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Catalytic conversion of alkynes to α-vinyl sulfides mediated by carbene-linker-carbene (CXC) rhodium and iridium complexes†

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The catalytic activity of a set of mono- and bimetallic Rh(I) and Ir(I) complexes bearing carbene-linker-carbene (CXC) bis-triazolylidene ligands (with X = O, N) coordinated in a bridging or chelating fashion was evaluated in the hydrothiolation of alkynes. The hydrothiolation of 1-hexyne with thiophenol in the absence of an external base or other additives was selected as a model reaction. All rhodium complexes are highly selective catalysts towards Markovnikov product formation and display superior activity compared to the related iridium derivatives. DFT calculations were carried out to rationalize the reaction mechanism and selectivity of this process. Neutral dinuclear $[Rh_2Cl_2(cod)_2(\mu\text{-}\mathbf{COC})]$ was found to be the most effective catalyst for this transformation. Its applicability was further studied towards the hydrothiolation of different alkyl and aryl alkynes using predominantly aryl thiols and proved to be one of the most active and selective catalysts towards the α-vinyl sulfide product to date.

Introduction

The structural pattern of α-vinyl sulfides makes these organic molecules important commodities for multiple synthetic applications. They are valuable building blocks extensively used as Michael acceptors, enolate surrogates, or intermediates towards different ring size heterocycles.[1–4] They are present in biologically active compounds and pharmaceuticals, and found application in materials science and total synthesis.[5–7] Thus, the development of atom-economical methods for the preparation of alkenyl sulfides such as the catalysed intermolecular functionalisation of alkynes (see Scheme 1, a) has been attracting much interest in recent years.

α-Vinyl sulfides are accessible *via* different synthetic strategies.[8–10] Not surprisingly, the use of transition metal catalysis provides substantial tunable control of the regioselectivity outcomes.[5] Rhodium catalysts are of particular interest. These species are often referred to as "chameleonic species"[8,11] because subtle modifications of the ancillary ligands significantly affect their activity and selectivity towards the Markovnikov (α-vinyl sulfides) or the anti-Markovnikov (*E*/*Z*-β-vinyl sulfides) addition products.[5,8,12–15] The most generally accepted mechanism involves the oxidative addition of the thiol S–H bond to the Rh(I) metal precursor to generate the corresponding Rh(III) intermediate as a first step (Scheme 1, b).[8,11] Then, the 1,2- or 2,1-alkyne insertion into the Rh–S or Rh–H bonds takes place to produce four possible reaction paths. Subsequent reductive elimination generates predominantly the α- or β-*E*-vinyl sulfides. For the oxidative addition route, an in-depth analysis by Castarlenas *et al.* highlighted two important factors that need to be considered when developing new rhodium complexes,[8] (i) the alkyne insertion into the Rh–H bond is energetically favored over the Rh–SR bond insertion, promoting the β-*E*/*Z* isomer formation and (ii) the marked *trans* influence of the hydride in the generation of the α-vinyl sulfide product, *i.e.* due to the control of the coordination of the acetylene *trans* to the hydride and favoring the attack of the thiolate *cis* to the alkyne. Thus, complexes that favor trigonal bipyramidal geometry around the metal center or have low stereochemical control typically favor the anti-Markovnikov addition.[13,16–18]

In contrast, complexes like $[Tp^*Rh(PPh_3)_2]$,[19,20] $[RhCl(NHC)(py)(\eta^2\text{-olefin})]$[13] and $[Rh\{\kappa^2\text{-O,N-}(C_9H_6NO)\}(\eta^2\text{-coe})(IPr)]$[21] promote alkyne insertion into the Rh–SR bond

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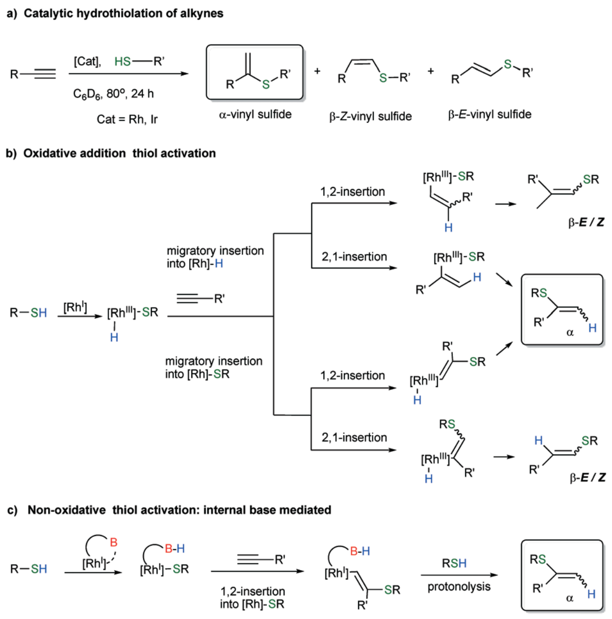


