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Fast Ruthenium-Catalysed Allylation of Thiols by Using Allyl Alcohols as Substrates

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Abstract: The allylation of aromatic and aliphatic thiols, by using allyl alcohols as substrates, requires only minutes at ambient temperature with either a Ru^{IV} catalyst, $[Ru(Cp^*)(\eta^3\text{-}C_3H_5)(CH_3CN)_2](PF_6)_2$ (**2**; Cp^* = pentamethylcyclopentadienyl) or a combination of $[Ru(Cp^*)(CH_3CN)_3](PF_6)$ and camphor sulfonic acid. Quantitative conversion is normal and the catalyst possesses high functional-group tolerance. The use of $[Ru(Cp^*)(CH_3CN)_3](PF_6)$ alone affords poor results. A comparison is made to the results from catalytic runs based on the use of carbonates rather than alcohols, by using **2** as the catalyst, and it is shown that the products from the alcohols are formed faster, so there is no advantage in using a carbonate substrate. The observed branched-to-linear (b/l) ratios when using substituted alcohols decrease with time suggesting that the catalysts isomerise the products. A new methodology from which one can select the desired isomeric product is proposed. DFT calculations and NMR spectroscopic measurements, by using an arene sulfonic acid as co-catalyst, suggest that η^6-complexes are not relevant for the catalytic system. Moreover, the DFT results indicate that 1) any η^6-complexes from the acids $RC_6H_4SO_3H$ result from deprotonation of the acid, 2) complexation of the thiol, via the deprotonated sulfur atom, is preferred over complexation of the O atom of the sulfonate, $RC_6H_4SO_3^-$ and 3) a sulfonate O-atom complex will be difficult to detect.

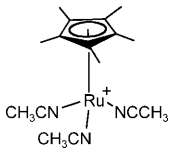
Keywords: alcohols · allylation · density functional calculations · NMR spectroscopy · ruthenium

Introduction

Ruthenium catalysts are finding increasing applications in organic synthesis.[1–4] Although allylation with various ruthenium complexes is well-known,[5,6] there has been renewed interest in applying [Ru(Cp*)]-based catalysts (Cp^* = pentamethylcyclopentadienyl) in allylation chemistry,[4e,6] as these complexes are capable of preferentially producing branched (rather than linear) allyl-organic products.

In a series of reports, we have recently suggested that the regioselectivity of the [Ru(Cp*)]-catalysed allylation reactions derives from orbital control[7,8] and that the reaction times can be markedly reduced by using a more labile, smaller coordination sphere.[9] This latter point is pertinent as, according to the literature, many of the allylation reactions with ruthenium are fairly slow, requiring a number of hours, and occasionally elevated temperatures.[5,6] Further, our new Ru^{IV} catalysts are capable of inducing novel Friedel–Crafts-type coupling chemistry[10] and allow allyl alcohols, rather than allyl carbonates or halides or acetates etc., to be used as substrates in this allylation chemistry, thereby avoiding unnecessary waste of the leaving group.[11]

With respect to the catalyst, oxidative addition reactions of **1** readily afford Ru^{IV} allyl salts.[8,12–14] that can be easily



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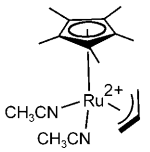

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transformed into $[Ru(Cp^*)(\eta^3\text{-}C_3H_5)(CH_3CN)_2](PF_6)_2$ (**2**). Salt **2** is an excellent catalyst for the allylation of indole derivatives, by using allyl alcohol substrates.[11b] Catalyst **2** is

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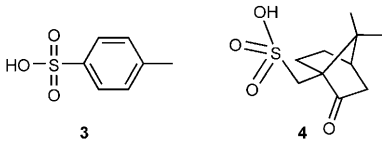
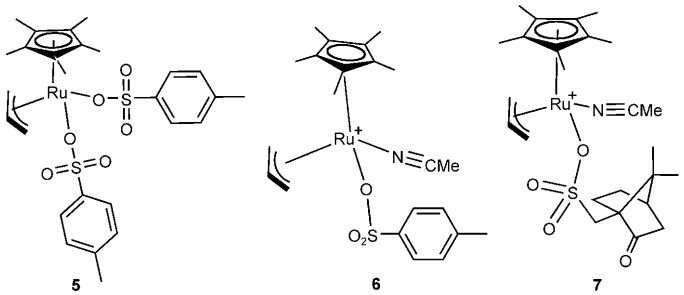
able to free one proton during the catalytic cycle thereby making water the leaving group in the oxidative addition reaction.[11a–c] Interestingly, a catalyst composed of HBF_4 and **1** does not improve either the reaction rate or the regioselectivity;[11b] however, the use of either *p*-toluene sulfonic acid (**3**) or camphor sulfonic acid (**4**) together with **1** markedly



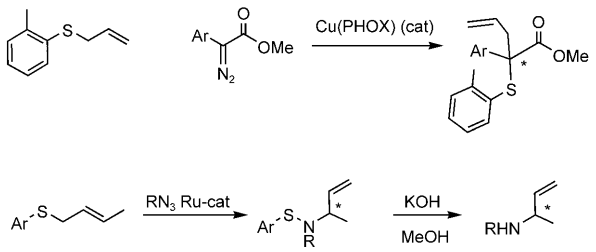
3 **4**

improves both the reaction kinetics and the product distribution.[11a,b] These results suggest coordination of the sulfonate anion and, subsequently, we have isolated and characterized the neutral Ru^{IV}–allyl, bis-sulfonate complex, **5**. De-



5 **6** **7**

spite this, we believe that **6** or **7**,[11a] as PF_6^- salts, are the active precursors. Herein, we extend our studies to the Ru-catalysed synthesis of allyl thioethers. In addition to their recognized preparative utility,[15] allyl thioethers have been called "privileged substrates" in cross-metathesis chemistry.[15a] Moreover, they are useful precursors in enantioselective syntheses,[15b,c] see Scheme 1, which shows the [Cu(PHOX)]-catalysed reaction (PHOX = phosphinooxazoline ligands)[15b] of an allyl thioether with a carbene precursor to afford a fully substituted new stereogenic centre (in 52–78% *ee*; *ee* = enantiomeric excess) and the synthesis of an allyl arylsulfonamide,[15c] by using a [Ru(salen)] catalyst that eventually affords the chiral amine with 78–86% *ee*. Further, thio–allyl compounds are known to possess some useful anticancer properties.[15f,1g]

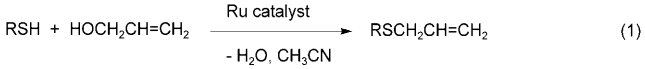


Scheme 1. Synthetic applications of allyl thioethers.

