediates and successive alkyne migratory insertion and reductive elimination steps. The regioselectivity of the catalytic outcome is determined by the alkyne migratory insertion into the Rh-S bond. The interplay of electronic and steric effects exerted by IPr, pyridine and hydride ligands accounts for the regioselective formation of branched vinyl sulfides as a consequence of the 1,2-insertion into the rhodium-thiolate bond. The encumbered and powerful electron donor NHC ligand directs the coordination of the pyridine *trans* to it, consequently blocking the coordination of the alkyne in this position. Simultaneously, the *trans* influence of the hydride paves the way to a *cis* thiolate-alkyne disposition that gives rise to the branched vinyl sulfide regioisomer. This mechanistic proposal is supported by DFT quantum-mechanical calculations. The rate-determining step is the alkyne migratory insertion leading to the C-S bond formation. The energy difference of 4.3 kcal mol^{-1} favoring the 1,2 over the 2,1-migratory insertion fully account for the observed regioselectivity.

The findings reported herein could be useful for the rational molecular design of new catalysts with improved regioselectivity in related addition processes such as hydroalkoxylation, hydrophosphination, hydroamination or hidroacylation among others. With the aim to improve activity and selectivity, catalysts design by modification of both NHC and ancillary ligands is currently investigated in our laboratories.

EXPERIMENTAL SECTION

General considerations. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. 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 starting material [Rh(μ-Cl)(IPr)(coe)]$_2$ (**1**) was prepared as previously described in the literature.[31b] ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300 MHz a Bruker Avance 400 MHz or a Bruker Avance 500 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external CFCl$_3$ (^{19}F). Coupling constants, J, are given in hertz. Spectral assignments were achieved by combination of ^{1}H-^{1}H COSY, ^{13}C APT and ^{1}H-^{13}C HSQC/HMBC experiments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. GC-MS analysis were run 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 μm with a 0.25 μm film thickness).

Preparation of [Rh(μ-Cl)(IPr)(η^2-CH$_2$=CH$_2$)]$_2$ (2). A yellow solution of **1** (300 mg, 0.236 mmol) in 10 mL of toluene at room temperature was bubbled with ethylene for 15 min. Then, the solvent was evaporated to dryness and subsequent addition of hexane caused the precipitation of a yellow solid which was washed with hexane (3 x 4 mL) and dried in vacuo. Yield: 240 mg (92%). Anal. Calcd. for C$_{58}$H$_{80}$N$_4$Cl$_2$Rh$_2$: C, 62.76; H, 7.26; N, 5.05. Found: C, 62.45; H, 7.15; N, 4.94. ^{1}H NMR (300 MHz, tol-d_8, 233 K): δ 7.3-7.1 (m, 12H, H$_{Ph-IPr}$), 6.19 (s, 4H, =CHN), 3.27 and 2.90 (both sept, J_{H-H} = 6.6, 8H, CHMe$_{IPr}$), 2.84 and 2.27 (both d, J_{H-H} = 12.6, 8H, CH$_2$=CH$_2$), 1.62, 1.47, 1.00, and 0.96 (all d, J_{H-H} = 6.6, 48H, CHMe$_{IPr}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (75.4 MHz, tol-d_8, 233 K): δ 179.7 (d, J_{C-Rh}= 62.3, Rh-C$_{IPr}$), 146.2 and 145.2 (both s, C$_q$), 137.0 (s, C$_q$N), 129.1 and 123.6 (s, CH$_{Ph-IPr}$), 123.7 (s, =CHN), 43.4 (d, J_{C-Rh} = 16.7, CH$_2$=CH$_2$), 28.5(s, CHMe$_{IPr}$), 25.8 and 23.3 (both s, CHMe$_{IPr}$).

Preparation of RhCl(IPr)(η^2-coe)(py) (3). A yellow solution of **1** (300 mg, 0.236 mmol) in 10 mL of toluene was treated with pyridine (200μl, 2.47 mmol) and stirred at room temperature for 15 min. Then, the solvent was evaporated to dryness and subsequent addition of hexane caused the precipitation of a yellow solid which was washed with hexane (3 x 4 mL) and dried in vacuo. Yield: 280 mg (83%). Anal. Calcd. for C$_{40}$H$_{55}$N$_3$ClRh: C, 67.07; H, 7.73; N, 5.87. Found: C, 66.83; H, 7.55; N, 6.02. ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 8.40 (d, J_{H-H} = 4.3, 2H, H$_{2-Py}$), 7.4-7.2 (m, 6H, H$_{Ph-IPr}$), 6.64 (s, 2H, =CHN), 6.55 (t, J_{H-H} = 5.4, 1H, H$_{4-Py}$), 6.20 (dd, J_{H-H} = 5.4, J_{H-H} = 4.3, 2H, H$_{3-Py}$), 4.52 and 2.61 (both sept, J_{H-H} = 6.4, 4H, CHMe$_{IPr}$), 3.12 (m, 2H, CH=CH$_{coe}$), 1.81, 1.47, 1.15, and 1.02 (all d, J_{H-H} = 6.4, 24H, CHMe$_{IPr}$), 1.8-0.8 (br, 12H, CH$_{2-coe}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (75.6 MHz, C$_6$D$_6$, 253 K): δ 183.3 (d, J_{C-Rh}= 54.0, Rh-C$_{IPr}$), 153.9 (s, C$_{2-Py}$), 149.3 and 146.6 (both s, C$_q$), 138.3 (s, C$_q$N), 135.1 (s, C$_{4-Py}$), 129.7, 128.9, 125.5, and 123.1 (all s, CH$_{Ph-IPr}$), 124.8 (s, =CHN), 122.9 (s, C$_{3-Py}$), 56.1 (d, J_{C-Rh} = 16.4, CH=CH$_{coe}$), 30.6, 30.4, and 27.3 (all s, CH$_{2-coe}$), 29.5 and 29.4 (both s, CHMe$_{IPr}$), 27.2, 27.1, 24.6, and 23.1 (all s, CHMe$_{IPr}$).

