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Ruthenium Catalysis

Decarbonylation of Salicylaldehyde Activated by *p*-Cymene Ruthenium(II) Dimer: Implication for Catalytic Alkyne Hydrothiolation

Sarangapani Modem,[a] Shravankumar Kankala,*[a,b] Ramesh Balaboina,[a] Narasimha Swamy Thirukovela,[a] Sreekantha B. Jonnalagadda,*[b] Ravinder Vadde,*[a] and Chandra Sekhar Vasam*[c,d]

Abstract: A stoichiometric C–H activation/decarbonylation of salicylaldehyde by $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ gave a carbonyl derivative $[(\eta^6\text{-}p\text{-cymene})RuCl(CO)(Ph\text{-}O)]$ (**1**) without the use of CO gas. A variety of polar phosphines were then incorporated into compound **1** to give new Ru^{II} cationic catalysts, $[(\eta^6\text{-}p\text{-cymene})Ru(CO)(Ph\text{-}O)L]BF_4$ (**2**–**8**). These were used to catalyse the hydrothiolation of alkynes with a range of thiols in aqueous THF to give anti-Markovnikov *E*-linear vinyl sulfides in high yields.

Introduction

Hydrofunctionalisation (or hydroelementation), the process of addition of heteroatom–hydrogen bonds across the C–C bonds of unsaturated molecules, is a 100 % atom-economical approach to the formation of new carbon–heteroatom bonds in sustainable organic synthesis.[1] In principle, this reaction can be promoted by free radicals,[2] strong acids,[3] bases,[4] or catalysts,[1d,5] and metal catalysts have been shown to have great potential to promote this process under mild conditions with a high degree of regio- and stereoselectivity. In contrast to the wide application of nitrogen, oxygen, and phosphorus nucleophiles in catalytic hydrofunctionalisation, the use of sulfur nucleophiles has remained relatively underexplored for a long time, due to the belief that sulfur compounds are effective poisons for metal catalysts. However, the fact that C–S-bond-containing structures are widespread, for example, the vinyl sulfides in natural products,[6] functional materials,[7] synthetic precursors/intermediates,[4b,8] and medicinal compounds,[9] has, in the last decade, stimulated interest in optimising the catalytic conditions for alkyne hydrothiolation.

[a] *Department of Chemistry, Kakatiya University, Warangal 506009, Telangana State, India*
E-mail: shravankankala@yahoo.com
vravichemku@gmail.com
[b] *School of Chemistry and Physics, University of Kwazulu-Natal, Westville Compus, Chiltern Hills, Durban 4000, South Africa*
E-mail: jonnalagaddas@ukzn.ac.za
[c] *Department of Chemistry, Satavahana University, Karimnagar, Telangana State, India*
[d] *Department of Pharmaceutical Chemistry, Telangana University, Nizamabad, Telangana State, India*
E-mail: vasamcs@yahoo.co.in

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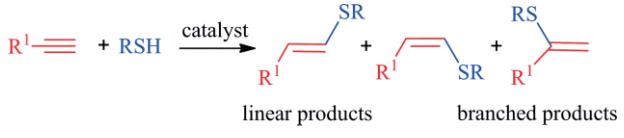
The mechanism of the hydrothiolation reaction of alkynes can be different from that of other addition reactions.[10] The mechanism of the hydrothiolation of alkynes begins either with (i) activation of the thiol, i.e., insertion of the alkyne into an initially formed metal thiolate [M]-SR or hydride thiolate H-[M]-SR species; or (ii) activation of the alkyne C–C triple bond, i.e., insertion of R-SH into a metal vinylidene species. The choice between these two possible mechanisms has been found to depend on the Lewis acidity of the metal precatalyst. The steric and electronic influence of ligands in the coordination sphere of the metal have been shown to determine the selectivity for Markovnikov (branched) or anti-Markovnikov (*E*/*Z* linear) vinyl sulfide products (Scheme 1). In this context, in the recent literature, a variety of metals, including platinum-group metals,[11] coinage-group metals,[12] lanthanides/actinides,[13] main-group metals,[14] and few early/late transition metals[15] have been investigated as efficient promoters for alkyne hydrothiolation. Nonetheless, control of the stereo- and regioselectivity under mild and environmentally friendly conditions still remains a challenging and highly desirable objective.



Scheme 1. Hydrothiolation of terminal alkynes.

In line with increasing awareness of green chemistry principles for sustainable chemical synthesis, reactions in aqueous media have received much attention.[16] Furthermore, water is able to exert an effect on the rates and selectivities of reactions as a result of hydrophobic interactions. In response to the factors described above, we now describe a method for the stereo-

selective anti-Markovnikov hydrothiolation of alkynes in aqueous media using serendipitously evolved homogeneous cationic [(η⁶-*p*-cymene)Ru(CO)(Ph-O)(phosphine)] catalysts. We recently reported the regioselective Markovnikov hydrothiolation of alkynes in aqueous media using Rh^{I}-phosphines.[17] In view of the versatility of metal-promoted regio- and stereoselective hydrothiolation, this time we planned to develop some new Ru^{II} catalysts based on polar phosphines. It should also be noted that previous reports of the use of Ru^{II} catalysts for hydrothiolation are very scarce.[11a]

