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Hydroxo–Rhodium–N-Heterocyclic Carbene Complexes as Efficient Catalyst Precursors for Alkyne Hydrothiolation

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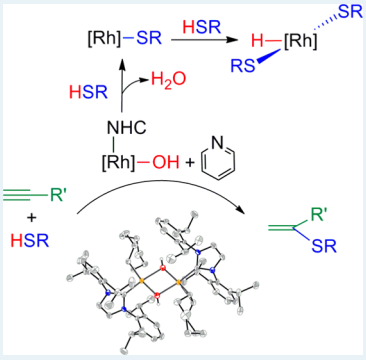
Supporting Information

ABSTRACT: The new Rh–hydroxo dinuclear complexes stabilized by an N-heterocyclic carbene (NHC) ligand of type $[Rh(\mu\text{-}OH)(NHC)(\eta^2\text{-olefin})]_2$ (coe, IPr (**3**), IMes (**4**); ethylene, IPr (**5**)) are efficient catalyst precursors for alkyne hydrothiolation under mild conditions, presenting high selectivity toward α-vinyl sulfides for a varied set of substrates, which is enhanced by pyridine addition. The structure of complex **3** has been determined by X-ray diffraction analysis. Several intermediates relevant for the catalytic process have been identified, including Rh^{I}-thiolato species $Rh(SCH_2Ph)(IPr)(\eta^2\text{-coe})(py)$ (**6**) and $Rh(SCH_2Ph)(IPr)(\eta^2\text{-HC}{\equiv}CCH_2Ph)(py)$ (**7**), and the Rh^{III}-hydride-dithiolato derivative $RhH(SCH_2Ph)_2(IPr)(py)$ (**8**) as the catalytically active species. Computational DFT studies reveal an operational mechanism consisting of sequential thiol deprotonation by the hydroxo ligand, subsequent S–H oxidative addition, alkyne insertion, and reductive elimination. The insertion step is rate-limiting with a 1,2 thiometalation of the alkyne as the more favorable pathway in accordance with the observed Markovnikov-type selectivity.



KEYWORDS: *homogeneous catalysis, N-heterocyclic carbene, rhodium, hydroxides, hydrothiolation, DFT calculations*

INTRODUCTION

The development of new and efficient transition-metal catalyzed transformations still continues to push forward organic synthesis and material science. That great level of success has been achieved mainly due to a detailed study of the factors that govern the reactivity of catalytic intermediate species whose understanding is essential in order to rationally design active and selective catalysts.[1] In this context, metal-alkoxides, and particularly hydroxides, represent a versatile type of derivatives that exhibit highly valuable catalytic applications as well as interesting utility as precursors for further elaborated organometallic complexes.[2] Metal-hydroxides can be directly involved in catalysis as key intermediates for several oxygen nucleophile additions,[3] or, alternatively, they can play the role of initiator, behaving as an internal base that triggers varied transformations such as hydrogenations,[4] arylations,[5] alkynylations,[6] and cyclizations,[7] among others.[8] Moreover, metal-hydroxo species are relevant synthetic organometallic precursors,[9] as well as intermediates in water-splitting processes[10] or advanced materials with interesting properties.[11]

The relative scarcity of late transition metal–hydroxo complexes[12] can be in part ascribed to the weakness of the M–OH bond due to a mismatch between the hard base nature of the hydroxo ligand and the soft acid character of the metal center.[2f] However, it has been shown that a bulky and powerful electron-donor ligand such as an N-heterocyclic carbene (NHC)[13] can stabilize these types of derivatives.[4c,5h,8c,9d,14] Following our interest in the development of selective organic transformations mediated by Rh–NHC catalysts,[15] and particularly on alkyne hydrothiolation[16] as a direct and an atom economical method for the preparation of vinyl sulfides,[17] we envisage the application of Rh–NHC–hydroxo derivatives as promising catalysts for this transformation. In this context, it is interesting to point out that the selectivity toward branched or lineal derivatives can be modulated as a function of the nature of the active organometallic catalyst.[18,19] If the more common catalytic alkyne hydrothiolation mechanism is operative, which encompasses thiol oxidative addition, alkyne insertion, and reductive elimination, the formation of vinyl sulfides can be achieved through *four* catalytic pathways, which arise from consecutive oxidative addition of the thiol to the metallic center and subsequent 1,2 or 2,1 insertion of the alkyne into Rh–H or Rh–SR bonds (Scheme 1). It becomes evident that the understanding of the factors that govern the

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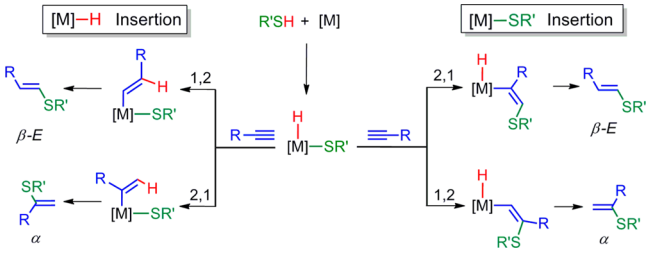
Scheme 1. Insertion Pathways for the Control of the Regioselectivity in Alkyne Hydrothiolation

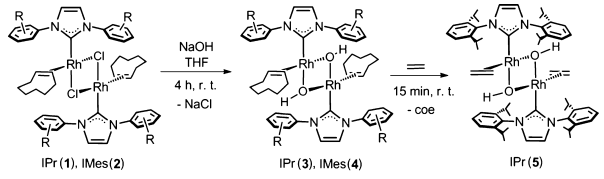


elemental steps of each divergent route is fundamental for the control of the selectivity outcome. In this direction, we have recently found that the addition of pyridine to Rh−NHC precursors directs the coordination of the alkyne *trans* to the hydride ligand, and consequently *cis* to the Rh−SR bond, thus blocking the hydrometalation pathways and allowing for the selective formation of α-vinyl sulfide via 1,2 insertion within the thiometalation route.[15f] Now, we report herein on the synthesis and catalytic application in alkyne hydrothiolation of new Rh−NHC−hydroxo complexes with particular emphasis on their influence on the reaction mechanism induced by the presence of the hydroxo bridging ligands in the catalyst precursors in comparison with the related chlorido bridged counterparts.