Preparation of RhCl(IPr)(η^2-CH$_2$=CH$_2$)(py) (4). The complex was prepared as described for **3** starting for **2** (300 mg, 0.270 mmol) and pyridine (220μl, 2.72 mmol). Yield: 290 mg (85%). Anal. Calcd. for C$_{34}$H$_{45}$N$_3$ClRh: C, 64.40; H, 7.15; N, 6.63. Found: C, 64.22; H, 7.02; N, 6.45. ^{1}H NMR (500 MHz, tol-d_8, 253 K): δ 8.32 (d, J_{H-H} = 4.5, 2H, H$_{2-Py}$), 7.3-7.1 (m, 6H, H$_{Ph-IPr}$), 6.54 (s, 2H, =CHN), 6.46 (t, J_{H-H} = 5.5, 1H, H$_{4-Py}$), 6.08 (dd, J_{H-H} = 5.5, J_{H-H} = 4.5 2H, H$_{3-Py}$), 4.09 and 3.08 (both sept, J_{H-H} = 6.5, 4H, CHMe$_{IPr}$), 2.52 and 2.03 (both d, J_{H-H} = 11.5, 4H, CH$_2$=CH$_2$), 1.91, 1.57, 1.23, and 1.13 (all d, J_{H-H} = 6.5, 24H, CHMe$_{IPr}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (125.6 MHz, tol-d_8, 253 K): δ 183.3 (d, J_{C-Rh}= 54.5, Rh-C$_{IPr}$), 151.5 (s, C$_{2-Py}$), 148.1 and 145.4 (both s, C$_q$), 137.4 (s, C$_q$N), 134.5 (s, C$_{4-Py}$), 129.1, 128.4, 124.2, and 122.7 (all s, CH$_{Ph-IPr}$), 123.7 (s, =CHN), 122.5 (s, C$_{3-Py}$), 41.6 (d, J_{C-Rh} = 15.4, CH$_2$=CH$_2$), 28.9 and 28.7 (both s, CHMe$_{IPr}$), 26.3, 26.1, 23.9, and 22.9 (all s, CHMe$_{IPr}$).

Preparation of RhCl(IPr)(η^2-coe)(2-picoline) (5). The complex was prepared as described for **3** starting for **1** (300 mg, 0.236 mmol) and 2-picoline (230μl, 2.329 mmol). Yield: 275 mg (80%). Anal. Calcd. for C$_{41}$H$_{57}$N$_3$ClRh: C, 67.43; H, 7.87; N, 5.75. Found: C, 67.74; H, 7.91; N, 5.68. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.43 (d, J_{H-H} = 5.2, 1H, H$_{6-Py}$), 7.49-7.11 (m, 6H, H$_{Ph-IPr}$), 6.71 and 6.61 (both d, J_{H-H} = 1.4, 2H, =CHN), 6.57 (dd, J_{H-H} = 7.9, J_{H-H} = 7.6, 1H, H$_{4-Py}$), 6.34 (d, J_{H-H} = 7.6, 1H, H$_{3-Py}$), 6.21 (dd, J_{H-H} = 7.9, J_{H-H} = 5.2, 1H, H$_{5-Py}$), 4.96, 4.16, 2.83 and 2.20 (all sept, J_{H-H} = 6.4, 4H, CHMe$_{IPr}$), 3.07 (m, 2H, CH=CH$_{coe}$), 2.75 (s, 3H, H$_{CH3-Py}$), 1.97, 1.65, 1.49, 1.33, 1.22, 1.11, 1.07 and 0.94 (all d, J_{H-H} = 6.4, 24H, CHMe$_{IPr}$), 1.8-0.8 (br, 12H, CH$_{2-coe}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (75.6 MHz, C$_6$D$_6$, 293 K): δ 185.7 (d, J_{C-Rh}= 53.5, Rh-C$_{IPr}$), 162.1 (s, C$_{2-Py}$), 153.0 (s, C$_{6-Py}$), 149.7, 149.4, 146.9 and 146.7 (all s, C$_q$), 138.5, 138.0 (both, C$_q$N), 135.0 (s, C$_{4-Py}$), 130.1, 129.9, 126.0, 125.5, and 123.4, 122.9 (all s, CH$_{Ph-IPr}$), 125.2 and 124.9 (both s, =CHN), 124.6 (s, C$_{3-Py}$), 119.9 (s, C$_{5-Py}$), 58.3, 52.5 (both d, J_{C-Rh} = 16.3, CH=CH$_{coe}$), 31.3, 30.0, 29.4, 29.3, 27.4, and 27.2 (all s, CH$_{2-coe}$), 29.9, 29.7, 29.2 and 29.0 (all s, CHMe$_{IPr}$), 27.9, 27.3, 27.1, 26.7, 25.0, 24.1, 23.5, and 22.5 (all s, CHMe$_{IPr}$), 26.9 (s, C$_{CH3-Py}$).