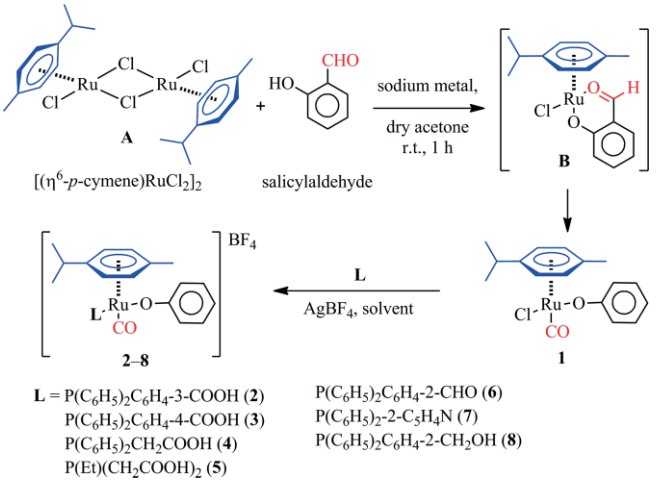
In this article, the results of our research findings are divided into two parts to explain the metal-mediated organic chemistry involved in (i) catalyst design, and (ii) hydrofunctionalisation. The first part demonstrates a serendipitously observed stoichiometric C–H activation/decarbonylation of salicylaldehyde mediated by [(η⁶-*p*-cymene)RuCl$_2$]$_2$ to produce [(η⁶-*p*-cymene)-RuCl(CO)(Ph-O)] (**1**) and [(η⁶-*p*-cymene)Ru(Ph-O)(CO)L]BF$_4$ (**2**–**8**). The second part concentrates on our main task of optimising the Ru^{II}-catalysed alkyne hydrothiolation conditions to produce anti-Markovnikov *E*-linear vinyl sulfides in environmentally benign aqueous media.

Results and Discussion

Stoichiometric Decarbonylation of Salicylaldehyde through C–H Activation with [(η⁶-*p*-Cymene)RuCl$_2$]$_2$

We planned to isolate Ru^{II} complex **B** (Scheme 2) and to incorporate polar phosphines into it by the exchange of chloride. Ru^{II}-η⁶-arene precursors have been proposed for the design of new Ru^{II} catalysts owing to the ring-slippage properties of η⁶-arene rings that facilitate fulfilment of the 18-electron rule during catalysis.[18] Nevertheless, as shown in Scheme 2, the stoichiometric reaction of [(η⁶-*p*-cymene)RuCl$_2$]$_2$ (**A**) with salicylaldehyde in dry acetone enabled a serendipitous C–H activation followed by a decarbonylation step on salicylaldehyde, and interestingly yielded a new piano-stool-structured neutral carbonyl derivative [(η⁶-*p*-cymene)RuCl(CO)(Ph-O)] (**1**), as determined by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy, and electrospray mass spectrometry.

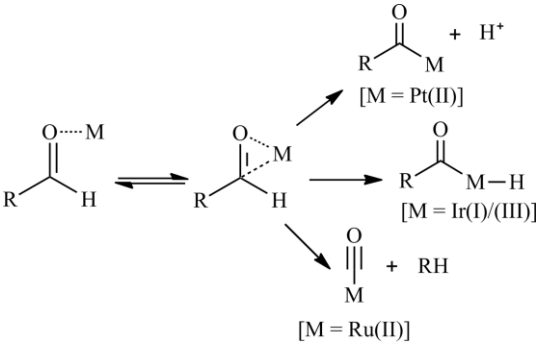
The IR spectrum of compound **1** shows a characteristic strong absorption band at $\tilde{\nu} \approx 1937$ cm^{-1}, which corresponds to Ru(C≡O). The absence of an absorption due to OH at $\tilde{\nu} \approx 3440$ cm^{-1}, and the presence of a new band at $\tilde{\nu} \approx 1032$ cm^{-1} in the same spectrum were ascribed to aryl C–O–Ru^{II} coordination of the phenoxide fragment that remained after the decarbonylation of salicylaldehyde. The metallated carbonyl carbon (i.e., Ru–CO) of compound **1** was observed in its ^{13}C NMR spectrum with a downfield chemical shift of $\delta \approx 190$ ppm, which is consistent with previously reported chemical shifts for Ru–CO coordination. Another downfield signal observed at $\delta \approx 160$ ppm was assigned to the aryl C–O–Ru^{II} carbon of the phenoxide ion fragment. The absence of signals in the ^{1}H NMR spectrum due to the aldehyde and hydroxyl group of salicylaldehyde confirms the above findings. The spectroscopic assignment of the chemical environments of the *p*-cymene and chloride moieties of compound **1** are given experimental section; they are consistent with previous reports.[19]



Scheme 2. Formation of compound **1** by an intramolecular pathway, and the subsequent synthesis of cationic Ru^{II} catalysts **2**–**8**.

The stoichiometric decarbonylation of various aldehydes through C–H activation catalysed by various transition-metal complexes, (V^{V}, Fe^{0}, Co$^{I/III}$, Ru$^{0/II}$, Rh$^{I/III}$, Pd^{II}, Os$^{VI/IV/0}$, Ir$^{I/III}$, Pt^{II} etc.) have been reported previously in some organic and organometallic syntheses.[20] The literature reveals that this process usually occurs either through oxidative addition or by an intramolecular pathway, and produces an (R)M(CO) derivative or intermediate (R = alkyl/aryl, M = metal). As a consequence, this phenomenon has been shown to give direct access to industrially valuable and labile metal–carbonyl catalysts without the need for poisonous CO gas.[21] However, the decarbonylation of salicylaldehyde mediated by Ru^{II} has not been reported before.

In the literature, it has been reported that during decarbonylation, the carbonyl fragment of the phenolic ligand (aromatic aldehydes) initially coordinates with the metal centre in an η^2 fashion. It then undergoes a rearrangement to give different M–CO bonds, as shown in Scheme 3. The π-bonded carbonyls[20p] (Pt^{II}, Ir^{I}, and Ru^{II}) can rearrange through hydrogen migrations to give each of the observed products with minimal geometric reorganisation. In our work, we assume that this reaction is intramolecular, and that it proceeds by a pathway different from that reported earlier for platinum(II) complexes.[22]



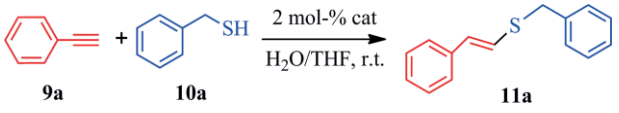
Scheme 3. π-Bonded metal carbonyls, and rearrangement to give a variety of M–CO bonds.