RESULTS AND DISCUSSION

Preparation of Rh−NHC−Hydroxo Complexes. Precedents for Rh^{I}−hydroxo derivatives stabilized by an NHC ligand of type Rh(cod)(NHC)(OH) (cod = 1,5-cyclooctadiene) have been very recently disclosed by the Nolan group.[5h,8e] Our interest was to prepare Rh^{I}−hydroxo complexes bearing labile mono-olefin ligands, such as ethylene or cyclooctene (coe), that presumably could be more active in alkyne hydrothiolation with regard to the cod counterparts, as previously shown in our group for the halogenated derivatives.[15f] Thus, treatment of the chlorido bridged $[Rh(\mu\text{-Cl})(NHC)(\eta^2\text{-coe})]_2$[20] (NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-carbene (IPr), **1**; 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-carbene (IMes), **2**) with NaOH in THF led to the hydroxo bridged dinuclear complexes $[Rh(\mu\text{-OH})(NHC)(\eta^2\text{-coe})]_2$ (IPr (**3**), IMes (**4**)), which were isolated as very air-sensitive yellow solids in 63% and 51% yields, respectively (Scheme 2). Mono-olefin was exchanged by

Scheme 2. Preparation of Rhodium Hydroxo-Bridge Dinuclear Compounds 3, 4, and 5



simply bubbling ethylene through a toluene solution of **3** to generate $[Rh(\mu\text{-OH})(IPr)(\eta^2\text{-ethylene})]_2$ (**5**) in 69% isolated yield. The more noticeable resonances in the ^1H NMR spectra of **3**−**5** are those corresponding to the hydroxo-bridges between −3.3 and −4.2 ppm. The $^{13}C\{^1H\}$ NMR spectra confirmed the presence of the corresponding carbene and η^2-olefin ligands. The dinuclear formulation of the complexes was further confirmed by an X-ray diffraction study of **3** (Figure 1).

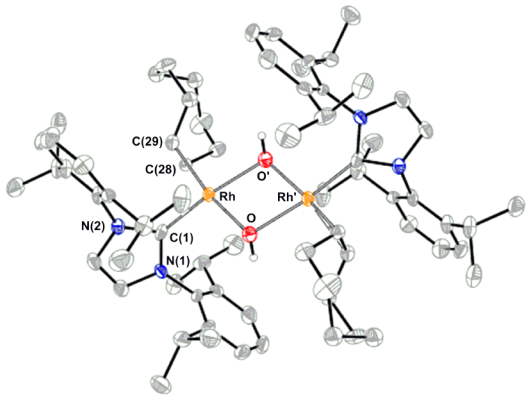


Figure 1. Molecular diagram of **3**. Selected bond lengths (Å) and angles (deg): Rh−C(1) 1.935(6), Rh−O 2.077(4), Rh−O′ 2.113(4), Rh−C(28) 2.095(6), Rh−C(29) 2.099(6), C(28)−C(29) 1.419(8); O−Rh−O′ 75.4(2), C(1)−Rh−O 97.9(2), C(1)−Rh−O′ 172.9(2).

Complex **3** displays slightly distorted square-planar rhodium centers with the NHC ligands disposed *anti* to each other and the wingtips of the IPr and the η^2-coe moiety located out of plane. The bridging Rh_2O_2 core is asymmetric, presenting different Rh−O bond distances of 2.077(4) and 2.113(4) Å, as in other Rh−NHC dinuclear complexes.[15f,21] The rhodium−carbene separation [Rh−C(1) 1.935(6) Å] compares well with previously reported rhodium−NHC single bond distances.[13b]

Catalytic Alkyne Hydrothiolation. The catalytic performance of complexes **3**−**5** in alkyne hydrothiolation was examined. The addition of thiophenol to phenylacetylene was chosen as a benchmark reaction. A 1:1 alkyne/thiol catalytic sample was monitored in an NMR tube in 0.5 mL of C_6D_6 using 2 mol % loading of the catalyst (Table 1 and Figure 2).

Table 1. Phenylacetylene Hydrothiolation with Thiophenol (1:1)[a]

Entry	Catalyst	aditive[b]	t(h)	Conversion %[c]	α/β-E	$TOF_{1/2}$
1	**3**	-	17	89	79/21	29
2	**3**		15	95	92/8	10
3	**4**	-	17	96	62/38	13
4	**4**		17	70	85/15	6
5	**5**	-	14	99	82/18	41
6	**5**		14	91	94/6	28
7	**3**	 + α-TH[d]	15	96	90/10	-

[a]Reaction conditions: 0.5 mL of C_6D_6, 2 mol % of catalyst, 25 °C, [alkyne] = [thiol] = 1.0 M. [b]10 equiv per mole of metal. [c]Formation of α + β-*E*-vinyl sulfides relative to phenylacetylene. [d]α-Terpinene.

The thiol was consumed after 17 h at 25 °C when using compound **3** as a catalyst precursor (Table 1, entry 1). The main product was the α-vinyl sulfide, but the selectivity reached only 79%. The formation of around 6% disulfide was detected by GC-MS analysis. The Rh-IMes catalyst **4** displayed lower catalytic activity and selectivity but also showed a decrease in the formation of disulfide (Table 1, entry 3). In contrast, catalyst **5**, bearing η^2-ethylene ligands, was more active and selective, showing a turnover frequency calculated at 50% conversion ($TOF_{1/2}$) of 41 h^{-1}. Although relatively low selectivity was attained, a clear tendency toward the α-isomer

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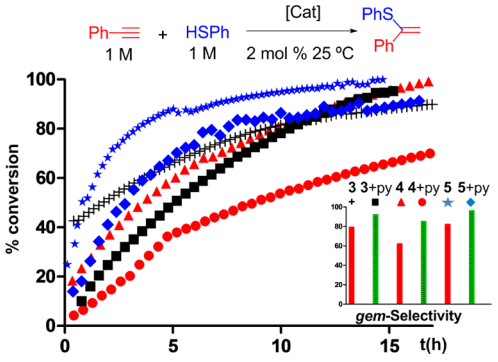


Figure 2. Monitoring of phenylacetylene hydrothiolation with thiophenol catalyzed by **3**−**5**, in the presence or absence of pyridine.

was observed for the hydroxo catalysts, in marked contrast to the chlorido bridged counterparts **1** and **2** with which only around 30% α-vinyl sulfide was obtained.[15f] We have previously shown that the addition of pyridine to Rh-NHC based catalytic systems results in a remarkable increase of selectivity toward *gem* products probably as a result of the stabilization of intermediate species.[15f,j,22] Pleasingly, selectivity toward α-vinyl sulfide was increased by the addition of 10 equiv of pyridine, up to 96% for **5**, although with a slight reduction in the catalytic activity (Table 1, entries 2, 4, 6, Figure 2). Moreover, the addition of pyridine reduced the formation of disulfide to trace amounts (<0.5%). Addition to α-terpinene (α-TH) as a radical scavenger to a catalytic sample of **3** and 10 equiv of pyridine did not significantly affect either the activity or the selectivity, thus excluding a mechanism via radical species operating with our catalytic system (Table 1, entry 7). Indeed, the absence of any β-Z-vinyl sulfide isomer throughout this study gives further evidence that the metal catalyst is not competing with a significant radical side reaction.