Preparation of RhCl(IPr)(η^2-CH$_2$=CH$_2$)(2-picoline) (6). The complex was prepared as described for **3** starting for **2** (300 mg, 0.270 mmol) and 2-picoline (270μl, 2.734 mmol). Yield: 270 mg (77%). Anal. Calcd. for C$_{35}$H$_{47}$N$_3$ClRh: C, 64.86; H, 7.31; N, 6.48. Found: C, 65.01; H, 7.45; N, 6.37. ^{1}H NMR (500 MHz, tol-d_8, 253 K): δ 8.21 (d, J_{H-H} = 5.3, 1H, H$_{6-Py}$), 7.37-7.09 (m, 6H, H$_{Ph-IPr}$), 6.59 and 6.49 (both d, J_{H-H} = 1.6, 2H, =CHN), 6.47 (dd, J_{H-H} = 8.0, J_{H-H} = 7.7, 1H, H$_{4-py}$), 6.14 (d, J_{H-H} = 7.7, 1H, H$_{3-Py}$), 5.93 (dd, J_{H-H} = 8.0, J_{H-H} = 5.3, 1H, H$_{5-Py}$), 4.32, 4.05, 3.05 and 2.59 (all sept, J_{H-H} = 6.7, 4H, CHMe$_{IPr}$), 2.58 (s, 3H, H$_{CH3-Py}$), 2.56, 2.35, 2.04 and 1.64 (all dd, J_{H-H} = 11.7, J_{H-H} = 8.8, 4H, CH$_2$=CH$_2$), 1.94, 1.70, 1.49, 1.40, 1.21, 1.13, 1.10 and 1.02 (all d, J_{H-H} = 6.7, 24H, CHMe$_{IPr}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (125.6 MHz, tol-d_8, 293 K): δ 184.9 (d, J_{C-Rh}= 53.8, Rh-C$_{IPr}$), 160.9 (s, C$_{2-Py}$), 151.7 (s, C$_{6-Py}$), 149.5 and 147.2 (both s, C$_q$), 137.4 (s, C$_q$N), 134.7 (s, C$_{4-Py}$), 129.1, 128.4, 125.4, and 122.8 (all s, CH$_{Ph-IPr}$), 124.1 (s, C$_{3-Py}$), 123.9 (s, =CHN), 120.5 (s, C$_{5-Py}$), 43.7 (d, J_{C-Rh} = 16.6, CH$_2$=CH$_2$), 25.4 (s, C$_{CH3-Py}$), 29.1 and 28.9 (both s, CHMe$_{IPr}$), 26.6, 26.1, 23.7, and 23.2 (all s, CHMe$_{IPr}$).

Preparation of RhCl(IPr)(η^2-coe)(4-picoline) (7). The complex was prepared as described for **3** starting for **1** (300 mg, 0.236 mmol) and 4-picoline (230μl, 2.329 mmol). Yield: 280 mg (81%). Anal. Calcd. for C$_{41}$H$_{57}$N$_3$ClRh: C, 67.43; H, 7.87; N, 5.75. Found: C, 67.81; H, 7.98; N, 5.87. ^{1}H NMR (300 MHz, tol-d_8, 253 K): δ 8.22 (d, J_{H-H} = 5.7, 2H, H$_{2-Py}$), 7.42-6.97 (m, 6H, H$_{Ph-IPr}$), 6.65 (s, 2H, =CHN), 6.08 (d, J_{H-H} = 5.7, 2H, H$_{2-Py}$), 4.46 and 2.61 (both sept, J_{H-H} = 6.3, 4H, CHMe$_{IPr}$), 3.05 (m, 2H, CH=CH$_{coe}$), 1.75, 1.46, 1.14, and 1.03 (all d, J_{H-H} = 6.3, 24H, CHMe$_{IPr}$), 1.7-0.8 (br, 12H, CH$_{2-coe}$), 1.50 (s, 3H, H$_{CH3-Py}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (75.6 MHz, tol-d_8, 253 K): δ 185.8 (d, J_{C-Rh}= 53.9, Rh-C$_{IPr}$), 153.0 (s, C$_{2-Py}$), 149.1 and 146.1 (both s, C$_q$), 146.2 (s, C$_{4-Py}$), 138.0 (s, C$_q$N), 129.7, 128.5, 125.0, and 122.7 (all s, CH$_{Ph-IPr}$), 124.4 (s, =CHN), 123.5 (s, C$_{3-Py}$), 55.4 (d, J_{C-Rh} = 16.5, CH=CH$_{coe}$), 30.3, 30.0, and 27.0 (all s, CH$_{2-coe}$), 29.1 and

29.0 (both s, $\underline{C}$HMe$_{IPr}$), 26.8, 26.7, 24.1, and 22.8 (all s, CH$\underline{Me}_{IPr}$), 20.2 (s, CH$_{3-Py}$).

