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

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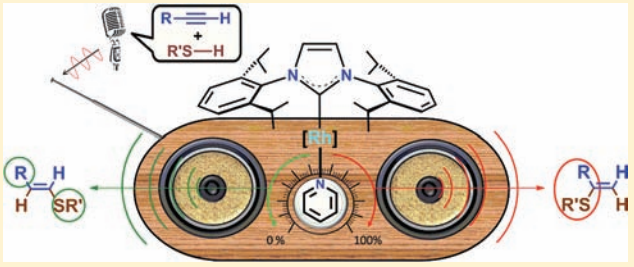
Supporting Information

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 formation of square-pyramidal thiolate−hydride active species in which the encumbered and powerful electron-donor IPr ligand directs coordination of pyridine trans to it, consequently blocking 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 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 migratory insertion of the alkyne into the rhodium−thiolate bond is the rate-determining step.

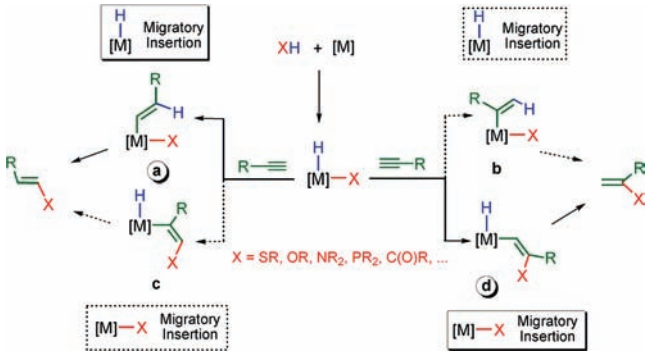


INTRODUCTION

Hydrothiolation of carbon−carbon multiple bonds is a direct and an atom economical method for 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, 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 a metal−hydride bond (**a**) gives rise to linear olefins (anti-Markovnikov or β-type products) whereas

Scheme 1. Pathways for Alkyne Migratory Insertion into M−H or M−X Bonds



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 valuable as synthetic intermedi-

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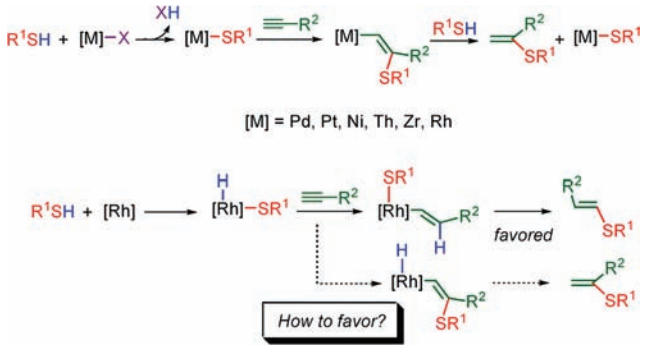
ates,[3] could be accomplished in a controlled manner if a method for directing alkyne insertion into metal−thiolate bonds is developed.

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 a hydride moiety (Scheme 2).[11−13,15c,21,22] In these catalytic systems the first step is

Scheme 2. Strategies Directed to Preparation of Branched Vinyl Sulfides



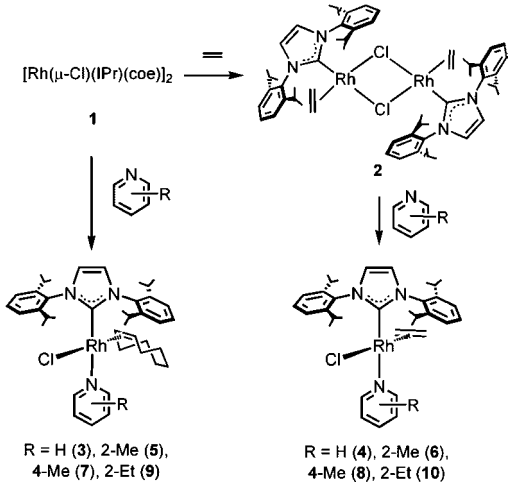
thiol-promoted protonolysis of an anionic ligand present in the precatalyst or alternatively formation of a bisthiolate complex accompanied with release of molecular hydrogen. However, in these cases it is difficult to inhibit formation of byproducts such as disulfide or bis(thio)alkenes. A priori, formation 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 does one 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, 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 formation of a 2,2-disubstituted alkenyl ligand and subsequently the branched vinyl sulfide. In particular, 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 elegantly shown for $Tp^*Rh(PPh_3)_2$ (Tp^* = hydrotris(3,5-dimethylpyrazolyl)-borate) by Love's group.[15b,d−f]

In order to succeed with our proposal, 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 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 stabilization of reactive intermediates but also for 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, this 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 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 $[Rh(\mu\text{-Cl})(NHC)(\eta^2\text{-olefin})]_2$[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. In particular, $[Rh(\mu\text{-Cl})(IPr)(\eta^2\text{-coe})]_2$ (**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 ethylene through a toluene solution of **1**, resulting in formation of the dimer $[Rh(\mu\text{-Cl})(IPr)(\eta^2\text{-}CH_2{=}CH_2)]_2$ (**2**) (Scheme 3), which was isolated as a yellow

Scheme 3. Synthesis of Rhodium−NHC Catalysts



solid in 92% yield. During preparation of the manuscript an alternative method for the synthesis of **2** was 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 $\mathbf{2}\cdot CH_2Cl_2$.[33]

Complex **2** showed dynamic behavior as evidenced in a ^1H 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 $\Delta H^{\ddagger}$ = 13.9 ± 0.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −1.3 ± 1.1 cal K^{-1} mol^{-1} for ethylene rotation and $\Delta H^{\ddagger}$ = 11.8 ± 0.4 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −1.5 ± 0.9 cal K^{-1} mol^{-1} for IPr rotation.

The chloro bridges in **1** and **2** were easily cleaved by nucleophilic pyridine ligands at room temperature, resulting in

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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 °C 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

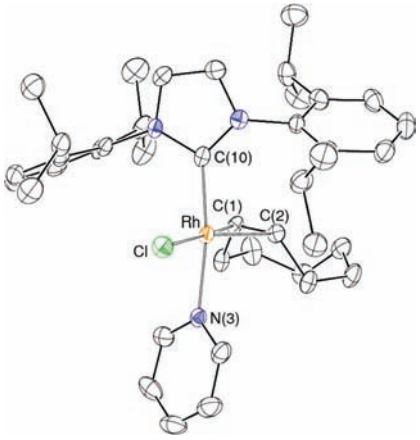

Figure 1. Molecular diagram of **3**. Selected bond lengths (Å) and angles (deg): Rh−Cl(1) 2.3886(13), Rh−N(3) 2.115(4), Rh−C(1) 2.149(4), Rh−C(2) 2.113(4), Rh−C(10) 1.986(4); Cl−Rh−N(3) 84.43(10), Cl−Rh−C(10) 86.21(12), Cl−Rh−Ct 166.02(14), N(3)−Rh−C(10) 169.36(15), N(3)−Rh−Ct 94.42(17), C(10)−Rh−Ct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

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]

The ^{1}H and ^{13}C{^{1}H} 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 ^{1}H VT-NMR study and the corresponding Eyring analysis were $\Delta H^{\ddagger}$ = 13.9 ± 0.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −1.7 ± 1.2 cal K^{-1} mol^{-1} for ethylene rotation and $\Delta H^{\ddagger}$ = 14.1 ± 0.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −0.7 ± 1.4 cal K^{-1} mol^{-1} for IPr rotation. The values obtained for rotation of ethylene in **4** are almost identical to that calculated for dimer **2**. In contrast, the barrier for rotation of IPr around the Rh−C axis in **4** is 2.3 kcal mol^{-1} higher than in **2**.

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** ($\Delta H^{\ddagger}$ = 15.1 ± 0.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −0.4 ± 1.9 cal K^{-1} mol^{-1}). Similar values for IPr rotation were calculated for complex **6** bearing a 2-picoline ligand ($\Delta H^{\ddagger}$ = 15.0 ± 0.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −1.6 ± 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

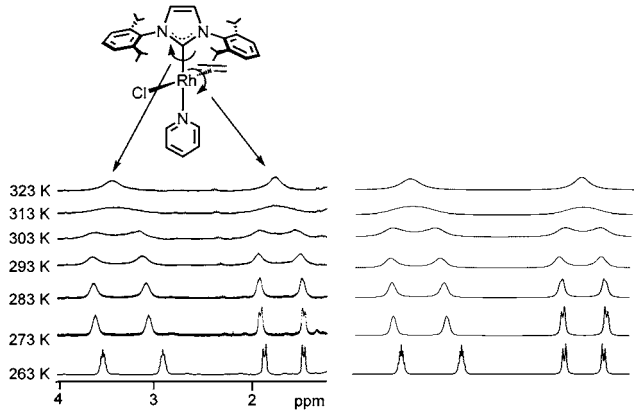

Figure 2. Variable-temperature ^{1}H NMR spectra of RhCl(IPr)-(pyridine)(η^2-ethylene) (**4**) in CD_2Cl_2 showing the coalescence of the CH−isopropyl and ethylene resonances: experimental (left) and calculated (right).

explained by hindered rotation of 2-picoline, which breaks the plane of symmetry.