We know of several reports[16–18] on catalytic S-allylation; however, these literature procedures are either not atom efficient, in that they waste the leaving group,[17] or have a narrow substrate scope. For example, palladium-catalysed allylation of aromatic thiols by allyl alcohols in water/hexane biphasic media[18] is applicable only to aromatic thiols. We show here that our Ru catalysts rapidly allylate various RSH compounds at room temperature in a few minutes, in high yields by using allyl alcohols as substrates.

Results and Discussion

Catalyst [Ru(Cp*)(CH_3CN)$_3$](PF_6) (1): Equation (1) shows the general reaction, and it is convenient to begin by noting a few results arising from the use of **1** as a catalyst.



(1)

Reaction of thiophenol with allyl alcohol, by using 5% of catalyst **1**, alone, gives 100% conversion to product, $PhSCH_2CH{=}CH_2$, in approximately 70 min; however, with R = *p*-AcC_6H_4, the reaction requires approximately 22 h to approach 90% conversion. Further, with R=$PhCH_2$, the reaction is even slower, approximately 22 h for 30% conversion. Clearly the reaction proceeds, but not always rapidly.

Catalyst salt 2: Table 1 gives results from a selection of thiol allylation reactions by using several RSH nucleophiles with alcohols as the substrates, all catalysed by salt **2**. A comparison of these results with those from experiments with **1** is informative. The reaction of PhSH with allyl alcohol (entry 10) is finished in 30 min and the reaction with *p*-AcC_6H_4SH (entry 15) is also complete within 30 min. Further, the reaction of $PhCH_2SH$ with allyl alcohol (entry 1) now requires only approximately 11 min for 100% conversion! Clearly, catalyst **2** is considerably faster than **1**. It is worth noting that **2** reveals a high functional-group tolerance (see entries 10–15).

Apart from this comparison, Table 1 shows that allyl alcohol (entries 1–15) can react rapidly with a variety of aromatic and aliphatic thiols to afford high yields of products frequently in <1 h. Entries 6–9 are especially noteworthy. 1,2-Ethane dithiol (entry 7) affords only a very modest amount of allylation product after several hours. This suggests that a potentially chelating five-membered ring complex, such as **8**, formed when two S atoms coordinate,[19a] might not be very active. This would be in keeping with the literature, which reports fairly slow reactions in which chelating ligands are involved.[5,6] In agreement with this idea we note that the use of $HS(CH_2)_3SH$ as a substrate (entry 8), which might form a six-membered chelate

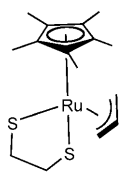


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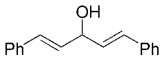
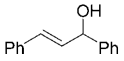
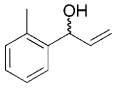
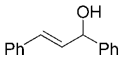
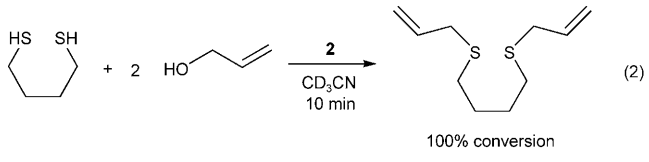
Table 1. Allylation of thiols by using **2** as the catalyst.[a]

Run	Thiol	Allyl substrate	*t*	Conv. [%]
1	$PhCH_2SH$		≤11 min	100
2	$HSCH_2CO_2Me$		30 min 18 h	>90% 100
3	Boc-Cys-OH		40 min	100
4	CySH		9 min	100
5	*t*BuSH		30 min	100
6			8 min	100
7[b]			10 min 5.5 h	11 16
8[b]			20 h	93
9[b]			10 min	100
10	PhSH		30 min	100
11	*p*-$MeOC_6H_4SH$		19 min	100
12	*p*-MeC_6H_4SH		22 min	100
13	*p*-ClC_6H_4SH		40 min	100
14	*p*-NCC_6H_4SH		12 min	100
15	*p*-AcC_6H_4SH		30 min	100
16[c]	PhSH		20 min	100
17[d]	PhSH		7 min	100
18	PhSH		≤6 min	100
19[e]	PhSH		15 min	100
20[f]	$PhCH_2SH$		1.5 h 17 h	≈80 100
21[g]	Boc-Cys-OH		6 min	100

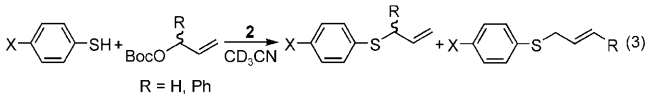
[a] CD_3CN (0.5 mL), allyl alcohol (0.07 mM), **2** (0.0035 mM), thiol (0.07 mM) (unless otherwise stated). [b] CD_3CN (0.5 mL), allyl alcohol (0.14 mM), **2** (0.0070 mM), thiol (0.07 mM). [c] branched-to-linear (b/l) ratios 3.1:1. [d] The product is PhCH=CHCH=CHCH(SPh)Ph and contains some impurities. [e] b/l 3:1. [f] b/l 0.6:1. [g] The observed ratio of diastereomers is approximately 2:1.

ring, also results in a very slow, but somewhat faster, diallylation reaction. However, by using the larger dithiol, $HS(CH_2)_4SH$ (entry 9, [Eq. (2)]), for which the chelate ring will not be so stable, the diallylation reaction is quite rapid and finished in approximately 10 min. Table 1, entries 16–19 show that a number of different allyl alcohols can serve as substrates in the reaction with PhSH.



(2)

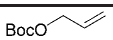
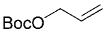
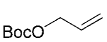
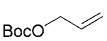
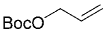
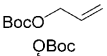
Carbonate chemistry: It is useful to compare these results, those which utilise allyl alcohols, with the rates for the **2**-catalysed allylation reactions of PhSH ([Eq. (3)], X = H) by using carbonates, under the same conditions. For the linear carbonate Boc-$OCH_2CH{=}CH_2$ (Boc = *tert*-butoxycarbonyl), after 90 min we find 84% conversion[19b] (vs. 30 min for 100% conversion with catalyst **2**), and for the branched carbonate, $PhCH(OBoc)CH{=}CH_2$, after 60 min we obtain 95% conversion (vs. 20 min for 100% conversion with **2**).



(3)

These results indicate that there is no advantage to be gained by using the carbonate as a leaving group. Table 2 gives results for the allylation of several thiophenols, by using allyl carbonates, under different conditions (3 instead of 5 mol% catalyst, and a three-fold excess of the thiophenol, instead of 1:1). Again, several of the thiophenols react much slower when carbonates are used as substrates.