Preparation of RhCl(IPr)(η^2-CH$_2$=CH$_2$)(4-picoline) (8). The complex was prepared as described for **3** starting for **2** (300 mg, 0.270 mmol) and 4-picoline (270μl, 2.734 mmol). Yield: 277 mg (79%). Calcd. for C$_{35}$H$_{47}$N$_3$ClRh: C, 64.86; H, 7.31; N, 6.48. Found: C, 65.15; H, 7.45; N, 6.52. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 8.23 (d, J_{H-H} = 6.0, 2H, H$_{2-Py}$), 7.34-7.00 (m, 6H, H$_{Ph-IPr}$), 6.60 (s, 2H, =CHN), 5.97 (d, J_{H-H} = 6.0, 2H, H$_{3-Py}$), 4.11 and 3.14 (both br, 4H, C$\underline{H}$Me$_{IPr}$), 2.52 and 2.12 (both br, 4H, CH$_2$=CH$_2$), 1.87-1.00 (br, 24H, CH$\underline{Me}_{IPr}$), 1.50 (s, 3H, H$_{CH3-Py}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (100.6 MHz, C$_6$D$_6$, 298 K): δ 184.6 (d, J_{C-Rh}= 53.7, Rh-C$_{IPr}$), 151.8 (s, C$_{2-Py}$), 147.4 and 147.2 (s, C$_q$), 146.8 (s, C$_{4-Py}$), 138.3 (s, C$_q$N), 130.1 and 128.7 (all s, CH$_{Ph-IPr}$), 124.8 (s, =CHN), 124.7 (s, C$_{3-Py}$), 42.1 (d, J_{C-Rh} = 16.9, CH$_2$=CH$_2$), 29.6 and 29.4 (both s, C$\underline{H}$Me$_{IPr}$), 26.8, 26.6, 24.1, 26.6 (both s, CH$\underline{Me}_{IPr}$), 20.5 (s, C$_{CH3-Py}$).

Preparation of RhCl(IPr)(η^2-coe)(2-ethylpyridine) (9). The complex was prepared as described for **3** starting for **1** (300 mg, 0.236 mmol) and 2-ethylpyridine (270μl, 2.36 mmol). Yield: 285 mg (81%). Anal. Calcd. for C$_{42}$H$_{59}$N$_3$ClRh: C, 67.78; H, 7.99; N, 5.65. Found: C, 68.19; H, 8.12; N, 5.82. ^{1}H NMR (500 MHz, tol-d_8, 253 K): δ 8.43 (d, J_{H-H} = 5.3, 1H, H$_{6-Py}$), 7.38-6.99 (m, 6H, H$_{Ph-IPr}$), 6.63 (dd, J_{H-H} = 8.9, J_{H-H} = 7.8, 1H, H$_{4-Py}$), 6.62 and 6.54 (both d, J_{H-H} = 1.4, 2H, =CHN), 6.39 (d, J_{H-H} = 7.8, 1H, H$_{3-Py}$), 6.20 (dd, J_{H-H} = 8.9, J_{H-H} = 5.3, 1H, H$_{5-Py}$), 4.93, 3.98, 3.11 and 2.90 (all sept, J_{H-H} = 6.6, 4H, CH$\underline{Me}_{IPr}$), 3.65 and 3.34 (both dq, J_{H-H} = 15.2, J_{H-H} = 7.5, 2H, CH$_{2-Py}$), 3.07 and 2.94 (both br, 2H, CH=CH$_{coe}$), 2.11, 2.02, 1.59, 1.40, 1.29, 1.22, 1.08 and 0.92 (all d, J_{H-H} = 6.6, 24H, CH$\underline{Me}_{IPr}$), 1.8-0.9 (br, 12H, CH$_{2-coe}$), 1.03 (dd, J_{H-H} = 7.5, J_{H-H} = 7.5, 3H, CH$_{3-Py}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (125.6 MHz, tol-d_8, 253 K): δ 184.7 (d, J_{C-Rh}= 53.4, Rh-C$_{IPr}$), 166.3 (s, C$_{2-Py}$), 152.3 (s, C$_{6-Py}$), 148.7, 148.6, 146.2, and 146.1 (all s, C$_q$), 137.9 and 137.2 (both s, C$_q$N), 134.8 (s, C$_{4-Py}$), 129.6, 129.4, 128.2, 125.6, 122.9, and 122.3 (all s, CH$_{Ph-IPr}$), 124.4 and 123.9 (both s, =CHN), 121.9 (s, C$_{3-Py}$), 119.6 (s, C$_{5-Py}$), 58.3, 51.6 (both d, J_{C-Rh} = 16.0, CH=CH$_{coe}$), 32.9 (s, CH$_{2-Py}$), 30.9, 30.4, 29.5, 29.4, 26.8, and 26.7 (all s, CH$_{2-coe}$), 29.5, 29.2, 28.7 and 28.5 (all s, C$\underline{H}$Me$_{IPr}$), 27.5, 26.6, 26.4, 26.2, 24.7, 23.5, 23.1 and 21.9 (all s, CH$\underline{Me}_{IPr}$), 13.4 (s, CH$_{3-Py}$).