The performance of hydroxo-catalyst precursor **3** with 10 equiv of pyridine was studied for a wide range of alkynes and thiols (Table 2). In general, selectivity to α-vinyl sulfide was very high, except for 1-ethynyl-1-cyclohexene and 2-ethynylpyridine, although catalytic activity was lower than that found for phenylacetylene and thiophenol. Aliphatic alkynes such as 1-hexyne and benzylacetylene afforded 86% and 93% Markovnikov-type addition products without isomerization to internal olefins (Table 2, entries 2 and 3). The presence of a heteroatom in the alkyne substituent does not hamper catalytic activity. For instance, propargyl methyl ether reacted with thiophenol with a conversion of 91% after 21 h and 91% selectivity to α-vinyl sulfide (Table 2, entry 4). In contrast, hydrothiolation of 2-ethynylpyridine showed an opposite selectivity toward the β-Z isomer (89%), which was not detected for other substrates throughout this study (Table 2, entry 5). Coordination of the pyridine moiety of the alkyne to the rhodium active species probably accounts for that unexpected result. Preferred hydrothiolation of a triple over a double C−C bond was observed for 1-ethynyl-1-cyclohexene, although with poor selectivity (Table 2, entry 6). Aliphatic thiols also reacted efficiently (Table 2, entries 7−9); particularly, hydrothiolation of a doubly protected cysteine derivative showed the highest selectivity of 95%. Interestingly, functionalization of cysteine is an important goal for the synthesis of biologically active derivatives.

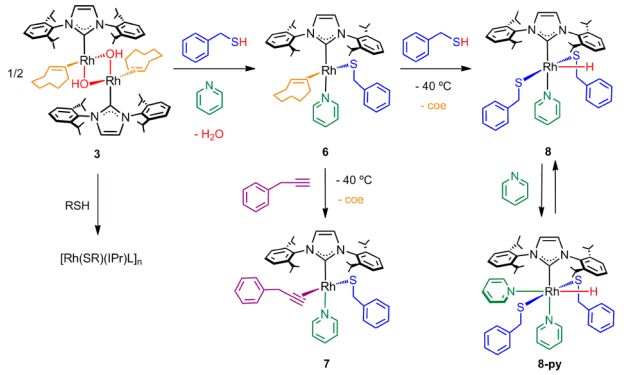
Table 2. Alkyne Hydrothiolation with 3 + 10 equiv py[a]

Entry	Alkyne	Thiol	t(h)	Conversion %	α/β-*E*
1			15	95	92/8
2			24	53	86/14
3			21	89	93/7
4			21	91	91/9
5			24	89	0/11/89[b]
6			24	50	66/34
7			24	53	86/14
8			22	98	95/5
9			22	91	91/9

[a]Reaction conditions: 0.5 mL of C_6D_6, 2 mol % of catalyst **3** plus 10 equiv of pyridine per mole of metal, 25 °C, [alkyne] = [thiol] = 1.0 M. [b]β-Z isomer.

Mechanistic Studies. In order to disclose the mechanism operating in the hydroxo Rh−NHC-based catalytic systems, a series of stoichiometric low temperature reactions with complex **3** have been performed (Scheme 3). Rather surprisingly, the

Scheme 3. Detected Intermediates Relevant to the Mechanism of Alkyne Hydrothiolation



hydroxo complexes **3**−**5** were stable toward bridge-cleavage by coordinating ligands, such as PPh_3 or pyridine, in contrast to the reactivity observed for their chlorido counterparts **1** and **2**.[15f] However, they are reactive toward acidic thiols such as thiophenol, benzylthiol, or *n*-butylthiol to generate unidentified mixtures of complexes, probably due to the formation of intricate thiolato bridged metallic structures.[23] In contrast, the addition of benzylthiol to **3** in the presence of pyridine at room temperature led to the formation of a new thiolato complex $Rh(SCH_2Ph)(IPr)(\eta^2\text{-coe})(py)$ (**6**).[24] The ^1H and $^{13}C\{^1H\}$ NMR spectra agree with the proposed structure. Particularly, the singlet at δ 2.68 ppm, which correlates with a CH_2−carbon signal at 35.0 ppm in the $^1H-^{13}C$ HSQC spectrum, can be ascribed to the benzylthiolato ligand, whereas the IPr and η^2-olefin show two doublets at 186.8 (J_{C-Rh} = 55.5 Hz) and 59.4 ppm (J_{C-Rh} = 12.9 Hz), respectively, in the $^{13}C\{^1H\}$ NMR spectrum. Moreover, the chlorido counterpart $RhCl(IPr)(\eta^2\text{-coe})(py)$, which was characterized by X-ray diffraction analysis, showed similar NMR data.[15f] Several attempts for isolation of the new complex were unsuccessful.

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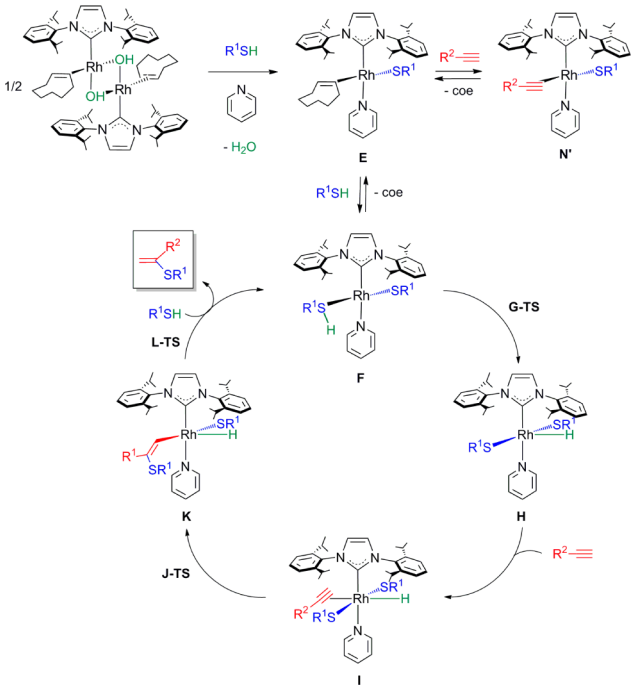
The next step was the study of the behavior of the metal−thiolato intermediate with alkynes. Treatment of a freshly prepared sample of **6** with 2 equiv of benzylacetylene at −40 °C gave rise to the formation of Rh(SCH_2Ph)(IPr)(η^2-HC≡CCH_2Ph)(py) (**7**) as a result of alkyne-coe ligand exchange (Scheme 3). The ^1H NMR spectrum of **7** displays, in addition to the typical signals for coordinated pyridine and IPr, a broad signal at δ 3.70 ppm (≡CH) and two doublets at 2.50 and 1.87 ppm (CH_2, J_{H-H} = 18.5 Hz) corresponding to the η^2-alkyne.[25] The CH_2 protons of the benzylthiolato ligand are also diastereotopic and appear as doublets at 3.47 and 3.10 ppm (J_{H-H} = 17.2). Moreover, the $^{13}C\{^1H\}$-APT NMR experiment at −40 °C shows three doublets at 185.4 (J_{C-Rh} = 56.5 Hz), 99.2 (J_{C-Rh} = 12.4 Hz), and 70.7 ppm (J_{C-Rh} = 12.5 Hz) corresponding to the IPr and the η^2-alkyne ligands, respectively.