Table 2. Allylation of *p*-RC_4H_4SH by using allyl carbonates with **2** as the catalyst.[a]

Run	R	Allyl substrate	*t*	Conv. [%]
1	H		30 min	100
2	Me		30 min 72 h	50 91
3	Cl		30 min 72 h	26 71
4	MeO		17 min	100
5	CN		55 min	100
6	Ac		45 min	100
7[b]	H		50 min	100
8[c]	Me		95 min	100
9[d]	Cl		240 min	95
10[e]	MeO		45 min	100
11[f]	CN		25 min	100
12[g]	COMe		30 min	100

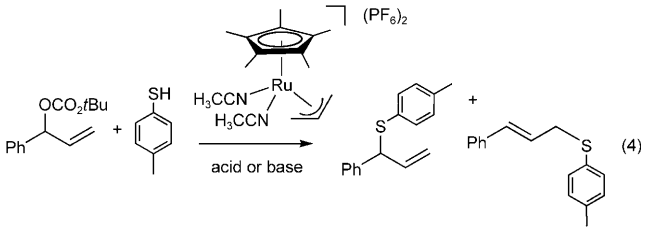
[a] CD_3CN (0.5 mL), allyl carbonate (0.07 mM), **2** (0.0021 mM), thiol (0.21 mM). [b] b/l 2.3:1. [c] b/l 1.4:1. [d] b/l 1.7:1. [e] b/l 1.4:1. [f] b/l 3.0:1. [g] b/l 1.3:1.

Table 3 shows the effect of adding either a base or a sulfonic acid on the rate of allylation of *p*-MeC_6H_4SH with the carbonate $PhCH(OBoc)CH{=}CH_2$ in the presence of **2** [Eq. (4)].

Table 3. Effect of added acid or base on the allylation of *p*-MeC_6H_4SH by $PhCH(OBoc)CH{=}CH_2$ with **2** as the catalyst (see Equation (3)).[a]

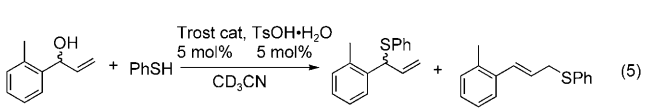
Acid/base	*t* [min]	Conv. [%]	b/l ratio
none	95	100	1.4:1
diisopropylethylamine	140	100	6.8:1
tributylamine	85	100	5:1
p-toluene sulfonic acid (**3**)	5	100	1:1
camphor sulfonic acid (**4**)	25	100	1:1.4

[a] CD_3CN (0.5 mL), allyl carbonate (0.07 mM), **2** (0.0021 mM), thiol (0.21 mM), acid or base (0.21 mM).



Addition of base is not very advantageous, whereas the sulfonic acid significantly accelerates this transformation. We note that addition of acid **3** markedly increases the reaction rate. Apart from the possible positive effect of the sulfonate anion as a ligand (see below), these results suggest that the thiophenol need not lose a proton to be effective in this chemistry. If proton loss were to be important, one might expect that base rather than acid would accelerate the reaction.

Catalyst system $[Ru(Cp^*)(CH_3CN)_3](PF_6)$/camphorsulfonic acid: Table 4 shows a set of similar reactions except that the catalyst is now formed from salt **1** plus acid **4** and presumably involves a Ru–O(sulfonate) bond.[11a] The reaction of PhSH with allyl alcohol (entry 5) now requires $\leq$10 min for full conversion at room temperature and thus is faster than with either **1** (70 min) or **2** (30 min). The reaction of thiophenol with the substituted allyl alcohol, $PhCH(OH)CH{=}CH_2$ (entry 17) requires $\leq$12 min, whereas with **2** full conversion requires approximately 20 min. This mixture clearly constitutes our fastest catalyst. Further, it also affords the best branched-to-linear (b/l) ratios. For example, for the reaction of $CH_2{=}CHCH(OH)$(*o*-tolyl) with PhSH (entry 15, Table 4, [Eq. (5)] we find 100% conversion after 8 min with

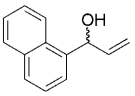
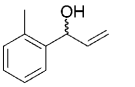
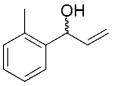


a b/l ratio of approximately 13:1 (rather than 3:1 with **2**). The catalytic reaction does not proceed by using the acid alone.

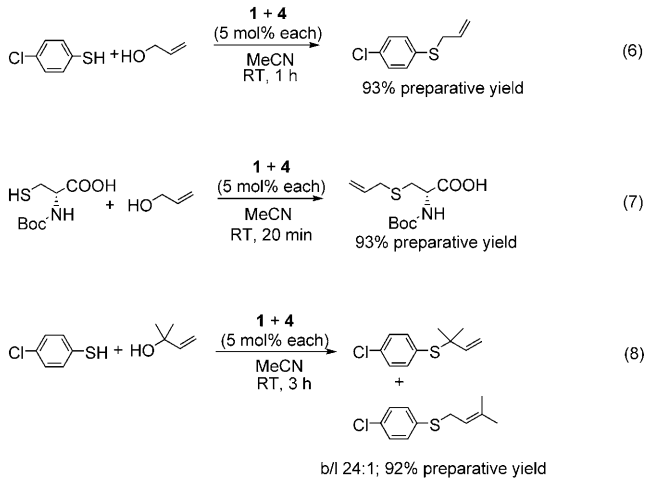
To demonstrate the synthetic value of the new catalytic system derived from **1** and **4** several reactions were carried out on a 0.28 mmol preparative scale in acetonitrile solution (0.14 M concentration of substrates), and the products isolated (see Equations (6–8) and the Experimental Section). Evaporation of the reaction mixture, preparation of a solution in dichloromethane (for N-Boc-Cys-OH, ethyl acetate was used as the solvent) and filtration affords the allyl thiol ethers in high yield and purity after removal of the solvent. This simple isolation procedure makes this chemistry very attractive.