Preparation of RhCl(IPr)(η^2-CH$_2$=CH$_2$)(2-ethylpiridine) (10). The complex was prepared as described for **3** starting for **2** (300 mg, 0.270 mmol) and 2-ethylpyridine (310μl, 2.71 mmol). Yield: 315 mg (86%). Anal. Calcd. for C$_{37}$H$_{53}$N$_3$ClRh: C, 65.53; H, 7.88; N, 6.20. Found: C, 65.89; H, 7.98; N, 6.33. ^{1}H NMR (500 MHz, tol-d_8, 253 K): δ 8.27 (d, J_{H-H} = 5.1, 1H, H$_{6-Py}$), 7.38-6.99 (m, 6H, H$_{Ph-IPr}$), 6.60 and 6.47 (both d, J_{H-H} = 1.5, 2H, =CHN), 6.57 (dd, J_{H-H} = 9.0, J_{H-H} = 7.7, 1H, H$_{4-Py}$), 6.27 (d, J_{H-H} = 7.7, 1H, H$_{3-Py}$), 6.09 (dd, J_{H-H} = 9.0, J_{H-H} = 5.1, 1H, H$_{5-Py}$), 4.42, 3.94, 3.15 and 2.45 (all sept, J_{H-H} = 6.6, 4H, CH$\underline{Me}_{IPr}$), 3.60 and 3.06 (both dq, J_{H-H} = 15.1, , J_{H-H} = 7.6, 2H, CH$_{2-Py}$), 2.62, 2.31, 2.04 and 1.62 (all dd, J_{H-H} = 11.7, J_{H-H} = 8.4, 4H, CH$_2$=CH$_2$), 1.96, 1.6, 1.51, 1.36, 1.21, 1.13, 1.09 and 1.01 (all d, J_{H-H} = 6.6, 24H, CH$\underline{Me}_{IPr}$), 0.96 (dd, J_{H-H} = 7.6, J_{H-H} = 7.6, 3H, CH$_{3-Py}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (125.6 MHz, tol-d_8, 253 K): δ 184.3 (d, J_{C-Rh}= 53.8, Rh-C$_{IPr}$), 165.5 (s, C$_{2-Py}$), 151.6 (s, C$_{6-Py}$), 148.7, 148.4, 146.2, and 145.7 (all s, C$_q$), 137.6 and 137.2 (both s, C$_q$N),

135.0 (s, C$_{4-Py}$), 129.8, 129.5, 128.2, 124.6, 123.0, and 122.6 (all s, CH$_{Ph-IPr}$), 124.4 and 123.7 (both s, =CHN), 122.1 (s, C$_{3-Py}$), 120.9 (s, C$_{5-Py}$), 44.5 and 36.9 (both d, J_{C-Rh} = 17.3, CH$_2$=CH$_2$), 31.8 (s, CH$_{2-Py}$), 29.4, 29.2, 28.8 and 28.6 (all s, C$\underline{H}$Me$_{IPr}$), 27.2, 26.6, 26.3, 26.1, 24.6, 23.3, 23.0 and 22.2 (all s, CH$\underline{Me}_{IPr}$), 13.6 (s, CH$_{3-Py}$).

In-situ preparation of RhClH(SPh)(IPr)(py) (11). A solution of **3** (23 mg, 0.032 mmol) in C$_6$D$_6$ (0.5 mL, NMR-tube) at 20 ºC was treated with thiophenol (2.3 μL, 0.034 mmol). ^{1}H NMR (500 MHz, C$_6$D$_6$, 293 K): δ 8.96 (d, J_{H-H} = 5.0, 2H, H$_{2-Py}$), 7.42-6.88 (m, 11H, H$_{Ph}$), 6.85 (s, 2H, =CHN), 6.26 (d, J_{H-H} = 7.6, 1H, H$_{4-Py}$), 5.95 (dd, J_{H-H} = 7.6-5.0, 2H, H$_{3-Py}$), 3.76 and 3.66 (both sept, J_{H-H} = 6.3, 4H, C$\underline{H}$Me$_{IPr}$), 1.96, 1.53, 1.26 and 1.10 (all d, J_{H-H} = 6.3, 24H, CH$\underline{Me}_{IPr}$), −26.55 (d, J_{Rh-H} = 48.5, 1H, Rh-H).