Scheme 1 a) Alkyne hydrothiolation catalysed by group 9 transition metals. b) and c) Rhodium-catalysed alkyne hydrothiolation activation mechanisms.

giving the Markovnikov product. Interestingly, a switch in the selectivity towards the α-vinyl sulfide was observed for some Rh(I)–NHC based complexes, after incorporating a pyridine ligand *trans* to the carbene moiety which prevents coordination of the alkyne in this position.[12,21] In some cases the addition of a 10 fold excess of pyridine to the reaction mixture is required to attain higher selectivities.[12,21] Parallel to this, the presence of strongly σ-donating NHC ligands bearing bulky substituents also positively impacted on the catalysis. In this context, our first report in the field involved a rhodium(I)–oxygen adduct featuring an anionic CNC bis(triazolylidene) based on the rigid carbazole framework functionalized with strong electron-donating 1,2,3-triazol-5-ylidenes (MICs).[22–24] High selectivity towards the Markovnikov product was displayed when alkyl thiols and aliphatic alkynes were used.[15] Encouraged by this result and aiming to study the effect of steric relaxation around the metal center, we prepared a series of monometallic Rh(I)–MIC complexes **A** [Rh(cod)(C^{Boc}**N**)] and **B** [Rh(CO)$_2$(C^{Boc}**N**)] bearing different chelating C–N ligands (Fig. 1).[14] Gratifyingly, neutral dicarbonyl complex **B** [Rh(CO)$_2$(C^{Boc}**N**)] featuring a hemi-labile tethered-NBoc amido-1,2,3-triazolylidene ligand acting as internal base proved to be very selective for the hydrothiolation of different alkynes with thiophenol through a non-oxidative reaction with metal–ligand cooperation (Scheme 1, c). Shortly after, a related highly selective Rh(I)–NHC complex bearing a N,O-pyridine-2-methanolato (N–O) bidentate supporting this mechanism has been reported.[11] More importantly, a series of preconditions that need to be satisfied to prevent the oxidative addition route were defined. These include the presence of an internal base along with a chelating ligand to control the potential equilibrium between mono- and dinuclear species and a π-acceptor ligand. Besides that, few examples of iridium complexes mediating this transformation are known. Only two cationic iridium catalysts featuring P–N bidentate ligands have been reported,[18,26] both displaying complete selectivity towards the β-*E*/*Z* vinyl sulfide product. On this basis, we foresaw that the availability of a set of rhodium and iridium complexes offering a palette of different coordination modes and nuclearities could contribute to gain more insight into the prerequisites for a selective catalyst in this transformation. Spurred by the success demonstrated in catalysis by metal complexes containing ancillary aliphatic pincer ligands,[27–30] we recently described the synthesis of a series of mono and dimetallic Rh(I) and Ir(I) complexes from readily available ether- and amine-bridged bis(triazolium) ligand precursors.[25] With this set of catalysts in hand, we herein evaluate their catalytic properties towards the hydrothiolation of alkynes to discriminate between the effects of (i) Rh(I) *vs.* Ir(I), (ii) mono- *vs.* dinuclear complexes and, (iii) chelating *vs.* non-chelating ligands (Fig. 1).

Results and discussion

We initiated a comparative catalytic study for the different Rh(I) complexes towards the hydrothiolation of 1-hexyne with thiophenol in deuterated benzene at 80 °C over a period of 24 h. The reaction conditions used during the evaluation of the catalytic properties of **A** and **B** were used as a benchmark.[14] Previously, we have shown that when the metal precursor [RhCl(cod)]$_2$ was combined with 2 equivalents of K_2CO_3 as the base, a mixture of the thiosubstituted alkene derivatives bis-β-*E*, β-*Z*-vinyl sulfide and the related bis-β-*Z*,

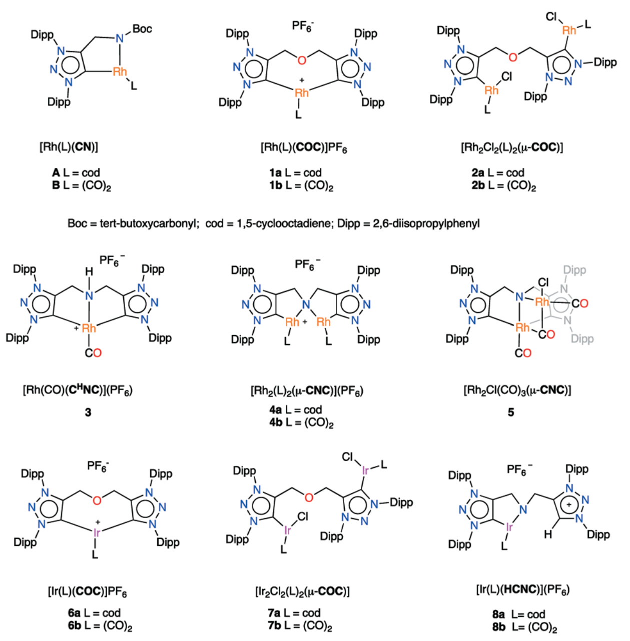
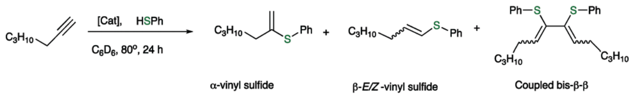