The presence of a substituent in the 2-position of pyridine affects not only 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 ΔH° = 14.4 ± 0.5 kcal mol^{-1} and ΔS° = 32.5 ± 1.3 cal K^{-1} mol^{-1}. The process is endothermic, whereas the slightly positive ΔS° agrees well with an increase of internal disorder in the products

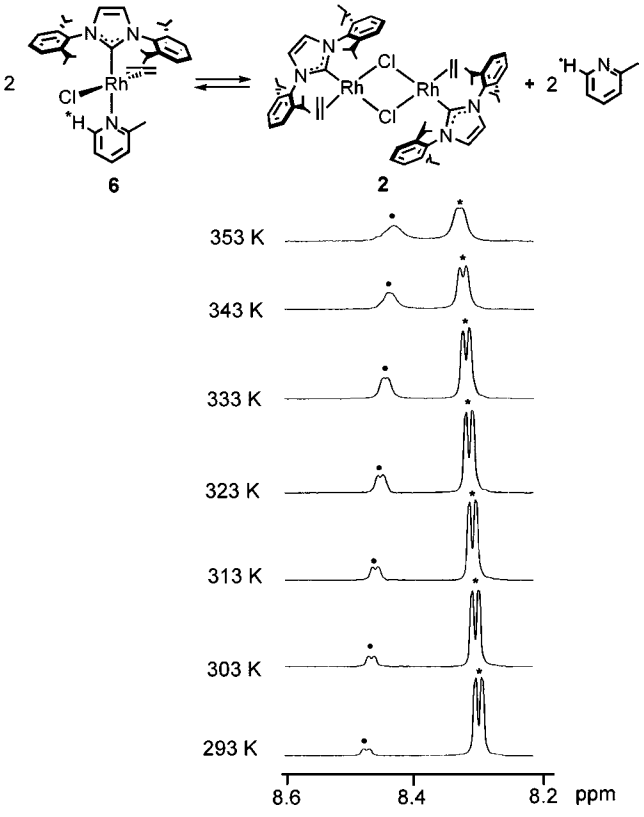

Figure 3. Variable-temperature ^{1}H NMR spectra in the *o*-pyridine proton region for the dynamic equilibrium between **6** and **2**.

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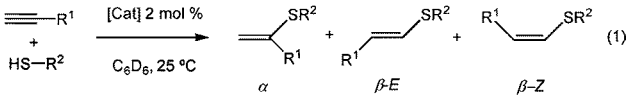
due to decoordination of 2-picoline. It seems clear that an ortho substituent on pyridine hinders coordination of the ligand to the metallic center. In accordance, the disubstituted 2,6-dimethylpyridine was found unable to cleave the chloro bridges in **1** and **2**.

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 studied that effect in the present transformation (eq 1).



(1)

Addition of thiophenol to phenylacetylene was chosen as the 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 °C 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 introduction of a IPr ligand compensates for the loss of activity. Then, other phosphane-free Rh−NHC derivatives were tested as catalyst 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.

Exchange of coe ligands by ethylene in dimer **2** enhanced the 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). In-situ addition of 1 equiv of pyridine to **1** and **2** gave similar results to **3** and **4**, respectively (entries 11 and 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 formation 37% of linear vinyl sulfides of mainly *Z* configuration probably via a 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, and 2-ethylpyridine ligands, respectively, was studied (entries 8, 9, and 10, respectively). Complex **8** gave

Table 1. Phenylacetylene Hydrothiolation with Thiophenol at 25 °C[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 	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]A 0.5 mL amount of C_6D_6 with 2 mol % of catalyst. [subs] = 1 M. [b]Determined at 50% conversion. [c]Yield of *β-Z*. [d]A 20 mol % of pyridine.

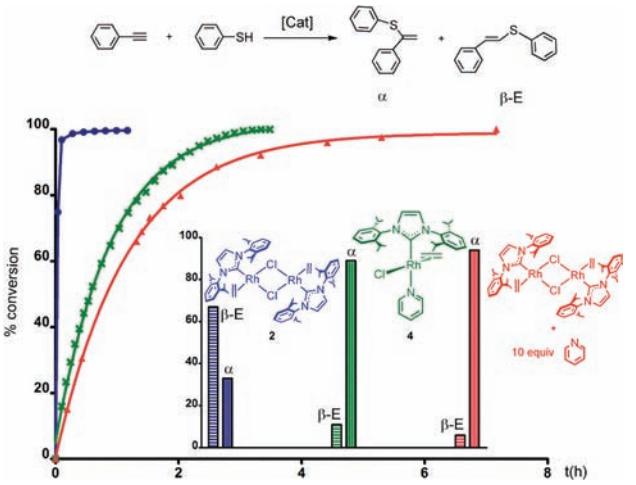


Figure 4. Catalytic activity and regioselectivity outcome in hydrothiolation of phenylacetylene with thiophenol for catalysts **2** (blue circles), **4** (green crosses), and **2** + 10 equiv of pyridine (red triangles).

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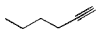
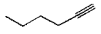
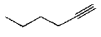
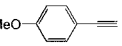
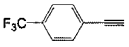
similar results to **4**, but catalysts **6** and **10**, bearing 2-substituted pyridines, showed a behavior between **2** and **4** in terms of both activity and selectivity. The hindered coordination of 2-picoline and 2-ethylpyridine, as shown in Figure 3, can be the reason for this result. Indeed, 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).

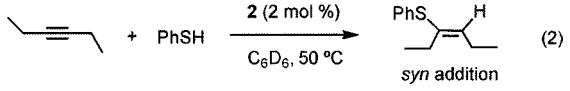
Compounds **1**−**4** are versatile catalyst precursors. They promote addition of thiophenol to different alkylic and aromatic alkynes (Table 2). The reaction rates for the alkylic

Table 2. Alkyne Hydrothiolation with Thiophenol[a]

Entry	Alkyne	Cat	T(°C)	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		**2** + 10 equiv py	25	18	99	10/90	7
9		**2** + 10 equiv py	25	4	99	3/97	45
10		**2** + 10 equiv py	50	18	99	10/90	7

[a]A 0.5 mL amount of C_6D_6 with 2 mol % of catalyst. [subs] = 1 M. [b]Exclusive formation of (*E*)-3-phenylsulfanyl-3-hexene.

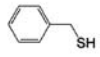
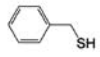
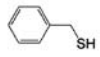
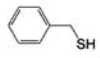
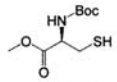
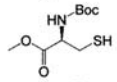
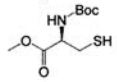
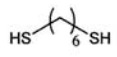
ones were lower than those observed for phenylacetylene, and thus, the reactions were performed at 50 °C. Strikingly, the "pyridine effect" on the regioselectivity was maintained. The amount of Markovnikov thioether product in the hydrothiolation of 1-hexyne was increased from 39/61 (**2**) to 22/78 using the pyridine complex **4** as catalyst (entries 1 and 2). Moreover, up to 96% of branched isomer was obtained using **2** + 10 equiv of pyridine as the 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 the complete chemoselectivity with exclusive addition of PhSH to the triple bond is noteworthy. 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. 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 a similar isomeric distribution (entry 10).

The scope of the catalysts was investigated using different thiols (Table 3). Again, the regioselectivity can be tuned by

Table 3. Hydrothiolation of Phenylacetylene with Different Thiols at 25 °C[a]

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

[a]A 0.5 mL amount of C_6D_6 with 2 mol % of catalyst. [subs] = 1 M. [b]Measured at full conversion. [c]Using 0.5 mol % of **2**. [d]Ratio between β-E,α and α,α.

pyridine addition. Benzyl hydrosulfide, $PhCH_2SH$, reacted much faster than PhSH (entries 1−4). In fact, full conversion was attained with **2** after the first recorded ^1H 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 previously shown for PhSH, catalyst **4** and the catalytic system **2** + 10 equiv of pyridine 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 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).

Mechanistic Proposal. A number of possible mechanisms for alkyne hydrothiolation have been postulated. The trans-addition products, β-Z vinyl sulfides, are mainly formed in the absence of catalyst via a radical pathway.[40] In our catalytic system inversion of regioselectivity promoted by pyridine addition does not proceed by radical intermediates as addition of a radical trap (BHT) did not influence either the activity or

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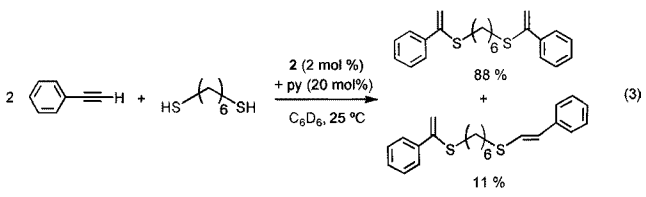

the selectivity. On the other hand, external attack of the thiol on a coordinated alkyne is unlikely as exclusive formation of the syn-addition *β-E* vinyl sulfide product was observed in the hydrothiolation of internal alkynes. In fact, we fail to detect any well-defined compound from addition of a 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, 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 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 °C to an NMR sample of **11** generated in situ led to smooth 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, 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 migratory insertion. Indeed, the observation that an electron-withdrawing group at the para position of the aromatic ring of phenylacetylene increases the activity is in accordance with this proposal. 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 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 with regard 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