In-situ preparation of RhClH(SPh)(IPr)(py)$_2$ (11-py). A solution of **1** (22 mg, 0.017 mmol) in toluene-d_8 (0.5 mL, NMR-tube) at -30 ºC was treated with pyridine (8 μL, 0.102 mmol) and thiophenol (2.3 μL, 0.034 mmol). The ^{1}H NMR was immediately recorded at low temperature. A mixture of **11** and **11-py** were observed in 1:2.5 ratio (at 293 K). Data for **11-py**: ^{1}H NMR (500 MHz, tol-d_8, 243 K): δ 9.58 and 9.31 (both br, 2H, H$_{o-Py-A}$), 9.06 (br, 2H, H$_{o-Py-B}$), 7.40-6.40 (br, 11H, H$_{Ph}$ and =CHN), 6.62 (br, 1H, H$_{p-Py-A}$), 6.24 (br, 1H, H$_{p-Py-B}$), 6.51 and 6.07 (both br, 2H, H$_{m-Py-A}$), 6.06 (br, 2H, H$_{m-Py-B}$), 4.37, 4.02, 3.51 and 3.26 (all br, 4H, C$\underline{H}$Me$_{IPr}$), 2.21, 1.67, 1.65, 1.60, 1.33, 1.22, 1.17 and 1.04 (all br, 24H, CH$\underline{Me}_{IPr}$), −16.27 (d, J_{Rh-H} = 15.4, 1H, Rh-H).

In-situ preparation of RhClH(SCH$_2$Ph)(IPr)(py)$_2$ (12-py). A solution of **1** (22 mg, 0.017 mmol) in toluene-d_8 (0.5 mL, NMR-tube) at -30 ºC was treated with pyridine (8 μL, 0.102 mmol) and benzylthiol (3.6 μL, 0.034 mmol). The ^{1}H NMR was immediately recorded at low temperature. ^{1}H NMR (500 MHz, tol-d_8, 223 K): δ 9.49 and 9.20 (both d, J_{H-H} = 4.9, 2H, H$_{o-Py--A}$), 9.44 (d, J_{H-H} = 5.2, 2H, H$_{o-Py-B}$), 7.40-6.90 (m, 11H, H$_{Ph}$), 6.72 and 6.49 (both br, 2H, =CHN), 6.61 (br, 1H, H$_{p-Py-A}$), 6.43 (br, 1H, H$_{p-Py-B}$), 6.42 and 5.96 (both br, 2H, H$_{m-Py-A}$), 6.24 (br, 2H, H$_{m-Py-B}$), 4.56, 3.97, 3.55 and 2.85 (all sept, J_{H-H} = 6.2, 4H, C$\underline{H}$Me$_{IPr}$), 2.45 and 2.20 (both d, J_{H-H} = 11.7, 2H, CH$_2$S), 2.06, 1.87, 1.71, 1.34, 1.32, 1.22, 1.16 and 0.93 (all d, J_{H-H} = 6.2, 24H, CH$\underline{Me}_{IPr}$), −17.10 (d, J_{Rh-H} = 15.2, 1H, Rh-H).

In-situ preparation of RhClH(SCH$_2$Ph)(IPr)(2-Etpy) (13). A solution **10** (19 mg, 0.026 mmol) in toluene-d_8 (0.5 mL, NMR-tube) at -50 ºC was treated with benzylthiol (3 μL, 0.028 mmol). The ^{1}H NMR was immediately recorded at low temperature. ^{1}H NMR (500 MHz, tol-d_8, 223 K): δ 7.68 (d, J_{H-H} = 5.0, 1H, H$_{6-Py}$), 7.40-7.00 (m, 11H, H$_{Ph}$), 6.60 (dd, J_{H-H} = 8.7, J_{H-H} = 7.6, 1H, H$_{4-Py}$), 6.59 and 6.56 (both br, 2H, =CHN), 6.20 (d, J_{H-H} = 7.6, 1H, H$_{3-Py}$), 6.02 (dd, J_{H-H} = 8.7, J_{H-H} = 5.0, 1H, H$_{5-Py}$), 3.82, 3.80, 3.50 and 3.31 (all sept, J_{H-H} = 6.2, 4H, CH$\underline{Me}_{IPr}$), 2.48-2.42 (m, 2H, CH$_{2-Py}$), 2.78 and 2.49 (both d, J_{H-H} = 12.5, 2H, CH$_2$S), 1.78, 1.73, 1.69, 1.58, 1.22, 1.17, 1.15 and 1.06 (all d, J_{H-H} = 6.2, 24H, CH$\underline{Me}_{IPr}$), 0.89 (dd, J_{H-H} = 7.5-7.3, 3H, CH$_{3-Py}$), −26.93 (d, J_{Rh-H} = 47.0, 1H, Rh-H).

Preparation of S-(phenylvinyl)-N-Boc-L-cysteine-methylester. A Schelnk tube containing 1 ml of toluene was charged with 11.1 mg (0.01 mmol) of catalyst **2**, 16 μL of pyridine (15.6 mg, 0.2 mmol), 200μL (229 mg, 1 mmol) of N-(tert-butoxycarbonyl)-L-cysteine methyl ester and 110 μL (102 mg, 1 mmol) of phenylacetylene were added. The yellow

