A hemilabile and cooperative N-donor functionalized 1,2,3-triazol-5-ylidene ligand for selective and base-free rhodium(I) catalyzed alkyn hydrothiolation reactions.


Abstract: A series of novel cationic and neutral Rh-complexes with an N-donor functionalized 1,2,3-triazol-5-ylidene (TRZ) ligand (where pendant N-donor is NHBoc, NH$_2$ or NMe$_2$ respectively) is described. Their catalytic activity was evaluated towards the hydrothiolation of alkynes. Among the catalysts, a neutral dicarbonyl complex featuring the tethered-NBoc amido-TRZ ligand proved very selective for alkyn hydrothiolation with an aryl thiol. Remarkably, the reaction could be carried out in the absence of pyridine or base additive. In addition, during the reaction course, no evidence for oxidative addition of the thiol S-H was observed, strongly suggesting a reaction pathway whereby a bifunctional ligand is involved. Experimental and theoretical mechanistic investigations suggest a ligand-assisted deprotonation of substrate thiol, hemilabile dissociation of amine from metal and thiolate coordination, which is indicative of a different reaction mechanism to those previously reported for related alkyn hydrothiolation reaction.

Introduction

The hydrothiolation of alkynes involves the atom-economical addition of the sulfur and hydrogen atom from a thiol group across a carbon-carbon unsaturated bond to generate vinyl sulfides. The structural motifs of vinyl sulfides as building blocks for biologically active compounds[1] and polymers[2] stimulate the development of efficient and selective synthetic methods for these valuable compounds. To this end, recent strategies have included the metal-catalyzed hydrothiolation of unsaturated carbon-carbon bonds, with the advantage of increased chemo-,

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Scheme 1. Thiol activation strategies in rhodium-catalyzed alkyn hydrothiolation.
to give the branched Markovnikov-products in excellent yields for the hydrothiolation of aryl alkynes with aryl thiols.\textsuperscript{40d}

In an effort to circumvent the use of additive pyridine, we recently reported the synthesis of a donating, monooanionic bis(1,2,3-triazol-5-ylidine)-based CNC-type pincer ligand with flanking mesionic carbene (MIC) moieties,\textsuperscript{8b} as supporting scaffold for [Rh\(^{1}\)(CNC)(μ-O\(_2\))], an air-stable selective precursor catalyst for the regioselective hydrothiolation of aliphatic alkynes with alkyl thiols.\textsuperscript{40k} However, similarly to the pyrazolylborate rhodium complexes reported by Love \textit{et al}.,\textsuperscript{8k} diminished regioselectivity for the branched α-vinyl sulfides was seen when aryl thiol and aryl alkynes were employed.\textsuperscript{40k} It was reasoned that a less encumbered bidentate ligand framework bearing a pendant nitrogen functionality could confer a bifunctional catalyst behaving as directing group and hemilabile ligand. First, negating the use of additive pyridine; and second, favoring intramolecular activation through the heterolytic cleavage of the thiol S-H bond over oxidative addition (see Scheme 1(b)) to improve the regioselectivity of the aryl substrates of alkyne hydrothiolation. Thus we set out to prepare a series of electron-rich Rh\(^1\) complexes containing a tethered N-donor-TRZ ligand \textbf{A}, \textbf{B} and \textbf{C} (Scheme 2)\textsuperscript{10} (where N-donor is NHBoc, NH\(_2\) or NMe\(_2\) respectively; TRZ = 1,2,3-triazol-5-ylidine) in order to exploit the possibility of both hemilability and ligand cooperativity for the activation of the thiol S-H bond.

\section*{Results and Discussion}

\subsection*{Synthesis and characterization of catalyst precursors}

The new ligand precursor 1,3-diaryl-1\(\text{H}\)-1,2,3-triazolium salts \textbf{A}–\textbf{C}\textsuperscript{11} were prepared by cycloaddition of the corresponding aryl alkynes and 1,3-bis(2,6-dipropoxyphenyl)triaz-1-ene according to an adapted literature procedure.\textsuperscript{12} The rhodium complexes 1–3 were prepared by reacting the free 1,2,3-triazol-5-ylidine ligands\textsuperscript{13} obtained after deprotonation of the corresponding triazolium salt precursors \textbf{A}, \textbf{B} or \textbf{C}, respectively with potassium hexamethyldisilazide (KHMDS) followed by addition to the metal precursor [RhCl(COD)]