The insertion of the alkyne into the Rh^I-thiolato bond could result in the formation of a new C−S bond.[26] However, for this process to be operative, a *cis* alkyne-thiolato disposition is required which is not the case in **7**. In fact, heating **7** to 40 °C for 4 h did not lead to the insertion of the alkyne into the Rh−S bond but rather resulted in the decomposition of the sample. The affinity of IPr and pyridine to adopt a mutually *trans* disposition in Rh^I square-planar complexes may account for the lack of the desired reactivity (see theoretical part for further details).[15f,27]

In view that alkyne-thiolato coupling within a Rh^I intermediate is hampered by the mutually *trans* configuration of both ligands in **7**, new catalytic pathways were explored. Thus, the addition of 1 equiv of benzylthiol to a freshly prepared toluene-d_8 solution of **6** at −40 °C led to the formation of the Rh^{III}−hydride−dithiolato complex RhH-(SCH_2Ph)$_2$(IPr)(py) (**8**). The ^1H NMR spectrum displays a shielded metal-hydride signal at −17.54 ppm, whereas a *trans* disposition of the two benzylthiolato ligands can be inferred by the presence of two doublets at 2.69 and 2.28 ppm (J_{H-H} = 12.2 Hz), integrating each by two protons, ascribed to the diastereotopic SCH_2 protons, which correlate in the $^1H-^{13}C$ HSQC experiment with only one resonance at 35.4 ppm, thereby confirming the chemical equivalence of both benzylthiolato ligands. Coordination of a second molecule of pyridine to **8** was observed at −80 °C, indicating a dynamic equilibrium process between **8** and **8-py**, as was previously observed for similar organometallic complexes (Scheme 3).[15f,j] Unfortunately, no intermediate species resulting from alkyne insertion into a rhodium-thiolato bond could be observed after the addition of phenylacetylene or benzylacetylene to **8**; instead, the formation of organic α-vinyl sulfides was observed, indicating that **8** is involved in the hydrothiolation process.

Reactivity studies on **3** strongly suggest that the Markonikov-selective alkyne hydrothiolation proceeds via Rh^{III}−hydride−dithiolato intermediates. A plausible mechanism is depicted in Scheme 4. The first step is the activation of the thiol by the hydroxo ligand to generate a Rh^I−thiolato intermediate stabilized by a pyridine ligand (**E**), similar to **6**. Then, thiol-coe ligand exchange generates a tetracoordinated Rh^I species (**F**) that undergoes oxidative addition of the thiol S−H bond to form Rh^{III}−hydride−dithiolato species (**H**) related to **8**. The higher *trans-influence* of the hydride ligand accounts for the disposition of the vacant site in **H** opposite to this ligand and thus directs coordination of the alkyne at this position in **I**. Then, 1,2 insertion of the alkyne into the Rh−S bond and subsequent hydride−alkenyl reductive elimination leads to the α-vinyl sulfide and a putative tricoordinated species that could

Scheme 4. Mechanistic Proposal for the Formation of α-Vinyl Sulfides



be stabilized by the coordination of alkene, alkyne, or thiol, being the last complex (**F**) which continues the catalytic cycle through S−H oxidative addition.

DFT Calculations on the Alkyne Hydrothiolation Mechanism. In order to support the mechanistic picture proposed in Scheme 4, a detailed computational study using DFT calculations (B3LYP method) has been carried out. Theoretical calculations dealing with alkyne hydrothiolation or insertion of an alkyne into metal−thiolato bonds are scarce.[15f,28] Because of the role of steric hindrance in the reaction regioselectivity, the full IPr ligand has been considered explicitly in the calculations. This mechanistic study starts at putative complex Rh(OH)(IPr)(py)(η^2-ethylene) (**A**) and includes the thiol deprotonation by the hydroxo ligand (Figure 3) and the proposed alkyne hydrothiolation catalytic cycle (see Scheme 4) via two thiometalation pathways leading to both α and β-E-vinyl sulfides (Figure 4). All energies are relative to the complex **A** and the corresponding reactants. The hydrometalation pathways have been also considered and reported in the Supporting Information.

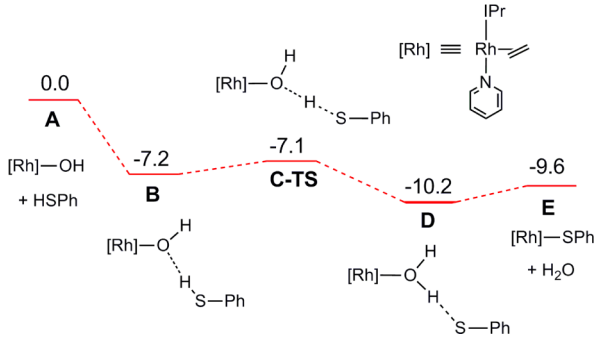


Figure 3. DFT calculated ΔE (in kcal mol^{-1}) energy profile for the thiol deprotonation by rhodium−hydroxo precursor.

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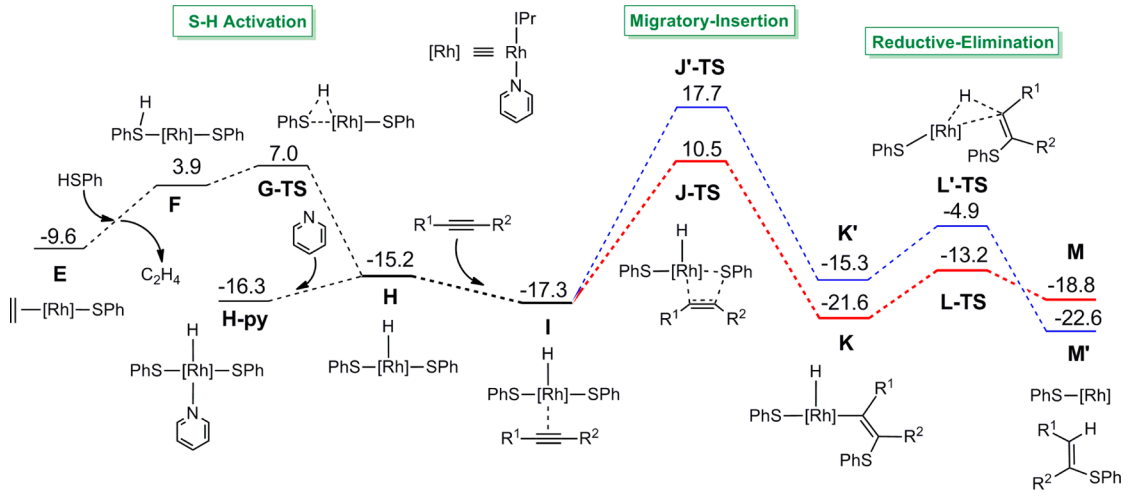

Figure 4. DFT calculated ΔE (in kcal mol^{-1}) along the energy surface of formation of vinyl sulfides through thiometalation. Structures **J** to **M** correspond to α-vinyl sulfide (R^1 = H, R^2 = Ph, red line), and structures **J′** to **M′** lead to linear vinyl sulfides (R^1 = Ph, R^2 = H, blue line).