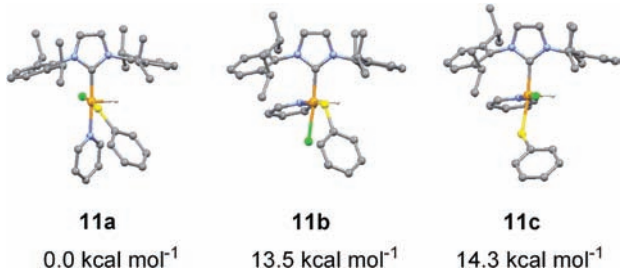

Figure 5. DFT-computed energies for the pentacoordinated square-pyramidal structures of **11**.

even decoordinates on increasing the steric demand on the NHC ligand.[44]

In contrast to the behavior observed for **3**, 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 a 1:2.5 ratio at 20 °C. The new saturated octahedral **11-py** results from coordination of pyridine ligand in **11**. A 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 ^{1}H 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, which shows the hydride region of the spectra, on lowering the temperature from 303 to 243 K the

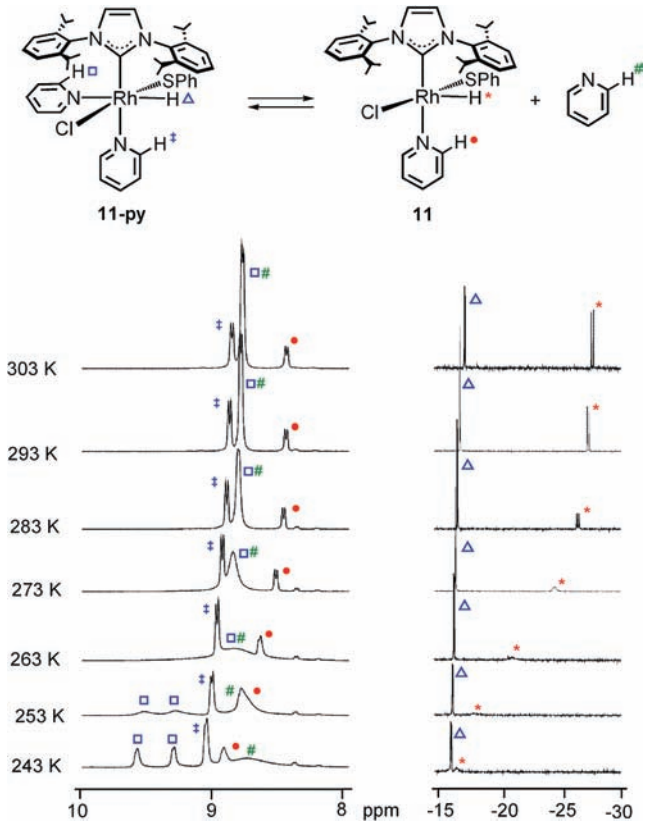

Figure 6. Stacked plot of variable-temperature ^{1}H NMR spectra in tol-d_8 in the *o*-pyridine (left) and hydride (right) regions of the equilibrium between **11** and **11-Py**.

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intensity of the hydride signal corresponding to **11** diminishes and shifts to lower field approaching 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** (red circles) integrate by 2 related to the hydride located at upfield shift, which suggests free rotation of the pyridine ligand that makes both *o*-protons equivalents. This resonance does not change much with temperature. In contrast, the ^{1}H NMR spectrum at 243 K of **11-py** displays three signals for the four 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 both *o*-pyridine protons of the ligand trans to IPr (blue daggers). In contrast, the signals corresponding to the pyridine ligand cis to IPr in **11-py** (blue squares) 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 (green pound signs). Interestingly, the hydride signal for **11** shifts to low field 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 saturation of the vacant site.[42]

Coordination of pyridine cis to IPr is not exclusively determined by the sterical pressure of the carbene ligand. Treatment of **1** with 1 equiv of benzylthiol and 3 equiv of pyridine per metal atom resulted in exclusive formation of a pyridine-saturated hydride complex RhClH(SCH$_2$Ph)(IPr)-(py)$_2$ (**12-py**) (Figure 7). The ^{1}H VT-NMR spectra of **12-py**

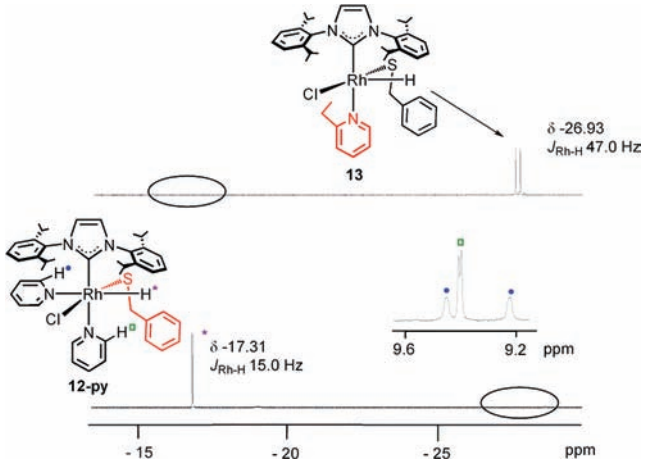
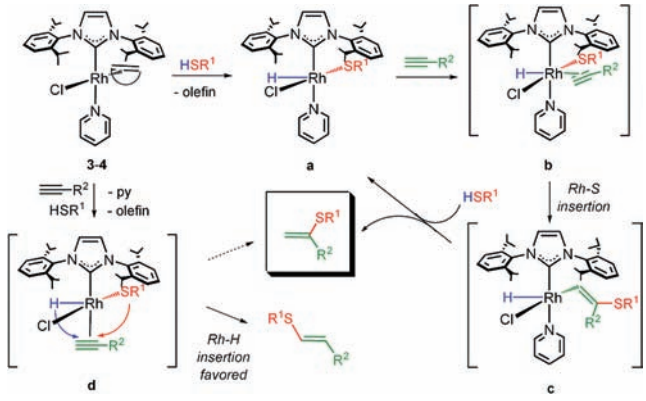


Figure 7. ^{1}H NMR spectra in tol-d_8 at 223 K for **12-py** (octahedral) and **13** (square pyramidal).

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 °C. In the *o*-pyridine region a doublet at 9.28 ppm (J_{H-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 formation of the saturated complex **13-py**, and thus, clean formation of square-pyramidal **13** was observed (δ −26.93 ppm, J_{Rh-H} = 47.0 Hz).

The unsaturated square-pyramidal species **a** similar to **11** is key for the explanation of the observed regioselectivity outcome (Scheme 4). The high trans influence of the hydride ligand

Scheme 4. Proposed Catalytic Cycle for the Regioselective Alkyne Hydrothiolation Leading to Branched Vinyl Sulfides



determines the stereochemistry of the complex and directs coordination of the incoming ligand (alkyne or pyridine) trans to it (**b**). Therefore, the alkyne is now located in cis disposition regarding thiolate ligand, thus favoring 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 to an increase of the concentration of **a** in the reaction media. Although formation of species such as **11-py** may retard alkyne coordination, resulting in an inferior catalytic activity, as observed for the catalytic system **2** + 10 equiv of pyridine, it could also help to prevent both decoordination of pyridine and isomerization of **a**, thus increasing the selectivity. In fact, decoordination of pyridine gives rise to a 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-substituted 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, driving the catalytic reaction through type **d** intermediates.

Consequently, a complex interplay between the 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

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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). To our knowledge, theoretical studies

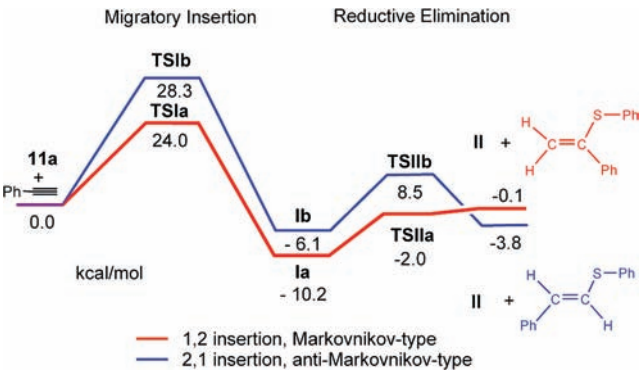

Figure 8. Computed potential-energy profile for the alkyne migratory insertion and reductive elimination for formation of vinyl sulfide.

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 the 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 the α or β carbon atom of the alkyne determines the configuration of the final product. Thus, both pathways for 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). The 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, formation of branched vinyl sulfides obtained via the 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).