Fig. 1 Schematic representation of mono- and dimetallic Rh(I) and Ir(I) complexes used in this study.[14,25]

Table 1 Screening of mono and bimetallic rhodium(I) catalysts for the model hydrothiolation of 1-hexyne with thiophenol[a]



Entry	Cat.	Mol% [Cat]	Conv. (%)	Prod. Distr. %	
				α	β-*Z*/β-*E*/bis-β–β
1	**[RhCl(cod)]$_2$**[14]	1	>99	8	2/2/89
2	**A**[14]	2	94	75	19/6/—
3	**B**[14]	2	34	>99	—/—/—
4	**1a**	1	68	96	2/2/—
5	**1b**	1	17	71	14/14/—
6	**2a**	1	88	92	3/5/—
7	**2a**	0.5	76	96	2/2/—
8	**2b**	1	15	82	9/9/—
9	**2b**	0.5	10	>99	—/—/—
10	**3**	1	44	95	3/3/—
11	**4a**	1	73	97	2/2/—
12	**4a**	0.5	58	>99	—/—/—
13	**4b**	1	37	>99	—/—/—
14	**4b**	0.5	31	>99	—/—/—
15	**5**	1	48	>99	—/—/—
16	**5**	0.5	49	93	4/4/—

[a] Reactions performed in C_6D_6 (0.5 mL) at 80 °C for 24 h using 1,4-di-*tert*-butylbenzene as internal standard, alkyne : thiol (1 : 1), 1 mol% catalyst (3.5×10^{-6} mol) for all compounds, as well as 0.5 mol% catalyst (1.75×10^{-6} mol) for binuclear compounds **2a–b**, **4a–b** and **5** (for comparison purposes). Conversion and product distribution of the α, β-*Z* and β-*E*-vinyl sulfide products were determined as the average of duplicate runs as determined from NMR integration based on 1-hexyne and thiophenol average referenced to 1,4-di-*tert*-butylbenzene.

β-*Z*-vinyl sulfide (Table 1, entry 1) was produced. In contrast, both metal complexes **A** [Rh(cod)(**C^{Boc}N**)] and **B** [Rh(CO)$_2$(**C^{Boc}N**)] displayed outstanding selectivity towards the branched vinyl sulfides with a catalyst loading of 2 mol% (entries 2 and 3, respectively), akin to some of the best rhodium-hydrothiolation catalysts so far reported in the literature.[31] Based on these precedents, we first explored the catalytic activity of both monometallic complexes (**1a** and **1b**) bearing the carbon–ether–carbon (COC) ligand. Complex **1a** [Rh(cod)(**COC**)](PF$_6$), showed greater conversion (68%) than the reference catalyst **B**, with lower catalyst loading (1 mol%) maintaining almost the excellent selectivity towards the α-vinyl sulfide product. In contrast, the related dicarbonyl derivative **1b** [Rh(CO)$_2$(**COC**)](PF$_6$), exhibited poor (17%) conversion and lower selectivity (entries 4 and 5, respectively, Table 1). Next, we assessed the catalytic performance of the corresponding dimetallic derivatives **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-**COC**)] and **2b** [Rh$_2$Cl$_2$(CO)$_4$(μ-**COC**)] using a 1 mol% catalyst loading (2 mol% metal content). Catalyst **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-**COC**)] showed 88% conversion, higher than the 68% found for **1a**, although with somewhat lower selectivity for the Markovnikov isomer. Again, the related tetracarbonyl derivative **2b**, [Rh$_2$Cl$_2$(CO)$_4$(μ-**COC**)], exhibited a poor conversion (15%) with lower selectivity (entries 6 and 8 respectively, Table 1). In order to compare the performance of dinuclear complexes **2a** and **2b** with monometallic compounds **1a** and **1b** under the same conditions, their activity using a 0.5 mol% catalyst loading (1 mol% Rh(I) contents) was tested. Catalyst **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-**COC**)] showed a 76% conversion, greater than **1a** and matching the selectivity observed for the α-vinyl sulfide. Again, the related tetracarbonyl derivative **2b** [Rh$_2$Cl$_2$(CO)$_4$(μ-**COC**)], exhibited poor conversion (10%) and even lower selectivity (entries 7 and 9 respectively, Table 1). Next, we investigated the activity of the cationic monometallic complex **3** [Rh(CO)(**C^{H}NC**)](PF$_6$), the neutral dimetallic complexes **4a** [Rh$_2$(cod)$_2$(μ-**CNC**)](PF$_6$), **4b** [Rh$_2$(CO)$_4$(μ-**CNC**)](PF$_6$) and **5** [Rh$_2$Cl(CO)$_3$(μ-**CNC**)] bearing the amino linked (CNC) ligand. Catalyst **3** [Rh(CO)(**C^{H}NC**)](PF$_6$), displaying tridentate coordination of the ligand, albeit exhibiting a moderate conversion of 44% using a catalyst loading of 1 mol%, was found to display fairly good selectivity towards the α-vinyl sulfide (entry 10, Table 1). The activity of the related dimetallic complexes was then evaluated, first using 1 mol% catalyst loading (2 mol% with respect to the metal). Catalyst **4a** [Rh$_2$(cod)$_2$(μ-**CNC**)](PF$_6$) displayed a fairly good conversion of 73% with excellent selectivity towards the α-vinyl sulfide (entry 11, Table 1). The conversion for the dicarbonyl derivative **4b** [Rh$_2$(CO)$_4$(μ-**CNC**)](PF$_6$) dropped to 37%, while matching the selectivity observed for **4a** (entry 13, Table 1). Interestingly, the performance of **4b** equals that observed for catalyst **B** [Rh(CO)$_2$(**C^{Boc}N**)] (entry 3, Table 1), where the ligand binding modes displayed by the two complexes, are at least partially similar bearing an internal base.