The initiation step of the catalytic process involves the activation of the thiol by the hydroxo ligand of complex **A** to generate a Rh^{I}–thiolato intermediate (**E**) similar to **6**, which is stabilized by 9.6 kcal mol^{-1}. The external protonation of the hydroxo ligand by the acidic thiol presents a very favorable energetic profile via intermediates **B** and **D** and the transition state **C-TS** (Figure 3).[29] Compound **E** may exchange the alkene ligand by another thiol molecule to yield **F**, which is the starting point of the catalytic cycle. The first step of this cycle is the S–H activation by the metal through the **G-TS** transition structure, leading to the hydride-dithiolato intermediate **H**, similar to **8**. The activation energy of this step is 16.6 kcal mol^{-1} (with respect to **E**), and it is exothermic. The vacant site in **H** is located *trans* to the hydride ligand, and both pyridine and alkyne ligands can be coordinated there. The former leads to a nonreactive species **H-py** with a relative energy of −16.3 kcal mol^{-1}, and the latter yields compound **I**, which is slightly more stable (−17.3 kcal mol^{-1}), and it can follow the catalytic cycle.

Because of the possible orientations of the coordinated alkyne, the profile bifurcates into the two pathways leading to α or β-E-vinyl sulfides. Hence, alkyne insertion into the Rh–S bond takes place through transition states **J-TS** and **J′-TS** with activation energies of 27.8 and 35.0 kcal mol^{-1}, respectively. Thus, according to transition state theory, the formation of the α-vinyl sulfide is kinetically more favorable due to the lower energetic barrier. Both transition states display a roughly metalacyclobutene structure including the metal, sulfur, and the two carbon atoms of the former alkyne (Figure 5). Inspection of the geometry of the structures reveals that **J-TS** is a more advanced transition structure than **J′-TS**, the Rh–C bond distance of 2.274 Å in **J-TS** being much shorter than that in **J′-TS** (2.655 Å). Another notable fact that arises from the comparison of both key transition states is that the phenyl group of the former alkyne suffers from higher steric hindrance from IPr substituents on **J′-TS** that may account for its relative destabilization. Also of note is the spatial structure of the Rh–hydride pentacoordinated species **K** and **K′** that can be described as a distorted trigonal bipyramid with C–Rh–S angles of 143.8° and 137.2°, respectively.

The cycle is closed by C–H reductive elimination through Y-shaped transition states, **L-TS** and **L′-TS**. The energetic barriers are considerably smaller than in the previous step, and the overall reaction is highly exothermic, −18.8 and −22.6 kcal

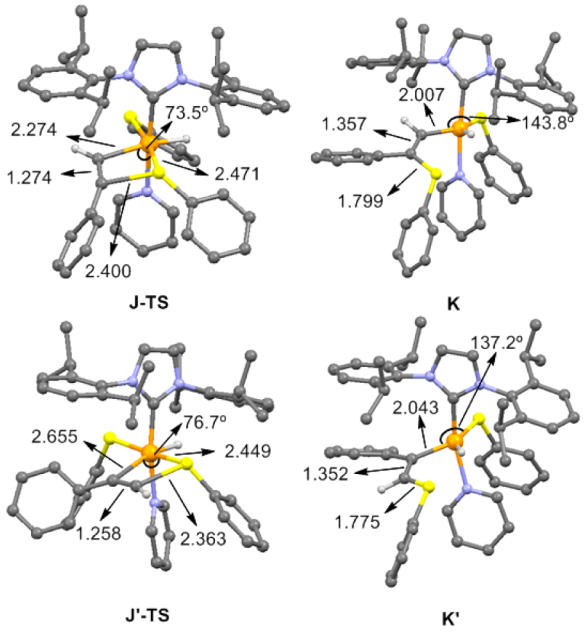

Figure 5. Optimized structures for the intermediates and transition states for migratory insertion including selected distances (Å) and angles (deg).

mol^{-1} for the α or β-E-vinyl sulfides, respectively. The hydrometalation pathways have also been computed but showed higher energetic barriers for the rate-limiting insertion step (see Supporting Information).

A possible alternative reaction pathway for alkyne hydrothiolation could be a nonoxidative process in which the insertion step takes place within a Rh^{I}–π-alkyne–thiolato species. The computed coe-alkyne ligand exchange and subsequent insertion step are presented in Figure 6. Compound **N′** represents a square-planar derivative similar to **7** in which isomerization to a *cis* alkyne–thiolate species **N** is necessary for the subsequent alkyne insertion into the Rh–SR bond to generate the rhodium–alkenyl intermediate **P**. In this case, the energetic barrier for the transition state **O-TS** is 32.8 kcal mol^{-1} (with regard to the lowest intermediate **N′**), higher than the energetic barrier calculated for **J-TS** (27.8 kcal mol^{-1}),

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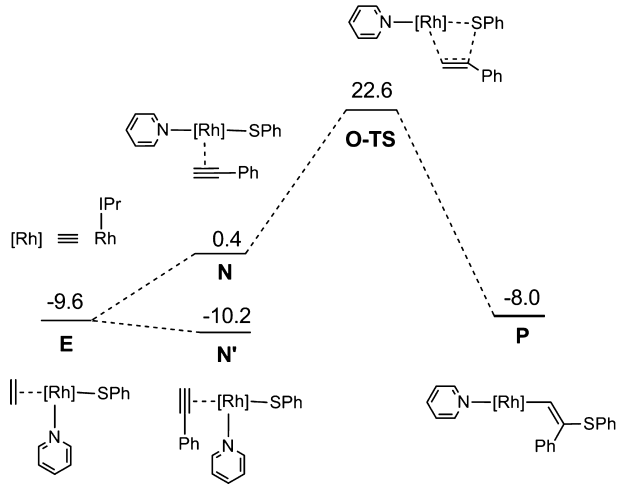

Figure 6. DFT calculated ΔE (in kcal mol^{-1}) energy profile for the insertion step within a Rh^{I}–π-alkyne–thiolato square-planar intermediate.

indicating that the pathway presented in Figure 4 is more favorable.