The formation of Ru^{II} compound **1** by decarbonylation was further evidenced by the fact that new cationic Ru^{II} complexes **2**–**8** (Scheme 2) were obtained in the presence of $AgBF_4$. A variety of polar phosphines were incorporated into the half-sandwich core of compound **1** simply by replacing the chloride group (Scheme 2). The spectroscopic and analytical characterisation data of complexes **2**–**8** are given in the Exp. Section. When we investigated the reactions of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with 2-hydroxy-1-naphthaldehyde and 2-vanillin, no decarbonylation was observed. This could be due to the variation in the steric and electronic properties of the substrates.

Catalytic Hydrothiolation

The efficacy of the cationic complexes $[(\eta^6\text{-}p\text{-cymene})Ru(Ph\text{-}O)(CO)(L)]BF_4$ (**2**–**8**) as catalysts for alkyne hydrothiolation was investigated in aqueous media (H_2O/THF, 7:3), and the results are presented in Table 1.

Table 1. Results of hydrothiolation using different Ru^{II} *p*-cymene catalyst.



9a **10a** **11a**

Entry	Catalyst	Time [h]	Yield [%][a]
1	no catalyst	16	57 (11:89:0)[b]
2	**2**	2	90 (74:26)
3	**2** + radical trap	2	90[c]
4	**3**	2	90 (74:26)
5	**4**	2	88 (72:28)
6	**5**	2	89 (73:27)
7	**6**	2	91 (75:25)
8	**7**	2	90 (74:26)
9	**8**	2	87 (71:29)

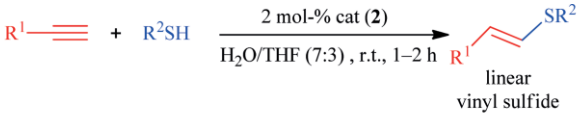
[a] Isolated yields after GC analysis of linear product (β-*E*). [b] Mixture of products [β(*E*:*Z*)/α] under reflux conditions. [c] Radical traps (2 mol-%).

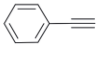
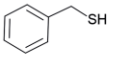
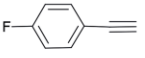
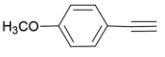
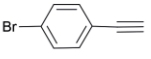
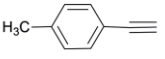
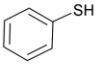
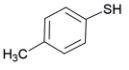
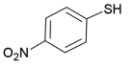
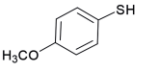
Initially, we investigated the hydrothiolation of phenyl acetylene (**9a**) with benzyl thiol (**10a**) in the presence of cationic Ru^{II} catalyst **2**, and compared the result with the uncatalysed hydrothiolation (without catalyst) of our previous report.[17] As shown in Table 1, the uncatalysed hydrothiolation between **9a** and **10a** proceeded only under refluxing conditions, and gave a mixture of linear (β; anti-Markovnikov) vinyl sulfides (Table 1, entry 1), in which the *Z*-isomer was the major product, as observed by us previously.[17] This reaction possibly occurred through a radical mechanism.

On the other hand, when Ru^{II} phosphine complex $[(\eta^6\text{-}p\text{-cymene})Ru(L)(CO)(Ph\text{-}O)]BF_4$ (**2**) was used as the catalyst, the hydrothiolation reaction occurred at room temperature and with good stereoselectivity, yielding anti-Markovnikov *E*-linear vinyl sulfide as the major product [β(*E*/*Z*) = 74:26] (Table 1, entry 2) after 2 h. The addition of radical traps {BHT (2,6-di-*tert*-butyl-4-methylphenol), TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl], and 4-methoxyphenol} to this reaction at room temperature had no effect on the product selectivity, yield, or reaction time (Table 1, entry 3). This shows that the reaction does not involve radicals, and proceeds by a catalytic path.

We then explored the potential of Ru^{II} phosphines **3**–**8** (Scheme 2) as catalysts, to see their effect on product selectivity and yield. The results summarised in Table 1 suggest that Ru^{II} phosphine derivatives **2**–**8** all efficiently controlled the stereoselectivity of the hydrothiolation reaction of **9a** with **10a**, to give *E*-linear vinyl sulfide **11a** as the major product (Table 1, entries 4–9) within a reaction time of 2 h. The characterisation data for **11a** is included in the Experimental Section. The major and minor isomers were separated by column chromatography. On the other hand, when we tried to run the model reaction with ruthenium dimer $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ and phosphine ligands in an aqueous medium, the reaction was sluggish, and a mixture of products was formed in poor yield. We also tested an alkyne hydrothiolation reaction using complex **1** (phosphine

Table 2. Hydrothiolation of terminal alkynes catalysed by Ru^{II} *p*-cymene catalyst.



Entry	Alkyne	Thiol	Product yield (%)[a] (*E*/*Z*)[b]
1	**9a** 	**10a** 	**11a** 90 (74/26)
2	**9b** 	**10a**	**11b** 92 (82/18)
3	**9c** 	**10a**	**11c** 94 (85/15)
4	**9d** 	**10a**	**11d** 88 (84/16)
5	**9e** 	**10a**	**11e** 92 (76/24)
6	**9a**	**10b** 	**11f** 86 (78/22)
7	**9b**	**10b**	**11g** 90 (80/20)
8	**9e**	**10b**	**11h** 86 (88/12)
9	**9a**	**10c** 	**11i** 90 (85/15)
10	**9e**	**10c**	**11j** 85 (72/28)
11	**9a**	**10d** 	**11k** 86 (70/30)
12	**9a**	**10e** 	**11l** 96 (78/22)
13	**9f** 	**10a**	**11m** 74 (64/36)

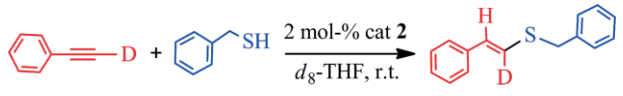
[a] Isolated yield after column chromatography. [b] *E*/*Z* ratio determined by ^1H NMR spectroscopy.

free) as the catalyst in aqueous media. However, the reaction was again slow, and produced a mixture of products including vinyl sulfides.