Although not indicated in Table 4, doubling the amount of acid **4** (5 mol% **1**, 10 mol% **4**) for reaction 7, does not accelerate the chemistry. After 10 min we find 100% conver-

Table 4. Allylation of thiols by using **1**+**4** the as catalyst.[a]

Run	Thiol	Allyl substrate	*t*	Conv. [%]	l/b ratio
1	$PhCH_2SH$		50 min	100	
2	Boc-Cys-OH		15 min	100	
3	CySH		55 min	100	
4	*t*BuSH		35 min	100	
5	PhSH		$\leq$10 min	100	
6	*p*-$MeOC_6H_4SH$		10 min	100	
7	*p*-MeC_6H_4SH		10 min	100	
8	*p*-ClC_6H_4SH		6 min	100	
9	*p*-NCC_6H_4SH		7 min	100	
10	*p*-AcC_6H_4SH		$\leq$5 min	100	
11	PhSH		16 min	100	1:0.54
12	PhSH		2.5 h	90–95%	only b
13	*p*-ClC_6H_4SH		3 h	100%	only b
14	PhSH		16 min 41 h 8 d	100	1:13 1:0.2 1:0
15	PhSH		8 min 15 min 6 d	100	1:13 1:8 1:0
16[b]	PhSH		15 min 16.5 h	100	1:10 1:11
17	PhSH		$\leq$12 min 230 min	100 100	1:2.9 1:0.2
18	$HSCH_2CO_2Me$		$\leq$11 min 15 h	100 100	1:2.8 1:0.6
19	$HSCH_2CO_2H$		12 min	$\approx$100	1:3.2
20	Boc-Cys-OH		20 min 48 h	100	1:4.2 1:0.8
21	$PhCH_2SH$		30 min 5 d	100 100	1:2.5 1:0
22	*t*BuSH		80 min 15 h	80–90 100	1:0.8 1:0.8

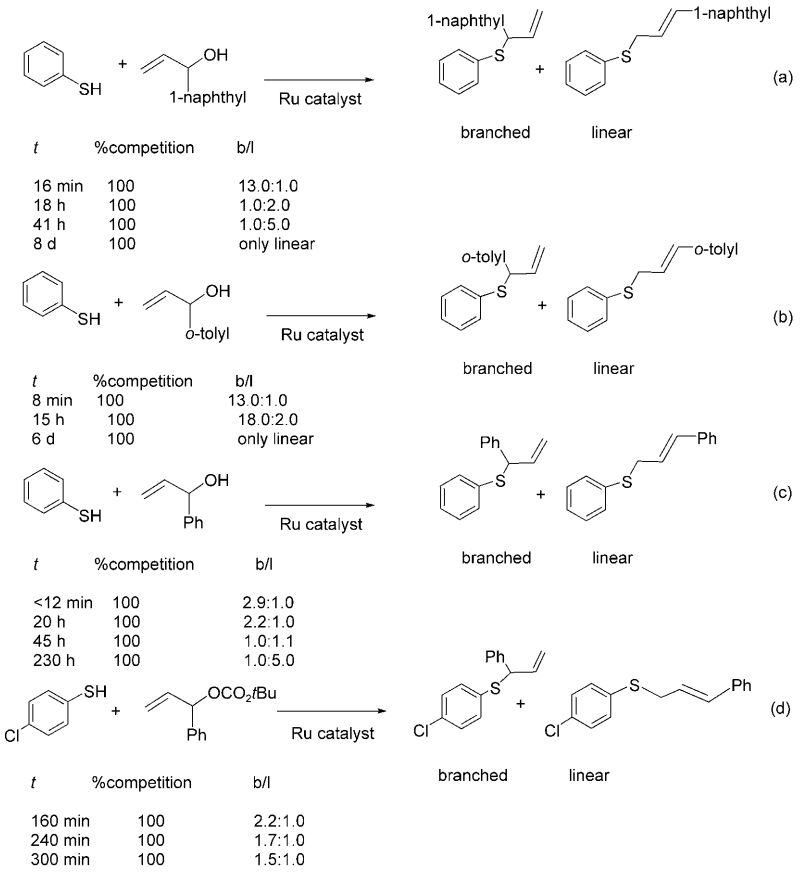
[a] CD_3CN (0.5 mL), allyl alcohol (0.07 mM), **1** (0.0035 mM), **4** (0.0035 mM), thiol (0.07 mM). [b] The reaction mixture was quenched after 4 min by addition of 25% aq. NH_3 (0.02 mL).



sion with a b/l ratio of 7.7:1. Doubling the amount of **1** (10 mol% **1**, 5 mol% **4**) also has little or no affect (after 10 min, 100% conversion with a b/l ratio of 6.0:1). As we will show, these rather different b/l ratios are due to isomerisation. We have suggested[11] a mechanism for this allylic alcohol-based allylation chemistry for indoles[11a,b] and presume that the thiol reactions proceed in a related fashion.

Isomerisation reactions: The observed branched-to-linear ratios for the allylation products are good, but not excellent. This prompted us to study the time dependence of the isomer distribution by means of ^{1}H NMR spectroscopy. Scheme 2 shows the results of these measurements for four catalysed reactions: Scheme 2a and b report on thiophenol with the bulky secondary alcohols (1-naphthyl)CH(OH)CH=CH_2 and (o-tolyl)-CH(OH)CH=CH_2 c) thiophenol with the more routine alcohol PhCH(OH)CH=CH_2, (all three reactions catalysed by **1**+**4**) and d) results from the reaction of *p*-Cl-thiophenol with the carbonate, PhCH(OC(O)O-*t*Bu)CH=CH_2, catalysed by **2**. These results show that the metal complex is capable of inducing isomerisation of the branched isomer to the linear isomer, in all four examples, albeit at different rates.[20] For the reaction involving PhCH(OH)CH=CH_2, catalysed by **1**+**4**, the linear product is now the major component after approximately 45 min. With the 1-naphthyl analogue, the isomerisation requires hours before the linear isomer dominates. For the carbonate chemistry, both the reaction and the isomerisation are fairly slow (ca. 95% converted after 4 h, and the branched isomer still dominates after 5 h). Assuming that the regioselectivity is orbital controlled,[8] and that the branched kinetic product is formed first, these new results indicate that literature-observed branched-to-linear ratios measured after many hours must be interpreted with caution. In any case, it is useful to know that, in some cases, if one waits long enough, the linear product can be obtained in an essentially pure form.

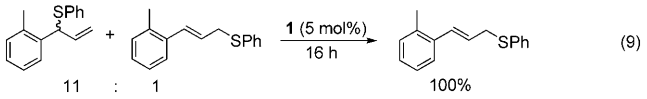
These observations on product isomerisation prompted us to consider how one might "preserve" the high b/l ratios observed with short reaction times. To this end, we have chosen to quench the reaction shown in Equation (5) with 25% aqueous NH_3 after only 3 min, thereby inhibiting the isomerisation by blocking several coordination positions. Analysis of the mixture of the above products, after column chromatography on silica gel, reveals a b/l ratio of 11:1 with 100% conversion (see Scheme 2 for comparison data). We have also quenched the reaction of (1-naphthyl)-CH(OH)CH=CH_2 with PhSH and find 98% conversion after 5 min with a b/l ratio of approximately 7:1. This ratio is unchanged after 24 h. The same reaction when quenched after 2 min afforded only 85% conversion, but a much larger, approximately 16:1, b/l ratio, which did not change after 3 h. Since the b/l ratios found for much longer catalyst



Scheme 2. Isomerisation from branched to linear isomers as a function of time.

contact times indicate mostly or exclusively linear products, as indicated in the scheme, this quenching provides us with an experimental methodology from which we can select the desired isomeric product. Of course, the quenching is successful because our catalyst is so fast. The subject of product isomerisation in connection with catalytic allylation has not been discussed in the literature and our approach represents the first proposed solution to this problem.