Interestingly, the activity and selectivity of the catalytic systems [Rh(μ-OH)(NHC)(η^2-olefin)]$_2$/py and [Rh(μ-Cl)(NHC)(η^2-olefin)]$_2$/py[15f] can be straightforwardly compared because the respective active species, RhH(SR)$_2$(IPr)(py) and RhHCl(SR)(IPr)(py), are closely related Rh^{III}–hydride species. Experimentally, it is found that the hydroxo-based [Rh(μ-OH)(NHC)(η^2-olefin)]$_2$/py catalytic system is less active but slightly more selective than the chlorido-based system. The calculated reaction mechanism is quite similar for both catalysts with the migratory insertion being the rate-limiting step and that decisive for shifting the catalytic outcome toward the formation of the thermodynamically less favorable product. The DFT studies show that the activation energies for the rate-limiting step are 27.8 and 24.0 kcal mol^{-1} for the [Rh]–OH and [Rh]–Cl catalysts, respectively. The different selectivity between [Rh]–OH and [Rh]–Cl catalysts can be explained considering the energy differences between the activation energies of the rate-limiting steps of the paths leading to α or β-E-vinyl sulfides, which are 7.2 and 4.3 kcal mol^{-1}, respectively. These values are in agreement with the better selectivity observed for the [Rh]–OH catalyst compared to [Rh]–Cl (Figure 7).

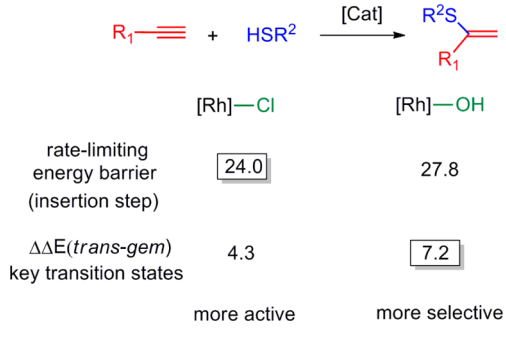

Figure 7. Comparative information on [Rh(μ-OH)(NHC)(η^2-olefin)]$_2$/py versus [Rh(μ-Cl)(NHC)(η^2-olefin)]$_2$/py catalytic systems from DFT studies (energies in kcal mol^{-1}).

CONCLUDING REMARKS

The catalytic system [Rh(μ-OH)(NHC)(η^2-olefin)]$_2$/py performs alkyne hydrothiolation selectively toward α-vinyl sulfides for a varied range of alkynes and thiols under mild conditions. Several intermediates relevant for the catalytic process have been identified by means of NMR low temperature experiments, including Rh^{I}–thiolato species, Rh(SCH$_2$Ph)(IPr)(η^2-coe)(py) and Rh(SCH$_2$Ph)(IPr)(η^2-HC≡CCH$_2$Ph)(py), and the Rh^{III}–hydride–dithiolato derivative RhH(SCH$_2$Ph)$_2$(IPr)-(py). Computational DFT studies reveal an operational mechanism consisting of sequential thiol deprotonation by a hydroxo ligand, subsequent thiol SH oxidative addition, alkyne insertion, and reductive elimination with the 1,2 thiometalation insertion as the rate-limiting step. Further work on the application of this catalytic system to other hydrofuntionalization reactions is currently being developed in our laboratories.

EXPERIMENTAL SECTION

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. THF was dried over sodium and distilled under argon prior to use; the other solvents were obtained oxygen- and water-free from a solvent purification system (Innovative Technologies). The organometallic precursors [Rh(μ-Cl)(NHC)(η^2-coe)]$_2$ (IPr, **1**; IMes, **2**)[20] were prepared as previously described in the literature. NMR spectra were recorded either on a Varian Gemini 2000 300 MHz, 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}). Coupling constants, J, are given in Hz. Spectral assignments were achieved by a combination of ^{1}H–^{1}H COSY, ^{13}C{^{1}H}-APT, and ^{1}H–^{13}C HSQC/HMBC experiments. GC-MS analyses were recorded on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system, using an HP-5MS 5% phenyl methyl siloxane column (30 m × 250 mm with a 0.25 mm film thickness). The nature of organic products was compared with previously reported data: phenyl (1-phenylvinyl) sulfide,[30] phenyl (hex-1-en-2-yl) sulfide,[31] phenyl (3-phenylprop-1-en-2-yl) sulfide,[17a] phenyl (3-methoxyprop-1-en-2-yl) sulfide,[19c] 2-(2-(phenylthio)vinyl)-pyridine,[18l] phenyl 1-(cyclohex-1-en-1-yl)vinyl sulfide,[32] benzyl (1-phenylvinyl) sulfide,[18c] phenyl S-(1-phenylvinyl)-N-Boc-L-cysteine-methylester,[15f] and butyl (1-phenylvinyl) sulfide.[33]

Preparation of [Rh(μ-OH)(IPr)(η^2-coe)]$_2$ (3). A yellow solution of **1** (160 mg, 0.126 mmol) in THF (20 mL) was treated with NaOH (130 mg, 3.25 mmol) and stirred at room temperature for 4 h. After filtration through Celite, the THF was removed in vacuo and *n*-hexane added to induce the precipitation of a yellow solid, which was washed with *n*-hexane (3 × 3 mL) and dried in vacuo. Yield: 89 mg (63%). Anal. Calcd for C$_{70}$H$_{102}$N$_4$O$_2$Rh$_2$: C, 67.95; H, 8.31; N, 4.53. Found: C, 67.63; H, 8.28; N, 4.42. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 7.4–7.1 (m, 12H, H$_{Ph\text{-}IPr}$), 6.31(s, 4H, =CHN), 3.44 (sept, J_{H-H} = 6.8, 8H, C<u>H</u>Me$_{IPr}$), 2.06 (m, 4H, =CH$_{coe}$), 1.71 and 1.05 (both d, J_{H-H} = 6.8, 48H, CH<u>Me</u>$_{IPr}$), 1.6–1.3 (br, 24H, CH$_{2\text{-}coe}$), −3.83 (s, 2H, OH). ^{13}C{^{1}H}-APT NMR (75.1 MHz, C$_6$D$_6$, 25 °C): δ 188.6 (d, J_{C-Rh} = 62.2, Rh–C$_{IPr}$), 145.7 (s, C$_{q\text{-}IPr}$), 137.9 (s, C$_q$N), 128.8 and 124.1 (s, CH$_{Ph\text{-}IPr}$), 123.5 (s, =CHN), 55.9 (d, J_{C-Rh} = 15.8, =CH$_{coe}$), 30.0, 28.3, and 26.8 (all s, CH$_{2\text{-}coe}$), 28.3 (s, <u>C</u>HMe$_{IPr}$), 25.6 and 24.0 (both s, CH<u>Me</u>$_{IPr}$).