The optimised conditions for the synthesis of **11a** were then used to study the hydrothiolation of a range of terminal alkynes and aryl/aliphatic thiols with different steric and electronic properties. These reactions were investigated in the presence of Ru^{II} phosphine catalyst **2** (Table 2). Again the formation of *E*-linear vinyl sulfides (**11b**–**11j**) as the major products was noticed in all the reactions (Table 2). The electronic effects influenced the product yield to some extent (up to 11 %) in all the reactions investigated.

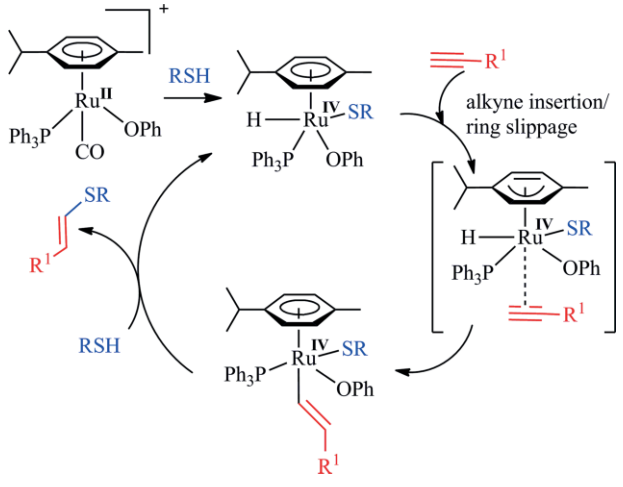
The alkynes and thiols bearing an electron-donating substituent at the *para* position gave better yields (Table 2, entries 3, 5, 9, and 12). On the other hand, those bearing an electron-withdrawing substituent at the *para* position gave slightly lower yields (Table 2, entries 4 and 11).

A deuterium-labelling hydrothiolation experiment (Scheme 4) was carried out in [D_8]THF to provide evidence for the assistance by the Ru^{II} phosphine catalyst in the anti-Markovnikov *syn*-addition. Upon the synthesis of 1,2-disubstituted deuterated vinyl sulfide, and in agreement with previous work,[11p] we propose that the product is formed through *syn*-addition. The reaction involving alkyne insertion into Ru–H is more favourable than that involving Ru–S, due to steric factors, as reported previously.[10a,10f,11p] The characteristic signal in the ^1H NMR spectrum for the deuterated product was observed at δ = 6.50 ppm. Further information is provided in the catalytic cycle.



Scheme 4. Reaction between deuterium-labelled phenylacetylene and benzylthiol.

Based on the results shown in Tables 1 and 2, and on previous literature, we have proposed an appropriate reaction mechanism for the Ru^{II}-phosphine-catalysed alkyne hydrothiolation reaction to selectively form the anti-Markovnikov *E*-linear product, as shown in Scheme 5. The presence of labile CO in transition-metal organometallic catalysts and the factors governing its coordination position to the metal during the operation of many catalytic cycles have already been discussed.[23]



Scheme 5. A plausible mechanism for the formation of linear vinyl sulfides.

Conclusions

In conclusion, this work presents an operationally simple and environmentally friendly transformation for the synthesis of carbonyl derivative [(η^6-*p*-cymene)RuCl(CO)(Ph-O)] (**1**) with no need for external CO gas. Compound **1** is a versatile precursor that can incorporate a variety of polar phosphines to give new Ru^{II} cationic catalysts [(η^6-*p*-cymene)Ru(Ph-O)(CO)L]BF_4 (**2**–**8**). These catalysts are efficient in alkyne hydrothiolation with aliphatic/aromatic thiols in aqueous THF to produce the anti-Markovnikov *E*-linear vinyl sulfides in excellent yields and with good stereoselectivity. Carbon monoxide has been found to be an important molecule for studying the reactivity of homogeneous catalysts and the implications for their use in organic synthesis. This protocol represents an improvement over existing methods.

Experimental Section

General Remarks: Commercially available reagents were used without further purification. Solvents were dried and deoxygenated by heating at reflux and storing over sodium. Microanalysis (C, H, N) was carried out using a Perkin–Elmer CHN analyser at 240 °C. IR spectra were recorded using KBr pellets with a Perkin–Elmer-283 spectrophotometer. ^1H, ^{13}C and ^{31}P NMR spectra were obtained with a Bruker MHz 270 NMR spectrometer, operating at 270 (for ^1H), 67.93 (for ^{13}C), and 109.29 (for ^{31}P) MHz, respectively. A MICROMASS-7070 spectrometer was used for mass spectra. UV/Visible spectra were recorded with a Shimadzu UV-160A double-beam spectrophotometer.

Procedure for the Synthesis of [(η^6-*p*-Cymene)Ru(CO)(Ph-O)Cl] (1): [(η^6-*p*-cymene)$RuCl_2$]$_2$ (0.612 g, 1 mmol) was suspended in acetone (15 mL), and a solution of the sodium salt of salicylaldehyde (0.288 g, 2 mmol) in acetone (10 mL) was added. The reaction mixture was stirred for 1 h. During the course of the reaction, the colour of the solution changed from red to pale yellow. Then volume of the solution was then reduced to 5 mL under vacuum, and diethyl ether (10 mL) was added dropwise to initiate the crystallisation of the product. The resulting pale yellow product was collected by filtration, and dried in vacuo (0.684 g, 76 %).

[(η^6-*p*-Cymene)Ru(Ph-O)(CO)Cl] (1): ^1H NMR (270 MHz, $CDCl_3$): δ = 1.25 (d, 3 H, isopropyl, *CH*$_3$), 2.17 (s, 3 H, toluyl, *CH*$_3$), 2.91 (sept, 1 H, isopropyl, *CH*), 5.36 (d, *J* = 6.3 Hz, 2 H, Ar-*H*$_A$), 5.48 (d, *J* = 6.3 Hz, 2 H, Ar-*H*$_B$), 6.92–7.80 (m, 5 H, Ar-H) ppm. ^{13}C NMR (67.93 MHz, $CDCl_3$): δ = 18.20, 22.18, 30.14, 84.28, 90.62, 97.52, 101.02, 121.24–135.98, 159.34, 196.12 ppm. IR: $\tilde{\nu}$ = 3447 (br., *p*-cymene), 1938 (ss, Ru–CO), 1032 (ms, aryl C–O–Ru), 307 (ms, Ru–Cl) cm^{-1}. $C_{17}H_{19}ClO_2Ru$ (391.86): calcd. C 52.11, H 4.89; found C 52.08, H 4.86.