It is interesting to compare the isomerisation rate for Trost's catalyst, **1**, with that for the Ru^{IV}-complex **2**. An isolated sample (via the quench) consisting of an 11:1 mixture of (*o*-tolyl)CH(SPh)CH=CH_2 and its linear isomer was treated with **1** (5 mol%) in CD_3CN for 3 h. The b/l ratio of the mixture changed from 11:1 to 0.33:1.0, and after 16 h, only the linear isomer could be observed [Eq. (9)].

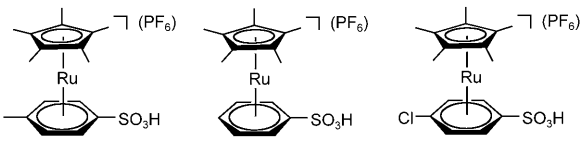


(9)

In a second experiment, treatment of the same isomeric mixture with complex **2** gave a b/l ratio of 1:0.9 after 19 h. Both catalysts isomerise the mixture, but [Ru(Cp*)-$(CH_3CN)_3$](PF_6) seems faster.

Co-catalyst *p*-toluene sulfonic acid (3) and η^6-arene complexes: The assumption that a sulfonate anion complexes the ruthenium provides an explanation for the more favourable kinetics and b/l ratios observed when using a catalyst made up of **1** together with **4**.[11a] However, a monosubstituted sulfonate complex has not yet been isolated. We have carried out some experiments by using **3**, an acid that is known[11a] to be capable of complexing Ru through the sulfonate oxygen. This alternative sulfonic acid is relevant as a model as it forms an excellent catalyst together with **1** in the allylation of indole[11a] and is quite effective in our thiol chemistry. The reaction of (*o*-tolyl)CH(OH)CH=CH_2 with PhSH (catalysed by a 1:1 mixture of **1** and **3**) at ambient temperature is complete in only 5 min with a b/l ratio of approximately 10:1 (see also Table 3). After 30 min the b/l ratio has been reduced to 3.5:1. The analogous reaction of (1-naphthyl)CH(OH)CH=CH_2 with PhSH by using **1** plus **3** is complete in 4 min with a b/l ratio of approximately 5:1. After 10 min, the b/l ratio has been reduced to 3.6:1.

Unfortunately, we found no evidence, by means of ^{1}H NMR spectroscopy, for a complex of **3** in acetonitrile solution. However, there is still the possibility that a transient O–sulfonate or an η^6-arene complex of the type [Ru(Cp*)(η^6-*p*-$CH_3C_6H_4SO_3H$)](PF_6) might be formed during the reaction. Alternatively, the aromatic moiety of any of the various *p*-RC_6H_4SH nucleophiles might well serve as a source of an arene donor. Of course, the S atom, either as RSH or as the thiolate, is certainly a possible ligand for ruthenium. To investigate the relative stability of such π species, an attempt was made to generate the complexes [Ru(Cp*)(η^6-*p*-$CH_3C_6H_4SO_3H$)](PF_6) (**9**), [Ru(Cp*)(η^6-$C_6H_5SO_3H$)](PF_6) (**10**) and [Ru(Cp*)(η^6-*p*-$ClC_6H_4SO_3H$)]-(PF_6) (**11**), by allowing [Ru(Cp*)$(CH_3CN)_3$](PF_6) to react with one equivalent of the corresponding arene sulfonic acid in acetone solution at room temperature. There are many known [Ru(Cp*)(η^6-arene)] salts.[21] The ^{1}H NMR spectra of the isolated[22a] crude yellow solids (see the Experimental Section) reveals signals at around $\delta = 6$ ppm which might[22a] correspond to the protons of η^6-arene products, plus minor but significant resonances between $\delta = 7$ and 8 ppm that can be assigned to the protons of the free arene sulfonic acid (Figure 1). The amount of uncomplexed arene increases



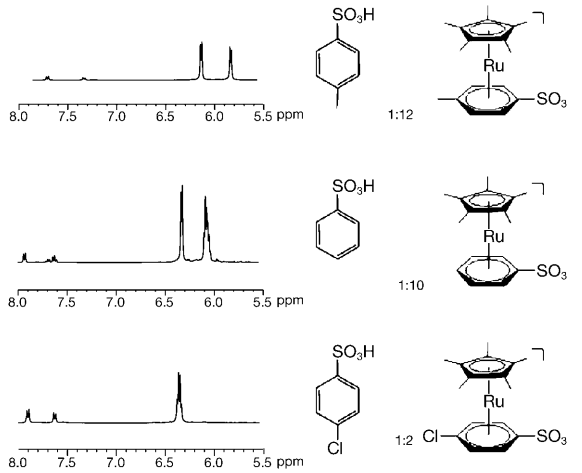


Figure 1. ^{1}H NMR spectra in the high-frequency region for the three zwitterionic [Ru(Cp*)(η^6-sulfonic acid anion)] complexes that were eventually shown to be **13**–**15**. The ratios free arene/complexed arene are shown (400 MHz, [D_6]acetone).

with the electron-withdrawing ability of the *para* substituent. The observed ratios of η^6-arene complex/free acid are 12:1, 10:1 and 2:1, respectively. At least in acetone solution, one can form an η^6-arene-type complex, even if these are not completely pure. We find no evidence for O complexation.

DFT calculations: If the arene of these phenyl sulfonic acids is not completely complexed in a weakly coordinating solvent such as acetone, it seems unlikely that they will be effective ligands in acetonitrile solution. Undoubtedly one could shift the equilibrium by addition of more sulfonic acid;[22b] however, in the catalytic reactions, the ratio of Ru to acid is 1:1. To pursue this point further we have calculated the relative stabilities of several η^6 complexes based on the chemistry of Equation (10) in acetone solution:

$$[Ru(Cp^*)(CH_3CN)_3]^+ + RC_6H_4X \rightarrow [Ru(Cp^*)(\eta^6\text{-}RC_6H_4X)]^+ + 3\,CH_3CN \quad (10)$$

in which R = H and X = SH for the thiol and R = Me, H or Cl for $X = SO_3H$.