It has been determined that 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 metallacyclobutene 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 (Rh–S) and 1.276 Å (C–C) in **TSIa** and 2.399 (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 (**TSIIb**) and −2.0 kcal mol^{-1} (**TSIIa**) being again the anti-Markovnikov pathway

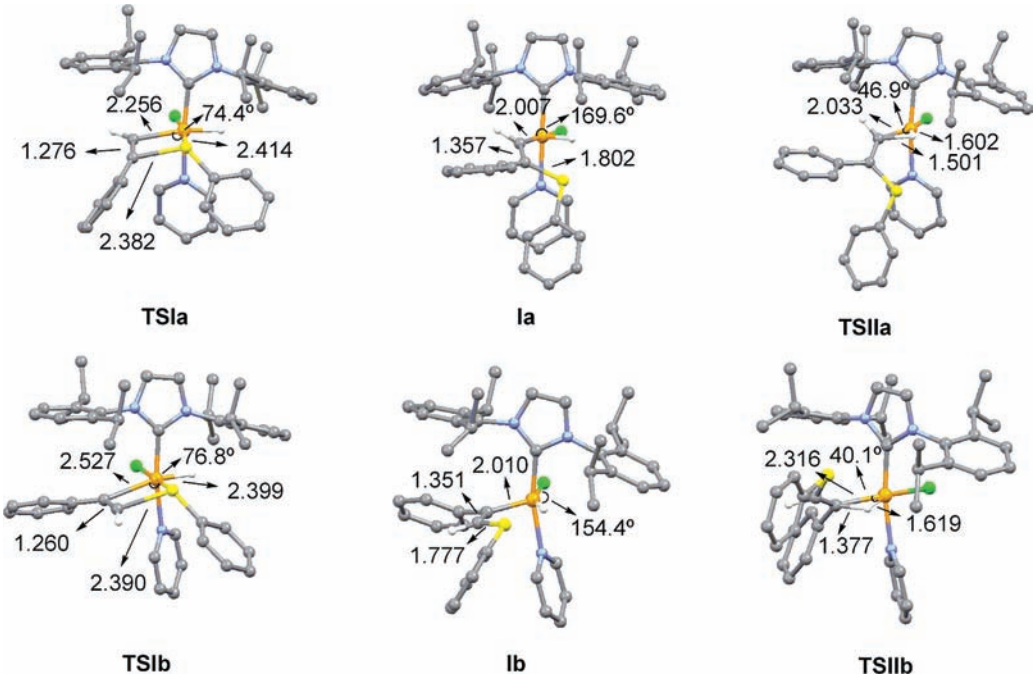

Figure 9. Optimized structures for the intermediates and transition states for migratory insertion and reductive elimination steps including selected distances (Å) and angles (deg).

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unfavorable. The final point corresponding to the unsaturated species RhCl(IPr) **II** and the respective coupled organic products is slightly more favorable for formation of linear vinyl sulfides (−3.8 vs −0.1 kcal mol^{-1}), although both pathways are thermodynamically less energetic that the starting point.

CONCLUSION

Herein we 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 mononuclear 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 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 coordination of the pyridine trans to it, consequently blocking 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 C−S bond formation. The energy difference of 4.3 kcal mol^{-1} favoring the 1,2- over the 2,1-migratory insertion fully accounts for the observed regioselectivity.

The findings reported herein could be useful for rational molecular design of new catalysts with improved regioselectivity in related addition processes such as hydroalkoxylation, hydrophosphination, hydroamination, or hydroacylation among others. With the aim to improve activity and selectivity, catalyst 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 a Varian Gemini 2000 Bruker ARX 300 MHz, Bruker Avance 400 MHz, or 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 × 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 precipitation of a yellow solid, which was washed with hexane (3 × 4 mL) and dried in vacuo. Yield: 240 mg (92%). Anal. Calcd for $C_{58}H_{80}N_4Cl_2Rh_2$: 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, C<u>H</u>Me$_{IPr}$), 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, CH<u>Me</u>$_{IPr}$). ^{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, <u>C</u>HMe$_{IPr}$), 25.8 and 23.3 (both s, CH<u>Me</u>$_{IPr}$).

*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 (200 μL, 2.47 mmol) and stirred at room temperature for 15 min. Then the solvent was evaporated to dryness, and subsequent addition of hexane caused precipitation of a yellow solid, which was washed with hexane (3 × 4 mL) and dried in vacuo. Yield: 280 mg (83%). Anal. Calcd for $C_{40}H_{55}N_3ClRh$: 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_6D_6, 298 K): δ 8.40 (d, J_{H-H} = 4.3, 2H, H$_{2\text{-}Py}$), 7.4−7.2 (m, 6H, H$_{Ph-IPr}$), 6.64 (s, 2H, =CHN), 6.55 (t, J_{H-H} = 5.4, 1H, H$_{4\text{-}Py}$), 6.20 (dd, J_{H-H} = 5.4, J_{H-H} = 4.3, 2H, H$_{3\text{-}Py}$), 4.52 and 2.61 (both sept, J_{H-H} = 6.4, 4H, C<u>H</u>Me$_{IPr}$), 3.12 (m, 2H, CH=CH$_{coe}$), 1.81, 1.47, 1.15, and 1.02 (all d, J_{H-H} = 6.4, 24H, CH<u>Me</u>$_{IPr}$), 1.8−0.8 (br, 12H, CH$_{2\text{-}coe}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (75.6 MHz, C_6D_6, 253 K): δ 183.3 (d, J_{C-Rh}= 54.0, Rh−C$_{IPr}$), 153.9 (s, C$_{2\text{-}Py}$), 149.3 and 146.6 (both s, C$_q$), 138.3 (s, C$_q$N), 135.1 (s, C$_{4\text{-}Py}$), 129.7, 128.9, 125.5, and 123.1 (all s, CH$_{Ph-IPr}$), 124.8 (s, =CHN), 122.9 (s, C$_{3\text{-}Py}$), 56.1 (d, J_{C-Rh} = 16.4, CH=CH$_{coe}$), 30.6, 30.4, and 27.3 (all s, CH$_{2\text{-}coe}$), 29.5 and 29.4 (both s, <u>C</u>HMe$_{IPr}$), 27.2, 27.1, 24.6, and 23.1 (all s, CH<u>Me</u>$_{IPr}$).

*Preparation of RhCl(IPr)(η^2-CH$_2$=CH$_2$)(py) (**4**).* The complex was prepared as described for **3** starting with **2** (300 mg, 0.270 mmol) and pyridine (220 μL, 2.72 mmol). Yield: 290 mg (85%). Anal. Calcd for $C_{34}H_{45}N_3ClRh$: 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$_{2\text{-}Py}$), 7.3−7.1 (m, 6H, H$_{Ph-IPr}$), 6.54 (s, 2H, =CHN), 6.46 (t, J_{H-H} = 5.5, 1H, H$_{4\text{-}Py}$), 6.08 (dd, J_{H-H} = 5.5, J_{H-H} = 4.5, 2H, H$_{3\text{-}Py}$), 4.09 and 3.08 (both sept, J_{H-H} = 6.5, 4H, C<u>H</u>Me$_{IPr}$), 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, CH<u>Me</u>$_{IPr}$). ^{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$_{2\text{-}Py}$), 148.1 and 145.4 (both s, C$_q$), 137.4 (s, C$_q$N), 134.5 (s, C$_{4\text{-}Py}$), 129.1, 128.4, 124.2, and 122.7 (all s, CH$_{Ph-IPr}$), 123.7 (s, =CHN), 122.5 (s, C$_{3\text{-}Py}$), 41.6 (d, J_{C-Rh} = 15.4, CH$_2$=CH$_2$), 28.9 and 28.7 (both s, <u>C</u>HMe$_{IPr}$), 26.3, 26.1, 23.9, and 22.9 (all s, CH<u>Me</u>$_{IPr}$).

*Preparation of RhCl(IPr)(η^2-coe)(2-picoline) (**5**).* The complex was prepared as described for **3** starting with **1** (300 mg, 0.236 mmol) and 2-picoline (230 μL, 2.329 mmol). Yield: 275 mg (80%). Anal. Calcd for $C_{41}H_{57}N_3ClRh$: 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_6D_6, 293 K): δ 8.43 (d, J_{H-H} = 5.2, 1H, H$_{6\text{-}Py}$), 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$_{4\text{-}Py}$), 6.34 (d, J_{H-H} = 7.6, 1H, H$_{3\text{-}Py}$), 6.21 (dd, J_{H-H} = 7.9, J_{H-H} = 5.2, 1H, H$_{5\text{-}Py}$), 4.96, 4.16, 2.83, and 2.20 (all sept, J_{H-H} = 6.4, 4H, C<u>H</u>Me$_{IPr}$), 3.07 (m, 2H, CH=CH$_{coe}$), 2.75 (s, 3H, H$_{CH3\text{-}Py}$), 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, CH<u>Me</u>$_{IPr}$), 1.8−0.8 (br, 12H, CH$_{2\text{-}coe}$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (75.6 MHz, C_6D_6, 293 K): δ 185.7 (d, J_{C-Rh}= 53.5, Rh−C$_{IPr}$), 162.1 (s, C$_{2\text{-}Py}$), 153.0 (s, C$_{6\text{-}Py}$), 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$_{4\text{-}Py}$), 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$_{3\text{-}Py}$), 119.9 (s, C$_{5\text{-}Py}$), 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$_{2\text{-}coe}$), 29.9, 29.7,

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29.2, and 29.0 (all s, $\underline{C}HMe_{IPr}$), 27.9, 27.3, 27.1, 26.7, 25.0, 24.1, 23.5, and 22.5 (all s, $CH\underline{Me}_{IPr}$), 26.9 (s, $C_{CH3\text{-}Py}$).