Procedure for the Synthesis of Catalysts 2–8: A Schlenk flask (100 mL) containing a sample of [(η^6-*p*-cymene)Ru(CO)(PhO)Cl] (0.5 mmol) in acetone (20 mL) was mixed with $AgBF_4$ (0.5 mmol). The reaction mixture was stirred for 15 min. The AgCl precipitate was removed, and the solution fraction was transferred into a second Schlenk flask. Then phosphine ligand (0.5 mmol) was added, and the reaction mixture was stirred for 4 h. The mixture was then

concentrated to 5 mL, and diethyl ether (10 mL) was added dropwise to initiate the crystallisation of product.

[(η⁶-p-Cymene)Ru(PhO)(CO)(P(C$_6$H$_5$)$_2$C$_6$H$_4$-3-COOH)]BF$_4$ (2): Yield 85 % (0.637 g). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.19 (d, 3 H, isopropyl, CH_3), 2.17 (s, 3 H, toluyl, CH_3), 1.29 (d, 3 H, isopropyl, CH_3), 2.92 (sept, 1 H, isopropyl, *CH*), 5.30 (d, J = 6.3 Hz, 2 H, Ar-H_A), 5.51 (d, J = 6.3 Hz, 2 H, Ar-H_B), 6.90–8.12 (m, 19 H, Ar-H), 12.01 (br., 1 H, *COOH*) ppm. ^{13}C NMR (67.93 MHz, $CDCl_3$): δ = 18.17, 22.17, 30.24, 84.29, 90.41, 96.92, 102.04, 120.23–136.41, 159.47, 172.23, 195.10 ppm. ^{31}P NMR (109.29 MHz, $CDCl_3$): δ = 29.80 ppm. IR: $\tilde{\nu}$ = 3446 (br., *p*-cymene), 1948 (ss, Ru–CO), 1720 (ss, COOH), 1098, 527 (ss, BF_4), 1034 (ms, aryl C–O–Ru), 510 (ms, Ru–P) cm^{-1}. $C_{36}H_{34}BF_4O_4PRu$ (749.51): calcd. C 57.69, H 4.57; found C 57.65, H 4.54.

[(η⁶-*p*-Cymene)Ru(PhO)(CO){P(C$_6$H$_5$)$_2$C$_6$H$_4$-4-COOH}]BF$_4$ (3): Yield 82 % (0.615 g); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.19 (d, 3 H, isopropyl, CH_3), 2.17 (s, 3 H, toluyl, CH_3), 1.29 (d, 3 H, isopropyl, CH_3), 2.92 (sept, 1 H, isopropyl, *CH*), 5.30 (d, J = 6.3 Hz, 2 H, Ar-H_A), 5.51 (d, J = 6.3 Hz, 2 H, Ar-H_B), 6.89–8.10 (m, 19 H, Ar-H), 12.04 (br., 1 H, *COOH*) ppm. ^{13}C NMR (67.93 MHz, $CDCl_3$): δ = 18.10, 22.11, 30.22, 84.29, 90.42, 96.92, 102.04, 120.24–136.45, 159.47, 172.24, 195.12 ppm. ^{31}P NMR (109.29 MHz, $CDCl_3$): δ = 30.05 ppm. IR: $\tilde{\nu}$ = 3442 (br., *p*-cymene), 1945 (ss, Ru–CO), 1720 (ss, COOH), 1096, 525 (ss, BF_4), 1030 (ms, aryl C–O–Ru), 512 (ms, Ru–P) cm^{-1}. $C_{36}H_{34}BF_4O_4PRu$ (749.51): calcd. C 57.69, H 4.57; found C 57.65, H 4.54.

[(η⁶-*p*-Cymene)Ru(PhO)(CO){P(C$_6$H$_5$)$_2$CH$_2$COOH}]BF$_4$ (4): Yield 78 % (0.536 g). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.20 (d, 3 H, isopropyl, CH_3), 2.16 (s, 3 H, toluyl, CH_3), 1.29 (d, 3 H, isopropyl, CH_3), 2.94 (sept, 1 H, isopropyl, *CH*), 3.60 (s, 2 H, CH_2), 5.34 (d, J = 6.3 Hz, 2 H, Ar-H_A), 5.56 (d, J = 6.3 Hz, 2 H, Ar-H_B), 6.76–8.09 (m, 15 H, Ar-H), 11.26 (br., 1 H, *COOH*) ppm. ^{13}C NMR (67.93 MHz, $CDCl_3$): δ = 18.15, 22.10, 30.24, 48.62, 84.20, 90.41, 96.94, 102.04, 120.02–136.62, 159.45, 170.25, 195.12 ppm. ^{31}P NMR (109.29 MHz, $CDCl_3$): δ = 30.25 ppm. IR: $\tilde{\nu}$ = 3448 (br., *p*-cymene), 1940 (ss, Ru–CO), 1095, 524 (ss, BF_4), 1038 (ms, aryl C–O–Ru), 514 (ms, Ru–P) cm^{-1}. $C_{31}H_{32}BF_4O_4PRu$ (688.11): calcd. C 54.16, H 4.69; found C 54.14, H 4.65.