To compare the performance of dimetallic amine-chelated **4a** and **4b** with ether-bridged **2a** and **2b** under the same reaction conditions, their activity was evaluated employing a 0.5 mol% catalyst loading (1 mol% with respect to the metal). Catalyst **4a** [Rh$_2$(cod)$_2$(μ-**CNC**)](PF$_6$) displayed a moderate 58% conversion, lower than that observed for **2a** but

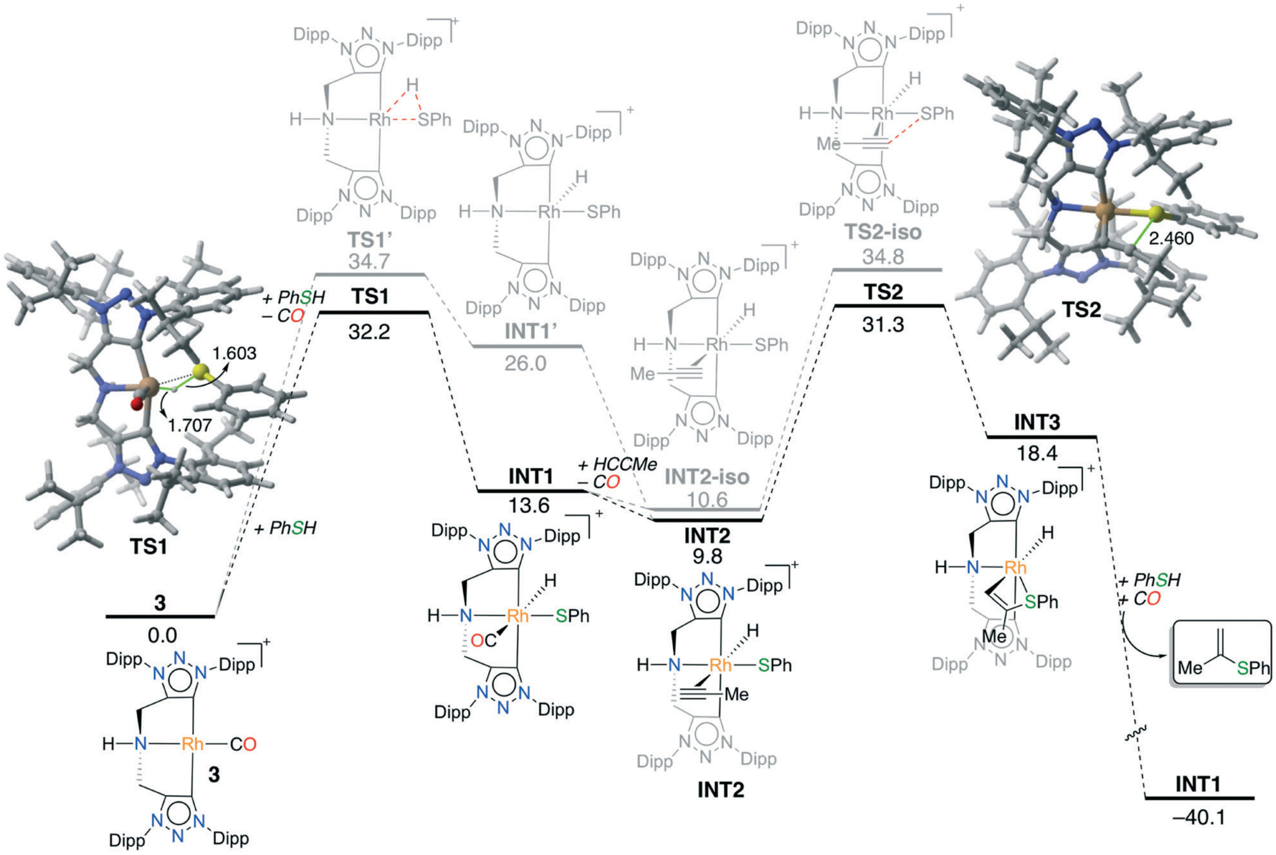


Fig. 2 Computed reaction profile for the reaction of PhSH and MeC≡CH catalysed by complex **3**. Relative free energies (within parentheses, ΔG_{298}, computed at 298 K) are given in kcal mol^{-1} whereas bond distances are given in Ångstroms. All data have been computed at the PCM(benzene)-B3LYP-D3/def2-SVP level.

matching the excellent selectivity observed for the α-vinyl sulfide (entry 12, Table 1). In contrast, **4b** $[Rh_2(CO)_4(\mu\text{-}\mathbf{CNC})](PF_6)$, exhibited a poor 31% conversion (entry 14, Table 1). Finally, we evaluated the activity of the neutral tricarbonyl dimetallic rhodium(I) complex **5** $[Rh_2Cl(CO)_3(\mu\text{-}\mathbf{CNC})]$, by first using 1 mol% catalyst loading (2 mol% with respect to the metal). Despite exhibiting a moderate conversion of 48%, excellent selectivity towards the α-vinyl sulfide product was observed (entry 15, Table 1). The conversion was maintained when catalyst loading was halved to 0.5 mol% (1 mol% with respect to the metal) with only a slight decrease in the observed selectivity towards the α-vinyl sulfide product.

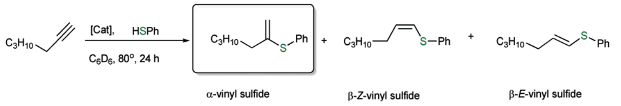
Density functional theory (DFT) calculations were carried out at the dispersion corrected PCM(benzene)-B3LYP-D3/def2-SVP level (see computational details in the ESI†) to gain more insight into the reaction mechanism and selectivity of the above transformations. To this end, we selected the process involving the Rh(I) catalyst **3**, which bears the $C^{H}NC$-pincer ligand and leads to an almost complete selective transformation towards the α-vinyl sulfide (see entry 10, Table 1). This system was chosen because, although displayed a lower conversion than the parent system **A**, allows us to understand the influence of the $C^{H}NC$-pincer ligand on the process.