\[\text{COD} = 1,5\text{-cyclooctadiene}\] (Scheme 2). The neutral metalloccyclic complex 1 [Rh(TRZ-NBoc)(COD)] (84\%), was obtained when 2.2 equivalents of base were added to precursor \textbf{A} prior to metalation. Employing the amino- and dimethylamine-functionalized triazolium salts as precursor ligands (\textbf{B} and \textbf{C}, respectively) with 1.2 equivalents of base led to the isolation of the cationic chelated complexes [Rh\textsuperscript{1}(TRZ-NR\(_2\))(COD)]

\[\text{COD} = 1,5\text{-cyclooctadiene}\] complexes 2, and 3. The dicarbonyl complexes [Rh\textsuperscript{1}(TRZ-NBoc)(CO)\(_2\)] (4) and [Rh\textsuperscript{1}(TRZ-NR\(_2\))(CO)\(_2\)]PF\(_6\) (5, R = H; 6, R = Me) were quantitatively prepared by treatment of the Rh(COD) complexes 1, 2 and 3, respectively, with CO (g) in dichloromethane (Scheme 2). The [Rh\textsuperscript{1}(TRZ-NBoc)(LL)] or [Rh\textsuperscript{1}(TRZ-NR\(_2\))(LL)]PF\(_6\) (LL = COD or (CO)\(_2\)) metal complexes 1–6, are all air and moisture stable. The carbene resonances of the cyclooctadiene complexes 1–3 are observed at 162.3 and 164.8 ppm, respectively. The \(^{13}\text{C}\) NMR spectra of the dicarbonyl complexes 4–6 display the carbene carbon doublet resonances at 164.8 and 169.7 ppm, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Solid-state structures of complexes 2 and 4 with 50\% probability ellipsoids. The PF\(_6\) counterion and hydrogens (except for the NH\(_2\) functional group) were omitted for clarity. Selected bond lengths (Å) and angles (°) for 2: C5–Rh1 2.029(2); Rh1–N4 2.165(2); Rh1–C31 2.052(2); Rh1–C32 2.173(2); Rh1–C35 2.132(2); Rh1–C36 2.111(2); C5–Rh1–N4 79.22(8); C5–Rh1–C31 164.76(10); C5–Rh1–C32 156.13(10); C5–Rh1–C35 156.13(10); C5–Rh1–C36 94.08(10); C5–Rh1–Me 156.13(10).}
\end{figure}

The IR spectra of 4–6 show the C-O stretching vibrations (1993, 2068 cm\(^{-1}\) for neutral complex 4; and 2027, 2090 cm\(^{-1}\) (5) and 2031, 2090 cm\(^{-1}\) (6), for the cationic complexes) within the range of previously reported Rh-TRZ complexes.\textsuperscript{14} Crystals suitable for X-ray diffraction could be obtained of complexes 1–4 (2 and 4, Figure 1; and 1 and 3, SI, Figure S31), and display pseudo-square planar geometry around the Rh(II) metal centre (Figure 1). As seen for the carbonyl ligands, the Rh\(_2\)CO\(_2\) bond lengths (2.017(2) – 2.045(3) Å) for the structures of 1–4 are in accordance with previously reported structures, and are relatively insensitive to changes in the electronic structure around the metal.\textsuperscript{14} For the cyclometallated complexes, however, the neutral amido complexes 1 and 4 display the expected shorter Rh-N bond distances (2.130(2) and 2.0924(18) Å, respectively), compared to the cationic amine complexes 2 and 3 (2.165(2) and 2.222(2) Å, respectively).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme2.png}
\caption{Synthesis of N-donor functionalized triazolylidene Rh(II) complexes 1–6.}
\end{figure}

Figure 1. Solid-state structures of complexes 2 and 4 with 50\% probability ellipsoids. The PF\(_6\) counterion and hydrogens (except for the NH\(_2\) functional group) were omitted for clarity. Selected bond lengths (Å) and angles (°) for 2: C5–Rh1 2.029(2); Rh1–N4 2.165(2); Rh1–C31 2.052(2); Rh1–C32 2.173(2); Rh1–C35 2.132(2); Rh1–C36 2.111(2); C5–Rh1–N4 79.22(8); C5–Rh1–C31 164.76(10); C5–Rh1–C32 156.13(10); C5–Rh1–C35 156.13(10); C5–Rh1–C36 94.08(10); C5–Rh1–Me 156.13(10).}
Catalytic and mechanistic studies

The catalytic activity of catalysts 1–6 was first investigated towards the 1-hexyne hydrothiolation with thiophenol, either in the presence or absence of the weak base $K_2CO_3$ (2 % mol) at 80 °C in deuterated benzene (Table 1). When the reaction was performed in the absence of rhodium catalyst (entry 1, Table 1), an almost 1:1 mixture of only the linear β-E and β-Z vinyl sulfide was obtained. This result contrasted with the reaction carried out with [RhCl(COD)]$_2$ in the presence of base (entry 2, Table 1) for which a mixture of the coupled products, the thio-substituted dienes, was obtained (identified as a mixture of the bis-β-E,β-Z vinyl sulfide and the bis-β-Z,β-Z vinyl sulfide, Figure S36).