[(η⁶-*p*-Cymene)Ru(PhO)(CO){P(Et)(CH$_2$COOH)$_2$}]BF$_4$ (5): Yield 88 % (0.547 g). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.20 (d, 3 H, isopropyl, CH_3), 2.15 (s, 3 H, toluyl, CH_3), 1.28 (d, 3 H, isopropyl, CH_3), 2.91 (sept, 1 H, isopropyl, *CH*), 2.50 (t, 3 H, CH_3 of Et), 3.05 (q, 2 H, CH_2 of Et), 3.62 (s, 4 H, CH_2), 5.32 (d, J = 6.3 Hz, 2 H, Ar-H_A), 5.54 (d, J = 6.3 Hz, 2 H, Ar-H_B), 7.25–7.89 (m, 5 H, Ar-H), 11.82 (br., 2 H, *COOH*) ppm. ^{13}C NMR (67.93 MHz, $CDCl_3$): δ = 18.17, 19.45, 22.17, 30.24, 46.24, 52.36, 84.29, 90.41, 96.92, 102.04, 120.25–136.44, 159.47, 172.23, 195.10 ppm. ^{31}P NMR (109.29 MHz, $CDCl_3$): δ = 30.34 ppm. IR: $\tilde{\nu}$ = 3440 (br., *p*-cymene), 1942 (ss, Ru–CO), 1712 (ss, COOH), 1094, 526 (ss, BF_4), 1032 (ms, aryl C–O–Ru), 524 (ms, Ru–P) cm^{-1}. $C_{23}H_{30}BF_4O_6PRu$ (622.09): calcd. C 44.46, H 4.87; found C 44.42, H 4.85.

[(η⁶-*p*-Cymene)Ru(PhO)(CO){P(C$_6$H$_5$)$_2$C$_6$H$_4$-2-CHO}]BF$_4$ (6): Yield 80 % (0.587 g). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.21 (d, 3 H, isopropyl, CH_3), 2.18 (s, 3 H, toluyl, CH_3), 1.30 (d, 3 H, isopropyl, CH_3), 2.94 (sept, 1 H, isopropyl, *CH*), 5.34 (d, J = 6.3 Hz, 2 H, Ar-H_A), 5.56 (d, J = 6.3 Hz, 2 H, Ar-H_B), 6.92–8.10 (m, 19 H, Ar-H), 9.24 (br., 1 H, *CHO*) ppm. ^{13}C NMR (67.93 MHz, $CDCl_3$): δ = 18.17, 22.18, 30.24, 84.28, 90.42, 96.92, 102.06, 120.25–136.42, 159.47, 164.25, 195.12 ppm. ^{31}P NMR (109.29 MHz, $CDCl_3$): δ = 30.22 ppm. IR: $\tilde{\nu}$ = 3445 (br., *p*-cymene), 1955 (ss, Ru–CO), 1662 (ss, CHO), 1102, 529 (ss, BF_4), 1034 (ms, aryl C–O–Ru), 512 (ms, Ru–P) cm^{-1}. $C_{36}H_{34}BF_4O_3PRu$ (734.13): calcd. C 58.95, H 4.67; found C 58.92, H 4.64.

[(η⁶-*p*-Cymene)Ru(PhO)(CO){P(C$_6$H$_5$)$_2$-2-C$_5$H$_4$N}]BF$_4$ (7): Yield 84 % (0.593 g). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.18 (d, 3 H, isopropyl, CH_3), 2.15 (s, 3 H, toluyl, CH_3), 1.28 (d, 3 H, isopropyl, CH_3), 2.91 (sept, 1 H, isopropyl, *CH*), 5.30 (d, J = 6.3 Hz, 2 H, Ar-H_A), 5.52 (d, J = 6.3 Hz, 2 H, Ar-H_B), 6.56–8.10 (m, 19 H, Ar-H) ppm. ^{13}C NMR (67.93 MHz, $CDCl_3$): δ = 18.15, 22.16, 30.24, 84.29, 90.42, 96.90, 102.05, 120.25–136.42, 156.10, 159.65, 195.10 ppm. ^{31}P NMR (109.29 MHz, $CDCl_3$): δ = 31.20 ppm. IR: $\tilde{\nu}$ = 3442 (br., *p*-cymene), 1954 (ss, Ru–CO), 1093, 524 (ss, BF_4), 1036 (ms, aryl C–O–Ru), 508 (ms, Ru–P) cm^{-1}. $C_{34}H_{33}BF_4NO_2PRu$ (707.13): calcd. C 57.80, H 4.71, N 1.98; found C 57.76, H 4.69, N 1.96.

[(η⁶-*p*-Cymene)Ru(PhO)(CO){P(C$_6$H$_5$)$_2$C$_6$H$_4$-2-CH$_2$OH}]BF$_4$ (8): Yield 85 % (0.625 g). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.17 (d, 3 H, isopropyl, CH_3), 2.18 (s, 3 H, toluyl, CH_3), 1.27 (d, 3 H, isopropyl, CH_3), 2.92 (sept, 1 H, isopropyl, *CH*), 3.46 (s, 2 H, CH_2-OH), 4.62 (s, 1 H, CH_2-*OH*), 5.31 (d, J = 6.3 Hz, 2 H, Ar-H_A), 5.53 (d, J = 6.3 Hz, 2 H, Ar-H_B), 6.82–8.04 (m, 19 H, Ar-H) ppm. ^{13}C NMR (67.93 MHz, $CDCl_3$): δ = 18.15, 22.17, 30.24, 56.84, 84.29, 90.42, 96.90, 102.06, 120.25–136.40, 159.45, 195.12 ppm. ^{31}P NMR (109.29 MHz, $CDCl_3$): δ = 30.46 ppm. IR: $\tilde{\nu}$ = 3438 (br., *p*-cymene), 3415 (OH), 1950 (ss, Ru–CO), 1099, 530 (ss, BF_4), 1034 (ms, aryl C–O–Ru), 518 (ms, Ru–P) cm^{-1}. $C_{36}H_{36}BF_4O_3PRu$ (736.15): calcd. C 58.79, H 4.93; found C 58.76, H 4.90.

General Procedure for the Catalytic Hydrothiolation of Terminal Alkynes with Thiols: Mononuclear Ru^{II} *p*-cymene catalyst **2** (0.20 mmol, 2 mol-%), water (7 mL), THF (3 mL), thiol (11 mmol), and alkyne (10 mmol) were combined in a round-bottomed flask (50 mL) equipped with a magnetic stirrer bar. The reaction mixture was stirred at room temperature for 1.5 h. After the reaction was complete, the mixture was diluted with dichloromethane (50 mL). The organic layer was dried (anhydrous Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product was subjected to column chromatography (silica gel, 60–120 mesh, *n*-hexane/EtOAc gradient) to give pure products.