According to the computed reaction profile shown in Fig. 2, the process begins with the oxidative addition reaction of PhSH to Rh(I) leading to the corresponding Rh(III) – intermediate **INT1**. The computed barrier of this step ($\Delta G^{\neq}$ = 31.5 kcal mol^{-1}, *via* **TS1**) and endergonicity of the process (ΔG_R = 13.6 kcal mol^{-1}) are compatible with the relatively high temperature required for the transformation (80 °C, see above). Alternatively, a dissociative mechanism involving the initial release of the CO ligand followed by a similar oxidative addition can be also envisaged. However, our calculations indicate that this alternative pathway *via* **TS1′** is not competitive from both kinetic ($\Delta G^{\neq}$ = 34.7 kcal mol^{-1}) and thermodynamic (ΔG_R = 26.0 kcal mol^{-1}) points of view. Intermediate **INT1** easily evolves into the next intermediate by exergonic replacement of the carbonyl ligand by the alkyne reactant. The two possible isomers that can be produced from this reaction step include an intermediate in which the alkyl substituent (methyl in our calculations) is proximal to the SPh ligand (**INT2**) and an intermediate where the terminal hydrogen atom of the alkyne occupies this position (**INT2-iso**). Our calculations indicate that these isomers are nearly degenerate being **INT2** (*i.e.* the intermediate leading to the favoured α-vinyl sulfide) 0.8 kcal mol^{-1} more stable than **INT2-iso**. Once **INT2** is formed, and in agreement with previous mechanistic studies,[8] the alkyne insertion into the Rh–S bond *via* **TS2** ($\Delta G^{\neq}$ = 21.5 kcal mol^{-1}) takes place leading to the formation of metallacycle **INT3**. Interestingly, our calculations indicate that the analogous Rh–S insertion reaction from the isomer **INT2-iso**, which would produce the corresponding β-sulfide *via* **TS2-iso**, proceeds with a higher activation barrier ($\Delta G^{\neq}$ = 24.2 kcal mol^{-1}) than the process involving **INT2**. The computed barrier energy difference ($\Delta\Delta G^{\neq}$ = 2.7 kcal mol^{-1}) is consistent with the observed almost complete selectivity towards the formation of the α-vinyl sulfide (95 : 5 see Table 1, entry 10). Strikingly, a lower energy barrier difference of $\Delta\Delta G^{\neq}$ = 2.4 kcal mol^{-1} was computed at 378 K (the temperature used in the experiments), which is translated into a 96 : 4 selectivity, therefore nearly matching the observed experimental ratio. Thus, it can be concluded that the origin of the selectivity of this transformation is mainly found in the alkyne insertion into the Rh–S bond.[32] Finally, the process ends up with a protonolysis reaction mediated by a new molecule of PhSH followed by coordination of the previously released CO ligand, which would produce the observed Markovnikov α-sulfide and **INT1**, the latter entering into a new catalytic cycle.