*Preparation of RhCl(IPr)(η^2-CH_2=CH_2)(2-picoline) (**6**).* The complex was prepared as described for **3** starting with **2** (300 mg, 0.270 mmol) and 2-picoline (270 μL, 2.734 mmol). Yield: 270 mg (77%). Anal. Calcd for $C_{35}H_{47}N_3ClRh$: 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, $H_{6\text{-}Py}$), 7.37−7.09 (m, 6H, $H_{Ph\text{-}IPr}$), 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, $H_{4\text{-}Py}$), 6.14 (d, J_{H-H} = 7.7, 1H, $H_{3\text{-}Py}$), 5.93 (dd, J_{H-H} = 8.0, J_{H-H} = 5.3, 1H, $H_{5\text{-}Py}$), 4.32, 4.05, 3.05, and 2.59 (all sept, J_{H-H} = 6.7, 4H, $C\underline{H}Me_{IPr}$), 2.58 (s, 3H, $H_{CH3\text{-}Py}$), 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, $CH\underline{Me}_{IPr}$). $^{13}C\{^1H\}$-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, $C_{2\text{-}Py}$), 151.7 (s, $C_{6\text{-}Py}$), 149.5 and 147.2 (both s, C_q), 137.4 (s, C_qN), 134.7 (s, $C_{4\text{-}Py}$), 129.1, 128.4, 125.4, and 122.8 (all s, CH_{Ph-IPr}), 124.1 (s, $C_{3\text{-}Py}$), 123.9 (s, =CHN), 120.5 (s, $C_{5\text{-}Py}$), 43.7 (d, J_{C-Rh} = 16.6, CH_2=CH_2), 25.4 (s, $C_{CH3\text{-}Py}$), 29.1 and 28.9 (both s, $\underline{C}HMe_{IPr}$), 26.6, 26.1, 23.7, and 23.2 (all s, $CH\underline{Me}_{IPr}$).

*Preparation of RhCl(IPr)(η^2-coe)(4-picoline) (**7**).* The complex was prepared as described for **3** starting with **1** (300 mg, 0.236 mmol) and 4-picoline (230 μL, 2.329 mmol). Yield: 280 mg (81%). Anal. Calcd for $C_{41}H_{57}N_3ClRh$: 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, $H_{2\text{-}Py}$), 7.42−6.97 (m, 6H, H_{Ph-IPr}), 6.65 (s, 2H, =CHN), 6.08 (d, J_{H-H} = 5.7, 2H, $H_{2\text{-}Py}$), 4.46 and 2.61 (both sept, J_{H-H} = 6.3, 4H, $C\underline{H}Me_{IPr}$), 3.05 (m, 2H, CH=CH_{coe}), 1.75, 1.46, 1.14, and 1.03 (all d, J_{H-H} = 6.3, 24H, $CH\underline{Me}_{IPr}$), 1.7−0.8 (br, 12H, $CH_{2\text{-}coe}$), 1.50 (s, 3H, $H_{CH3\text{-}Py}$). $^{13}C\{^1H\}$-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, $C_{2\text{-}Py}$), 149.1 and 146.1 (both s, C_q), 146.2 (s, $C_{4\text{-}Py}$), 138.0 (s, C_qN), 129.7, 128.5, 125.0, and 122.7 (all s, CH_{Ph-IPr}), 124.4 (s, =CHN), 123.5 (s, $C_{3\text{-}Py}$), 55.4 (d, J_{C-Rh} = 16.5, CH=CH_{coe}), 30.3, 30.0, and 27.0 (all s, $CH_{2\text{-}coe}$), 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, $CH_{3\text{-}Py}$).

*Preparation of RhCl(IPr)(η^2-CH_2=CH_2)(4-picoline) (**8**).* The complex was prepared as described for **3** starting with **2** (300 mg, 0.270 mmol) and 4-picoline (270 μL, 2.734 mmol). Yield: 277 mg (79%). Anal. Calcd for $C_{35}H_{47}N_3ClRh$: 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_6D_6, 298 K): δ 8.23 (d, J_{H-H} = 6.0, 2H, $H_{2\text{-}Py}$), 7.34−7.00 (m, 6H, H_{Ph-IPr}), 6.60 (s, 2H, =CHN), 5.97 (d, J_{H-H} = 6.0, 2H, $H_{3\text{-}Py}$), 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, $H_{CH3\text{-}Py}$). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (100.6 MHz, C_6D_6, 298 K): δ 184.6 (d, J_{C-Rh}= 53.7, Rh−C_{IPr}), 151.8 (s, $C_{2\text{-}Py}$), 147.4 and 147.2 (s, C_q), 146.8 (s, $C_{4\text{-}Py}$), 138.3 (s, C_qN), 130.1 and 128.7 (all s, CH_{Ph-IPr}), 124.8 (s, =CHN), 124.7 (s, $C_{3\text{-}Py}$), 42.1 (d, J_{C-Rh} = 16.9, CH_2=CH_2), 29.6 and 29.4 (both s, $\underline{C}HMe_{IPr}$), 26.8, 26.6, 24.1, 26.6 (both s, $CH\underline{Me}_{IPr}$), 20.5 (s, $C_{CH3\text{-}Py}$).

*Preparation of RhCl(IPr)(η^2-coe)(2-ethylpyridine) (**9**).* The complex was prepared as described for **3** starting with **1** (300 mg, 0.236 mmol) and 2-ethylpyridine (270 μL, 2.36 mmol). Yield: 285 mg (81%). Anal. Calcd for $C_{42}H_{59}N_3ClRh$: 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, $H_{6\text{-}Py}$), 7.38−6.99 (m, 6H, H_{Ph-IPr}), 6.63 (dd, J_{H-H} = 8.9, J_{H-H} = 7.8, 1H, $H_{4\text{-}Py}$), 6.62 and 6.54 (both d, J_{H-H} = 1.4, 2H, =CHN), 6.39 (d, J_{H-H} = 7.8, 1H, $H_{3\text{-}Py}$), 6.20 (dd, J_{H-H} = 8.9, J_{H-H} = 5.3, 1H, $H_{5\text{-}Py}$), 4.93, 3.98, 3.11, and 2.90 (all sept, J_{H-H} = 6.6, 4H, $C\underline{H}Me_{IPr}$), 3.65 and 3.34 (both dq, J_{H-H} = 15.2, J_{H-H} = 7.5, 2H, $CH_{2\text{-}Py}$), 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, $CH_{2\text{-}coe}$), 1.03 (dd, J_{H-H} = 7.5, J_{H-H} = 7.5, 3H, $CH_{3\text{-}Py}$). $^{13}C\{^1H\}$-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, $C_{2\text{-}Py}$), 152.3 (s, $C_{6\text{-}Py}$), 148.7, 148.6, 146.2, and 146.1 (all s, C_q), 137.9 and 137.2 (both s, C_qN), 134.8 (s, $C_{4\text{-}Py}$), 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, $C_{3\text{-}Py}$), 119.6 (s, $C_{5\text{-}Py}$), 58.3, 51.6 (both d, J_{C-Rh} = 16.0, CH=CH_{coe}), 32.9 (s, $CH_{2\text{-}Py}$), 30.9, 30.4, 29.5, 29.4, 26.8, and 26.7 (all s, $CH_{2\text{-}coe}$), 29.5, 29.2, 28.7, and 28.5 (all s, $\underline{C}HMe_{IPr}$), 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, $CH_{3\text{-}Py}$).

*Preparation of RhCl(IPr)(η^2-CH_2=CH_2)(2-ethylpiridine) (**10**).* The complex was prepared as described for **3** starting with **2** (300 mg, 0.270 mmol) and 2-ethylpyridine (310 μL, 2.71 mmol). Yield: 315 mg (86%). Anal. Calcd for $C_{37}H_{53}N_3ClRh$: 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, $H_{6\text{-}Py}$), 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, $H_{4\text{-}Py}$), 6.27 (d, J_{H-H} = 7.7, 1H, $H_{3\text{-}Py}$), 6.09 (dd, J_{H-H} = 9.0, J_{H-H} = 5.1, 1H, $H_{5\text{-}Py}$), 4.42, 3.94, 3.15, and 2.45 (all sept, J_{H-H} = 6.6, 4H, $C\underline{H}Me_{IPr}$), 3.60 and 3.06 (both dq, J_{H-H} = 15.1,, J_{H-H} = 7.6, 2H, $CH_{2\text{-}Py}$), 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, $CH_{3\text{-}Py}$). $^{13}C\{^1H\}$-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, $C_{2\text{-}Py}$), 151.6 (s, $C_{6\text{-}Py}$), 148.7, 148.4, 146.2, and 145.7 (all s, C_q), 137.6 and 137.2 (both s, C_qN), 135.0 (s, $C_{4\text{-}Py}$), 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, $C_{3\text{-}Py}$), 120.9 (s, $C_{5\text{-}Py}$), 44.5 and 36.9 (both d, J_{C-Rh} = 17.3, CH_2=CH_2), 31.8 (s, $CH_{2\text{-}Py}$), 29.4, 29.2, 28.8, and 28.6 (all s, $\underline{C}HMe_{IPr}$), 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, $CH_{3\text{-}Py}$).