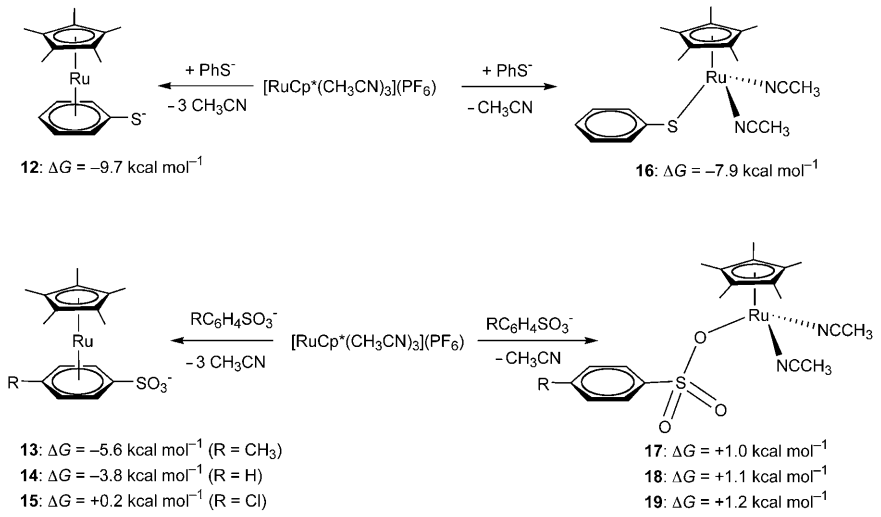
We find that ΔG is positive in all cases, so that replacement of the three CH_3CN ligands of $[Ru(Cp^*)(CH_3CN)_3]^+$ by one η^6-arene ligand is always thermodynamically unfavourable. The ΔG value, 1.9 kcal mol^{-1}, is smaller for PhSH, than for any of the three presumed sulfonic acid salts, **9**–**11**: 4.8, 6.0 and 10.3 kcal mol^{-1}, respectively, suggesting that, if at all, the thiol would most likely form the π complex. Clearly, these values do not correspond to the experimental results. Nevertheless, we note that the ΔG values calculated for the three acids correlate with the electron-donating characteristics of the η^6-arene ligand, that is, a better electron-donating group favours a more stable η^6-arene complex. The electron-donating ability of the arene ligands is associated with the charge calculated (by means of a Natural Population Analysis, NPA) for the η^6 ligands in the various complexes. Stronger arene donors are associated with larger positive charges on the arene ligands, so that in **9**–**11** one finds +0.32 for $R = CH_3$, +0.30 for R = H and +0.28 for R = Cl. The corresponding value for $[Ru(Cp^*)(\eta^6\text{-}C_6H_5SH)]^+$ is +0.38.

We next considered the possibility that the anions,[21i,22a] rather than the neutral acid species, were π-bonded and have calculated the ΔG values for the reaction shown in the bottom section of Scheme 3. Here, we are assuming that the arene substrate can lose one proton to afford **12**–**15**, and that HPF_6 will be the side product.[22c] The corresponding ΔG values calculated for the formation of the neutral η^6 zwitterionic species **12**–**15** are now −9.7, −5.5, −3.8 and 0.2 kcal mol^{-1}, respectively, and thus predict more stable η^6 complexes.[22a] Note that 1) these values are in much better agreement with the NMR spectroscopic observations and 2) the ΔG value for the anionic chloro-arene is practically zero, at the accuracy level of the method employed (see Computational Details), so that this result agrees reasonably with the 2:1 ratio observed by NMR spectroscopy. Again, these ΔG values follow the trend of the electron-donating capability of the ligand. The stronger electron arene donors will have in total less negative charge corresponding to more stable η^6 complexes. The charges calculated for the arene ligands in **12**--**15** are: −0.39 for PhS^-, −0.53 for $R = CH_3$ and $X = SO_3^-$, −0.55 for R = H and $X = SO_3^-$ and −0.57 for R = Cl and $X = SO_3^-$.

It is worth noting (at the top of Scheme 3) that the calculations predict that the thiolate, anion, PhS^-, should complex via the S atom affording, **16**, a relatively stable complex with a ΔG value of −7.9 kcal mol^{-1}.[22c] If this were correct, then each thiol reagent shown in the catalysis tables would indeed afford a slightly different catalyst, thereby explaining some of the varying observations with respect to the reaction times and product distributions. Continuing, the complexes **17**–**19**, formed by complexation of an O atom from the sulfonic acid, are predicted to be not very stable; this is consistent with our observations that the sulfonic acids **3** and **4** do not readily complex via the O atom to any major extent (in CH_3CN solution).

Conclusions

The catalytic allylation of both aromatic and aliphatic thiols by using a variety of allyl alcohols as substrates proceeds rapidly to completion within minutes at ambient temperature, with catalyst **2**, or a combination of $[Ru(Cp^*)(CH_3CN)_3](PF_6)$ (**1**) and camphor sulfonic acid (**4**). In many cases, 100% conversion is attained in 15 min or less. Many other catalysts require either many hours and/or elevated temperatures.[5,6] Both catalysts work well and tolerate a wide variety of substituents on the S atom; however, the catalyst from **1** and **4** (or **3**) is the fastest. A comparison with the results from catalytic runs based on the use of carbonates rather than alcohols clearly shows that there is no advantage in using an allyl precursor with a carbonate (or acetate etc.) leaving group. The branched-to-linear ratios for the products from experiments that use substituted alcohols decrease with time; however, we have shown that one can select the desired isomeric product by either rapidly quenching with NH_3 (to afford the branched product) or by simply waiting (which gives mostly linear product). The



Scheme 3. Results from the DFT calculations (for acetone solutions).

DFT results indicate that 1) the stable η^6 complexes derived from the acids $RC_6H_4SO_3H$ result from deprotonation of the acid rather than simple η^6-arene coordination, 2) complexation of the thiol, via the deprotonated sulfur atom, is preferred over the O atom of the sulfonate, $RC_6H_4SO_3^-$ and 3) a sulfonate O-atom complex will be difficult to detect, especially in acetonitrile solution. Presumably, for the catalyst consisting of **1** plus **4** (or **3**), we are generating a very small amount of a quite active catalyst.