Table 1. Selection of precatalysts in the presence or absence of $K_2CO_3$ for the model hydrothiolation of 1-hexyne with thiophenol.

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[a] $^*$Reactions performed at 80 °C with 2 mol% of [cat.] in 0.5 mL C$_6$D$_6$ using anisole as internal standard. [b] 2 mol% of $K_2CO_3$. [c] Conversion after 24 h calculated by NMR integration based on internal standard anisole integration. [d] Unidentified precipitate observed.

In contrast, the metal complexes 1–6 displayed excellent selectivity towards the branched vinyl sulfides after 24 hours when 2 mol % of $K_2CO_3$ was added (Table 1, entry 3, 5, 7, 8, 10 and 12), comparable to some of the best rhodium-hydrothiolation catalysts to date.$^{[4]}$ In the case of the cationic complexes 2 and 5 [Rh(TRZ-NH$_3$)(LL)]$^+$ (LL = COD or (CO)$_2$, respectively), the formation of the coupled thio-substituted dienes, in conjunction with the formation of the desired α-vinyl sulfide and the linear products, were seen when the reaction was performed in the absence of $K_2CO_3$ (Table 1, entry 6 and 11). The presence of this coupled bis-vinyl sulfide product is suggestive of a reaction pathway that includes the presence of two thiolate ligands on the rhodium metal center, similarly as the mechanism proposed by Mizobe et al that follows oxidative addition of two thiolate ligands and concomitant release of molecular hydrogen.$^{[42]}$

However, if 2 mol % of the base was added (Table 1, entry 5 and 10), none of the coupled product was observed, and a complete selectivity switch was seen to favor the formation of the α-vinyl sulfide product. This is anticipated for a situation where [Rh]-SR insertion of the alkylene is favored over [Rh]-H insertion.$^{[39]}$ To rule out the possibility of NH$_2$-deprotonation of the amino catalyst precursors 2 and 5 by the weak base to yield the neutral amido complexes, the reactions were repeated with the analogous dimethylamine complexes [Rh(TTRZ-NMe$_3$)(LL)]$^+$ (LL = COD, 3 or (CO)$_2$, 6). Similar conversions and selectivity were seen for dimethylamine-complexes 3 and 6 (Table 1, entry 1 and 7 and 12) compared to the amino-complexes derivatives 2 and 5, and the possible bifunctional role of the TRZ-NH$_3$ ligand was dismissed. Instead, base-promoted deprotonation of the thiophenol, and coordination of the resultant thiolate with concomitant de-coordination of the NR$_2$ (R = H, Me) seemed more likely. To test this hypothesis, stoichiometric reactions were performed where 1 equivalent of thiophenol and $K_2CO_3$ was added to both complexes 5 and 6 (see SI). The FT-IR spectra of these complexes displayed a shift of the N-H stretching frequencies from 3331 and 3285 cm$^{-1}$ for 5, to 3311 and 3240 cm$^{-1}$, respectively, thus indicating dissociation of the NH$_2$-moiety; while for the NMe$_2$-complex 6, the ν(CO) bands shifted from 2030 and 2090 cm$^{-1}$ to 2008 and 2076 cm$^{-1}$, respectively, more closely correlating with the carbonyl vibration bands observed for the neutral Rh$^+$ complex 4 (1993, 2068 cm$^{-1}$).

In both cases, these results point to the hemilabile action of the NR$_2$-ligands of the cationic complexes, followed by coordination of the deprotonated thiol to yield a neutral Rh$^+$ intermediate. In addition, no Rh-H upfield shift was observed in the $^1$H NMR spectra, nor was the ν(Rh-H) vibration observed in the 2200 – 2300 cm$^{-1}$ region in the IR spectra. This result was also supported by computational calculations of the possible pathways for 5, comparing (a) an N-donor function that does not act in a cooperative or hemilabile fashion (SI, Figure S44); (b) a possible N-H effect by deprotonation of the amine-group by the weak non-coordinating base combined with a hemilabile functionality (SI, Figure S45); (c) deprotonation of the thiol by the weak base, with no N-H effect and solely a hemilabile function (SI, Figure S46), with oxidative addition of a second thiophenol molecule, and finally, the most energetically favourable pathway: (d) deprotonation of the thiol by the weak base, decoordination of hemilabile –NH$_2$ and substitution by thiophenolate (no oxidative addition and no [Rh]-H intermediate formed) (SI, Figure S47).