*In-Situ Preparation of RhClH(SPh)(IPr)(py) (**11**).* A solution of **3** (23 mg, 0.032 mmol) in C_6D_6 (0.5 mL, NMR tube) at 20 °C was treated with thiophenol (2.3 μL, 0.034 mmol). ^{1}H NMR (500 MHz, C_6D_6, 293 K): δ 8.96 (d, J_{H-H} = 5.0, 2H, $H_{2\text{-}Py}$), 7.42−6.88 (m, 11H, H_{Ph}), 6.85 (s, 2H, =CHN), 6.26 (d, J_{H-H} = 7.6, 1H, $H_{4\text{-}Py}$), 5.95 (dd, J_{H-H} = 7.6−5.0, 2H, $H_{3\text{-}Py}$), 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 °C was treated with pyridine (8 μL, 0.102 mmol) and thiophenol (2.3 μL, 0.034 mmol). ^{1}H NMR was immediately recorded at low temperature. A mixture of **11** and **11-py** was observed in a 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, $H_{o\text{-}Py\text{-}A}$), 9.06 (br, 2H, $H_{o\text{-}Py\text{-}B}$), 7.40−6.40 (br, 11H, H_{Ph} and =CHN), 6.62 (br, 1H, $H_{p\text{-}Py\text{-}A}$), 6.24 (br, 1H, $H_{p\text{-}Py\text{-}B}$), 6.51 and 6.07 (both br, 2H, $H_{m\text{-}Py\text{-}A}$), 6.06 (br, 2H, $H_{m\text{-}Py\text{-}B}$), 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_2Ph)(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 °C was treated with pyridine (8 μL, 0.102 mmol) and benzylthiol (3.6 μL, 0.034 mmol). ^{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, $H_{o\text{-}Py\text{-}A}$), 9.44 (d, J_{H-H} = 5.2, 2H, $H_{o\text{-}Py\text{-}B}$), 7.40−6.90 (m, 11H, H_{Ph}), 6.72 and 6.49 (both br, 2H, =CHN), 6.61 (br, 1H, $H_{p\text{-}Py\text{-}A}$), 6.43 (br, 1H, $H_{p\text{-}Py\text{-}B}$), 6.42 and 5.96 (both br, 2H, $H_{m\text{-}Py\text{-}A}$), 6.24 (br, 2H, $H_{m\text{-}Py\text{-}B}$), 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_2S), 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_2Ph)(IPr)(2-Etpy) (**13**).* A solution **10** (19 mg, 0.026 mmol) in toluene-d_8 (0.5 mL, NMR-tube) at −50 °C was treated with benzylthiol (3 μL, 0.028 mmol). ^{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, $H_{6\text{-}Py}$), 7.40−7.00 (m, 11H, H_{Ph}), 6.60 (dd, J_{H-H} = 8.7, J_{H-H} = 7.6, 1H, $H_{4\text{-}Py}$), 6.59 and 6.56 (both br, 2H, =CHN), 6.20 (d, J_{H-H} = 7.6, 1H, $H_{3\text{-}Py}$), 6.02 (dd, J_{H-H} = 8.7, J_{H-H} = 5.0, 1H, $H_{5\text{-}Py}$), 3.82, 3.80, 3.50, and 3.31 (all sept, J_{H-H} = 6.2, 4H, $C\underline{H}Me_{IPr}$), 2.48−2.42 (m, 2H, $CH_{2\text{-}Py}$), 2.78 and 2.49 (both d, J_{H-H} = 12.5, 2H, CH_2S), 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, $CH_{3\text{-}Py}$), −26.93 (d, J_{Rh-H} = 47.0, 1H, Rh−H).

Preparation of S-(Phenylvinyl)-N-Boc-L-cysteine-methylester. A Schlenk tube containing 1 mL of toluene was charged with 11.1 mg

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(0.01 mmol) of catalyst **2**; 16 μL of pyridine (15.6 mg, 0.2 mmol), 200 μL (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 min at room temperature and then filtered through silica gel in order to remove the catalyst. Finally, the solution was concentrated under vacuum and analyzed by NMR. 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, $H_{o\text{-}Ph}$), 7.23−7.18 (m, 3H, $H_{m+p\text{-}Ph}$), 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, $CH_{3\text{-}tBu}$). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (125.6 MHz, C_6D_6, 298 K): δ 171.0 (s, C−C=O), 155.1 (s, N−C=O), 144.1 (s, C=CH_2), 139.3 (s, $C_{q\text{-}Ph}$), 128.5 (s, $C_{p\text{-}Ph}$), 128.4 (s, $C_{m\text{-}Ph}$), 127.5 (s, $C_{o\text{-}Ph}$), 113.3 (s, =CH_2), 79.4 (s, $C_{q\text{-}tBu}$), 53.2 (s, N−CH), 51.7 (s, O−CH_3), 34.3 (s, S−CH_2), 28.1 (s, $CH_{3\text{-}tBu}$).

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, $H_{o\text{-}Ph}$), 7.25−7.15 (m, 3H, $H_{m+p\text{-}Ph}$), 6.65 (d, J_{H-H} = 15.6, 1H, S−CH=), 6.59 (d, J_{H-H} = 15.6, 1H, =HC−Ph), 5.73 (d, J_{H-H} = 8.0, 1H, NH), 4.81 (dt, J_{H-H} = 8.0−4.8, 1H, N−CH), 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, $CH_{3\text{-}tBu}$). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (125.6 MHz, C_6D_6, 298 K): δ 170.8 (s, C−C=O), 155.0 (s, N−C=O), 136.9 (s, $C_{q\text{-}Ph}$), 129.1 (Ph-CH=CH), 128.6 (s, $C_{m\text{-}Ph}$), 127.1 (s, $C_{p\text{-}Ph}$), 125.8 (s, $C_{o\text{-}Ph}$), 121.6 (s, C=CH−S), 79.5 (s, $C_{q\text{-}tBu}$), 53.8 (s, N−CH), 51.9 (s, O−CH_3), 35.4 (s, S−CH_2), 28.0(s, $CH_{3\text{-}tBu}$).

Preparation of Phenyl(1-(4-(trifluoromethyl)phenyl)vinyl)sulfane. The product was prepared as described for *S*-(phenylvinyl)-*N*-Boc-L-cysteine-methylester starting with 1-ethynyl-4-(trifluoromethyl)-benzene (158 μL, 1 mmol). The reaction time was 4 h, 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, $H_{2\text{-}Ph-CF3}$), 7.38 (m, 2H, $H_{o\text{-}Ph\text{-}S}$), 7.33 (d, J_{H-H} = 8.1, 2H, $H_{3\text{-}Ph-CF3}$), 7.05 (m, 2H, $H_{m\text{-}Ph\text{-}S}$), 6.99 (m, 1H, $H_{p\text{-}Ph\text{-}S}$), 5.51 and 5.39 (both s, C=CH_2). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (125.6 MHz, C_6D_6, 298 K): δ 143.6 (s, C=CH_2), 142.3 (s, $C_{1\text{-}Ph-CF3}$), 133.3 (s, $C_{q\text{-}Ph\text{-}S}$), 132.0 (s, $C_{o\text{-}Ph\text{-}S}$), 130.2 (q, J_{C-F} = 32.4, $C_{4\text{-}Ph-CF3}$), 129.2 (s, $C_{m\text{-}Ph\text{-}S}$), 127.6 (s, $C_{2\text{-}Ph-CF3}$), 127.5 (s, $C_{p\text{-}Ph\text{-}S}$), 125.3 (q, J_{C-F} = 3.8, $C_{3\text{-}Ph-CF3}$), 124.5 (q, J_{C-F} = 272.6, CF_3), 117.61 (s, *C* = CH_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 with 1,6-hexanedithiol (40 μL, 0.5 mmol) with a molar ratio of 1,6-hexanedithiol:phenylacetilene = 1:2. The reaction time was 0.7 h, conversion was complete, and a ratio of 88/12 of branched-branched/branched-linear hydrothiolation product was obtained. ^{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, $H_{o\text{-}Ph}$), 7.3−7.1 (br, 6H, $H_{m+p\text{-}Ph}$), 5.51 and 5.24 (both s, 4H, C=CH_2), 2.54, 1,50 and 1,17 (br, 12H, $CH_{2\text{-}alkylic}$). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (75.4 MHz, C_6D_6, 298 K): δ 145.8 (s C=CH_2), 140.1 (s, $C_{q\text{-}Ph}$), 128.4 (s, $C_{m\text{-}Ph}$), 128.3 (s, $C_{p\text{-}Ph}$), 127.3 (s, $C_{o\text{-}Ph}$), 110.3 (s, C=CH_2), 31.9, 28.4, and 28.3 (all s, $CH_{2\text{-}Alkylic}$).

Standard Catalytic Conditions. In a NMR tube 0.01 equiv of catalyst was dissolved in 0.5 mL of C_6D_6, and then 0.5 mmol of thiol and 0.5 mmol of alkyne were added. Alkyne conversion to vinyl sulfide and conversion was quantified by integration of the ^{1}H NMR spectrum. Reaction product formation was also monitored at periodic time intervals using GC-MS analyses.

Molecular Structure Determination for Complexes 2 and 3. Single crystals for 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 semi-empirical absorption correction was applied using the SADABS program.[49] Structures were solved by the 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 the 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 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 × 0.186 × 0.154 mm, a = 10.2222(4) Å, b = 12.2208(5) Å, 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(Mo Kα) = 0.742 mm^{-1}, D_{calcd} = 1.35 g cm^{-3}, min and max transmission factors 0.804 and 0.907, 16 152 reflections measured (1.73 ≤ θ ≤ 30.52°, sin θ/λ ≤ 0.715 Å^{-1}), 7570 independent reflections (R_{int} = 0.0161); number of data/restraints/parameters 7570/0/322. 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 × 0.161 × 0.057 mm, a = 10.374(3) Å, b = 10.874(3) Å, 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(Mo Kα) = 0.571 mm^{-1}, D_{calcd} = 1.301 g cm^{-3}, min and max abs correction factors 0.813 and 1.139, 18 989 reflections measured (1.96 ≤ θ ≤ 26.37°, sin θ/λ ≤ 0.625 Å^{-1}), 7439 independent reflections (R_{int} = 0.0667); number of data/restraints/parameters 7439/6/455. 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 calculations have been performed with the Gaussian09 package[51] at the B3LYP level.[52] The rhodium atom was 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 structures on the potential energy surface.