Benzyl(styryl)sulfane (11a):[15] Yield 90 %, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.01 (s, 2 H), 6.26 (d, J = 11.4 Hz, 1 H), 6.40 (d, J = 10.8 Hz, 1 H), 6.54 (d, J = 15.8 Hz, 1 H), 6.73 (d, J = 15.4 Hz, 1 H), 7.18–7.35 (m, 9 H), 7.48 (d, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.24, 39.6, 124.42, 125.23, 125.60, 126.85, 127.45, 127.82, 128.52, 128.14, 128.52, 129.62, 137.42, 137.94, 138.60 ppm. MS (EI, 70 eV): m/z = 227 [M + H]$^+$. $C_{15}H_{14}S$ (226.08): calcd. C 79.60, H 6.23, S 14.17; found C 79.58, H 6.22, S 14.15.

Benzyl(4-fluorostyryl)sulfane (11b):[16] Yield 92 %, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.02 (s, 2 H), 6.30 (d, J = 11.2 Hz, 1 H), 6.45 (d, J = 11.4 Hz, 1 H), 6.54 (d, J = 15.4 Hz, 1 H), 6.68 (d, J = 15.4 Hz, 1 H), 7.01–7.10 (m, 2 H, Ar-H), 7.25–7.49 (m, 7 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.72, 39.64, 114.53, 115.60, 115.85, 123.40, 124.52, 125.43, 126.52, 126.92, 127.22, 128.64, 128.85, 130.24, 132.84, 133.10, 137.52, 159.40, 162.92 ppm. MS (EI, 70 eV): m/z = 245 [M + H]$^+$. $C_{15}H_{13}FS$ (244.33): calcd. C 73.74, H 5.36, S 13.12; found C 73.72, H 5.34, S 13.10.

Benzyl(4-methoxystyryl)sulfane (11c): Yield 94 %, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.34 (s, 3 H), 3.97 (s, 2 H), 6.28 (d, J = 10.1 Hz, 1 H), 6.42 (d, J = 10.4 Hz, 1 H), 6.51 (d, J = 15.0 Hz, 1 H), 6.65 (d, J = 15.5 Hz, 1 H), 7.35–7.06 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.30, 37.62, 39.65, 56.64, 123.12, 125.06, 125.61, 126.10, 127.28, 128.54, 128.72, 128.90, 129.05, 129.20, 129.44, 134.22, 134.30, 136.22, 136.45, 137.20, 137.52 ppm. MS (EI, 70 eV): m/z = 257 [M + H]$^+$. $C_{16}H_{16}OS$ (256.09): calcd. C 74.96, H 6.29, S 12.51; found C 74.94, H 6.28, S 12.49.

Benzyl(4-bromostyryl)sulfane (11d): Yield 88 %, pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.05 (s, 2 H), 6.40 (d, J = 10.6 Hz, 1

H), 6.49 (d, *J* = 11.2 Hz, 1 H), 6.56 (d, *J* = 15.3 Hz, 1 H), 6.68 (d, *J* = 15.3 Hz, 1 H), 7.02–7.10 (m, 2 H), 7.25–7.48 (m, 7 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.35, 39.34, 114.90, 115.25, 115.52, 123.88, 124.65, 125.50, 126.72, 126.93, 127.30, 128.64, 128.76, 130.24, 132.90, 133.06, 137.22, 159.64, 162.92 ppm. MS (EI, 70 eV): *m/z* = 305 $[M + H]^+$. $C_{15}H_{13}BrS$ (303.99): calcd. C 59.02, H 4.29, S 10.51; found C 59.12, H 4.32, S 10.49.

Benzyl(4-methylstyryl)sulfane (11e): Yield 92 %, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 3.96 (s, 2 H), 6.18 (d, *J* = 10.8 Hz, 1 H), 6.38 (d, *J* = 10.5 Hz, 1 H), 6.51 (d, *J* = 15.0 Hz, 1 H), 6.65 (d, *J* = 15.4 Hz, 1 H), 7.06–7.34 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.35, 37.62, 39.64, 123.12, 125.04, 125.61, 126.06, 127.45, 128.52, 128.74, 128.92, 129.02, 129.15, 129.42, 134.20, 134.35, 136.63, 136.90, 137.52, 137.65 ppm. MS (EI, 70 eV): *m/z* = 241 $[M + H]^+$. $C_{16}H_{16}S$ (240.10): calcd. C 79.95, H 6.71, S 13.34; found C 79.92, H 6.69, S 13.32.

Phenyl(styryl)sulfane (11f): Yield 86 %, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.54 (d, *J* = 10.5 Hz, 1 H), 6.60 (d, *J* = 10.5 Hz, 1 H), 6.72 (d, *J* = 15.3 Hz, 1 H), 6.90 (d, *J* = 15.4 Hz, 1 H), 7.25–7.52 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.35, 125.92, 126.80, 127.06, 127.14, 127.52, 128.25, 128.64, 129.02, 129.72, 129.94, 131.76, 135.13, 136.42 ppm. MS (EI, 70 eV): *m/z* = 213 $[M + H]^+$. $C_{14}H_{12}S$ (212.07): calcd. C 79.20, H 5.70, S 15.10; found C 79.18, H 5.68, S 15.06.

(4-Fluorostyryl)(phenyl)sulfane (11g):[15] Yield 90 %, white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.45 (d, *J* = 10.5 Hz, 1 H), 6.55 (d, *J* = 10.5 Hz, 1 H), 6.67 (d, *J* = 15.3 Hz, 1 H), 6.81 (d, *J* = 15.3 Hz, 1 H), 6.95–7.07 (m, 2 H), 7.20–7.48 (m, 7 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.04, 115.32, 115.40, 115.75, 123.00, 125.52, 126.15, 126.94, 127.25, 127.48, 127.55, 129.15, 129.82, 130.06, 130.32, 130.54, 132.64, 135.02, 135.82, 160.55, 163.82 ppm. MS (EI, 70 eV): *m/z* = 231 $[M + H]^+$. $C_{14}H_{11}FS$ (230.06): calcd. C 73.01, H 4.81, S 13.92; found C 73.00, H 4.78, S 13.90.