In contrast, for the neutral amido complexes 1 and 4 [Rh(TRZ-NBoc)(LL)] (LL = COD or (CO)$_2$, respectively), the formation of the mixture of C-C coupled thio-dienes was not observed even in the absence of base (Table 1, entry 4 and 9). Catalyst 4 was proven to be the most selective towards the α-vinyl sulfide,
although lower conversions were obtained. A mercury drop-test was performed on catalyst precursor 4 with no resulting significant change in either the conversion or regioselectivity of the catalyst, thereby indicating that a heterogeneous catalytic mode of action can be excluded.\textsuperscript{[115]}

In order to gain more insight about the reaction mechanism, we decided to explore the stoichiometric reactivity of 4 with substrate thiophenol to investigate the possibility of a cooperative\textsuperscript{[116]} and/or hemilabile catalyst activation mechanism. Both NMR and FT-IR spectra were recorded after addition of first 1 equivalent of thiophenol, and excess thiophenol in a separate experiment, to 4 [Rh(THZ-NBoc)(CO)]\textsubscript{2} in the absence of base, at room temperature (see SI, Figures S37 – S42). We did not observe any evidence for the formation of Rh-hydride species by NMR and IR spectra, even when recording the spectra after heating at 80°C. In the \textsuperscript{1}H and \textsuperscript{13}C NMR spectra, clear evidence for the protonation and dissociation of the resulting –NHBoc moiety was seen, and coordination of the thiolate ligand (see SI, Figures S39, S40). The NBoc-C\textsubscript{2}H\textsubscript{5} chemical shift, observed as a singlet peak at 4.71 ppm (see SI, Figure S41), is consistent with the fragmentation pattern/loss of carbonyl (calculated exact isotopic mass = 729.2788) (Figure S43, SI), \textsuperscript{[13]} and \delta(CO) = 186.0 (d, J = 7.24 Hz) and CO resonances (\delta 189.7, d, J = 63Hz; 189.9, d, J = 59 Hz) (SI, Figure S38) to \delta(Rh-C\textsubscript{2}H\textsubscript{5}) = 168.2 (d, J = 41 Hz) and \delta(CO) = 186.0 (d, J = 65 Hz), 191.0 (d, J = 59 Hz) (SI, Figure S40) is observed. In addition, the coordination of the thiolate is confirmed by the downfield shifted thiophenolate C\textsubscript{Boc} resonance of the phenyl ring observed at 155.5 ppm, and the downfield shift of the \textalpha-CH of the phenyl resonating at 7.89 ppm (d, J = 7.24 Hz) and 134.2 ppm, in the \textsuperscript{1}H and \textsuperscript{13}C NMR spectrum, respectively. The reaction mixture was analyzed by high resolution electrospray-ionization mass spectrometry, and the molecular ion peak of the thiolate complex INT\textsuperscript{2} was observed as [M-(CO)]\textsuperscript{+} = [Rh(NH\textsubscript{2}Boc-TRZ)(SPh)]\textsuperscript{+} = 729.2746 (calculated exact isotopic mass = 729.2788) (Figure S43, SI), consistent with the fragmentation pattern/loss of carbonyl ligands expected for carbonyl complexes during mass spectrometry ionization.

Similarly, the IR spectrum of INT\textsuperscript{2} after addition of 1 equivalent of thiophenol to 4, supported the protonation and dissociation of the –NHBoc moiety, with coordination of the thiolate ligand. The ν(CO) bands observed shifted from 1993, 2068 cm\textsuperscript{-1} to 1998, 2060 cm\textsuperscript{-1} after thiophenol addition, and a new broad N-H stretching frequency is observed at 3367 cm\textsuperscript{-1} (absent from the IR spectrum of 4). The small shift in the carbonyl stretching frequencies indicate that no oxidation of the Rh\textsuperscript{I} metal center had taken place, only exchange of the amido ligand for the thiolato ligand. In addition, the C=O vibration of the Boc-group shifted from 1624 cm\textsuperscript{-1} in 4, to 1720 cm\textsuperscript{-1} for INT\textsuperscript{2} after thiophenol addition. This stretching frequency more closely resembles the C=O stretching frequency observed for the precursor salt A (1715 cm\textsuperscript{-1}), supporting the dissociation of the –NHBoc moiety from the Rh(I) metal center and resultant higher energy NH-stretching frequency. If a second equivalent or excess of thiophenol was added, a mixture of unidentified products was obtained, although no evidence of dithiolate coordination or Rh-H bond formation was obtained in either the measured NMR or IR spectra, even after heating the reaction mixtures at 80 °C. Importantly, both the IR carbonyl stretching frequencies and the \textsuperscript{13}C NMR carbene resonance are indicative of a Rh\textsuperscript{III} metal center, and not a Rh\textsuperscript{II} metal center as would be expected as a result of oxidative addition.