Determination of Rotational Barriers. Full line-shape analyses 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 $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by linear least-squares fit of the Eyring plot. Errors were computed by published methods.[48]

■ ASSOCIATED CONTENT

Supporting Information

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

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Meng, D.; Chen, W.; Zhao, W. *J. Nat. Prod.* **2004**, *70*, 824. (b) Sader, H. S.; Johnson, D. M.; Jones, R. N. *Antimicrob. Agents Chemother.* **2004**, *48*, 53. (c) Szilágyi, Á; Fenyvesi, F.; Mayercsik, O.; Pelyvás, I. S.; Bácskay, I.; Fehér, P.; Váradi, J.; Vecsernyés, M.; Herczegh, P. *J. Med. Chem.* **2006**, *49*, 5626.

(2) (a) Dvorak, C. A.; Schmitz, W. D.; Poon, D. J.; Pryde, D. C.; Lawson, J. P.; Amos, R. A.; Meyers, A. I. *Angew. Chem., Int. Ed.* **2000**, *39*, 1664. (b) Ceruti, M; Balliano, G.; Rocco, F.; Milla, P.; Arpicco, S.; Cattel, L.; Viola, F. *Lipids* **2001**, *36*, 629. (c) Johannesson, P.; Lindeberg, G.; Johansson, A.; Nikiforovich, G. V.; Gogoll, A.; Synnergren, B.; LeGrèves, M.; Nyberg, F.; Karlén, A.; Hallberg, A. *J. Med. Chem.* **2002**, *45*, 1767.

(3) Schaumann, E. *Top. Curr. Chem.* **2007**, *274*, 1.

(4) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075.

(5) (a) Chou, S.-S. P; Wey, S.-J. *J. Org. Chem.* **1990**, *55*, 1270. (b) Surasani, S. R.; Peddinti, R. K. *Tetrahedron Lett.* **2011**, *52*, 4615.

(6) (a) Boaz, N. W.; Fox, K. M. *J. Org. Chem.* **1993**, *58*, 3042. (b) Majumdar, K. C.; Kundu, U. K.; Ghosh, S. K. *Org. Lett.* **2002**, *4*, 2629. (c) Fernandez de la Pradilla, R.; Tortosa, M.; Viso, A. *Top. Curr. Chem.* **2007**, *275*, 103. (d) Liu, Z.; Mehta, S. J.; Lee, K.-S.; Grossman, B.; Qu, H; Gu, X.; Nichol, G. S.; Hruby, L. J. *J. Org. Chem.* **2012**, *77*, 1289.

(7) Mizuno, H.; Domon, K.; Masuya, K.; Tanino, K.; Kuwajima, I. *J. Org. Chem.* **1999**, *64*, 2648.

(8) (a) Liu, Z.; Rainier, J. D. *Org. Lett.* **2005**, *7*, 131. (b) Macnaughtan, M. L.; Gary, J. B.; Gerlach, D. L.; Johnson, M. J. A.; Kampf, J. W. *Organometallics* **2009**, *28*, 2880.

(9) (a) Sabarre, A.; Love, J. *Org. Lett.* **2008**, *10*, 3941. (b) Braun, M.-G.; Zard, S. Z. *Org. Lett.* **2011**, *13*, 776. (c) Jin, W.; Du, W.; Yang, Q.; Yu, H.; Chen, J.; Yu, Z. *Org. Lett.* **2011**, *13*, 4272. (d) Zhu, Y.; Xie, M.; Dong, S.; Zhao, X.; Lin, L.; Liu, X.; Feng, X. *Chem.—Eur. J.* **2011**, *17*, 8202. (e) Cui, Y.; Floreancing, P. E. *Org. Lett.* **2012**, *14*, 1720.

(10) McDonald, J. V.; Corbin, J. L.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2056.

(11) (a) Kuniyasu, H.; Ogawa, A.; Sato, K.-I.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902. (b) Bäckvall, J.-E. *J. Org. Chem.* **1994**, *59*, 5850. (c) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, J. *J. Am. Chem. Soc.* **1999**, *121*, 5108. (d) Kondoh, A.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2007**, *9*, 1383. (e) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P.; Khrustalev, V. N.; Antipin, M. Y.; Timofeeva, T. V. *J. Am. Chem. Soc.* **2007**, *129*, 7252. (f) Mitamura, T.; Daitou, M.; Nomoto, A.; Ogawa, A. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 413.

(12) (a) Ogawa, A.; Kawakami, J.-I.; Mihara, M.; Ikeda, T.; Sonoda, N.; Irao, T. *J. Am. Chem. Soc.* **1997**, *119*, 12380. (b) Ananikov, V. P.; Beletskaya, I. P. *Pure Appl. Chem.* **2007**, *79*, 1041.

(13) (a) Han, L.-B.; Zhang, C.; Yazawa, H.; Shimada, S. *J. Am. Chem. Soc.* **2004**, *126*, 5080. (b) Ananikov, V. P.; Orlov, L. V.; Beletskaya, I. P. *Organometallics* **2006**, *25*, 1970. (c) Malyshev, D. A.; Scott, N. M.; Marion, N.; Stevens, E. D.; Ananikov, V. P.; Beletskaya, I. P.; Nolan, S. P. *Organometallics* **2006**, *25*, 4462. (d) Ananikov, V. P.; Gayduck, K. A.; Orlov, N. V.; Beletskaya, I. P.; Khrustalev, V. N.; Antipin, M. Y. *Chem. Eur.* **2010**, *16*, 2063.

(14) Koelle, U.; Rietmann, C.; Tjoe, J.; Wagner, T.; Englert, U. *Organometallics* **2005**, *14*, 703.

(15) (a) Burling, S.; Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P. *Dalton Trans.* **2003**, 4181. (b) Cao, C.; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614. (c) Misumi, Y.; Seino, H.; Mizobe, Y. *J. Organomet. Chem.* **2006**, *691*, 3157. (d) Fraser, L. R.; Bird, J.; Wu, Q.; Cao, C.; Patrick, B. O.; Love, J. A. *Organometallics* **2007**, *26*, 5602. (e) Shoai, S.; Bichler, P.; Kang, B.; Buckley, H.; Love, J. A. *Organometallics* **2007**, *26*, 5778. (f) Yang, J.; Sabarre, A.; Fraser, L. R.; Patrick, B. O.; Love, J. A. *J. Org. Chem.* **2009**, *74*, 182. (g) Yang, Y.; Rioux, R. M. *Chem. Commun.* **2011**, *47*, 6557. (h) Liu, J.; Lam, J. W. Y.; Jin, C. K. W.; Ng, J. C. Y.; Shi, J.; Su, H.; Yeung, K. F.; Hong, Y.; Faisal, M.; Yu, Y.; Wong, K. S.; Tang, B. Z. *Macromolecules* **2011**, *44*, 68. (i) Zhao, H.; Peng, J.; Cai, M. *Catal. Lett.* **2012**, *142*, 138.

(16) Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P. *Dalton Trans.* **2009**, 3599.

(17) Delp, S. A.; Munro-leighton, C.; Goj, L. A.; Ramírez, M. A.; Gunnoe, T. B.; Petersen, J. L.; Boyle, P. D. *Inorg. Chem.* **2007**, *46*, 2365.

(18) Corma, A.; González-Arellano, C.; Iglesias, M.; Sánchez, F. *Appl. Catal., A* **2010**, *375*, 49.

(19) Higuchi, Y.; Atobe, S.; Tanaka, M.; Kamiya, I.; Yamamoto, T.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Organometallics* **2011**, *30*, 4539.

(20) Yadav, J. S.; Reddy, B. V. S.; Raju, A.; Ravindar, K.; Baishya, G. *Chem. Lett.* **2007**, *36*, 1474.

(21) Weiss, C. J.; Marks, T. J. *J. Am. Chem. Soc.* **2010**, *132*, 1053.

(22) (a) Weiss, C. J.; Wobser, S. D.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 2062. (b) Weiss, C. J.; Wobser, S. D.; Marks, T. J. *Organometallics* **2010**, *29*, 6308.

(23) (a) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 379. (b) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368. (c) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596.

(24) Examples where reductive elimination is proposed as the key step: (a) Ghosh, R.; Zhang, X.; Achord, P.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2007**, *129*, 853. (b) Hyatt, I. F. D.; Anderson, H. K.; Morehead, A. T., Jr.; Sargent, A. L. *Organometallics* **2008**, *27*, 135. (c) González-Rodríguez, C.; Pawley, R. J.; Chaplin, A. B.; Thompson, A. L.; Weller, A. S.; Willis, M. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 5134.

(25) (a) Bassetti, M.; Casellato, P.; Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Martín-Vaca, B. *Organometallics* **1997**, *16*, 5470. (b) Marchenko, A. V.; Gérard, H.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 1244. (c) Li, X.; Vogel, T.; Incarvito, D.; Crabtree, R. H. *Organometallics* **2005**, *24*, 62. (d) Di Tommaso, S.; Tognetti, V.; Sicilia, E.; Adamo, C.; Ruso, N. *Inorg. Chem.* **2010**, *49*, 9875.

(26) Some examples of 2,1 alkyne addition into a M-H bond: (a) Weng, W.; Parking, S.; Ozerov, O. V. *Organometallics* **2006**, *25*, 5345. (b) She, L.; Li, X.; Sun, H.; Ding, J.; Frey, M.; Klein, H.-F. *Organometallics* **2007**, *26*, 566.