(4-Methylstyryl)(phenyl)sulfane (11h):[15] Yield 86 %, pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 6.45 (d, *J* = 10.8 Hz, 1 H), 6.60 (d, *J* = 10.8 Hz, 1 H), 6.75 (d, *J* = 15.2 Hz, 1 H), 6.84 (d, *J* = 15.6 Hz, 1 H), 7.12–7.45 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.15, 121.70, 124.72, 125.90, 126.61, 126.94, 127.32, 128.62, 129.05, 129.32, 129.44, 129.82, 132.34, 133.65, 135.54, 136.32, 136.95, 137.45 ppm. MS (EI, 70 eV): *m/z* = 227 $[M + H]^+$. $C_{15}H_{14}S$ (226.08): calcd. C 79.60, H 6.23, S 14.17; found C 79.58, H 6.20, S 14.15.

Styryl(*p*-tolyl)sulfane (11i):[15] Yield 90 %, pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 6.45 (d, *J* = 10.8 Hz, 1 H), 6.54 (d, *J* = 10.6 Hz, 1 H), 6.65 (d, *J* = 15.6 Hz, 1 H), 6.86 (d, *J* = 15.4 Hz, 1 H), 7.10–7.50 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.04, 126.42, 126.90, 127.05, 128.24, 128.60, 129.92, 130.55, 132.62, 136.54, 137.35 ppm. MS (EI, 70 eV): *m/z* = 227 $[M + H]^+$. $C_{15}H_{14}S$ (226.08): calcd. C 79.60, H 6.23, S 14.17; found C 79.58, H 6.20, S 14.15.

(4-Methylstyryl)(*p*-tolyl)sulfane (11j):[17] Yield 85 %, white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 6 H), 6.38 (d, *J* = 10.2 Hz, 1 H), 6.50 (d, *J* = 10.6 Hz, 1 H), 6.65 (d, *J* = 15.2 Hz, 1 H), 6.81 (d, *J* = 15.4 Hz, 1 H), 7.10–7.42 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.35, 123.10, 125.92, 126.05, 126.32, 126.85, 128.70, 128.92, 129.15, 129.44, 129.65, 129.70, 129.91, 130.02, 130.42, 130.56, 131.22, 131.75, 134.10, 137.06, 137.25, 137.42 ppm. MS (EI, 70 eV): *m/z* = 241 $[M + H]^+$. $C_{16}H_{16}S$ (240.10): calcd. C 79.95, H 6.71, S 13.34; found C 79.92, H 6.68, S 13.32.

(4-Nitrophenyl)(styryl)sulfane (11k):[18] Yield 86 %, yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.34 (d, *J* = 15.6 Hz, 1 H), 6.49 (d, *J* = 15.2 Hz, 1 H), 6.52 (d, *J* = 10.2 Hz, 1 H), 6.88 (d, *J* = 10.4 Hz, 1 H), 7.31–7.33 (m, 2 H), 7.39–7.42 (m, 2 H), 7.49–7.55 (m, 3 H), 8.15–8.17 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.72, 124.04, 124.25, 126.65, 127.15, 128.12, 128.55, 128.74, 129.02, 129.22, 132.15, 135.60, 145.80, 146.15 ppm. MS (EI, 70 eV): *m/z* = 258 $[M + H]^+$. $C_{14}H_{11}NO_2S$ (258.05): calcd. C 65.35, H 4.31, S 12.46; found C 65.32, H 4.29, S 12.44.

(4-Methoxyphenyl)(styryl)sulfane (11l):[15] Yield 96 %, white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 6.40 (d, *J* = 10.2 Hz, 1 H), 6.55 (d, *J* = 10.5 Hz, 1 H), 6.63 (d, *J* = 15.2 Hz, 1 H), 6.92 (d, *J* = 15.4 Hz, 1 H), 6.78–6.89 (m, 2 H), 7.20–7.28 (m, 2 H), 7.26–7.50 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.32, 114.80, 125.75, 126.90, 126.85, 127.12, 128.30, 128.64, 128.72, 128.90, 132.92, 133.44, 136.62, 159.40 ppm. MS (EI, 70 eV): *m/z* = 243 $[M + H]^+$. $C_{15}H_{14}OS$ (242.08): calcd. C 74.34, H 5.82, S 13.23; found C 74.32, H 5.80, S 13.20.

Benzyl(3,3-dimethylbut-1-enyl)sulfane (11m): Yield 74 %, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (s, 9 H), 3.95 (s, 2 H), 5.82 (d, *J* = 15.2 Hz, 1 H), 5.95 (d, *J* = 15.4 Hz, 1 H), 6.31 (d, *J* = 10.5 Hz, 1 H), 6.40 (d, *J* = 10.5 Hz, 1 H), 7.10–7.29 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.12, 32.48, 34.75, 41.62, 120.36, 125.44, 127.52, 129.40, 148.60 ppm. MS (EI, 70 eV): *m/z* = 207 $[M + H]^+$. $C_{13}H_{18}S$ (206.35): calcd. C 75.67, H 8.79, S 15.54; found C 75.65, H 8.78, S 15.52.

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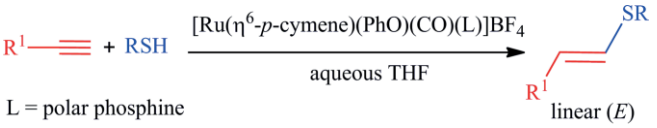
Ruthenium Catalysis



A serendipitously discovered stoichiometric C–H activation/decarbonylation of salicylaldehyde by $[(\eta^6\text{-}p\text{-cymene})\text{-}RuCl_2]_2$ gave $[(\eta^6\text{-}p\text{-cymene})RuCl(CO)\text{-}(Ph\text{-}O)]$ (**1**) without the need for external CO gas. Polar phosphines were incorporated into **1** to give cationic Ru^{II} catalysts **2**–**8**. These were used in the hydrothiolation of alkynes to selectively give anti-Markovnikov *E*-linear vinyl sulfides in aq. THF.

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