Density Functional Theory (DFT) calculations were additionally carried out to further evaluate the mechanism of the alkyne hydrothiolation reaction catalyzed by rhodium(II) complex 4 (vide supra). To this end, we computed the corresponding reaction profile involving the PhSH and HC≡CMe reactants in the presence of the model Rh\textsuperscript{II} catalyst 4M (where the bulky Dipp substituents on the triazolylidene ring were replaced by phenyl groups). The results are shown in Figure 3, which gathers the corresponding relative free energies (\Delta G\textsubscript{298}, at 298 K) computed at the dispersion corrected B3LYP-D3/det2-SVP level (see computational details below).

From the data in Figure 3, it can be suggested that the process begins with the formation of the initial intermediate INT\textsuperscript{1}, characterized by the occurrence of an intermolecular hydrogen bond involving the PhSH reactant and the NBoc moiety of the
catalyst. Once this initial intermediate is formed, facile thiolate/NHBoc ligand displacement occurs to produce the Rh(I) complex \( \text{INT2} \). The ease of this ligand exchange becomes evident in view of the high exergonicity \( \Delta G_R = -18.4 \text{ kcal/mol} \).

Figure 3. Computed reaction profiles for the reaction of PhSH and H\( \equiv \text{CMe} \) in the presence of model catalyst 4M. Relative free energies (\( \Delta G_{298} \), at 298 K) and bond distances are given in kcal/mol and angstroms, respectively. All data have computed at the B3LYP-D3/def2-SVP level.

from the separate reactants) and the rather low activation barrier \( \Delta G^\ddagger = 1.4 \text{ kcal/mol} \), via \( \text{TS1} \)) computed for this reaction step. Endergonic replacement of a CO ligand by the alkyne occurs next to produce intermediate \( \text{INT3} \) (\( \Delta G_R = 12.3 \text{ kcal/mol} \)). From this intermediate, insertion of the thiolate ligand into the coordinated alkyne takes place leading to the alkenyl-Rh(I) complex \( \text{INT4} \). This slightly endergonic step (\( \Delta G_R = 4.1 \text{ kcal/mol} \)) occurs through the transition state \( \text{TS2} \), a saddle point associated with the concomitant formation of the new C–S bond and Rh–S cleavage (\( \Delta G^\ddagger = 19.8 \text{ kcal/mol} \)).

Final protonolysis of the Rh–C bond (very likely assisted by a new molecule of PhSH) leads to the formation of the observed alkene regenerating the catalyst by coordination of the previously released CO ligand. The high exergonicity computed for this final step (\( \Delta G_R = -20 \text{ kcal/mol} \)) compensates for the previous endergonic insertion reaction and drives the complete catalytic cycle forward.

The proposed reaction mechanism (without the consideration of external base) given in Figure 4, therefore includes the dissociation of the hemilabile protonated ligand and thiolate coordination to the metal center to form \( \text{INT2} \). The spectroscopic detection of this intermediate is compatible with its computed thermodynamic stability (see above). Subsequent alkyne coordination by replacing one of the carbonyl ligands (\( \text{INT3} \)), is followed by alkenyl binding to metal center (\( \text{INT4} \)) after the thiolate group migration. Finally, protonolysis either by a second thiophenol molecule (Path 1, Figure 4) or deprotonation of the pendant NHBoc ligand (Path 2, Figure 4), yields product vinyl sulfide and catalyst. In a final stoichiometric reaction, 1 equivalent of alkyne was added to the stoichiometric reaction mixture (4 + HSPh → \( \text{INT2} \)), but did not lead to product formation, even after heating to 80 °C. For this reason, it can be concluded that protonolysis of the alkenyl complex \( \text{INT4} \) by a second thiophenol molecule is more likely (Path 1, Figure 4). Repetition of the stoichiometric reaction with 1 equivalent of \( \text{K}_2\text{CO}_3 \) yielded the same results.