Experimental Section

General information: All air-sensitive manipulations were carried out under a nitrogen atmosphere. All solvents were dried over an appropriate drying agent and then distilled under nitrogen. CD_3CN was dried over molecular sieves and stored under nitrogen. [D_6]Acetone was distilled over $CaSO_4$ and stored under nitrogen. All commercially available starting materials were purchased from commercial sources and used as received. ^{1}H, ^{13}C and 2D NMR spectra were recorded with Bruker DPX-250, 300, 400 and 500 MHz spectrometers at room temperature. Chemical shifts are given in ppm and referenced to TMS for ^{1}H NMR spectra. Mass spectra were obtained from the analytical service of the ETHZ. The allyl alcohols used in the allylation reactions were synthesised according to a modified literature procedure.[11a]

NMR spectroscopic procedure for monitoring the allylation of thiols by using 1 and 4 as the catalyst: The thiol (0.07 mmol) was added to a solution of CD_3CN (0.5 mL) containing the allylic alcohol (0.07 mmol), [Ru(Cp*)(MeCN)$_3$](PF$_6$) (0.0018 g, 0.0035 mmol) and (1*S*)-(+)-10-camphorsulfonic acid (0.008 g, 0.0035 mM), in an oven-dried NMR tube, and the mixture was monitored at ambient temperature.

Examples of preparative syntheses of allylthiols

(*S*)-Allyl-*p*-chlorothiophenol: 4-Chlorothiophenol (0.041 g, 0.28 mmol) was added to a solution of allyl alcohol (20 μL, 0.29 mmol), [Ru(Cp*)(MeCN)$_3$](PF$_6$) **1**) (0.0071 g, 0.014 mmol) and (1*S*)-(+)-10-camphorsulfonic acid (0.0033 g, 0.014 mM) in MeCN (2 mL). The reaction mixture was stirred at room temperature for 1 h and then evaporated in vacuo at 40 °C. The resulting residue was dissolved in CH_2Cl_2 and filtered through a plug of silica gel. Evaporation of the resulting solution afforded the pure product as a transparent liquid (0.048 g, 93 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.28 (s, 4H), 5.96–5.80 (m, 1H), 5.15 (d, 1H, J = 13.3 Hz), 5.10 (d, 1H, J = 5.5 Hz), 3.55 ppm (d, 2H, J = 6.8 Hz); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 134.7, 133.6, 132.6, 131.7, 129.3, 118.3, 37.8 ppm; HRMS-EI: *m*/*z*: calcd for C_9H_9ClS: 184.0108 [*M*]$^+$; found: 184.0107.

(*S*)-Allyl-*N*-Boc-cysteine: By using *N*-Boc-cysteine (0.062 g, 0.28 mmol) instead of 4-chlorothiophenol, a 20 min reaction time, and ethyl acetate as the eluent, (*S*)-allyl-*N*-Boc-cysteine was obtained as an oil (0.068 g, 93 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.72 (br s, 1H), 5.85–5.71 (m, 1H), 5.38 (br s, 1H), 5.16 (d, 1H, J = 15.0 Hz), 5.16 (d, 1H, J = 11.0 Hz), 4.55 (br s, 1H), 3.18 (d, 2H, J = 7.1 Hz), 3.02–2.88 (m, 2H), 1.47 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.9, 155.8, 134.0, 118.4, 80.9, 53.4, 35.6, 32.9, 28.6 ppm; HRMS-ESI: *m*/*z*: calcd for $C_{11}H_{19}NNaO_4S$: 284.0927; found: 284.0925 [*M*+Na]$^+$.

(*S*)-(α,α-Dimethylallyl)-*p*-chlorothiophenol: 4-Chlorothiophenol (0.041 g, 0.28 mmol) was added under nitrogen to a solution of 2-methyl-3-buten-2-ol (30 μL, 0.28 mmol), [Ru(Cp*)(MeCN)$_3$](PF$_6$) (0.0071 g, 0.014 mmol) and (1*S*)-(+)-10-camphorsulfonic acid (0.0033 g, 0.014 mM) in MeCN (2 mL). The reaction mixture was stirred at room temperature for 3 h and then quenched with 25 % aqueous ammonia (0.08 mL). The resulting mixture was evaporated in vacuo at 40 °C. The obtained residue was dissolved in CH_2Cl_2 and filtered through a plug of silica gel. Evaporation of the resulting solution afforded 0.055 g (92 % yield) of the product (b/l 24:1) as a transparent liquid. The branched isomer slowly isomerises to the linear one when stored as a solution in $CDCl_3$. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.43 (d, 2H, J = 8.4 Hz), 7.32 (d, 2H, J = 8.4 Hz), 5.98 (dd, 1H, J_1 = 17.4, J_2 = 10.5 Hz), 4.96 (d, 1H, J = 10.5 Hz), 4.75 (d, 1H, J = 17.4 Hz), 1.38 ppm (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 144.7, 138.5, 135.1, 131.4, 128.6, 111.8, 50.4, 27.3 ppm.

The following three complexes, originally thought to be salts **9–11**, are assigned the structures **13**–**15**.

[Ru(Cp*)(η^6-C$_6$H$_5$SO$_3$)] (13): Benzene sulfonic acid (18.6 mg, 0.118 mmol) was added to a solution of [Ru(Cp*)(CH$_3$CN)$_3$](PF$_6$) (59.6 mg, 0.118 mmol) in acetone (3 mL). The cloudy yellow reaction mixture was stirred for 2 h at room temperature and the solvent removed under vacuum. The resulting yellow solid was washed three times with diethyl ether and dried under high vacuum (HV). The product was found to be a 1:10 mixture of benzene sulfonic acid and **13**. Yield: 60.1 mg; ^{1}H NMR (400 MHz, [D_6]acetone): δ = 1.94 (s, 15H; C_5Me_5), 5.96 (m, 3H), 6.22 (d, 2H, J = 5.6 Hz), 7.53 (m, 3H, benzene sulfonic acid), 8.82 ppm (d, 2H, J = 7.6 Hz, benzene sulfonic acid).

[Ru(Cp*)(η^6-*p*-MeC$_6$H$_4$SO$_3$)] (14): *p*-Toluene sulfonic acid monohydrate (22.6 mg, 0.119 mmol) was added to a solution of [Ru(Cp*)(CH$_3$CN)$_3$](PF$_6$) (60.0 mg, 0.119 mmol) in acetone (3 mL). The cloudy yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting yellow solid was washed three times with diethyl ether and dried under HV. The product was found to be a 1:12 mixture of *p*-toluene sulfonic acid and **14**. Yield: 54.5 mg; ^{1}H NMR (400 MHz, [D_6]acetone): δ = 1.90 (s, 15H; C_5Me_5), 2.19 (s, 3H), 2.34 (s, 3H; *p*-toluene sulfonic acid), 5.82 (d, 2H, J = 5.6 Hz), 7.12 (d, 2H, J = 5.6 Hz), 7.32 (d, 2H, J = 7.6 Hz; *p*-toluene sulfonic acid), 7.69 ppm (d, 2H, J = 7.6 Hz; *p*-toluene sulfonic acid).