solution was stirred for 30 minutes at r.t. and then filtered through silica gel, in order to remove the catalyst. Finally the solution was concentrated under vacuum and analyzed by NMR. The conversion was complete and a ratio of 90/10 of branched/linear hydrothiolation product was obtained. **S-(1-phenylvinyl)-N-Boc-L-cysteine-methylester**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.58 (d, J_{H-H} = 6.8, 2H, H_{o-Ph}), 7.23-7.18 (m, 3H, H_{m+p-Ph}), 5.70 (d, J_{H-H} = 8.4, 1H, NH), 5.44 and 5.38 (both s, 2H, =CH_2), 4.79 (dt, J_{H-H} = 8.4 J_{H-H} = 4.9, 1H, NCH), 3.34 (s, 3H, OCH_3), 3.14 and 2.97 (dd, J_{H-H} = 13.7, J_{H-H} = 4.9, 2H, SCH_2), 1.49 (s, 9H, CH_{3-tBu}). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (125.6 MHz, C_6D_6, 298 K): δ 171.0 (s, C-$\underline{C}$=O), 155.1 (s, N-$\underline{C}$=O), 144.1 (s, $\underline{C}$=CH_2), 139.3 (s, C_{q-Ph}), 128.5 (s, C_{p-Ph}), 128.4 (s, C_{m-Ph}), 127.5 (s, C_{o-Ph}), 113.3 (s, =$\underline{C}H_2$), 79.4 (s, C_{q-tBu}), 53.2 (s, N-$\underline{C}$H), 51.7 (s, O-$\underline{C}H_3$), 34.3 (s, S-$\underline{C}H_2$), 28.1 (s, $\underline{C}H_{3-tBu}$). **S-(2-phenylvinyl)-N-Boc-L-cysteine-methylester**. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.61 (d, J_{H-H} = 6.9, 2H, H_{o-Ph}), 7.25-7.15 (m, 3H, H_{m+p-Ph}), 6.65 (d, J_{H-H} = 15.6, 1H, S-C$\underline{H}$=), 6.59 (d, J_{H-H} = 15.6, 1H, =$\underline{H}$C-Ph), 5.73 (d, J_{H-H} = 8.0, 1H, NH), 4.81 (dt, J_{H-H} = 8.0-4.8, 1H, N-C$\underline{H}$), 3.38 (s, 3H, O-CH_3), 3.23 and 3.11 (dd, J_{H-H} = 14.1-4.8, 2H, S-CH_2), 1.47 (s, 9H, CH_{3-tBu}). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (125.6 MHz, C_6D_6, 298 K): δ 170.8 (s, C-$\underline{C}$=O), 155.0 (s, N-$\underline{C}$=O), 136.9 (s, C_{q-Ph}), 129.1 (Ph-$\underline{C}$H=CH), 128.6 (s, C_{m-Ph}), 127.1 (s, C_{p-Ph}), 125.8 (s, C_{o-Ph}), 121.6 (s, C=$\underline{C}$H-S), 79.5 (s, C_{q-tBu}), 53.8 (s, N-$\underline{C}$H), 51.9 (s, O-$\underline{C}H_3$), 35.4 (s, S-$\underline{C}H_2$), 28.0(s, $\underline{C}H_{3-tBu}$).

Preparation of Phenyl(1-(4-(trifluoromethyl)phenyl)vinyl)sulfane. The product was prepared as descrive for S-(phenylvinyl)-N-Boc-L-cysteine-methylester starting for 1-ethynyl-4-(trifluoromethyl)benzene (158 μL, 1 mmol). The reaction time was 4h, the conversion was complete and a ratio of 97/3 of branched/linear hydrothiolation product was obtained. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.53 (d, J_{H-H} = 8.1, 2H, $H_{2-Ph-CF3}$), 7.38 (m, 2H, H_{o-Ph-S}), 7.33 (d, J_{H-H} = 8.1, 2H, $H_{3-Ph-CF3}$), 7.05 (m, 2H, H_{m-Ph-S}), 6.99 (m, 1H, H_{p-Ph-S}), 5.51 and 5.39 (both s, C=C$\underline{H}_2$). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (125.6 MHz, C_6D_6, 298 K): δ 143.6 (s, $\underline{C}$=CH_2), 142.3 (s, $C_{1-Ph-CF3}$), 133.3 (s, C_{q-Ph-S}), 132.0 (s, C_{o-Ph-S}), 130.2 (q, J_{C-F} = 32.4, $C_{4-Ph-CF3}$), 129.2 (s, C_{m-Ph-S}), 127.6 (s, $C_{2-Ph-CF3}$), 127.5 (s, C_{p-Ph-S}), 125.3 (q, J_{C-F} = 3.8, $C_{3-Ph-CF3}$), 124.5 (q, J_{C-F} = 272.6, $\underline{C}F_3$), 117.61 (s, C=$\underline{C}H_2$). ^{19}F NMR (470 MHz, C_6D_6, 298K): δ -62.39 (s, CF_3).