Table 2. Scope of the base-free hydrothiolation of terminal alkynes with thiophenol using catalyst precursor 4\( ^{\text{\small[a]}} \). Endergonic replacement of a CO ligand by the alkyne occurs next to produce intermediate \( \text{INT3} \) (\( \Delta G_R = 12.3 \text{ kcal/mol} \))\( ^{\text{\small[b]}} \).

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\( ^{\text{\small[a]}} \) Reactions performed at 80 °C with 2 mol% of [4], in 0.5 mL C\( _6 \)D\( _6 \), and anisole as internal standard. \( ^{\text{\small[b]}} \) Conversion calculated after 24 h based on NMR integration of the internal standard anisole. \( ^{\text{\small[c]}} \) Unidentified precipitate observed. \( ^{\text{\small[d]}} \) An additional 4% unidentified byproduct was observed. \( ^{\text{\small[e]}} \) 2 mol% of \( \text{K}_2\text{CO}_3 \) added.
In addition, a perusal of table 1 reveals that in the case of metal complex 2, the lack of ligand-assisted deprotonation of the thiophenol, can only be circumvented by using a catalytic amount of base in order to have excellent regioselectivity. The evidence for ligand-assisted deprotonation of the thiophenol by 4 prompted us to widen the range of both aliphatic and aryl substrates with various functional groups for the base-free hydrothiolation reaction (Table 2), using complex 4 as catalyst. Again, no coupled bis-β,β-vinyl sulfide products were observed, and the reaction was selective to the branched α-vinyl sulfides, thus demonstrating the good functional group tolerance exhibited by the catalyst. Addition of 2 mol% of K$_2$CO$_3$ (entry 2, Table 2) leads to an increase in the yield of the reaction, but as previously seen (Table 1, entries 8 and 9), accompanied by a slight decrease in selectivity. Notably, the strategy of using a bidentate, hemilabile ligand in a cooperative fashion to deprotonate and activate the substrate thiol (especially thiophenol) proved successful in preventing Rh-H formation, so that alkyl insertion into the resultant Rh-SR bond favors α-isomer product formation.

**Conclusions**

The performance of a range of cationic and neutral bidentate N-donor functionalized 1,2,3-triazol-5-ylidene Rh(I) complexes as catalyst precursors for the alkene hydrothiolation reaction was investigated. The strategy of combining an electron-donating (TRZ) bidentate ligand with a tethered coordinating $N$-moiety was followed, as a design approach to yield a catalyst that activates the substrate thiol via deprotonation by the ligand. In addition, direction of the site of attack of the incoming substrate thiol, and insertion of substrate alkene into resulting (Rh)-SR bond for improved Markovnikov-addition regioselectivity of the hydrothiolation reaction, were targeted. For the cationic N-donor (TRZ-NH$_2$) complexes 2 and 5, no evidence for a ligand-assisted bifunctional reaction mechanism for the catalytic hydrothiolation could be found, which is supported by the similar results obtained for the dimethylamino-analogues 3 and 6. Instead, stoichiometric and computational studies indicated only the hemilabile action of the NR$_2$-moiety was observed, as a design approach to yield a catalyst that activates the substrate thiol via deprotonation by the ligand. In contrast, the neutral amidine complexes 1 and 4 demonstrated ligand-assisted activation of the thiol substrates to circumvent the use of directing ligand pyridine or base in the hydrothiolation reaction. A pathway that includes thiol deprotonation by the pendant amido of the triazolylidene ligand, and hemilabile dissociation of the ligand N-donor was postulated for catalyst precursor 4, following spectroscopic and computational studies. Excellent regioselectivity towards the branched vinyl sulfide products was shown by catalyst precursor 4, yielding the notoriously harder-to-come-by α-vinyl sulfides with aryl substituents, specifically for the case when both substrate alkyne and thiol contains aromatic substituents.