[Ru(Cp*)(η^6-*p*-ClC$_6$H$_4$SO$_3$)] (15): *p*-Chloro sulfonic acid (23.1 mg, 0.120 mmol) was added to an acetone (3 mL) solution of [Ru(Cp*)(CH$_3$CN)$_3$](PF$_6$) (60.4 mg, 0.120 mmol). The cloudy yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting yellow solid was washed three times with diethyl ether and dried under HV. The product was found to be a 1:2 mixture of *p*-chloro sulfonic acid and **15**. Yield: 64.6 mg. ^{1}H NMR (400 MHz, [D_6]acetone): δ = 2.02 (s, 15H; C_5Me_5), 6.35 (m, 4H), 7.73 (d, 2H, J = 8.4 Hz; *p*-chloro sulfonic acid), 7.32 ppm (d, 2H, J = 8.4 Hz; *p*-chloro sulfonic acid).

Attempt to prepare a Ru–thiolate complex: *p*-Me-Thiophenol (9.8 mg, 0.079 mmol) was added to a solution of [Ru(Cp*)(CH$_3$CN)$_3$](PF$_6$) (40.0 mg, 0.079 mmol) in MeCN (2 mL). Diisopropylethylamine (0.07 mL, 0.396 mmol) was added and the pale-yellow solution turned deep purple, which suggested the presence of a new Ru species. The reaction mixture was stirred for 30 min at room temperature after which time the solvent was reduced under vacuum. Diethyl ether was added to precipitate 13.1 mg of a brown solid which was found by ^{1}H NMR spectroscopy to be mainly *p*-Me-thiophenol. This brown solid was removed by filtration and on further addition of diethyl ether to the filtrate, 27.2 mg of a red crystalline solid precipitated. This was collected, washed three times with diethyl ether and dried under vacuum. NMR spectroscopic studies are consistent with the formulation: [HN(CH$_2$CH$_3$)(CHMe$_2$)$_2$][Ru(Cp*)(*p*-MeC$_6$H$_4$S)$_2$(CH$_3$CN)] for approximately 80 % of the red crystalline solid. ^{1}H NMR (500 MHz, CD_3CN): 1.35 (m, 15H; 5 methyl groups from the ammonium ion), 1.46 (s, 15H; Cp*), 2.37 (s, 6H; methyl groups of *p*-Me-thiophenol), 3.19 (d of q, 2H, J = 7.5, 4.5 Hz; ethyl CH$_2$), 3.71 (m, 2H; isopropyl C*H*Me$_2$), 6.22 (1H, J_{NH} = 52.5 Hz; R$_3$N$^+$*H*), 7.21 (d, 2H, J = 7.5 Hz; *p*-Me-thiophenol), 7.34 ppm (d, 2H, J = 7.5 Hz; *p*-Me-thiophenol); ^{13}C NMR (125 MHz, CD_3CN): δ = 10.3 (Cp* C*C*H$_3$), 16.8 (CH$_2$*C*H$_3$), 18.1 (CH(*C*H$_3$)$_2$), 20.7 (*p*-*C*H$_3$-thiophenol), 43.5 (*C*H$_2$CH$_3$), 55.5 (*C*H(CH$_3$)$_2$), 97.1 (Cp* *C*CH$_3$), 129.7 (*meta* thiophenol carbon atoms), 132.1 (*ortho* thiophenol carbon atoms), 136.5 (*ipso* thiophenol carbon atom), 140.3 ppm (*para* thiophenol carbon atom); MS: *m*/*z*: 843 (2Cp*, 2Ru, 3*p*-Me-thiophenol), 719 (2Cp*, 2Ru, 2*p*-Me-thiophenol), 629 (2Cp*, 2Ru, 1*p*-Me-thiophenol 1S).

Computational details: The calculations were performed by using the GAUSSIAN 03 software package[23] and the PBE1PBE functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25 % mixture of Hartree–Fock[24a] exchange with DFT[24b] exchange correlation, given by Perdew, Burke and Ernzerhof functional (PBE).[25] The optimised geometries were ob-

tained with the LanL2DZ basis set[26] augmented with a *f*-polarization function[27] for Ru and a standard 6–31G(d,p)[28] for the remaining elements (basis b1). Frequency calculations were performed, yielding no imaginary frequency modes, and confirming the nature of the stationary points as minima. Atomic charges were obtained by using a Natural Population Analysis (NPA).[29]

The reaction energy values reported were obtained from single-point energy calculations by using a VTZP basis set (basis b2) and the geometries optimised at the PBE1PBE/b1 level. Basis b2 consisted of a standard 3–21G[30] with an added *f*-polarization function[27] for Ru and a standard 6–311++G(d,p)[31] for the remaining elements. Solvent (acetone) effects were considered in the PBE1PBE/b2//PBE1PBE/b1 energy calculations by using the Polarizable Continuum Model (PCM) initially devised by Tomasi and co-workers[32] as implemented on GAUSSIAN 03,[33] and, thus, the calculated energy differences can be taken as free energy.[34] The molecular cavity was based on the united atom topological model applied on UAHF radii, optimised for the HF/6–31G(d) level.

Acknowledgement

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[22] a) As a consequence of the DFT results, a ^{19}F NMR spectrum of the isolated sample thought to be **9** was measured. This spectrum shows only a weak doublet for the PF_6^- anion. Addition of a known amount of a ^{19}F standard allows us to estimate that this sample contains very little of this anion (ca. 7% of what it should contain if structure **9** were correct). Consequently, the isolated species, thought to be **9**–**11**, are best described as **13**–**15**, in agreement with the literature;[21i] b) as noted, the experiments with one equivalent of arene gave mixtures. With respect to **13**, addition of a second equivalent of *p*-$CH_3C_6H_4SO_3H$ to the acetone solution containing **1** results in complete conversion of **1**; however, the isolated product was not pure; c) a mixture of **1** with two equivalents of PhSH and *N*,*N*-diisopropylethylamine allowed the isolation of a complex that contains two thiol moieties per ruthenium. However, based on mass spectrometry, this material appears to be a dinuclear species with bridging thiolate anions (see the Experimental Section). Moreover, this complex was not active as a catalyst. See also reference [19a] for thiolate complexes of Ru.

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