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Preparation of [Rh(μ-OH)(IMes)(η^2-coe)]$_2$ (4). The complex was prepared as described for **3** starting from **2** (303 mg, 0.274 mmol) and NaOH (130 mg, 3.25 mmol). A yellow solid was obtained. Yield: 146 mg (51%). Satisfactory microanalysis figures could not be obtained due to high air-sensitivity. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 6.85 (s, 2H, $CH_{Ph\text{-}IMes}$), 6.01 (s, 4H, =CHN), 2.47 (s, 12H, $CH_{3\text{-}o\text{-}IMes}$), 2.47 (s, 6H, $CH_{3\text{-}m\text{-}IMes}$), 1.6−1.0 (br, 28H, $=CH_{coe}$, $CH_{2\text{-}coe}$), −3.31 (s, 2H, OH). ^{13}C{^{1}H}-APT NMR (75.1 MHz, C_6D_6, 25 °C): δ 187.8 (d, J_{C-Rh} = 59.1, Rh−C_{IMes}), 138.2 (s, $C_{qo\text{-}IMes}$), 137.0 (s, C_qN), 138.2 (s, $C_{qm\text{-}IMes}$), 128.9 (s, $CH_{Ph\text{-}IMes}$), 121.9 (s, =CHN), 55.6 (d, J_{C-Rh} = 16.4, $=CH_{coe}$), 30.7, 28.1, and 27.3 (all s, $CH_{2\text{-}coe}$), 20.9 (s, $CH_{3\text{-}o\text{-}IMes}$), 19.1 (s, $CH_{3\text{-}m\text{-}IMes}$).

Preparation of [Rh(μ-OH)(IPr)(η^2-CH_2=CH_2)]$_2$ (5). Ethylene was bubbled through a yellow solution of **3** (159 mg, 0.121 mmol) in toluene (10 mL) at room temperature for 15 min to give a yellow solution. Then, the solution was concentrated to ca. 1 mL and *n*-hexane added to induce the precipitation of a yellow solid, which was washed with *n*-hexane (3 × 3 mL) and dried in vacuo. Yield: 96 mg (69%). Anal. Calcd for $C_{58}H_{82}N_4O_2Rh_2$: C, 64.92; H, 7.70; N, 5.22. Found: C, 64.78; H, 7.90; N, 5.00. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.2−7.1 (m, 12H, $H_{Ph\text{-}IPr}$), 6.23 (s, 4H, =CHN), 3.11 (sept, J_{H-H} = 6.8, 8H, C<u>H</u>Me_{IPr}), 1.74 (br, 8H, CH_2=CH_2), 1.59 and 1.01 (both d, J_{H-H} = 6.8, 48H, CH<u>Me</u>$_{IPr}$), −4.24 (s, 2H, OH). ^{13}C{^{1}H}-APT NMR (75.1 MHz, C_6D_6, 25 °C): δ 186.8 (d, J_{C-Rh} =59.5, Rh−C_{IPr}), 146.4 (s, $C_{q\text{-}IPr}$), 137.4 (s, C_qN), 128.9 (s, $CH_{p\text{-}Ph\text{-}IPr}$), 123.8 (s, $CH_{m\text{-}Ph\text{-}IPr}$), 122.7 (s, =CHN), 40.0 (d, J_{C-Rh} = 16.5, CH_2=CH_2), 28.6 (s, <u>C</u>HMe_{IPr}), 25.6 and 23.7 (both s, CH<u>Me</u>$_{IPr}$).

***In-situ* formation of Rh(SCH_2Ph)(IPr)(py)(η^2-coe) (6).** A solution **3** (32 mg, 0.026 mmol) in toluene-d_8 (0.5 mL, NMR tube) at room temperature was treated with benzylthiol (6.1 μL, 0.052 mmol) and pyridine (8.7 μL, 0.11 mmol). ^{1}H NMR (400 MHz, tol-d_8, −10 °C): δ 8.51 (d, J_{H-H} = 5.5, 2H, $H_{2\text{-}py}$), 7.4−6.8 (11H, H_{Ph}), 6.62 (s, 2H, =CHN), 6.48 (t, J_{H-H} = 7.6, 1H, $H_{4\text{-}py}$), 6.14 (dd, J_{H-H} = 7.6, 5.5, 2H, $H_{3\text{-}py}$), 4.62 and 2.65 (both sept, J_{H-H} = 6.7, 4H, C<u>H</u>Me_{IPr}), 3.36 (br, 2H, $=CH_{coe}$), 2.68 (s, 2H, CH_2S), 1.6−1.0 (br, 12H, $CH_{2\text{-}coe}$), 1.77, 1.53, 1.11, and 1.03 (all d, J_{H-H} = 6.7, 24H, CH<u>Me</u>$_{IPr}$). ^{13}C{^{1}H}-APT NMR (100.6 MHz, tol-d_8, 25 °C): δ 186.8 (d, J_{C-Rh} = 55.5, Rh−C_{IPr}), 154.4 (s, $C_{2\text{-}py}$), 148.2 and 145.6 (both s, $C_{q\text{-}IPr}$), 147.0 (C_qS), 137.1 (s, C_qN), 134.8 (s, $C_{4\text{-}py}$), 129.3, 129.1, 128.8, 124.3, 123.3, and 124.3 (all s, CH_{Ph}), 123.1 (s, =CHN), 122.4 (s, $C_{3\text{-}py}$), 59.4 (d, J_{C-Rh} = 12.9, $=CH_{coe}$), 35.0 (s, CH_2S), 30.3, 30.1, and 29.1 (all s, $CH_{2\text{-}coe}$), 28.8 and 28.6 (both s, <u>C</u>HMe_{IPr}), 26.8, 26.6, 24.5, and 22.5 (all s, CH<u>Me</u>$_{Pr}$).