**Experimental Section**

All air and moisture sensitive synthetic procedures were performed under a N$_2$ (g) or Ar (g) atmosphere using standard Schlenk techniques. All solvents were purified and distilled over Na$_2$ (s) (hexane, diethyl ether, benzene and THF) or CaH$_2$ (dichloromethane and acetone) under N$_2$ (g) atmosphere. A Bruker AVANCE III- 300-12 MHz or 400.21 MHz spectrometer was used for NMR experiments. Chemical shifts are reported as δ (in ppm) and reported downfield from TMS and referenced to the residual solvent chemical shifts. Coupling constants (J) are reported in Hz. The NMR spectra were analysed using MNeova (Mestrelab research) and the residual solvent chemical shifts were chosen as the default reference shifts in the software. Solution FT-IR spectra (v(CO)) were recorded on a Bruker ALPHA FT-IR spectrophotometer with a NaCl cell, using CH$_2$Cl$_2$ as solvent. The range of absorption measured was from 4000–600 cm$^{-1}$. Mass spectral analyses were performed on a Waters Synapt G2 HDMS by direct infusion at 5 μL/min with positive electron spray as the ionization technique. The m/z values were measured in the range of 400-1500 with acetoneitrile as solvent for 1–4, and dichloromethane for 5 and 6. Prior to analysis, a 5 mM sodium formate solution was used to calibrate the instrument in resolution mode.

**Preparation of complexes 1–3.**

A Schlenk tube in the glove box was charged with the precursor triazolium salt A$^{11}$ (1.40 g, 2.1 mmol) and 2.2 eq. KHMS (0.93 mg, 4.6 mmol). Freshly distilled, deaerated THF (ca. 15 mL) was cannula transferred into this Schlenk tube at -78 °C. The solution was stirred at this temperature for ca. 30 min, before allowing to warm up to -50 °C. The deprotonated NBoc-functionalized carbene was then slowly transferred dropwise (via cannula) into a THF suspension of 0.5 eq. [Rh(COD)Cl]$_2$ (0.54 g, 1.1 mmol) at -78 °C. The reaction mixture was stirred overnight whilst slowly allowing to warm up to RT. The solvent was evaporated to complete dryness in vacuo followed by extraction with hexanes, to yield of 1. Crystallization from a dichloromethane solution layered with hexane, yielded crystals of 1 suitable for X-ray diffraction.

Cationic complexes 2 and 3 were prepared in a similar procedure as described above, using ligand precursors B (1.00 g, 1.8 mmol) and 1.2 eq of KHMS (0.43 g, 2.2 mmol) and C (1.10 g, 1.9 mmol)$^{11}$ with 1.2 eq of KHMS (0.46 g, 2.3 mmol), respectively.

**[Rh(TRZ-NBoc)(COD)]** (1) Yellow powder. Yield: 1.30 g (84%). $^1$H NMR$^{16}$ (300 MHz, CDCl$_3$): δ = 7.47 (dd, 2H, J = 7.82 Hz, H$_2$), 7.26, 7.23 (d, 2H, J = 7.80 Hz, H$_2$), 5.38 (br, 2H, H$_2$), 4.10 (s, 2H, H$_2$), 3.35 (br, 2H, H$_2$), 2.52 (sept, 2H, J = 6.75 Hz, H$_2$), 2.25 (m, 2H, H$_2$), 2.10, 1.80, 1.67 (br m, 6H, H$_2$), 1.37 (d, J = 6.79 Hz, 6H, H$_2$), 1.23, 1.06, 1.03 (d, 18H, J = 6.79 Hz, 6.80 Hz, 6.90 Hz, H$_2$). $^{13}$C[H] NMR (75 MHz, CDCl$_3$): $^1$δ = 146.3 (C$_4$), 162.3 (d, J = 51.6 Hz, C$_5$), 157.3 (C$_5$), 142.5 (C$_{12,14}$), 134.6, 131.1 (C$_7$), 131.7, 131.6 (C$_{12}$), 124.5, 123.6 (C$_{10}$), 95.8, 65.5 (C$_{20,22}$) 65.8 (C$_8$), 49.7 (C$_{13}$), 28.5 (C$_{10}$), 28.7, 28.6 (C$_{12,14}$), 31.7, 29.4, 28.9, 26.4. 23.8, 22.4 (C$_{13,15,21,22}$). HRMS: m/z: [M+H]$^+$calculated: 729.3615; observed: 729.3607;