Next, we explored the performance of the six Ir(I) complexes (Table 2), for comparison to the rhodium(I) derivatives in the same transformation. Initially, we studied the two cationic diolefinic **6a** [Ir(cod)(**COC**)](PF$_6$) and dicarbonyl **6b** [Ir(CO)$_2$(**COC**)](PF$_6$) mononuclear Ir^{I} complexes, bearing the (COC) ligand acting as chelate (Fig. 1). In this case, **6a** displayed a 91% conversion, using 1 mol% catalyst loading, slightly lower than the 94% observed for the neutral Rh(I) complex **A** [Rh(cod)(**CN**)] bearing the less bulky (CN) ligand (Fig. 1), but higher than the 68% registered for the cationic Rh(I) analogue **1a** [Rh(cod)(**COC**)](PF$_6$) bearing the (COC) (Table 1, entries 2 and 4 respectively). In contrast, the related dicarbonyl derivative **6b**, [Ir(CO)$_2$(**COC**)](PF$_6$), exhibited a moderate 51% conversion albeit higher than that found for the neutral Rh(I) complex **B** [Rh(CO)$_2$(**CN**)] featuring the bidentate (CN) ligand or the Rh(I) counterpart **1b** [Rh(CO)$_2$(**COC**)](PF$_6$) containing the (COC) ligand (Table 1, entries 3 and 5 respectively). The selectivity of the dicarbonyl complex Ir(I) **6b** is markedly higher than that observed for the diolefinic Ir(I) **6a** (Table 2, entries 1 and 2 respectively), and slightly higher than that found for the dicarbonyl Rh(I) complex **1b** (Table 1, entry 5). However, this species displays a lower selectivity when compared to the diolefinic Rh(I) complex **1a**, inferior selectivity to the 96% α-isomer product distribution obtained for diolefinic Rh(I) complex **1a** [Rh(cod)(**COC**)](PF$_6$) is indicated. Next, we assessed the performance of the corresponding neutral dimetallic derivatives **7a** [Ir$_2$Cl$_2$(cod)$_2$(μ-**COC**)] and **7b** [Ir$_2$(CO)$_4$(μ-**COC**)] containing the (COC) ligand acting as bridge. First, we used a catalyst loading of 1 mol% (2 mol% metal content). As a result, the dinuclear tetraolefinic Ir(I) catalyst **7a** [Ir$_2$Cl$_2$(cod)$_2$(μ-**COC**)] displayed 81% conversion (Table 2, entry 3) *versus* the 88% previously observed for the related dinuclear tetraolefinic Rh(I) derivative **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-**COC**)] (Table 1, entry 6). Moreover, in addition to the lower conversion observed in comparison with the Rh(I) analogue **2a**, catalyst **7a** also proved to exhibit a poor selectivity. The related tetracarbonyl Ir(I) derivative **7b** [Ir$_2$(CO)$_4$(μ-**COC**)] (1 mol% catalyst loading, 2 mol% Ir(I) content), exhibited a low conversion of 38% (Table 2, entry 5) and matching the selectivity to its rhodium(I) counterpart **2b** [Rh$_2$(CO)$_4$(μ-**COC**)] (Table 1, entry 8).