***In Situ* Formation of Rh(SCH_2Ph)(IPr)(η^2-HC≡CCH_2Ph)-(py) (7).** A freshly prepared solution of **6** in toluene-d_8 (0.5 mL, NMR tube) from **3** (32 mg, 0.026 mmol), benzylthiol (6.1 μL, 0.052 mmol), and pyridine (8.7 μL, 0.11 mmol) was treated with benzylacetylene (6.0 μL, 0.048 mmol) at −40 °C. ^{1}H NMR was immediately recorded at low temperature. ^{1}H NMR (400 MHz, toluene-d_8, −40 °C): δ 8.44 (overlapped with free py, $H_{2\text{-}py}$), 7.2−6.9 (16H, H_{Ph}), 6.52 and 6.30 (both d, J_{H-H} = 2.2, 2H, =CHN), 6.38 (t, J_{H-H} = 7.1, 1H, $H_{4\text{-}py}$), 5.97 (dd, J_{H-H} = 7.1, 5.1, 2H, $H_{3\text{-}py}$), 4.36, 4.04, 3.28, and 2.26 (all sept, J_{H-H} = 6.7, C<u>H</u>Me_{IPr}), 3.70 (br, 1H, HC≡C), 3.47 and 3.10 (both d, J_{H-H} = 17.2, 2H, CH_2S), 2.50 and 1.87 (both d, J_{H-H} = 18.5, 2H, ≡CCH_2), 1.99, 1.65, 1.59, 1.15, 1.13, 1.06, 1.01, and 0.94 (all d, J_{H-H} = 6.7, CH<u>Me</u>$_{IPr}$). ^{13}C{^{1}H}-APT NMR (100.5 MHz, toluene-d_8, −40 °C): δ 185.4 (d, J_{C-Rh} = 56.5, Rh−C_{IPr}), 152.4 (s, $C_{2\text{-}py}$), 147.6, 147.0, 145.5, and 145.1 (all s, $C_{q\text{-}IPr}$), 139.7 and 138.9 (both s, C_qN), 138.0 (s, C_qS), 136.0 (s, $C_{q\text{-}Ph}$), 133.7 (s, $C_{4\text{-}py}$), 130−122 (CH_{Ph}), 123.2 and 122.7 (both s, =CHN), 122.6 (s, $C_{3\text{-}py}$), 99.2 (d, J_{C-Rh} = 12.4, HC≡<u>C</u>), 70.7 (d, J_{C-Rh} = 12.5, H<u>C</u>≡C), 32.8 (s, CH_2S), 31.5 (s, ≡C<u>C</u>H_2), 29.27, 28.9, 28.6, and 28.5 (all s, <u>C</u>HMe_{IPr}), 27.0, 26.1, 25.2, 25.1, 24.0, 23.37, 23.0, and 22.8 (all s, CH<u>Me</u>$_{IPr}$).

***In Situ* Formation of RhH(SCH_2Ph)$_2$(IPr)(py) (8) and RhH(SCH_2Ph)$_2$(IPr)(py)$_2$ (8-py).** A freshly prepared solution of **6** (0.5 mL of toluene-d_8, NMR tube) from **3** (32 mg, 0.026 mmol), benzylthiol (6.1 μL, 0.052 mmol), and pyridine (8.7 μL, 0.11 mmol) was treated with benzylthiol (6.1 μL, 0.052 mmol) at −40 °C and measured immediately. Complexes **8** and **8-py** are in dynamic equilibrium. ^{1}H NMR (300 MHz, tol-d_8, −40 °C): δ 8.95 (d, J_{H-H} = 5.0 2H, $H_{2\text{-}py}$), 7.4−6.4 (16H, H_{Ph}), 6.31 (br, 2H, =CHN), 6.33 (t, J_{H-H} = 7.4, 1H, $H_{4\text{-}py}$), 6.12 (dd, J_{H-H} = 7.4, 5.0, 2H, $H_{3\text{-}py}$), 3.58 and 3.43 (both sept, J_{H-H} = 6.5, 4H, C<u>H</u>Me_{IPr}), 2.69 and 2.38 (both d, J_{H-H} = 12.2, 4H, CH_2S), 1.89, 1.21, 1.08, and 0.84 (all d, J_{H-H} = 6.5, 24H, CH<u>Me</u>$_{IPr}$), −17.54 (d, J_{H-Rh} = 20.2, Rh−H). ^{1}H NMR (300 MHz, tol-d_8, −80 °C): δ 9.47 (br, 2H, $H_{2\text{-}pyb}$), 9.08 (br, 2H, $H_{2\text{-}pya}$), −17.32 (d, J_{H-Rh} = 19.4, Rh−H). ^{13}C{^{1}H}-APT NMR (75.1 MHz, tol-d_8, −40 °C): δ 176.6 (d, J_{C-Rh} = 52.7, Rh−C_{IPr}), 153.8 (s, $C_{2\text{-}py}$), 147.5 and 145.8 (both s, $C_{q\text{-}IPr}$), 146.4 (s, C_qS), 137.3 (s, C_qN), 135.1 (s, $C_{4\text{-}py}$), 129.5, 129.1, 128.5, 123.7, and 123.1 (all s, CH_{Ph}), 125.5 (s, =CHN), 123.7 (s, $C_{3\text{-}py}$), 35.4 (s, CH_2S), 29.1 and 28.3 (both s, <u>C</u>HMe_{IPr}), 27.5, 27.2, 23.6, and 22.8 (all s, CH<u>Me</u>$_{Pr}$).

Standard Conditions for the Catalytic Alkyne Hydrothiolation. In a NMR tube, 0.01 equiv of catalyst was dissolved in 0.5 mL of C_6D_6, and then 0.50 mmol of thiol and 0.50 mmol of alkyne were added. The alkyne conversion to vinyl sulfide was quantified by integration of the ^{1}H NMR spectra. Reaction product formation was also monitored at periodic time intervals by using GC-MS analysis. One equivalent of α-terpinene relative to thiol was used in the radical scavenger experiment.

Crystal Structure Determination. X-ray diffraction data were collected at 100(2) K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using narrow ω rotation (0.3°) on a Bruker APEX DUO CCD diffractometer. Intensities were integrated and corrected for absorption effects with SMART,[34] SAINT-PLUS,[35] and SADABS[36] programs, included in APEX2 package. The structures were solved with the Patterson method and refined using full matrix least-squares on F^2, with SHELXS-97 and SHELXL-97 programs, respectively.[37]

Crystal Data for Compound ***3***. $C_{70}H_{102}N_4O_2Rh_2$; M = 1237.38; yellow block 0.114 × 0.086 × 0.050 mm^3; triclinic; $P\bar{1}$; a = 11.021(5), b = 11.519(5), c = 14.052(6), α = 68.604(7), β = 73.514(6), γ =74.287(6)°; Z = 1; V = 1564.5(11) Å^3; D_c =1.313 g/cm^3; μ = 0.575 mm^{-1}; minimum and maximum absorption correction factors 0.8058 and 0.9649; $2\theta_{max}$ = 50.70°; 11 059 reflections collected, 5529 unique (R_{int} = 0.1060); number of data/restraints/parameters 5529/0/349; final GOF 0.951; R_1 = 0.0628 (3305 reflections, $I > 2\sigma(I)$); $wR(F^2)$ = 0.1317 for all data; largest difference peak 0.906 e/Å^3. Two carbon atoms of the coe ligand were found to be disordered. They were included in the model in two different positions with complementary occupancy factors (0.60/0.40(1)).

Computational Details. The geometry of all structures has been optimized with the G09 program package[38] at the DFT level using the B3LYP method[39] combined with the 6-31G(d,p) basis set for H, C, N, Cl, and S atoms[40] and the SDD pseudopotential[41] for Rh. The nature of the stationary

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points has been confirmed by frequency analysis, and intrinsic reaction paths have been traced connecting the transition structures with the respective minima.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic information files containing full details of the structural analysis of complex **3** (CIF format). Energetic profile of the alkyne hydrothiolation catalytic cycle via an alternative hydrometalation pathway (Figure S1), selected NMR spectra, and Cartesian coordinates for theoretical calculations. 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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