**[Rh(TRZ-NH$_2$)COD)](PF$_3$)** (2) Yellow powder. Yield: 1.10 g, 79 %. $^1$H NMR$^{16}$ (300 MHz, CD$_2$Cl$_2$): δ = 7.63, 7.56 (dd, 1H, J = 7.85 Hz, 7.82 Hz, H$_2$), 7.41, 7.35 (d, 2H, J = 7.86 Hz, 7.83 Hz, H$_2$), 4.63 (m, 2H, H$_2$), 3.89 (t, 2H, J = 5.0 Hz, H$_2$), 3.68 (m, 2H, H$_2$), 3.61 (bt, 2H, H$_2$), 2.45 (sept, 2H, J = 6.79 Hz, H$_2$), 2.22 (m, 4H+ 2H, H$_2$), 1.89, 1.79 (m, 2H, H$_2$), 1.43, 1.30, 1.15, 1.11 (d, 2H, J = 6.77 Hz, 6.83 Hz, 6.81 Hz, 6.89 Hz, H$_2$), 1.37 (d, J = 6.79 Hz, 6.80 Hz, H$_2$), 1.23, 1.06, 1.03 (d, 18H, J = 6.79 Hz, 6.80 Hz, 6.90 Hz, H$_2$). $^{13}$C[H] NMR$^{16}$ (75 MHz, CD$_2$Cl$_2$): δ = 164.8 (d, J = 51.9 Hz, C$_4$), 156.8 (C$_4$), 145.6, 145.7 (C$_{12,14}$), 134.7, 130.4 (C$_4$), 133.2, 132.3 (C$_6$), 125.6, 124.7 (C$_{10}$), 93.7 (d, J = 8.26 Hz, C$_8$), 74.2 (d, J = 13.1 Hz, C$_{31}$), 41.8 (C$_9$), 32.2, 29.5 (C$_{12,14}$), 25.7, 25.1, 23.9, 23.2 (C$_{13,15,21,22}$). $^{31}$P NMR (121 MHz, CD$_2$Cl$_2$): δ = -144.5 ppm (hept, J =
Preparation of complexes 4–6.

The dicarbonyl complexes 4, 5 and 6 were prepared from the corresponding COD complexes 1 (0.54 g, 0.74 mmol), 2 (0.47 g, 0.61 mmol) or 3 (0.32 g, 0.40 mmol), respectively, by dissolving the precusor metal complex in ca. 20 mL dichloromethane. CO (g) was bubbled through the solution at room temperature for 5 min until the colour of the solution ceases to lighten. The solution was stirred for ca. 15 min in the CO (g) atmosphere, before the solvent was evaporated. Subsequent washing with hexanes yielded the pure complexes.

Crystal structure determination

Single crystal X-ray diffraction data were collected on a Bruker Apex II CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on nylon loops then immediately placed in a cold stream of N₂ at 150 K. Structures were solved and refined using Olex2 and SHELXTL. A satisfactory refinement of the crystal structure of complex 4 was only obtained after squeeze methodology was applied in order to eliminate residual electronic density of the solvent, which could not be refined otherwise.¹⁹ CCDC-1504559 (A), 1504560 (B), 1504561 (C), 1504562 (2) and 1504563 (4), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for compound 2

\[\text{C}_{2}\text{H}_{13}\text{N}_{4}\text{Fe}_{2}\text{PF}_3\text{Rh} (M=774.67 g/mol); monoclinic, space group P2_1/n (no. 14).} \]
\(a = 11.664(5) \text{ Å, } b = 12.5642(6) \text{ Å, } c = 24.8822(11) \text{ Å, } \beta = 102.418(2)^{\circ}; V = 3561.2(3) \text{ Å}^3; Z = 4, T = 150.15 \text{ K, } \mu(\text{MoKα}) = 0.586 \text{ mm}^{-1}, D_{\text{calc}} = 1.445 \text{ g/cm}^3, 121530 \text{ reflections measured (4.664} \leq 2\theta \leq 52 \text{.924}^{\circ}), 7303 \text{ unique (} R_{\text{int}} = 0.0460, R_{\text{free}} = 0.0151 \text{) which were used in all calculations. The final } R_{\text{f}} \text{ was 0.0330 (} l > 2\sigma(l) \text{) and } wR_{\text{f}} \text{ was 0.0893 (all data).} \]

DFT calculations

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.²⁰ Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP²¹ in conjunction with the D3 dispersion correction suggested by Grimme et al.²² using the double-\(\tilde{C}\) quality plus polarization def2-SVP basis set²³ for all atoms. This level is denoted B3LYP-D3/def2-SVP. Reactants and products were characterized by frequency calculations,²⁴ and have positive definite Hessian matrices. Transition structures (TSs) show only one negative eigenvalue in their diagonalised force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.²⁵

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Keywords: rhodium(I) • hydrothiolation • 1,2,3-triazol-5-ylidene (TRZ) • mesoionic carbene (MIC) • hemilabile


[18] See Supporting Information for full NMR spectra and atom numbering scheme.


A ligand-assisted acid-base thiol activation strategy for the regioselective hydrothiolation of alkynes mediated by a Rh\textsuperscript{I} catalyst