In order to compare the performance of the neutral and bimetallic **7a**, **b** with cationic and monometallic **6a** and **6b** under the same conditions, we assessed their activity using a 0.5 mol% catalyst loading (1 mol% Ir(I) content). Neutral catalyst **7a** [Ir$_2$Cl$_2$(cod)$_2$(μ-**COC**)] displayed a 59% conversion, much lower than the 91% conversion observed for cationic **6a** and showing a similar poor selectivity. In the case of the related tetracarbonyl derivative **7b** [Ir$_2$(CO)$_4$(μ-**COC**)], the lower catalyst loading (0.5 mol%) resulted in a similar conversion to that found for a 1 mol% catalyst loading of the same catalyst (Table 2, entry 6), although it negatively impacted the selectivity. Finally, we evaluated the

Table 2 Hydrothiolation of 1-hexyne and thiophenol catalysed by iridium(I) mono- and dimetallic complexes **6a–b**, **7a–b**, and **8a–b**[a]



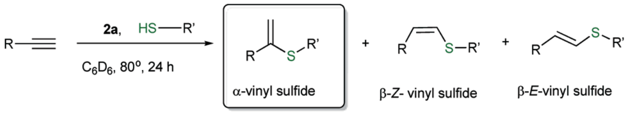
				Prod. Distr. %		
Entry	Cat.	Mol% [Cat]	Conv. (%)	α	β-*Z*	β-*E*
1	**6a**	1	91	43	12	45
2	**6b**	1	51	79	14	7
3	**7a**	1	81	45	13	43
4	**7a**	0.5	59	47	24	30
5	**7b**	1	38	83	8	8
6	**7b**	0.5	37	67	17	17
7	**8a**	1	35	92	8	—
8	**8b**	1	41	62	29	10

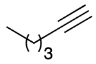
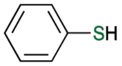
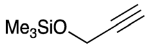
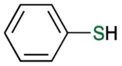
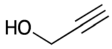
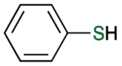
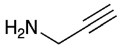
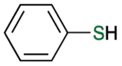
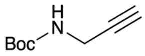
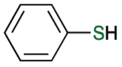
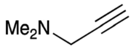
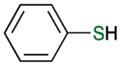
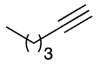
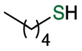
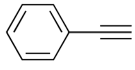
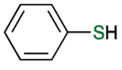
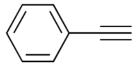
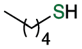
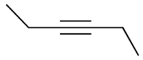
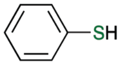
[a] Reactions performed in C$_6$D$_6$ (0.5 mL) at 80 °C for 24 h using 1,4-di-*tert*-butylbenzene as internal standard, alkyne : thiol (1 : 1), 1 mol% catalyst (3.5 × 10^{-6} mol) for all compounds, as well as 0.5 mol% catalyst (1.75 × 10^{-6} mol) for binuclear compounds **7a–b** (for comparison purposes). Conversion and product distribution of the α, β-*Z* and β-*E*-vinyl sulfide products were determined as the average of duplicate runs as determined from NMR integration based on 1-hexyne and thiophenol average referenced to 1,4-di-*tert*-butylbenzene.

performance of the neutral diolefinic **8a** [Ir(cod)(**^{H}CNC**)](PF$_6$) and dicarbonyl **8b** [Ir(CO)$_2$(**^{H}CNC**)](PF$_6$) monometallic Ir(I) complexes containing the (CNC) ligand and bearing a pendant triazolium arm (Fig. 1). Moderate conversions of 35 and 41%, respectively, were obtained (Table 2, entries 7 and 8). However, a marked difference was observed in terms of selectivity. Diolefinic catalyst **8a** was found to be very selective towards the α-vinyl sulfide, proving to be one of the most selective Ir(I) catalysts for this transformation.[8,18,26] At variance, the dicarbonyl derivative **8b** [Ir(CO)$_2$(**^{H}CNC**)](PF$_6$) showed to be significantly less selective. This is the opposite trend than that observed for Rh(I) catalysts **A** [Rh(cod)(**CN**)] and **B** [Rh(CO)$_2$(**CN**)] bearing the bidentate (CN) ligand with a proven non-oxidative addition mechanism.[13] After screening all catalysts displayed in Fig. 1, it was found that the top two performing catalysts are the olefinic Rh(I) based cationic **1a** [Rh(cod)(**COC**)](PF$_6$) and neutral **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-**COC**)] bearing the (COC) ligand (Table 1, entries 4 and 6). In general, the observed trend is that all Rh(I) complexes having either the (COC) or (CNC) ligand exhibited very good selectivity towards the α-vinyl sulfide outperforming the related Ir(I) derivatives, with the exception of the olefinic neutral complex **8a**. In parallel, the (COC) Ir(I) complexes bearing carbonyl groups, although less effective than the rhodium derivatives, displayed higher selectivity than their olefinic counterparts. Next, **1a** [Rh(cod)(**COC**)](PF$_6$) and neutral **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-**COC**)] were employed to further explore reaction conditions optimization. Towards this aim, the temperature (40 and 80 °C) and reaction time (12 and 24 hours) were investigated towards the addition of thiophenol across the unsaturated bond of 1-hexyne (see Table S1†).