(27) (a) Ohtaka, A.; Kuniyasu, H.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2002**, *124*, 14324. (b) Ogata, K.; Toyota, A. *J. Organomet. Chem.* **2007**, *692*, 4139.

(28) Sola, E.; García-Campubí, A.; Andrés, J. L.; Martín, M.; Plou, P. *J. Am. Chem. Soc.* **2010**, *132*, 9111.

(29) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Praetorius, J. M.; Crudden, C. M. *Dalton Trans.* **2008**, 4079. (c) Arduengo, A. J., III; Iconaru, L. I. *Dalton Trans.* **2009**, 6903. (d) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612.

(30) (a) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543. (b) Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402. (c) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343. (d) Herrmann, W. A.; Öfele, K.; Schneider, S. K.; Herdtweck, E.; Hoffmann, S. D. *Angew. Chem., Int. Ed.* **2006**, *45*, 3859. (e) Würtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523. (f) Jiménez, M. V.; Pérez-Torrente, J. J.; Bartolomé, M. I.; Gierz, V.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2008**, *27*, 224. (g) Zhu, Y.; Fan, Y.; Burgess, K. *J. Am. Chem. Soc.* **2010**, *132*, 6249. (h) Malik, H. A.; Surmunen, G.

J.; Montgomery, J. *J. Am. Chem. Soc.* **2010**, *132*, 6304. (i) Ho, C.-Y.; He, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 9182.
(31) (a) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516. (b) Yu, X. Y.; Patrick, B. O.; James, B. R. *Organometallics* **2006**, *25*, 4870. (c) Yu, X.-Y.; Sun, H.; Patrick, B. O.; James, B. R. *Eur. J. Inorg. Chem.* **2009**, 1752. (d) Zenkina, O. V.; Keske, E. C.; Wang, R.; Crudden, C. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 8100.
(32) (a) Di Giuseppe, A.; Castarlenas, R.; Pérez-Torrente, J. J.; Lahoz, F. J.; Polo, V.; Oro, L. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 3938. (b) Palacios, L.; Miao, X.; Di Giuseppe, A.; Pascal, S.; Cunchillos, C.; Castarlenas, R.; Pérez-Torrente, J. J.; Lahoz, F. J.; Dixneuf, P. H.; Oro, L. A. *Organometallics* **2011**, *30*, 5208.
(33) Zenkina, O. V.; Keske, E. C.; Wang, R.; Crudden, C. M. *Organometallics* **2011**, *30*, 6423.
(34) (a) Cramer, R. *J. Am. Chem. Soc.* **1964**, *86*, 217. (b) Wickeneiser, E. B.; Cullen, W. R. *Inorg. Chem.* **1990**, *29*, 4671. (c) Tejel, C.; Villoro, J. M.; Ciriano, M. A.; López, J. A.; Eguizábal, E.; Lahoz, F. J.; Bahkmutov, V. I.; Oro, L. A. *Organometallics* **1996**, *15*, 2967. (d) Friedman, L. A.; Meiere, S. H.; Brooks, B. J.; Harman, W. D. *Organometallics* **2001**, *20*, 1699. (e) Albietz, P. J.; Cleary, B. P.; Paw, W.; Eisenberg, R. *Inorg. Chem.* **2002**, *41*, 2095. (f) McBee, J. L.; Escalada, J.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 12703.
(35) (a) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663. (b) Burling, S.; Douglas, S.; Mahon, M. F.; Nama, D.; Pregosin, P. S.; Whittlesey, M. K. *Organometallics* **2006**, *25*, 2642. (c) Ritleng, V.; Barth, C.; Brenner, E.; Milosevic, S.; Chetcuti, M. J. *Organometallics* **2008**, *27*, 4223. (d) Vélez, C. L.; Markwick, P. R. L.; Holland, R. L.; DiPasquale, A. G.; Rheingold, A. L.; O'Connor, J. M. *Organometallics* **2010**, *29*, 6695. (e) Ragone, F.; Poater, A.; Cavallo, L. *J. Am. Chem. Soc.* **2010**, *132*, 4249. (f) Busetto, L; Cassani, M. C.; Femoni, C.; Mancinelli, M.; Mazzanti, A.; Mazzoni, R.; Solinas, G. *Organometallics* **2011**, *30*, 5258.
(36) (a) Krug, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 2694. (b) Bontemps, S.; Gornitzka, H.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1611.
(37) (a) Selent, D.; Scharfenberg-Pfeiffer, D.; Reck, G.; Taube, R. *J. Organomet. Chem.* **1991**, *415*, 417. (b) Hahn, C.; Sieler, J.; Taube, R. *Polyhedron* **1998**, *17*, 1183. (c) Nguyen, D. H.; Pérez-Torrente, J. J.; Lomba, L.; Jiménez, M. V.; Lahoz, F. J.; Oro., L. A. *Dalton Trans.* **2011**, *40*, 8429.
(38) Rubio, M.; Suárez, A.; del Rio, E.; Galindo, A.; Álvarez, E.; Pizzano, A. *Organometallics* **2009**, *28*, 547.
(39) Lee, S. I.; Park, S. Y.; Park, J. H.; Jung, I. G.; Choi, S. Y.; Chung, Y. K.; Lee, B. Y. *J. Org. Chem.* **2006**, *71*, 91.
(40) (a) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1035. (b) Kondoh, A.; Takami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2005**, *70*, 6468. (c) Hoyle, C. E.; Bowman, C. N. *Angew. Chem., Int. Ed. Engl.* **2010**, *49*, 1540.
(41) (a) Mueting, A. M.; Boyle, P.; Pignolet, L. H. *Inorg. Chem.* **1984**, *23*, 44. (b) Osakada, K.; Hataya, K.; Yamamoto, T. *Inorg. Chem.* **1993**, *32*, 2360. (c) Osakada, K.; Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3271. (d) Circu, V.; Fernandes, M. A.; Carlton, L. *Polyhedron* **2003**, *22*, 3293.
(42) (a) Evans, D. R.; Huang, M.; Senagish, W. M.; Chege, E. W.; Lam, Y.-F.; Fettinger, J. C.; Williams, T. N. *Inorg. Chem.* **2002**, *41*, 2633. (b) Seino, H.; Yoshikawa, T.; Hidai, M.; Mizobe, Y. *Dalton Trans.* **2004**, 3593. (c) Oster, S. S.; Grochowski, M. R.; Lachicotte, R. J.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2010**, *29*, 4923. (d) Jiménez, M. V.; Lahoz, F. J.; Lukešová, L.; Miranda, J. R.; Modrego, F. J.; Nguyen, D. H.; Oro, L. A.; Pérez-Torrente, J. J. *Chem.—Eur. J.* **2011**, *17*, 8115.
(43) (a) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442. (b) Kuznetsov, V. F.; Lough, A. J.; Gusev, D. G. *Inorg. Chim. Acta* **2006**, *359*, 2806. (c) Salem, H.; Shimon, L. J. W.; Leitus, G.; Weiner, L.; Milstein, D. *Organometallics* **2008**, *27*, 2293. (d) Findlater, M.; Cartwright-Sykes, A.; White, P.; Schauer, C. K.; Brookhart, M *J. Am. Chem. Soc.* **2011**, *133*, 12274.
(44) (a) Sandford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314. (b) Urbina-Blanco, C. A.; Leitgeb, A.; Slugovc, C.; Bantreil, X.; Clavier, H.; Slawin, A. M. Z.; Nolan, S. P. *Chem.—Eur. J.* **2011**, *17*, 5045.
(45) (a) Rappert, T.; Nürnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156. (b) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089.
(46) (a) Schollhammer, P.; Cabon, N.; Capon, J.-F.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Organometallics* **2001**, *20*, 1230. (b) Ikada, T.; Mizobe, Y.; Hidai, M. *Organometallics* **2001**, *20*, 4441. (c) Kuniyasu, H.; Yamashita, F.; Terao, J.; Kambe, N. *Angew. Chem Int. Ed.* **2007**, *46*, 5929.
(47) (a) Sharpless, K. B.; Patrick, D. W.; Truesdale, L. K.; Biller, S. A. *J. Am. Chem. Soc.* **1975**, *97*, 2305. (b) Romão, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197. (c) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 6750. (d) Kamiya, I.; Nishinaka, E.; Ogawa, A. *J. Org. Chem.* **2005**, *70*, 696. (e) Emmert, M. H.; Cook, A. K.; Xie, Y. J.; Sanford, M. S. *Angew. Chem., Int. Ed. Engl.* **2011**, *50*, 9409. (f) Ye, X.; Liu, G.; Popp, B. V.; Stahl, S. S. *J. Org. Chem.* **2011**, *76*, 1031.
(48) (a) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 1383. (b) Zheng, W.; Ariafard, A.; Lin, Z. *Organometallics* **2008**, *27*, 246. (c) Wang, M.; Cheng, L.; Wu, Z. *Dalton Trans.* **2008**, 3879.
(49) (a) *SADABS: Area Detector Absorption Correction*; Bruker-AXS: Madison, WI, 1996. (b) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
(50) Sheldrick, G. M. *SHELXL-97 Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, 1997.
(51) Firsch, M. J.; et al. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2004. The full reference is given in the Supporting Information.
(52) Lee, C.; Parr, R. G.; Yang, W. *Phys. Rev. B* **1988**, *37*, B785. Becke, A. D. *J. Phys. Chem.* **1993**, *98*, 64.
(53) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
(54) Morse, P. M.; Spencer, M. O.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.