Preparation of 1,6-bis((1-phenylvinyl)thio)hexane. The product was prepared as described for S-(phenylvinyl)-N-Boc-L-cysteine-methylester starting for 1,6-hexanedithiol (40 μL, 0.5 mmol) with a molar ratio 1,6-hexanedithiol:phenylacetilene = 1:2. The reaction time was 0,7 h, the conversion was complete and a ratio of 88/12 of branched-branched/branched-linear hydrothiolation product was obtained. **1,6-bis((1-phenylvinyl)thio)hexane**: ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.72 (dd, J_{H-H} = 8.1, J_{H-H} = 1.2, 4H, H_{o-Ph}), 7.3-7.1 (br, 6H, H_{m+p-Ph}), 5.51 and 5.24 (both s, 4H, C=C$\underline{H}_2$), 2.54, 1,50 and 1,17 (br, 12H, $CH_{2-alkylic}$). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (75.4 MHz, C_6D_6, 298 K): δ 145.8 (s $\underline{C}$=CH_2), 140.1 (s, C_{q-Ph}), 128.4 (s, C_{m-Ph}), 128.3 (s, C_{p-Ph}), 127.3 (s, C_{o-Ph}), 110.3 (s, C=$\underline{C}H_2$), 31.9, 28.4 and 28.3 (all s, $\underline{C}H_{2-Alkylic}$).

Standard catalytic conditions. In a NMR tube 0.01 equivalent of catalyst were dissolved in 0.5 mL of C_6D_6 and then 0.5

mmol of thiol and 0.5 mmol of alkyne were added. The alkyne conversion to vinyl sulfide and the conversion was quantified by integration of the ^{1}H-NMR spectrum. Reaction product formation was also monitored at periodic time intervals by using GC-MS analyses.

Molecular Structure Determination for complexes 2 and 3. Single crystals for the X-ray diffraction study of **2** and **3** were grown by slow diffusion of *n*-hexane into a saturated solution of the complexes in toluene. Intensity data for both complexes were collected at low temperature (100(2)K) 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 SADABS program.[49] The structures were solved by Patterson method and completed by successive difference Fourier syntheses. Refinements were carried out by full-matrix least-squares on F^2 with SHELXL-97,[50] including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms for the ethylene molecules in **2** were obtained from difference Fourier maps and refined as free isotropic atoms; the rest of hydrogens were included in calculated positions and refined as riding atoms. In the case of **3**, two regions of disorder were observed and modeled with two moieties with complementary occupancy factors. Only two residual peaks above 1.00 e$^-$/Å^3 were observed in **3**, but were located in close proximity of the rhodium atoms.

Crystal data for **2**: $C_{58}H_{80}Cl_2N_4Rh_2$, M = 1109.98, triclinic, space group $P\bar{1}$, orange crystal 0.191 x 0.186 x 0.154 mm, a = 10.2222(4), b = 12.2208(5), c = 13.5228(5) Å, α = 101.2870(5), β = 110.5192(5), γ = 111.5633(4)°, V = 1365.44(9) Å^3, Z = 1, μ(MoKα) = 0.742 mm^{-1}, D_{calc} = 1.35 g cm^{-3}, min & max. trans. factors 0.804 and 0.907. 16152 reflections measured (1.73 ≤ θ ≤ 30.52°, senθ/λ ≤ 0.715 Å^{-1}), 7570 independent reflections (R_{int} = 0.0161); number of data/restrains/parameters 7570/0/322. The final R_1 and $wR(F^2)$ values were 0.0216 and 0.0553 for $I > 2\sigma(I)$, and 0.0227 and 0.0560 for all data, respectively; S = 1.035 for all data.

Crystal data for **3**: $C_{40}H_{55}ClN_3Rh$, M = 716.26, triclinic, space group $P\bar{1}$, yellow crystal 0.213 x 0.161 x 0.057 mm, a = 10.374(3), b = 10.874(3), c = 17.559(4) Å, α = 85.301(3), β = 75.467(3), γ = 72.538(3)°, V = 1829.1(8) Å^3, Z = 2, μ(MoKα) = 0.571 mm^{-1}, D_{calc} = 1.301 g cm^{-3}, min & max. absorp. correc. factors 0.813 and 1.139. 18989 reflections measured (1.96 ≤ θ ≤ 26.37°, senθ/λ ≤ 0.625 Å^{-1}), 7439 independent reflections (R_{int} = 0.0667); number of data/restrains/parameters 7439/6/455. The final R_1 and $wR(F^2)$ values were 0.0570 and 0.1263 for $I > 2\sigma(I)$, and 0.0893 and 0.1372 for all data, respectively. The goodness of fit on F^2 was 1.006.

Computational Details. All the calculations have been performed with the Gaussian09 package[51] at the B3LYP level.[52] The rhodium atom was were represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set.[53] The remaining atoms (C, H, N, O, Cl, S) were represented by a 6-31G(d) basis set. Full optimizations of geometry without any constraint were performed, followed by analytical computation of the Hessian matrix to

confirm the nature of the stationary points as minima or transition structure on the potential energy surface.

Determination of rotational barriers. Full line-shape analysis of the dynamic ^{1}H NMR spectra of **2, 3, 4** and **6** were carried out using the program gNMR (Cherwell Scientific Publishing Limited). The transverse relaxation time, T_2, was estimated at the lowest temperature. Activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained by linear least-squares fit of the Eyring plot. Errors were computed by published methods.[48]

ASSOCIATED CONTENT

Crystalographic data and processing parameters for compounds **2** and **3**, determination of thermodynamic parameters of the equilibrium between **6** and **2**, cartesian coordinate for theoretical calculated compounds, and complete Reference 51. This material is available free of charge via the Internet at http://pubs.acs.org.

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