In the case of the best performing catalyst from this study, Rh(I) **2a–b**, and the most selective Ir(I) catalyst **8a–b**, the decrease in the π-basicity of the metal centre for carbonyl co-ligands (**b**) *vs.* cod-substituted complexes (**a**), accompanied by a loss in selectivity could be indicative of a decrease in the ease of oxidative addition in a catalytic cycle that differs from that of **A**/**B** (and includes oxidative addition of the thiol substrate). It was concluded that the best performing catalyst is **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-COC)] at 80 °C and 24 h using a 0.5 mol% catalyst loading (see Table S1,† entry 7). Following the identification of **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-COC)] as the catalyst of choice, the substrate scope of both aliphatic and aryl substrates for the base-free hydrothiolation of terminal

Table 3 Substrate scope of the base-free hydrothiolation of various alkyl and aryl terminal alkynes and thiols, catalysed by complex **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-COC)][a]



Entry	Alkyne	Thiol	Conv./yield (%)	α/β-*Z*/β-*E*
1			87/85	96/2/2
2			83/70	83/8/8
3			93/76	90/5/5
4			82/76	92/6/1
5			90/78	94/0/6
6			77/60	>99/0/0
7			80/70	87/6/6
8			79/46[b]	47/31/22
9			69/58	51/32/17
10			26/11	—/9/91

[a] Reactions performed in C$_6$D$_6$ (0.5 mL) at 80 °C for 24 h using 1,4-di-*tert*-butylbenzene as internal standard, alkyne : thiol (1 : 1), 0.5 mol% (1.75 × 10^{-6} mol) **2a**. Conversion and yields were determined as the average of duplicate runs as determined from NMR integration based on 1-hexyne and thiophenol average referenced to 1,4-di-*tert*-butylbenzene. [b] Unidentied precipitate observed.

alkynes, under the optimized reaction conditions, was expanded (Table 3). Catalyst **2a** revealed good functional group tolerance with no coupled bis-β-, β-vinyl sulfide products detectable. By examination of the results gathered in Table 3, we can confirm that the neutral dimetallic complex **2a** [$Rh_2Cl_2(cod)_2$(μ-**COC**)] proved to be very selective towards the branched α-vinyl sulfide product when aliphatic alkynes and both aryl and alkyl thiols were used as substrates in the absence of an internal base or hemilabile ligand function (Table 3, entries 1–7). In contrast, only moderate selectivities were obtained for aryl alkynes (Table 3, entries 8–9), especially in the case where both the alkyne and thiol contain an aryl group (entry 8). Finally, we evaluated the catalytic activity of complex **2a** [$Rh_2Cl_2(cod)_2$(μ-**COC**)] in the base-free hydrothiolation of an internal alkyne such 3-hexyne with thiophenol under the same reaction conditions (Table 3, entry 10). A lower conversion of 26% was observed with preferential formation of (*E*)-3-phenylsulfanyl-3-hexene, in comparison with the high yield reported for the formation of this *E*-isomer.[13]

Conclusions

The catalytic activity of a series of mono- and dimetallic rhodium(I) and iridium(I) complexes bearing carbene-linker-carbene (CXC) bis-triazolylidene ligands (with X = O, N) ligands were assessed in the hydrothiolation model reaction of the terminal 1-hexyne with thiophenol. The catalytic studies revealed that, in general, the Rh(I) complexes outperformed the related Ir(I) derivatives, both in terms of activity and selectivity. Among them, the rhodium complexes bearing the (COC) ether bridged bis-triazolylidene ligand have shown superior activity and selectivity towards the sought after branched α-vinyl sulfide product, in comparison with related Rh(I) counterparts featuring the (CNC) amino bridged derivative. Finally, the neutral dimetallic rhodium(I) complex **2a** containing the carbene–ether–carbene (COC) ligand proved to be the best catalyst in terms of activity and selectivity for a series of aliphatic alkynes and different thiols, demonstrating good functional group tolerance. Notably, the identified best-performing rhodium catalyst **2a** and selective iridium catalyst **8a** employed in this study, the absence of a basic, hemilabile coordinating moiety and the selectivity improvement observed for cod co-ligands instead of stronger π-acidic carbonyl ligands, point to an alternative catalytic mechanism for these complexes, compared to the non-oxidative route exemplified by catalysts **A**/**B**. Indeed, DFT calculations carried out for the transformation involving the Rh(I) catalyst **3** suggest that the process involves an initial oxidative addition step followed by a selectivity-determining step consisting of the alkyne insertion into the Rh–S bond.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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32 As proposed previously (see ref. 8), an alternative alkyne insertion into the Rh–H bond can be also envisaged. However, this process is not feasible from **INT2** (or **INT2-iso**) as the hydride ligand is placed *trans* to the alkyne. Despite that, our calculations indicate that the analogous intermediate where the hydride is placed *cis* to the alkyne ligand is 5.7 kcal mol^{-1} less stable than the *trans* isomer **INT2**, which suggests that the Rh–H insertion pathway is not operative in this transformation.